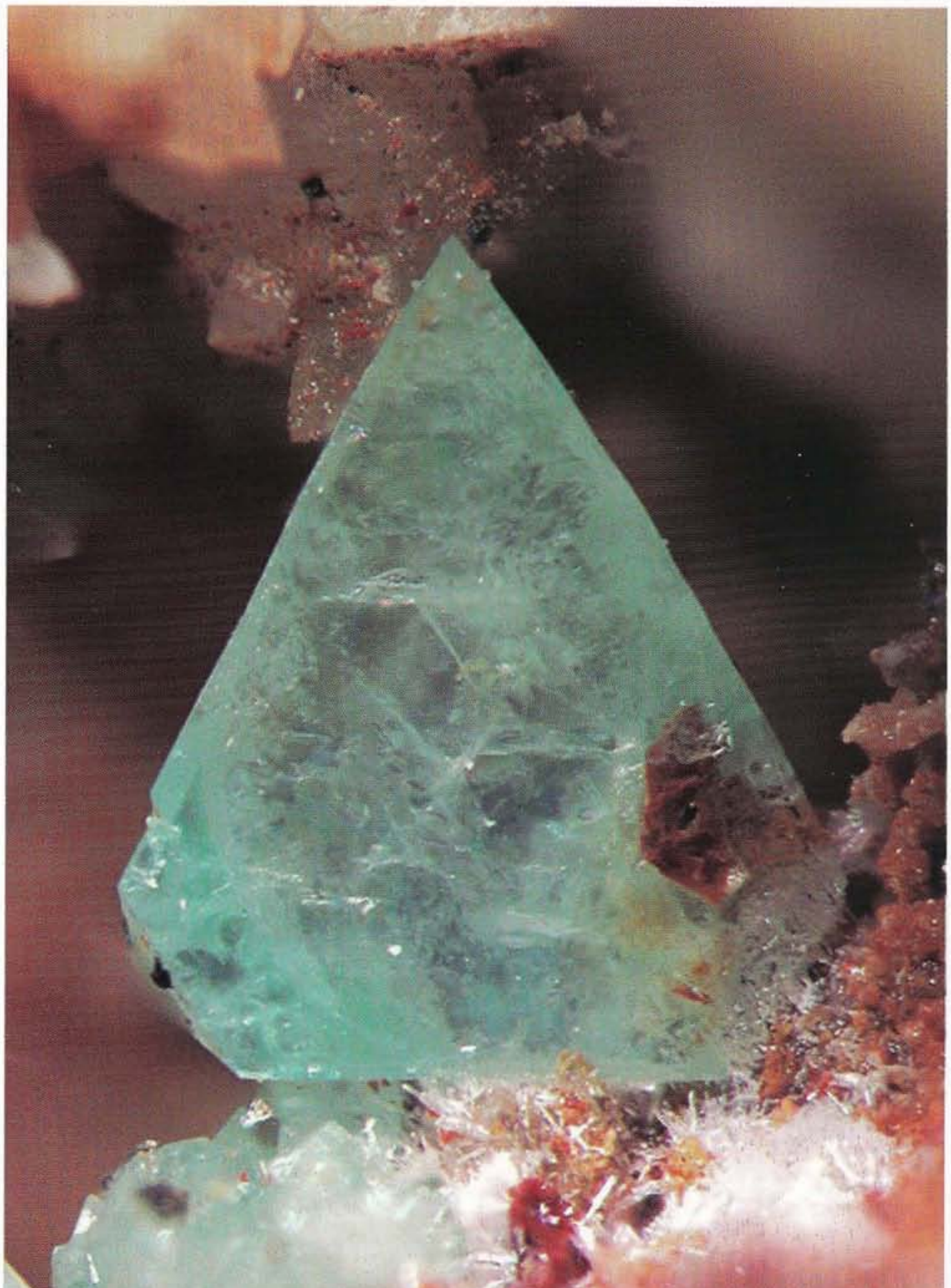
JOURNAL OF *The Russell Society*

Volume 11, 2008



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JOURNAL OF THE RUSSELL SOCIETY

The journal of British Isles topographical mineralogy

EDITOR:

Norman Moles, School of Environment and Technology, University of Brighton,
Cockcroft Building, Lewes Road, Brighton, BN2 4GJ

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

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Typography, Design and Printed by: Q3 Digital/Litho, Loughborough, Leicestershire LE11 1LE

Published by: The Russell Society. Registered Charity No. 803308.

ISSN 0263 7839

FRONT COVER:
Susannite ($Pb_4(SO_4)(CO_3)_2(OH)_2$) crystal 2.1 mm tall with characteristic trigonal symmetry, from Red Gill Mine, Caldbeck Fells, Cumbria, described by Bridges *et al.* in this volume. Specimen from the Peter Briscoe collection; David Green photograph.

BACK COVER:
Botryoidal pink rhodochrosite 45 mm across with black acicular manganite and some overgrowths of white botryoidal baryte, from Durnford Quarry, near Bristol, England. Chris Finch collection; David Green photograph. Photograph originally published in the UK Journal of Mines & Minerals no. 29 (2008).

NOTES FOR CONTRIBUTORS

TYPESCRIPTS

If possible, prepare papers in electronic format using Microsoft Word and send the file(s) as email attachment(s) to the Editor. Do not embed figures and tables within the text, but indicate where they should be inserted. Use 1.5 line spacing and number pages in the footer. At the end of the manuscript provide figure captions and any tables with their captions. Each paper will normally be reviewed by two referees. Submission of a paper to the Journal is taken to imply that it has not been considered for publication elsewhere. Material accepted for publication can not be published elsewhere in the same form without the consent of the Editor.

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

FORMAT AND PRESENTATION

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

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

FIGURES

All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Fig. 1, etc.

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

TABLES

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

TERMINOLOGY

Authors should adhere to the nomenclature and terminology of the International Mineralogical Association. The most recent Fleischer's Glossary of Mineral Species (at present the 10th edition, by Mandarino and Back 2008) can be used as a guide to mineral nomenclature, but where this conflicts with Hey's Mineral Index (1993) or Mineralogical Magazine and Mineralogical Abstracts usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (Acta Crystallographica, **22**, 45 (1967)).

ABBREVIATIONS

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

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

REFERENCES

References should be indicated in the text thus: (Brown, 1967) or 'as stated by Brown (1967)'; (Green and Brown, 1985) for two authors; (Green *et al.*, 1986) for three or more authors. If two or more references would give rise to identical citations in the text, they may be distinguished by appending 'a', 'b', etc. to the publication year. A list of references in alphabetical order should form the last section of each paper. Some examples of the style used are given below; note that journal names are given in full. Papers in press may be included provided they have been accepted for publication and the journal name is given.

Personal communications and unpublished work (except M.Sc. and Ph.D. theses), should not be included here but can be cited in the text, thus: (A. Brown, *personal communication* or *personal communication*, 1992), (B.C. Green, unpublished work). Likewise, references to Newsletters and similar publications will normally be cited in the text but not included in the reference list.

Bannister, F.A., Hey, M.H. and Claringbull, G.F. (1950). Connellite, buttgenbachite and tallingite. *Mineralogical Magazine*, **29**, 280-286.

Dewey, H. (1923). *Copper Ores of Cornwall and Devon*. Memoirs of the Geological Survey: Special Reports on the Mineral Resources of Great Britain, vol. **27**.

Heddle, M.F. (1901). *The Mineralogy of Scotland* (ed. by J.G. Goodchild), vol. **1**, p. 25. David Douglas, Edinburgh.

Jackson, N.J. (1977). *The Geology and Mineralization of the St Just District*. Unpublished Ph.D. thesis, University of London.

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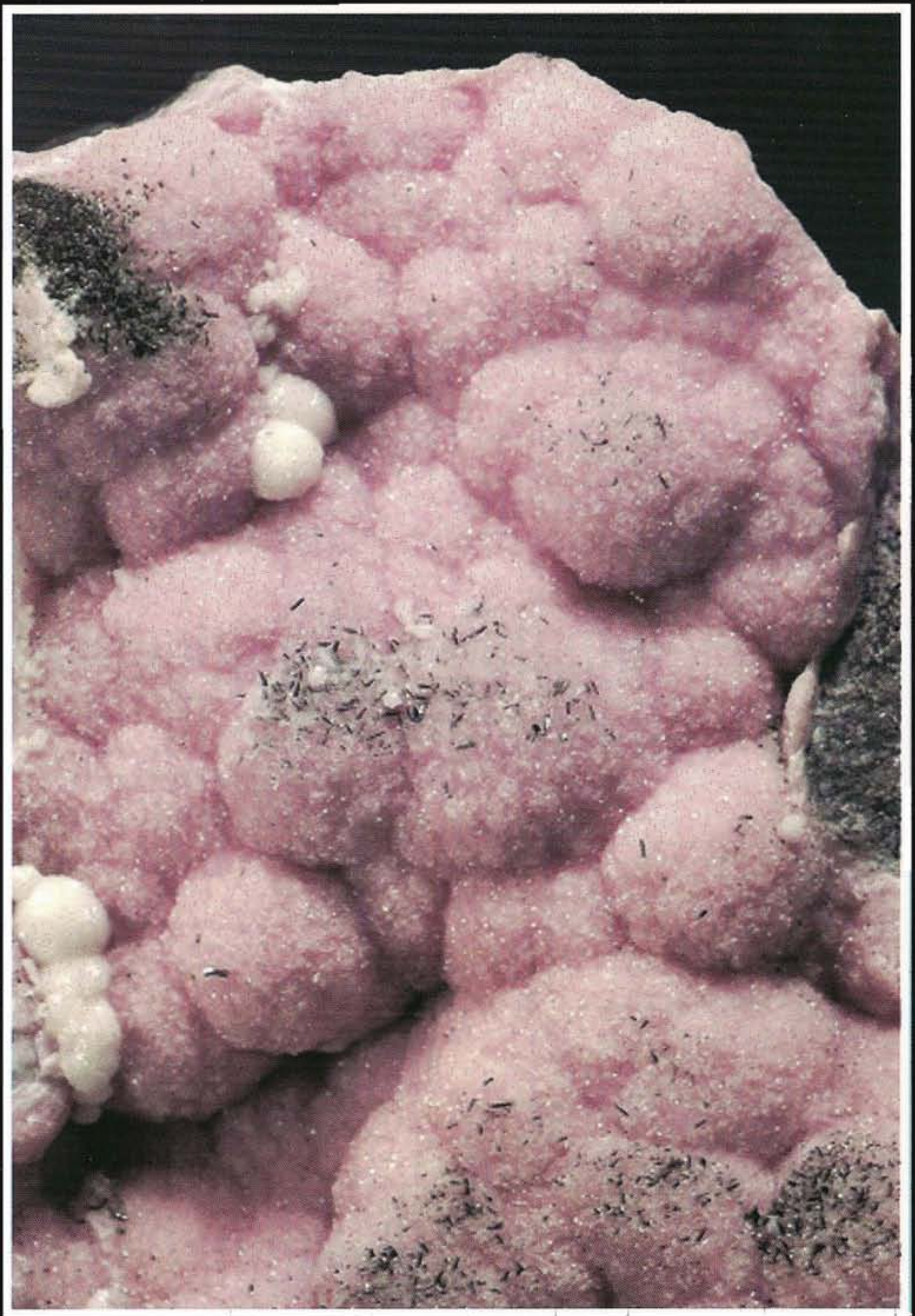

Journal of the Russell Society

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Volume 11, 2008

Editorial

Volume 11 is another 'bumper issue' with a fortuitous mix of articles, long and short, on minerals and localities throughout Britain and Ireland. These are illustrated with over 100 colour photographs. The editor is again indebted to the authors for providing excellent material, and to the reviewers for checking and suggesting improvements. Amongst the articles are descriptions of the first British occurrences of kombatite, calcioancylite-(Ce), heulandite-Sr and heulandite-Ba, and a review of the occurrences of the uncommon copper vanadate minerals volborthite and tangeite. Strontianite is described from County Mayo in Ireland, and post-mining stalactitic ranciéite from Parys Mountain (Mynydd Parys) in Anglesey. Short contributions record the first English occurrences of the calcium zeolite scolecite, and also from Cornwall, the lead tungstate stolzite. Rounding off the volume are reviews of two seminal mineral books published in 2008: 'Minerals of Northern England' by Bob Symes and Brian Young; and 'Minerals of Britain and Ireland' by Andy Tindle.

I am particularly pleased to include extracts from a comprehensive report by Lynda Garfield and David Wellings on mineral occurrences on Barry Island and adjacent areas of the Glamorgan coast. While the mineral species themselves are not especially rare or spectacularly formed, Lynda and David's report provides a fascinating insight to the geological history of the area, and their meticulous records set a precedent for others to emulate.

The first three articles in this volume, comprising half the total page length, are on the wonderfully varied mineralogy of the Caldbeck Fells in Cumbria. David Green and co-authors provide a comprehensive review of the mineralogy of higher Roughton Gill and draw attention to several rare and unusual minerals in samples collected during the decade before the restriction on collecting was introduced in 2000. They present a good case for collecting further material, from the screes and *in situ* vein structures, which may otherwise be lost to future research. Similarly, Trevor Bridges and co-authors document from the Red Gill Mine a significant number of new species found since Cooper and Stanley's 1990 compilation. In the third article, Trevor Bridges and David Green provide evidence for baryte formation in supergene environments and discuss the interesting chemical problem this raises.

Current opportunities for mineral collecting in Britain and Ireland do not compare with the halcyon days of the Victorian collectors and indeed of the relatively restriction-free period in the mid–20th Century. Nonetheless discoveries are still being made, some spectacular, as evidenced by the cover photographs and articles in this volume and in volume 29 (2008) of the UK Journal of Mines & Minerals. Michael Wolfe, compiler of the Mineral News article in UKJMM 29, remarked that "a resurgence in metal mining in Britain is almost certain to produce material of interest to collectors" [and to researchers, I would add]. We can only hope that the financial crisis besetting Britain and the World in the latter half of 2008, does not scupper investment in these mining ventures.

Scottish Natural Heritage has recently published a Scottish Fossil Code (a flier and the full document are available to view and download from www.snh.org.uk) which encourages responsible collecting of, and care for, fossil specimens. The code declares that "fossil collecting is an essential activity that provides the basic material and data for the science of palaeontology". We all need an equivalent declaration to raise the profile of mineral collecting, which provides the basic material and data for the science of mineralogy!

Norman Moles

Journal of the Russell Society, **11**, 3-28 (2008)

A REVIEW OF THE MINERALOGY OF THE ROUGHTON GILL MINES, CALDBECK FELLS, CUMBRIA: PART 2
THE ROUGHTON GILL SOUTH VEIN ON BALLIWAY RIGG

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

Trevor F. BRIDGES
10 Springfield, Ovington, Prudhoe, NE42 6EH

Michael S. RUMSEY
The Natural History Museum, Cromwell Road, London, SW7 5BD

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

Andrew G. TINDLE
Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA

The Roughton Gill South Vein crops out along a strike length of a few hundred metres in intrusive igneous rocks of the Carrock Fell Complex on the southeastern flank of Balliway Rigg in higher Roughton Gill, Caldbeck Fells, Cumbria. A number of mine workings exploited the vein in this area, but they are small and have left little mineralised spoil. A considerable amount of veinstone is present in natural scree on Balliway Rigg and this is the source of almost all the specimens we have examined. The primary mineralisation comprises galena, chalcopyrite and sphalerite in a quartz-carbonate gangue with some baryte. Weathering has removed most of the primary carbonate at the surface exposures of the vein, producing extensive screes containing bleached white quartz.

About fifty supergene minerals are described. Pyromorphite, mimetite, cerussite, hydrocerussite, malachite, goethite and 'chrysocolla' are widespread and abundant. An oxidised galena vein at the southwestern end of the exposure produced a suite of rare lead-bearing supergene minerals including lanarkite, leadhillite, mattheddleite, scotlandite and susannite. Most of the other rare supergene species were found in loose blocks of veinstone. Minerals reported for the first time from the Roughton Gill mines as a result of this study include bario-pharmacosiderite, cesàrolite, chenite, cinnabar, connellite, coronadite, cryptomelane, kintoreite, lepidocrocite, phosphohedyphane, romanèchite, segnitite and silver.

Published data describing the minerals of the Caldbeck Fells is complicated by the claims of Arthur Kingsbury, some of which are fraudulent. Kingsbury visited higher Roughton Gill from 1950 on, and claimed a number of unusual minerals from the locality in papers published between 1957 and 1960. Some of his specimens are clearly genuine, but the members of the alunite-jarosite group and carminite give cause for concern, as they do not resemble the well provenanced specimens we have examined in this study.

INTRODUCTION

The Caldbeck Fells, at the northern edge of the English Lake District, hosts one of the most remarkable and diverse mineral assemblages in the British Isles (Young, 1987; Cooper and Stanley, 1990, 1997; Tindle, 2008). The workings at the head of the Dale Beck valley, which are often collectively described as the Roughton Gill mines, are perhaps the best known of all Caldbeck Fells localities. Their mineralogical fame rests with the remarkable specimens of hemimorphite, pyromorphite and plumbogummite that were collected during the last major working of the mines in the Victorian era. These are eagerly sought by modern day collectors and displayed in museums across the world. Superb specimens of linarite were also claimed in the nineteenth century, but although linarite occurs at the Roughton Gill mines, there is good evidence to suggest that the best specimens originated in the nearby workings of Red Gill Mine (Bridges *et al.*, 2008).

The mineralogy of a number of localities in the Dale Beck valley including the Silver Gill mines (Green *et al.*, 2005), Brae Fell Mine (Bridges *et al.*, 2006), and Red Gill Mine (Bridges *et al.*, 2008) has recently been reviewed. There has also been a recent detailed description of the mineralisation at the Driggith and Sandbed mines (Green *et al.*, 2006), which lie on the strike extension of the Roughton Gill South Vein. In the studies completed so far, the mineralogy of sites that are well defined geographically and geologically is described, following the topographic conventions established by Cooper and Stanley (1990). This has proved difficult when dealing with workings that are as complex and diverse as the Roughton Gill mines. We have therefore divided the mines into smaller areas (Fig. 1) and will concentrate on each of these in turn. Our review of the mineralogy of the Silver Gill mines (Green *et al.*, 2005) should be considered to be the first of these. This report, which describes minerals from the Roughton Gill South Vein on the flank of Balliway Rigg in higher Roughton Gill, is the second. A third study, led by TFB, will describe the minerals on the extensive spoil heaps derived from the 30-, 60- and 90-fathom levels of Roughton Gill Mine. We also plan to review the Mexico Mine workings and material found at the exposures of the South Vein on Iron Crag. All the workings in this area are notified as a Geological

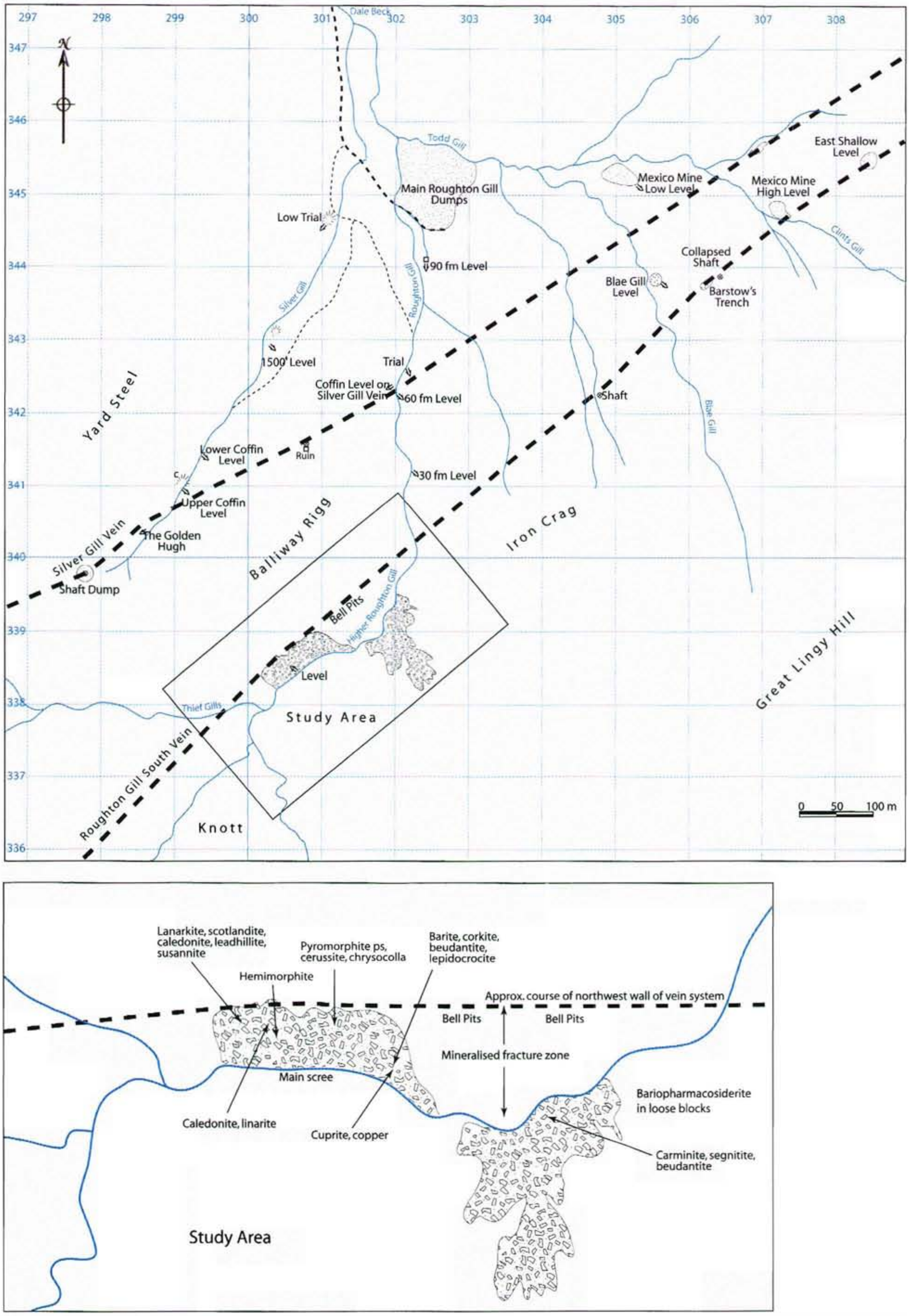

Figure 1. A sketch plan of the workings in higher Roughton Gill showing the extent of the study area and its relationship to the nearby workings at the head of the Dale Beck valley. Approximate locations of some of the more unusual mineral discoveries are marked, but unfortunately most of the specimens were collected before the widespread availability of hand-held GPS and it has not been possible to give precise grid references. ps = pseudomorph.

Conservation Review (GCR) site as part of Skiddaw Massif Site of Special Scientific Interest (SSSI); they are also of archaeological interest and are designated as 'Red Zone' by the Lake District National Park Authority (LDNPA). This means the collecting of geological specimens is effectively forbidden.

The objective of this study is to review and expand upon the existing knowledge and understanding of the mineralogy of the site. A full description of a remarkable assemblage of rare lead minerals that were collected in 1988-9 *in situ* at the southwest end of the South Vein is included (this discovery was made just as Cooper and Stanley (1990) was being finalised and is only briefly noted in their account). There are also a surprising number of more recent discoveries, including some remarkable plumbogummite specimens, rich specimens containing cuprite, copper and connellite, and two supergene arsenate assemblages, both of which include members of the alunite-jarosite group with highly variable chemical compositions. In common with our previous work there is a re-examination of any data based on specimens claimed to have been collected by Arthur Kingsbury, which was summarised in good faith by Hartley (1984), but which in some cases has been shown to be doubtful or fraudulent (Ryback *et al.*, 1998; 2001; Tindle, 2008). A careful re-examination of Kingsbury's material is important, to set the record straight and to make his collection more useful to researchers in the future.

Roughton Gill (the name is derived from the ancient Norse word for roaring) drains boggy moorland on the northern flank of Knott, which at 2329 feet is the most commanding of the fells in the northern half of the Skiddaw Massif. A fan shaped group of tributary streams, which are collectively described as the Thief gills, coalesce to produce a short, steeply incised, hanging valley, which is generally described in the mineralogical literature as higher Roughton Gill. The valley has a fairly shallow gradient for about 300 m until the stream turns north and tumbles in a series of steep cascades towards the 90-fathom level dumps of Roughton Gill mine. Here it joins with a number of other tributary streams including Silver Gill and Todd Gill, and later with Swinburn Gill, to form Dale Beck.

The Roughton Gill mines exploited two major northeast-southwest trending vein systems, and include workings that can be attributed to many different periods of mining (Postlethwaite, 1913; Shaw, 1970; Adams, 1988; Cooper and Stanley, 1990; Smith *et al.*, 2001; Jecock *et al.*, 2001). It is worthwhile noting in these introductory paragraphs that there is some inconsistency in relation to the naming of the veins: we follow the convention established by Cooper and Stanley (1990) which describes the Roughton Gill North and South veins as part of the same fracture system, although separated by large 'horses' or plates of country rock. This nomenclature is based on observations made in the underground workings; the two separate veins are not at all obvious in the relatively poor scree covered surface exposures in higher Roughton Gill, where the mineralisation appears to be developed within a wide fracture system containing parallel running quartz veins. In our work and in Cooper and Stanley (1990) the Silver Gill Vein is the name used to describe the second major northeast-southwest trending mineralised fracture system that crosses the head of the Dale Beck valley, 100 – 200 m to the northwest of the South Vein (Fig. 1). Readers should note that some publications describe the Silver Gill Vein as the Roughton Gill North Vein and also that the sketch plan (Fig. 1) is a considerable simplification of the structure of the vein system.

This study concentrates on the mineralisation that is present along natural exposures of the Roughton Gill South Vein on the flank of Balliway Rigg in higher Roughton Gill. A few grassed-over bell pits and some small trials lie within the study area, which is defined in the accompanying sketch map (Fig. 1). Little is known of the history of these workings; they were excluded from the detailed archaeological surveys produced by Jecock *et al.* (2001), although they are probably ancient and likely to be of importance in framing an understanding of mining in the area (e.g. Smith *et al.*, 2001). They are marked in some detail on a plan of the Roughton Gill mines dated 1825, which is reproduced in Cooper and Stanley (1990, p.58) and in a different version in Adams (1988, p.71). A short description of the mining landscape has recently been produced by Tyler (2006): in higher Roughton Gill he notes a shallow level driven from the northeast to undercut the South Vein, a short level driven directly toward the vein from the gill bed and two levels near the confluence of the Thief gills, which are described as Dobson's Dam Trial and Thief Gill Lead Mine. Although the remains of some of these workings are evident, they are of peripheral interest in this description as relatively little mineralised spoil is present on the dumps.

The various workings at the head of the Dale Beck valley are simply and collectively described as Roughton Gill Mine in most early accounts of the mineralogy of the area (e.g. Greg and Lettsom, 1858). Indeed the term 'Roughton Gill' was used in the nineteenth century as a 'catch-all' to describe almost any working in the Dale Beck valley (see Bridges *et al.*, 2008). For this reason, relatively little use has been made of the abundant material in nineteenth century museum collections labelled 'Roughton Gill'.

The Roughton Gill workings began to be differentiated in the studies of Davidson and Thomson (1951), a trend continued by Arthur Kingsbury (Kingsbury and Hartley, 1957a,b; 1958; 1960; Hartley, 1984), who produced extremely detailed labels to accompany some of the specimens in his collection and described a considerable number of unusual minerals from the South Vein in higher Roughton Gill. Most of the modern collections we have examined clearly differentiate specimens collected in higher Roughton Gill from those found in other parts of the sett.

GEOLOGY

The classic account of the geology of the Caldbeck Fells and surrounding areas is provided by Eastwood *et al.* (1968) in a sheet memoir that accompanies the one-inch map. In the forty years since it was published the area has been re-surveyed (e.g. British Geological Survey, 1997), and there has been a considerable re-interpretation of its geological history (see for example Cooper *et al.*, 2004, for an in-depth discussion of the Skiddaw Group, which crops out just to the southwest of our study area). The rocks within the study area belong almost entirely to the Carrock Fell Complex and are briefly described by Eastwood *et al.* (1968), who note ilmenite-rich melagabbros with a variable amount of pink felsic granophyric material in patches and irregular veins. A modern and accessible account of these rocks is provided by David Millward in Stephenson *et al.* (2000); this description is based primarily on his interpretation.

The Carrock Fell Complex comprises multiple sheet-like intrusions with mafic and felsic components. It is emplaced between the rocks of the Skiddaw and Eycott Volcanic groups and crops out over an area about 6km from east to west and 2km from north to south between Carrock Fell and the headwaters of Roughton Gill. At its western edge at the head of the Dale Beck valley, the complex contains three small and rather unusual felsic intrusions, which extend along the Roughton Gill and Dry Gill Fault systems. These are the Iron Crag and Red Covercloth microgranites and the Harestones Rhyolite.

In higher Roughton Gill, the northwestern wall of the vein system, which occupies a major fault, is made up of apatite-bearing ferrodiorite, an intrusive igneous rock which is part of the Carrock Division of the Carrock Fell Complex. The vein system is largely contained by the feldspar-phyric Iron Crag Microgranite, a fault bounded intrusive igneous body that post-dates the rocks of the Carrock Division and may be unrelated to them (Stephenson *et al.*, 2000). To the southwest of our study area, there is an interesting subhorizontal contact where the rocks of the Carrock Fell Complex are overlain by andesitic rocks of the Eycott Volcanic Group. As the vein is followed further in this direction, it passes into mudstones, siltstones and sandstones of the Bitter Beck Formation, which is part of the Ordovician Skiddaw Group. It is not well mineralised in these strata.

The Roughton Gill South Vein occupies the south-western part of an extensive NE-SW trending mineralised fracture system that can be traced between the Thief gills and the northeastern edge of the Caldbeck Fells near Wood Hall. Five separate northeast-southwest trending veins are mapped crossing Iron Crag to the northeast of our study area by the British Geological Survey (1997). The three northern veins appear to be part of the fracture system described by Cooper and Stanley (1990) as the Silver Gill Vein, whereas the two southern ones are continuous with the fracture system exploited by the Sandbed and Driggith mines, which is described as the Roughton Gill South Vein.

The vein exposures in higher Roughton Gill are poor and transient and archaeological concerns have made it impossible to get a clear picture of the structure. Our limited observations suggest that the fracture system is in excess of thirty metres wide and that it contains predominantly quartz veins varying from a few millimetres to more than a metre in width, with a general northeast-southwest trend.

MATERIAL SOURCES

Our review summarises published data, but is primarily based on analyses of specimens of reliable provenance. Restrictions introduced in 2000 to protect the archaeological remains in higher Roughton Gill mean we have not been able to do any field collecting at the site. Since most specimens were collected before the widespread use of hand-held GPS technology, it has not always been possible to provide as accurate a provenance as we would have liked. Nonetheless we are confident that all of the specimens we describe originated from the study area. The sketch map (Fig. 1) provides an approximate guide to where some of the more unusual minerals were found.

We have been fortunate to have been allowed access to the extensive collection of Norman Thomson, including material collected from the 1940s onward, and to a number of more recent collections which have excellent associated data. The principal public collection examined in this study was at the Natural History Museum (NHM), which includes the Arthur Kingsbury Collection. Private collections belonging to Richard Bell (also comprising material from the late Mike Rothwell and John Dickinson), Peter Briscoe, William Creighton, David Charlton, Tony Rigby, David McCallum, Mike Leppington, Trevor Bridges, and George Wilson were also examined.

ANALYTICAL TECHNIQUES

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

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

Certain minerals require quantitative chemical analyses in addition to XRD and EDS data to identify them to species level. Analyses by wavelength dispersive spectrometry (WDS) were carried out in a limited number of cases to establish precise chemical compositions. Crystallites were hand-picked from the specimens under study, embedded in resin and polished to produce a flat surface. Analyses were made at 20 kV, 20 nA with a 15 micron beam diameter using a Cameca SX100 electron microprobe. Count times of 10 seconds were used to minimise decomposition during data collection. A significant amount of WDS data on the lead-bearing minerals of the alunite-jarosite group and on the closely related species pyromorphite, mimetite and phosphohedyphane are included as chemical formulae in the descriptions that follow.

MINERALS

Most of the minerals described below were collected from loose blocks found in natural screes below the Roughton Gill South Vein in higher Roughton Gill. Although it seems very likely that they originated from the southwest-northeast trending vein system, it is impossible to be absolutely certain in every case. A few specimens (largely of supergene arsenates) were collected from a scree on the east side of the valley (see Fig. 1 for the precise localities), these are probably also part of the

South Vein mineralisation as the fracture zone is relatively wide, but it is impossible to be absolutely sure as no *in situ* exposure was found. They are described here because of their close spatial association.

Where an identification is based on modern analysis or a sound literature reference, the sub-title is capitalised; if there is some uncertainty associated with an identification or further investigation is required the sub-title is given in lower case; where identifications are likely to be based on fraudulent specimens, or the minerals are not part of the natural assemblage, the sub-title is italicised.

Acanthite, Ag_2S

Characteristic minute spiky clusters of the silver sulphide mineral acanthite (identified by EDS) have developed on all of the silver specimens we have examined while they were in storage. This chemical process affects supergene silver from many localities, notably the nearby Red Gill Mine (Bridges *et al.*, 2008) and Force Crag Mine (Green *et al.*, 1997). Acanthite cannot be considered a part of the natural mineral assemblage since it develops after specimens have been collected. Storage in a low humidity environment seems to prevent the chemical reaction, which if allowed to proceed unchecked can completely replace the silver on a specimen in a period of a few years.

ANGLESITE, $PbSO_4$

A few anglesite specimens displaying blocky to bladed crystals up to about 5 mm in length were collected in the late 1980s at the southwest end of the scree that stretches along the flank of Balliway Rigg in higher Roughton Gill. Others have been found in the galena-rich blocks of vein quartz that are exposed by periodic flooding (Fig. 2). The largest crystal found in this study is a broken white blade 14 mm long in a quartz cavity with wulfenite and calcium-rich pyromorphite. Anglesite is most commonly found with bindheimite, caledonite, linarite and sulphur and is often associated with partly oxidised galena.

Anglesite crystals from Roughton Gill up to 25 mm in length are in the collection of the Natural History Museum (Cooper and Stanley, 1990), but they are not well localised. Anglesite was noted by Hartley (1984) as part of the assemblage that he had collected with Arthur Kingsbury in the 1950s from the South Vein, but there are no notable specimens in the Kingsbury Collection.

Figure 2. Steeply pyramidal anglesite crystals up to 5 mm long in a cavity in quartz with somewhat corroded octahedral galena. Mike Leppington Collection.

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

Aurichalcite occurs rarely as pale blue to turquoise millimetre-size aggregates of radiating, lath-like crystals and occasionally as randomly disposed blue to blue-green blades in cavities in quartz veinstone. In higher Roughton Gill, and at many of the other localities in the immediate area, aurichalcite is less common than the chemically similar mineral rosasite.

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

An azurite specimen in the R. J. King collection at the National Museum Wales, with crystals up to 15 mm long, is reputed to be from higher Roughton Gill (Cooper and Stanley, 1990). If genuine it is by far the best example of the species from the Caldbeck Fells. No similar specimens have ever been found, and the history of the specimen, which was obtained from an old collection by the north-of-England mineral dealer W. F. Davidson, is sufficiently uncertain that we consider the occurrence remains unproven. The presence of large crystals of azurite, a mineral which requires a relatively high partial pressure of CO_2 to crystallise, is geochemically unlikely in the Caldbeck Fells.

BARIOPHARMACOSIDERITE, $Ba_{0.5}Fe_4(AsO_4)_3(OH)_4{\cdot}6H_2O$

Bariopharmacosiderite (formerly barium pharmacosiderite) is the current IMA approved name for the barium-dominant member of the pharmacosiderite group. It is common in small amounts in the Caldbeck Fells (e.g. Tindle, 2008), but often confused with pharmacosiderite. The two species are easily distinguished by chemical analysis. Three specimens from the scree on the eastern side of Roughton Gill were examined by EDS and all proved to be bariopharmacosiderite. The best specimens, with areas to several square centimetres encrusted in dark green pseudo-cubic crystals to 2 mm (Fig. 3) were found in scree on the east side of Roughton Gill at the extreme northeastern edge of the study area (Tony Rigby, *personal communication*). Bariopharmacosiderite occurs in thin fractures in iron and manganese oxide rich wallrock and is often partially coated by minute spherules of an iron oxide mineral.

Yellow-brown to pale green pseudo-cubic crystals and occasional anhedral masses of bariopharmacosiderite with beudantite and carminite have been collected from scree blocks a few metres east of the beck, nearer to the main vein exposure.

Figure 3. Dark green cubic crystals of bariopharmacosiderite up to 1 mm on edge collected from loose scree on the east side of the valley. Tony Rigby Collection.

BARYTE, $BaSO_4$

Primary white baryte is a generally late-stage component of the vein filling along the South Vein in higher Roughton Gill. Occasional colourless to white, tabular to blocky crystals, which are probably supergene in origin, occur with lead and copper secondaries in cavities in vein quartz. Well formed millimetre-size white, rhombic baryte crystals, which are clearly supergene since they occasionally encrust lepidocrocite, occur on specimens from an iron and arsenate bearing assemblage at the northeast end of the vein exposure (Fig. 4). Smaller, but otherwise similar crystals are present in an arsenate-rich assemblage found in scree on the east side of higher Roughton Gill.

Figure 4. Blocky white baryte crystals up to about 0.3 mm across with colourless transparent outer zones associated with minor yellow beudantite from screes below the South Vein on the west side of the valley. Mike Leppington Collection.

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

Beaverite was claimed from the outcrop of the South Vein on Balliway Rigg by Kingsbury and Hartley (1957b, 1960), but was not noted in an unpublished manuscript describing the minerals of the area in 1951. The specimens in the Kingsbury collection are rather non-descript, comprising beaverite, galena and somewhat corroded cerussite. They are not similar in appearance to any material of undoubted provenance collected in the recent past, and given Kingsbury's proven propensity for mislabelling and the probable late date of collection, they cannot be considered trustworthy.

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

Beudantite was identified by XRD and WDS as yellow to brown euhedral rhombic crystals up to about 0.2 mm on edge, which are sometimes aggregated into spherical masses (Fig. 5). It also forms crusts on iron-stained quartz. Beudantite occurs with baryte and lepidocrocite in cellular quartz veinstone found in screes at the northeast end of the exposure of the vein in higher Roughton Gill. Screes on the east side of the valley produced well formed yellow to dark brown rhombic to pseudo-cubic crystals in an iron-stained matrix. The exact source of these latter specimens, which are sometimes associated with well-crystallised carminite, is unknown.

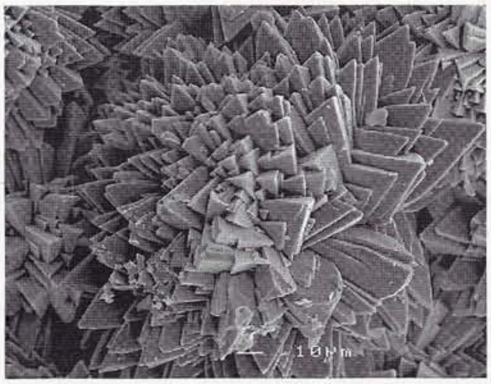

Figure 5. SEM photograph showing radiating rhombic aggregates of beudantite up to about 0.05 mm on edge.

Average chemical formulae determined by WDS for two beudantite grains from the east side of the valley are:
$Pb_{1.11}Cu_{0.04}Fe_{2.76}Al_{0.31}(AsO_4)_{1.19}(SO_4)_{0.67}(PO_4)_{0.14}(OH,H_2O)_6$ and
$Pb_{1.12}Cu_{0.04}Fe_{2.64}Al_{0.11}(AsO_4)_{1.30}(SO_4)_{0.69}(PO_4)_{0.01}(OH,H_2O)_6$.
A grain from the west side of the valley yielded:
$Pb_{1.10}Cu_{0.05}Fe_{2.60}Al_{0.11}(AsO_4)_{1.22}(SO_4)_{0.78}(PO_4)_{0.01}(OH,H_2O)_6$.

Beudantite was noted with carminite at Balliway Rigg in an unpublished manuscript prepared by Arthur Kingsbury in 1951. It was later described with a variety of other minerals including, jarosite, plumbojarosite and beaverite by Kingsbury and Hartley (1960). The claimed Roughton Gill alunite-jarosite group specimens in the Kingsbury collection are not particularly spectacular but they do not give the impression of a coherent group, which were all collected from the same locality. Many of the other specimens on which the 1960 'carminite and beudantite' paper is based, including for example beudantite with olivenite from Dry Gill Mine, and beudantite from Ingray Gill, are almost certainly fraudulent. Kingsbury's beudantite specimens cannot be considered trustworthy.

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Bindheimite was identified by EDS as pale yellow powdery encrustations in cavities in quartz-galena matrix with cerussite, caledonite, leadhillite and malachite. It is quite common in cavities in quartz veinstone near partially oxidised galena, but the friable, powdery nature means that most specimens do not survive washing in water.

Arthur Kingsbury considered his discovery of bindheimite in 1950 on the flank of the South Vein in higher Roughton Gill to be the first British occurrence of the mineral (see Cooper and Stanley, 1990). There are half a dozen large bindheimite bearing specimens in the Kingsbury Collection that are almost certainly from Balliway Rigg, but not explicitly labelled as such. They appear very similar to material collected from the locality in the recent past and there is no reason to doubt their authenticity. Unfortunately, the only specimen labelled

Balliway Rigg in Kingsbury's collection is atypical: rather than the usual powdery pale yellow coating, the bindheimite forms more solid infills in cavities within an iron-oxide rich quartz matrix.

BORNITE, Cu_5FeS_4

Metallic purple bornite was identified on a single specimen in intimate intergrowth with chalcopyrite. Minerals such as bornite, which are characteristic of the zone of supergene sulphide enrichment, are rare in higher Roughton Gill, most of the chalcopyrite in the South Vein is oxidised to goethite.

Bournonite, $PbCuSbS_3$

Bournonite was noted intergrown with galena from workings on the South Vein in higher Roughton Gill in an unpublished manuscript by Arthur Kingsbury (Cooper and Stanley, 1990). We have been unable to find any bournonite labelled from higher Roughton Gill in the Kingsbury Collection, but the mineral has been found as microscopic inclusions in galena on the strike extension of South Vein at Driggith Mine (Stanley and Vaughan, 1981). Although the record is quite likely to be correct, it is perhaps best considered unproven.

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

A brochantite occurrence in 'Thief Gills' (which in fact refers to the outcrop of the South Vein on Balliway Rigg, Norman Thomson, *personal communication*) was noted by Davidson and Thomson (1951). Brochantite was identified in this study as drusy crusts on goethite and as occasional earthy masses and encrustations associated with partially oxidised sulphides on vein quartz.

CALCITE, $CaCO_3$

Calcite is uncommon in the quartz veinstone at higher Roughton Gill. A few rather etched translucent white crystals up to about 3 mm long with shallow pyramidal terminations were identified by EDS in this study.

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

A number of small but rich caledonite specimens were collected in the late 1980s at the southwest end of the South Vein exposure on Balliway Rigg. Caledonite occurs here in a variety of habits, varying from pale blue velvety encrustations (Fig. 6), and radiating sprays of acicular crystals (Fig. 7), both of which are common, to deep blue elongated prismatic crystals, which are rather rare. The largest crystals are a little under a millimetre in length and encrust cavities in quartz-galena matrix up to about 10 mm across. Leadhillite, susannite and mattheddleite are common associated species. More recently, specimens to large hand size displaying millimetre sized caledonite crystals associated with dark blue bladed linarite in cavities in vein quartz were found at the top of the scree exposure near the southwestern end (Tony Rigby, *personal communication*). The crystals often occur as sky-blue laths, and more occasionally as striated prisms (Fig. 8) lining cavities in white vein quartz with linarite, leadhillite and susannite.

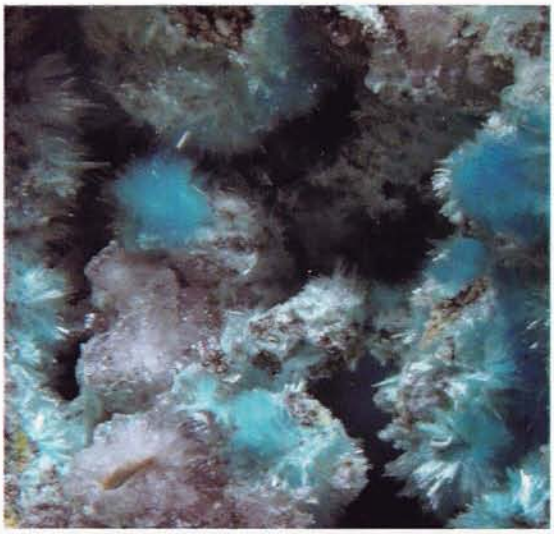

Figure 6. Feathery caledonite crystal aggregations up to 0.7 mm across from the lead vein at the southwestern end of the exposure. David McCallum Collection.

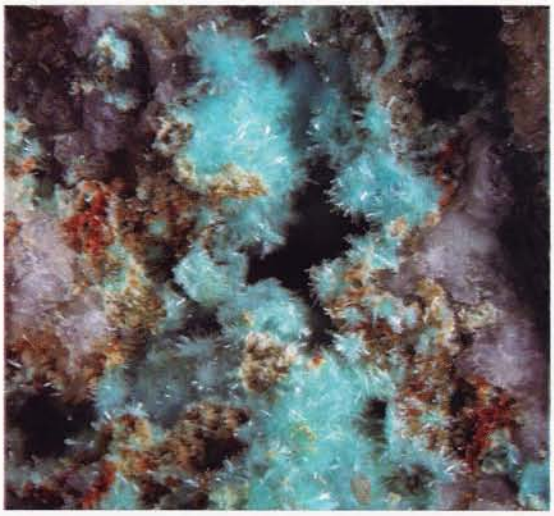

Figure 7. Acicular pale blue caledonite up to about 0.4 mm in length from the lead vein at the southwestern end of the exposure. David McCallum Collection.

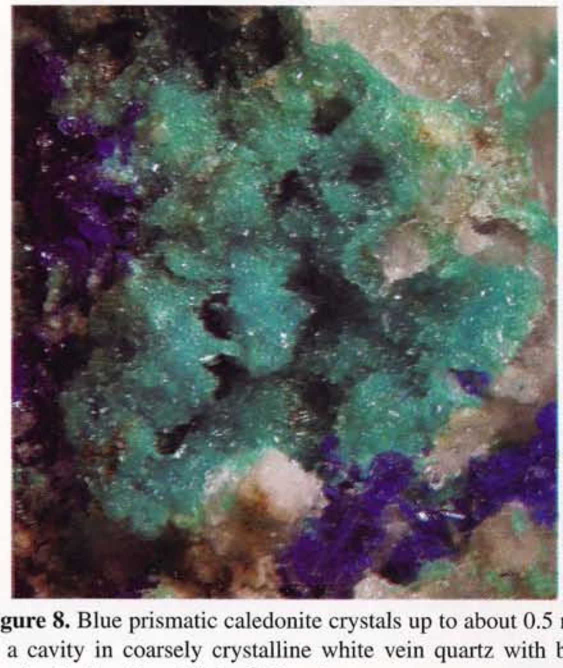

Figure 8. Blue prismatic caledonite crystals up to about 0.5 mm in a cavity in coarsely crystalline white vein quartz with blue linarite blades. Tony Rigby Collection.

The outcrop of the South Vein on the flank of Balliway Rigg appears to be the only area of the 'Roughton Gill mines' where caledonite is at all common. It was noted by Davidson and Thomson (1951) and by Hartley (1984) from the South Vein in this area and it may be that this is the source of some nineteenth century specimens that are labelled 'Roughton Gill'. The crystal habit in higher Roughton Gill is typically rather fine and feathery, in contrast to the more blocky habit that is characteristic of Red Gill Mine. A particularly rich specimen of feathery caledonite with susannite from the Henry Ludlam collection (which is labelled 'Roughton Gill') is figured in Cooper and Stanley (1990, p.129).

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

Carminite was identified by XRD (to differentiate it from mawbyite) and EDS in material found in a scree on the east side of the valley at the northeastern end of the study area. Characteristic deep red pointed prismatic crystals up to about 0.1 mm in length (Figs 9 and 10) accompany segnitite in small cavities in thin veins in quartz-rich wallrock. Carminite is also almost certainly present as minutely drusy deep red resinous encrustations in specimens found loose in screes on the west side of the valley, but they are too small for analysis by XRD.

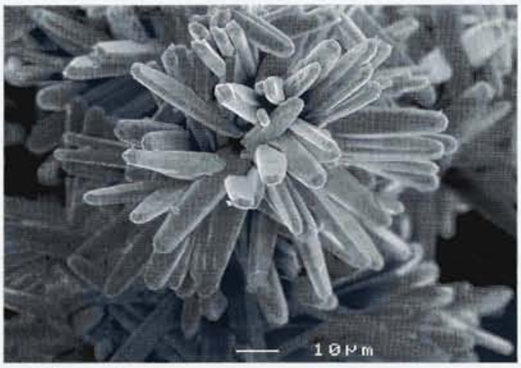

Figure 9. SEM photograph showing steeply pyramidal carminite crystals up to about 0.03 mm in length with four or six shallow terminating faces, from screes on the east side of the valley.

Figure 10. Deep carmine red carminite with crystals up to about 0.2 mm long associated with yellow-brown segnitite and a pale green corroded mass of bariopharmacosiderite. Mike Leppington Collection.

Carminite was claimed from the outcrop of the South Vein in higher Roughton Gill by Kingsbury and Hartley (1960). The Kingsbury specimens are different from any that we have collected, but they closely resemble classic material from Tintic, Utah, USA. They comprise mimetite, beudantite and carminite, with grey copper sulphides, chalcopyrite and arsenopyrite. The sulphide assemblage is unlike anything we have found along the exposure of the South Vein in higher Roughton Gill. The Kingsbury carminite specimens are likely to be fraudulent.

CERUSSITE, $PbCO_3$

Cerussite is common and widespread along the exposure of the South Vein in higher Roughton Gill. It occurs as colourless to white, acicular, blocky, prismatic and tabular crystals, which are commonly twinned (Fig. 11). Pyromorphite epimorphs after cerussite were described by Davidson and Thomson (1951) from 'Thief Gills' and excellent specimens up to 40 mm in length were collected in the relatively recent past by William Creighton (Fig. 12). Cerussite is intergrown with hydrocerussite on some specimens and it is occasionally found with caledonite (Fig. 13).

Figure 11. Thin platy cerussite twins to 3 mm on iron stained quartz matrix. David McCallum Collection.

Figure 12. Pyromorphite as pseudomorphs and epimorphs up to 40 mm long after cerussite and hydrocerussite. Manchester Museum Collection, accession number N15561.

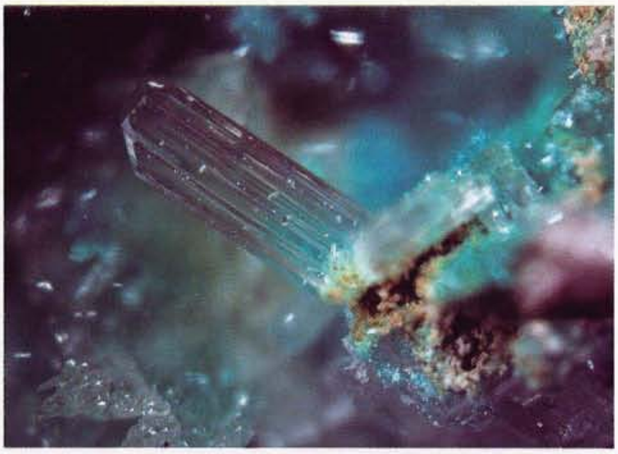

Figure 13. A striated colourless cerussite crystal 2.5 mm in length in a cavity lined with prismatic caledonite and susannite. Mike Leppington Collection

CESÀROLITE, $PbH_2Mn_3O_8$

Cesàrolite is an uncommon lead manganese oxide that was reported for the first time in the British Isles at Eaglebrook Mine, Ceredigion, Wales (Cotterell, 2006); it also occurs at Frongoch Mine in the same general area (Cotterell, 2007). Relatively few manganese oxide minerals were available for study from the exposures in higher Roughton Gill, despite comments about their relative abundance in a number of articles (e.g. Davidson and Thomson, 1951). Cesàrolite was identified by a combination of XRD and EDS as a dull, black, rather earthy botryoidal crust on a single specimen in the Mike Leppington Collection. This is the first report of cesàrolite in the Caldbeck Fells, although it has previously been identified by XRD at Short Grain (NY 3130 3585) (authors' unpublished data).

CHALCOPYRITE, $CuFeS_2$

Chalcopyrite is the commonest primary copper mineral in the vein exposure. It occurs as idiomorphic masses in quartz veinstone, these are sometimes bright and unoxidised, but more commonly partly replaced by goethite. Blue and green oxidation rims commonly surround chalcopyrite.

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

Chenite is a rare mineral that has been reported from three localities in the Caldbeck Fells: Driggith Mine, Short Grain and Red Gill Mine (Green and Hubbard, 1996; Green *et al.*, 2006; Bridges *et al.*, 2008, Tindle, 2008). The two chenite specimens we have examined in this study are in the Mike Leppington Collection. Characteristic pale blue monoclinic blades up to 0.25 mm in length occur in cavities in vein quartz. Insufficient material was available for analysis by XRD, but a comparison of the EDS spectrum of the specimen with undoubted chenite is considered sufficient to differentiate it from caledonite, the only other lead copper sulphate with which it might be confused.

Chrysocolla, $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$

The name 'chrysocolla' is in common use to describe any blue or green botryoidal amorphous-looking copper silicate mineral from the Caldbeck Fells. 'Chrysocolla' is a difficult mineral to characterise as neither the formula nor the crystal structure are well defined. A study of 'chrysocolla' from Arizona (Sun, 1963) concluded that it was not a definite chemical compound, but a hydrogel containing SiO_2, CuO and H_2O with minor Al_2O_3, CaO and MgO. A more recent examination of material from the walls of mine levels in Ireland also clearly showed the presence of copper-bearing silica gels (Moreton, 2007). X-ray diffraction data published by the Joint Commission on Powder Diffraction Standards is widely variable and even modern mineralogical texts (e.g. Anthony *et al.*, 1995) include a question mark in parentheses after the crystal system.

Three 'chrysocolla' specimens were examined by XRD in this study, all produced broad amorphous scatter without discrete peaks. This is not unusual, and since 'chrysocolla' commonly appears to produce very diffuse XRD peaks of low intensity; the technique is perhaps not well suited to characterising such specimens. Analyses by EDS reveals the presence of copper and silicon, sometimes with minor aluminium and this is taken to be indicative of 'chrysocolla' *sensu lato*, even though the specimens might be better described as amorphous copper silicate gels.

Chrysocolla is common at the vein exposures in higher Roughton Gill. It occurs as blue botryoidal crusts with yellow to yellow-green pyromorphite (Fig. 14), hemimorphite or hydrocerussite and as thick blue to green vein infillings, the latter being coloured by included malachite. Chrysocolla commonly replaces and encrusts malachite (Fig. 15).

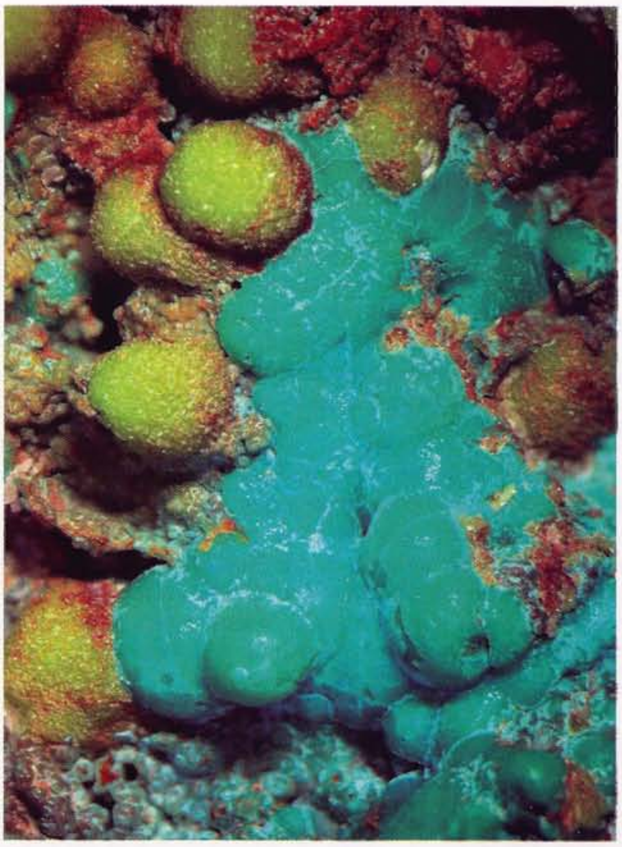

Figure 14. Botryoidal blue green 'chrysocolla' with yellow pyromorphite. Peter Briscoe Collection.

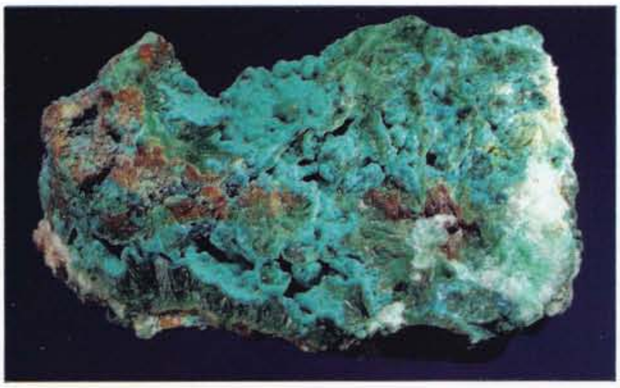

Figure 15. A rich mass of malachite, 75 mm across, containing numerous small cavities lined with thin blue encrustations of 'chrysocolla'. Tony Rigby Collection.

CINNABAR, HgS

Cinnabar is uncommon but widespread in the Caldbeck Fells. It was first described from Potts Gill Mine and Dry Gill Mine (Neall and Leppington, 1994) and has since been reported at a few other localities (e.g. Green *et al.*, 2006; Bridges *et al.*, 2008). In higher Roughton Gill, thin earthy crusts of brick red cinnabar are rarely found encrusting pyromorphite in small cavities in quartz veinstone. They are typically less than 0.1 mm thick, and usually contain only mercury and sulphur, although antimony, possibly as admixed bindheimite, is sometimes also present. In common with other Caldbeck Fells occurrences, the cinnabar from higher Roughton Gill is clearly supergene in origin, it is most probably formed by the oxidation of slightly mercurian sphalerite.

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

Connellite is often found where copper veins oxidise in saline environments. It is stable at lower chloride ion activities than the members of the atacamite group (Pollard *et al.*, 1990) and is also sometimes found in the supergene oxidation zones of base metal orebodies. In these assemblages it is commonly associated with cuprite. In the Caldbeck Fells, connellite has been reported from Silver Gill (Green *et al.*, 2005), and from the Sandbed and Driggith mines, which lie along the strike extension of the Roughton Gill South Lode (Green *et al.*, 2006). It was also recently recorded from Saddleback Old Mine in the southeastern quadrant of the Skiddaw Massif (Briscoe *et al.*, 2008).

Minute acicular blue connellite crystals up to 0.08 mm long, occur with pale green acicular malachite in cavities in massive cuprite at an exposure at the northeastern end of the screes in higher Roughton Gill. A recent cautionary note by Leverett *et al.* (2008) raises the possibility of confusion with the nitrate-bearing mineral buttgenbachite, however, no nitrate was detected in our analyses and sulphur was clearly present.

COPPER, Cu

A small number of specimens of cuprite, goethite and chalcedonic quartz, with minor copper and connellite were collected from screes at the northeastern end of the vein exposure in higher Roughton Gill in the 1990s. The largest masses of copper are a little over 2 mm across and are intimately associated with cuprite.

CORKITE, $PbFe_3(PO_4)(SO_4)(OH)_6$

Corkite was identified by XRD and WDS as sharp yellow to brown rhombs up to 0.1 mm on edge. They are sometimes aggregated into spherical masses (Fig. 16) up to about 0.3 mm across and also form drusy crusts and scatterings of crystal aggregates that can cover areas to many square centimetres. All of the specimens we have identified as corkite are from the screes below the South Vein on the west side of the beck. Similar looking specimens with carminite from the east side are much richer in arsenate and are either beudantite or segnitite. Corkite specimens are commonly found in thin quartz veins and fractures in highly altered wallrock. Average chemical formulae determined for two crystal groups are: $Pb_{1.18}(Fe_{2.87},Al_{0.21})(PO_4)_{0.58}(SO_4)_{0.93}(AsO_4)_{0.50}(OH,H_2O)_6$ and $Pb_{1.18}(Fe_{2.92},Al_{0.21})(PO_4)_{1.32}(SO_4)_{0.68}(AsO_4)_{0.01}(OH,H_2O)_6$. These data show the wide variability in the composition of alunite-jarosite group minerals, in the first formula phosphate only just exceeds arsenate and the mineral is very close to the composition boundary with beudantite; arsenate is almost completely absent from the second formula, which is close to the composition boundary with kintoreite.

Figure 16. Spherical aggregations of yellow corkite up to 0.25 mm across on iron stained quartz from screes on the west side of the valley. Identified by XRD and WDS. Mike Leppington Collection.

CORONADITE, $Pb(Mn^{4+},Mn^{2+})_8O_{16}$

Coronadite is rare in the Caldbeck Fells. It was reported by Hartley (1959) from Dry Gill Mine and is sometimes assumed to be fairly common there, but recent research has shown that almost all of the black manganese oxide that accompanies Dry Gill campylite is romanèchite.

A specimen from the Mike Leppington Collection comprising black minutely botryoidal crusts with a dark metallic fracture was identified by XRD and EDS as coronadite. Examination of the fracture surfaces under a scanning electron microscope showed the botryoidal aggregates were made up of minute acicular crystals a few µm across.

COVELLITE, CuS

Dark purple metallic rims and encrustations around galena and other sulphides are almost certainly covellite. Covellite occasionally also occurs as metallic blue to purple hexagonal plates in small cavities in quartz veinstone. It was noted without description by Hartley (1984) and there is no reason to doubt this record.

CRYPTOMELANE, $K_{1-1.5}(Mn^{4+},Mn^{2+})_8O_{16}$

Cryptomelane is a member of the coronadite group of minerals (see Back and Mandarino, 2008), which includes several manganese oxide minerals with very similar XRD patterns. A small specimen of a massive compact and rather hard manganese oxide from the Mike Leppington Collection was identified as cryptomelane (with $K > Ba$) by a combination of XRD and WDS. A few tiny cavities in the compact, massive cryptomelane are lined with minute acicular black crystals containing potassium and manganese but no detectable barium, a composition that is near ideal end-member cryptomelane.

CUPRITE, Cu_2O

Several specimens containing relatively pure veinlets of cuprite up to a few millimetres in thickness in a matrix of chalcedonic quartz and goethite (Fig. 17) were found in scree below the South Vein at the northeast end of the exposure. In places the cuprite is intergrown with malachite, 'chrysocolla' and contains millimetre size blebs of copper and occasional connellite crystals. The specimens, which were identified by EDS, are among the richest cuprite specimens known from the Caldbeck Fells.

DOLOMITE, $CaMg(CO_3)_2$

Dolomite is abundant at the Roughton Gill mines (e.g. Davidson and Thomson, 1951). It is not particularly common in higher Roughton Gill, where quartz is by far the most abundant gangue mineral, but can nonetheless be found as weathered cream to brown masses. It is worthwhile noting that unfortunately, no specimens were available for analysis in this study, and the possibility that some material may be ankerite cannot be dismissed.

GALENA, PbS

Galena is common along the vein exposure in higher Roughton Gill, and erosion occasionally reveals large and heavy blocks in coarsely crystalline quartz. The largest crystals we have identified in this study are slightly oxidised cubo-octahedra about 2 mm on edge in cavities in veinstone overgrowing stumpy pyramidal quartz. Much of the diverse supergene assemblage along the South Vein is generated by the oxidation of galena, which is the only primary lead mineral present in any quantity.

Figure 17. Cuprite veinlets up to 3 mm in thickness, the one on the left hand side showing extensive alteration to malachite and 'chrysocolla', in a matrix of iron stained chalcedonic quartz. Mike Leppington Collection.

A variety of rare minerals were collected from a highly oxidised galena vein up to about 50 mm wide, which was exposed at the southwest end of the scree in higher Roughton Gill in 1988. Pyromorphite and cerussite are common in vein quartz surrounding galena masses, and linarite and caledonite are often present near the contact between galena and the surrounding matrix if any copper sulphides are present. Anglesite, lanarkite and mattheddleite are usually closely associated with oxidising galena.

GOETHITE, α-FeO(OH)

Goethite is widespread as powdery limonitic to dark brown compact botryoidal masses in cavities and fractures in vein quartz. It was identified by XRD. It occasionally occurs as stalactitic masses and where larger voids are present in the vein, as botryoidal crusts up to several centimetres thick, which can cover specimens to large hand size (Fig. 18).

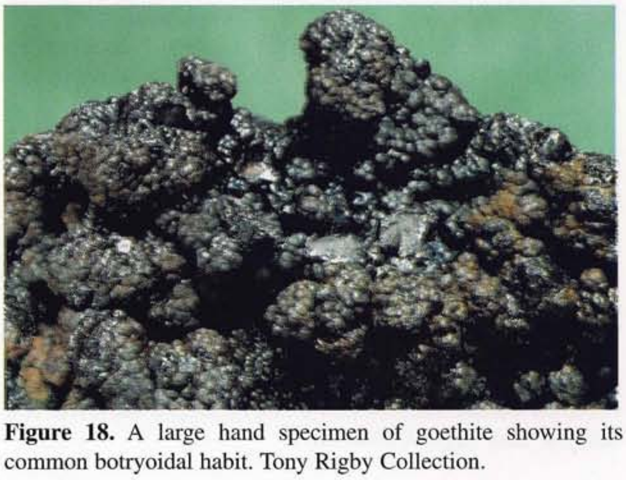

Figure 18. A large hand specimen of goethite showing its common botryoidal habit. Tony Rigby Collection.

HEMATITE, $\alpha\text{-}Fe_2O_3$

A specimen of dark red to brown gossanous material containing numerous small cavities lined with earthy red powder was identified by XRD as hematite. It is clearly supergene.

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$

Hemimorphite is relatively common as radiating sprays of millimetre-sized colourless to white platy crystals, which are occasionally associated with 'chrysocolla', aurichalcite, rosasite and in one case mottramite. A few specimens show white radiating crystal aggregates grading into pale blue crusts. Although blue hemimorphite has occasionally been found in higher Roughton Gill, it is unlikely to be the source of the fine nineteenth century specimens that the mines are famous for. Nonetheless, Cooper and Stanley (1990) note pale blue botryoidal hemimorphite *in situ* and a few specimens showing white to blue zoned crusts of hemimorphite in fissures in iron stained quartz were collected from the southwest end of the screes in the late 1990s (Fig. 19). An unusually rich specimen of pale blue-grey drusy hemimorphite collected from the southwest end of the scree is illustrated in Fig. 20.

Figure 19. A cavity in iron-stained quartz veinstone about 40 mm in length encrusted in blue botryoidal hemimorphite, which on fracture surfaces shows well developed white and blue banding. Tony Rigby Collection.

Figure 20. A large hand specimen, *ca.* 70 mm across, the upper surface of which is richly covered in botryoidal blue-grey hemimorphite with a drusy crystal surface. Found by Neil Hubbard and now part of the Tony Rigby Collection.

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

Hydrocerussite is widespread and relatively common along the exposure of the South Vein in higher Roughton Gill. Heinrich Neumann of Leeds University collected specimens in what he described as Thief Gill in 1949. This was the first locality for the mineral in the Caldbeck Fells and only the second in England at the time. Arthur Kingsbury collected further material on a field-trip with Peter Embrey in 1950. They are preserved in the Kingsbury collection at the NHM and appear genuine.

Hydrocerussite was identified by XRD in a variety of habits in this study. It occurs as thin bright pearly plates, which loosely encrust cavities in vein quartz; as aggregates of discoidal crystals up to 3 mm across; as well formed rhombs up to 3 mm across; and as platy hexagonal crystals with a perfect one-directional cleavage up to about 5 mm on edge. Platy aggregates occasionally occur which seem to be composed of alternating layers of cerussite and hydrocerussite. Pyromorphite occasionally forms pseudomorphs and epimorphs after cerussite and hydrocerussite.

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

Hydrozincite was identified by XRD as white earthy crusts up to about 1 mm thick, sometimes covering areas to several square centimetres. Close examination under a high power stereo-microsope shows the crusts are made up of minute lath-like pearly crystals.

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

Jarosite was identified by EDS as drusy crusts of pale slightly pearly brown crystals a few tens of micrometres across in cavernous iron-stained quartz matrix in loose screes on the east side of the valley.

Jarosite was claimed from several locations in the Caldbeck Fells by Kingsbury and Hartley (1958). These include higher Roughton Gill where jarosite is described with beudantite, beaverite and 'chrysocolla' in chalcedonic quartz. No material similar to the rather non-descript Kingsbury specimens has been discovered in our investigations and bearing in mind Arthur Kingsbury's propensity for mis-labelling specimens it must be regarded with some scepticism.

KINTOREITE, $PbFe_3(PO_4)_2(OH,H_2O)_6$

Kintoreite, the lead, iron and phosphate dominant member of the alunite-jarosite group, was described from Broken Hill mine, New South Wales, Australia by Pring *et al.* (1995). It can only be identified with certainty by a combination of XRD and WDS. Systematic surveys of the composition of alunite-jarosite group minerals from the Caldbeck Fells have revealed kintoreite at Burdell Gill (Tindle, 2008), Coombe Height and higher Roughton Gill. Some of the specimens from the first two localities are close to end-member composition with little substitution of sulphate or arsenate for phosphate. The specimens from higher Roughton Gill are rather more complex in their chemistry, but still fall within the kintoreite composition field. Small groups of sharp yellow rhombic kintoreite crystals up to about 0.1 mm on edge occur in cavities in thin quartz veins from the screes below the South Vein on the west side of the beck. The most phosphate-rich composition we have analysed has a chemical formula that can be written: $Pb_{1.15}(Fe_{3.01},Al_{0.12})(PO_4)_{0.94}(AsO_4)_{0.79}(SO_4)_{0.27}(OH,H_2O)_6$. Since lead, iron and phosphate are dominant, and there are less than 0.5 sulphate groups per formula unit, this is kintoreite (Pring *et al.*, 1995, p.145).

LANARKITE, $Pb_2O(SO_4)$

A small number of lanarkite specimens were found in an oxidised galena vein at the southwest end of the scree on the South Vein in 1988. In all about ten small hand specimens and perhaps thirty micromount-sized fragments were collected. Lanarkite occurs as colourless to white lath-like crystals up to 5 mm long in cavities up to about 20 mm across. The largest (slightly corroded) specimen is figured in Cooper and Stanley (1990, p.101). Fresh unaltered lanarkite crystals are present on relatively few specimens (Fig. 21), most show some degree of alteration or dissolution. Some crystals are completely replaced by leadhillite, and leadhillite epimorphs after lanarkite are present on a number of specimens. Drusy mattheddleite commonly overgrows lanarkite (Fig. 22) and it is occasionally associated with fibrous velvety caledonite. Although many of the specimens are associated with partly oxidised galena, galena is not present in every case.

Figure 21. Bladed lanarkite crystal groups up to 3 mm in length scattered with mattheddleite from a vein at the southwestern end of the exposure. David Green Collection.

Figure 22. Lanarkite blades up to 4 mm long spanning cavities in highly oxidised galena matrix from a vein at the southwestern end of the exposure. David Green Collection.

The first claim of lanarkite in the Caldbeck Fells was made by Arthur Kingsbury, who described three small specimens from Brae Fell Mine in an unpublished manuscript on the minerals of the northern Lake District in 1951: these were examined in detail by Bridges *et al.* (2006) who consider it unlikely that they are from Brae Fell Mine and therefore that they are fraudulent. Lanarkite was noted by Hartley (1984) from higher Roughton Gill, also on the basis of material collected by Kingsbury. The specimen in the Kingsbury collection at the NHM is described by Cooper and Stanley (1990) and comprises radiating sprays and crystal sections to 20 mm with leadhillite. In common with the Brae Fell specimens, it is almost certainly a fragment of an old specimen from the Leadhills-Wanlockhead district in Scotland. It is amazingly large, a single isolated example, strongly resembles Leadhills specimens and is unlike anything ever collected by anyone else at Roughton Gill.

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

Blocky pseudo-hexagonal leadhillite crystals up to about 4 mm across were found in cavities in oxidised galena in a vein at the southwestern end of the scree on Balliway Rigg in 1988 (Fig. 23). They are typically associated with caledonite, mattheddleite (Fig. 24) and lanarkite and occasionally occur as pseudomorphs and epimorphs after the latter species. Leadhillite is widespread but uncommon along the vein exposure. It occurs in a variety of habits varying from thin tabular to prismatic in quartz blocks containing partly oxidised galena. It is sometimes associated with anglesite, cerussite or linarite. Excellent thin tabular leadhillite crystals up to 4 mm across were found with linarite by William Creighton in the 1990s (Fig. 25).

Figure 23. Thick pseudo-hexagonal blocky leadhillite crystals up to 2 mm across on slightly oxidised galena from a vein at the southwestern end of the exposure. David McCallum Collection.

Figure 24. Hexagonal leadhillite crystals up to 2.5 mm across coated in drusy mattheddleite from a vein at the southwestern end of the exposure on Balliway Rigg. Peter Briscoe Collection.

Figure 25. Blue bladed linarite crystals to about 1.5 mm, closely associated with leadhillite. Specimen collected by William Creighton, now in the Peter Briscoe Collection.

Fine lustrous pale yellow leadhillite crystals to 10 mm in the Kingsbury Collection at the NHM are described by Cooper and Stanley (1990). While these may be genuine, they are much larger than any that have been reported since, and given Kingsbury's penchant for claiming old-time specimens from the Leadhills-Wanlockhead district as Caldbeck Fells, they should be treated with caution.

LEPIDOCROCITE, γ-FeO(OH)

Lepidocrocite was identified by XRD as drusy crusts of sub-millimetre size dark reddish brown to black tabular crystals (Fig. 26) and as lustrous black reniform crusts with blocky white supergene baryte and yellow to yellow-brown beudantite in small cavities in iron-rich quartz collected from the screes below the South Vein. It sometimes forms epimorphs after supergene baryte (Fig 27). Small hand specimens covered in black botryoidal lepidocrocite, which has a dark red-brown colour on fracture surfaces, are associated with beudantite and segnitite in screes on the east side of higher Roughton Gill.

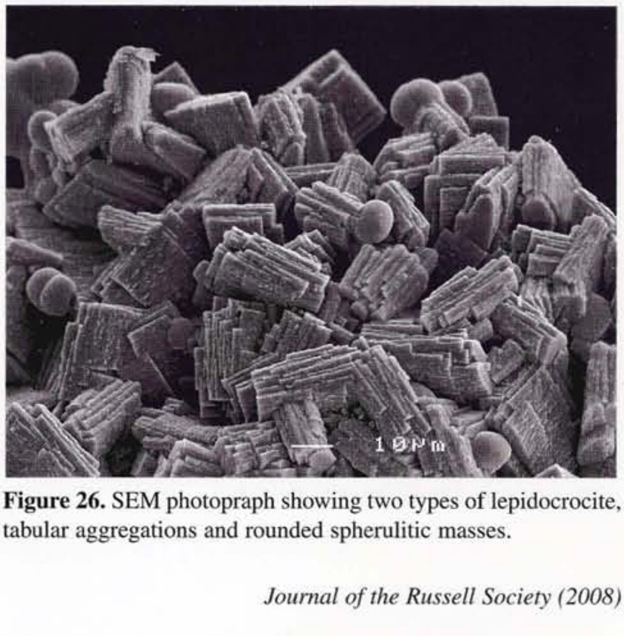

Figure 26. SEM photopraph showing two types of lepidocrocite, tabular aggregations and rounded spherulitic masses.

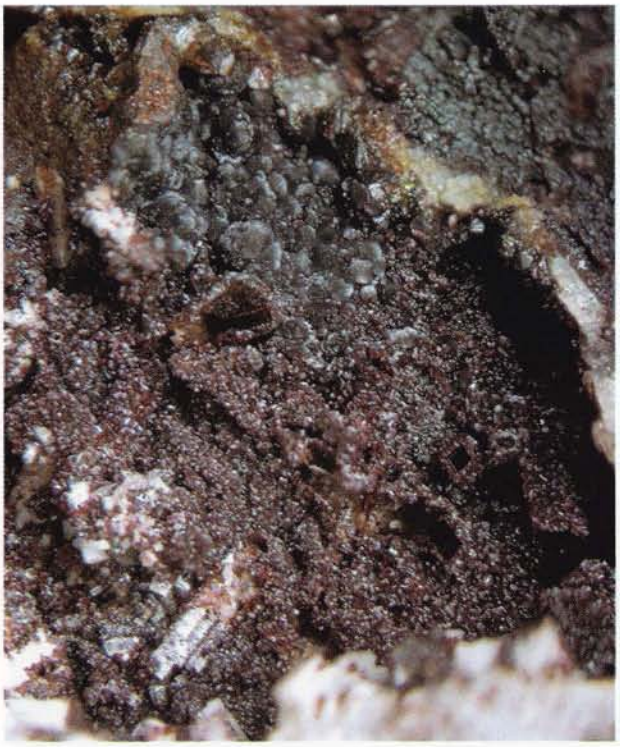

Figure 27. Dark reddish brown drusy crustiform to botryoidal lepidocrocite with epimorphs up to about 0.3 mm across after blocky botryoidal baryte at the lower right and unaltered baryte crystals at the lower left. Minor yellow beudantite is also present on this specimen from the Mike Leppington Collection.

Figure 28. Dark blue blocky linarite crystals to about 3.5 mm in length with cerussite. Mike Leppington Collection.

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

Although many early records note Roughton Gill as a locality for fine specimens of linarite, it seems likely that most of the specimens claimed for the locality originated in the nearby workings of Red Gill Mine (see Bridges *et al.*, 2008 for a detailed discussion). Linarite occurs as blocky to elongated tabular crystals (Fig. 28) and azure-blue crusts around partly oxidised sulphides. It is not particularly common, but a few rich specimens were collected in the 1990s. The best display fragile deep azure blue bladed linarite crystals in cavities and fractures in vein quartz, with occasional undamaged crystals up to about 5 mm in length and broken crystals up to 12 mm long (Fig. 29). Leadhillite and caledonite are common associates and linarite crystals are sometimes partly replaced by brochantite. Linarite-rich lenses, presumably produced by the oxidation of mixed copper and lead sulphides, in quartz veinstone are commonly surrounded by iron-stained quartz, pyromorphite, chrysocolla and malachite (Fig.30).

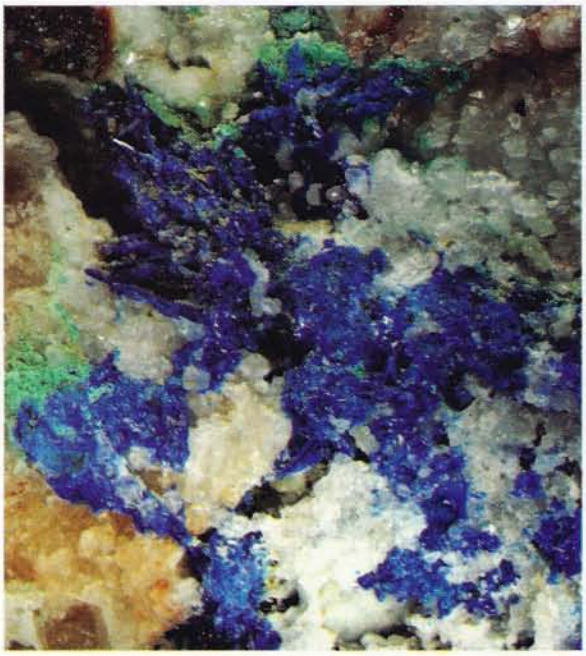

Figure 29. A fracture surface in vein quartz with cavities lined with deep azure blue linarite, one of the finest specimens known from higher Roughton Gill, with broken crystal blades up to 12 mm in length. Tony Rigby Collection.

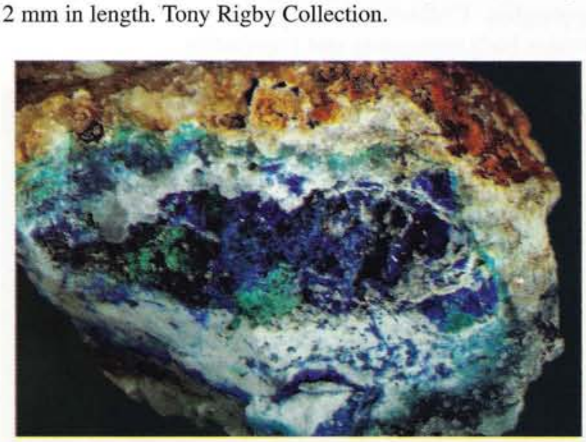

Figure 30. A rich specimen displaying a supergene assemblage that is typical of a number of locations in the Caldbeck Fells. Deep blue linarite and caledonite occur in a 40 mm wide cavity within white vein quartz, surrounded by an iron-stained halo containing pyromorphite, minor malachite and cerussite. Tony Rigby Collection.

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

The Roughton Gill mines are well known for malachite, which according to Shaw (1970), was a significant component of the ore worked from the South Vein. Malachite is probably the second most abundant supergene copper mineral (after 'chrysocolla') at the exposure of the South Vein in higher Roughton Gill. It occurs as pale to dark green crusts, fibrous masses and locally as emerald green acicular crystals and crystal groups up to about 10 mm long (Fig. 31). The most common associates are cerussite and 'chrysocolla'.

Figure 31. Dark green bundles of malachite about 8 mm in length overgrown by a second generation of lighter green malachite. Tony Rigby Collection.

MANGANITE, $MnO(OH)$

Manganite or pyrolusite was noted from the Thief gills by Davidson and Thomson (1951). Manganese oxide minerals require careful analysis to characterise them to species level, but a single specimen from the Mike Leppington Collection analysed by EDS and XRD contains both manganite and coronadite.

Figure 32. Mattheddleite crystals up to about 0.2 mm long as radiating aggregates with pale blue susannite (centre left). David McCallum Collection.

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

Mattheddleite was reported by Cooper *et al.* (1988) from four locations in the Caldbeck Fells including the exposure of the South Vein in higher Roughton Gill. A considerable number of specimens were collected from a lead vein at the southwest end of the South Vein on Balliway Rigg in late 1988 and these are briefly described by Cooper and Stanley (1990). In all, about 50 mostly micromount-size fragments were found in a highly oxidised galena vein (Figs 32 and 33). Mattheddleite occurs as drusy crusts lining small cavities and as minute acicular crystals seldom exceeding 0.2 mm in length scattered on other supergene minerals (Fig. 34). The most common associations are with lanarkite, caledonite, leadhillite and susannite.

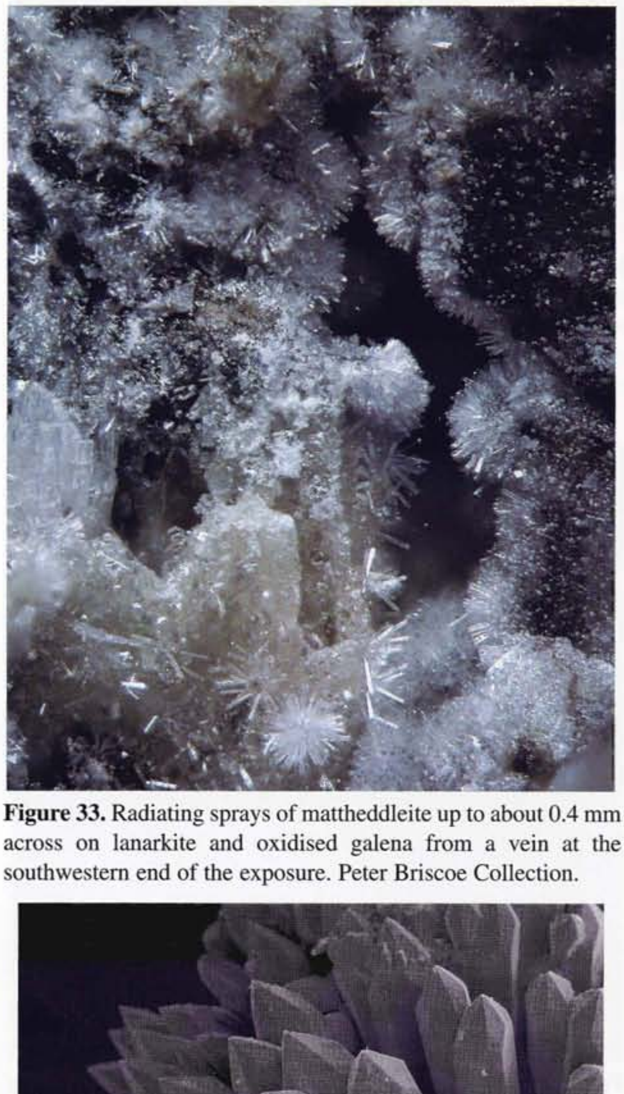

Figure 33. Radiating sprays of mattheddleite up to about 0.4 mm across on lanarkite and oxidised galena from a vein at the southwestern end of the exposure. Peter Briscoe Collection.

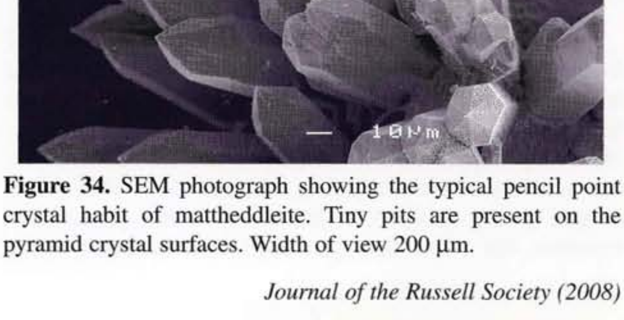

Figure 34. SEM photograph showing the typical pencil point crystal habit of mattheddleite. Tiny pits are present on the pyramid crystal surfaces. Width of view 200 µm.

MIMETITE, $Pb_5(AsO_4)_3Cl$

Pyromorphite and mimetite are well known at the Roughton Gill mines. A remarkable stalactitic example is illustrated as figure 87 of Cooper and Stanley (1990). Reconnaissance surveys of the composition of 'pyromorphite' specimens from higher Roughton Gill by EDS indicate that about a third are mimetite. Yellow is the commonest colour, although mimetite may also be green, brown or white. It occurs as squat to elongated hexagonal prisms (Fig. 35), as curved 'rice grains', and rounded barrels that are similar to campylite. There is no reliable way to distinguish pyromorphite from mimetite by visual means. Some mimetite crystals have calcium-rich surfaces (Fig. 36).

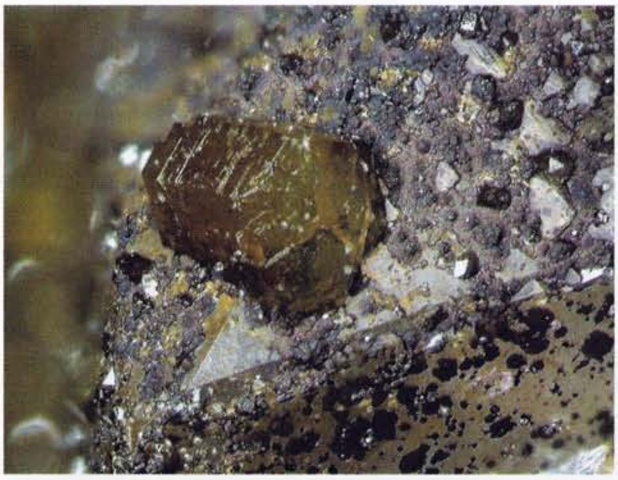

Figure 35. A bright yellow mimetite crystal, which is 1.2 mm long, with rounded pyramidal terminations. David McCallum Collection.

Figure 36. Yellow drusy mimetite crystals (identified by WDS), with calcium-rich surfaces. David McCallum Collection.

MOTTRAMITE, $PbCu(VO_4)(OH)$

Mottramite is rare. It was identified by EDS as minute olive green pyramidal crystals on hemimorphite and 'chrysocolla' and as scattered yellow to yellow-brown blocky crystals on lavender blue plumbogummite (Figs 37 and 38). It also occurs as minute brown pyramidal crystals on green pyromorphite. The largest crystals are a few tenths of a millimetre across.

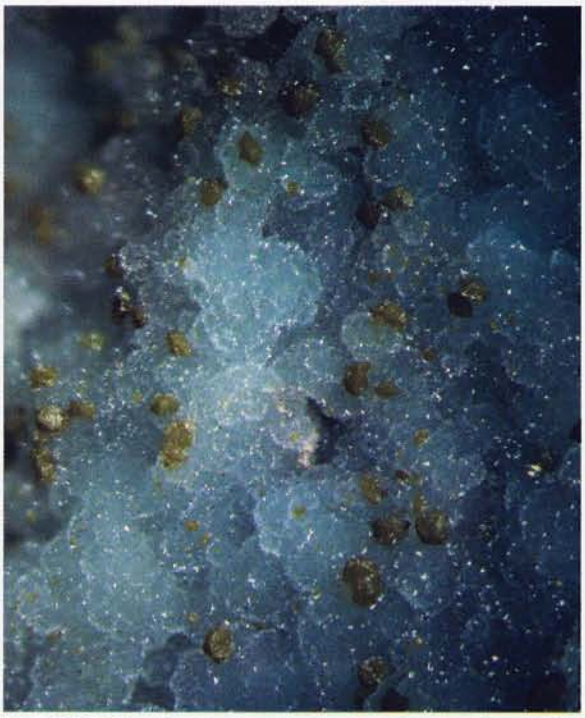

Figure 37. Yellow-brown mottramite crystals up to about 0.2 mm across on pale blue drusy plumbogummite. Mike Leppington Collection.

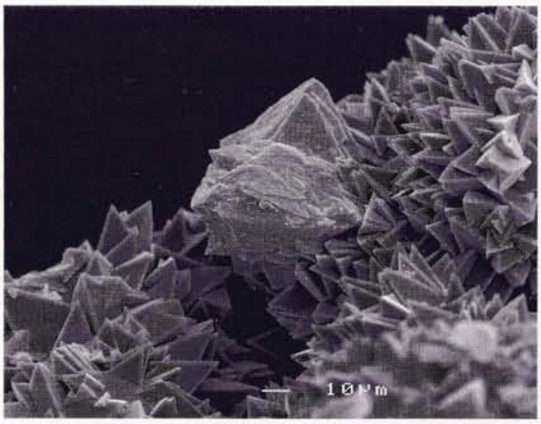

Figure 38. SEM photograph of a mottramite crystal 0.05 mm across on a bed of sharp drusy plumbogummite.

PHOSPHOHEDYPHANE, $Pb_3Ca_2(PO_4)_3Cl$

As part of a survey of the composition of 'pyromorphite' from higher Roughton Gill a number of specimens were examined by EDS. Most proved to be either pyromorphite or mimetite but the spectra in one or two cases suggested that sufficient calcium might substitute for lead to produce a composition in either the hedyphane or phosphohedyphane composition fields. Surprisingly, the specimen that appeared to be the most calcium-rich when examined by EDS (Fig. 36) proved to be a calcium poor mimetite when analysed by WDS. This is most likely due to calcium enrichment near the crystal surfaces (our EDS analyses usually examine crystal surfaces, whereas WDS requires polished fragments and so determines the composition within crystal fragments).

Figure 39. Botryoidal green crust of mixed pyromorphite and phosphohedyphane, showing the common botryoidal habit. Julie Ballard Collection.

A pale to dark green botryoidal calcium-rich pyromorphite crust (Fig. 39), which was also analysed by WDS, had a composition that was sufficiently calcium-rich at several points for it be described as phosphohedyphane. The most calcium-rich composition has a formula (calculated on the basis of three PO_4 anions) that can be written $Pb_{4.1}Ca_{1.3}(PO_4)_{3.0}Cl_{1.1}$. The boundary between phosphohedyphane and pyromorphite is reached where calcium is present at more than 20 mol% of the total calcium plus lead present (Kampf *et al.*, 2006; A. Kampf, *personal communication*). Calcium is strongly zoned in the botryoidal crust, varying between 1 mol% and 24 mol% of the total calcium plus lead. In three of the analyses it exceeded 20 mol%.

PLUMBOGUMMITE, $PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$

The history of the discovery of plumbogummite and of the early confusion with hemimorphite and smithsonite is summarised by Cooper and Stanley (1990). There is no record of the precise provenance of plumbogummite in the mine, although the suggestion by Meirs (1900) that most of the specimens were found in the early 1830s mitigates against the workings in higher Roughton Gill, which were exhausted by that time. The date correlates with extensive activity on the 60-fathom level, which may well be the original locality. Davidson and Thomson (1951) record that fine specimens were restricted to the extreme south side of the main dumps (below the 60-fathom level).

The first report of plumbogummite from the South Vein in higher Roughton Gill is due to Arthur Kingsbury, who recorded specimens "*along the back of the south vein, on the flank of Balliway Rigg, from just above the waterfall to the junction of higher Roughtongill with the northern Thief Gill*" in an unpublished manuscript completed in 1951. A number of superb specimens, with very precise labels are preserved in the Kingsbury collection at the NHM. A fine dark blue plumbogummite specimen with no pyromorphite in association was collected from higher Roughton Gill by Norman Thomson sometime after 1951, but it is unlike the material in the Kingsbury collection.

The only contemporary discovery of blue plumbogummite from higher Roughton Gill that we are aware of is due to David Charlton, who with the late Ken Savage uncovered a few rich specimens from an isolated exposure in the 1990s. These are unlike the classic plumbogummite-pyromorphite combinations from Roughton Gill; they comprise rich pale lavender blue encrustations of plumbogummite in sugary quartz, which sometimes overgrow highly elongated prismatic pyromorphite and are occasionally overgrown by minute yellow-brown mottramite crystals (Figs 40 and 41).

Figure 40. Drusy lavender blue plumbogummite aggregates about 4 mm tall surrounding partly corroded pyromorphite in quartz veinstone. Mike Leppington Collection.

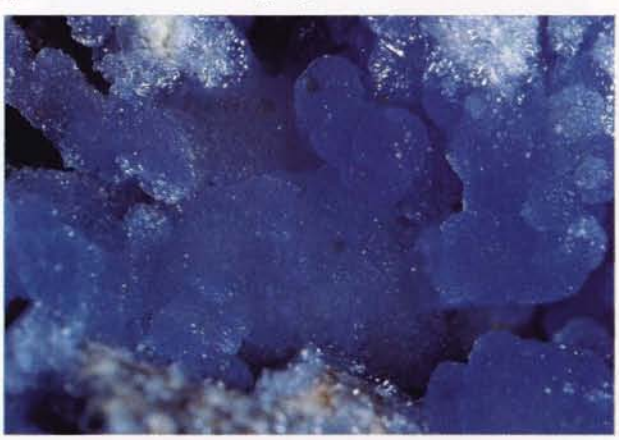

Figure 41. Plumbogummite as a blue minutely botryoidal encrustation on vein quartz. Specimen from the collection of the late Ken Savage. *ca.* 15 mm.

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

The lead-bearing minerals of the alunite-jarosite group (see Back and Mandarino, 2008) require XRD and quantitative chemical analysis if they are to be identified to species level. We have investigated the chemical composition of a number of grains of alunite-jarosite group minerals by WDS. A single analysis of a dark brown pseudo-cubic crystal from the east side of the valley was sufficiently sulphate-rich, (see Scott, 1987; Birch *et al.*, 1992; and Pring *et al.*, 1995 for discussions of the classification of these minerals) to place it just within the plumbojarosite composition field. The chemical formula, $Pb_{2.1}(Fe_{5.8},Al_{0.2})(SO_4)_{3.0}(AsO_4)_{1.0}(OH,H_2O)_{12}$, is unusually lead-rich for plumbojarosite. It contains twice the amount of lead found in specimens of ideal end-member composition. This is almost certainly the result of its borderline chemical composition, with the maximum possible amount of trivalent arsenate substituting for divalent sulphate. This allows more lead to be accommodated in the structure than would normally be possible, while maintaining charge balance.

Plumbojarosite was described from an outcrop of the South Vein in Higher Roughton Gill with galena, cerussite, 'chrysocolla', carminite, beudantite, jarosite and beaverite by Kingsbury and Hartley (1960). The specimens are dissimilar to those that we have collected and must be regarded with suspicion.

Psilomelane

The hard manganese oxides that occur in the Caldbeck Fells were commonly described using the 'catch all' term psilomelane (see Cooper and Stanley, 1990). We have identified cryptomelane, cesàrolite, coronadite, manganite and romanèchite from higher Roughton Gill by XRD, WDS and EDS. Further studies of the manganese oxides would be useful.

PYRITE, FeS_2

Pyrite is uncommon in the vein, which is extensively weathered. There are two specimens in the Mike Leppington Collection. One, which was identified by EDS, shows pyrite as typical small silvery masses intergrown with brassy yellow chalcopyrite. The other comprises small broken masses of silvery pyrite with other sulphides in quartz veinstone on a specimen which was retained for its unusual supergene copper minerals.

Pyrolusite, MnO_2

Pyrolusite or manganite was noted in one of the Thief gills by Davidson and Thomson (1951). Our analyses have only confirmed manganite, but very few specimens were available for study. Further field and analytical work is required to establish the diversity of manganese oxide minerals in the area.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$

Pyromorphite is the most abundant supergene mineral in the screes in higher Roughton Gill. It occurs commonly across the whole of the surface exposure of the South Vein. Although pyromorphite is abundant in higher Roughton Gill, the crystals are smaller and the specimens nowhere near as large or fine as those found in the vein exposures to the northeast. Pyromorphite occurs in a wide variety of colours and habits including green botryoidal to stalactitic masses; green, yellow and orange-yellow hexagonal barrels; yellow hexagonal plates; elongated green prisms (Fig. 42) and orange brown lenticular crystals. Crystals are typically up to a millimetre or two in length and rarely exceed 5 mm. Perhaps the most remarkable pyromorphite specimens from higher Roughton Gill are the pseudomorphs and epimorphs after cerussite and hydrocerussite. These typically show drusy yellow-green to green microcrystalline crusts surrounding and replacing prismatic cerussite. William Creighton collected particularly fine specimens of this type in the early 1990s.

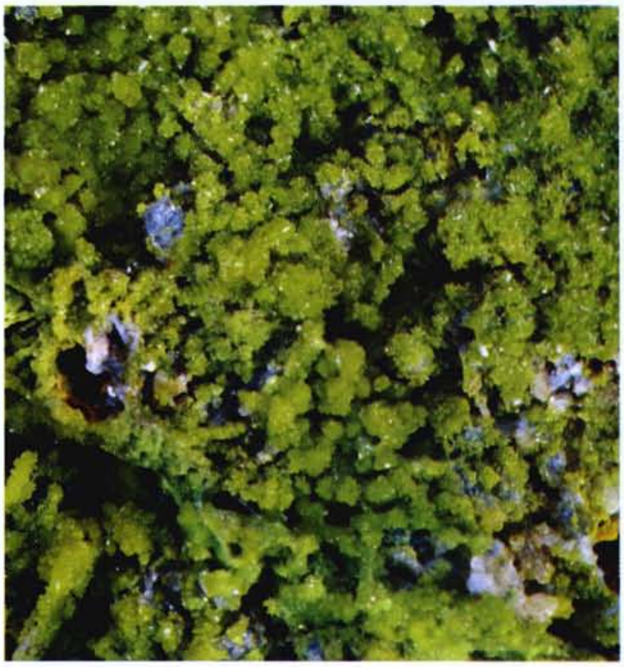

Figure 42. Drusy green pyromorphite crusts on white vein quartz. David McCallum Collection.

QUARTZ, SiO_2

Quartz is the major vein filling along the exposure of the South Vein in higher Roughton Gill. It varies in texture from compact, massive, white, fine-grained almost chalcedonic infillings to loose saccharoidal masses and white coarsely crystalline masses with numerous cavities containing stumpy pyramidal crystals. Although several distinct textures are present in the specimens we have examined it has not been possible to determine whether they relate them to different stages of vein mineralisation due to the lack of opportunity for suitable fieldwork. It nonetheless seems likely that more than one episode of mineralisation is involved and an examination of the distribution of the primary minerals across they vein system would make a very worthwhile study.

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

Acicular crystals up to 0.3 mm long with the characteristic light green colour and EDS spectrum of redgillite occur rarely in thin fractures in sphalerite-rich veinstone with partly oxidised copper sulphides. However, montetrisaite, a dimorph of redgillite has recently been approved by the IMA (IMA 2007-009) and an abstract of an as yet unpublished paper posted online. Close proximity to the redgillite type locality - Silver Gill (Green et al. 2005) - suggests this is the more likely mineral at higher Roughton

Gill, but full confirmation requires XRD for which there is insufficient material at present.

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

A hard botryoidal mineral with a sooty black exterior and a sub-metallic lustre on the somewhat foliated fracture surfaces was identified by a combination of XRD and EDS as romanèchite. Romanèchite occurs in white vein quartz with green pyromorphite in the screes on the north-west side of the valley.

ROSASITE, $(Cu,Zn)_2CO_3(OH)_2$

Surprisingly, rosasite was not described from Britain until 1957, when Kingsbury and Hartley noted it from seven localities including the exposure of the South Vein in higher Roughton Gill. This is not listed as a rosasite locality by Hartley (1984), but the Roughton Gill finds have been duplicated by many other collectors (see Cooper and Stanley, 1990) and there is no reason to doubt their authenticity. Rosasite typically occurs as blue-green crusts and spherulitic aggregates, typically about 0.5 mm across, which are commonly associated with hemimorphite (Fig. 43). The richest specimens originate in the lower workings in Roughton Gill, but small hand specimens can be found in the screes below the South Vein in the current study area.

SCORODITE, $FeAsO_4 \cdot 2H_2O$

Scorodite was identified using EDS by the late Mike Rothwell on specimens collected from the east side of higher Roughton Gill. It occurs as brown to grey crusts as part of an arsenate-rich assemblage that also includes beudantite, carminite and segnitite.

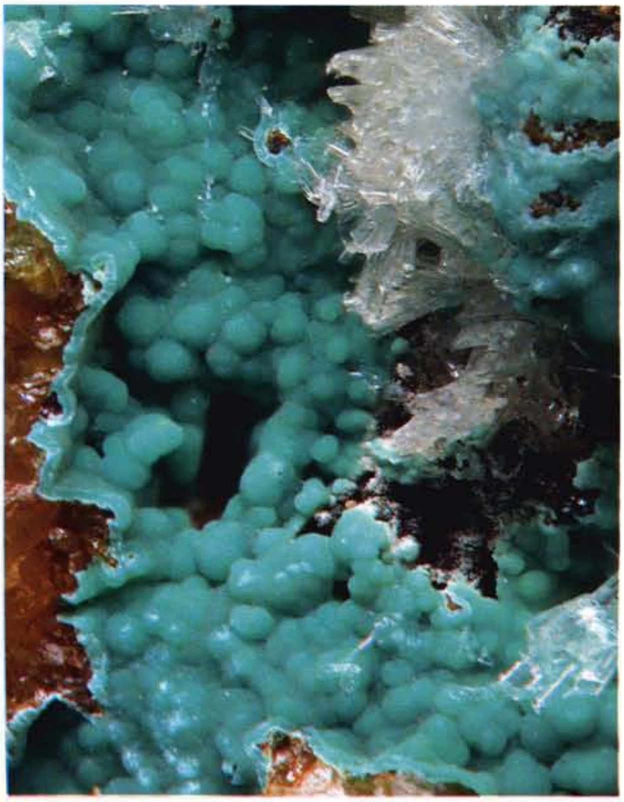

Figure 43. Characteristic botryoidal blue-green rosasite crusts about 0.1 mm thick with spherules up to about 0.3 mm across and white platy hemimorphite. Mike Leppington Collection.

Figure 44. Pointed brown scotlandite crystals up to 0.2 mm in length on oxidised galena from the lead vein at the southwestern end of the exposure. David Green Collection.

SCOTLANDITE, $PbSO_3$

A handful of scotlandite specimens were collected in 1988 from a galena vein exposed in steep scree at the south-west end of the exposure of the South Vein in higher Roughton Gill (Green, 1989). A single small hand specimen (which was donated to the NHM) and five tiny fragments (now preserved as micromounts) displaying translucent pointed pale brown scotlandite crystals to 0.6 mm were found (Fig. 44). The pointed crystal morphology is described by Neall *et al.* (2006) as type 1 scotlandite. More recently a single specimen with colourless chisel-shaped crystals to up 1.5 mm long (described by Neall *et al.*, 2006 as type 2 scotlandite) has been identified. Scotlandite occurs either on its own, or with leadhillite, susannite or bindheimite, in cavities in highly oxidised galena.

SEGNITITE, $PbFe_3(AsO_4)_2(OH,H_2O)_6$

Segnitite, the lead, iron and arsenate dominant member of the alunite-jarosite group (Birch, 1992) is rare in the British Isles (see Tindle, 2008). It was identified by XRD and WDS as pale yellow to yellow-brown rhombs up to about 0.1 mm on edge, which commonly form small drusy aggregations and crusts. Segnitite occurs with carminite and beudantite in fractures in quartz-rich rock in screes on the east side of the valley. The source of these specimens *in situ* is unknown. Analyses of the data for two grains of segnitite produced a formula that can be written $Pb_{1.08}(Fe_{2.55},Al_{0.48})(AsO_4)_{1.75}(SO_4)_{0.21}(PO_4)_{0.04}(OH,H_2O)_6$.

SILVER, Ag

Silver was first reported from the Caldbeck Fells at Red Gill Mine (Wirth, 1989) and has since been reported from Brae Fell Mine, Short Grain Low Level and Driggith Mine (see Tindle, 2008). Many of the original specimens from Red Gill Mine have subsequently altered to acanthite (Bridges *et al.*, 2008). The presence of acanthite on several of the specimens we have examined in this study is almost certainly due to the oxidation of tiny masses of supergene silver, although we have only been able to positively identify silver by EDS on one tiny specimen.

SPHALERITE, ZnS

Sphalerite is much less abundant than either galena or chalcopyrite in the highly oxidised vein exposures in higher Roughton Gill, although it is relatively common in mine spoil derived from the deeper levels. Occasionally, complex millimetre-size red to red-brown crystals with a resinous lustre occur in cavities in vein quartz and dark brown more compact masses are sometimes found intergrown with other sulphides.

SULPHUR, S

Sulphur was identified by EDS as pale yellow to colourless rounded crystals with a resinous lustre in cavities in galena. On the few specimens we examined the galena was rather etched but its surfaces did not appear to be dulled by oxidation, perhaps indicating that sulphur is a late-stage hypogene mineral.

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

Millimetre-size colourless to pale blue rhombohedral crystals of susannite, some highly elongated, are quite common on specimens collected from the lead vein at the southwest end of the vein exposure in higher Roughton Gill (Figs 45 and 46). In addition to the relatively common rhombohedral crystal habit, two specimens with a more unusual morphology were identified by XRD. These comprise highly elongated trigonal prisms, growing from their points and very gradually tapering upward to a large flat termination (Fig. 47). This habit is very similar to the bechererite crystal habit (see for example Green *et al.*, 2005), it even displays the striations perpendicular to the c-axis that are an occasional feature of that species.

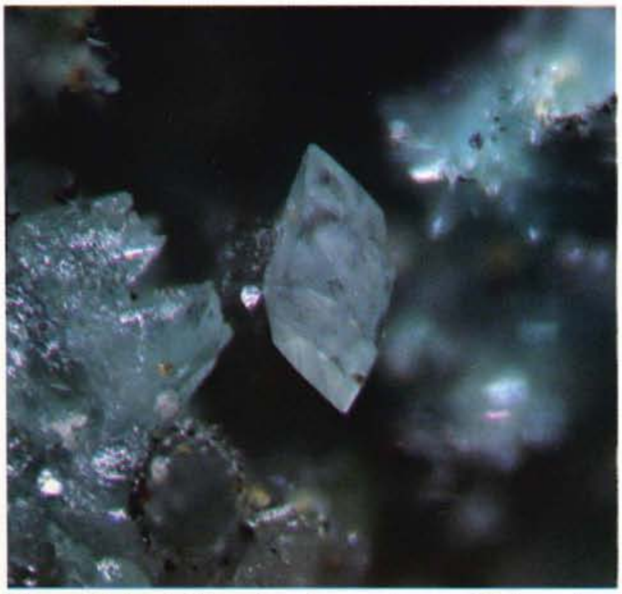

Figure 45. A pale blue trigonal susannite crystal 0.5 mm long. David McCallum Collection.

Figure 46. A typical blue trigonal susannite crystal 1.4 mm in length. Richard Bell Collection.

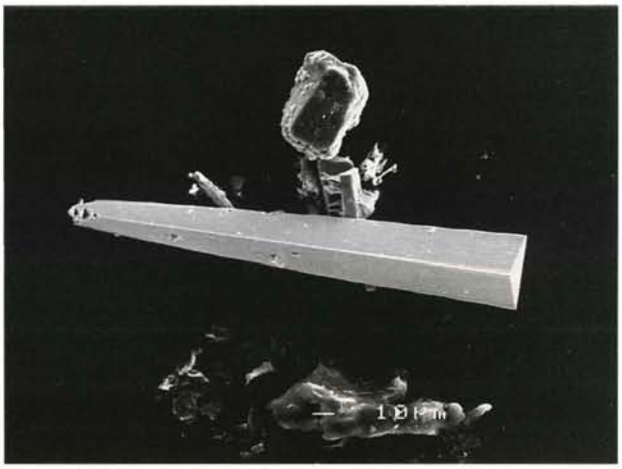

Figure 47. SEM photograph illustrating an unusual crystal habit of susannite, a trigonal prism growing from a point and gradually increasing in size along its length to a pinacoid termination.

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

Tetrahedrite-tennantite with an intermediate composition is listed from higher Roughton Gill by Hartley (1984). We have been unable to trace the specimen in the Kingsbury Collection at the NHM. Tetrahedrite has been confirmed along the easterly strike extension of the Roughton Gill South Vein at Driggith Mine (Stanley and Vaughan, 1981), but tennantite remains unconfirmed. There is no reference to tetrahedrite or tennantite from higher Roughton Gill in any of Kingsbury's X-ray catalogues and it may be that specimens were found independently by Jack Hartley. A more extensive investigation of the primary mineralisation is required to resolve this problem.

TENORITE, CuO

Tenorite was claimed in small amounts at the Roughton Gill mines by a number of early workers (see

Cooper and Stanley, 1990). An XRD examination of some massive and rather dull looking black patches collected by Norman Thomson in higher Roughton Gill, which were thought to be a black copper sulphide, revealed the presence of tenorite on a single specimen.

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

A tetrahedrite-tennantite intermediate is listed from higher Roughton Gill without description by Hartley (1984), but we have been unable to trace the specimen in the Kingsbury Collection at the NHM. Since tetrahedrite has been confirmed along the strike extension of the Roughton Gill South Vein at Driggith Mine (Stanley and Vaughan, 1981), and the specimen does not appear to be linked to Kingsbury, there seems no reason to doubt the report, but whether it represents tetrahedrite or tennantite is unknown.

WULFENITE, $PbMoO_4$

Wulfenite was described from the outcrop of the South Vein in higher Roughton Gill by Rothwell and Mason (1992), who added a caveat that the specimens may have been found in the nearby workings in Silver Gill and dropped by collectors. Field-work since that time indicates that the wulfenite definitely occurs along the exposure of the South Vein as it has been collected in a number of different areas in fresh scree exposures. It is a rare associate of pyromorphite and anglesite and occurs as millimetre sized yellow to orange-yellow tablets (Fig. 48) and as thin orange plates.

Figure 48. A butterscotch yellow wulfenite crystal 1.1 mm across with a large pinacoid face associated with bladed white anglesite and minutely drusy white calcium-rich pyromorphite. Mike Leppington Collection.

DISCUSSION

Restrictions on fieldwork resulting from the 'Red Zone' classification of the localities in higher Roughton Gill has limited the scope of this investigation, which is primarily based on the specimens in a small number of collections, with the inevitable biases that that introduces. Nonetheless, we have added considerably to the mineralogy of the site and have identified a considerable number of species that have not been reported previously: fifty-nine species are considered to be genuine, six require further work and two are considered suspect. This compares favourably to the fewer than fifty confirmed minerals for the whole of 'Roughton Gill', listed by Cooper and Stanley (1990), and only nineteen from higher Roughton Gill listed by Hartley (1984). Minerals reported for the first time in this study include bariopharmacosiderite, cesàrolite, chenite, cinnabar, connellite, coronadite, cryptomelane, kintoreite, lepidocrocite, phosphohedyphane, romanèchite, segnitite and silver.

The main supergene assemblage in the screes below the vein is dominated by cerussite, pyromorphite, goethite, hemimorphite, mimetite, malachite and 'chrysocolla'. These are common and themodynamically stable phases in the conditions encountered at the surface of the Earth. They can form over quite a wide range of carbonate ion activity (aCO_3^{2-}), partial pressure of carbon dioxide (pCO_2) and pH. This assemblage is typical of the weathering of low temperature lead-zinc-copper veins and similar to many other localities in the Caldbeck Fells (e.g. Cooper and Stanley, 1990).

The unusual supergene assemblage containing relatively large crystals of lanarkite, with leadhillite and susannite, found in oxidised galena at the southwest end of Balliway Rigg in the late 1980s, is of significant mineralogical and geochemical interest and is worthy of further study. Authentic specimens of lanarkite are extremely uncommon in the Caldbeck Fells (Bridges *et al.*, 2006, 2008; Green *et al.*, 2006) and we know of no other discovery of large crystals *in situ*. The lanarkite typically forms in cavities in partly oxidised galena near the centre of a galena vein that varied up to 50 mm wide and was exposed over a strike length of about 5 m. The cavities in which the lanarkite occur are generally surrounded by hydrocerussite, cerussite, pyromorphite and residual galena. These minerals appear to have formed a seal protecting most of the lanarkite from alteration. Leadhillite, susannite and caledonite are sometimes found with lanarkite. In order to demonstrate the very unusual conditions that must have prevailed in the galena vein at some time in the past, two stability diagrams are presented (Figs 49 and 50). The necessary thermochemical data for the species involved are taken from the compilation of Robie *et al.* (1978) for anglesite and the more common ions in solution. The data of Taylor and Lopata (1984) have been used for cerussite and hydrocerussite, and that of Abdul-Samad *et al.* (1982a, 1982b) for leadhillite and lanarkite respectively. In the system lead-sulphate-pH-pCO_2 at a pCO_2 of 0.000141 (1.41×10^{-4}), the conditions under which cerussite and hydrocerussite can co-exist at equilibrium is shown in Fig. 49. At pCO_2 higher than this, cerussite is stable under high pH conditions and at lower pCO_2 hydrocerussite is stable. Log activity sulphate ion ($\log.aSO_4^{2-}$) when anglesite or leadhillite are forming would usually be of the order of -3 ± 0.5 and it can be seen that leadhillite has quite a wide stability field in the range of pH 6 to 7.7. A low level of carbonate ion entering a system of oxidising galena can stabilise leadhillite; higher carbonate ion would stabilise cerussite or hydrocerussite and lower or no carbonate ion would stabilise anglesite.

Figure 50 shows the same system at the very low pCO_2 of 5×10^{-8}. Lanarkite now has a narrow field of

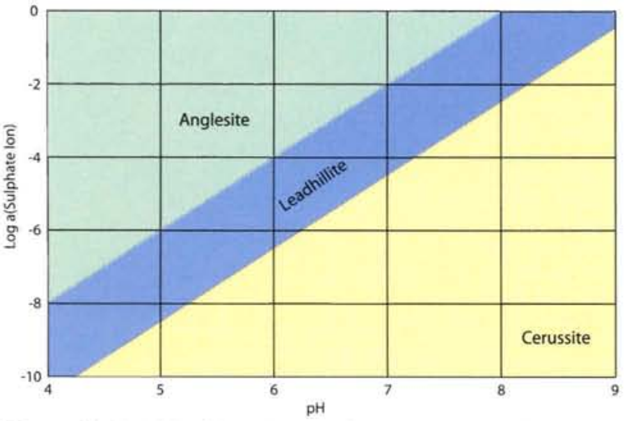

Figure 49. Stability field diagram for the system lead-sulphate-pH- pCO_2 at a pCO_2 of 0.000141 (1.41×10^{-4}), the conditions under which cerussite and hydrocerussite are in equilibrium.

stability between anglesite and leadhillite, a field that would be wider at even lower pCO_2. It can be seen that the whole diagram has moved towards a higher pH, e.g. the leadhillite field at $\log.aSO_4^{2-}$ of -3 now extends from pH 7.7 to 8.8. Achieving these conditions requires the addition of a strong base to the system, the most likely source for which would be weathering of the mafic minerals in the ferrodiorite that forms the northwest wall of the vein. Weathering of the wallrock is clearly demonstrated by the abundance of silicate minerals such as hemimorphite and 'chrysocolla' in the supergene assemblage. It is unlikely that these silicates could have been formed by supergene alteration of the vein assemblage alone as the only silicate mineral present, quartz, appears unaltered even in the highly weathered surface exposures.

Figure 51. Lanarkite blades up to 4 mm in length in a cavity in highly oxidised galena have been almost completely pseudomorphed by drusy leadhillite. David Green Collection.

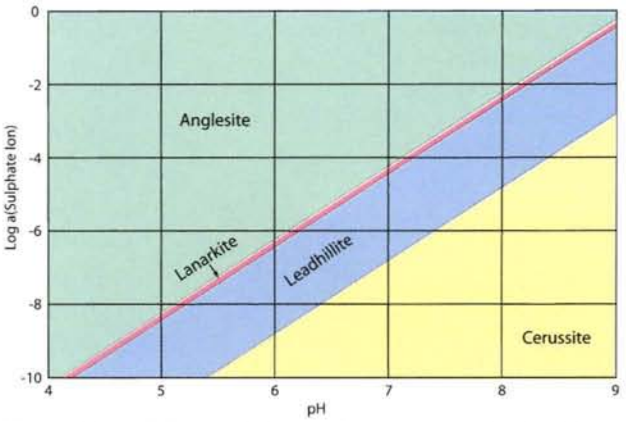

Figure 50. Stability field diagram for the system lead-sulphate-pH- pCO_2 at a pCO_2 of 5×10^{-8}, the conditions under which lanarkite has a narrow stability field between anglesite and leadhillite.

The survival of the lanarkite crystals to the present day would depend on their isolation from the environment, since lanarkite is not thermodynamically stable at the surface. This isolation seems to have been provided by the hydrocerussite, cerussite and unoxidised galena that surrounds the cavities in which the lanarkite occurs. On occasion this isolation has failed and the lanarkite has been wholly or partially pseudomorphed by leadhillite (Fig. 51), a process which CO_2 alone can effect.

Mimetite is fairly common along the South Vein in higher Roughton Gill. There are also rich local occurrences of bariopharmacosiderite, beudantite, carminite, scorodite and segnitite. Rich crusts of beudantite occur with baryte and lepidocrocite in quartz veins in scree below the South Vein at the northeast end of the exposure. Bariopharmacosiderite, beudantite, carminite, segnitite and scorodite have also been identified in a similar assemblage in scree on the opposite side of the valley. At both occurrences the arsenate minerals occur in thin quartz veins and fractures in altered, metasomatised quartz-rich wallrock. On a few specimens, the arsenate minerals occur in irregular cavities, which appear to have been produced by the dissolution of sulphides. Similar structures in which pyrite and arsenopyrite have partly oxidised to produce carminite, mimetite, beudantite and segnitite in quartz have been found at other localities in the Caldbeck Fells including Sandbed Mine and Deer Hills (Cooper and Stanley, 1990; Green *et al*, 2006). Since the arsenate assemblages in higher Roughton Gill were found in loose scree at some distance from the main vein exposure and are not found in thick quartz veins, they may represent the highly oxidised remnant of a distinct and separate primary assemblage. This certainly appears to be the case along the strike extension of the vein at Sandbed Mine, where lead veins cut earlier arsenopyrite and pyrite bearing assemblages (Green *et al.*, 2006). Supergene arsenate minerals tend to be concentrated on the southeast edge of the vein system whereas phosphates appear to be more common along the northwest edge. Unfortunately, most of our material was found in loose scree. A more detailed geochemical examination of the veins *in situ* would be of interest to determine how the arsenic to phosphorus ratios vary across the vein system.

It is interesting to compare the mineralisation on the South Vein in higher Roughton Gill with the Silver Gill Vein in Silver Gill (described recently by Green *et al.*, 2005) as the two veins occupy approximately parallel running fractures a few hundred metres apart. The primary mineralogy appears to be quite similar, comprising galena, sphalerite and chalcopyrite in quartz veinstone with minor baryte and carbonates. There are some differences in the supergene assemblages. Arsenate-bearing minerals, notably mimetite, are quite common along the South Vein, but rather rare in Silver Gill (and also in most of the mines on the west side of the Dale Beck valley).

The 'Leadhills type' assemblage including minerals such as caledonite, lanarkite, leadhillite, susannite and matt-heddleite is well developed on the South Vein, but extremely rare in Silver Gill. In contrast, in Silver Gill the post-mining copper sulphate supergene assemblage including the minerals of the langite group, schulenbergite and ramsbeckite, is quite common. This assemblage is absent along the South Vein, where specimens were collected from natural scree.

Arthur Kingsbury claimed to have found four of the lead-bearing members of the alunite-jarosite group at localities in the Caldbeck Fells in papers published between 1957 and 1960 (Kingsbury and Hartley, 1957b, 1958, 1960). These describe beaverite, jarosite, plumbojarosite and beudantite (and also carminite) from many localities including higher Roughton Gill. The claims are problematic for two reasons. The first is the well established tendency for Kingsbury to claim specimens from places where they were not collected (Ryback *et al.*, 1998, 2001). The specimens in the Kingsbury Collection do not look like the well provenanced material we have examined from higher Roughton Gill in this study, or even as if they are a coherent group from the same locality. A second reason for re-examining Kingsbury's claims is the difficulty in identifying the lead bearing members of the alunite-jarosite group to species level. The discoveries of kintoreite and segnitite in the 1990s, and of the extensive solid solutions that are possible between the different lead-bearing group members, mean that XRD is not wholly reliable: in many cases, WDS is also required (e.g. Birch *et al.*, 1992; Pring *et al.*, 1995; Kolitsch and Pring, 2001).

There seems little to be gained from a re-investigation of Kingsbury's material using WDS because of the doubts regarding provenance. Instead, we have examined as many reliable specimens of alunite-jarosite group minerals as possible using XRD and WDS, and in the process confirmed beudantite, corkite, jarosite, kintoreite, plumbogummite, plumbojarosite and segnitite from higher Roughton Gill. With the exception of blue plumbogummite (but not the occasionally yellow brown crystals of plumbogummite that also occur) none of these minerals can be identified by visual means alone, and even XRD supported by EDS is not reliable in every case.

Although the archaeological remains in higher Roughton Gill are likely to be of importance in framing an understanding of the history of mining in the area, the geological features including the minerals that are present are also of great scientific value. The screes derived from the South Vein in the areas we describe appear largely natural. Our investigation of material collected from them in the decade between the publication of Cooper and Stanley (1990) and the restriction of collecting in 2000 has resulted in the discovery of a considerable number of rare, unusual and interesting minerals. The screes are relatively extensive and gradually replenished by natural weathering and erosion. We believe there is a good case for collecting some of the material they contain, which will otherwise be lost to future research, and also for making a detailed examination of the vein exposures. This study has been limited by our inability to collect representative specimens of some of the commoner minerals for analysis, it would also have been useful to have been able to clear some of the scree to examine the *in situ* vein structures and if necessary to collect samples from them and the surrounding rocks. Together with an examination of the ore mineralogy, this might have helped to establish the chronology of what is almost certainly a paragenetically complex primary fracture filling. If carefully planned this need not conflict with the archaeological interest at the site. Further work on the primary mineralisation and vein paragenesis, the remarkably diverse manganese oxide mineralisation (we identified five different species in the six specimens we had available for study!) and the chemistry of the lead-bearing alunite-jarosite group minerals at the site is also desirable.

ACKNOWLEDGEMENTS

Thanks are due to the Department of Earth Sciences at the University of Manchester for access to analytical equipment. Private collections belonging to Richard Bell (also comprising material from the late Mike Rothwell and John Dickinson), David McCallum, Peter Briscoe, Norman Thomson, George Wilson, David Middleton, Tim Neall, William Creighton, Tony Rigby and Max Wirth were also examined, and all added to the article. MSR would like to thank Alan Hart and Chris Stanley of the NHM for further information regarding Kingsbury specimens from the locality. Notes compiled by the late George Ryback were very useful when trying to track down hard-to-find Kingsbury specimens. An extensive review provided by Brian Young provided an opportunity to consider the manuscript in some detail at a late stage which provided a great deal of food for thought.

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Journal of the Russell Society, **11**, 29-47 (2008)

A REVIEW OF THE MINERALISATION AT RED GILL MINE, CALDBECK FELLS, CUMBRIA, ENGLAND

Trevor F. BRIDGES
10 Springfield, Ovington, Prudhoe, NE42 6EH

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

Michael S. RUMSEY
The Natural History Museum, Cromwell Road, London, SW7 5BD

C. Michael Leppington
1 Harrot Hill, Cockermouth, Cumbria, CA13 0BL

The Red Gill Mine workings are situated in Swinburn Gill, a minor tributary to the Dale Beck valley in the northern Caldbeck Fells, Cumbria. The mine exploited an approximately WNW-ESE trending quartz-baryte-chalcopyrite-galena vein, mainly on the west side of the gill. The primary minerals have been altered by a period of supergene enrichment, followed by lengthy intense oxidation. The vein is deficient in carbonates and as a result the oxidation has given rise to a suite of rare minerals including excellent specimens of caledonite, leadhillite and especially linarite, which could be collected into fairly recent times.

The mine has been known for these rare minerals since the 1860s, and it has long been suspected that spectacular specimens of linarite labelled 'Roughton Gill Mine' (or 'Cumberland') actually originated from Red Gill Mine. Mineralogical evidence to support this view is presented.

Cooper and Stanley (1990) present a long and impressive list of minerals identified at the site. Nevertheless, a further 11 species have been identified since 1990, including rarities such as redgillite, scotlandite, sulphur, mottramite and cinnabar. Of particular interest is a specimen of vanadinite, which was definitely found at the site, but does seem remarkably good considering it is the only specimen found out of 25 tests on pyromorphite.

The Kingsbury Collection in the Natural History Museum contains several specimens collected by Kingsbury in 1951. All of these are typical of the site and there is no reason to doubt their provenance. However, Kingsbury also claimed to have found gold and an excellent specimen of linarite from a bell pit lower down Swinburn Gill. The former is considered fraudulent and the latter probably came from elsewhere.

INTRODUCTION

The main workings of Red Gill Mine are situated in the northern Caldbeck Fells, Cumbria, in a side valley (Swinburn Gill) branching approximately SSW off the Dale Beck valley near its southern end. About 1 km up the minor valley, near the point where Swinburn Gill meets Red Gill, there are the remains of level entrances, small dumps and an area probably used for dressing ore. While the mine was never much more than a trial, it is one of the best known localities in the Lake District, due to the excellent specimens of caledonite, leadhillite and especially linarite that are believed to have originated from the site in the mid 1800s and into recent times. As a result, the locality has always been well researched and Cooper and Stanley (1990) report an impressive list of rare and interesting species. This review has been prompted as further unusual species have been found since 1990 and evidence regarding the potential fraudulent finds claimed by Arthur Kingsbury and published in various later works (Hartley, 1984, Young, 1987, Cooper and Stanley, 1990) have become increasingly apparent (Ryback *et al.*, 1998 & 2001).

This paper is part of an ongoing programme to review mining sites in the Caldbeck Fells. It is the third review of sites in the Dale Beck valley, earlier reviews being of the Silver Gill workings (Green *et al.*, 2005a) and Brae Fell Mine (Bridges *et al.*, 2006).

HISTORY

The earliest history of working at the site is shrouded in mystery. It is close to the known Elizabethan workings in Silver Gill and Shaw (1970) suggests that some of the levels, including No. 2 Level, were worked at that time. However, this level was accessible for a period in the 1970s and 1980s and a photograph taken at that time (Fig. 1) does not show a typical hand-picked Elizabethan level.

Figure 1. No.2 (Old Dutch) Level as it appeared in 1979.

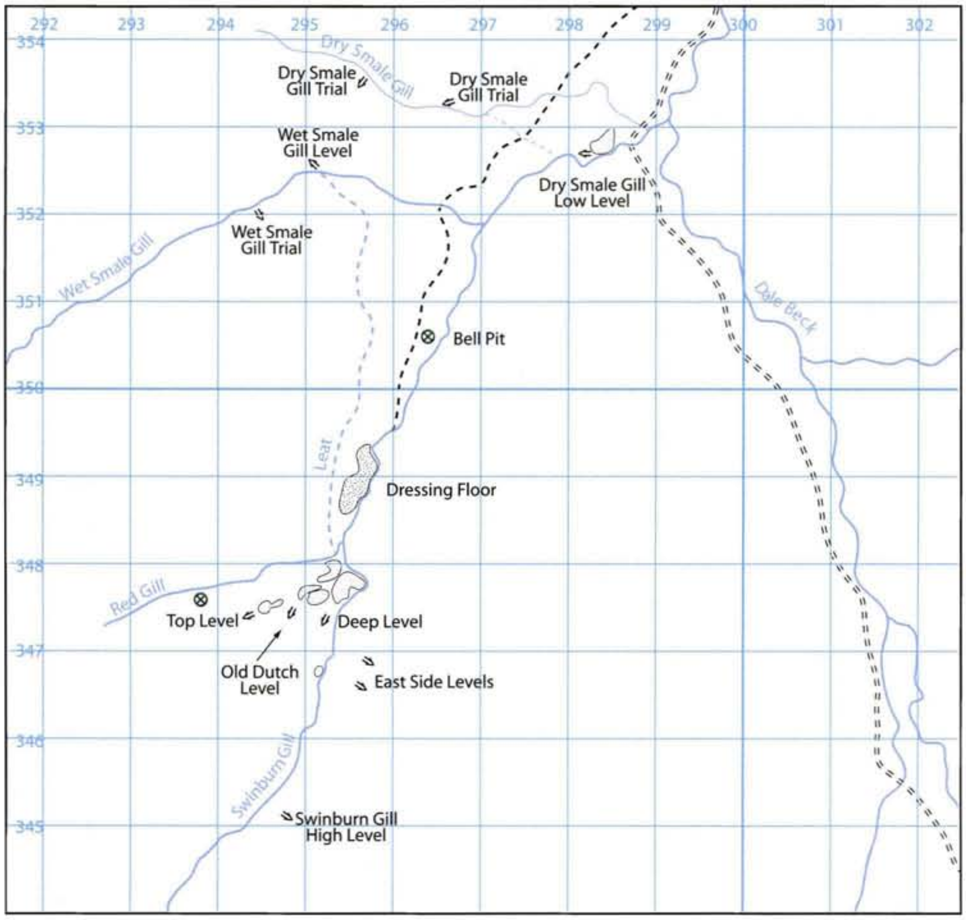

Figure 2. Sketch plan of the main workings of the Red Gill Mine sett, but also showing other nearby workings.

Manuscript references to Red Gill Mine date back to *ca.*1700 and 1724 (Cooper and Stanley, 1990), but the main period of working seems to have been between 1861 and 1871 (Shaw, 1970; Cooper and Stanley, 1990).

The history of collecting is confused by the proximity of the workings to the much larger Roughton Gill Mine. A review of the early specimen material and documentation in the Natural History Museum (NHM) demonstrates the problems regarding early collecting and locality provenance.

During the 1840s, 1850s and early 1860s the extant documentation produces a confusing array of specimens and localities:

1843. The oldest specimen of linarite from the region is registered in the main NHM collections as BM 15637. It was bought from 'Mr Wright' and is specifically attributed to 'Roughten-gill'.

1850. A specimen of caledonite and linarite ('blue sulphate') is registered by Robert Philips Greg in the Allan-Greg Collection Catalogue as specimen AG9. It was attributed only to 'Cumberland' at the time of registration, but was later updated by Greg (?) to read 'Red Gill, Cumberland'.

1852. Four specimens of linarite are registered in the Allan-Greg Collection Catalogue as A.G. 3, 4 and 5). One of these is the spectacular specimen figured by Cooper and Stanley (1990, p 103).

1854. Dana records caledonite and linarite from 'Roughten Gill, Cumberland'. This appears to be the first published reference for these minerals at a specific locality in the Caldbeck Fells.

1858. Greg and Lettsom record that linarite and caledonite occur at 'Red Gill' and 'Roughtengill' in Caldbeck. This appears to be the earliest published reference to Red Gill. Leadhillite is also mentioned, occurring at Red Gill only.

1860. Caledonite specimen BM 31463 purchased by the British Museum from the sale of a Mr Nuttall's minerals. Originally registered as 'Roughten Gill, Cumberland', this is later changed to 'Red Gill' by the British Museum curator Thomas Davies, but the date and reason for the change are not known.

1863. Despite many caledonite, leadhillite and linarite specimens being obtained between 1843 and 1863, it is not until 1863 that an entry in the main NHM registers specifies 'Red Gill' at the time of the original acquisition. This specimen was also purchased from 'Mr. Wright' and registered as caledonite, BM 35501.

In addition to those above, there are several excellent linarite specimens of the same era in other collections at the NHM. Notable specimens in the Henry Ludlam Collection are also labelled various spellings of 'Roughton Gill', 'Red Gill' or merely 'Cumberland'.

During the 1860s and 1870s, linarite appears to have become more prolific in quantity and was then dominantly provenanced from Red Gill as evidenced by a collection of Bryce-Wright invoices to Henry Ludlam preserved at the NHM.

Figure 3. Photograph of the main Red Gill Mine workings.

After 1880, the main phase of linarite collection from Red Gill seems to have slowly ebbed away. Very good specimens were still being obtained, but in ever decreasing quality and size as shown by specimens in the Russell Collection (1880-1910) and those from Davidson and Thomson (1940-1950).

By the 1950s, Davidson and Thomson (1951) reported that linarite, caledonite and leadhillite still occur at Red Gill, but are rare to the point where they failed to find the latter two at Roughton Gill.

During the period 1940s to 1980s many good but small specimens were collected from the Red Gill site and for a period around 1980 underground access to the No. 2 level was possible and provided good specimen material. In fact, small but significant specimens could be collected until the late 1990s when collecting was banned by the Lake District National Park Authority (LDNPA) in order to preserve the remaining archaeology, a ban that remains in place today.

Our study is mainly based on material of reliable provenance collected between the 1940s and the 1990s. However, reference is made to the old specimens of linarite and caledonite labelled from 'Cumberland', 'Roughton Gill' and 'Red Gill' where appropriate.

LOCATION

Figure 2 is a sketch plan of the Red Gill Mine workings, showing the relationship to the other mines and trials in the area of Swinburn Gill. For the purpose of this study, only workings to the south of the bell pit at NY 2964 3506 (but including this bell pit) are considered. The workings lower down the gill, close to the junction with the main Dale Beck valley, will be the subject of future studies.

On ascending Swinburn Gill from the lower workings, the first feature is the bell pit, which is almost completely grassed over, suggesting a near absence of minerals containing heavy metals. Very small crystals of malachite, linarite, caledonite, cerussite and leadhillite have been found in quartz matrix (Mike Leppington Collection), but mineralisation was clearly not well developed. Interestingly, Kingsbury claimed to have found a superb linarite specimen here, which will be discussed later.

Figure 3 is a photograph of the main Red Gill site from the north. In the photograph, the two areas of scree in the foreground appear to be natural. Beyond these, to the right of the group of four sheep is an area of spoil normally referred to as the dressing floor, but there is a feature at its south end (NY 2954 3486) which could be a collapsed level. South of this area, at the junction of Red Gill and Swinburn Gill, is an area dominated by white quartz (NY 2952 3480). The geological map shows a level at this point, but there is no sign of it today and the area looks more like an ore pile or sorting area.

Beyond the 'dressing floor', the entrances to the three main levels are marked by the obvious depressions that can be seen on Figure 3. The lowest is No. 1 (Deep or Bottom) Level at NY 2951 3474, with its triangular shaped dump nearby. Above this is No. 2 (Old Dutch) Level at NY 2948 3475, with its dump below the depression. Further up the hillside is No. 3 (Top) Level at NY 2944 3475, with a small dump below the depression, but the main dump is to the right on the photograph and runs down into Red Gill. These three levels, their dumps and the dressing floor are the main workings and are the source of all the specimens for the mineralogical notes that follow, unless clearly stated otherwise.

There are other, less significant workings in both Swinburn Gill and Red Gill that are not apparent on Figure 3. In Red Gill itself, above No. 3 Level, is a shaft on the line of the vein at NY 2938 3476. Below this, in the bottom of the gill (NY 2940 3478) is a feature which the geological map interprets as a level, but may just be where the dump from the shaft has washed out. The spoil from the shaft is dominated by quartz with traces of galena, chalcopyrite, pyromorphite, cerussite and stains of copper minerals, mainly malachite.

About 40 m higher up Swinburn Gill than No. 1 Level is a dump at NY 2951 3468 with no obvious source. Nearby in the stream bed at NY 2951 3466 is the possible site of a completely filled level, from which the dump could be derived. However, this would have been very subject to flooding, unless collapse of the dump has caused silting up of the stream bed. Quartz and baryte are abundant on this dump, ankerite is common and there is some calcite.

High on the east slopes of Swinburn Gill are two levels at NY 2958 3469 and NY 2966 3465. Since these are nearly side by side it seems likely the first exploited the continuation of the main vein and the second the nearby mineralised fault (see later). However, the geological map shows both to be on the continuation of the Red Gill Vein. There is far more veinstuff on the first, more northerly dump, and about 50 specimens from here were available for research. In the text that follows this is referred to as the main East Side Level. The dominant minerals visible on the spoil heap are quartz and baryte, with some ankerite, galena and chalcopyrite. The second smaller dump contains less veinstuff, but the primary mineralogy seems similar.

Much further up Swinburn Gill the geological map shows two levels to one side of a small NNE-SSW mineralised fault on the eastern slopes. We failed to find these levels, an experience shared by Davidson and Thomson many years ago (Norman Thomson, *personal communication*). However, there are the remains of a single level at NY 2948 3451 (called Swinburn Gill High Level on Figure 2), which is 20 to 30 m away and appears to be actually on the strike of the vein. A small amount of mineralisation associated with this consisted of quartz with ankerite and minor galena.

As stated above, No. 2 Level was accessible for a number of years in the late 1970s and early 1980s. Shaw (1970, p. 45) shows a cross-section through the workings, but this does not seem to match observations when the workings were open. The cross-section shows access to the No. 2 Level was through a shaft from the surface, which first passed through the No. 3 Level. In the 1980s access to both No. 2 and No. 3 Levels was through horizontal passages, partly collapsed at the surface. The levels led to stopes on the vein and there was a shaft linking the two levels.

GEOLOGY (Based on the British Geological Survey 1:10,000 series sheet 23 SE)

The Red Gill workings are situated close to the southern edge of the Eycott Volcanic Group (EVG) suite of lavas, sills and volcaniclastic rocks (Ordovician) that host much of the mineralisation of the Caldbeck Fells. A complex of approx. ENE-WSW and NNE-SSW fractures fault the EVG rocks against outcrops of the Hope Beck and Bitter Beck sedimentary formations (mudstones and siltstones), also of Ordovician age, just to the south of the workings. The main workings were on a partly mineralised fault, about 1.5km long, terminating to the west on the west side of Brae Fell at NY 286 349 and to the east on the top of the ridge between Swinburn Gill and the main Dale Beck valley at NY 296 347. The fault trends WNW-ESE at the mine, but changes to E-W further west. The fault lies entirely in the EVG, mainly lavas, except for a short section between NY 2934 3477 and NY 2939 3475 where there is a coarse lapilli tuff and tuff breccia to the north of the fault. The mineralised section runs from NY 2923 3482 for approximately 450 m to NY 2966 3463, traversing the valley bottom, and consists of a Pb-Cu-quartz-baryte vein typical of the E-W veins of the Caldbeck Fells. Figure 4 shows the main vein in No. 2 Level, taken in 1979. The vein is well oxidised, the dominant mineral is quartz and the blue mineral is mainly copper-bearing silica gel, often called chrysocolla.

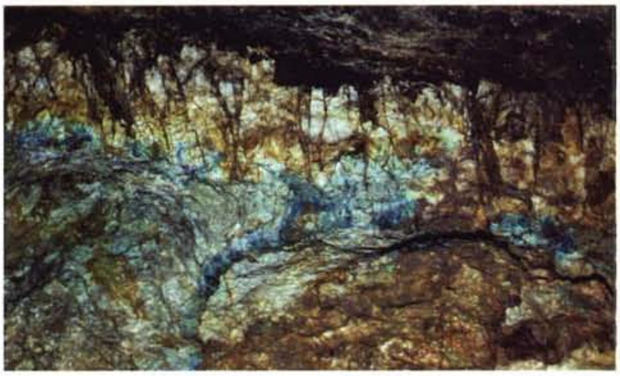

Figure 4. The vein in No. 2 Level as it appeared in 1979.

To the south of the main vein the geological map shows another mineralised fault, which in the vicinity of the workings is nearly parallel to the main vein and about 40 m away. The dominant minerals are abundant quartz and baryte with ankerite and calcite.

Further south on the east side of the gill the geological map shows a short section of a roughly NNE-SSW fault, mineralised between NY 2949 3454 and NY 2946 3446. Little mineralisation is visible, but there is quartz with some ankerite and galena.

Note that about 750 m to the west of the site there is a section of mineralised fault marked 'Ba', on the geological map, and worked from a shaft and level at NY 287 348. This working does not form part of this study.

METHOD

Except when clearly stated otherwise, the identifications and descriptions that follow are based on over 500 specimens mainly in private collections, collected in the last 70 years and of excellent provenance. However, older individual specimens in the literature are discussed under the relevant sections. One significant reference is Hartley (1984) who listed minerals claimed to have been collected by Arthur Kingsbury.

Much of the relevant material in the collections had already been identified by X-ray diffractometry (XRD). Where this was lacking, samples were taken for analysis by energy dispersive X-ray spectroscopy (EDS) using a scanning electron microscope (SEM). When the identification was still not fully confirmed, material was then sampled for XRD. All specimens were studied using a stereomicroscope for their morphological characteristics and mineralogical associations.

It should be noted that most of the minerals referred to in Cooper and Stanley (1990) were previously reported by other authors, e.g. Young (1987) in his 'Glossary of the minerals of the Lake District and adjoining areas'. In this review, precedence is given to the Cooper and Stanley reference, since this is considered the definitive work on the Caldbeck Fells and is more descriptive.

THE MINERALS

Minerals which have not been fully identified or are of dubious provenance, are shown in italics in the text that follows. Minerals which, as a result of this study are now considered not to occur at Red Gill Mine are shown in brackets.

(ACANTHITE, Ag_2S)

Most of the relatively small specimens of native silver found at the site (see later) have developed very fine pointed needles of acanthite during storage in collections, often to the point where the original silver has been nearly completely replaced.

ANGLESITE, $PbSO_4$

Cooper and Stanley (1990), note that anglesite is more common at Red Gill Mine than anywhere else in the Caldbeck Fells and describe crystals as often occurring as small glass clear blades, but rarely as crystals up to 25 mm long, which generally span cavities.

Figure 5. A transparent prismatic anglesite crystal with well developed pyramidal terminations 3.5 mm long. One of many different habits of the mineral from Red Gill. David Middleton Collection.

In this study crystals up to 15 mm have been observed bridging cavities. Free standing 'sword shaped' glass clear crystals, which can reach 3 mm in length, and much larger cloudy white blades are common. Anglesite also occurs as equant rhombic crystals, reaching 6 mm on edge, the smaller crystals again often being lustrous and glass clear (Fig. 5). Particularly interesting is a specimen of fibrous anglesite in the Max Wirth Collection (Fig. 6), which has been confirmed by XRD.

Figure 6. Unusual acicular to almost fibrous anglesite crystals up to 0.7 mm in length with minor caledonite lining a vein in quartz matrix. Max Wirth Collection.

Anglesite usually occurs in cavities in quartz lined with small pyramidal crystals, often iron stained, but sometimes in irregular cavities that appear to have resulted from the oxidation of galena. Associated minerals include many other species, but particularly cerussite, linarite, caledonite and leadhillite and its polymorphs.

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

Ankerite is abundant on the dump higher up the gill and on the dumps below the levels on the east side of the gill. On the main workings it has only been found on one specimen, which could possibly have been transported down the gill from the higher dump.

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

Aurichalcite is very rare, but it has been found as aggregates of greenish-blue feathery crystals, a few tenths of a millimetre in length, in iron stained quartz, sometimes associated with hemimorphite. (Identification confirmed, XRD 1418)

BARYTE, $BaSO_4$

As noted by Cooper and Stanley, (1990), primary baryte is plentiful at the mine. It mainly occurs as compact white bladed masses with spear shaped terminations on crystals. It is also common on the dump to the south of the main workings and on the dumps up the east side of Swinburn Gill.

More interesting are numerous small colourless or white, rhombic or diamond shaped tablets, reaching 3 mm on the longest diagonal and up to 0.5 mm thick, associated with cerussite and malachite on iron stained quartz. Some of the crystals show clear signs of partial dissolution and they all appear to be supergene in origin. Excellent examples exist where crystals are perched on supergene minerals such as cerussite, malachite and caledonite. This occurrence is included in a discussion on supergene baryte by Bridges and Green (2008).

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Pale yellow earthy coatings of bindheimite are common in cavities generated by the oxidation of galena. It is commonly associated with cerussite, anglesite, susannite and leadhillite. (Identification confirmed by EDS).

BROCHANTITE, $Cu_4SO_4(OH)_6$

Cooper and Stanley (1990) note that brochantite 'is now very rare at this locality, although excellent specimens may be seen in old collections'. Davidson and Thomson (1951) noted that in their experience 'caledonite is some fifty times more common than brochantite here'.

The rarity of the mineral in crystalline form, is confirmed by the current study, but it has been found as bright emerald green crusts and blocky crystals up to 0.5 mm across, associated with goethite, linarite, oxidised chalcopyrite and grey copper sulphides (Fig. 7). Thin microcrystalline crusts also occur on material from the main East Side Level.

Figure 7. Tabular emerald-green brochantite crystals up to 0.3 mm long beside a large linarite crystal. Collected by Peter Briscoe in 1983 from the No. 2 Level dumps.

Far more common on the main site, however, are crusts of brochantite with an earthy appearance. These are usually closely associated with grey copper sulphides and chalcopyrite, and appear to have resulted from the oxidation of these sulphides. (Identification confirmed XRD 1414). Earthy brochantite is common on early specimens of linarite.

CALCITE, $CaCO_3$

Cooper and Stanley (1990) report the presence of deeply etched lenticular crystals of calcite from the small dump in Swinburn Gill, just south of the No. 1 Level. They also note the presence of epimorphs with scalenohedral morphology in quartz from the No. 2 Level dump, indicating the presence of the mineral here in the past.

In the current study calcite has only been found on two specimens from the main workings, one from No. 2 Level and one from the bottom of the No. 1 Level dump, which could have been transported down from the vein higher up the gill. Quartz epimorphs with scalenohedral morphology, possibly after calcite, occur on the dumps below both of the east side levels. Primary carbonates are very rare on the main workings.

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

The presence of this rare mineral, specifically at Red Gill Mine, was first reported by Greg and Lettsom (1858). Cooper and Stanley (1990) note that crystals can reach 5 mm but are generally smaller than this. Hartley (1984) records caledonite from material collected by A.W.G. Kingsbury. Several specimens in the Kingsbury Collection contain caledonite and all are entirely typical of the locality.

The collections of the NHM contain many excellent specimens, but particularly noteworthy is a specimen in the Russell Collection which has a cavity containing crystals up to 5 mm across (Fig. 8).

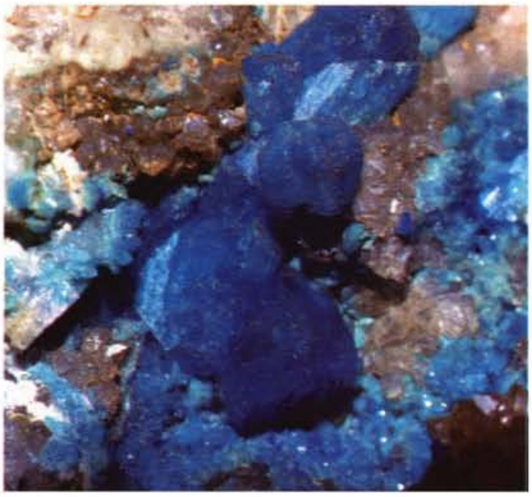

Figure 8. Dark blue caledonite crystals up to 5 mm on edge of an unusual blocky habit. One of relatively few specimens of Red Gill caledonite in the collection of Sir Arthur Russell now held at the NHM.

Figure 9. A spray of striated sky blue caledonite crystals up to 3.5 mm in length from the No. 3 Level. Richard Bell Collection.

Considering its world-wide rarity, caledonite remained relatively common at Red Gill into the late 1990s. It occurred in a variety of crystal forms and of colour varying from turquoise to green. Most common are blocky crystals usually no more than 3 mm on the longest dimension, but flat bladed crystals (Fig. 9) and needles also occur, varying from very fine to elongated blades up to 3 mm long by 0.7 mm wide, though, again, usually much smaller than this. Both forms often completely line cavities in quartz. Common associated minerals are leadhillite, linarite, cerussite, anglesite and mattheddleite. It often overcoats the first three minerals.

CERUSSITE, $PbCO_3$

Cerussite, first reported by Greg and Lettsom (1858), has been recorded numerous times since and exists as an accessory phase in many collections world wide. The cerussite specimens (Hartley, 1984) in the Kingsbury Collection are again typical of the locality.

Figure 10. Prismatic cerussite crystals up to 3.5 mm on edge on botryoidal goethite. David Middleton Collection.

In this study it remains one of the commonest supergene minerals, occurring in 'jackstraw' needles up to 10 mm long, blocky crystals to 3 mm, striated blades up to 5 mm, which can be glass clear, and good twinned pseudo-hexagonal crystals up to 3 mm. Pseudomorphs of anglesite up to 5 mm long also occur and, in one case, leadhillite seems to have been replaced (Mike Leppington Collection). Cerussite is commonly associated with linarite, caledonite, leadhillite and forms attractive specimens with malachite. Figures 10 and 11 show good examples of small cerussite crystals that show classic pseudo-hexagonal twinning and further examples of twinned cerussite can be seen in Cooper and Stanley (1990, p. 89).

Figure 11. Thin tabular cerussite crystals up to 2 mm across with well developed hexagonal twinning. David Middleton Collection.

It is also common on specimens from the main East Side Level as pseudo-hexagonal and jackstaw crystals up to 10 mm long.

CHALCOPYRITE, $CuFeS_2$

The recorded output of chalcopyrite concentrate in the period 1861 to 1866 (Shaw, 1970) is no more than c.2.5 tonnes, significantly less than the galena output. It is nevertheless a common mineral on specimen material, generally occurring as small blebs in quartz, often associated with galena. Very frequently it shows replacement by goethite and grey copper sulphides. It is present on some of the specimens in the Kingsbury Collection, again all typical of the site.

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

Chenite is very rare at Red Gill but has been found as minute pale blue bladed crystals up to 1 mm in length, associated with elyite and hydrocerussite on a specimen collected in 1985 from the dressing floor below the site. It has also been found on a specimen from No. 3 Level, again as minute bladed crystals with elyite. (Identification confirmed by XRD).

CHRYSOCOLLA, $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$

First reported by Greg and Lettsom (1858) and several times since, blue to green crusts and coatings, often with a greasy lustre, which are referred to as chrysocolla, are quite common on specimens from the mine and often have desiccation cracks. Occasionally the form is of botryoidal crusts, a good example of which is illustrated in Cooper and Stanley, (1990, p. 90). The latter authors note that pseudomorphs after malachite occur and in this study pseudomorphs after linarite have been observed. Hartley (1984) records its presence on material collected by Kingsbury.

However, two specimens of typical material were analysed by XRD in this study. One was a pale turquoise blue specimen with occasional desiccation cracks and the second was pale green with a conchoidal fracture and waxy lustre. Long, high resolution XRD scans were performed on relatively thick powder specimens of both. The blue specimen produced no crystalline peaks whatever, while the green specimen produced a faint malachite pattern on a broad amorphous background. EDS showed copper and silicon to be the only heavy metal elements present and in variable amounts.

'Chrysocolla' has been reported from numerous localities in the Caldbeck Fells, but we are not aware of specimens that have been confirmed by XRD. Furthermore, the XRD patterns that are supposed to be characteristic of chrysocolla (published in the JCPDS index) are widely variable. Moreton (2007) investigated soft copper bearing gels from Tankardstown Mine, Co. Waterford in some detail and made comparisons with similar deposits from elsewhere and with material similar to the 'mineral' often called chrysocolla from the Caldbeck Fells. He concluded that these deposits are best referred to as 'copper-bearing silica gel'. However, 'chrysocolla' is in such common use that the name will be retained in the text that follows, but placed in inverted commas to indicate it is not a true species.

CINNABAR, HgS

Cinnabar is rare in the Caldbeck Fells, having only been reported from four localities (Neall and Leppington, 1994; Green *et al.*, 2006). At Red Gill it has been identified by EDS as minute specks of earthy red coatings in small cavities in highly oxidised veinstone from the main East Side Level and a further example has been noted from the No. 2 Level dumps, where it is associated with hemimorphite. These earthy coatings are typical of its occurrence in supergene environments, e.g. see Bridges and Young (1998).

COVELLINE, CuS

Millimetre size metallic purple crystalline masses in vein quartz containing brochantite were identified by XRD as covelline (XRD 1411). It is relatively common as dark sometimes iridescent metallic rims surrounding other sulphides, particularly galena and is also common as masses of post-collecting thin metallic hexagonal plates on specimens containing copper sulphides.

CUPRITE, Cu_2O

This mineral is reported by Cooper and Stanley (1990) on the basis of a study by Berg (1985). Our research indicates that it is very rare, but has been found as small bright red specks associated with grey copper sulphides, cerussite, leadhillite and pyromorphite. One interesting specimen consists of cuprite enclosed in glass clear hexagonal crystals 0.5 mm across and presumed to be leadhillite (Mike Leppington Collection).

DIGENITE, Cu_9S_5
DJURLEITE, $Cu_{31}S_{16}$
CHALCOCITE, Cu_2S

Cooper and Stanley (1990) note that chalcocite and digenite have been reported from Red Gill Mine, but early identifications of chalcocite have to be regarded with suspicion, since only relatively recently has it become possible to distinguish the grey copper sulphides from each other and even then only with some difficulty. Digenite was reported by Davidson and Thomson (1951) on the basis of an XRD study at the NHM.

In this study, only djurleite has been confirmed (3 samples). Grey copper sulphides, with the general formula $Cu_{2-x}S$, are quite common as small blebs in quartz and often occur as partial or total replacements of chalcopyrite and galena, indicating a period of supergene enrichment at the site. It is worth noting that several of the early linarite specimens have relatively large amounts of grey copper sulphide in their matrix.

DOLOMITE, $CaMg(CO_3)_2$

Dolomite is very uncommon at Red Gill Mine. It has been identified on a specimen in the Mike Leppington collection as a thin vein filling in milky quartz, where occasional cavities contained typical saddle shaped crystals. Dolomite post-dates both quartz and sphalerite on the specimens examined and is clearly a late stage primary mineral.

ELYITE, $Pb_4Cu(SO_4)(OH)_8$

Briscoe (1986) reported elyite from a specimen collected in 1985 between the stream and the old dressing floor at Red Gill Mine. This was the first report of the mineral from a natural setting in the UK, as opposed to its relatively common occurrence in lead smelter slags. The elyite occurred as minute purple crystals on a fracture in galena-chalcopyrite matrix and associated with chenite and hydrocerussite. Since 1985, the mineral has been found as minute lath-like crystals associated with chenite and an unidentified mineral from the No. 3 Level (Fig. 12) and also on the No. 2 Level dump. It remains one of the rarest minerals at the site.

Figure 12. Elyite crystals *ca.* 0.3 mm long with pale blue chenite from the No. 3 Level in 1989. Richard Bell Collection.

GALENA, PbS

This was the main ore worked, with c.28 tons of concentrate being sold in the period 1861 to 1866 (Shaw, 1970). Shaw noted the presence of galena on several of the dumps and it has been recorded several times before and since. It is a common constituent on many Red Gill specimens and is present on some of the specimens in the Kingsbury Collection and was reported by Hartley (1984). Again, the specimens are typical of the site.

In this study it is observed to be a common constituent of specimens, usually in quartz and often partly oxidised. Replacement by grey copper sulphides is also common. Rarely, small, lustrous crystals of galena occur in cavities in quartz. A single specimen found has microcrystalline lustrous crusts of galena associated with anglesite and is probably supergene in origin. See Green *et al.* (2005b) for a full discussion of this phenomenon.

GOETHITE, α-$FeO(OH)$

Limonitic brown ochreous deposits are common in mineralised quartz and are probably mainly goethite. Rarely dark brown radiating material up to 1 mm thick occurs as botryoidal crusts on quartz.

(GOLD, Au)

Kingsbury donated a group of 6 fragments of gold in quartz matrix, purporting to be from the bell pit below Red Gill Mine, to the NHM in 1960, which he claimed to have collected in 1953. This is after the 1951 date when it is believed Kingsbury started behaving fraudulently (Ryback *et al.*, 1998 & 2001). The specimens are relatively rich and the gold occurs in the quartz and in minor limonite lined cavities in the quartz. The quartz has dark glassy areas and is typical of high temperature formation. Gold has not been found at Red Gill in the current study and it has to be concluded that this claim is fraudulent.

Sweet (1960) discussed a specimen of gold in the Bouglise Collection labelled Cumberland, England, but altered by Bouglise to read 'Leadhills, Ecosse', although no reason for the change is given. The specimen consists of minute grains and crystals of gold in quartz gossan, associated with linarite, caledonite, cerussite and hemimorphite. Sweet compared the specimen with material from Leadhills and Red Gill and noted that it more nearly resembled typical Red Gill mineralisation than Leadhills. She also noted that Kingsbury had claimed gold from the area and this may have coloured her thinking. She finally expresses the opinion that a Caldbeck Fells locality seems the more likely, but stops short of suggesting this to be Red Gill. We would point out that hemimorphite is rare at Red Gill and as stated above, despite the fact that Red Gill is one of the most intensively researched localities in the Caldbeck Fells, no-one else has ever found gold there. On the whole it seems safest to delete gold from the Red Gill list of minerals.

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$

Cooper and Stanley (1990) reported hemimorphite from Red Gill as small colourless crystals and globular aggregates. It is rare on the main site, but has been found in this study on several specimens as small compact white spheres reaching 0.8 mm diameter and as typical thin, colourless and lustrous bladed crystals up to 0.5 mm long, forming radiating aggregates.

Hemimorphite is much more common on material from the main East Side Level, where it occurs as crusts of small radiating blades up to 1 mm long.

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

Hydrocerussite was reported from Red Gill Mine by Hartley (1984) on the basis of specimen material claimed to have been collected by Kingsbury. It was not observed during stereomicroscopic examination of material in the Kingsbury Collection, but it is easily overlooked. There seems to be no reason to doubt the report.

Crystals, which are rare at the mine, mainly consist of extremely thin flat plates with an irregular hexagonal cross-section and usually with a pearly lustre. Individual plates reach 1.5 mm across (Fig. 13). Much more abundant are white masses up to 5 mm across, superficially resembling cerussite, but with a distinct cleavage and often surrounded by cerussite, an association confirmed by XRD. In addition to the more common forms above, it has been identified (by XRD) as euhedral translucent rhombs to 0.5 mm on edge, crystallised on mattheddleite and closely associated with caledonite (Fig. 14).

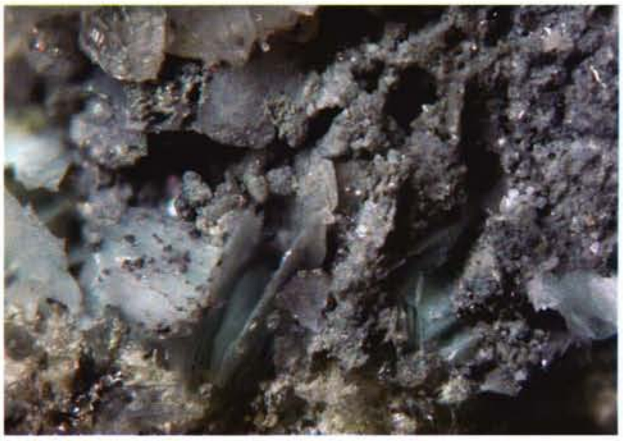

Figure 13. Plates of hydrocerussite to 3 mm from the No. 2 Level dumps.

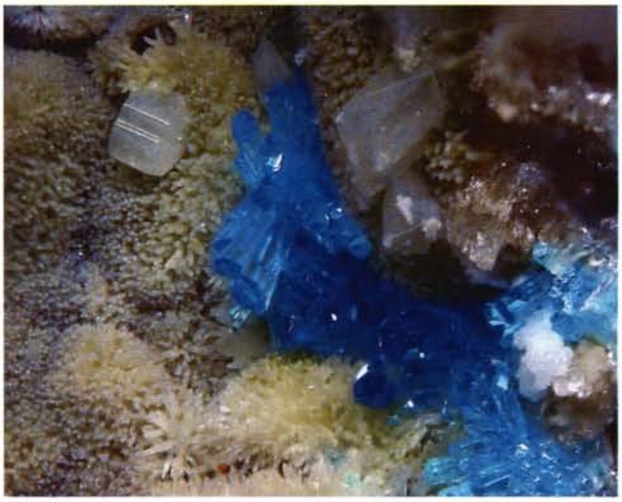

Figure 14. Hydrocerussite rhombs up to 0.5 mm on edge overgrowing mattheddleite with bright blue prismatic caledonite, from the No. 2 Level dumps. Minute pale brown to green encrustations of an unknown copper lead silicate coat the tip of some of the mattheddleite crystals on this specimen.

Two specimens of thin blades with a pearly lustre have been found on specimens from the main East Side Level.

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

Hydrozincite is extremely rare, but has been noted as a typical white encrustation a few millimetres across associated with hemimorphite.

LANARKITE, $Pb_2(SO_4)O$

This very rare mineral was first identified at Red Gill Mine by XRD at Leeds University on a specimen collected by David Middleton. It occurred as minute pale blue tapering bladed crystals on altered galena.

LANGITE, $Cu_4(SO_4)(OH)_6{\cdot}2H_2O$

Cooper and Stanley, (1990) reported langite from Red Gill Mine as deep royal blue crystals with caledonite, identified by XRD at Leeds University. It remains a very rare mineral at the site, but has been found as minute pseudo-hexagonal crystals and anhedral flakes associated with brochantite and covelline on fractured surfaces of a grey copper sulphide.

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

Hartley (1984) reported leadhillite on material collected by Kingsbury and it is present on specimens in his collection. There is no reason to doubt the provenance.

Red Gill Mine has long been noted for producing excellent leadhillite specimens. Greg and Lettsom recorded it as 'found recently' in 1858. Cooper and Stanley, (1990) state crystals up to 35 mm across have been found, but in this study crystals more than 10 mm across are very rare. Crystals are usually thin tabular hexagons, but crystals with elongated prisms occur. Crusts of small hexagonal tablets covering several square centimetres on quartz have also been found. Most crystals are colourless and translucent, but glass clear examples occur (Figs. 15 & 16). Numerous associated minerals include anglesite, susannite, linarite, caledonite, bindheimite and cerussite.

Figure 15. Tabular hexagonal leadhillite crystals up to 4 mm across scattered with small caledonite crystals and minor mattheddleite. Collected by Peter Briscoe from the dressing floor.

Figure 16. Thin tabular hexagonal leadhillite crystals up to 4 mm across with a 1.1 mm linarite crystal in direct contact. Roy Starkey Collection.

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

As with caledonite, Greg and Lettsom (1858) were the first to report linarite specifically from Red Gill Mine. As stated above, many of the Caldbeck Fells early splendid linarite specimens in the NHM collections were originally labelled from Cumberland and Roughton Gill, with the labels sometimes altered to Red Gill. Only since the 1860s are specimens directly labelled from Red Gill Mine. It is now commonly thought that the majority of these old time specimens came from the No. 2 Level.

Figure 17 shows a classic early Red Gill Mine specimen in the Ludlam Collection, the specimen being supplied by Bryce-Wright. Note that early specimens from Roughton Gill are figured in the 'Discussion', where the associated minerals are described and their potential significance considered.

Figure 17. Linarite labelled 'Red Gill Mine, Cumberland'. The specimen width is 80 mm. (Ludlam Collection No. 7450). © NHM.

The Kingsbury Collection contains several specimens with linarite, all but one of which appear genuine. The single exception is documented from the 'Bell Pit' lower down Swinburn Gill and is considered further in the 'Discussion'.

In this study, numerous beautiful specimens of bladed crystals up to 6 mm long have been found in cavities in quartz matrix (Fig. 18). Many of these specimens also have a range of other supergene minerals in direct association with the linarite or elsewhere on the specimen. These minerals include anglesite, bindheimite, caledonite, cerussite, grey copper sulphide, malachite and leadhillite. The last association is of particular interest and is discussed later. Coatings of small crystals on copper sulphides also occur and are probably post-mining in origin. Cooper and Stanley (1990) note that linarite has been found pseudomorphed by malachite and brochantite.

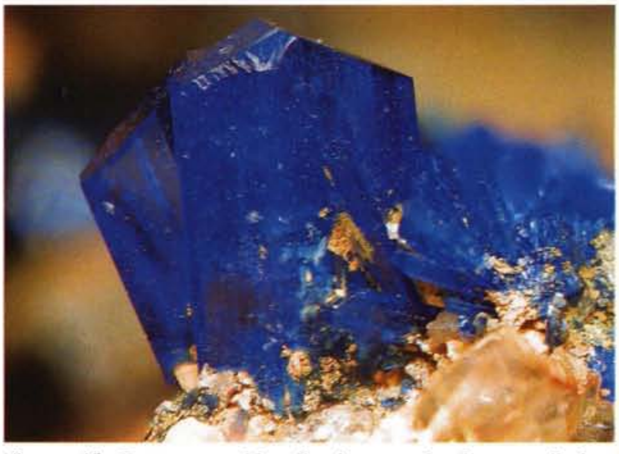

Figure 18. Deep azure blue linarite crystals, 3 mm tall, in a ferruginous matrix from the No 2 Level dumps. David Middleton specimen.

On the Main East Side Level dump the small number of specimens of linarite found all appear to be post-mining in origin.

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

Macphersonite, the rarest of the basic lead-sulphate-carbonates, has been identified at Red Gill by XRD on a single specimen, which was briefly described by Cooper *et al.* (1988). It occurs as a complex grey translucent crystalline mass, 4 mm across, in a cavity in quartz veinstone with susannite, caledonite and mattheddleite (Fig. 19).

Figure 19. Twinned macphersonite aggregate 1.5 mm across collected in 1987 on the No. 2 level dump by David Green.

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

Malachite is listed by Hartley (1984) based on Kingsbury material and it is present on specimens in his collection at the NHM. There is no reason to doubt their provenance. Cooper and Stanley (1990) reported malachite as sprays or spherical aggregates of small emerald green crystals and note that it is commonly pseudomorphed by 'chrysocolla'. Miers (1897) reported it as pseudomorphing linarite.

Figure 20. Green radiating aggregated needles of malachite up to 2 mm long with minor cerussite.

It remains fairly common at the main site and on material from the main East Side Level, the common forms being assemblies of radiating needles up to 5 mm long (Fig. 20), which sometimes form irregular hemispheres, and as 'furry' mats coating cavities in quartz up to 15 mm across. By far the most common associated mineral is cerussite, but associations with linarite and 'chrysocolla' are also common.

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

Mattheddleite is not rare at Red Gill. It was first reported by Cooper *et al.* (1988) on material from the No. 2 level as sprays or crusts, associated with caledonite, leadhillite, susannite and lanarkite and is figured twice by Cooper and Stanley (1990, p. 102 & 108). Mattheddleite typically occurs as drusy crusts and radiating sprays of minute colourless to white hexagonal crystals terminated by a sharp 'pencil point'. The largest crystals found in this study reach just over 0.5 mm in length, but are typically less than 0.1 mm long. Figure 21 shows typical radiating crystals of mattheddleite with caledonite and leadhillite and Figure 22 a cluster of terminated crystals.

Figure 21. Radiating white mattheddleite sprays with individual crystals up to 0.5 mm long on blue blocky caledonite with white thin tabular leadhillite crystals up to 4 mm across, a typical association at Red Gill. From the dressing floor and in the Peter Briscoe Collection.

Figure 22. A highly magnified image of a radiating cluster of mattheddleite crystals up to 0.23 mm long showing the typical 'pencil point' terminations. David Middleton Collection.

Mattheddleite is commonly associated with caledonite, leadhillite and susannite and is also found with anglesite and bindheimite.

MOTTRAMITE, $PbCu(VO_4)(OH)$

Mottramite occurs as a yellow brown encrustation on green pyromorphite on a specimen in the Mike Leppington Collection. The crusts are resolved into characteristic curved boat shaped crystals up to about 30 micrometres across by scanning electron microscopy. EDS shows Cu, V and Pb to be present in the appropriate ratios for mottramite. The mineral is easily overlooked and may be more common than this single specimen indicates.

(PLUMBOGUMMITE, $PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$)

Noted by Berg (1985) on the basis of visual identification, Cooper and Stanley (1990) express the opinion the mineral is probably 'chrysocolla'. It has not been found in the current study.

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

Originally reported by Hartley (1984), psilomelane is a discredited species and most old material identified as 'psilomelane' is romanèchite. However, in this study the latter mineral has not been identified, earthy black barium-manganese deposits proving to be amorphous by XRD.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$
MIMETITE, $Pb_5(AsO_4)_3Cl$
VANADINITE, $Pb_5(VO_4)_3Cl$

Pyromorphite was reported by Hartley (1984) on Kingsbury specimen material. It is visible on some of the specimens in his collection and all are typical of the site.

The mineral is common at Red Gill Mine, usually occurring in fractures surrounding partly oxidised masses of galena-rich veinstone. The form is usually crusts of yellow to green prismatic to blocky hexagonal crystals (Fig. 23). It is also often found as thin inconspicuous crystalline crusts on the outside of specimens of quartz with linarite, caledonite and leadhillite. It is much rarer on specimen material from the main East Side Level.

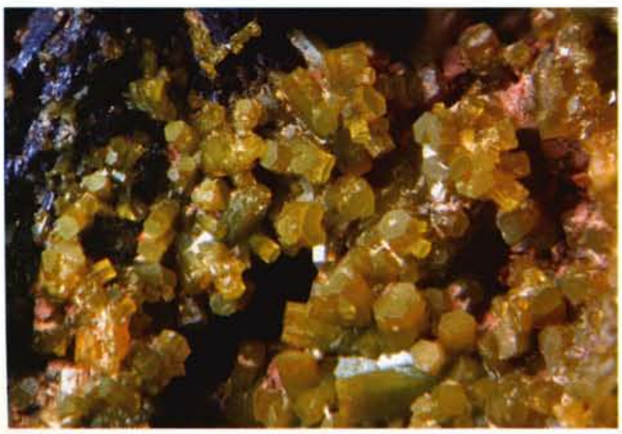

Figure 23. Yellow-green barrel shaped pyromorphite crystals 0.5 mm long from high up Red Gill itself. From the J. George Wilson Collection.

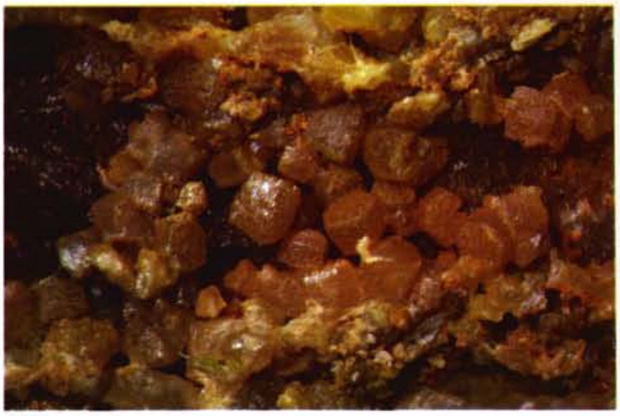

Figure 24. Pale brown blocky hexagonal vanadinite crystals up to 0.9 mm across (XRD and EDS confirmed) associated with green pyromorphite from the Norman Thomson Collection. The specimen is entirely typical of Red Gill Mine.

Mimetite was reported from Red Gill Mine by Cooper and Stanley (1990) on the basis of a specimen supplied by Mick Cooper and confirmed by XRD at Leeds University. Since mimetite was found at the neighbouring workings in Silver Gill (Green, *et al.*, 2005a) and at Brae Fell Mine (Bridges *et al.*, 2006) a further detailed search for it was conducted at Red Gill Mine. Twenty five specimens were examined by EDS but no arsenic was found. However, a single specimen proved to be near end member vanadinite (Fig. 24), the identity confirmed by XRD. This is a remarkably good specimen and raises the question as to whether it actually originated from Red Gill. It was unquestionably found there and the whole specimen is typically Red Gill, with caledonite, linarite, cerussite and earthy bindheimite in small cavities elsewhere on the specimen. If inadvertently dropped at the site by other collectors, it is difficult to see from where it could have originated.

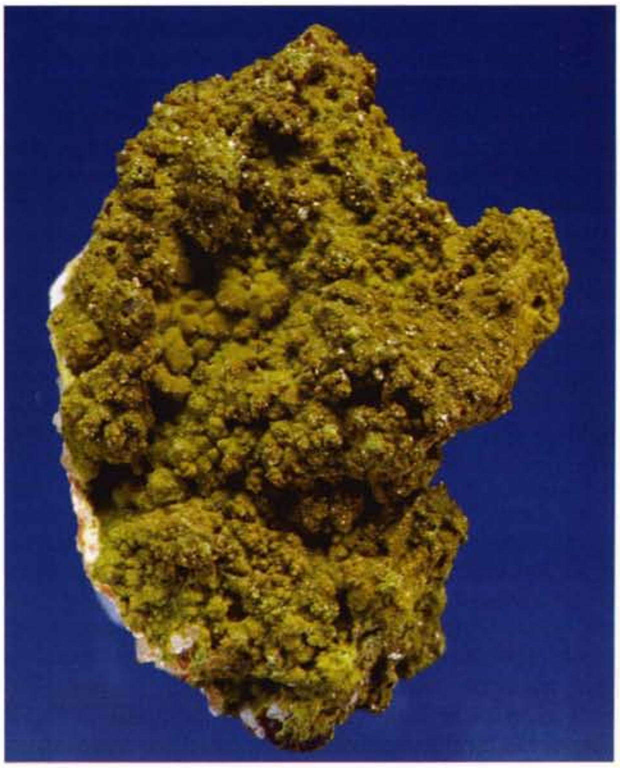

Figure 25. A well crystallised pyromorphite specimen 60 mm in tall from high up Red Gill. David McCallum Collection.

In addition to the above, where pyromorphite is essentially an accessory mineral, rich specimens of pyromorphite were found in the early 1980s where the Red Gill vein is exposed in scree above the mine site on the south side of Red Gill, (J. George Wilson, *personal communication*). They comprise specimens of cellular quartz, up to large cabinet size, encrusted with millimetre-size dark green barrel shaped crystals of pyromorphite (Fig. 25).

QUARTZ, SiO_2

Quartz was the main gangue mineral of the vein and is common on the dumps. Most of the minerals occur in a matrix of quartz. Crystals are common in vugs and are generally pyramidal and usually fairly small, rarely exceeding 10 mm across. However, many of the supergene species occur in irregular cavities in quartz where a primary mineral has been wholly or partially oxidised away.

QUEITITE, $Pb_4Zn_2(SiO_4)(Si_2O_7)(SO_4)$

This rare lead-zinc silicate-sulphate mineral was first found in Britain from Red Gill Mine by the late Mike Rothwell in 1987 on the No. 2 level dump and reported by Braithwaite *et al.*, (1989). Figure 26 shows part of the original specimen.

Figure 26. One of the best queitite specimens collected by the late Mike Rothwell on the No. 2 Level dump in 1987. The field of view is 6 mm across and the queitite is partly overgrown by a few pale blue susannite crystals. Richard Bell Collection.

The site remains one of the very few world-wide localities where this rare species has been recorded. Due to its rarity it is worthwhile recording the discovery in detail. The original description of the specimen, which broke into several fragments is as follows:

"The material consists predominantly of massive cerussite with subordinate quartz and represents the contents of a small cavity from the Red Gill vein. The cavity also contains leadhillite, susannite and caledonite in addition to the quietite, all deposited after the cerussite. The queitite forms a white drusy and minutely botryoidal encrustation (with a silky fibrous fracture), about 0.5 mm thick, on leadhillite and susannite, the latter in typical pale blue steep rhombohedra. A thin discontinuous layer of a somewhat granular yellow unidentified material, perhaps pyromorphite-mimetite, underlies some of the quietite, but was not seen in association with the leadhillite-group minerals. Caledonite was the last mineral to form."

A battery of analytical techniques was used to characterise the material including XRD (University of Leeds and NHM), semi-quantitative energy dispersive X-ray spectrometry (NHM) and infra-red absorption spectroscopy (University of Manchester).

Since rare species such as queitite have a peculiar fascination for collectors and curators, it is worth recording the fate of the specimens twenty years after they were found. All of the original specimens were from a relatively small piece of veinstone which broke during collection and was subsequently trimmed to produce ten separate fragments. One was donated to the NHM, others were given to Richard Bell (2), John Dickinson (1), David Green (1), Mike Leppington (2) and the British Micromount Society Collection (1) with the best two being retained by Mike Rothwell. The specimens belonging to Mike Rothwell and John Dickinson were bequeathed to Richard Bell who currently has four specimens registered in his collection.

In addition to the above, a further specimen, also confirmed by XRD, has been found by Neil Hubbard in a block from the stream bank near the dressing floor.

The rarity of queitite places a responsibility on anyone who owns a specimen to curate it carefully.

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

The name redgillite confers a measure of mineralogical immortality on Red Gill Mine, although as a result of crystallographic difficulties encountered in the description of the species (IMA:2004-016), the type specimen is in fact from the nearby workings in Silver Gill (Pluth *et al.*, 2005 and Green *et al.*, 2005a). The name redgillite has been in colloquial use among mineralogists since the late 1980s, long before the species was formally described. Specimens from sites in mid-Wales and the Caldbeck Fells were first recognised in the mid-1980s and a photograph of a remarkable specimen from Red Gill, which sadly appears to have been lost, is reproduced in Cooper and Stanley (1990, p. 133).

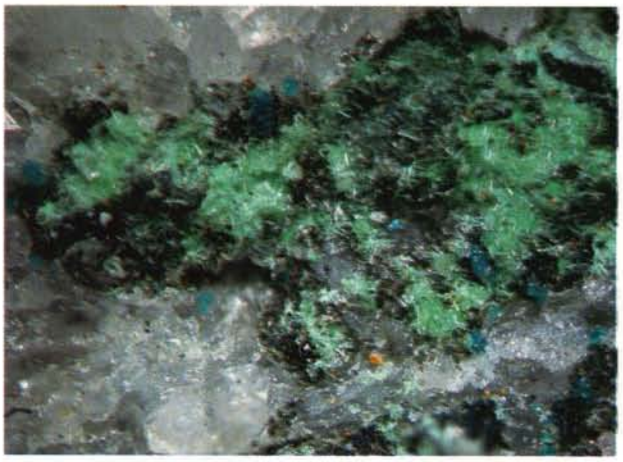

Figure 27. Redgillite crystals up to 0.1 mm across, associated with small blue langite crystals from No. 3 Level. David Green Collection.

Redgillite occurs at Red Gill Mine as radiating sprays of pale to grass green acicular to long prismatic crystals which are usually less than 1 mm in length (Fig. 27). It typically occurs in thin fractures in sulphide-rich matrix associated with other copper sulphate minerals, notably langite and is probably post-mining in origin.

SCOTLANDITE, $PbSO_3$

This very rare mineral was reported from Red Gill by Neall *et al.*, (2006) on the basis of XRD analysis at Manchester Museum. It occurs as minute (<0.3 mm) thin prismatic crystals in a quartz and highly oxidised galena matrix and in association with mattheddleite and leadhillite and in one case is overgrown by caledonite. One particularly good specimen, in the Mike Leppington Collection, consists of several small cavities in similar matrix with numerous crystals up to 0.5 mm on the longest dimension

SERPIERITE, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6{\cdot}3H_2O$

This extremely rare mineral at Red Gill was reported by Cooper and Stanley (1990) as soft, pale blue micaceous aggregates on cerussite, identified by XRD (NHM) on a specimen in the Peter Braithwaite Collection. It is probably a dump formed mineral.

SILVER, Ag

Native silver was first reported from Red Gill by Wirth (1989) as minute arborescent growths. A small number of specimens have been found since and one particularly good specimen in the Richard Bell collection consists of arborescent wires up to 2 mm long on iron stained quartz (Fig. 28). As stated previously most of the specimens are altering to acanthite in collections.

Figure 28. A relatively unaltered specimen of silver as somewhat blackened arborescent masses 2 mm long in white vein quartz. Richard Bell Collection.

SPHALERITE, (Zn,Fe)S

This mineral is reported by Cooper and Stanley (1990) on the basis of a study by Berg (1985). It is surprisingly rare at the site, but does occur as small brown blebs, with typical cleavage, associated with galena and chalcopyrite in quartz matrix and as small (*ca.* 3 mm) crystals in quartz from the main site and the main East Side Level.

SULPHUR, S

Sulphur is rare, but occurs as crusts of pale yellow crystals usually associated with oxidised galena and often also with covelline. Individual crystals reach 1 mm, but are generally smaller than this.

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

Susannite is not uncommon at Red Gill. Thin hexagonal prisms, c. 0.2 mm across and up to 2 mm long, usually with a tapering pyramidal termination are the commonest form. Larger crystals are often tapering pyramids, up to 1 mm across, and usually no more than 3 mm long. Small crystals are often colourless and opaque, but larger crystals are usually pale blue and translucent. Figure 29 is of a group of typical small susannite crystals. Rarely doubly terminated pyramidal crystals occur (Fig. 30) and, even more rarely, crystals can be glass clear. Common associates are caledonite, leadhillite and linarite. It is interesting to note that small crystals of visually identified susannite occur on one of the specimens in the Kingsbury Collection, but was apparently not recognised.

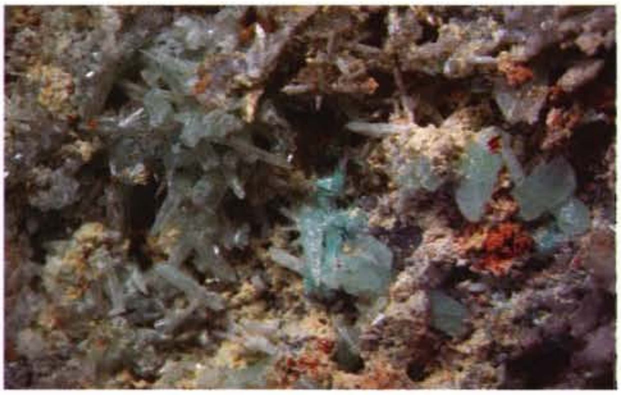

Figure 29. Well formed elongated susannite prisms up to 1.3 mm long, tapering to a three-sided point with probable leadhillite and caledonite. Trevor Bridges Collection.

Figure 30. A single pale blue susannite 2.1 mm tall with characteristic trigonal symmetry. Peter Briscoe Collection.

WROEWOLFEITE, $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$

A single specimen of wroewolfeite, comprising bladed crystals up to 0.5 mm long, in a cavity in chalcopyrite matrix, was identified by XRD at Leeds University (Fig. 31). The specimen was collected on the middle level dumps in the late 1980s (Cooper and Stanley, 1990, authors unpublished data).

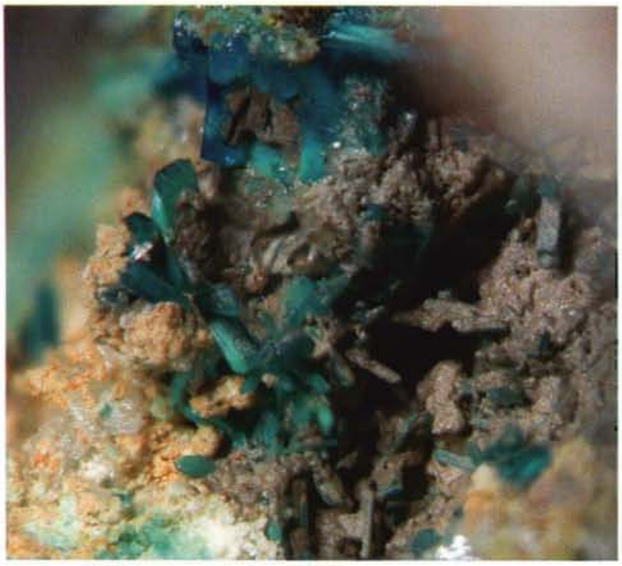

Figure 31. Characteristic blue bladed wroewolfeite crystals up to 0.2 mm from the No. 2 Level dump. David Green Collection.

UNIDENTIFIED MINERALS

Lead-copper sulphate

In a study of the mineralisation at the Driggith and Sandbed mines a poorly characterised lead-copper sulphate from Driggith Mine (Green *et al.*, 2006, p. 35 and Fig. 58) was described. Identical material, comprising radiating sprays of pale blue acicular to feathery crystals up to 0.1 mm in length, occurs with elyite from the top level at Red Gill Mine. It is worthwhile pointing out that although the mineral is described as a sulphate, it could be a sulphite or even possibly a thiosulphate.

Copper-lead silicate

A pale brown frothy cellular boxwork overgrowing mattheddleite was examined by EDS, which showed it to be a copper-lead silicate with a composition similar to material which has been identified in almost identical parageneses from the Leadhills district in southern Scotland. Some specimens from Leadhills have been identified as creasyite and others are described as creasyite-like phases (Steve Rust, *personal communication*). There is insufficient material from Red Gill for more complete analytical work.

DISCUSSION

The primary mineralisation of the main workings of Red Gill Mine is predominantly galena and chalcopyrite in a gangue of quartz with some baryte. As such it is reasonably typical of the approximately E-W veins of the Caldbeck Fells, apart from the apparent scarcity of sphalerite, as evidenced by the small amount found in this study and the paucity of supergene zinc minerals. Also noteworthy is the rarity of primary carbonates such as calcite, dolomite and ankerite on the main site. Pyrite has not been found in the present study but since this mineral is readily oxidised, the abundant presence of limonitic ochre suggests it may have been present in reasonable quantity at one time, although the oxidation of chalcopyrite also produces limonite.

The primary mineralisation may not be special, but the supergene mineralisation most certainly is. It seems likely that the structure of the vein, and its relationship to the hillside, has permitted supergene alteration to take place at some depth over a long period of time. Initially, there appears to have been a lengthy period of sub-watertable supergene enrichment resulting in the partial replacement of galena and chalcopyrite by grey copper sulphides. As the watertable fell, due to erosion, a long period of oxidation must have ensued to account for the formation of the excellent specimens of linarite, anglesite, caledonite, susannite and leadhillite and rarer interesting species such as mattheddleite, hydrocerussite, queitite, redgillite and elyite.

Most of the specimens in the Kingsbury Collection in the NHM are entirely typical of recently collected material and there is no need to doubt their provenance or that Kingsbury collected the specimens himself. It is interesting to note that these specimens were all collected in 1950, which is before the 1951 date when it is considered Kingsbury commenced his fraudulent behaviour (Ryback *et al.*, 1998 & 2001). However, there are two exceptions, the first of which is a group of gold specimens from Swinburn Gill, which Kingsbury claimed to have collected in 1953 at a date when he did not collect any other Red Gill specimens. This gold is almost certainly fraudulent. The second exception is an excellent specimen of linarite, with 10 mm blades in a cavity 40 mm by 20 mm, which Kingsbury claimed to have found from the bell pit lower down Swinburn Gill in 1950. This site is very poorly mineralised and almost certainly the specimen did not originate there. However, it has the appearance of a Red Gill specimen and looks quite fresh, without the patina of an old time specimen. Its true provenance must remain uncertain.

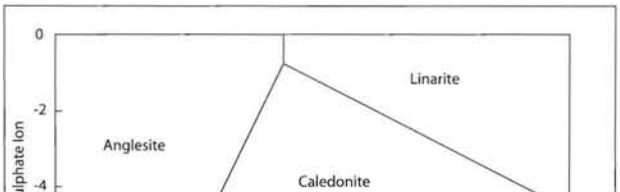

Figure 32. Stability diagram for the system lead-copper-sulphate-pH- pCO_2 at $a Cu^{2+}$ of 10^{-8} and pCO_2 of 0.000141, conditions under which cerussite and hydrocerussite are in equilibrium. The association of these two minerals is common at Red Gill.

The close association of leadhillite and linarite in small cavities, often intergrown with each other is common at Red Gill Mine. Figure 16 shows a typical example of the association. Figure 32 shows a stability field diagram for the system lead-copper-sulphate-pH-pCO_2. The necessary thermochemical data for the species involved are taken from the compilation of Robie *et al.* (1978) for anglesite and the more common ions in solution. The data of Taylor and Lopata (1984) have been used for cerussite and hydrocerussite and that of Abdul-Samad *et al.* (1982) for leadhillite, caledonite and linarite. It can be seen that in terms of sulphate ion activity (aSO_4^{2-}) the caledonite field extends over three orders of magnitude. The association of linarite and leadhillite would therefore be expected to be extremely rare at best, but in addition to being fairly common at Red Gill Mine it has been observed at higher Roughton Gill and at four other localities in the UK, despite the overall rarity of leadhillite. Furthermore, the scale of the caledonite field would indicate that low levels of copper ion, entering an environment where lead minerals are forming, should result in the formation of caledonite. In fact linarite is by far more common in these circumstances, associations with anglesite and cerussite being common from numerous localities in the UK. Since it is unlikely that kinetic effects could account for the association of leadhillite with linarite, the thermochemical properties of the three minerals would seem to require re-assessment.

It is worth discussing in more detail the provenance of the early 19th Century linarite specimens. Davidson and Thomson (1951) and Cooper and Stanley (1990) both express doubts about the early linarite specimens attributed to Roughton Gill Mine, doubts with which the current authors concur. The reasons for this are mineralogical and this study provides a suitable opportunity for discussing them in some detail.

Mining sites often have a distinct mineralogical character which endures through the ages and means that in many cases, specimens are instantly recognisable. A classic example is the campylite and plumbogummite from Dry Gill Mine in the Caldbeck Fells. Applying this philosophy to the Red Gill and Roughton Gill mines, the latter has produced excellent specimens of pyromorphite into the period covered by this study. The mine was also noted for fine specimens of plumbogummite and pale blue botryoidal hemimorphite, small specimens of which were found during this study. The 90 fathom level dumps of Roughton Gill Mine are rich in pyromorphite, bladed hemimorphite crystals and 'chrysocolla'. Also common, are cerussite, crystalline brochantite and the supergene carbonates rosasite, aurichalcite and malachite. Anglesite, linarite and grey copper sulphides are rare. An inspection of over 100 Roughton Gill specimens revealed only 2 specimens of linarite (one a dump formed crust) and no caledonite, leadhillite or the earthy form of brochantite. This assemblage indicates the solutions effecting the oxidation had a near neutral pH, and reasonably high carbonate ion activity (aCO_3^{2-}) and pCO_2 in order to stabilise the supergene carbonates in particular and to destabilise leadhillite and anglesite. It should be noted that these comments only apply to the main lower dumps of Roughton Gill Mine, not Higher Roughton Gill Mine, which is often called Thief Gill or Balliway Rigg. The mineralogy of this site, which is the subject of another review (Green *et al.* 2008), is more similar to Red Gill than to the main Roughton Gill site, although on a very much smaller scale.

The contrast between Roughton Gill and Red Gill Mine is amazing considering the localities are only approximately 1km apart. Red Gill Mine has produced excellent specimens of linarite, caledonite, leadhillite (and its polymorphs), cerussite and anglesite from the mid 1800s until the present. Recent specimens are smaller than in the past, but they are still very good. Other significant and relatively common minerals are grey copper sulphides, hydrocerussite and earthy as opposed to crystalline brochantite. Hemimorphite and crystalline brochantite are rare and even malachite is not abundant. This mineral assemblage indicates formational conditions which started with a period of supergene enrichment leading into conditions of oxidation with relatively low pH, aCO_3^{2-} and pCO_2 in order to stabilise leadhillite and its polymorphs, hydrocerussite and indeed to permit the formation of significant amounts of anglesite. For a full treatment of the background to the geochemical conditions outlined above see Williams (1990).

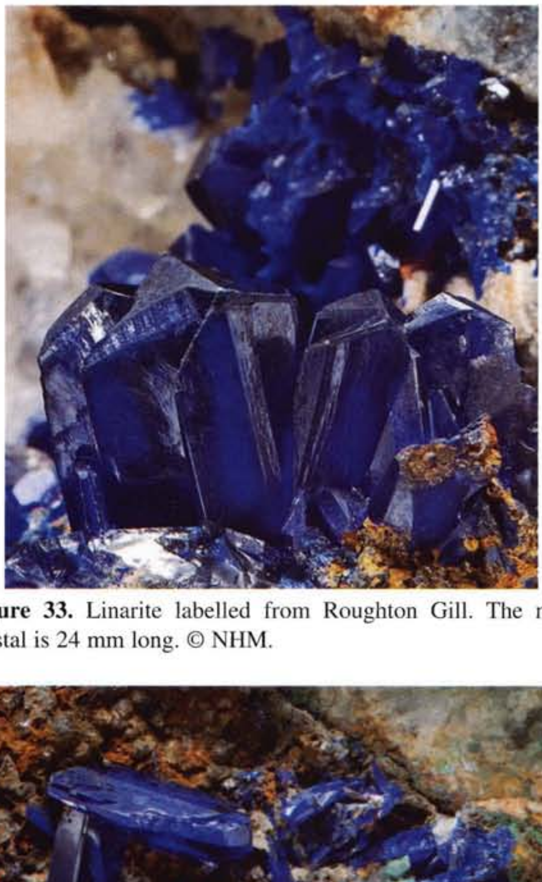

Figure 33. Linarite labelled from Roughton Gill. The main crystal is 24 mm long. © NHM.

Figure 34. Linarite labelled from Roughton Gill. The main crystal is 16 mm long. © NHM.

Figures 33, 34 and 35 show superb specimens of linarite attributed to Roughton Gill Mine and in the main

NHM Collections. These and other early Roughton Gill specimens commonly have grey copper sulphides and earthy brochantite as associated species, as do early and recent Red Gill specimens. The older specimens tend to be richer in the grey copper sulphides, which has some bearing on a possible formational mechanism which is discussed later. There are two particularly interesting specimens in the Ludlam Collection in the NHM. Figure 36 is of a specimen of linarite with caledonite and leadhillite attributed to Roughton Gill Mine which can be compared with Figure 17 of linarite from Red Gill Mine. The matrices of the specimens are very similar.

Figure 35. Linarite labelled from Roughton Gill. The upright crystal is 14 mm high. © NHM.

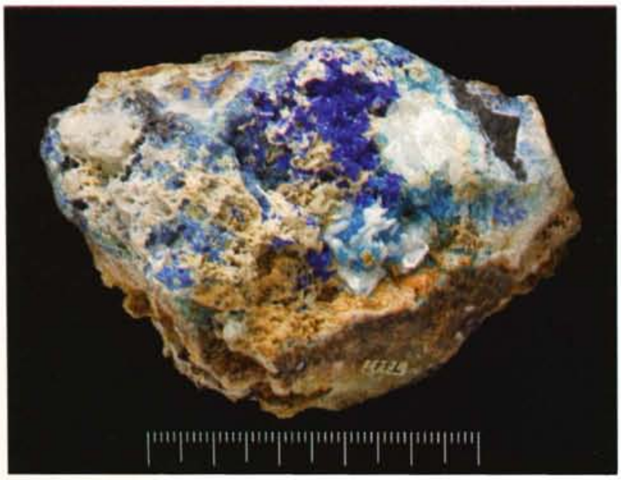

Figure 36. Linarite with caledonite and leadhillite, labelled from Roughton Gill Mine. The specimen is 85 mm wide. (Ludlam Collection No. 7447). © NHM.

Based on the discussion above it is nearly inconceivable that the specimen of linarite with caledonite and leadhillite (Fig. 36), in the Ludlam Collection, could have come from Roughton Gill as opposed to Red Gill. Furthermore, the associated grey copper sulphides and earthy brochantite of the early 'Roughton Gill' specimens point to a Red Gill origin for all the specimens. While the case cannot be regarded as proven, it really is most probable that all the early classic linarite specimens labelled Cumberland and Roughton Gill actually came from Red Gill Mine.

The unusual nature of the mineralogy at Red Gill Mine makes it worth enlarging on a possible mechanism to account for the mineral assemblage. The thermochemical data, on which the following discussion is based, are as for those used to prepare the stability diagram above, combined with data and diagrams in the classic works of Garrels and Christ (1965) and Williams (1990). As stated above the primary vein seems to have consisted of quartz, baryte, chalcopyrite, galena and possibly pyrite with very little sphalerite and carbonates. A period of sub-watertable supergene enrichment, greater than elsewhere in the Caldbeck Fells, seems to have occurred to account for the relatively abundant grey copper sulphides at the site. As the watertable fell, oxidation set in at relatively low pH, due to the sulphuric acid released by the oxidation of chalcopyrite (and possibly pyrite) and lack of neutralising carbonates. The lack of the latter also resulted in low pCO_2. Under these conditions, oxidation over an extended period of time of chalcopyrite, grey copper sulphides and galena, could give rise to the large linarite crystals and minerals such as anglesite. It is also possible that high $a\mathrm{Cu}^{2+}$, high $a\mathrm{SO_4}^{2-}$ and low pH gave rise to the formation of small pockets of antlerite or its precursor compound 'antlerite dihydrate' $Cu_3SO_4(OH)_4 \cdot 2H_2O$, (Pollard *et al.*, 1992). In a recent paper Yoder *et al.*, 2007 conclude the latter mineral is $Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$, but this compound does not dehydrate to antlerite and that of Pollard and his colleagues does (identity confirmed by XRD), indicating that the different experimental techniques employed have produced two different compounds. In addition, the report of Yoder *et al.* does not suggest a mechanism for the formation of antlerite in the temperature range 10 to 40°C, leaving the work of Pollard *et al.* seeming to provide a better interpretation of natural systems. Finally, oxidation under low pH conditions explains the formation of native sulphur, which only forms at low pH, and the rarity of cuprite, which commonly forms from the oxidation of grey copper sulphides at near neutral pH, but not at low pH.

With time and gradual depletion of the sulphides, pH would rise and $a\mathrm{SO_4}^{2-}$ fall. This would allow some gradual increase in $a\mathrm{CO_3}^{2-}$ permitting the formation of minerals such as caledonite, cerussite, hydrocerussite, malachite, leadhillite and the latter's polymorphs. These conditions would destabilise any antlerite (or its dihydrate) that is present and Bridges *et al.* (2005) suggest that the earthy form of brochantite may often result from the decomposition of this mineral. This could explain the fact that earthy brochantite is relatively common at the site.

The silica required for the copper-bearing silica gel and the other silicate minerals such as mattheddleite and queitite, is presumably derived from wall rock weathering. Wall rock weathering probably also accounts for the formation of the very rare high pH minerals such as lanarkite, elyite and redgillite, minerals which still demand a very low $a\mathrm{CO_3}^{2-}$ and pCO_2. Such weathering would also provide the phosphate for the formation of pyromorphite. The low levels of chloride ion required for some of the minerals always seems to be present in the environment.

Minerals such as native silver and cinnabar are relict phases from sulphide oxidation and the oxidation of galena would also provide the antimony for the formation of bindheimite.

While much of the above is speculative, it does provide a possible geochemical model to account for the mineralogy of this remarkable site.

Finally, the specimen material from the main East Side Level indicates more alkaline conditions prevailed there giving rise to relative abundance of cerussite and malachite and a rarity of sulphates. Hemimorphite is also much more common. In some respects the assemblage is intermediate between that of the main Red Gill site and Roughton Gill, which is of course where the site is placed.

SPECIMENS

In addition to the collections of the NHM, specimen material from this study have been placed in the collections of The Manchester Museum and the Hancock Museum, Newcastle upon Tyne.

ACKNOWLEDGEMENTS

We should like to acknowledge the help received from Richard Bell, Peter Briscoe, Neil Hubbard, David McCallum, David Middleton, Roy Starkey, George Wilson and the late Max Wirth and especially to Norman Thomson for allowing inspection and where necessary analysis of specimen material in their collections. It has been a classic example of co-operation among amateurs in furthering the needs of science. We should like to thank Harry Taylor, NHM Image Resources, for the excellent photographs included as Figures 17 and 33 to 36. The copyright of the photographs remains with the NHM. MSR would like to thank Austin Woodbridge for his help with curating the Ludlam Collection, used by Roy Starkey in preparing a lecture and TFB would like to thank Roy Starkey for an interesting discussion on this collection. In particular we should like to thank Julie Ballard whose photographic skills provided many of the other photographs figured in this study.

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Journal of the Russell Society, **11**, 48-50 (2008)

BARYTE FORMATION IN SUPERGENE ENVIRONMENTS IN THE CALDBECK FELLS, CUMBRIA

Trevor F. BRIDGES
10 Springfield, Ovington, Prudhoe NE42 6EH

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

The occurrence of baryte crystals, on specimens which clearly formed in a supergene environment, is described from several localities in the Caldbeck Fells, Cumbria. In many cases the baryte has crystallised on minerals of undoubted supergene origin such as cerussite and malachite. It is suggested that bacteriogenic reduction of the sulphate in primary baryte mobilised barium as its soluble sulphide, and that this later re-deposited as supergene baryte in oxidising conditions. Further examples of this phenomenon have been noted from Derbyshire.

INTRODUCTION

Supergene baryte is common in the Northern Pennine Orefield as an alteration of witherite (barium carbonate) and barytocalcite and alstonite (both barium, calcium carbonate). It mostly occurs as a surface encrustation, but on occasion may completely replace the original mineral. The form is usually crusts of small thin transparent or white flakes and tablets often with a diamond shape. It is most common as a dump alteration mineral, but has been observed *in situ*, for example at Nentsberry Haggs Mine. The mechanism for its formation is simply that sulphates and even sulphuric acid are formed by the oxidation of heavy metal sulphides and these react with the barium carbonate. At atmospheric temperatures, baryte is far more stable (less soluble) than all of the barium carbonate minerals.

Recent research in the Caldbeck Fells has revealed that, at several sites, baryte occurs closely associated with supergene minerals in cavities in quartz matrix, with no real evidence that barium carbonates were ever present in the area. Details of several occurrences follow.

OCCURRENCES OF SUPERGENE BARYTE

At the first seven locations considered in this study, the supergene baryte crystals are small and are often very similar in morphology to the supergene baryte of the Northern Pennine Orefield. The final locality - Dry Gill Mine - differs from the others in that the supergene baryte crystals are far more numerous and are significantly larger.

Silver Gill Workings. NY 298 340 to NY 301 345

The workings at Silver Gill were mainly on a NE-SW vein in which quartz, galena and chalcopyrite are the main primary minerals. Green *et al.* (2005) summarised the supergene mineralogy of the site and reported small transparent blades of baryte from the upper workings. The crystals occur with malachite on goethite encrusted quartz, clearly indicating that they are of supergene origin.

Brae Fell Mine. NY 298 357

Brae Fell Mine worked an approximately E-W quartz-baryte-galena-chalcopyrite vein in lavas and volcanic sediments of the Ordovician Eycott Volcanic Group. The mineralogy of the site has been summarised by Bridges *et al.* (2006) who reported that small (*ca.* 1 mm) clear and opaque white crystals of baryte occur in cavities in limonite stained quartz and in one case enclosing a supergene copper mineral. Some of the baryte crystals resemble one form of anglesite with which they may be easily confused at first sight.

Red Gill Mine. NY 295 348

This mine worked an approximately E-W quartz-baryte-galena-chalcopyrite vein. In the study several specimens consisting of small colourless or white rhombic or diamond shaped tablets, up to 3 mm long and up to 0.5 mm thick were found associated with cerussite and malachite on iron stained quartz. One excellent example consists of transparent 1 mm diamond shaped crystals perched on caledonite crystals (M. Woodward collection), but similar crystals have also been observed on cerussite and malachite. Figure 1 shows a typical example of white crystals associated with malachite.

Figure 1. Blocky white crystals of supergene baryte up to 2.5 mm long associated with malachite from Red Gill Mine, Caldbeck Fells, Cumbria.

Roughton Gill Mine. NY 303 343

Roughton Gill Mine mainly exploited the approximately NE-SW trending Roughton North and South Veins. These are quartz-baryte-sulphide veins which are noted for carrying large quantities of pyromorphite. Extremely thin blades of baryte occur encrusting ochres of limonite and wad. Individual crystals reach 5 mm long, but are less than 1 mm in height. The crystals are usually transparent and rosasite is in association on two of the specimens examined.

Dump from shaft on Deer Hills. NY 3145 3625

On this small dump, quartz is virtually the only gangue mineral and the vein material is very highly oxidised. Various arsenate minerals such as carminite and mimetite dominate the supergene assemblage. Small tabular crystals of baryte up to 1 mm long occur in cavities in quartz lined with beudantite and carminite. The baryte crystals, which are white or clear, can be seen to enclose carminite on some specimens.

Trial on Low Pike. NY 320 358

This trial explored a quartz-baryte vein, in which primary baryte appears to be more abundant than at all the other sites considered here. The veinstone contains numerous cavities and fractures, which contain tabular crystals of baryte, up to 2 mm long, which can be seen to grow on or engulf supergene minerals such as bayldonite, philipsburgite and pseudomalachite. In some cases the baryte appears green due to inclusions of these minerals.

Saddleback Old Mine. NY 332 286

Strictly this mine is just outside the Caldbeck Fells but is included for completeness. It worked a quartz-baryte-galena vein in mudstones and siltstones of the Kirkstile Formation of the Ordovician Skiddaw Group. A tabular crystal of baryte on dark brown goethite, which is clearly supergene, is figured by Briscoe *et al.*, (2008, Fig. 3) in a recent description of the mineralogy of the site.

At all of the above localities, the supergene baryte crystals are small and are often very similar in morphology to the supergene baryte of the Northern Pennine Orefield. The final locality in this study is different to the others in that the supergene baryte crystals are by far more numerous and also significantly bigger.

Dry Gill Mine. NY 324 245

Dry Gill Mine is well known for splendid specimens of the variety of mimetite called campylite which occurred in approximately E-W quartz-baryte veins with abundant manganese oxides. While much of the baryte is unquestionably of hypogene origin, baryte that has formed in supergene conditions is common. On many of the specimens examined, the most common sequence of deposition of the supergene minerals is mimetite coated by plumbogummite, followed by further mimetite which may be prismatic or of campylite habit. Crystals of baryte up to 15 mm long, occur here, coated by plumbogummite, crystallised on plumbogummite, enclosed by mimetite and growing on mimetite. Baryte also occurs crystallised on goethite and wad. Interestingly, some of the baryte crystals show signs of corrosion, even though the associated crystals of plumbogummite and mimetite are unaffected. The crystals discussed above are mainly tabular and in some respects are similar to common forms of primary baryte, but, in addition to these, small crystals up to 1.5 mm and very similar to those at the other localities occur. Figure 2 shows supergene baryte crystals encrusting hexagonal mimetite crystals and Figure 3 tabular supergene baryte associated with mimetite on limonite.

Figure 2. Blocky white crystals of supergene baryte up to 0.8 mm long overgrowing tabular hexagonal mimetite crystals from Dry Gill Mine, Caldbeck Fells, Cumbria.

Figure 3. Tabular supergene baryte crystals up to 5 mm long on 'limonite' with an unusual stalactitic morphology from Dry Gill Mine, Caldbeck Fells, Cumbria.

DISCUSSION

There can be little doubt that the baryte occurrences outlined above have formed in supergene conditions and are not of hypogene origin, unlike the bulk baryte deposits of the Caldbeck Fells. The formation of supergene baryte requires the mixing in solution of barium ions (Ba^{2+}) and sulphate ions (SO_4^{2-}) in the oxidation zone of a deposit.

Normally sulphate will always be present in oxidation zones, but mobilising barium ions is more problematic. Several possible mechanisms are now considered.

The low solubility of baryte means it is unlikely the crystals have formed by simple dissolution of baryte followed by later precipitation.

There is no real evidence that barium carbonates were ever present in the area. Shaw (1970) reports that assays of baryte, in an unspecified baryte working, showed up to 0.5% $BaCO_3$ and that 'Examination of the lode with an ultra violet lamp has shown spots of witherite in some parts of the solid barytes lode, but it could not be discerned with the naked eye in ordinary light'. However, a low level of calcite could have the same effect. In any case, the barium carbonates all have a low solubility and normally replacement with baryte takes place at the site of the carbonate.

It is theoretically possible that these crystals could have formed as the result of very late stage hydrothermal solutions, similar to the solutions observed in several of the coal mines of north-east England, reaching the oxidising environments in the veins. The nature of these solutions, which carry $BaCl_2$, is described and discussed by Edmunds (1975) and Dunham (1990). These solutions would readily react with sulphate to form baryte and did so in the coal mines, blocking up pipework. However, these solutions only occurred at depth in the coal mines and there is no evidence whatsoever that such solutions were encountered in the relatively shallow workings of the Caldbeck Fells.

The problems of the above mechanisms, combined with the obvious corrosion of the primary baryte crystals at Dry Gill Mine suggests another mechanism is required. Green *et al.* (2005) report the existence of supergene galena at a number of localities and attribute this to oxidising conditions occasionally reverting to reducing conditions for periods long enough for some formation of galena. They suggest that changes in the level of the water table could easily account for this. Baryte subjected to the same process can be reduced to barium sulphide by bacteriogenic processes and barium sulphide is very soluble in water. If this migrates to an oxidising environment it will revert to baryte, which may well be obviously supergene as described above. That baryte can be readily reduced in this manner has been demonstrated by Ulrich *et al.* (2003) in a landfill situation. They observed that the bacteria in landfill leachate could reduce significant amounts of baryte to barium sulphide in a matter of days. However, for this process to work in an oxidising mineral vein, sulphate ion activity ($a\mathrm{SO}_4^{2-}$) must be very low or the bacteria will preferentially reduce sulphate in solution. Such conditions will only arise when oxidation is well advanced and this probably accounts for the fact that the supergene baryte is associated with sulphate free minerals, the only exception observed being the association with caledonite at Red Gill Mine and this latter mineral is a sulphato-carbonate. For further information on the dissolution of baryte see Bridges and Green (2006).

There is clearly no reason why supergene baryte should not be present in other suitable orefields, where there is a source of primary baryte and deep oxidation of the orebodies. An exhaustive study of other localities has not been undertaken, but inspection of material from the Leadhills-Wanlockhead orefield failed to reveal any examples. However, in the Derbyshire orefield baryte, which appears to be supergene in origin, has been noted at three localities. At Wapping Mine, Matlock (SK 294 574) extensive crusts of small clear flat blades of baryte, up to 5 mm across, occur on calcite and limonite, often incorporating the latter mineral. At an opencast working on Bonsall Moor, Matlock (SK 249 594), small clusters of 1 mm white crystals occur associated with and partly on hemimorphite in fluorite. At Millclose Mine, Matlock (NY 263 618) clear blades and white needles of baryte occur in cavities with other supergene minerals and in one case can be seen to be crystallised on smithsonite. There are almost certainly many more localities.

ACKNOWLEDGEMENTS

Thanks are due to Peter Briscoe, David McCallum, Roy Starkey, the late Max Wirth and especially Norman Thomson for allowing inspection and where necessary analysis of specimen material, relevant to this study, in their collections. TFB would also like to thank Brian Young for a most interesting discussion on the occurrence of baryte in supergene environments.

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Journal of the Russell Society, **11**, 51-53 (2008)

THE FIRST BRITISH OCCURRENCE OF KOMBATITE, $Pb_{14}(VO_4)_2O_9Cl_4$, FROM THE "WESLEY MINE" NEAR WESTBURY ON TRYM, BRISTOL

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

The mineralised manganese deposits of the Mendip region in Somerset have produced some of the rarest mineral species known within the British Isles. The region contains three type localities which have produced six type specimens, two of which are still yet to be found outside the region. All six type species are lead-based oxychlorides and a total of nine different lead-based oxychlorides are currently known from the area. This paper gives the description of one more; kombatite, ideally $Pb_{14}(VO_4)_2O_9Cl_4$, from "Wesley Mine", near Westbury on Trym. Although not a new species to science, kombatite is new to the British Isles and its occurrence at "Wesley Mine" is only the second reported occurrence worldwide.

INTRODUCTION

Kombatite, ideally $Pb_{14}(VO_4)_2O_9Cl_4$, was described as a new species by Rouse *et al.* (1986) from the Kombat Mine in Namibia. Here it occurred as tiny 0.2 mm anhedral bright yellow grains embedded within calcite veins in hausmannite (Anthony *et al.*, 2000). It has remained extremely rare, only a few specimens are known and the occurrence reported here, a single grain from a single specimen from the "Wesley Mine", represents the first natural material found outside the original locality.

GEOLOGY

The mineralized manganese deposits of the Mendip region in Somerset have produced some of the rarest mineral species known within the British Isles. The region contains three type localities: Merehead Quarry (also known as Torr Works Quarry), Higher Pitts Farm (also known as Priddy) and "Churchill" (exact locality uncertain). These localities have produced six type specimens: mendipite, chloroxiphite, diaboleite, mereheadite, parkinsonite and symesite. All six types are lead-based oxychlorides and a total of nine different lead-based oxychlorides are currently known from the area.

The specimen identified as kombatite, lead-based oxychloride number ten for the Mendip area, comes from the "Wesley Mine" (also known as Didsbury College Mine) near Westbury on Trym and Henbury in the Bristol City Unitary Authority. Little is known about the original workings of "Wesley Mine", which were discovered by accident during excavations for an extension to the foundations of Wesley Theological College in 1983 (Alabaster, 1989). It is recorded that there was active mining for manganese, iron and lead in the Bristol area during the 17th, 18th and 19th Centuries, but the era and purpose of "Wesley Mine" remains unknown. There is a possibility that "Wesley Mine" corresponds to a site known to be active in 1756 called "Pope's Work", a small copper mine near Henbury where a man named Pope discovered a few small veins of copper-ore which he was exploiting (Catcott, 1756; Gough, 1930); however, there are reports of other unnamed workings for lead in the Henbury and Westbury-on-Trym region (Savage, 1989), that could also correspond to "Wesley Mine". For a complete overview of the geological setting and mineralogy of "Wesley Mine", consult the paper by Alabaster (1989).

KOMBATITE SPECIMEN

The specimen consists largely of calcite adhering to a small amount of manganese oxide. The kombatite is found as a single bright orange grain, about 2 mm in length, embedded within the calcite (Figures 1 and 2). It is irregular in shape and has a pronounced cleavage causing the grain to fracture into discrete layers.

Figure 1. Specimen BM 1989,93 showing the overall form of the specimen and an arrow pointing to the "parkinsonite" which has now been identified as the rare species kombatite. This could be world's largest example of a kombatite crystal at around 2 mm in length as the original reports of kombatite from Kombat Mine were sub 1 mm. Photograph courtesy the Natural History Museum.

Figure 2. Close up of the kombatite grain from "Wesley Mine", showing the strong cleavage and consequent layered fracturing on the grain surface. The surrounding material is calcite. Photograph courtesy the Natural History Museum.

ID	SiO_2	Cl	V_2O_5	CuO	As_2O_5	PbO	SO_3	Cr_2O_3	MoO_3	Total
1	0.04	4.26	3.48	<dt	1.90	90.65	<dt	0.23	0.25	99.85
2	0.04	4.27	3.40	<dt	1.99	89.66	<dt	0.22	0.20	98.82
3	0.05	4.31	3.38	0.06	1.88	89.39	<dt	0.19	0.34	98.63
4	0.03	4.41	3.80	<dt	1.31	89.78	<dt	0.25	0.45	99.03
5	0.03	4.36	3.60	<dt	1.51	89.92	<dt	0.23	0.40	99.07
6	0.04	4.34	3.46	<dt	1.81	89.42	<dt	0.23	0.40	98.72
7	0.04	4.36	3.41	<dt	1.83	89.76	<dt	0.24	0.38	99.04
8	0.06	4.24	2.57	<dt	3.10	89.31	<dt	0.16	0.13	98.61
9	0.05	4.29	3.49	0.06	1.73	89.45	<dt	0.23	0.38	98.71
10	0.03	4.44	3.66	<dt	1.51	90.20	<dt	0.23	0.47	99.54
11	0.02	4.33	3.42	<dt	1.82	89.90	<dt	0.26	0.34	99.11

Table 1. Wt.% analyses of 11 points performed on a fragment removed from specimen BM 1989,93. Standards were: vanadinite (Pb, Cl, V), gallium arsenide (As), copper metal (Cu), molybdenum metal (Mo), chromium oxide (Cr), wollastonite (Si) and baryte (S). Totals have been corrected for the Chlorine, Oxygen equivalency. <dt indicates below detection limits. Errors are such that wt% analysis to 2 decimal places is valid.

The specimen was part of a suite of rocks collected by C. Alabaster in 1983 from the "Wesley Mine" and kindly donated to the BM(NH), now NHM, for the dual purposes of representing the now inaccessible locality and helping to characterise parkinsonite, a rare lead molybdenum oxychloride found there (Symes *et al.,* 1994). This particular specimen was registered as BM 1989,93 and initially identified as a parkinsonite specimen. It clearly matches Alabaster's 1989 description of orange, vanadium rich parkinsonite from "Wesley Mine".

At a later unrecorded date at the NHM, a precession x-ray pattern was obtained from the grain that seemed to indicate that it had a "sahlinite-like" structure rather than the very similar but different parkinsonite structure. This fact, together with a suspected find of sahlinite from Merehead Quarry, prompted the author to investigate the specimen further. Quantitative chemical analyses using wavelength dispersive x-ray spectroscopy (WDX) on a Cameca SX100 Microprobe were performed at 11 points on a tiny portion of the specimen that had been mounted into a polished epoxy block. The analyses as shown in Table 1, accurate to 2 decimal places, revealed the true identity of the specimen to be kombatite, the vanadium analogue of sahlinite, rather than an orange parkinsonite. An averaged formula based on 21 structural anions, and complete tetrahedral co-ordination of V, As, Cr and Si, can be written:

$Pb_{13.83}Mo_{0.08}[(VO_4)_{1.29},(AsO_4)_{0.56},(CrO_4)_{0.10},(SiO_4)_{0.02}]O_{8.86}Cl_{4.20}$

DISCUSSION

In the original description of the locality, Alabaster (1989) indicates that within the 25 or so specimens thought to contain parkinsonite, the grains varied in colour from orange to deep blood red. The orange grains were investigated separately, determined as being vanadium containing and noted as having a different crystalline form and mineralogical association. However they were still eventually identified as parkinsonite. This was probably due to the incompletely characterized state of parkinsonite at this stage, prior to its official publication in 1994. With this in mind, it is suggested here that all the "orange parkinsonites" from "Wesley Mine" are likely to be kombatite and not parkinsonite, which probably corresponds only to the deeper blood-red samples. A further "orange parkinsonite" from the "Wesley Mine" exists in the collections at the NHM, registered as BM 1989,94 and will be investigated in due course.

Probable vanadium rich parkinsonites are known to exist from Kombat Mine, Namibia (Welch *et al.,* 1996; C. Stanley, *personal communication*) so it is feasible that some samples from "Wesley Mine" may also fall in between the two species. Interestingly, as Mo(VI) and V(V) occupy different structural sites within the two minerals, it is thought that V-rich parkinsonites are composed of intercalated, yet, distinct, layers of kombatite and parkinsonite at an atomic scale, and does not represent a solid solution. However, as As(V) and V(V) do occupy the same site, it is possible that the As-rich, Mo-poor analyses observed in this study (Table 1) may dominantly represent true solid solution between kombatite and sahlinite, rather than intercalated layers of each. Although testing this is beyond the scope of this project.

After calculating site occupancy from wt% data in table 1, Analysis 8 indicates that the vanadium site is occupied here by 48.4% V, 46.2% As, 3.6% Cr and 1.7% Si, This is very nearly As(V) dominant and opens up the possibility that other examples from the "Wesley Mine" may be As dominant and would thus be correctly identified as the rare mineral sahlinite.

The reason for the difference in colour of the "Wesley Mine" specimen when compared to those from the type locality is unknown, but might be due to the presence of around 0.25 wt% chromium.

CONCLUSIONS

Kombatite is the tenth positively identified lead-based oxychloride found within the Mendip manganese deposits and investigative work is currently underway regarding a further four. The region shows similarities to the famous deposits at Mammoth St. Anthony, USA (Bideaux, 1980), Kombat Mine, Namibia (Dunn, 1991) and Långban in Sweden (Holtstam and Langhof, 1999) and is clearly of significant international importance and warrants further study (Turner, 2006).

Some of the lead oxychlorides also have important industrial usages, kombatite is a so called "aurivillius phase" (Aurivillius, 1982) the structure of which is important for research within the semi-conductor industry. Further investigation of the lead based oxychlorides in the Mendip region may lead to significant discoveries of new minerals and mineral structures important to this industry.

ACKNOWLEDGEMENTS

I would like to thank Rick Turner for re-igniting my interest in the mineralogy of the Mendip region, John Spratt and Anton Kearsley of the NHM for help with Electron Microprobe analyses, Mark Welch and Chris Stanley also of the NHM for overall comments and Chris Alabaster, for his foresight when preserving and recording information about the "Wesley mine" before it was covered by buildings.

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ADDENDUM

After the submission of this paper, qualitative EDX analysis upon an irregular fragment of a similar grain with a yellowish hue on the second specimen, revealed a chemistry dominated by Pb, Cl, As & O without any vanadium. This grain is now a candidate for an occurrence of sahlinite at "Wesley Mine" and both WDX and XRD analysis will be performed upon it at a later date. These results will be published in a future volume of the Journal of the Russell Society.

Journal of the Russell Society, **11**, 54-58 (2008)

A REVIEW OF THE OCCURRENCES OF THE COPPER VANADATE MINERALS VOLBORTHITE AND TANGEITE IN THE BRITISH ISLES

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

Neil HUBBARD
30 Thirlmere Road, Barrow upon Soar, Leicestershire, LE12 8QQ

Francis INCE
78 Leconfield Road, Loughborough, Leicestershire, LE11 3SQ

The uncommon copper vanadate mineral volborthite is described from three new British locations: Newhurst Quarry in Leicestershire, Littleham Cove in Devon, and Wheal Edward in Cornwall. A report of volborthite from Bardon Hill Quarry in Leicestershire is substantiated and a tentative record added for Dean Quarry in Cornwall. At the Leicestershire localities, volborthite occurs with other vanadium-bearing supergene minerals in copper deposits that are concentrated around the sub-Triassic unconformity. At Littleham Cove, it occurs in vanadium-rich nodules in continental red-bed sequences of Permo-Triassic age and at Wheal Edward it is found with supergene uranium minerals in vein mineralisation associated with the Land's End Granite. A lead-rich variety of the rare calcium copper vanadate mineral tangeite is described from New Cliffe Hill Quarry, another Leicestershire locality where vanadium minerals are found in supergene copper mineralisation at the sub-Triassic unconformity. It occurs as rich pale green felted masses in cavities in a ferruginous dolomite vein with calcite and baryte.

INTRODUCTION

Volborthite, $Cu_3V_2O_7(OH)_2{\cdot}2H_2O$, is an uncommon mineral that was first noticed by the Russian palaeontologist A. F. von Volborth on a specimen from an unknown locality in the foothills of the Ural Mountains (Pekov, 1998). It is typically found in the oxidation zones of vanadium-rich copper deposits as rosettes of olive to yellow-green pseudohexagonal scaly crystals or as green to yellow-green spheroidal aggregates and crusts (Anthony *et al.*, 2000).

Volborthite cannot be distinguished from the visually similar species tangeite and vésigniéite without recourse to analysis, ideally by X-ray diffractometry (XRD). Analyses by energy dispersive spectrometry (EDS) provide a guide to identification if insufficient material is available for analysis by XRD as they distinguish volborthite from both vésigniéite and tangeite, which contain barium and calcium respectively; EDS also discriminates the as yet un-named zinc-bearing analogue of volborthite, which has recently been approved as a new mineral by the IMA Commission on New Minerals and Mineral Names (IMA No. 2007-026). In spite of the visual similarities, volborthite is not closely related to either vésigniéite and tangeite; it contains the pyrovanadate (V_2O_7) group whereas tangeite and vésigniéite are orthovanadates (containing VO_4).

Tangeite is a rare member of the adelite-descloizite group (Back and Mandarino, 2008). The name was first used in 1925 by A. E. Fersman to describe a basic calcium copper vanadate, with a composition $CaCu(VO_4)(OH)$, from the Tyuya-Muyun deposit, Fergana, Kyrgyzstan (see Pekov, 1998 for an interesting discussion of the history of the species). The mineral calciovolborthite, also usually described as $CaCu(VO_4)(OH)$, and now generally considered to be identical to tangeite, was described in 1848 from Friedrichsroda, Thuringia, Germany. If the normal rules of mineral nomenclature were applied, calciovolborthite would take precedence, but a re-examination of material from Friedrichsroda only identified vésigniéite, $BaCu_3(VO_4)_2(OH)_2$, at that locality (Guillemin, 1956). Following further research, the Commission on New Minerals and Mineral Names accepted a proposal that the name tangeite should be used to describe $CaCu(VO_4)(OH)$ (Basso and Zefiro, 1994). As the type specimen of calciovolborthite has not been traced, some uncertainty surrounds the use of that name: it was recently discredited and was considered to be synonymous with either tangeite or vésigniéite by Burke (2006).

Volborthite and tangeite were first described from the British Isles in vanadium-rich nodules exposed in rocks of the Mercia Mudstone Group at the Butterley and Blaby Brick Pit, Glen Parva, Leicestershire (King and Dixon, 1971). Volborthite forms yellow-green crusts surrounding blue-green masses of tangeite. The minerals occur as encrustations on the surfaces of vanadiferous nodules; as shell-like, multi-coloured encrustations, which are the relics of vanadiferous nodules; on the etched surfaces of gypsum; and on joints in the rock in the immediate vicinity of nodules. The brick pit locality is almost certainly identical to 'Blaby mine', which is described as a volborthite locality by Anthony *et al.* (2000).

In addition to the Butterley and Blaby Brick Pit, the only well substantiated record of volborthite in the British Isles is at New Cliffe Hill Quarry, Stanton under Bardon, Leicestershire, where crusts of oily green to yellowish-green volborthite coat fractures in diorite (Hubbard *et al.*, 2005). The only additional report of tangeite is at Penrhyn Quarry near Bethesda in Wales, where 'calciovolborthite' was claimed on the basis of a single specimen in the private collection of a Danish mineralogist (Bevins, 1994). This record is unconfirmed.

Our review of supergene copper vanadates in Britain was prompted by the re-discovery of a small collection of remarkable volborthite specimens that were found in the late 1970s at Newhurst Quarry. More recently, rich specimens of plumbian tangeite were found at the nearby New Cliffe Hill Quarry. Both finds are easily the best from the British Isles and worthy of record on that basis alone.

Descriptions of specimens from further British localities, are included as a comparison.

LOCALITIES

The text below describes four locations where volborthite has been confirmed by XRD and includes data on a fifth tentative discovery. Tangeite is described from a single new locality. We have been unable to trace any further information on the occurrence at Penrhyn Quarry in Wales or to add to the published descriptions of specimens from the Butterley and Blaby Brick Pit: these localities are not considered further.

NEWHURST QUARRY

At Newhurst Quarry (SK 485 179) near Shepshed in Leicestershire, Triassic sandstones and siltstones of the Sherwood Sandstone and Mercia Mudstone groups unconformably overlie extensively folded and faulted Precambrian rocks of the Charnian Supergroup (Carney *et al.*, 2001). In common with other nearby sites, an oxidised copper-dominated mineral assemblage is present in the rocks surrounding the unconformity. Supergene vanadium-bearing minerals are widespread, but uncommon, in this assemblage. Three vanadium-bearing supergene minerals, mottramite, vanadinite and vésigniéite, the latter being the first British occurrence at the time (see King and Wilson, 1976), were described in a recent review of the mineralogy of the site (Ince, 2005).

In April 2008, the Central Branch of the Russell Society organized a mineral, rock and fossil identification day at the Charnwood Museum, Loughborough. During the day Peter Lord, a former member of the Russell Society, described some remarkable volborthite specimens that were collected at Newhurst Quarry in the late 1970s. These were identified at the Natural History Museum, London (NHM), but were not widely known, so Peter kindly made them available for further study. We were unable to trace the analytical records at the NHM (Mike Rumsey, *personal communication*), so an isolated crystal group was detached for analysis by XRD: this provided an excellent match for volborthite (XRD reference number MANCH:XRD1427)

Figure 1. Unusually rich thin tabular pistachio green volborthite crystals up to 1.5 mm on edge encrusting hematite-stained calcite from Newhurst Quarry. Peter Lord collection.

Peter's collection comprised ten specimens, which were recovered from the north face of the quarry in the late 1970s. The occurrence was in a breccia associated with a fault or shear zone which contained angular wallrock clasts cemented by scalenohedral calcite crystals and earthy hematite.

Volborthite occurs as dark green drusy crystalline encrustations in void spaces between calcite crystals (Fig. 1), the largest covering an area of about 20 x 20 mm. On some specimens a pseudo-hexagonal platy to thick tabular form is well developed. The largest single crystals of this habit just exceed 1 mm on edge and are often slightly curved (Fig. 2). The smaller crystals commonly aggregate into rosettiform groups, some resembling the well known hematite 'iron-roses' of Switzerland.

Figure 2. Tabular pseudo-hexagonal volborthite on calcite, the crystal group 1 mm across from Newhurst Quarry. Frank Ince collection.

Minute radiating aggregates of pale green acicular crystals are associated with volborthite on most of the specimens. They are typically less than 0.2 mm across and the individual crystals are normally only a few hundred nanometres thick. Initial investigations by EDS revealed copper, calcium and vanadium and consequently tangeite, the only known calcium copper vanadate, was suspected. Subsequent analysis by XRD indicated that the mineral was a member of the mixite group, the pattern providing a good match for mixite, zálesíite and agardite, which are structurally similar (XRD reference number MANCH:XRD1446). Further EDS analyses revealed the presence of arsenic as well as calcium, copper and vanadium. The aggregates were tentatively identified as a vanadium-rich variety of the calcium copper arsenate zálesíite, a determination recently confirmed by WDS analyses (Andrew Tindle, *personal communication*).

Figure 3. Pale mint green acicular sprays of zálesíite crystals up to 0.1 mm long on calcite from Newhurst Quarry. Peter Lord collection.

The only other supergene mineral identified by XRD on the specimens is malachite, which occurs as inclusions in a copper silicate gel. Small encrustations with a visual similarity to tyrolite are present, but it did not produce a useful XRD pattern.

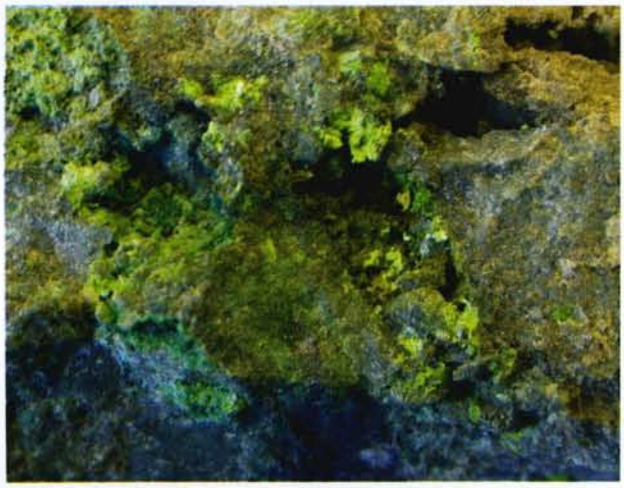

Figure 4. Volborthite from Bardon Hill Quarry. Leicester University specimen 110207. Photograph: 20 mm x 15 mm.

BARDON HILL QUARRY

Volborthite specimens reported from the Triassic breccias exposed at Bardon Hill Quarry, Coalville, Leicestershire (SK 456 133) were not considered fully substantiated in a recent review of the mineralogy of the site by Ince (2007). Analyses at the Universities of Leicester and Manchester during this study confirm the presence of volborthite as a yellow-green encrustation on a specimen (L1436) in the Leicester University collection (Fig. 4: Kay Hawkins, *personal communication* and MANCH:XRD1473). The XRD pattern is not a perfect match to volborthite as it has a relatively high signal to noise ratio and only shows the reflections from the (0.0.l) planes clearly, however this is not unusual in minerals which display a high degree of preferred orientation when ground for XRD. Specimens which had been tentatively labelled 'volborthite' in the Neil Hubbard collection and at the National Museum Wales proved to be vésigniéite, a mineral which is also intimately mixed with volborthite on the Leicester University specimen.

NEW CLIFFE HILL QUARRY

A remarkable suite of supergene copper minerals was exposed at the sub-Triassic unconformity and infilling fractures in the underlying diorite at New Cliffe Hill Quarry near Stanton under Bardon in Leicestershire (SK 462 107) in the early 1990s. In a recent summary, Hubbard *et al.* (2005) describe four supergene vanadium minerals, mottramite, vanadinite, vésigniéite, and volborthite, from the locality. In April 2005 a number of specimens displaying rich felted aggregates and masses of acicular pale green crystals on calcite and baryte (Fig. 5), partially filling cavities in a ferruginous dolomite vein, were collected from an access road approximately two thirds the way down the quarry at its western end (well away from the original copper occurrence). Analyses produced a tangeite-like XRD pattern (XRD reference number MANCH:XRD1440), while EDS showed that copper, vanadium, calcium and lead were the major elements present with an atomic number greater than 10. This is sufficient to identify the specimens as lead-rich tangeite.

Figure 5. Rich pale green tangeite fibres in wispy masses to 2 mm long with white baryte and hematite-stained calcite from New Cliffe Hill Quarry. Neil Hubbard collection.

LITTLEHAM COVE

At Littleham Cove (SY 039 803) near Budleigh Salterton on the south coast of Devon, red-bed mudstones and siltstones of the Upper Permian Littleham Mudstone Formation are exposed in rapidly eroding sea cliffs. The sedimentary sequence contains dark coloured vanadiferous nodules, which are known locally as 'fish eyes'. A suite of poorly characterised copper, silver, cobalt, arsenic, uranium and vanadium-rich minerals is found in the nodules. Volborthite occurs as yellow-green to yellow-brown spherules up to about 0.4 mm across in fractures and cavities in dark coloured vanadium-bearing nodules to ca. 50 mm across (Fig. 6: XRD reference number MANCH:XRD766).

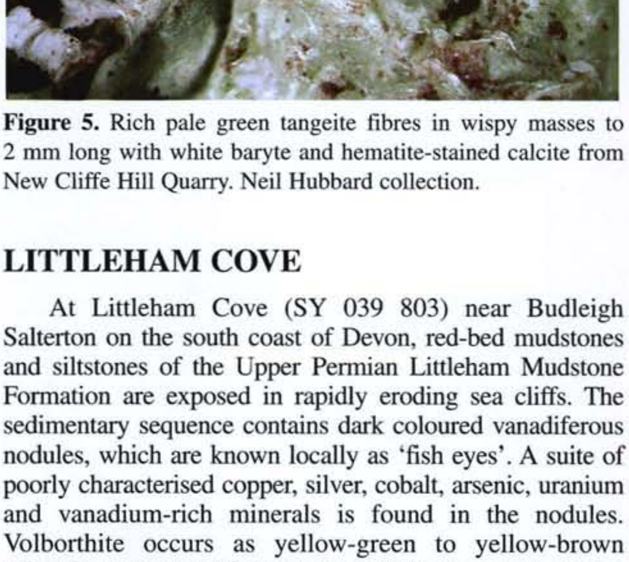

Figure 6. Orange-brown volborthite spherules up to 0.4 mm in diameter in a fracture in a vanadiferous nodule from Littleham Cove. Jorn Caen collection.

WHEAL EDWARD

Wheal Edward (SW 360 328) in the parish of St Just in west Cornwall worked copper and tin bearing lodes associated with the Land's End Granite. The site is perhaps best known to mineralogists for the suite of uranium-bearing supergene minerals that were at one time common on the dumps. Volborthite is a rare member of the supergene assemblage, occurring as dark-green rosettes and yellow-green balls up to 0.4 mm across associated with metazeunerite (Fig. 7). It was found in spoil from the Second World War workings on Cliff Lode and identified by XRD at the Natural History Museum (film number 7107F).

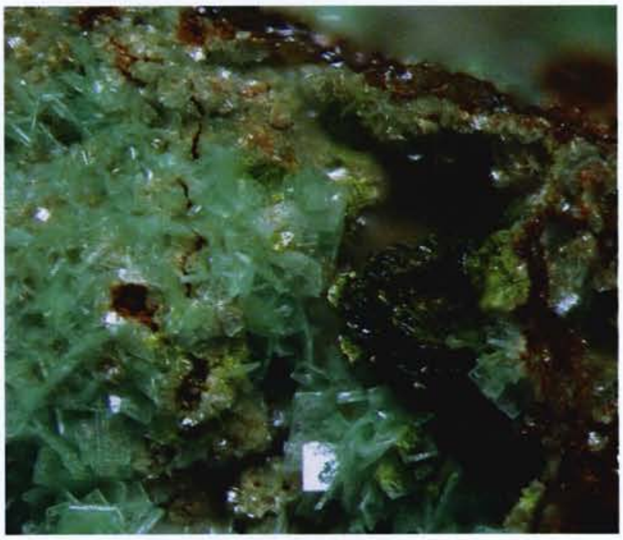

Figure 7. Pistachio green volborthite aggregate with crystals to about 0.2 mm and pale green tabular metazeunerite from Wheal Edward. Neil Hubbard collection.

DEAN QUARRY

Dean Quarry near St Keverne in Cornwall (SW 803 204), produced crushed aggregate and armour-stone from the gabbroic rocks of the Lizard Ophiolite. The site is well known for zeolites, particularly analcime and natrolite, which occasionally occur in superbly crystallised specimens. Traces of vanadium-bearing minerals are sometimes present in the zeolite-bearing assemblages, in calcite veins, and in fractures in the surrounding rocks (Jeremy Hooper, *personal communication*).

A mineral which is almost certainly volborthite occurs as minute yellow to yellow green spherules (up to about 0.3 mm across) in fractures in the rock. Insufficient material was available for analysis by XRD, but EDS produced a trace which is typical of volborthite. Identification can only be tentative without a confirmatory analyses by XRD, but the data is included in the hope that a detailed examination of further specimens will reveal sufficient material.

DISCUSSION

Its close visual similarity to vésigniéite, tangeite and a number of supergene uranium-bearing minerals makes volborthite an easy mineral to overlook, and it may be more common than the few British records suggest. Continental red-bed sequences such as the Sherwood Sandstones and Mercia Mudstones are widespread in the British Isles and are relatively enriched in vanadium (e.g. Harrison *et al.*, 1975; Holmes *et al.*, 1982; van-Panhuys *et al.*, 1996). Volborthite and other supergene copper vanadates are a possibility wherever these rocks host copper deposits.

Vanadium is commonly enriched in the magnetite that is common in mafic igneous rocks (e.g. Cawthorn *et al.*, 2005). When these are weathered, supergene vanadium minerals are sometimes also found.

The volborthite occurrence at Littleham Cove is in a geologically similar environment to the original British volborthite and tangeite occurrence at the Butterley and Blaby Brick Pit in Leicestershire (King and Dixon, 1971). In both cases the minerals are directly associated with diagenetic vanadium-rich nodules in continental red-bed sequences. The other localities in Leicestershire are associated with copper mineralisation which is concentrated around the sub-Triassic unconformity (e.g. Ince, 2005; 2007; Hubbard *et al.*, 2005).

The green acicular mineral associated with volborthite at Newhurst Quarry is worthy of further investigation. The outer layers may represent an as yet undescribed vanadate analogue of zálesíite. Extensive P-for-As substitution is known in mixite group minerals (e.g. Frost *et al.*, 2005), but there is little data on vanadium substitution and no vanadium-bearing minerals are included in the group by Back and Mandarino (2008).

Although the crystal habit of tangeite can mimic the tabular pseudo-hexagonal habit of vésigniéite and volborthite (e.g. Anthony *et al.*, 2000), it occurs as distinctive felted masses in the specimens we have examined from New Cliffe Hill Quarry. These are not unlike some of the early material from the type locality in Kyrgyzstan (Pekov, 1998). The specimens from New Cliffe Hill Quarry are remarkably rich and it is unfortunate that they seem to have been wetted before they were collected.

Although the XRD pattern is not a perfect match for tangeite, this is not unusual (again due to preferred orientation) in material with a fibrous or acicular crystal morphology. The presence of lead, probably substituting for calcium, is also likely to affect the crystal structure (and hence the XRD data). This type of substitution does not appear to have been reported previously, but unfortunately, the fibrous crystal morphology, with crystals typically much less than a micrometre across, made preparation of samples for quantitative analysis by WDS extremely difficult and no useful data was collected. It is clear from inspection of the EDS spectra that calcium is present at a greater concentration than lead and it can therefore be described as a lead-rich tangeite.

This article illustrates how easily interesting specimens and data can be lost. The Newhurst Quarry volborthite specimens are almost certainly the best ever found in Britain, but without their chance re-discovery earlier this year, they may have never come to light. Detailed investigations by one of us (Ince, 2005) which produced a comprehensive review of the mineralogy of the site failed to reveal them, even though an identification was made at the NHM, since precise data on the locality had not been kept or may never have been known (Michael Rumsey, *personal communication*). The same comment applies to the rich if somewhat water damaged tangeite specimens from New Cliffe Hill Quarry which only came to be investigated through a series of coincidences.

ACKNOWLEDGEMENTS

Thanks are due to Peter Lord, who brought the specimens from Newhurst Quarry to our attention and kindly made material available for analysis. Chris Jewson submitted material from Dean Quarry for analysis and Jeremy Hooper made a considerable number of analyses of the vanadate minerals, which will be the subject of a future paper. Tim Neall investigated specimens from Littleham Cove in detail and isolated several specimens which later proved to be volborthite. Clive Minker brought the material from New Cliffe Hill Quarry, which had been originally collected by Nick Peters, to our attention and Nick Peters and Colleen Thomson are thanked for providing additional information and specimens. Last but by no means least, Kay Hawkins (Geology Department, Leicester University) is thanked for providing XRD confirmation of the volborthite from Bardon Hill Quarry.

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Journal of the Russell Society, **11**, 59-63 (2008)

RANCIÉITE FROM MYNYDD PARYS, AMLWCH, ANGLESEY, WALES

Tom F. COTTERELL
Amgueddfa Cymru - National Museum Wales, Cathays Park, Cardiff, CF10 3NP

David A. JENKINS
Llys Geraint, Allt Bryn Eglwys, Bethesda, Gwynedd, LL57 4AX.

Black stalactitic aggregates precipitating on the roof of the Joint (45 fm.) level at Mynydd Parys have been identified as the Ca-rich phyllomanganate mineral ranciéite. The walls and floor of the tunnel are thickly coated by ochre precipitated during the flow of acidic (pH 3.5) iron charged water produced by the decay of pyrite within the mine workings. The presence of ranciéite on the roof of the tunnel indicates a flow of neutral pH water through the rocks above. The source of manganese is unclear, but is probably related to carbonates within local rocks. Small quantities of base metals present within the ranciéite are thought to have been leached from the underlying ochre. This is the first record of ranciéite in Wales.

INTRODUCTION

Ranciéite, $(Ca,Mn^{2+})Mn^{4+}_4O_9 \cdot 3H_2O$, is a phyllomanganate mineral of the birnessite family (Giovanoli, 1969) that forms as a product of weathering or alteration of manganese deposits and manganese-bearing minerals in Ca-rich environments such as limestones (Bardossy and Brindley, 1978), travertines and marbles (Nimfopoulos *et al.*, 1997; Ertl *et al.*, 2005) and in tuffs of basaltic to dacitic composition (Richmond *et al.*, 1969; Barrese *et al.*, 1986). A solid solution series exists with takanelite, $(Mn^{2+},Ca)Mn^{4+}_4O_9 \cdot H_2O$ (Kim, 1991) and with the recently discovered Zn analogue (Kim *et al.*, 2002). Distinction between ranciéite and takanelite has, in the past, proved problematic due to analytical errors that have crept into the literature: Kim (1991) demonstrated that the original description of takanelite produced by Nambu and Tanida (1971) was in fact ranciéite with todorokite and braunite impurities and provided new X-ray diffraction data on takanelite from Janggun Mine, Korea. Ertl *et al.* (2005) performed structure modelling of the first well crystallized ranciéite using the Rietveld method and difference-Fourier summations to determine that it is probably trigonal in structure, in contrast to the monoclinic structure of birnessite. Ertl *et al.* (2005) also produced the most detailed X-ray powder diffraction data to date.

In the British Isles, ranciéite is rare. It has been identified by XRD as a pink-brown powdery phase on a specimen in the Natural History Museum, London, labelled as from 'near Newbiggin', Teesdale, Co. Durham (Ryback and Tandy, 1992). No further details have emerged as to the exact locality. A photograph displaying velvety clusters of ranciéite microcrystals on saponite from The Gobbins, Co. Antrim, Northern Ireland is presented in Tindle (2008). The method of identification, although not stated, is XRD supported by EDS (David Green, *personal communication*). Tindle (2008) also records an occurrence of ranciéite, at Mynydd Parys, near Amlwch, Anglesey, Wales, on the basis of information provided by the present authors. It is this occurrence that is described in detail in this article.

Mynydd Parys, or Parys Mountain as it is also known, is the site of two famous copper mines (Parys Mine and Mona Mine) that dominated the world's copper markets at the end of the eighteenth century. The geology consists of a thick sequence of Ordovician-Silurian shales and volcanic extrusives and tuffs, overlying metamorphic Precambrian basement (Jenkins *et al.*, 2000). The orebodies, which have been proved to >400 m depth, consist of a major polymetallic sulphide deposit of volcanogenic massive sulphide (VMS) type. The ore contains large quantities of fine-grained pyrite that decays rapidly on exposure to the atmosphere. The resultant acidic products have caused environmental problems, including acid mine drainage (AMD). Somewhat ironically, the drainage water was a good source of copper in the past, with Cu/CuO being precipitated by addition of scrap iron in a system of specially built ponds: the remarkably efficient process reduced copper in solution from 70 to 4 mg/litre and yielded up to 50 tonnes of copper per year. Modern exploration by Anglesey Mining Plc. has delineated a resource of 6.5 M tonnes with a combined average grade of over 10 % Zn, Cu and Pb, with minor Au and Ag beneath the old workings.

At Mynydd Parys, ranciéite occurs as post-mining, dark brown to black, soft, porous, stalactitic aggregates several centimetres across (Figs. 1 and 2), in the Joint (45 Fm.) level accessed via Dyffryn Adda adit. The precipitation of ranciéite is ongoing, but is restricted to only two or three small areas on or near the roof of the tunnel approximately 400 metres from the adit entrance. Thick ochre caused by the flow of acidic iron-rich water from the main workings at Mynydd Parys coats the tunnel walls over which the ranciéite precipitates. Access to the site involves wading through ochre, the disturbance of which causes the Afon Goch to flow orange with iron-charged solutions.

Figure 1. Stalactitic ranciéite (grey-black) forming on the roof of Dyffryn Adda adit level. The ranciéite aggregate is approximately 10 cm across. David A. Jenkins photo.

Figure 2. Close-up of stalactitic ranciéite shown in Fig. 1.

EXPERIMENTAL

Initial identification of ranciéite was made in 2000 by DAJ using X-ray diffraction (X-ray number 2919c) at University of Wales, Bangor. However, accurate identification of 7 Å phyllomanganate minerals (ranciéite, takanelite, birnessite, *etc.*) requires both X-ray diffraction and chemical data (Kim, 1993). Therefore, samples were submitted to Amgueddfa Cymru – National Museum Wales (abbreviated to Amgueddfa Cymru from now on) for further study. A powdered sample (taken from the original material – now registered as Amgueddfa Cymru specimen NMW 2007.35G.M.1) was mounted on a low background silicon wafer using acetone and X-ray diffraction was performed using a PANanalytical X'Pert PRO X-ray diffractometer fitted with an X'Celerator detector. The operating conditions included CuK_{α} radiation run at 40 kV 30 mA. The sample was rotated at half a revolution per second using a sample spinner and a circular area 20 mm in diameter analysed for 30 minutes covering the angles from 5 to 75° 2θ. The resultant diffraction pattern, XRD no. NMW X-1552, was investigated using X'Pert Highscore search and match software and shown to be consistent with ranciéite (Table 1).

Further material was mounted in a polished block (registered as NMW 2007.35G.M.1a) suitable for detailed

Ranciéite												Takanelite	
1		2		3		4		5		6		7	
d (Å)	*I*	d (Å)	*I*	d (Å)	*I*	d (Å)	*I*	d (Å)	*I*	d (Å)	*I*	d (Å)	*I*
7.490	100	7.57	s	7.56	100	7.66	100	7.481	100	7.503	100	7.25	s
3.740	14	3.77	m	3.77	20	3.74	20	3.744	70	3.726	39	3.619	wb
						2.50	8	2.497	6				
2.463	10	2.46	mw	2.46	12			2.469	1	2.458	32	2.451	m
2.342	6	2.34	m	2.35	10			2.341	2	2.346	19	2.347	w
2.064	2	2.06	m	2.06	10			2.061	4	2.060	8		
								1.874	10	1.858	2		
1.758	2	1.76	m	1.76	8			1.751	6	1.762	9		
								1.498	4	1.504	3		
								1.494	6				
1.425	4	1.423	m	1.42	7			1.423	<1	1.420	26	1.429	m
1.397	2			1.40	5			1.397	3	1.405	14		
								1.331	1				
								1.280	1				
								1.249	17				
								1.217	<1				
								1.172	<1				
								1.113	2				
								1.070	3				

Table 1. Comparative X-ray powder diffraction data for ranciéite and takanelite.

1. Ranciéite from Paxton's Cave, near Boiling Springs, Virginia, U.S.A. PDF no. 022-0718.
2. Ranciéite from Oriente Province, Cuba (Richmond *et al.*, 1969).
3. Ranciéite from Itéa, Greece (Bardossy and Brindley, 1978).
4. Ranciéite from Kato Nevrokopi, Greece (Nimfopoulos *et al.*, 1997).
5. Ranciéite from Friesach, Carinthia, Austria (Ertl *et al.*, 2005).
6. Ranciéite from Mynydd Parys, Anglesey, Wales. (This study, XRD no. NMW X-1552).
7. Takanelite from Janggun Mine, Korea (Kim, 1991).

analysis by energy dispersive X-ray spectroscopy (EDS). A CamScan Maxim Scanning Electron Microscope (SEM) fitted with an Oxford Instruments energy dispersive X-ray spectrometer and analytical software was used for this stage. The resultant analyses (Table 2) produced low totals, due in part to the porosity of the material and secondly because of structural water, which is normally calculated by difference. The important factor in distinguishing between ranciéite and takanelite is the proportion of CaO to (MnO_2+MnO+Mn_2O_3). Published chemical data (Frondel *et al.*, 1960; Richmond *et al.*, 1969; Nambu and Tanida, 1971; Bardossy and Brindley, 1978; Barrese *et al.*, 1986; Kim, 1991; Kim, 1993; Ertl *et al.*, 2005) produce %CaO/(MnO_2+MnO+Mn_2O_3) values in the range 8.5-13.7 for ranciéite and 4.3-0.33 for takanelite. As both minerals form a solid solution series (Kim, 1993) a much greater range of values are predicted. Material from Mynydd Parys produces a %CaO/(MnO_2+MnO+Mn_2O_3) value of 10.7 consistent with ranciéite.

Individual stalactites consist of dendritic aggregates (Fig. 3). The difference in density highlighted in backscattered electron mode relate to porosity, rather than

	Ranciéite						Takanelite
	1	2	3	4	5	6	7
SiO_2	0.41	0.62	0.7	0.24	b.d.	0.11	n.d.
MnO_2	71.9	75.04	64.8	62.01	69.21	56.55	74.01
Mn_2O_3	-	-	-	-	7.08	-	-
MnO	-	3.31	3.0	-	0.88	-	10.42
Al_2O_3	0.14	0.12	5.6	1.18	b.d.	0.41	trace
Fe_2O_3	n.d.	0.12	2.9	0.3	0.18	-	0.26
CuO	-	0.02	-	-	-	0.84	-
ZnO	-	-	-	2.54	-	0.57	-
CaO	6.11	8.10	6.1	6.83	10.56	6.04	3.64
BaO	2.85	-	-	-	0.20	trace	trace
MgO	1.53	0.16	0.32	0.63	0.21	0.59	0.59
K_2O	0.86	0.26	0.12	0.25	0.55	0.43	0.33
Na_2O	0.53	0.12	0.11	n.d.	b.d.		
H_2O^+		11.09					
H_2O^-		1.53					
H_2O			13.69		11.13		11.50
P_2O_5	0.17	0.10	-	-	-	-	-
As_2O_5	0.18	-	-	-	-	-	-
SO_3	-	-	-	-	-	0.29	-
TiO_2	0.21	-	0.01	-	-	-	-
SrO	-	-	trace	-	-	-	-
Cl	0.12	-	-	-	-	trace	-
Total	85.07	100.59	97.65	73.98	100.00	65.83	100.75
%CaO/(MnO_2+MnO+ Mn_2O_3)	8.5	10.3	9.0	11.0	13.7	10.7	4.3

Table 2. Chemical composition of ranciéite and takanelite.

1. Ranciéite from Mazzano Romano, Italy (Barrese *et al.*, 1986). Average of 16 EPMA spot analyses.
2. Ranciéite from Oriente Province, Cuba (Richmond *et al.*, 1969).
3. Ranciéite from Itéa, Greece (Bardossy and Brindley, 1978). Wet chemical analysis.
4. Ranciéite from Kato Nevrokopi, Greece (Nimfopoulos *et al.*, 1997). Average of 18 EPMA spot analyses.
5. Ranciéite from Friesach, Carinthia, Austria (Ertl *et al.*, 2005). Average of 10 EPMA.
6. Ranciéite from Mynydd Parys, Anglesey, Wales. (This study). Average of three EDS analyses on NMW 2007.35G.M.1a. Low total attributed to porosity. Assuming H_2O is between 10-15 % of chemical composition, then around 20-25 % of the sample is pore space.
7. Takanelite from Janggun Mine, Korea (Kim, 1991). By EPMA, Mn and H_2O by wet chemical analysis.

b.d. = below detection limit; n.d. = not determined.

chemical variation. The central part of dendrites has high porosity (dark grey in Fig. 3) whereas the edges are compact and denser (white).

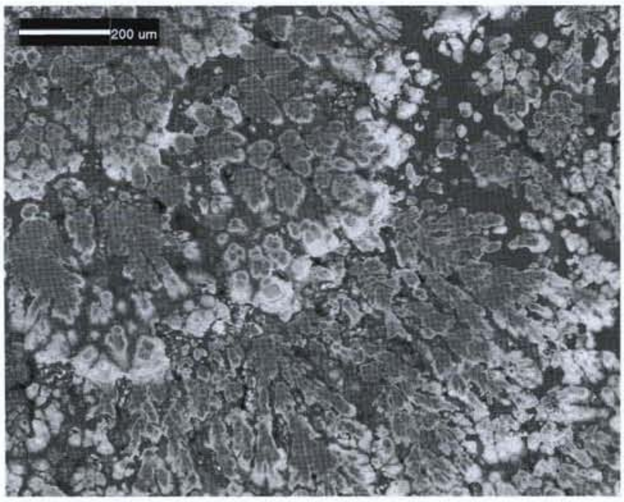

Figure 3. Back-scattered electron image of dendritic ranciéite in polished section. Amgueddfa Cymru specimen, no. NMW 2007.35G.M.1a. Amgueddfa Cymru image.

DISCUSSION

The discovery of ranciéite at Mynydd Parys is unusual for a number of reasons. Firstly, the overriding environment at Mynydd Parys is highly acidic. AMD has and remains a major issue right across the mine site: acidity levels as high as 2.4 pH have been recorded (Thomas, 2000; Butler, 2000; Jenkins *et al.*, 2000) in the Afon Goch (South) draining from the mine and although the level in Dyffryn Adda adit is lower at 3.5 pH (Thomas, 2000; Jenkins *et al.*, 2000) it is still significantly acidic. Ranciéite on the other hand typically precipitates at neutral to alkaline conditions (c. 7-8 pH) (Nimfopoulos *et al.*, 1997).

Secondly, the source of manganese at Mynydd Parys is not directly apparent: no manganese-bearing minerals have been reported from the mine (Jenkins *et al.*, 2000). The carbonates, ankerite, calcite, dolomite and siderite have all been recorded as gangue minerals and all have the potential to contain small amounts of manganese. All of these carbonates have the potential to be weathered readily under acidic conditions, thus releasing any manganese into solution. However, if manganese was carried from the mine workings in the acidic drainage water it would, (a) remain in solution until the conditions are right for precipitation (neutral to alkali conditions), but with a constant flow of acidic water these conditions are unlikely to be reached in the drainage level, (b) only be precipitated in contact with the drainage water and not on the roof of the tunnel well above the current level of drainage water.

Analysis of mine drainage water in Dyffryn Adda adit (Thomas, 2000; Jenkins *et al.*, 2000) shows levels of manganese that are not particularly high (3.65 μg/ml or 0.000365%, *c.f.* manganese comprises approximately 0.085 % of the Earth's crust, although concentrations above 0.1 % are recorded in some ultrabasic rocks – Petrie, 1999). This suggests that the source of manganese is localised rather than the mine waters being enriched. The most likely reason for this is that strata intersecting the level near the sample site must carry localised manganese-bearing carbonates. Weathering of these carbonates would produce a neutral to alkali value (pH 7-8) at which ranciéite usually precipitates. Whole rock analyses of some of the local shales indicate 0.5-2.5 % MnO, whereas carbonate gangue minerals (ferro-dolomite to ankerite) containing 1-2 % Mn have been recorded in deep cores (T. Barrett, *personal communication*).

At the sample site in the Joint (45 Fm.) level, ranciéite precipitates over rusty ochre (Fig. 1) which was previously deposited on the roof and walls of the tunnel under acidic conditions when mine drainage water levels were higher. It is possible that the seepage water bearing the manganese enters the tunnel at a high pH and is lowered to neutral pH on contact with the acidic ochre, but no measurements have been made to test this theory.

In respect to certain other factors of deposition the environment at Mynydd Parys is well suited. Ranciéite is typically a late stage mineral, usually forming as a result of weathering processes: the conditions of deposition reflect this, generally being under high humidity, at atmospheric pressure and very low temperature (around 25°C) (Nimfopoulos *et al.*, 1997). Humidity levels within the drainage adit at Mynydd Parys are typically high, the temperature is low (in the range 7-10°C), pressure remains at atmospheric levels and ongoing precipitation as stalactites clearly represents late stage deposition.

The presence of appreciable Cu and Zn in ranciéite from Mynydd Parys is interesting, if perhaps not unexpected, after all these metals reflect the ore mineralogy of the mine workings. However, this is not necessarily what one would expect from water issuing from the host rocks in a section of tunnel far removed from the main orebodies. High levels of Cu and Zn are recorded in water samples from right across the mine site, but data for Dyffryn Adda adit (Thomas, 2000; Jenkins *et al.*, 2000) suggests that Cu, Zn and Fe levels are quite low. This probably relates to the precipitation of ochre, which removes Fe and probably also Cu and Zn from solution, thus leaving a somewhat less acidic, metal poor water to flow from the adit mouth. As noted earlier, the manganese-bearing solutions appear to be derived from seepage through the host rocks, rather than mine drainage water, but they invariably coat the underlying ochre. The presence of Cu and Zn in the Mynydd Parys ranciéite can therefore be explained by the leaching of these metals from the underlying ochre as ranciéite precipitation takes place.

Base metals are themselves uncommon in published ranciéite occurrences, but this relates to the fact that there are very few accounts of occurrences in base metal sulphide deposits. The most significant discovery was that of a Zn-analogue of ranciéite at Dongnam mine, Korea (Kim *et al.*, 2002) where supergene oxidation of rhodochrosite-sulphide ore in hydrothermal veins resulted in the formation of zoned crystals of ranciéite and Zn-dominant ranciéite.

The neutral to alkaline conditions required for the precipitation of ranciéite are rare at Mynydd Parys – therefore this occurrence of rancieite in such conditions represents an interesting local anomaly. A similar localised occurrence of post-mining deposition of manganese is known in the smaller Morfa Du mine to the northwest. Initial XRD analysis (NMW X-1843) indicates that this is also a 7 Å phyllomanganate mineral similar in structure to dehydrated ranciéite (Kim, 1993), but chemical data is required for definitive identification.

ACKNOWLEDGEMENTS

The authors wish to thank Lionel Joynson for assistance with fieldwork and Tim Barrett for access to analytical data on manganese concentrations in rocks at Mynydd Parys and for discussions regarding manganese mineralogy. The authors would also like to thank Amanda Valentine of Amgueddfa Cymru for preparation of polished blocks and Mike Lambert also of Amgueddfa Cymru for assistance with EDS analysis and SEM imaging. Finally, David Green is thanked for providing details of a recent discovery of ranciéite in Northern Ireland.

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Journal of the Russell Society, **11**, 64-70 (2008)

EXTRACTS FROM 'MINERALS OF THE GLAMORGAN COAST: BARRY ISLAND AND ADJACENT AREAS'

Lynda GARFIELD
16 Penffordd, Pentyrch, Cardiff CF15 9TJ

David WELLINGS
15 Liscum Way, Barry, Vale of Glamorgan CF62 8AB

This article comprises a summary and extracts of a larger report published by the authors, which is available from them in electronic format on DVD. The report describes the minerals found along a stretch of the Glamorgan coast, from south of the Atlantic Trading Estate (ST137671) westwards along the south coast of Barry Island, to west of Cold Knap Point (ST101660). The outcrop comprises several headlands of Carboniferous Limestone, overlain unconformably by late Triassic and early Jurassic sedimentary rocks. In the limestones, minerals include calcite, dolomite, galena, baryte and quartz, with very minor sphalerite, chalcopyrite and sulphide alteration products, interpreted as the products of Mississippi Valley Type (MVT) mineralisation. In the Triassic rocks, evaporite minerals include calcite, gypsum (variety selenite), celestine and very minor strontianite, almost all within nodules in mudstones.

Comparisons along the outcrop have led to some interesting conclusions: (1) The MVT mineralisation is considered to be of both pre-late Triassic and post-Triassic age. (2) A reactivated fault zone orientated 340° close to the Cadoxton River is postulated to account for significant differences in the geology and mineralisation of the Carboniferous Limestone either side of this zone. (3) The occurrence of celestine in Triassic nodules is more extensive than previously reported. (4) There may have been some small scale mining activity on Bendrick Rock.

INTRODUCTION

The main object of the survey was to find mineral localities on Barry Island and adjacent areas, to identify the minerals, and to record their location. The area of interest extends along the length of the local coastal Carboniferous Limestone outcrop. It offers excellent cliff exposure and particularly extensive exposure down to low water. The survey involved a significant amount of literature searching to locate previous mineral finds, and an extensive systematic field study from 2004 to 2008.

Previously, Howard (1894/5, 1895/6) gave the most detailed account of the minerals of the area. More recent accounts have tended merely to repeat previous reports. The geology has been well documented, however these accounts rarely record any mineralisation.

The field study looked for all the previously indicated mineral localities; not all are now identifiable or accessible. It also included a search for further mineral localities. Overall, the minerals may not be as outstanding in quantity or quality as those found in other parts of the Carboniferous Limestone and Triassic outcrops in South Wales, but numerous new finds were made. Rather more mineralisation then previously known about was identified, especially on Bendrick Rock. It is interesting that, given the area's proximity to Cardiff, and for Barry Island its location on very well trodden ground, much had not been previously reported.

METHOD

A variety of existing reports were studied to identify previously recorded mineral localities. The field study included the coastal rocks down to those exposed during the lowest tides, around 6 m below mean sea-level. Only areas accessible to the public were included.

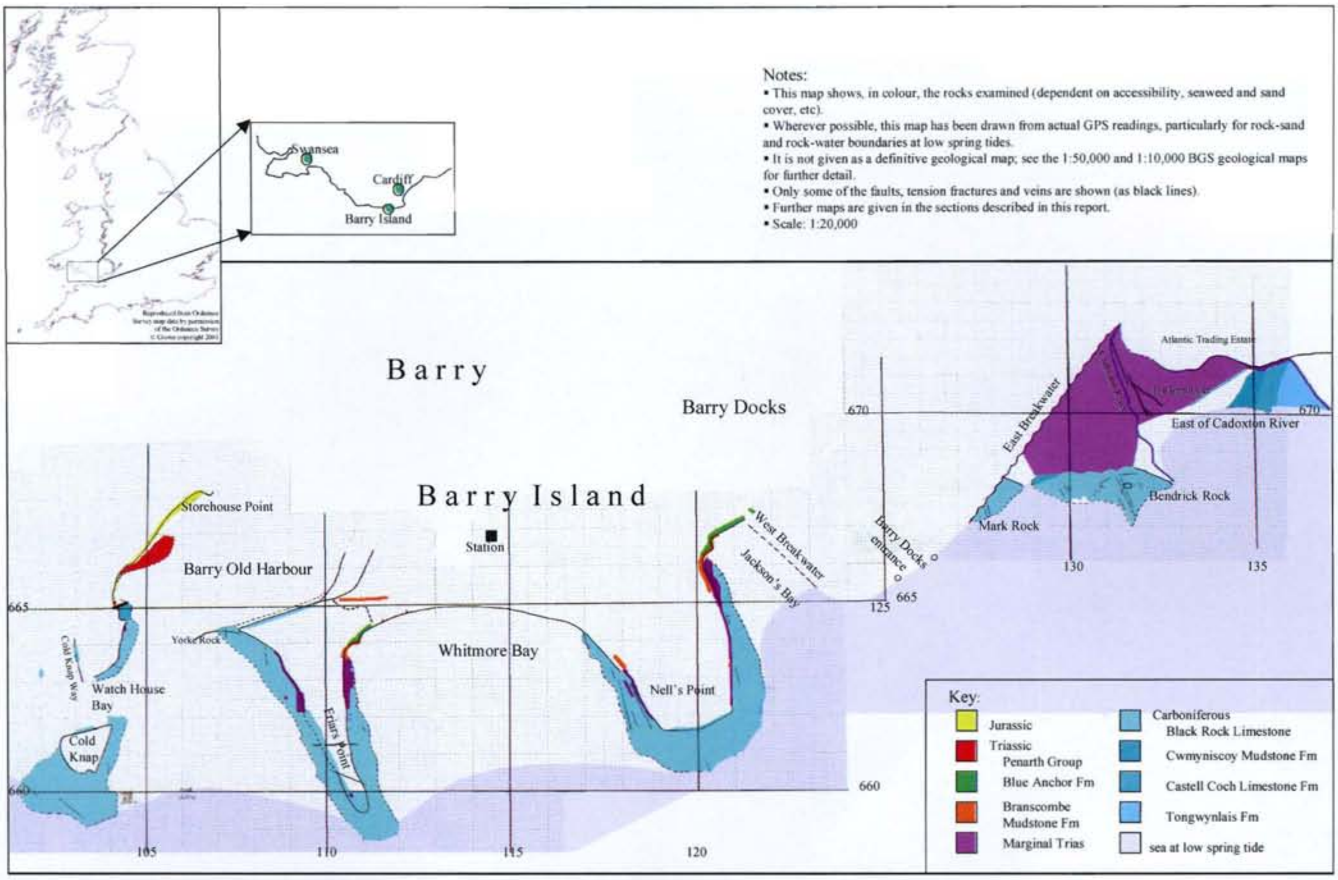
Locations were recorded as National Grid references as accurately as possible using a GPS personal navigator, backed up with photographs to show the geology, the terrain, and almost all the mineral finds.

Minerals found were identified primarily by their appearance, hardness, and response to dilute acids. Some samples were taken for microscope examination, density measurements, reaction with hot acids, UV light fluorescence, and X-ray diffraction analysis (XRD) at the Amgueddfa Cymru - National Museum Wales geology department, also one sample by EDS (energy dispersive X-ray analysis on the Scanning Electron Microscope).

RESULTS

The results of the investigations, with photographs, are described in the full report (Garfield and Wellings 2008) under five sections, each based around a part of the local Carboniferous Limestone outcrop (Fig. 1). These are, from east to west: East of the Cadoxton River (EC); Bendrick Rock (BR) and Mark Rock (MR); Jackson's Bay (JB) and Nell's Point (NP); Friars Point (FP); Storehouse Point (SP) to Cold Knap Point (CK). Some relevant historic data is also included.

In addition, the detailed descriptions from the 2004-8 field study are given separately as data sheets with accompanying photo compilations. Full copies of these, including a DVD with the original photo files, have been deposited with the Amgueddfa Cymru - National Museum Wales and the British Geological Survey (BGS) Wales office for posterity, should other interested bodies wish to make further investigations. A few representative mineral samples have been deposited with the Amgueddfa Cymru - National Museum Wales.



Notes:

- This map shows, in colour, the rocks examined (dependent on accessibility, seaweed and sand cover, etc).
- Wherever possible, this map has been drawn from actual GPS readings, particularly for rock-sand and rock-water boundaries at low spring tides.
- It is not given as a definitive geological map; see the 1:50,000 and 1:10,000 BGS geological maps for further detail.
- Only some of the faults, tension fractures and veins are shown (as black lines).
- Further maps are given in the sections described in this report.
- Scale: 1:20,000

Figure 1. Map of Barry Island and adjacent areas, with outline geology.

GEOLOGY

Bendrick Rock, Nell's Point, Friars Point, and Cold Knap are headlands of hard grey fossiliferous partially dolomitised Carboniferous Limestone, dipping 25° to 70° to the south, originally deposited in shallow tropical seas around 350 million years ago. Deposition of a thick sequence followed, including coal-bearing strata, ending about 300 million years ago. During the Variscan orogeny the rocks were folded, faulted and uplifted, with subsequent erosion of a considerable thickness of strata. The limestones now lie on the southern limb of a local east-west anticline. This, and numerous small thrusts, indicate south-north compression. The limestones are crossed by many later vertical fractures, bearing mostly 340° to 360°, referred to here just as "tension fractures", indicative of east-west extension. Some show movement and many are varyingly infilled with calcite.

Around 215 million years ago, during the late Triassic, the area had drifted northwards. It now lay on the north margin of a large inland hypersaline lake, in an arid to semi-arid climate. Modern day equivalents are playa lake and/or coastal sabkha environments. The Carboniferous Limestone formed hills and/or islands. These correspond to the limestone headlands seen today, but the hills/islands then were probably a little larger and more extensive. From time to time the lake level rose, and/or the land dropped, resulting in a succession of wave-cut platforms with paleo-cliffs behind. Rock falls are preserved as breccias full of fragments of Carboniferous Limestone, some of which are quite large, up to a few metres in size, cemented by lime rich muds. These breccias are termed "marginal Trias", as are conglomerates, sandstones, siltstones and limestones deposited close to the margins of the lake.

The gently dipping predominantly red coloured beds both overlying and extending laterally from the marginal Trias, e.g. as seen in the cliffs of Jackson's Bay, were deposited as fine grained muds and silts within the lake. Gypsum nodules formed in soils in the vicinity. These nodules have subsequently been altered, mainly to calcite. Occasionally gypsum (variety selenite) and strontium minerals (celestine and very minor strontianite) can be found in them. The red dominated beds are now assigned to the upper part of the Branscombe Mudstone Formation (formerly the "red mudstones", before that the Keuper Marl).

The lake was invaded by seawater around 205-210 million years ago, the hills/islands eventually becoming completely buried by very late Triassic to early Jurassic sediments. A major WSW-ENE fault of post-Liassic age, the Cold Knap Fault, is seen in a zone of disturbance north of Watch House Bay.

Barry Island is renowned internationally for the unconformity between the Carboniferous and Triassic rocks, representing around 140 million years of geological time. Of particular note are up to seven successive wave-cut platforms, with paleo-cliffs at their rear and wave-cut notches at the base of the cliffs. There are three Sites of Special Scientific Interest (SSSI) / Geological Conservation Review (GCR) sites in the area, including "the Bendricks" for dinosaur footprints.

This geological outline is based on observations made during this study complemented by more detailed descriptions, notably Howe *et al.* (2004), Howells (2007), Hounslow and Ruffell (2006), Waters and Davies (2006), and Waters and Lawrence (1987).

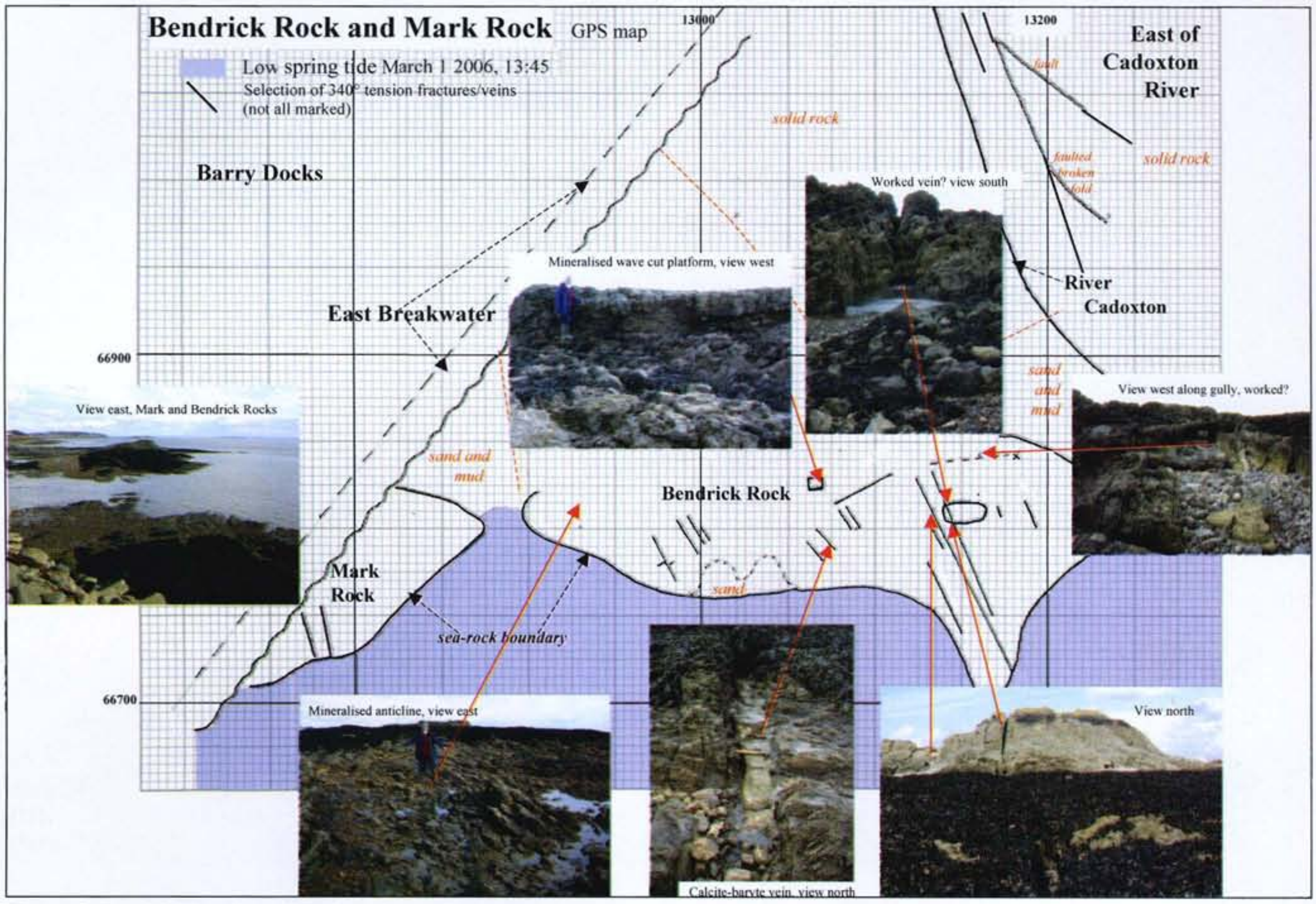


Figure 2. Bendrick Rock and Mark Rock, map with photographs.

PRIMARY MINERALS

CALCITE, $CaCO_3$

Many of the tension fractures in the Carboniferous Limestone are infilled with calcite veins. Some of these veins contain coarse white crystalline calcite often showing several stages of infilling. Some veins are up to a metre thick, some can be traced for a hundred metres or more, all appear to be vertical. Some contain other minerals such as baryte, dolomite, quartz, galena, sphalerite, pyrite or chalcopyrite, but there appears to be little comparison between them. For example the main 340° fault on Bendrick Rock is infilled with coarse white calcite up to a metre thick, but 10 m to the east there is another thinner more irregular bifurcating vein which contains galena, baryte, sphalerite, calcite and dolomite. Only one vein has been found with well shaped crystals of calcite (Fig. 3). The tension fractures and calcite filled veins do not extend up into the Trias. There are some other thick calcite veins within the Carboniferous Limestone, of varying orientation.

Disseminations of irregular veinlets occur in the Carboniferous Limestone, notably on Bendrick Rock. Analysis of one of these shows 50% carbonate (calcite and dolomite) in association with baryte, galena and quartz. Occasionally these are also noted in marginal Trias. Crystalline calcite is found in the nodules in the Triassic mudstones of Jackson's Bay and Whitmore Bay. Some very thin veins of pink calcite run at an angle in some of the mudstones.

Figure 3. Cockscomb baryte on calcite, Bendrick Rock. Field of view 5 cm. (Cover photograph of the report)

DOLOMITE, $CaMg(CO_3)_2$

In the absence of good crystalline material, differentiation in the field between calcite and dolomite is difficult, although dolomite is definitely present in the limestone, as indicated by the literature (Howells, 2007), XRD analyses and chemical tests.

BARYTE, $BaSO_4$

Baryte occurs relatively widely on Bendrick and Mark Rocks as white, pink to orange coloured centimetre thick irregular veinlets, usually with calcite, dolomite and galena, which can stand proud on the surface of the

Carboniferous Limestone. It is also found, in small concentrations, in some of the calcite veins in the tension fractures and in some east-west gullies. In one vein on Bendrick Rock, baryte occurs as cockscomb crystals in cavities with crystalline calcite (Fig. 3).

On Nell's Point and Friars Point baryte is similarly present, but it is not as noticeable as on Bendrick Rock. It has not been noted on Cold Knap, the west side of Barry Old Harbour, or in the Carboniferous Limestone east of the Cadoxton River. It has not been found in Triassic rocks except for two small nodules in the marginal Trias east of the Cadoxton River, boulders of marginal Triassic breccia on the west side of Nell's Point, and very occasionally in the lowest Triassic rocks immediately above the unconformity on Bendrick Rock. The mineral is confirmed by XRD analyses.

Figure 4. Galena in calcite vein, Yorke Rock, east side Barry Old Harbour. Field of view 10 cm. (Photo FP35)

GALENA, PbS

On Bendrick Rock and Mark Rock galena is also relatively widespread, where it is found as groups of crystals and thin veins in the Carboniferous Limestone, as crystals and thin veinlets in the calcite veins within the tension fractures and gullies, and in the irregular veinlets in association with baryte, calcite and dolomite. Further west, galena becomes less noticeable. It is present as crystals and thin veins in the limestone and calcite veins on both Nell's Point and Friars Point. It also occurs in irregular veinlets on Nell's Point, and on the joint planes of the limestone at the south end of Friars Point. It has only been found in Triassic rocks in very minor amounts in association with baryte at the localities mentioned above, and as suspected detrital galena eroded from the Carboniferous Limestone on Bendrick Rock and in Jackson's Bay. It has not been noted, as with baryte, on Cold Knap, the west side of Barry Old Harbour, or in the Carboniferous Limestone east of the Cadoxton River. The mineral is confirmed by XRD analyses.

SPHALERITE, ZnS

Sphalerite occurs as fresh resinous pale yellow to mid brown crystals within small samples taken from the central part of the calcite vein 10 m east of the fault on Bendrick Rock. It is confirmed by XRD analysis, in association with calcite, galena and dolomite. It has also been identified in a rather weathered vein towards the west end of Bendrick Rock; XRD results indicate only secondary zinc minerals, but a small amount of sphalerite has been seen under the microscope. It has not been noted at any other locality in this survey, although it was reported from the base of the marginal Trias in Jackson's Bay (The Russell Society Newsletter **16**, 1988).

CHALCOPYRITE, $CuFeS_2$

Chalcopyrite has been found at only two localities, as very minor occurrences. A very small amount of malachite is noted at one of these.

CELESTINE, $SrSO_4$ and STRONTIANITE, $SrCO_3$

Celestine in the Trias has been known for nearly two centuries within the nodules in the red mudstones, where it can still occasionally be found, notably at the west side of Jackson's Bay. It is actually more extensive than previously reported, with further localities found during this field study at the north-west corner and the east side of Whitmore Bay. Some of these are in grey as well as red mudstones.

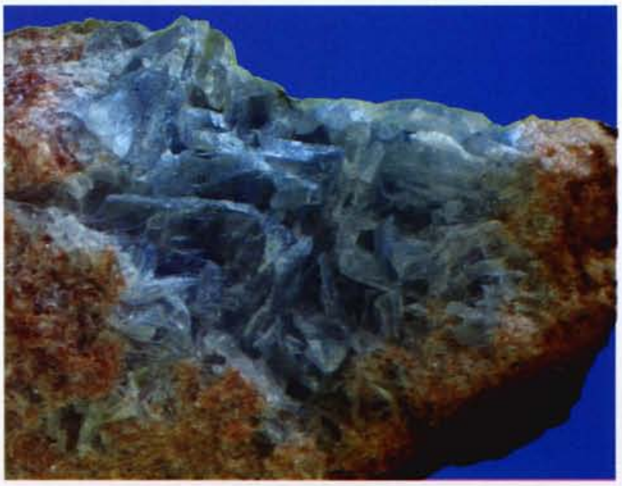


Figure 5. Celestine nodule found 1987, west side Jackson's Bay (Mary Hyde sample). Filed of view 6 cm. (Photo JB23)

The celestine found shows several forms, for example large blue crystalline masses (Fig. 5), white-buff masses, and millimetre sized clear to pale brown friable crystals in nodules that appear to erode quite quickly. Two XRD analyses confirm celestine, one EDS analysis gives 99 wt% $SrSO_4$. Strontianite has also been found, in very minor amounts, on celestine within a nodule from the north-west corner of Whitmore Bay.

Figure 6. Celestine and strontianite in Blue Lias limestone, Storehouse Point. Field of view *ca.* 14 mm. (Photo SP8)

In the Jurassic Blue Lias rocks close to Storehouse Point, there are very minor occurrences of celestine in voids within fossils with even smaller amounts of needles of strontianite (Fig. 6). No strontium minerals have been identified during this survey in the Carboniferous Limestone, however several earlier accounts report barytocelestine, now not recognised as a separate mineral species.

GYPSUM, $CaSO_4{\cdot}2H_2O$

Gypsum variety selenite (Fig. 7) occurs occasionally in the nodules in the Triassic mudstones. So far only three localities are known, all on the west side of Jackson's Bay.

Figure 7. Selenite from a nodule, west side Jackson's Bay. Field of view 16 cm. (Photo JB17)

QUARTZ, SiO_2

Quartz occurs as small nodules within the Carboniferous Limestone on a bedding plane on Bendrick Rock, and as crystals in small cavities on a bedding plane just south of Yorke Rock. At both locations there are numerous chert horizons, some of which show silicified fossil material. Some of the fossils in a sample from Yorke Rock have been replaced by a form of silica referred to as "beekite" in several earlier publications, e.g. North (1916) who describes it as "a chalcedonic form of silica" and of "frequent occurrence" in the Carboniferous Limestone in the district. It has not otherwise been searched for in the current survey.

XRD analyses confirm the presence of quartz, and indicate that there is more quartz present than identified visually in the mineralised veins and veinlets, at least on Bendrick Rock.

PYRITE, FeS_2, GOETHITE, FeO.OH

Pyrite, a fairly common mineral, has been noted in small quantities at a number of locations. It frequently shows alteration to goethite.

At one locality east of the Cadoxton River, iron oxides, most probably goethite, fill joints and penetrate the bedding of the Carboniferous Limestone.

SECONDARY MINERALS

In this survey, much of the area under investigation is covered by the sea at least twice a day. The rest of the area is subject to sea spray. Under these conditions, interesting secondary minerals can form from the reaction, particularly of sulphides, with sea water, such as phosgenite (lead carbonate chloride). Secondary minerals have not been specifically looked for in this survey, but it is noted that galena sometimes shows whitish deposits on its surface. These are considered to be cerussite ($PbCO_3$) but have not been followed up further. In a sample from a tension fracture exposed at low water on Bendrick Rock, microscope examination shows weathered galena and some irregular cavities which resemble weathered sphalerite. There is some suspected pale yellow bindheimite ($Pb_2Sb_2O_6(O,OH)$). Small white clusters which fluoresce blue look very much like hydrozincite ($Zn_5(CO_3)_2(OH)_6$). Follow up examination by XRD analysis shows cerussite and smithsonite ($ZnCO_3$).

GENESIS OF THE MINERALISATION

The known mineral localities on Barry Island and adjacent areas are considered to form the following associations:

- calcite/carbonate-baryte-galena in Carboniferous Limestone (this includes mineralisation in the tension fractures, east-west gullies, and disseminations of irregular veinlets),
- evaporite minerals principally in nodules in Triassic mudstones,
- to a lesser extent, other relatively thick calcite veins of various orientations,
- to a lesser extent, iron oxides in Carboniferous Limestone,
- and to an even lesser extent, sulphide alteration minerals.

In examining the genesis of the mineralisation, the most recent and the most comprehensive account is that of Bevins and Mason (2000), covering Glamorgan and

Gwent. They identify eight types of mineralisation. Four are very similar to the associations identified and listed above, namely:

- Mississippi Valley Type lead-zinc-barium
  The association of calcite/carbonate-baryte-galena in Carboniferous Limestone is considered to be of this type,
- evaporite related deposits,
- oxide iron ores,
- supergene alteration of the MVT mineralisation.

Mississippi Valley Type lead-zinc-barium

Mississippi Valley Type (MVT) deposits consist of veins and replacement bodies which have been precipitated from low-temperature, highly saline metalliferous brines expelled from deep sedimentary basins. These are typically found within limestone–dominated districts, with minerals precipitated when the brines reacted with limestone, dissolving it and replacing it typically with fluorite, baryte, calcite, sphalerite and galena (Mineralogy of Wales, 2007).

In the South Wales-Mendip orefield, mineral deposits of this type have been worked at several localities over the last two millennia, some sites being relatively large, others very small. There are a few reported small localities, some previously worked, fairly close to Barry Island (Mike Munro, *personal communication*). The mineralisation, with galena and baryte dominant, also carries varying amounts of sphalerite, quartz, pyrite, chalcopyrite, calcite and fluorite. It is found mainly in limestones, mostly of early Carboniferous age but also of early Jurassic age, occasionally in marginal Trias (Bevins and Mason 2000).

At Ogmore, 25km further west, the mineralisation is considered to be "by far the most important metallogenic site in the South Wales MVT Orefield". Mineralisation takes a variety of forms. Reactivated Variscan structures are invoked as pathways for mineralising hydrothermal fluids, which are considered to have been generated within the Jurassic marine basin. They then "migrated out and upwards to mineralise… the Carboniferous limestones, the marginal Trias and basal Lias". In the latter, minerals were "deposited from fluids exhaled into the marginal Liassic sediments near to surface" around topographic highs of Carboniferous Limestone. "Minor metallogenic events may have affected the area as recently as mid Tertiary times" (Bevins and Mason 2000).

On Barry Island and adjacent areas the calcite/carbonate-galena-baryte association shows many of the features of MVT type mineralisation described from Ogmore. Although the occurrences are relatively minor in extent, they do show several forms, and they do appear to be of differing ages including a possible older pre late-Triassic phase.

On Barry Island and adjacent areas the 340°-360° tension fractures do not extend up into the overlying Trias, nor do the calcite vein infillings. An approximate east-west tensional regime of pre-late Triassic age is thus indicated. The emplacement of at least some of the calcite must be similarly related. Are the baryte-sulphide minerals in these veins also related, or were they introduced later? The presence of galena-bearing clasts of Carboniferous Limestone within basal marginal Trias, close to an outcrop of galena-bearing in situ Carboniferous Limestone on Bendrick Rock suggests (some) galena emplacement of pre-late Triassic age, as does the finding of what appears to be detrital galena scattered nearby in the Trias very close to the unconformity, similarly in Jackson's Bay.

The few other instances of mineralisation in the marginal Trias indicate a (very) late or post-Triassic age, as do the two small nodules in the Trias east of the Cadoxton River.

So, as observed so far, the evidence does suggest at least some pre-late Triassic mineralisation, with some later post-Triassic mineralisation and/or remobilisation. Closer examination of the mineralisation, particularly on Bendrick Rock, is indicated. Age dating of the various associations of galena would be useful.

Why is the Carboniferous Limestone outcrop east of the Cadoxton River so different from that of Bendrick Rock, 500 m to the west? There must have been some movement between the Carboniferous Limestone rocks of these two areas, because of the difference in age, dip, fracture patterns and mineralisation. The movement and erosion must have been before the Trias was deposited. In contrast the "faulted broken fold" in the Trias and the associated 340° disturbances just to the east of the Cadoxton River indicate movement of post-Triassic age. However the 340° direction is a pre-late Triassic feature. This suggests a re-activated fault zone, close to the Cadoxton River.

The Carboniferous Limestone of Bendrick Rock, in comparison with the nearby exposures to the west on Barry Island, contains more chert, hosts more galena and baryte and calcite veins, is reportedly more dolomitised, and it formed an hill/island in Triassic times as it does now. Perhaps a re-activated fault zone just east of the Cadoxton River controlled in some way the circulation of hydrothermal fluids in the area? There is plenty of scope for further investigation.

Observations on Bendrick Rock suggest that it has quite possibly been worked for minerals in the past, but without a more definite indication in the literature or the finding of old artefacts, this cannot be taken any further. However, Bendrick Rock is recommended for consideration as a RIGS (Regionally Important Geological or Geomorphological Site) or SINC (Site of Importance for Nature Conservation) designation on account of the level of mineralisation found there.

Evaporite-related deposits

The more interesting evaporite minerals are those in the nodules in the Triassic mudstones. Composed mostly of calcite, a few carry sulphates of calcium and strontium; it is these sulphate bearing nodules which are of particular interest.

It is probable that the nodules were originally deposited as gypsum or even anhydrite. "Similar sulphate nodules form today at shallow depths in shoreline sediments around tropical coasts such as the Persian Gulf, where they are known as sabkhas" (Thomas, 1998). The nodules "formed as clusters of gypsum crystals growing within the soil in an arid environment", "which has since been recrystallised to calcite" (Howe *et al.*, 2004).

The gypsum was replaced by the less soluble calcium carbonate when carbonate bearing waters circulated through the mudstones at some time during diagenesis. However, it is not clear (and different people hold different views on this) as to how this process occurred. Mineralogical changes during diagenesis can be numerous in evaporite sequences. Regarding the celestine, was it deposited as an evaporite mineral, similar to gypsum, or was it introduced during diagenesis?

Regarding the source of the strontium, it has been suggested that strontium was present in the aragonite or calcite of the fossils in the Carboniferous Limestone, and that this was subsequently released from the calcite during dolomitisation of the limestone. Bevins and Mason (2000) suggest that there might have been "localised remobilisation of Sr during a more widespread mineralising event" i.e. the MVT mineralisation.

Iron oxides

Bevins and Mason (2000) note that weak iron ore mineralisation is widespread throughout South Wales, wherever the relevant geology is exposed. The larger deposits are interpreted as having formed "by the repeated infill of solution voids in dolomitised limestone". Over the years, various mechanisms for their formation have been put forward, notably either iron rich fluids formed during oxidising conditions during arid Triassic times percolating downwards into the underlying Carboniferous Limestone and hematising and/or filling cavities in the limestone with iron oxides, and/or episodic iron bearing hydrothermal fluids circulating through the limestones, Variscan fracture systems acting as a major control, perhaps even as an early phase of MVT hydrothermal mineralisation (Bevins and Mason, 2000). The iron oxides east of the Cadoxton River appear to be of this type, deposited along joint planes and bedding, but very minor in extent.

ACKNOWLEDGMENTS

The authors wish to thank staff of the Amgueddfa Cymru - National Museum Wales especially Tom Cotterell for help with identification and XRD analyses. They also thank Tom Sharpe (Geologists' Association - South Wales Group); Geraint Owen (The Russell Society and Geologists' Association - South Wales Group) University of Swansea; Adrian Humpage and staff of the British Geological Survey office, Tongwynlais; Mike Munro (Welsh Mines Society); Tom Clemett, Barry; Barry Library, Cardiff Central Library, Cardiff University Library and Glamorgan Record Office; and members of the Wales and West branch of The Russell Society.

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Journal of the Russell Society, **11**, 71-72 (2008)

THE MINERALS OF MONEEN QUARRY, CASTLEBAR, CO. MAYO, IRELAND

Stephen MORETON
33 Marina Avenue, Great Sankey, Warrington, Cheshire, WA5 1HY, UK

Strontianite, celestite, fluorite, gypsum, calcite, dolomite and sphalerite occur in small cavities, often in fossil shells, in the Carboniferous limestone exposed in Moneen quarry, Castlebar, Co. Mayo. Quartz, pyrite and bitumen are rare associates.

INTRODUCTION

Moneen Quarry is a large working limestone quarry, operated by Roadstone Provinces Plc, on the outskirts of Castlebar, Co. Mayo in the west of Ireland (Irish grid ref. M 162908). The rock type is Lower Carboniferous limestone and contains fossils of corals and shells, the latter commonly Nautiloids.

Small cavities occasionally occur in the fossil shells, and sometimes also without any apparent association with fossils. Cavities are scarce, often being confined to particular beds within the limestone, and even then, only parts of those beds, as can be seen in the quarry face. They are rarely more than 10 cm across, but contain a variety of minerals, and when these do not completely infill the cavities they can afford small, well crystallised specimens, as described below.

MINERALS

Bitumen, C_nH_{2n+2}

Bitumen occurs very rarely as black spots, *ca.* 1 mm across, on dolomite.

CALCITE, $CaCO_3$

Calcite is ubiquitous. It is translucent white and usually of a stumpy scalenohedral habit, although some curious lozenge shaped crystals have also been found. The crystals rarely exceed 10 mm. Mammillated encrustations also occur, often with celestite blades.

CELESTITE, $SrSO_4$

After calcite, this is probably the most common mineral present. Frequently it completely infills the cavities as white to pale lilac platy masses. When freely grown crystals are present they are invariably white and usually of a thin platy habit up to 20 mm long, more rarely as wedge or lozenge shapes up to 10 mm. Identification was by XRD of several separate samples, and of one composite sample.

XRF analysis of a composite sample indicated a modest barium content in addition to the expected strontium: 6.2 % BaO, 3.0 % CaO, 0.1 % MgO, 24.7 % SO_3, 50.0 % SrO, 0.5 % SiO_2, 15.3 % lost in furnace. The calcium must be substituting for strontium, it is unlikely to be present as adhering calcite as the sample was acid-washed prior to analysis. Theory predicts 43.6 % SO_3 for pure $SrSO_4$ (less when Ba is present, more when Ca is present). As the method involves fusing the sample at 1250 °C with a lithium tetraborate flux, much volatile SO_3 is likely to be lost, making this a poor method for quantitative determination of sulphate, hence the low value.

DOLOMITE, $Ca,Mg(CO_3)_2$

White or pale cream-coloured dolomite is occasionally found as an early phase lining some of the cavities. Crystals rarely exceed 4 mm.

FLUORITE, CaF_2

Pale to deep purple fluorite is sometimes present as spots amongst the calcite lining the cavities. Rarely, free grown cubes up to 8 mm have been found.

Figure 1. Fluorite, 8 mm cube on calcite, Moneen Quarry. S. Moreton specimen and photograph.

GYPSUM, $CaSO_4{\cdot}2H_2O$

Massive, white, granular gypsum sometimes completely fills the cavities. It may enclose blades of celestite indicating it post-dates this mineral. Rarely, colourless crystals up to several millimetres have also been found. These may be partially overgrown with strontianite. Identification was by XRD of three separate samples. Chemical tests confirmed the presence of calcium and sulphate. Loss in a furnace at 1100 °C was 20.8 %, which is very close to the theoretical water content of 20.9 %.

PYRITE, FeS_2

Pyrite sometimes occurs disseminated in the limestone around the margins of the cavities.

QUARTZ, SiO_2

A single, colourless, double terminated 10 mm crystal in a dolomite-lined cavity was found in 2000, and a distorted 7 mm prism in 1997.

SPHALERITE, ZnS

Spots up to 15 mm across of brown, yellow and occasionally bright orange-red sphalerite sometimes occur in calcite-filled cavities. Free grown crystals are very rare, one such is greenish and nearly 10 mm across.

STRONTIANITE, $SrCO_3$

Strontiantite is commonly present as tufts and druses of acicular crystals up to 4 mm in length. These are usually snow-white but sometimes translucent. It is always the last mineral to be deposited. A few exceptional examples up to 2 cm long were found on the first visit in 1995, but these were so delicate they did not survive attempts to recover them from the large boulder containing them. None of this size have been seen since. Identification was by XRD of several separate samples, and of one composite sample.

XRF analysis of a composite sample gave 5.6 % BaO, 8.2 % CaO, 0.1 % MgO, 2.7 % SO_3, 52.6 % SrO, 0.1 % SiO_2, 30.6 % lost in furnace. The material has a similar barium content to the celestite. The high calcium content may be due to adhering calcite, as the sample could not be acid washed to remove this. The loss may be taken to be CO_2 and is close to the theoretical value for pure $SrCO_3$ (29.8 %). Effervescence in acid confirmed the presence of carbonate.

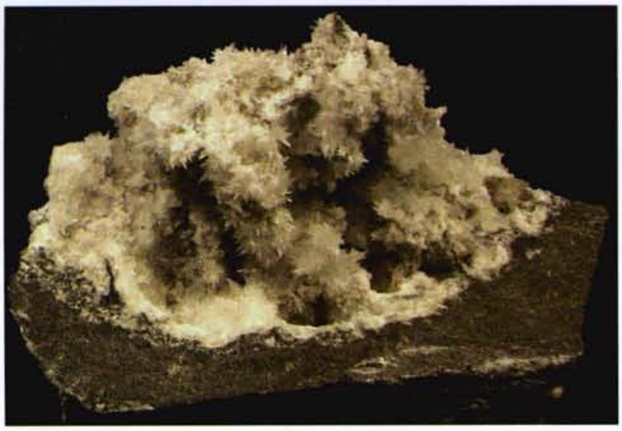

Figure 2. Strontianite, *ca.* 2 mm crystals, Moneen Quarry. Collected by R. Lawson, photograph by S. Moreton.

DISCUSSION

The similarity with Trearne quarry, near Beith, Ayrshire, is obvious. At Treane, small cavities, often in fossil shells in the limestone, contain a suite of minerals that overlaps with that at Moneen quarry, in particular the fluorite and strontium minerals (Todd, 1989). The circumstances of formation may be similar. Curiously, at Moneen quarry, although the two strontium minerals, strontianite and celestite, are quite common, they only occasionally occur together on the same specimen.

The minerals described here are already well known from localities in the UK. However, as the only previous reports of Irish strontianite are 19th century (mentioned in Ryback and Moreton, 1993), and have not been repeated in recent times, Moneen quarry is possibly the best modern Irish location for the mineral. Or at least the best accessible one, as strontianite (identified by EDAX) has also been found at Galmoy mine, Co. Kilkenny, where it occurs with honeyblende sphalerite and calcite (author's unpublished observation). Unfortunately, requests to this mine by the author, for access or specimens, have so far been refused.

Sadly Moneen quarry is nearing the end of its life, being located on the edge of a growing town, and with the quarry now approaching its limits. This, therefore, seemed an opportune time to record what was found. What will happen after closure is not clear, but the quarry's location on the edge of a large town with a good road network would make it a prime landfill site.

As specimens will soon be unobtainable, a suite of examples has been donated to the National Museum of Ireland.

CURRENT SITUATION

Due to health and safety concerns access to the quarry is only by prior appointment, and will include a safety induction video and a chaperon.

ACKNOWLEDGEMENTS

The author is indebted to the management of Moneen quarry for permission to visit intermittently over a ten year period from 1995. Robert and John Lawson of Moorland Minerals assisted greatly in collecting, and Peder Aspen (formerly Edinburgh University) and David Green (Manchester Museum) carried out some of the XRD work and the EDAX. A former Galmoy mine employee is also thanked for the strontianite specimen from there.

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Journal of the Russell Society, **11**, 73-79 (2008)

BARIUM ZEOLITES AND CALCIOANCYLITE-(Ce) FROM GUISACHAN QUARRY, TOMICH, HIGHLAND, SCOTLAND

Neil HUBBARD
30 Thirlmere Road, Barrow upon Soar, Leicestershire, LE12 8QQ

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

Andrew G. TINDLE
Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA

A mineral assemblage comprising calcite, calcioancylite-(Ce), edingtonite, harmotome, pyrite and marcasite is present in thin fractures in psammitic rocks of the Loch Eil Group at Guisachan Quarry, about a kilometre to the south of Tomich, Strathglass, Highland Region, Scotland. Edingtonite is uncommon in the British Isles and this is the first report of calcioancylite-(Ce). The formula can be written $(Ba_{0.95},K_{0.05},Na_{0.02})[Al_{1.93}Si_{3.06}O_{10}]\cdot nH_2O$ for edingtonite and $(Ba_{2.06},K_{0.23},Na_{0.35})[Al_{4.75}Si_{11.25}O_{32}]\cdot nH_2O$ for harmotome. The edingtonite is a little richer in silica than most published analyses, but the zeolite formulae are otherwise typical. The calcioancylite-(Ce) has a formula that can be written $(Ce_{1.57},La_{0.60},Nd_{0.59},Pr_{0.09})(Ca_{0.72},Sr_{0.35})(CO_3)_4(OH)_{2.9}\cdot 1.1H_2O$. It is cerium-dominant, with a relatively high proportion of rare earths and a consequent depletion of the elements of group two. The calcium to strontium ratios vary between 1.4 and 2.9.

INTRODUCTION

Our investigation of the mineralisation at Guisachan Quarry began with the chance discovery of harmotome in the stone used to make a forest track in Strathglass, about 60km southwest of Inverness. The source of the aggregate was traced to Guisachan Quarry, in reality little more than a borrow pit, which is intermittently worked by Forest Enterprise to produce crushed stone for road construction (Fig 1). Guisachan Quarry is situated about a kilometre to the south of the settlement of Tomich on a wooded hillside on the south side of the valley of the River Glass (NH 3091 2670). It is developed within the Upper Garry Psammite, a heavily fractured pink to dark grey medium grained metamorphosed clastic rock, with some fine grained pelitic components. This in turn is part of the Loch Eil Group, which extends for many tens of kilometres immediately to the north and west of the Great Glen Fault, and forms a substantial part of the early Neoproterozoic basinal sediments of the Moine Supergroup in the Northern Highlands Terrane of Northern Scotland (May and Highton, 1997; Woodcock and Strachan, 2000).

Figure 1. Guisachan Quarry as it stood in 2003. Photo Roy Starkey.

Careful investigation of the minerals present in thin fractures in the psammitic rocks which are exposed at the quarry has revealed edingtonite, calcioancylite-(Ce), the iron sulphides pyrite and marcasite, and abundant calcite in addition to harmotome. Since zeolite group minerals are of interest to mineralogists and collectors, and calcioancylite-(Ce) is known from relatively few localities worldwide, a description was thought worthwhile.

Harmotome, $Ba_2(Na,K,Ca_{0.5})[Al_5Si_{11}O_{32}]\cdot 12H_2O$, has the same framework structure as the minerals of the phillipsite series, but the name was retained in the most recent review of zeolite nomenclature on the basis of long usage (Coombs *et al.* 1998). Although it was discovered in the mines at St Andreasberg in Germany in the last quarter of the eighteenth century (Dana, 1883), it is generally agreed that Haüy provided the formal description of the species in 1801. Harmotome is widespread in low temperature barium-rich hydrothermal vein systems in the British Isles and has been reported at a few localities in vesicles in mafic igneous rocks (Tindle, 2008).

Edingtonite, $Ba[Al_2Si_3O_{10}]\cdot 4H_2O$, has a peculiar fascination for British mineralogists. It was described by Wilhelm Karl von Haidinger in 1825 and named for Thomas Edington who had collected a single specimen at Duntiglenan near Old Kilpatrick West Dunbartonshire in 1823 (Meikle and Todd, 1995). Several further localities in the Carboniferous lavas around Old Kilpatrick were known by the time Greg and Lettsom produced their compilation of the mineralogy of Britain and Ireland in 1858; these records are repeated by Heddle (1901) and more precise details are provided by Meikle and Todd (1995), who also describe a new locality: Loanhead Quarry near Beith, North Ayrshire. Harmotome and prehnite are typical associates of edingtonite at all of the localities in the Carboniferous lavas around Glasgow.

Edingtonite is otherwise rare in the British Isles. It occurs as crystals to 20 mm associated with calcite, harmotome and prehnite on joint planes in a dolerite intrusion at Squilver Quarry in Shropshire (Hubbard and

Enamy, 1993). It has recently been described from the Conlig and Whitespots lead mines in Co. Down as minute crystals on calcite and dolomite in a late stage low temperature hydrothermal assemblage which also includes harmotome (Moles, 2007). A further and as yet unpublished locality is in the Precambrian rocks at Dolyhir Quarry in the Welsh borderlands where edingtonite occurs very rarely as minute crystals in thin fractures with harmotome (Tom Cotterell, *personal communication*).

The ancylite group comprises seven orthorhombic and monoclinic rare earth carbonates (Back and Mandarino, 2008), which are typically found in nepheline syenites and carbonatites (Anthony *et al.*, 2003). The only member of the group reported from the British Isles is ancylite-(Ce), which was first found as pale violet micro-crystals associated with platy baryte, drusy quartz and calcite on the Bellsgrove Lodge dump, near Strontian, Highland Region, Scotland (Livingstone, 1993). It has subsequently been recorded at a number of the other mines in the hills north of Strontian as part of a late stage hydrothermal assemblage which includes the barium zeolites harmotome and brewsterite and the rare earth carbonate-silicate kainosite-(Y) (Green and McCallum, 2005).

Calcioancylite-(Ce) is a rare member of the ancylite group with a complicated and interesting history (Pekov, 1998). The type locality was not specified in the first description of the species (Chernik, 1904), it may be in western Russia, one of the Baltic states, Poland, or even Finland; the name was not used either, as Chernik considered the mineral to be a variety of ancylite. Some subsequent references to "calcio-ancylite", including the first use of that name, describe a mineral which would now be classified as a calcium-rich variety of ancylite (Pekov *et al.*, 1997). The modern definition of calcioancylite as a separate species with Ca>Sr was introduced by Palache *et al.* (1951). Subsequent investigations of its chemistry and crystallography summarised by Pekov *et al.* (1997) and Larsen and Gault (2002), have produced a complex formula, which is probably best written $(Ca,Sr)_{4-x}(REE)_x(CO_3)_4(OH)_x{\cdot}(4-x)H_2O$, where x varies between 2.1 and 3.0 (see Back and Mandarino, 2008). This is sometimes simplified to $(Ce,Ca,Sr)CO_3(OH,H_2O)$.

MINERALOGY

The minerals were collected *in situ* and from loose blocks exposed by intermittent operations at Guisachan Quarry on site visits (mostly by NH) from 2001 onward. They occur almost entirely as inconspicuous submillimetre size crystals in thin fractures in the psammite. The more unusual species, calcioancylite-(Ce), edingtonite and harmotome were identified by a combination of X-ray diffractometry (XRD) and wavelength dispersive X-ray spectrometry (WDS). The WDS data is relatively extensive and is tabulated under a separate heading following the mineral descriptions.

CALCIOANCYLITE–(Ce), $(Ce,Ca,Sr)CO_3(OH,H_2O)$

Pink to grey pyramidal crystals of calcioancylite-(Ce) are occasionally present in fractures in the psammitic rock at Guisachan Quarry. On a few specimens they are richly scattered on the fracture surfaces, with as many as fifty tiny crystals in an area of a square centimetre or so, however their similarity in colour to the speckled pink to grey rock matrix and their small size make them inconspicuous even when examined under a stereomicroscope (and almost impossible to see in the field!). The largest crystals found in this study are about 1 mm on edge; they are typically pink in colour and scattered in ones and twos in fractures with abundant calcite, harmotome and occasional edingtonite (Figs 2 and 3).

Figure 2. A pale pink pseudotetragonal crystal of calcioancylite-(Ce) with included iron sulphides, 0.8 mm on edge.

The name ancylite is derived from the Greek word for curved, in allusion to the rounded or distorted crystal habits seen at some localities. The crystals from Guisachan Quarry are typically well formed pseudotetragonal bipyramids, with eight large plane faces. The corners of the crystals are often modified by paired faces which are usually only resolved under a scanning electron microscope (SEM) (Fig. 4). The underlying orthorhombic symmetry is sometimes betrayed by elongation along one of the perpendicular axes, which alters the apparently bipyramidal crystal shape to a squat prism.

Figure 3. Calcioancylite-(Ce), 0.5 mm on edge, on slightly corroded white calcite with tiny pyrite cubes.

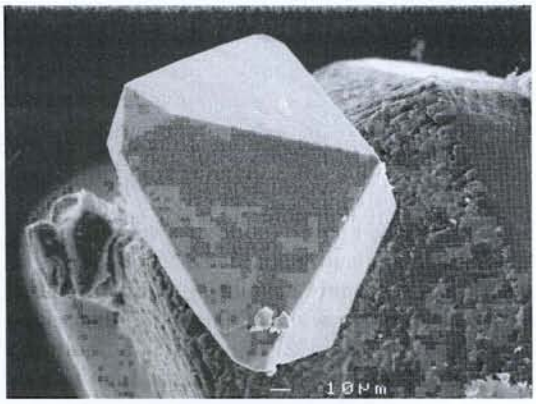

Figure 4. Bipyramidal crystal of calcioancylite-(Ce) with a pair of small prism faces modifying the corners.

Calcioancylite-(Ce) is commonly associated with calcite crystals which often appear partly dissolved (Fig. 5). Many crystals are overgrown by a scattering of pyrite cubes, which are at the limit of resolution of a stereomicroscope, but easily resolved using scanning electron microscopy (Fig. 6).

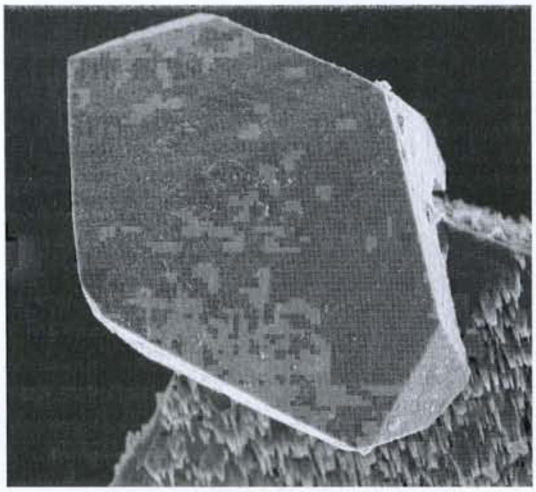

Figure 5. Calcioancylite-(Ce) on corroded calcite.

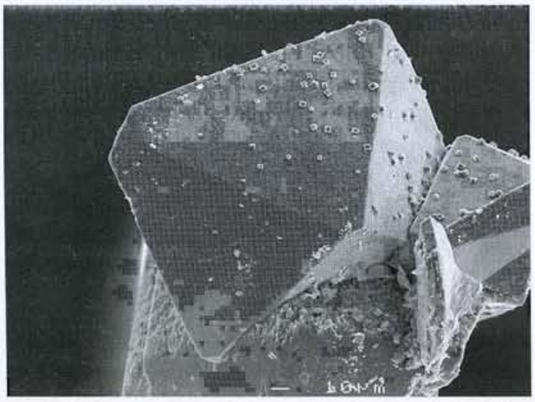

Figure 6. Calcioancylite-(Ce) on slightly corroded calcite with minute scattered pyrite cubes on the pyramid faces.

CALCITE, $CaCO_3$

Calcite is common as translucent white modified rhombohedral crystals up to several millimetres on edge, which often span the fractures in which they crystallise. Calcite also locally cements the brecciated psammite. Both edingtonite and calcioancylite-(Ce) are occasionally found growing on calcite.

EDINGTONITE, $Ba[Al_2Si_3O_{10}]\cdot4H_2O$

Edingtonite occurs as inconspicuous colourless to white crystals that rarely exceed a millimetre on edge and are usually much smaller. A few hand specimens covered in millimetre-size crystals have been found, but edingtonite is much less common than harmotome, and specimens of any size are exceedingly rare. Crystals are usually found scattered on fracture surfaces in the psammitic rock (Fig. 7) and can form continuous crusts to 40 mm across. They also occur on calcite, which may be slightly corroded (Fig. 8). The crystal habit is usually a flat bipyramid, although equant wedge shaped crystals similar to those reported at the type locality (see Tschernich, 1990) also occur. A few specimens with edingtonite crystals as drusy aggregates up to 3 mm across have been collected.

Figure 7. Blocky translucent edingtonite crystals up to 1.5 mm on edge.

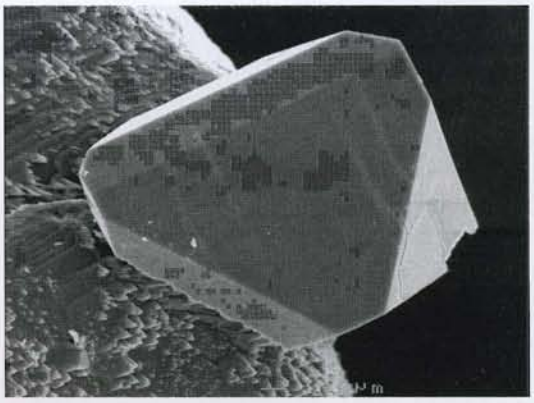

Figure 8. A single sharp edingtonite crystal on slightly corroded calcite.

Oxide	Grain P20, wt% value					Grain P21, wt% value		
SiO_2	38.80	39.19	39.54	38.47	38.81	39.11	37.99	38.67
Al_2O_3	20.79	21.10	21.04	20.71	20.78	20.47	20.60	20.47
MgO	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
CaO	0.01	0.03	0.00	0.02	0.01	0.08	0.02	0.00
Na_2O	0.10	0.10	0.15	0.10	0.10	0.13	0.07	0.10
K_2O	0.35	0.46	0.53	0.38	0.47	0.61	0.33	0.58
SrO	0.06	0.00	0.06	0.02	0.02	0.04	0.09	0.05
BaO	31.20	30.98	30.17	30.89	30.75	29.78	31.11	30.11
Total	91.46	92.10	91.62	90.76	91.07	90.43	90.35	90.13
H_2O	8.54	7.91	8.39	9.24	8.93	9.59	9.65	9.89
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 1. Composition data for two crystals of edingtonite from Guisachan Quarry, coded P20 and P21. Standards used are: Si, Al and K=K-feldspar, Ca=bustamite, Na=jadeite, Sr=synthetic $SrTiO_3$, Ba=baryte. Trace quantities of other elements detected including titanium, zinc, chlorine, fluorine, iron and manganese are not quoted in the table, but are included in the total. Water is calculated by difference.

HARMOTOME, $Ba_2(Na,K,Ca_{0.5})[Al_5Si_{11}O_{32}]\cdot 12H_2O$

Harmotome is the commonest zeolite in the fracture assemblage. It occurs as squat to prismatic colourless to white cruciform twins, which sometimes reach as much as 5 mm in length (Fig. 9), but are usually less than 2 mm. Most of the cruciform twins appear to be on the Perrier law, which is characterised by the absence of intersecting sector striations on the outermost faces of the crystals (Tschernich, 1990). Some of the smaller crystals are simple pseudo-hexagonal morvenite twins.

MARCASITE, FeS_2

Prismatic to tabular tarnished marcasite crystals up to about 1 mm in length, but usually much smaller, occur rarely on calcioancylite-(Ce) and harmotome.

Figure 9. Prismatic cross-twinned harmotome, 4 mm tall.

PYRITE, FeS_2

Pyrite is uncommon in the fracture-hosted mineral assemblage. It occurs as minute cubic crystals on and in calcioancylite-(Ce) and sometimes overgrows or is included in the outer layers of crystals of harmotome. Slightly tarnished cubic crystals up to about 1 mm on edge are sometimes scattered on fractures surfaces and pyrite also occasionally occurs as well formed octahedrons and pentagonal dodecahedrons.

ANALYTICAL DATA

Quantitative chemical analyses of harmotome, edingtonite and calcioancylite-(Ce) were made by wavelength dispersive spectrometry (WDS) on a Cameca SX100 electron microprobe. It was fitted with wavelength dispersive spectrometers and calibrated using a range of natural and synthetic materials which are noted in the accompanying tables. Crystals were hand picked from the specimens under study, embedded in resin, and polished to produce a flat surface. The zeolite analyses were made at 20kV and 20nA with a 20 micron beam diameter, count times of ten seconds were typically used to minimize volatilisation. A PAP correction procedure was employed to refine the data (Pouchou and Pichoir, 1985), which is presented as weight percent oxides in Tables 1 and 2.

Extensive interferences and the difficulty of obtaining reliable standards make routine WDS analyses of minerals that contain rare earth elements (REE) difficult. The data we have gathered for three grains of calcioancylite-(Ce) is presented in Table 3. It only includes the common REE, calcium and strontium, which are quoted as weight percent oxides. Analytical conditions were 20kV and 20nA using a 15 micron beam diameter on a Cameca SX100 electron microprobe fitted with 5 wavelength dispersive spectrometers.

CRYSTAL CHEMISTRY

Zeolites are problematic to analyse by microprobe techniques because of their instability under the electron beam. Their surfaces may appear to be aluminium

Oxide	Grain P22, wt% value					Grain P23, wt% value				
SiO_2	49.29	50.13	49.15	51.68	50.21	49.63	48.98	49.39	50.34	49.63
Al_2O_3	17.41	17.33	17.72	18.04	17.78	18.83	18.15	17.62	17.93	17.59
MgO	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.02
CaO	0.05	0.02	0.07	0.03	0.05	0.32	0.09	0.05	0.11	0.09
Na_2O	0.85	0.77	0.80	0.45	1.34	0.91	0.95	0.77	0.34	0.76
K_2O	0.58	0.53	0.70	0.60	0.59	0.98	0.90	0.80	0.68	0.74
SrO	0.04	0.07	0.09	0.00	0.00	0.00	0.06	0.06	0.05	0.00
BaO	23.30	22.99	23.02	22.96	24.11	23.13	23.19	23.14	23.32	23.32
Total	91.68	91.97	91.72	93.86	94.28	93.91	92.48	91.97	92.96	92.29
H_2O	8.35	8.03	8.30	6.14	5.72	6.09	7.53	8.03	7.04	7.71
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2. Composition data for two crystals of harmotome from Guisachan Quarry, coded P22 and P23. Standards used are: Si, Al and K=K-feldspar, Ca=bustamite, Na=jadeite, Sr=synthetic $SrTiO_3$, Ba=baryte. Trace quantities of other elements detected including titanium, zinc, chlorine, fluorine, iron and manganese are not quoted in the table, but are included in the total. Water is calculated by difference.

deficient due to minor hydrolytic damage which causes the leaching of aluminium (Bish and Boak, 2001), but as the probe uses freshly ground and polished surfaces this would not have been a problem in this case. Analytical problems can be mitigated by using short counting times and defocusing the beam. The reliability of the data can then be checked by calculating the charge balance error, which should be less than ten percent (Passaglia and Sheppard, 2001). The data of Tables 4 and 5 suggest that our analyses are reliable; the largest charge balance error for edingtonite is less than four percent and for harmotome less than eight percent.

The H_2O content calculated by difference in our zeolite analyses is rather smaller than those quoted by Anthony *et al.* (2003) for 'ideal' compositions. Volatilisation effects or a genuinely different H_2O content could explain the differences between the values. The gradually decreasing H_2O values we have observed in many other zeolite analyses suggests the former and for this reason the formulae are simply written as $\cdot nH_2O$.

The R-value, Si/(Si + Al), is commonly used as a measure of the ratio of silicon to aluminium in zeolite frameworks (Passaglia and Sheppard, 2001). Edingtonite, like many other rare zeolites, crystallises with a very

Oxide	P334, wt%		Grain P335, wt %					Grain P337, wt%				
La_2O_3	10.7	10.9	10.7	9.8	10.2	10.0	9.6	11.7	11.7	11.8	11.7	10.7
Ce_2O_3	27.1	26.2	28.3	27.9	27.3	27.1	26.4	28.1	27.9	27.8	28.1	27.5
Pr_2O_3	2.9	2.9	3.1	2.9	3.3	3.1	3.0	2.7	2.7	2.7	2.7	2.9
Nd_2O_3	9.3	10.0	9.7	10.3	10.5	10.7	10.5	8.6	8.6	8.9	9.2	10.3
CaO	4.3	3.8	3.7	4.1	4.1	4.3	4.2	4.1	3.9	4.0	4.0	4.3
SrO	4.9	4.9	4.4	3.0	3.0	2.9	3.2	4.7	4.3	4.5	4.5	3.7
Total	59.2	58.7	59.8	58.0	58.5	58.1	57.0	59.9	59.2	59.7	60.1	59.5

Oxide	Grain P337, wt%									
La_2O_3	10.1	10.1	9.6	9.5	9.6	9.8	9.3	8.9	9.6	9.0
Ce_2O_3	27.4	27.0	27.4	27.1	26.5	27.5	26.6	26.5	26.1	25.4
Pr_2O_3	3.2	3.0	2.9	3.2	2.9	3.4	3.1	3.2	2.9	2.8
Nd_2O_3	10.5	11.0	11.4	11.3	11.8	12.2	12.2	11.1	9.9	10.9
CaO	4.5	4.5	4.6	4.3	4.3	4.5	4.4	4.1	4.6	4.9
SrO	3.4	3.4	2.9	3.1	3.1	3.3	3.3	4.6	5.1	5.0
Total	59.1	59.0	58.8	58.4	58.3	60.7	58.9	58.4	58.2	58.1

Table 3. Composition data for three grains of calcioancylite-(Ce) from Guisachan Quarry, coded P334, P335 and P337. Other elements analysed but not detected include barium and thorium, small amounts of fluorine and iron are ignored for the purpose of this analysis. Standards used for La, Ce, Pr, Nd were synthetic REE glasses prepared by Edinburgh University probe lab and containing 1 REE each together with Si, Al & Ca. Ca = bustamite, Fe = hematite, Sr = synthetic strontium titanite, Ba = baryte, Th = synthetic ThO_2, F = synthetic LiF.

Calculated Formula	Balance Error%	R-value
$(Ba_{0.96},K_{0.04},Na_{0.01})[Al_{1.93}Si_{3.06}O_{10}]\cdot nH_2O$	-2.9	0.61
$(Ba_{0.95},K_{0.05},Na_{0.02})[Al_{1.94}Si_{3.06}O_{10}]\cdot nH_2O$	-1.3	0.61
$(Ba_{0.92},K_{0.06},Na_{0.02})[Al_{1.93}Si_{3.07}O_{10}]\cdot nH_2O$	0.1	0.60
$(Ba_{0.96},K_{0.04},Na_{0.02})[Al_{1.94}Si_{3.05}O_{10}]\cdot nH_2O$	-2.4	0.61
$(Ba_{0.95},K_{0.05},Na_{0.02})[Al_{1.93}Si_{3.06}O_{10}]\cdot nH_2O$	-2.1	0.61
$(Ba_{0.92},K_{0.07},Na_{0.02})[Al_{1.90}Si_{3.09}O_{10}]\cdot nH_2O$	-2.4	0.62
$(Ba_{0.98},K_{0.04},Na_{0.02})[Al_{1.94}Si_{3.04}O_{10}]\cdot nH_2O$	-3.6	0.61
$(Ba_{0.94},K_{0.07},Na_{0.01})[Al_{1.92}Si_{3.07}O_{10}]\cdot nH_2O$	-2.2	0.62

Table 4. Edingtonite formulae calculated for specimens from Guisachan Quarry using 10 structural oxygen atoms, based on the data of table 1. Cations present at a level of less than 0.01 per formula unit are not included in the formulae. Column one gives the calculated formula. The balance error is (Na+K)+2(Ba)-(Al))/((Na+K)+2(Ba))x100 (see Passaglia and Sheppard, 2001). The R value is Si/(Si+Al).

limited range of R-values. In a survey of the crystal chemistry of the zeolite group, Passaglia and Sheppard (2001) noted that the R-values for edingtonite from the five localities they had data for were restricted to the range from 0.59 to 0.61. The specimens from Guisachan Quarry are a slightly more silica-rich, the highest R-value being 0.619 and the average 0.613. This is higher than most other reports, with the exception of a remarkably high value (of 0.787) recorded for edingtonite from Loanhead Quarry on the basis of analyses at the University of Wolverhampton (see Meikle and Todd, 1995). In common with all of the edingtonite analyses we are aware of, barium is the dominant extra-framework cation at Guisachan Quarry: an average formula can be written $(Ba_{0.95},K_{0.05},Na_{0.02})[Al_{1.93}Si_{3.06}O_{10}]\cdot nH_2O$ and in all of our analyses barium makes up more than 90mol% of the exchangeable cations.

Calculated Formula	Balance Error%	R-value
$(Ba_{2.09},K_{0.19},Na_{0.38})[Al_{4.70}Si_{11.28}O_{32}]\cdot nH_2O$	-1.8	0.71
$(Ba_{2.04},K_{0.17},Na_{0.34})[Al_{4.63}Si_{11.37}O_{32}]\cdot nH_2O$	0.2	0.71
$(Ba_{2.06},K_{0.23},Na_{0.35})[Al_{4.77}Si_{11.23}O_{32}]\cdot nH_2O$	0.2	0.70
$(Ba_{1.98},K_{0.19},Na_{0.19})[Al_{4.69}Si_{11.39}O_{32}]\cdot nH_2O$	7.4	0.71
$(Ba_{2.11},K_{0.19},Na_{0.58})[Al_{4.69}Si_{11.23}O_{32}]\cdot nH_2O$	-6.6	0.71
$(Ba_{2.02},K_{0.31},Na_{0.39})[Al_{4.95}Si_{11.06}O_{32}]\cdot nH_2O$	0.9	0.69
$(Ba_{2.06},K_{0.29},Na_{0.42})[Al_{4.86}Si_{11.13}O_{32}]\cdot nH_2O$	-1.0	0.70
$(Ba_{2.07},K_{0.26},Na_{0.34})[Al_{4.73}Si_{11.26}O_{32}]\cdot nH_2O$	-0.9	0.70
$(Ba_{2.05},K_{0.22},Na_{0.15})[Al_{4.75}Si_{11.31}O_{32}]\cdot nH_2O$	4.5	0.70
$(Ba_{2.08},K_{0.24},Na_{0.34})[Al_{4.71}Si_{11.27}O_{32}]\cdot nH_2O$	-1.7	0.71

Table 5. Harmotome formulae calculated for specimens from Guisachan Quarry using 32 structural oxygen atoms and based on the data of table 2. Cations present at a level of less than 0.1 per formula unit are not included in the formulae. Column two gives the calculated formula. The balance error is (Na+K)+2(Ba)-(Al))/((Na+K)+2(Ba))x100 (see Passaglia and Sheppard, 2001). The R value is Si/(Si+Al).

The chemical formula for harmotome, $(Ba_{2.06},K_{0.23},Na_{0.35})[Al_{4.75}Si_{11.25}O_{32}]\cdot nH_2O$, is fairly typical. There are almost exactly two atoms of barium per formula unit and potassium and sodium are the only other major extra-framework cations. The average R-value of 0.703 is not unusual (Passaglia and Sheppard, 2001) and all of the individual values are well within the relatively wide natural variability found in the mineral.

The analytical data for calcioancylite-(Ce), which is summarised in Table 3, does not include data for the heavy rare earth elements (REE) from samarium on. None of these is likely to be present in significant amounts, although they might add a few wt% to the totals. The relatively low totals, which average about 60 wt%, are primarily due to the presence of carbonate, hydroxyl and water of crystallisation, none of which is amenable to determination by conventional microbeam techniques. Our data compare well with that published for ancylite group minerals by Pekov *et al.* (1997); the analytical totals are particularly close to calcioancylite-(Ce) from the Polar Urals.

Calcium is the dominant group 2 element in all of the grains we have analysed, the molar ratio of calcium to strontium varying between 1.4 and 2.9. Cerium is the dominant rare earth element, it exceeds the next most abundant REE by a factor of two in every case. This clearly shows that the specimens from Guisachan Quarry are calcioancylite-(Ce). Calculating formulae using the assumptions of Pekov *et al.* (1997), but using a cation sum of 4.0 rather than 2.0 for comparison with Back and Mandarino (2008), the chemical formula can be written: $(Ce_{1.57},La_{0.60},Nd_{0.59},Pr_{0.09})(Ca_{0.72},Sr_{0.35})(CO_3)_4(OH)_{2.9}\cdot 1.1H_2O$. The value of x, which is a measure of the amount of REE present averages 2.92 and varies between 2.7 and 3.0; this is at the upper end of the 2.1 to 3.0 range quoted for natural material by Back and Mandarino (2008), indicating that the calcioancylite-(Ce) from Guisachan Quarry is relatively REE rich.

DISCUSSION

The sequence of mineralisation at Guisachan Quarry is relatively simple. Calcite was the first mineral to be deposited, a period of dissolution followed, then harmotome, edingtonite and calcioancylite-(Ce) crystallised at about the same time; these were followed at a late stage by pyrite and marcasite. Localities in the British Isles which provide an interesting comparison include the Strontian mines on Loch Sunart and Dolyhir Quarry in the Welsh Borderlands. Pyrite and marcasite are present as inclusions in the zeolites at Strontian and REE minerals are represented by ancylite-(Ce) and kainosite-(Y). The REE minerals present at Dolyhir Quarry include synchysite-(Ce) and ewaldite, and they occur in the same thin fractures as harmotome and edingtonite.

The late stage zeolite and REE-bearing mineralisation at both Strontian and Dolyhir Quarry is associated with low temperature hydrothermal veins containing base metals. There is no evidence of hydrothermal veins containing base metals in the area immediately around Guisachan Quarry, although it is interesting to note that harmotome was recorded by Russell (1946) in lead-bearing veins at Loch na Meine Mine about 14 km to the northeast. The pervasive mineralisation in thin fractures belongs to a late stage of mineralisation which clearly post-dates the development of the metamorphic fabric. Given the wide area over which the meta-sedimentary Loch Eil Group crops out, it may be that this style of mineralisation is more widespread than is currently recognised. Indeed, harmotome has been collected by one of us (NH) *in situ*, at a forestry track cutting (NH 341 321) approximately 6 km northeast of Guisachan Quarry.

A selection of specimens from Guisachan Quarry has been presented to the Hunterian Museum at the University of Glasgow.

ACKNOWLEDGEMENTS

We would like to thank the staff of Forest Enterprise who gave permission to examine the geology and collect specimens from Guisachan Quarry. Tom Cotterell is thanked for information about edingtonite from Dolyhir Quarry, and Roy Starkey for providing a photograph of the locality.

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HEULANDITE-Sr AND HEULANDITE-Ba, TWO ZEOLITE GROUP MINERALS NEW TO BRITAIN FROM WHITESMITH MINE, STRONTIAN, HIGHLAND REGION, SCOTLAND

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

Andrew G. TINDLE
Department of Earth Sciences, Open University, Milton Keynes, Bucks, MK7 6AA

Neil HUBBARD
30 Thirlmere Road, Barrow upon Soar, Leicestershire, LE12 8QQ

David McCALLUM
67 Church Street, Mexborough, South Yorkshire, S64 0HG

Brian JACKSON
National Museums of Scotland, Chambers Street, Edinburgh, EH1 1JF

The zeolite group minerals heulandite-Ba and heulandite-Sr have been identified in a late-stage assemblage in veins and fractures in schist and gneiss at Whitesmith Mine, Strontian, Highland Region, Scotland.

They are commonly associated with calcite, pyrite and brewsterite, and more rarely with strontianite. The most barium-rich composition is: $(Ba_{1.88},Sr_{1.67},Ca_{1.04},K_{0.29},Na_{0.18})[Al_{9.97}Si_{26.11}O_{72}]\cdot nH_2O$, and the most strontium-rich: $(Ba_{1.44},Sr_{1.99},Ca_{1.00},K_{0.27},Na_{0.57})[Al_{9.62}Si_{26.36}O_{72}]\cdot nH_2O$. The elements of group two, calcium, strontium and barium, are the dominant extraframework cations, and they almost always make up more than 80 mol% of the total extraframework cations present. The frameworks are rich in aluminium, and include some of the most aluminous compositions yet determined for minerals of the heulandite series.

INTRODUCTION

The Strontian mines in the Highland Region of Scotland are well known to mineralogists as the type locality for strontianite and for the zeolite group minerals brewsterite (Strontian is the type locality for brewsterite-Sr) and harmotome (Livingstone, 2002). A small number of specimens of another zeolite group mineral, heulandite were found at Whitesmith Mine in the late 1970s. The recent discovery of further specimens has prompted this account of its occurrence and composition.

Minerals of the heulandite series occur in a wide variety of geological environments and have been reported from a considerable number of localities in the British Isles (*e.g.* Tschernich, 1992; Dyer *et al.*, 2006; Tindle, 2008). They are aluminosilicates with a negatively charged framework of tetrahedrally coordinated units containing large channels in which positively charged ions and water molecules sit. Aluminium can replace silicon in the aluminosilicate framework, which does not have a fixed composition; it becomes more negatively charged as the ratio of aluminium to silicon increases. The positive ions (usually described as extraframework cations) are almost always drawn from the elements of groups one and two of the periodic table. The wide range of chemical compositions that are possible because of the presence of exchangeable cations and the variable aluminosilicate frameworks mean that natural zeolites are classified primarily according to their framework topology and only then according to their composition. In most cases a unique framework topology defines a mineral series, which is split into species on the basis of the dominant extraframework cation (Coombs *et al.*, 1997).

The definition of the heulandite series is unusually complex since, uniquely among the members of the zeolite group, it shares a framework topology with clinoptilolite (Coombs *et al.*, 1997). Heulandite is defined as the mineral with an Si:Al ratio in the framework of less than four, whereas in clinoptilolite the ratio is greater than or equal to four. This nomenclature is rooted in long-established usage, and seems to have some benefit in distinguishing minerals that occur in different geological environments. It merits a short chapter in a recent review of the minerals of the zeolite group to which readers are referred for a more detailed discussion (Bish and Boak, 2001).

In the heulandite series, the calcium dominant species heulandite-Ca is very common, heulandite-K and -Na are rarer, but still well known, and heulandite-Sr and -Ba have only been reported from a few localities worldwide (Tschernich, 1992; Passaglia and Sheppard, 2001; Larsen *et al.*, 2005).

WHITESMITH MINE

Five major mines were developed on lead veins in the hills north of Strontian in the eighteenth and nineteenth centuries. From east to west, they are Fee Donald, Bellsgrove, Middleshop, Whitesmith, and Corrantee (e.g. Tschernich, 1992). The first and last of the mines, Fee Donald and Corrantee, are separated from the central group by rough moorland and are reasonably well defined. The central mines, Bellsgrove, Middleshop, and Whitesmith, are more closely spaced. They worked the Strontian Main Vein along a strike length of about 2 km between Whitesmith Whim Shaft and Oliphant's Dam

(NM 823 659 to NM 843 658). The topography of this area was considerably altered by a modern mine, which was developed on the Strontian Main Vein in the 1980s to provide baryte for the North Sea oil industry (Mason and Mason, 1984).

The Strontian veins are hosted by middle to upper amphibolite facies metamorphic rocks (gneiss and schist) of the Glenfinnan Group (part of the Moine Supergroup) at Corrantee Mine. They are near the contact between the granodiorites of the Strontian Complex (Caledonian) and the Ardgour Granite Gneiss (Moine) between Whitesmith Mine and Bellsgrove Mine. The veins at Fee Donald Mine are wholly within the Ardgour Granite Gneiss. The Moine country rock was thermally metamorphosed by the Strontian pluton, which has a 3km wide high-grade thermal aureole and a migmatic overprint in the form of granitic segregations, which disrupt the metamorphic fabric for up to half a kilometre from the contact. At Whitesmith Mine, the Strontian Main Vein is developed within an east-west trending 'crush zone' in the Ardgour Granite Gneiss. The crush zone also hosts a suite of metasomatised Permo-Carboniferous dykes which predate the mineral veins. These altered dykes and the veins are cut, often at a high angle, by a suite of later mafic dykes of early Tertiary age.

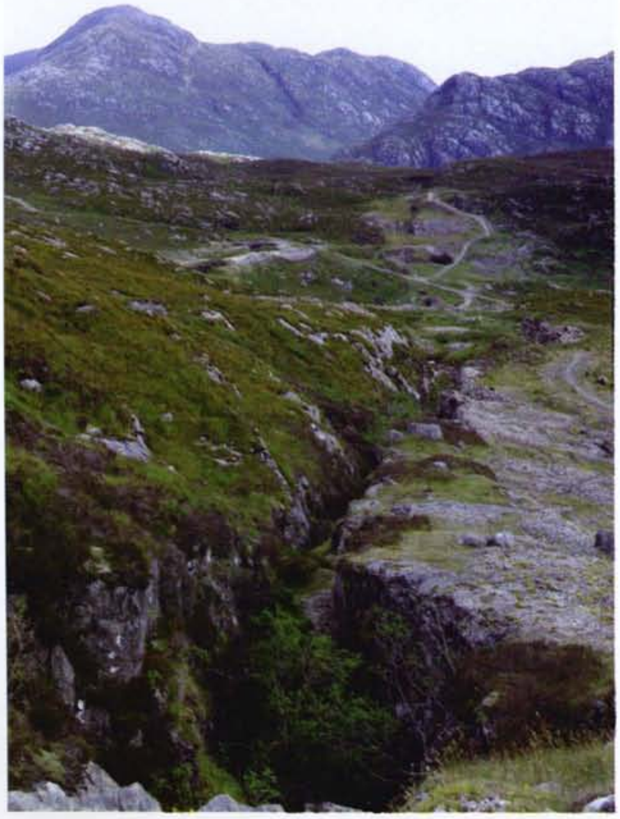


Figure 1. Whitesmith Mine photographed from the west end of the old opencut in July 2007. A near vertical east-west vein runs for more than 2km across moorland to the east and was worked by the Whitesmith, Middleshop and Bellsgrove mines. This photograph was taken from the highly dangerous Whim Shaft at the extreme west end of the Whitesmith Opencut.

Whitesmith Mine (Fig. 1) is named for John Whitesmith, who worked at Strontian in the first half of the eighteenth century. The mine is wrongly identified on Ordnance Survey maps, which position it near to the ruined baryte mine processing plant. A review of eighteenth and nineteenth century plans and surveys of the area shows that this is not the case. Our description uses the survey of the Strontian mines compiled by Arthur Russell (1919) to identify the mines, supplemented by Ball's (1807) estate plan which marks and names many of the shafts.

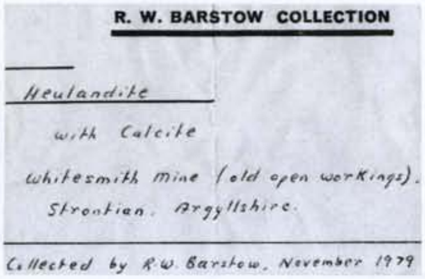
Whitesmith Mine worked the Strontian Main Vein via a shallow adit driven from the east (the entrance, now obliterated, was at *ca.* NM 8287 6588) and a series of shafts. The deepest of these, Whim Shaft (NM 8231 6595) at the west end of the sett, is in excess of 100 fathoms according to Russell (1919). The eastern workings of Whitesmith Mine were obliterated in the 1980s by the baryte mining operation, but the western workings remain much as they were abandoned in the nineteenth century. The position of the Old Sump Crosscut (NM 8249 6593), Whin Dyke Shaft (NM 8251 6593) and Hugh's Shaft (NM 8239 6594), which are marked on Ball's (1807) estate plan can still be identified along an opencut that runs east-west for about 300 m.

The mineralisation comprises major calcite and baryte with significant quantities of the base metal sulphides galena and sphalerite. These are typically deposited in a rhythmic sequence parallel to the vein walls, often producing a well defined symmetrical filling where the veins are narrow (where the veins are wider the textures are often much more complex). In some areas, the north wall of the vein is made up of brecciated clasts of gneiss, the interstices of which are coated in drusy brown brewsterite. Brewsterite also occurs in cavities and fractures in the vein, where it is sometimes associated with radiating groups of crystalline strontianite. Harmotome is relatively rare, although it occasionally occurs as characteristic white blocky crystals in cavities and fractures. The zeolite group minerals and most of the strontianite are part of a late-stage fracture assemblage that post-dates the major vein mineralisation. At Whitesmith Mine, this assemblage also includes ancylite-(Ce), chamosite, minor calcite and kainosite-(Y) (described recently by Green and McCallum, 2005) and the mineral which is subject of this paper, heulandite.

HEULANDITE

Heulandite was first found at Whitesmith Mine by the well known mineral dealer Richard Barstow (1947 – 1982), who made his one and only trip to the locality with his long-standing collecting partner David Lloyd late in 1979 (David Lloyd, *personal communication*). Barstow and Lloyd collected 'brewsterite' specimens along the length of the old opencut, but when they were unwrapped and examined, a few looked a little different. They were identified as heulandite, a mineral not previously known from Strontian. Most of the specimens were sold, but Barstow and Lloyd retained the two best for their personal collections. They display blocky colourless crystals up to about 8 mm in length, with a slightly pearly lustre, in cavities with hexagonal 'nailhead' calcite, cubo-octahedral pyrite and occasional brewsterite (Figs 2 and 3). It seems likely that this first group of heulandite specimens were collected from the north wall of the Whitesmith Opencut at the west end near Whim Shaft, although with the passage of time it is impossible to be absolutely certain. A few other collectors found similar specimens at about the same time, but their precise locality is lost.

Figure 2. The best heulandite specimen collected by Richard Barstow in 1979 from the Whitesmith Opencut. Heulandite crystals to 8 mm are associated with flat-topped hexagonal calcite. Neil Hubbard Collection.



R. W. BARSTOW COLLECTION

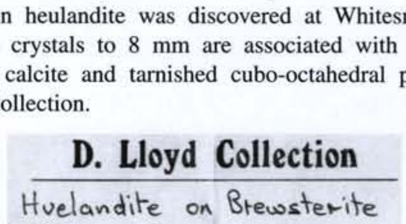
Heulandite

with Calcite

Whitesmith mine (old open workings).
Strontian. Argyllshire.

Collected by R.W. Barstow. November 1979

Figure 3. David Lloyd's heulandite specimen from the trip in 1979, when heulandite was discovered at Whitesmith Mine. Heulandite crystals to 8 mm are associated with flat-topped hexagonal calcite and tarnished cubo-octahedral pyrite. Neil Hubbard Collection.



D. Lloyd Collection

Huelandite on Brewsterite
WRitesmith section
Strontian
Argyllshire

S.C. 14.11.79

The next interesting discovery was made in 2003 as part of a systematic survey of the Strontian mines by a small group of collectors including two of us (DG and DM). A careful examination of the south wall of the opencut in the area below Hugh's Shaft revealed several parallel-running baryte veins containing numerous cavities lined with drusy brewsterite, acicular brown strontianite and very rare heulandite (Fig. 4). In all about ten heulandite specimens were collected. The finest of these, which was found by David McCallum, contained a large cavity lined with acicular brown strontianite and a scattering of colourless coffin-shaped heulandite crystals to about 4 mm. It is now in the collection of the National Museum of Scotland (NMS).

Figure 4. Transparent blocky heulandite crystal 5 mm long with brown acicular strontianite from the south wall of the main vein below Hugh's Shaft. David McCallum Collection.

In 2008, a small collapse on the south wall of the opencut, about 40 m to the west of Hugh's Shaft, afforded an opportunity to examine another mineralised area (briefly described by Wolfe *et al.*, 2008). Numerous thin calcite veins run parallel to the local cleavage and where the rock is folded, larger cavities and fractures lined with brewsterite and occasional weathered strontianite are present. Heulandite was found as small inconspicuous crystals in calcite veins along a strike length of about 2 m. It was moderately common in and around an otherwise unremarkable calcite vein up to about 25 mm wide. The vein comprised two calcite cheeks between 5 and 10 mm in thickness, which commonly met, but sometimes opened to produce a narrow central cavity lined with calcite, pyrite, brewsterite and heulandite. Where the vein intersected perpendicular veins and fractures, larger cavities lined with brewsterite, calcite and heulandite occasionally developed, the best of these contained heulandite crystals up to 18 mm long (Figs 5 and 6).

Figure 5. A single well formed heulandite crystal 4 mm tall on calcite collected from the south wall of the Whitesmith Opencut about 40 m west of Hugh Shaft. David McCallum Collection.

Figure 6. Heulandite , 4 mm across, from the south wall of the Whitesmith Opencut about 40 m west of Hugh Shaft. David McCallum Collection.

EXPERIMENTAL

A considerable amount of data is needed to identify the minerals of the heulandite series to species level. Initially a few small crystals were detached and analysed by X-ray diffractometry (XRD). The crystal grains were finely ground, and applied in solvent suspension to a glass slide. The thin film so produced was mounted in an X-ray diffractometer (Cu Kα radiation, 40 kV, 20 mA) and its diffraction pattern recorded from 5° to 50° in 2θ. Software was used to match the pattern to known standards.

The XRD data allows a mineral to be identified as a member of the heulandite or clinoptilolite series, but quantitative chemical data is required if it is to be identified to species level. A few crystals were prepared for quantitative chemical analyses by wavelength dispersive spectrometry (WDS) on a Cameca SX100 electron microprobe. They were hand picked, embedded in resin, and polished to produce a flat surface. Analyses were made at 20 kV and 20 nA with a 20 micron beam diameter. Count times of ten seconds were used to minimise volatilisation. A PAP correction procedure was used to refine the data (Pouchou and Pichoir, 1985). More than eighty analyses on five different grains were collected, producing more data than can be easily tabulated in a report such as this. A complete set of the original analyses is lodged with the editor; selected data is presented in Table 1.

Analytical problems are often encountered when the chemistry of zeolite group minerals is investigated using WDS, largely because of their instability under the electron beam. These can be reduced by using short data gathering times and by defocusing the beam. An independent check can be made on the quality of the data by calculating the charge balance error, which should be less than ten percent if the analyses to be considered reliable (see Passaglia and Sheppard, 2001 for a fuller discussion). The mean charge balance error in our analyses (84 data points) is -0.9%, with maximum and minimum values of +3.9% and –6.6% respectively. This indicates that the results can be considered reliable.

CRYSTAL CHEMISTRY

Heulandite formulae are normally calculated on the basis of 72 structural oxygen atoms (Back and Mandarino, 2008). A full tabulation of the chemical formulae derived from our data would be unduly long, but some formulae are of interest. The maximum and minimum formula values for various important elements are listed in table 2.

The elements of group two, calcium, strontium and barium, are the dominant extraframework cations in all of the analyses. They average 85 mol% of all of the cations present, with low and high values of 79 mol% and 94 mol% respectively. There are relatively large amounts of

Oxide	High Ba	Low Ba	High Sr	Low Sr	High Ca	Low Ca	High K	Low K	High Na	Low Na	High R	Low R
SiO_2	49.92	57.21	53.54	54.75	57.89	50.64	55.85	53.70	54.51	54.44	55.43	49.92
Al_2O_3	16.17	16.22	16.58	15.72	16.35	15.57	16.53	15.99	16.61	15.42	15.86	16.17
CaO	1.85	2.86	1.90	2.34	2.93	1.75	2.69	1.97	2.38	2.16	2.56	1.85
Na_2O	0.18	0.37	0.59	0.08	0.31	0.15	0.22	0.08	0.78	0.03	0.22	0.18
K_2O	0.39	0.91	0.38	0.51	0.59	0.39	1.18	0.29	0.54	0.52	0.88	0.39
SrO	5.50	6.95	6.95	4.97	7.13	5.89	6.93	5.31	6.52	5.78	6.67	5.50
BaO	9.16	4.13	7.44	8.19	4.27	8.58	5.28	9.20	6.07	7.47	5.54	9.16
H_2O	16.83	11.31	12.61	13.45	10.50	17.02	11.30	13.47	12.60	14.18	12.84	16.83

Table 1. Representative composition data quoted as wt% oxide values for heulandite from Whitesmith Mine, Strontian, Scotland. Standards used are Si, K, Al = K-feldspar; Ca = bustamite; Na = jadeite; Sr = synthetic $SrTiO_3$; Ba = Baryte. Water is calculated by difference to produce a sum of 100 wt%. Sharp eyed readers will note that the wt% SrO in column 6 slightly exceeds the value in column 4, however the data of column 4 produce a slightly higher Sr value in the calculated formula when it is normalised to 72 structural oxygens, effectively because calculated chemical formulae measure the molar ratios of the different elements, not the absolute values. Other elements including Fe and Mg were analysed but were not found in significant quantities.

Calculated Formula	Balance Error %	R value	Note
$(Ba_{1.88},Sr_{1.67},Ca_{1.04},K_{0.29},Na_{0.18})[Al_{9.97}Si_{26.11}O_{72}]\cdot nH_2O$	3.5	0.724	Most Ba
$(Ba_{0.76},Sr_{1.90},Ca_{1.45},K_{0.61},Na_{0.34})[Al_{9.00}Si_{26.95}O_{72}]\cdot nH_2O$	-2.3	0.750	Least Ba
$(Ba_{1.44},Sr_{1.99},Ca_{1.00},K_{0.27},Na_{0.57})[Al_{9.62}Si_{26.36}O_{72}]\cdot nH_2O$	-0.7	0.733	Most Sr
$(Ba_{1.58},Sr_{1.42},Ca_{1.23},K_{0.36},Na_{0.08})[Al_{9.12}Si_{26.94}O_{72}]\cdot nH_2O$	2.5	0.747	Least Sr
$(Ba_{0.82},Sr_{1.93},Ca_{1.50},K_{0.50},Na_{0.29})[Al_{8.90}Si_{26.99}O_{72}]\cdot nH_2O$	-4.7	0.752	Most Ca
$(Ba_{1.76},Sr_{1.78},Ca_{0.98},K_{0.29},Na_{0.16})[Al_{9.58}Si_{26.44}O_{72}]\cdot nH_2O$	1.1	0.734	Least Ca
$(Ba_{0.99},Sr_{1.92},Ca_{1.38},K_{0.80},Na_{0.21})[Al_{9.58}Si_{26.44}O_{72}]\cdot nH_2O$	-3.3	0.741	Most K
$(Ba_{1.79},Sr_{1.53},Ca_{1.05},K_{0.21},Na_{0.07})[Al_{9.38}Si_{26.71}O_{72}]\cdot nH_2O$	3.9	0.740	Least K
$(Ba_{1.16},Sr_{1.84},Ca_{1.24},K_{0.37},Na_{0.73})[Al_{9.51}Si_{26.48}O_{72}]\cdot nH_2O$	-0.6	0.736	Most Na
$(Ba_{1.45},Sr_{1.66},Ca_{1.15},K_{0.37},Na_{0.02})[Al_{9.02}Si_{27.01}O_{72}]\cdot nH_2O$	1.1	0.750	Least Na
$(Ba_{1.88},Sr_{1.67},Ca_{1.04},K_{0.29},Na_{0.18})[Al_{9.97}Si_{26.11}O_{72}]\cdot nH_2O$	3.5	0.724	Highest Al:Si
$(Ba_{1.06},Sr_{1.73},Ca_{1.42},K_{0.62},Na_{0.16})[Al_{8.64}Si_{27.21}O_{72}]\cdot nH_2O$	-6.6	0.759	Lowest Al:Si

Table 2. Heulandite formulae calculated on the basis of 72 structural oxygen atoms. Column one gives calculated formulae. The balance error is ((Na+K)+2(Ba+Sr+Ca)-(Al))/((Na+K)+2(Ba+Sr+Ca))x100 (see Passaglia and Sheppard, 2001). The R-value is Si/(Si+Al).

the heavier group two elements, strontium and barium, in comparison to most other analyses (*e.g.* Passaglia and Sheppard, 2001). Twelve of the analyses fall within the heulandite-Ba composition field, the remaining seventy-two are heulandite-Sr.

DISCUSSION

The minerals of the heulandite and clinoptilolite series are relatively common in nature. Heulandite occurs as well formed crystals in cavities in volcanic rocks and in pegmatites (Tschernich, 1992), whereas the more silica-rich clinoptilolite is abundant in diagenetically altered volcaniclastic sediments as an intergranular cement (Bish and Boak, 2001). In Scotland, excellent crystalline specimens of heulandite have been reported in amygdales in the basaltic rocks of the Inner Hebrides and around Glasgow (see for example the classic work of Heddle, 1901), but this is the first report of an occurrence in a low temperature hydrothermal vein in the British Isles.

The composition of the specimens from Strontian is unusual. They are rich in the heavy alkaline earth elements, strontium and barium, and also in aluminium. The most comparable data we have found is on material from Campegli Mine, Liguria, Italy (Lucchetti *et al.*, 1982), the type locality for heulandite-Sr, which has a formula that can be written $(Ba_{0.14},Sr_{2.10},Ca_{1.76},K_{0.22},Na_{0.40}Mg_{0.02})[Al_{9.19}Si_{26.94}O_{72}]\cdot nH_2O$ (R = 0.746) and on specimens from Kongsberg, Norway, the type locality for heulandite-Ba, which have an average composition that can be written $(Ba_{2.49},Sr_{0.30},Ca_{1.41},K_{0.37},Na_{0.33})[Al_{8.96}Si_{27.01}O_{72}]\cdot nH_2O$ (R = 0.751) (Alf Olav Larsen, *personal communication*; Larsen *et al.*, 2005). The Norwegian localities for heulandite-Ba and heulandite-Sr, afford perhaps the best comparison to Strontian. At two localities near Kongsberg, heulandite, which is rich in barium and strontium, occurs in late stage hydrothermal quartz-calcite veins with minerals of the brewsterite series, harmotome, calcite and pyrite. A third geologically distinct Norwegian locality for heulandite-Ba and -Sr is at Sjoa in alpine-type veins with quartz, hematite, rutile, anatase, chlorite and brewsterite. The first two localities have considerable geological and mineralogical similarities to the Strontian lead mines.

Strontium is the dominant extraframework cation in most of the analyses and calcium and barium are also usually present at more than one atom per formula unit. The barium content is rather more variable than the other extraframework cations. One way to illustrate this chemical variability is to use a ternary plot (Fig. 7). The data of Fig. 7 occupy a relatively small area of the possible composition space, and are extended along the barium axis. This relative homogeneity of composition is in contrast to brewsterite, for which we have also collected considerable data (Tindle, 2008), where compositions near the strontium and barium dominant end-members and at all points in between have been discovered.

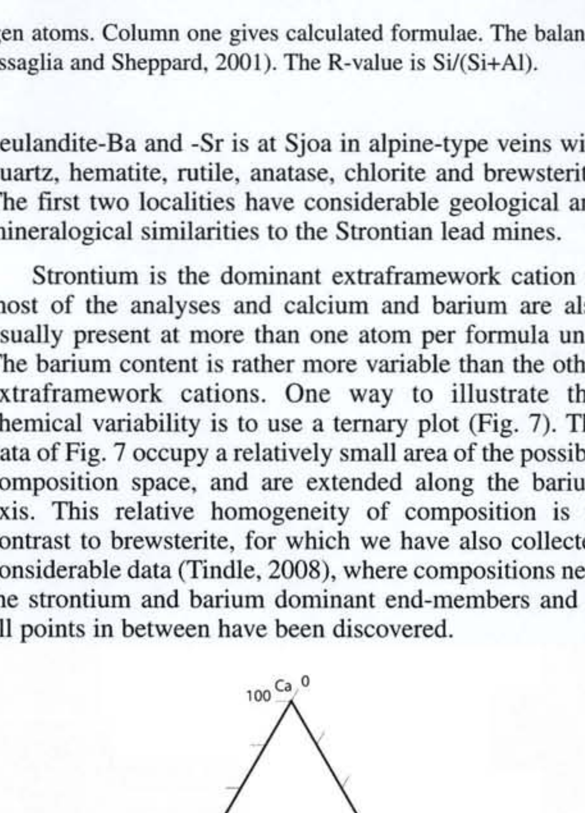


Figure 7. A ternary plot constructed with axes that show the mol% of divalent cations in five heulandite specimens (84 analyses) from Whitesmith Mine. The data occupy a relatively small area of the possible composition space.

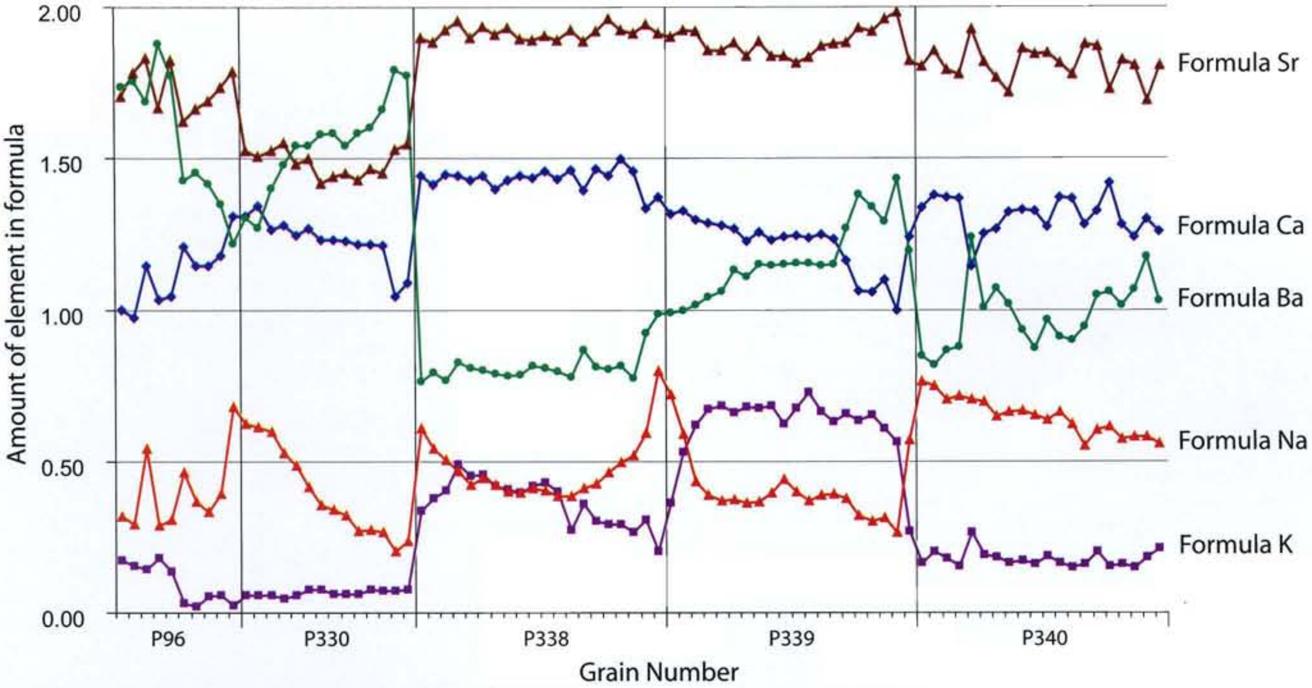


Figure 8. A graphical illustration of the cationic composition of heulandite from Whitesmith Mine (quoted as cations per formula unit based on 72 structural oxygen atoms). There are 84 analyses of five separate grains.

A compilation of 84 analysis points, showing the variation in composition among the extraframework cations for five different crystal grains, is given in Fig. 8. It is clear on examining this plot that the amount of Ba present has a somewhat antipathetic correlation with Ca. Interestingly, a similar correlation between Ba and Sr + Ca was noted in heulandite from Sjoa in Norway by Larsen *et al.* (2005).

The molar percentage of Si in the framework (which is obtained by multiplying the R-value by 100) varies between 72.4 mol% (Si:Al = 2.62) and 75.9 mol% (Si:Al = 3.15), with a mean value of 75.0 mol% (Si:Al = 3) and standard deviation of 0.9 mol%. The mean is toward the high silicon end of an assymetric distribution that includes compositions which are extremely aluminium-rich (it is interesting to note that Bish and Boak (2001) state that heulandite crystals with Si:Al <2.6 do not occur).

Our most aluminium-rich formula has 9.97 atoms per formula unit; if plotted in the composition field illustrated by Bish and Boak (2001, p.212) it would be the most aluminium-rich composition in a very extensive data-set (and very near the top of the graph, which only extends to 10 atoms per formula unit). No other formula we are aware of, including the compilations of Passaglia and Sheppard (2001) and of Larsen *et al.* (2005), is more aluminium-rich.

Iron is sometimes present in heulandite series minerals, where it is thought to occupy framework sites (*e.g.* Bish and Boak, 2001). Since this might be of relevance to this discussion of the framework composition, all of our analyses included determinations for FeO. Iron was almost always below the limit of detection of the microprobe system, the highest measured values being less than 0.05 wt%. It is not present in significant amounts.

If the amount of aluminium in the zeolite framework is plotted against the sum of divalent cations an interesting correlation emerges (Fig. 9). Those analyses with the highest aluminium content correlate with the largest number of divalent cations. Large amounts of aluminium in the framework produce a large negative charge excess, which must be balanced by the positive charges of the extraframework cations to produce a stable structure. Divalent cations may be favoured because they have a higher positive charge density, which may be important in the limited space in the zeolitic channels. Alternatively it may be that the unusual chemical conditions in the vein system produce aluminium-rich heulandite.

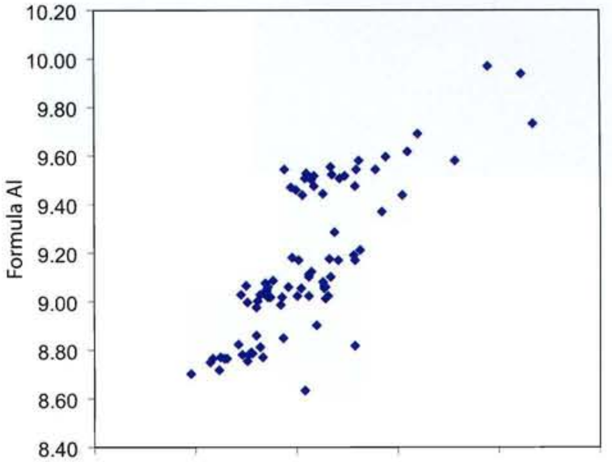


Figure 9. A plot of aluminium in the heulandite structure versus the sum of divalent cations, which clearly suggests a positive correlation between the two.

ACKNOWLEDGEMENTS

We would like to thank David Lloyd who supplied information about the discovery of heulandite at Strontian in 1979 and Peter Briscoe who generously allowed analyses of a specimen prior to its acquisition by the NMS, and also assisted in the fieldwork and with provision of specimens for analysis. Trevor Bridges kindly made another sample available for analysis. Dan MacDonald allowed access to the site and we are grateful for his continued interest and support. DG would like to thank the Department of Earth Sciences at the University of Manchester for access to analytical equipment. John Faithfull and Alan Dyer provided very helpful reviews.

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Journal of the Russell Society, **11**, 87-87 (2008)

SCOLECITE FROM CORNWALL, THE FIRST OCCURRENCES IN ENGLAND

Oneta M. WILSON
50 Agnes Street, Levenshulme, Manchester, M19 3AZ

Alan DYER
Institute of Materials Research, Cockcroft Building, University of Salford, M5 4WT

Vincent A.D. HOLYER
2, Valley Gardens, Voguebeloth, Illogan, Redruth, TR 6 4EE

Craig D.WILLIAMS
School of Applied Science, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1SB

Scolecite is the calcium structural analogue of the sodium zeolite natrolite. It was named by Gehlen and Fuchs (1913) because it "curls like a worm" (Greek skolek = worm) when heated.

Gottardi and Galli (1975) list scolecite as a common zeolite mineral. In the British Isles, well-known occurrences are at Talisker Bay, Isle of Skye, on Ben More, Isle of Mull (Livingstone, 2002) and from several localities in Northern Ireland (Walker, 1960). It does not have a type-locality (Back and Mandarino, 2008). Here we report the first confirmed occurrences of this zeolite at two localities in Cornwall.

Cornwall provides the most abundant source of zeolites in England and the majority of zeolites recorded from this county come from the Lizard Peninsula. Holyer (1972) lists analcime, chabazite, heulandite, natrolite, stilbite from some 13 localities and more recently clinoptilolite has been confirmed by Dyer *et al.* (2006) at Wheal Hazard, St.Just. An entry in Mindat (www.mindat.org) records harmotome at Greystones quarry, Levant, Callington.

One of us (OMW) has collected samples from Henscarth, which lies on the north side of Mullion Cove. The collecting site (NGR SW 666 179) was on the cliff above the passage way in front of the Mullion Cove Hotel. The material occurs in veins within the Traboe hornblende schist close to unfaulted contacts with serpentine – a common setting where zeolites are found on the Lizard.

The Mullion Cove material was of white acicular crystals. The material was analysed by powder XRD diffraction at the University of Wolverhampton using a Phillips PW1710 interfaced with a searchable zeolite database.

An excellent match with JCPDF 41-1355 confirmed the presence of scolecite and the absence of any other major mineral phase. XRF showed it to be a calcium aluminosilicate with some sodium present, comparable to an analysis of a Pune scolecite quoted in Gottardi and Galli (1985). The Hensgarth material is the first fully analysed scolecite from an England locality and it can be commented that it is rare to find scolecite within veins in a schist. Tshernich (1992) notes only one similar occurrence – in veins in a biotite schist found at Grosse Sidelhorn, Nr. Baregg, Oberaar, Switzerland, as reported by Parker (1973).

A very similar sample was collected (by VADH) from veins in the Devonian Crousa gabbro at Dean Quarry, St. Keverne (NGR SW 803 204). No XRD was carried out on this sample but calcium was shown to be present by chemical testing. The sample is in Plymouth Museum. Mindat, and Golley and Williams (1995), list scolecite at Dean Quarry but without a defining reference.

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Journal of the Russell Society, **11**, 88-90 (2008)

STOLZITE FROM PENBERTHY CROFT MINE, ST HILARY, CORNWALL

David MOULDING
Merlin House, Castle Green, Helston, Cornwall, TR13 8EZ

Jeremy HOOPER
48 St Julitta, Luxulyan, Bodmin, Cornwall, PL30 5ED

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

Stolzite, ideally $PbWO_4$, was described in the early part of the nineteenth century from the mines near Zinnwald on the border between Germany and the Czech Republic. The name honours Joseph Stolz (1803–1896) who made early investigations of the chemistry of the species (Greg and Lettsom, 1858; Anthony *et al.*, 2003). Stolzite is typically found in the supergene zones of lead or tungsten rich orebodies. It is visually indistinguishable from the widespread and well known lead molybdate wulfenite, and a solid solution extends between the two. Stolzite is rare, usually occurring as inconspicuous microcrystals, although there are a few localities for more spectacular specimens with centimetre-sized crystal on specimens to small cabinet size, notably Broken Hill, New South Wales, Australia (Birch, 1999) and the Ste Lucie Mine, Marvejols, France.

Although stolzite has been described from eight localities in the British Isles, the first two reports, which date from the mid to late nineteenth century, are doubtful. The first and most controversial record appeared in the *Mineralogy of Great Britain and Ireland* (Greg and Lettsom, 1858: 410–11): Robert Philips Greg described "minute but measurable crystals, on macled crystals of black carbonate of lead from Force Craig lead mine near Keswick", and provided a chemical analysis and a crystal drawing to support his identification. Sir Arthur Russell (1944) cast doubt on the record following extensive research on the Allan-Greg collection, as it was not substantiated by either a specimen or a catalogue entry. His views are echoed by more recent workers (e.g. Cooper and Stanley, 1990). Stolzite was tentatively identified by Patrick Dudgeon (1890) at Girthorn near Gatehouse of Fleet, Dumfries and Galloway, but this record is also unsubstantiated. Undoubted British localities are limited to Carrock Mine, Poddy Gill, and Brandy Gill in the Caldbeck Fells, Cumbria (Cooper and Stanley, 1990); Whytes Cleugh, Wanlockhead, Dumfries and Galloway (Livingstone, 1992); Hingston Down Quarry, Calstock, Cornwall (Green *et al.*, 1996; Weiss *et al.*, 2007) and Cheesewring Quarry, Linkinhorne, Cornwall (Green *et al.*, 1996). To these we add Penberthy Croft Mine, St Hilary, Cornwall.

Penberthy Croft Mine is located about 1.5km north-east of the village of Goldsithney in the parish of St. Hilary, Cornwall (SW 555 324). It produced copper and tin from predominantly east-west striking lodes hosted by metasedimentary rocks of the Mylor Slate Formation (Goode and Taylor, 1988; Betterton, 2000). According to Dines (1956), 23 shafts were sunk to exploit the lode system along a strike length of about 1.5 km. The surface remains of these workings can be traced for a little over a kilometre. Several distinct mineral assemblages are present on the dumps. The main stage of mineralisation comprises high-temperature hypothermal to mesothermal Sn-Cu-As-W bearing veins in quartz-chlorite matrix. Later low temperature Pb-Zn mineralisation in a quartz-carbonate matrix occupied north-south trending cross-courses. Both of these assemblages were subjected to extensive and prolonged oxidation, and it is probably fair to say that Penberthy Croft Mine is best known for the varied assemblage of supergene minerals that this produced (Camm and Merry, 1991; Betterton, 2000).

In August 2007, one of us (DM) collected a 50 x 50 x 35 mm specimen of quartz-chlorite veinstone, with an unusual polyhedral cavity about 20 mm across, from the Ducketts shaft dump (SW 5564 3241) at Penberthy Croft Mine. Examination under a hand lens revealed a few well formed dark brown bipyramidal crystals with a superficial resemblance to anatase. Subsequent investigation using a stereomicroscope showed that a considerable fraction of the inner surface of the cavity was covered in inconspicuous colourless, pale buff to pale brown bipyramids. Crystals of both types were examined by energy dispersive spectrometry (EDS), which showed that lead and tungsten were the only heavy elements present (analyses ED369a,b by JH). An analysis by X-ray diffractometry (XRD) produced a least-squares fitting parameter that was a much better match to stolzite than either the structurally similar mineral wulfenite (note Mo would not necessarily show up in an EDS analysis since it is masked by lead) or the monoclinic lead tungstate mineral raspite (X-ray reference number MANCH:XRD1471).

The largest stolzite crystal on the specimen is an isolated double-terminated dark brown tetragonal bipyramid, which is 1.1 mm in length (Fig. 1). The pale brown to buff crystal aggregates lining the polyhedral cavity are made up of smaller crystals, not usually exceeding 0.5 mm long. They cover areas up to 4 mm across and are commonly aggregated into masses that exhibit parallel growth (Fig. 2). Most of the crystals are bounded by eight well developed faces belonging to the common steeply pyramidal form n {110}; this is sometimes truncated by the pinacoid c {001}, which is most often present on the larger crystals, and occasionally modified by Â {111}. Less steeply pyramidal forms are present on a few crystals, but they are too small to measure reliably.

Figure 1. The largest stolzite crystal found on the specimen from Ducketts Shaft dump at Penberthy Croft Mine, a dark brown bipyramid 1.1 mm tall. David Moulding collection, M.1058.

Figure 2. Aggregates of steeply pyramidal stolzite crystals, with the specular reflections deliberately captured to illustrate parallel crystal growth. This 10 x 6 mm image is part of the interior of a polyhedral cavity about 20 mm across which at one time contained scheelite. David Moulding collection, M.1058.

Careful examination of the corners of the cavity revealed a number of etched pale yellow grains with a resinous lustre, which almost certainly represent the original mineral that occupied it. Analysis by XRD showed this to be scheelite ($CaWO_4$) (X-ray reference number MANCH:XRD1472). The high-temperature vein mineralisation, which is common across southwest England, is divided into two distinctive sub-assemblages at Penberthy Croft Mine. In the upper parts of the mine, there is a chalcopyrite-dominated assemblage with arsenopyrite, sphalerite and pyrite; this is replaced at depth by an arsenopyrite-dominated assemblage with minor scheelite and stannite (Betterton, 2000). The specimen almost certainly belongs to this latter assemblage, indicating that the oxidising solutions penetrated deeply into the lode system.

In an oxidising environment, there is little difficulty in accounting for chemical conditions required for stolzite to form. The tungstate ions were almost certainly supplied by the dissolution of scheelite, which formerly occupied the polyhedral cavity we have described. Lead-rich solutions derived from the oxidation of galena in the cross-courses were clearly also present, as is evidenced by the remarkable variety of supergene lead-bearing minerals recorded by Betterton (2000).

The geological environment, a high temperature vein containing primary tungsten minerals, is similar to the stolzite occurrences at Hingston Down Quarry (Green *et al.*, 1996) and to an as yet undescribed occurrence at Cligga Mine, Perranzabuloe, Cornwall. It may be that stolzite is more widespread in this type of assemblage, which is widely developed in southwest England, than previously suspected. It occurs in many similar high-temperature quartz-wolframite-scheelite veins worldwide (Anthony *et al.*, 2003)

Penberthy Croft Mine was especially popular with mineral collectors in the last decades of the twentieth century. Their detailed investigations culminated in the comprehensive mineralogical account produced by Betterton (2000). The discovery of well formed crystals of the rare lead tungstate stolzite shows that there are still opportunities to extend the list of the unusual species present at even the most extensively studied localities.

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BOOK REVIEWS

"Minerals of Northern England" by R.F. Symes and B. Young

(NMS Enterprises Limited, Edinburgh, 208 pp., 2008. Price £30.00. ISBN: 978-1-905267-01-9)

The North of England has long been famous as a source of fine mineral specimens and this book, by perhaps the two most knowledgeable authors in their field, amply describes the geology and mining history of the area which has made it so.

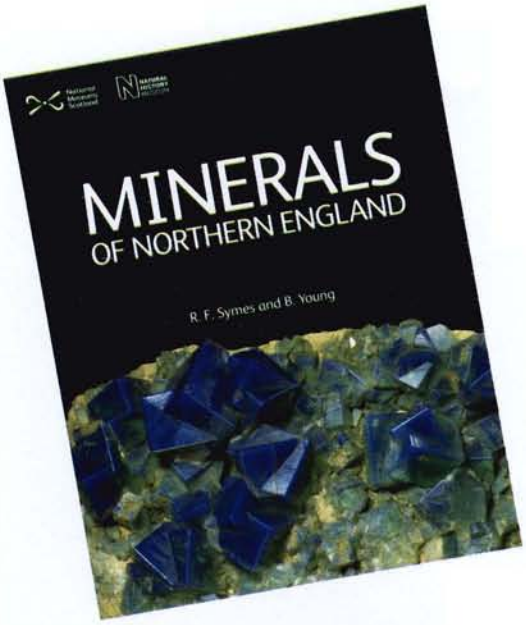
After the introduction, a chapter on the geological background gives a 500 million year history of the area which is written in such a way as to be understandable by those with little or no geological background. The connection between conditions under which the rocks were formed, their geological history and their present day appearance and usage is well explained. This is followed by a chapter on the mineralisation. This splits the region into three main areas, the Lake District, the Northern Pennine Orefield and the Cumbrian Iron Orefield. The different types of mineral deposits in the Lake District, their geology and mineralisation, is explained. The North Pennine Orefield is split into the Alston and Askrigg Blocks for descriptive purposes. The discovery of the Weardale granite and the effect of this, the Whin Sill and the differing wallrocks on the mineralisation are well covered. The section on the Cumbrian iron orefield covers the geology and formation of the hematite deposits which have produced many of the mineral specimens that the area is justly famous for. The following chapter 'The Mines and Minerals' again splits the region into the three main areas with further subdivisions. The principal mines, their history, geology and mineralisation in each area are then described. There are useful maps showing the position of the mines in each area. There is also some human history, history of the mining companies and an insight into the production and processing of some of the ores. Inevitably, some of A.W.G. Kingsbury's fraudulent records get a mention here. Some of the previous chapter is repeated here and perhaps the two chapters could have been combined.

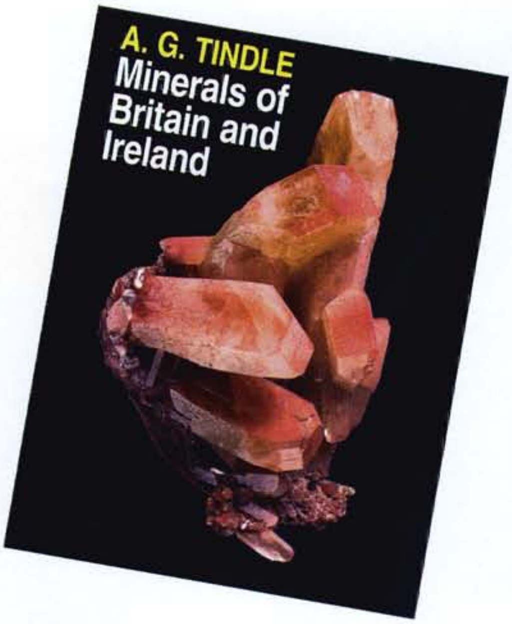
The chapter 'Collectors and Collections' gives a history of mineral collecting in the area from the Woodward collection (1665-1728) to the present day. The major collectors and collections are described here including Sir Arthur Russell. There are fascinating letters to Russell from mine owners which help to explain why he was able to acquire such a fine collection of minerals from the region. The local craft of spar boxes is described and illustrated.

The final chapter 'Introduction to the Minerals' is perhaps the one which we have all brought the book for and you would expect, from the book's title, to be the major part of the book. But only seven minerals, calcite, baryte, fluorite, hematite, witherite, alstonite and barytocalcite, are described. This is followed by pictures of 23 different minerals. Most of the figured specimens are from the collection of the Natural History Museum and as you would expect, there are many fine specimens but unfortunately, the image reproduction does not always do them justice.

The book is a fascinating read and I would recommend it to everyone. It has been well edited, it is difficult to find errors, and it is well illustrated, despite some of the rather lack-lustre reproduction, it is just a pity that the chapter on the minerals is so relatively brief. The only major omission that I noticed was the world class boracite occurrence at Boulby mine.

Neil Hubbard





"Minerals of Britain and Ireland" by A.G. Tindle

(Terra Publishing, Harpenden, 616pp., 2008. Price £95.00. ISBN 978-1-903544-22-8)

This is a large and comprehensive work which, after an introduction mentioning that the confirmed mineral species described from Britain and Ireland represent more than 25 % of the worldwide total, includes several maps indicating the principal localities. In the main part of the book, the minerals are listed alphabetically, and where the occurrences are widespread geographically, they are listed in a standard order: England, Wales, Scotland and Ireland. The classification used is based on that in *Fleischer's Glossary of Mineral Species*, with confirmed species appearing in bold type; synonyms and discredited species are all listed, but appear in light grey type.

A mass of data is presented for each mineral, including details of each reported occurrence with the appropriate reference, the economic importance of the mineral and notes on its morphology in each locality. Some of the more important and collectable species are given several pages (e.g galena has thirteen pages of double columns and sphalerite has nine). Stilbite and strontianite both get two pages. The author obviously has had to be more restrictive in his treatment of the far more abundant rock-forming silicates: plagioclase feldspar get short shrift as it is not a species, the fuller entries being reserved for the individual members of the series. Similarly for the K-feldspars, where orthoclase gets four columns with three photos, and microcline and anorthoclase each have a single column.

To cope with the amount of detail on each occurrence, the typeface used is necessarily rather small and the sheer density of the information presented could have made for a rather indigestible appearance. The decision made early on to make the book an illustrated volume was crucial, and the author was fortunate to obtain numerous first-rate mineral photographs from colleagues, mostly in colour, with the locality and size of specimen included in the caption. Most are magnified views, but as illustrations of the species being described they also serve to give most pages a more arresting impact.

There is an extensive list of references as well as tables listing biographic information on all those individuals who have had minerals named after them. Tables A1—A8 collectively contain 464 mineral names that in one way or another have a British or Irish connection.

On first examination, this is in some ways a compulsive book – as once picked up the reader will find more and more fascinating entries and will get involved in cross-referencing to other species listed as being associated! It is large and weighty in all senses, but encourages one to dip in further. The author has clearly invested many, many hours, days, months and years in this project, which began we are told with his intention to compile, for his personal satisfaction, a list of all known mineral species from Britain and Ireland, spurred on later by the realization that an up-to-date listing was long overdue.

The mineralogical community now owes a debt of gratitude to him for the very detailed work in which the original scheme was expanded in such a way as to present this very detailed account of all the minerals in Britain and Ireland, including the offshore islands and even Rockall in the coverage. An enormous amount of effort was surely entailed in chasing up obscure references and sifting through hundreds of publications from both home and abroad which have yielded further data. The author has indeed been fortunate in obtaining willing cooperation from both amateur and professional mineralogists and mineral collectors, as well as expert mineral photographers. Andy Tindle is to be congratulated on giving us this useful and very comprehensive compendium.

R.A. Howie