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FRONT COVER: A pink quartz crystal, 2.5 mm in length, on specular hematite, collected in 2018 on a Russell Society field trip to Cloud Hill Quarry, Breedon on the Hill, Leicestershire. John Chapman specimen and photo.

BACK COVER: A painting of a cabinet specimen (17 × 20 cm) of calcite on fluorite, heavily included by an unknown black sulphide, from Ladywash Mine, Eyam, Derbyshire. Don Edwards specimen and painting.
JOURNAL OF THE RUSSELL SOCIETY

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EDITORIAL

Welcome to volume 22 of the Journal of the Russell Society. At the start of this editorial, thanks are extended once again to Malcolm Southwood, whose software tools for managing the workflow have made the changeover trouble-free. A big thank you also to contributors, editorial board members and referees, whose conscientious work has made this edition possible. John Chapman’s excellent images are scattered through several articles, communicating far more than words ever could and Peter Briscoe’s understated colour palette has brought a new level of professionalism to the location maps. Volume 22 owes a great deal to our new typesetter, Robert Preston, who has relieved Frank Ince of some of the responsibilities of Journal Manager.

It is traditional for new editors to begin with an entreaty to readers to consider writing an article. This is simply a request to share knowledge and enthusiasm. The more inexperienced (or cavalier) may go on to claim that the process is straightforward and painless. Not so! An article will absorb a certain quantum of time and effort. Authors often find that ‘the doing’ makes it worthwhile (although this may only be evident in retrospect). An article at least ensures that information is placed on permanent record. In these less-than-certain times, look around and ask yourself: are collections and their associated data safe?

The nuts and bolts of the writing process are described in an updated Guide for Authors, which is available on the Society website. It explains the content and structure of articles and the minutiae of grammar and style, but is not recommended as a starting point. The Guide is detailed and prescriptive, but offers little to the ‘creative process’. A better strategy is to contact a member of the editorial board. All are experienced authors and will be happy to offer advice and support.

Articles in this issue are linked by that most appealing property of minerals, their colour. For readers with a little time on their hands Light and Color in Nature and Art (Williamson and Cummins, 1983) provides an excellent introduction to the subject and is often available for next-to-nothing via internet booksellers. The same, sadly, is not true of Kurt Nassau’s classic Physics and Chemistry of Color, which provides a technical perspective.

Opening the batting in this year’s JRS, Steve Rust describes a specimen obtained in 1973 by John Jones from the Hucklow Edge Vein at Ladywash Mine in Derbyshire. His sharp eyes spotted the rare copper sulpharsenide enargite. Steve’s article illustrates the value of referees. All articles are scrutinised by two independent and knowledgeable experts who check facts and make comments on interpretations. This should reassure prospective authors as it helps to avoid mistakes and ensure accuracy. Arsenic-bearing minerals are rare in Derbyshire; the literature (e.g. Ford et al., 1993) records only arsensopyrite, enargite and mimetite. During a review of the Ladywash article, John Jones pointed out a probable error in the last of these. In 1872, when lead mining was in decline, local smelters purchased 326 tons of ‘linnets’ which had been stockpiled at sixteen different lead mines. Some of this material was described as ‘brown linnets’, and it was assumed, on the basis of colour, that ‘brown linnets’ were mimetite. John points out that there is no evidence for this. Colour is not a reliable guide to the composition of lead-bearing apatite-group minerals; modern analyses show that all Derbyshire ‘linnets’, brown or otherwise, are pyromorphite.

Ladywash Mine may be the premier specimen locality in Derbyshire, a county which is not lacking in mineralogical superlatives. It furnished the front cover illustration for Minerals of the English Midlands (Starkey, 2018). Don Edwards, who started Tideswell Dale Rockshop in 1971, recalled that in the early years one of the miners supplied a van load every week. And yet there is little recorded in the literature of the specimens it produced. A Ladywash calcite makes a worthy frontispiece (Fig. 1) and one of Don’s paintings features on the back cover. A detailed article is overdue!

In the discussion section of his article, Steve observes that Russell Society members have had access to New Milldam Mine, which works the same vein system as Ladywash, for many years. Collections have surely matured sufficiently to merit a descriptive article? Wulfenite (Figs 2 and 3) is one of a suite of poorly recorded minerals that will be familiar to many readers.
Figure 1. One of many fine specimens from Ladywash Mine, near Eyam, acquired by John Jones. Roy Starkey specimen and photo.
Moving on, Michael McMullen delves into the dark and sooty world of manganese oxides. It is one of nature’s ironies that these black powders were formerly used in the production of bleach and to remove undesirable colours from glass. Michael describes a fantastic piece of rescue collecting at Laverockbraes, a classic locality for well crystallised manganite, which now lies buried beneath the suburb of Grandhome, north-northwest of Aberdeen. We remain with Michael for a report of orange-red wulfenite at Roar Hill on the eastern edge of the Cairngorms. In recent decades, wulfenite has become something of a barometer of mineralogical discovery in the British Isles. Sir Arthur Russell considered his report of wulfenite from Loch na Mèine near Struy in 1946 was only the fifth British occurrence. There are now two dozen in Scotland alone and probably more than a hundred in the British Isles.

The next contribution, by Stephen Moreton and Robert Lawson, describes octahedral purple fluorite and associated minerals from Lettermuckoo Quarry in Co. Galway, Ireland.

Remaining in the purple region of the colour wheel, manganese is the chromophore in pale amethyst-purple veinlets of barium-rich muscovite from Benallt Mine on the Lleyn Peninsula, a site well known to Society members. Tom Cotterell and his team from National Museum Wales describe the material in two articles which extract a considerable amount of information from a small dataset.

Attractive green amazonite from Ben Loyal in the far north of Scotland, which rivals the best collected in the nineteenth century, is described by Roy Starkey and Chris Finch. As with many allochromatic minerals, the colour of Ben Loyal amazonite bleaches on long exposure to the elements. Roy and Chris have been able to preserve many beautiful examples of this most desirable Scottish ‘species’.

The mines of the Caldbeck Fells in Cumbria are best known for their colourful suites of copper-, lead- and zinc-bearing supergene minerals. Descriptions of many sites of mineralogical interest, based primarily on specimens in the Mike Leppington Collection, appeared in the *Journal of the Russell Society* between 2005 and 2011. After a hiatus of almost a decade, Mike and his team return with a description of the minerals of the little known Smale Gill trials.

Rounding off, Brian Young and Andy Hopkirk describe pseudomorphs and epiomorphs involving fluorite from a number of locations in the Northern Pennine Orefield (see also Fig. 4). Brian and Andy also contribute a description of smithsonite pseudomorphs after rugose corals from Middle Fell near Alston. This makes an interesting comparison with an earlier description of corals replaced by hemimorphite at Grovebeck Mine in Swaledale (Young, 2013).
Finally in this editorial, Michael McMullen has asked that members be made aware of restrictions on collecting at the Glenbuchat elbaite locality. The site was described by Starkey and McMullen (2017) and has since attracted unwanted attention. Please note that with immediate effect no one will be allowed to visit this site between the months beginning April until the end of September. Visitors will be able to visit ONLY during the period October to the end of March.

This restriction is being imposed due to the unscrupulous actions of some visitors walking across the moor disturbing and in some cases destroying grouse nesting areas.

The moor is heavily monitored by gamekeepers who are all in radio contact. Anyone seen on this part of the moor during the restricted period will be stopped, questioned and asked to empty their bags of specimens. Those refusing will have their vehicle photographed and will be prosecuted for mineral theft.

REFERENCES

Figure 4. Pseudomorphs hold a particular fascination for collectors with an interest in chemistry. In some cases it is fairly easy to see how one species replaces another, but there are specimens where the process is obscure. In this remarkable specimen from the North Swaledale Mineral Belt, deep green pyromorphite replaces fluorite cubes a little less than 1 mm on edge (the modifications to the edges show that the pseudomorph can only be after fluorite). Charles Lamb Collection, photo John Chapman.
ENARGITE FROM LADYWASH MINE, EYAM, DERBYSHIRE

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The uncommon copper sulpharsenide enargite occurs as metallic grey-black crystals up to about 0.75 mm on edge with chalcopyrite, galena, pyrite and sphalerite on a fluorite specimen from the workings on Hucklow Edge Vein at Ladywash Mine near Eyam in Derbyshire. The occurrence has strong mineralogical similarities with the two other enargite localities in the South Pennine Orefield at Gregory Mine and Millclose Mine. In each case, enargite occurs as a late-stage primary phase in low-temperature fluorite-dominated hydrothermal vein mineralisation. Arsenic-bearing primary minerals are relatively rare in the Pennine orefields; comparable mineralisation is briefly described and discussed.

INTRODUCTION

Ladywash Mine [SK 218 775] situated on Eyam Edge about 1 km north of the village of Eyam, worked the eastern end of the Hucklow Edge vein system. The mine dates from the early eighteenth century, but the locality is best known to collectors as a relatively modern operation which produced remarkable specimens of calcite, fluorite, marcasite and sphalerite in the third quarter of the twentieth century when the veins were being reworked for fluorspar (Rodgers, 1977; Bramley, 1991; Ford et al., 1993; Starkey, 2018).

Enargite, ideally Cu₃AsS₄, has been identified on a specimen from Ladywash Mine in the John Jones Collection, which was recently acquired by Crystals Classics Fine Minerals of Somerset. John’s collection, which was built over a period of more than 50 years, had a particularly strong focus on the minerals of Derbyshire.

HISTORY

There are documentary references to lead mines near Great Hucklow as early as the eleventh century (Sharp and Stamp, 1912). Many small mines were in operation in the Medieval Period. The first references to Ladywash Mine date from the early part of the eighteenth century, when the lead veins below Eyam Edge were being opened up (Hunter, 2015). The veins at Ladywash extend into the Monsal Dale Limestone, where water ingress was a major problem. Stoke Sough was driven from the River Derwent in the late 1720s and had reached the Ladywash workings by the middle of the century, draining all of the productive ground.

Ladywash Mine was worked intermittently for lead until the mid nineteenth century, but its mineralogical fame rests on the twentieth century reworking for fluorspar (Bramley, 1991) which extended the workings from the bottom of Ladywash Shaft through many of the adjacent mines. Such was the scale of the reworking that the nineteenth century operations [SK 2158 7705] are described as Old Ladywash Mine in some texts (e.g. Stevenson et al., 1971). They are not discussed further here. To collectors, Ladywash Mine has become synonymous with the twentieth century operations, which extend for more than 2 km west of the shaft bottom.

As the value of fluorspar began to increase at the end of the nineteenth century, many of the old spoil heaps along Eyam Edge were reprocessed. When the tips were exhausted, some of the mines were reopened as considerable reserves remained in situ in the cheeks of the veins1. Ladywash and the nearby New Engine Mine were worked in the inter-war years by Ashover Mines Ltd. In 1937, when their operation was winding down, the agent for the nearby Glebe Mines inspected the workings. Ladywash Shaft was reopened and a cross-cut which reached Old Edge Vein at a depth of 160 m was driven. A large unworked section of Old Edge Vein was discovered almost immediately and it provided considerable fluorspar. As most of the productive ground lay to the west of the shaft bottom, Ladywash Shaft was enlarged and it became the principal haulage route for fluorspar from 1949 onward.

The Glebe Mines were acquired by Laporte Minerals Ltd in 1959. Ladywash Mine continued to produce fluorspar, working steadily westward through the vein system. A new processing facility at Cavendish Mill was opened in 1965 and the mine supplied much of the feed. Although the deposits were not exhausted, increasing haulage costs as the workings extended further along Hucklow Edge Vein, the limited capacity of the shaft, and the inevitable variability in commodity prices eventually rendered the mine uneconomic. It was placed on care and maintenance on 16 March 1979 and subsequently abandoned. The headgear and much of the plant were removed but some of the original mine buildings remain and the shaft is still intact as it provides a second exit from the workings of New Milldam Mine.

New Milldam Mine was opened as a trackless decline in 1987 at the west end of the Hucklow Edge vein system. It came into production in 1991 and gradually worked toward the area that had been exploited by Ladywash Mine. The mine was sold to Glebe Mines Ltd in 1999 and was acquired by Ineos Fluor in 2007 after the failure of a tailings dam at Cavendish Mill. Ineos Fluor ceased

1 Fluorspar reserves along the vein system are estimated at about three million tonnes by the British Geological Survey (2010).
production in 2010, but the mine restarted in a small way in 2012 when it was acquired by British Fluorspar. The haulage level currently extends for more than 4 km along Hucklow Edge Vein and the mine produces about 65,000 tonnes of fluorspar and 10,000 tonnes of baryte per year (Colman, 2019). Calcite is also produced and mixed sulphide and supergene mineral concentrates are shipped to China for processing (Neil Hubbard, personal communication, 2019).

GEOLOGY

Mineralisation in the South Pennine Orefield is reviewed in Ford and Worley (2016) and the geological setting of the mines along Hucklow and Eyam edges is summarised in Ford (2012). Lower Carboniferous rocks of the Peak Limestone Group, which host the vein deposits, crop out in Middleton Dale south of the village of Eyam, where they are quarried for roadstone. They dip gently to the northeast and are overlain as the land rises to the north by mudstone and sandstone of the Namurian Millstone Grit Group.

The Hucklow Edge vein system is a stratabound deposit. The mineral veins exploited at Ladywash and neighbouring mines lie within wrench faults, which developed in the closing stages of the Variscan Orogeny (Ford and Worley, 2016). They are productive in the top part of the massive Monsal Dale Limestone Formation and in the overlying Eyam Limestone Formation. The veins disappear as the faults pass into the overlying shales and do not extend into the underlying Cressbrook Dale Lava, which is at least 72 m thick at Ladywash Mine (Hunter, 2015).

A gradual increase in the thickness of the Cressbrook Dale Lava eastwards from Great Hucklow towards Eyam (Hunter and Shaw, 2011) is accompanied by a reduction in the thickness of the Monsal Dale Limestone above it, so that the vertical extent of the vein system reduces from west to east. The Eyam Limestone Formation is rather variable in thickness and consists of thinly bedded limestone and mudstone with chert bands and extensive fossil-rich reefs. Mineralising fluids ponded in fractures in the Eyam Limestone, just below the overlying shales, producing orebodies that were locally very rich.

The carbonate rocks, which host the vein deposits are overlain by mudstone, most of which is assigned to the Bowland Shale Formation. The mudstone forms the scarp slope of Eyam Edge, which is capped by thick competent sandstones of the Namurian Millstone Grit Group. The shaft at Ladywash Mine, which is about 300 m north of the Edge, reaches the surface in shale and siltstone of the Hebden Formation.

2 The mudstone was formerly described as the Edale Shale and at its base the thin Longstone Mudstone Member, which is currently assigned to the Widmerpool Formation, is sporadically present.

SPECIMEN DESCRIPTION

The mines around Eyam were known for fine mineral specimens in the nineteenth century, but only Water Grooves Mine receives specific mention (for calcite) in Greg and Lettsom (1858). Their quality is such that they are the only calcite specimens from the county noted specifically in Sinkankas (1964). Ladywash Mine became famous in the mid twentieth century when remarkable calcite specimens were found (Braithwaite, 1983; Starkey, 2018), although surprisingly little has been recorded about the circumstances of their discovery. As well as calcite, Ladywash Mine produced fine baryte, chalcopyrite, fluorite, galena, marcasite and sphalerite. One such specimen was acquired by John Jones in July 1973. It is number 991 in his collection, and is described as fluorite with pyrite inclusions, sphalerite and minor chalcopyrite from Hucklow Edge Vein, Ladywash Mine, Eyam.

The specimen measures 12 × 9 cm and consists of colourless intergrown fluorite cubes up to 15 mm on edge with later cuboctahedral galena and black crystalline sphalerite. Brassy yellow chalcopyrite crystals overgrow much of the fluorite (Fig. 1) and minute square flattened metallic pyrite crystals are present as inclusions near to the crystal surfaces.

Scattered crystals of metallic dark grey-black enargite, (about ten in total) up to about 0.75 mm on edge are present. They are typically tabular (Fig. 2) to short prismatic with asymmetric modifications (Fig. 3). Some are closely associated with twinned black sphalerite crystals and striated sphenoidal chalcopyrite. A simple blocky prismatic crystal bounded by prominent six-sided c {001}, with large square {100} and smaller rectangular {110} forms which combine to produce a stout prism, is illustrated in Figure 4. The habit is very similar to that described from Gregory Mine in Cooper (1995).

Figure 1. Brassy yellow sphenoidal chalcopyrite up to 3 mm across scattered on the surface of a cubic fluorite crystal with minor galena on the right hand side. Ladywash Mine, Eyam, Derbyshire. Crystal Classics specimen; photo Steve Rust.
The identification has been confirmed by X-ray powder diffraction (Fig. 5) at Amgueddfa Cymru – National Museum Wales (X-ray reference number NMW X-3657).

DISCUSSION

Enargite is typically found as a late-stage primary mineral in low-temperature hydrothermal veins. Most of the dozen or so British localities listed in Tindle (2008) fall within this category. There is no obvious geological pattern to these occurrences. Surprisingly, enargite is not recorded from areas such as the Caldbeck Fells in Cumbria or from Cornwall and Devon, which are otherwise famous for their copper and arsenic minerals.

Arsenic-bearing minerals of any sort are rare in the South Pennine Orefield and in the neighbouring deposits.

Figure 2. Dark grey blocky enargite, 0.5 mm on edge, with brassy yellow chalcopyrite on pale grey fluorite which contains flattened pyrite inclusions. Ladywash Mine, Eyam, Derbyshire. Crystal Classics specimen; photo Steve Rust.

Figure 3. Complex rather asymmetric enargite crystal, 0.75 mm on edge, associated with flattened black sphalerite and striated brassy yellow chalcopyrite. Ladywash Mine, Eyam, Derbyshire. Crystal Classics specimen; photo Steve Rust.

Figure 4. Highly magnified image of a blocky prismatic enargite crystal. Six-sided c \{001\} faces are bounded by two large square \{100\} and four smaller rectangular \{110\}, which form a stout prism. The small triangular modification is probably \{011\}. Slight damage on the corner shows incipient cleavage, which can be used to distinguish enargite from the chemically similar tennantite, which has no cleavage. Ladywash Mine, Eyam, Derbyshire. Crystal Classics specimen; photo Steve Rust.
of the Askrigg Block. They are less abundant and diverse than in the deposits of the Alston Block, where rich primary nickel arsenide mineralisation has been described at a number of localities (Bridges, 1982; Young et al., 1985; Dunham, 1990) and a diverse range of supergene arsenates has been identified (Bridges and Young, 1998; Bridges and Green, 2005, 2006; David Green, personal communication, 2019). In some cases, the arsenic mineralisation in the North Pennine Orefield is spatially associated with the Whin Sill, however local concentrations of arsenic-bearing minerals have been recorded well away from any igneous bodies (Young and Pacey, 2016).

In the Askrigg Block, Dunham and Wilson (1985: pp. 90–91) record tetrahedrite-tennantite at Stennerskeugh Clouds (where arsenic is dominant and the composition is antimony-bearing tennantite) and at Cumpston Hill (where antimony is dominant and the composition is arsenic-bearing tetrahedrite). Their report is based on analyses originally reported in Small (1982). A single specimen of ‘stibioluzonite’ in galena is noted at an undisclosed locality (Dunham and Wilson, 1985: p. 91). As this is described as a “sulphantimonide”, it may refer to the antimony-dominant mineral famatinite³, which is reported from Melbecks Moor, near Gunnerside in Swaledale by Vaughan and Ixer (1980). Minute crystals of famatinite and luzonite are recorded in calcite near Scaleber Bridge, about 3 km SSE of Settle on the southwestern edge of the Askrigg Block, by Ixer and Stanley (1998).

In the South Pennine Orefield, the only arsenic-bearing species noted in Tindle (2008) are arsenopyrite, enargite and mimetite. Of these, it seems very likely that the records of mimetite, summarised in Ford et al. (1993), are errors which have propagated in the literature on the basis of early misinterpretations of the terms ‘brown linnets’ and ‘brown lead ore’ (John Jones, personal communication, 2019). Pyromorphite is common in Derbyshire, but mimetite has not been identified by modern analytical methods. Claims of arsenopyrite from the South Pennine Orefield, summarised in Tindle (2008), include specimens from High Rake near Hucklow and Eyam, and also seem worthy of further investigation. It seems possible that some may be misidentifications of marcasite. Tennantite and zincolivenite have been reported from Ecton Hill in Staffordshire, but they are inconspicuous and rare (Braithwaite et al., 2009).

The first record of enargite from the South Pennine Orefield is on an old (1804 catalogue date) specimen in the collection of Georgiana, Duchess of Devonshire, from the Gregory Mine, near Ashover (Cooper, 1995). Groups of grey, flat-topped, six-sided crystals up to about 2 mm across were identified by XRD at the Natural History Museum [and are figured in colour in Starkey (2018: p. 103)]. Similar crystals have been visually identified on a specimen from Millclose Mine, South Darley (Neil

³ In modern nomenclature, stibioluzonite is an antimony-bearing variety of luzonite, a sulpharsenide which is dimorphous with enargite; famatinite forms a solid-solution series with luzonite in which antimony replaces arsenic.

Figure 5. The results of an analysis of a crystal of enargite from Ladywash Mine by powder X-ray diffraction at Amgueddfa Cymru – National Museum Wales (analysis NMW X-3657). The blue lines are the positions of the diffraction peaks for enargite and the red curve the measured diffraction intensity. The match between the two is excellent.
Hubbard, personal communication, 2019). These occurrences have mineralogical and paragenetic similarities to the occurrence reported here at Ladywash Mine.

Igneous bodies are present at all three enargite locations and it may be that (as at some localities in the North Pennine Orefield) they supplied the small amounts of arsenic required for enargite and arsenopyrite to form. Unfortunately, detailed records of the precise geological situation in which the specimens were collected were not made and this assertion is purely speculative.

It is hoped that this description and the accompanying photos of enargite will encourage members to re-examine their specimens. Russell Society members have had access to material from New Milldam Mine, which works the same vein system as Ladywash Mine, for many years. Enargite is a relatively inconspicuous mineral and it is possible that further specimens remain undiscovered in collections.

ACKNOWLEDGEMENTS

Thanks are due to Crystal Classics Fine Minerals Ltd for allowing the specimen to be described and studied. Tom Cotterell of Amgueddfa Cymru – National Museum Wales is thanked for the analysis by XRD. Neil Hubbard kindly shared information about unreported occurrences of enargite in Derbyshire and Don Edwards shared some of his reminiscences of specimens from Ladywash Mine. John Jones shared information from his collection catalogue and is thanked for observation about ‘linnets’ in Derbyshire. Don Edwards, David Green, Neil Hubbard and John Jones are thanked for comments which improved the manuscript.

REFERENCES


MANGANITE FROM LAVEROCKBRAES, GRANDHOME, ABERDEEN

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Excavations in the late Devensian Banchory Till in the area around NJ 917 111, west of Laverockbraes Farm, about 5 km NNW of the city of Aberdeen, have produced some of the finest specimens of manganite from the British Isles. Lustrous striated prismatic crystals up to about 10 mm in length occur in cavities in massive manganese oxides. The ore was discovered at the beginning of the nineteenth century as an indirect result of canal building. Its principal use appears to have been as a raw material in the production of chlorine bleach. The last definite record of work dates from the 1840s, although anecdotal evidence suggests there may have been a reworking in the last half of the nineteenth century. In 2016, the site was cleared, excavated and landscaped during preparatory work for a large housing development. This provided a unique opportunity to rescue specimens from an area that had been heavily overgrown and inaccessible to mineralogical study for more than a century. The Laverockbraes deposit represents mineralisation deposited by oxidising iron- and manganese-rich fluids in fractures, which locally coalesced to produce ore-grade sections.

INTRODUCTION

With the demise of the British mining industry and the advent of increasingly protective legislation, access to sites of mineralogical interest is becoming challenging. On occasion, opportunities which can be beneficial to collectors, landowners, statutory stakeholders and museums present themselves. The rescue collecting of manganese minerals prior to the construction of Grandhome, a new suburb of the City of Aberdeen, was one such opportunity.

In the early part of the nineteenth century, two rich deposits of manganese ore were discovered to the west of Bridge of Don, about 5 km NNW of the centre of Aberdeen. The deposit near Hill of Danestone is on land which was developed in the 1980s. No geological survey work or rescue collecting was carried out at the time. The workings lie near to the current site of Danestone Primary School [c. NJ 918 102]. Archaeological notes compiled in 2002 describe a “Manganese Mine” which had “Workings, supposedly extensive, representing about ten years work”; and go on to state that “Nothing is visible of any extractive workings at this location, which lies in the grounds of a school” (CANMORE, 2002). The second deposit, about 500 m west of Laverockbraes Farm, is the subject of this study.

Small manganese deposits are relatively common in the Aberdeen area. Manganite, pyrolusite and romanèchite were found as rich crystalline blocks in till at Bridge of Don Industrial Estate [NJ 9407 1087] (Chew, 1978; Nicholson, 1989).

HISTORY

The history of manganese mining in late eighteenth and early nineteenth century Britain is intimately connected with the introduction and development of chlorine bleaching. Manganese oxides were also used as pigments, in chemical manufacturing and in glass making. It is one of nature’s ironies that the black sooty powders proved essential in the production of bleach and that they could remove undesirable colour from glass. Manganese had limited uses in metal alloys at the time, its extensive use as an additive to control impurities in steel only began after Henry Bessemer developed the process which bears his name in the mid-1860s. This post-dates the principal periods of working at Laverockbraes.

In the middle of the eighteenth century, bleaching was a long, tedious and expensive process. Cloth was soaked in alkaline lyes for several days and spread out in ‘bleaching fields’ to whiten in the sun; it was then soaked in sour milk, washed and spread out to whiten once more. Each whitening could take several weeks, and as several repetitions were required, the whole process commonly took up an entire summer. Weak sulphuric acid replaced sour milk in the latter part of the eighteenth century, but the process remained slow and expensive until the late 1780s, when it was found that a solution made using the newly discovered gas, chlorine, was an effective bleaching agent. It reduced the bleaching time from months to days and eventually to just a few hours.

There seem to have been several independent introductions of chlorine bleaching into Britain (Thomson, 1824; Partington, 1962). The first successful experiments involved James Watt, in 1786. In the next year Patrick Copland [or Copeland], professor of Natural Philosophy at Marischal College in Aberdeen, learned of the chlorine bleaching process from Professor de Saussure, with whom he and his patron, the Duke of Gordon, had spent three weeks in Geneva. The knowledge was brought back to Aberdeen, and Alexander and Patrick Milne of Gordon, Barron and Company, who operated the Woodside Cotton Mill, took it up. The proprietors of nearby Grandholm Mills also needed bleach. Numerous advertisements over the next sixty years refer to bleaching facilities operated by Leys Masson and Company at “Grandholm Mills” or “Grandholm Works” (Hamish Johnston, personal communication, 2019).
Chlorine bleaching was well established in Scotland by the early 1790s, when ‘prepared manganese, properly ground and fit for immediate use’ was advertised to bleachers and paper makers. Initially, chlorine gas bubbled through lime-water was used. This had the disadvantage that the gas had to be produced near the bleaching works. It was not until the end of the decade that the Scottish chemist Charles Tennant developed the safer and more convenient calcium hypochlorite ‘bleaching powder’.

Demand for ‘manganese oxide’ was significant. In 1804 James Sowerby (1804: pp. 179–180) noted that its major uses were:

“in glass-houses in small quantities, to clear and discolour glass by giving up some of its oxygen, and so completing the vitrification of the iron or other colouring ingredients. It is used as a pigment or an ingredient in printer’s ink, and to procure oxygen gas from, for many purposes, viz. as a medicine; or for oxygenizing muriatic acid for bleaching, &c”.

A little more than a decade later Robert Jameson (1816: p. 324) noted:

“All the oxymuriatic acid used in bleacheries, and for the purpose of destroying contagious matter, is prepared from manganese, and the usual materials of muriatic acid”.

In this context oxymuriatic acid is an old chemical term for elemental chlorine, which was absorbed by slaked lime to produce calcium hypochlorite. As the century progressed and manganese ores began to be differentiated it became clear that some were more effective than others. Pyrolusite was particularly good as an additive in glass making and Greg and Lettsom (1858) note that it was superior to manganite in the production of chlorine gas.

The principal British manganese mines in the first decade of the nineteenth century were at Upton Pyne in Devon, where 3000 tons of black oxide per annum were produced (Starkey, 2018). According to Berger (1811) the last mine at Upton Pyne had been abandoned by about 1811, but others had been opened at Newton St Cyrus. At the same time Cornish manganese ore was “shipped direct to Lancashire, where for some years it has been employed in the bleaching of cotton” (Berger, 1811: p. 179). Manganese from Devon was commonly advertised for sale in the second decade of the nineteenth century and Thomson (1836: p. 503) records that in the 1830s the mines around Upton Pyne “supplied most of the manganese consumed in Great Britain, amounting annually to about 30,000 tons”. Despite these large volumes, demand exceeded supply and alternative sources were sought. The rich Mendip manganese ores were contaminated with lead, which made them unsuitable in many applications and exploration extended into remote areas of north Wales and Scotland (Tom Cotterell, personal communication, 2018).

The Grandhome Estate, northwest of Aberdeen, has been owned by the Paton family since 1684 and has a long association with cloth manufacturing. In the late eighteenth century John Paton (1745–1827), the head of the family, leased a piece of land to Messrs Hadden and Leys for the purpose of building a canal, which among other desiderata would bring water to the mills along the River Don. A preliminary survey of the route was made by Captain George Taylor in 1793. Work appears to have commenced in earnest in about 1801, after the Aberdeen Canal Bill had received its third reading in the House of Commons. The canal opened, somewhat unsuccessfully, in 1805, and with more robust lock gates in 1806 (Graham, 1969).

Paton family archives indicate that the excavations for the new canal exposed small amounts of manganese ore on the Haugh, a flat section of land near the River Don beside Grandhome House2. Subsequent exploration in the surrounding country by Dr William Dyce (1770–1835) revealed rich ore at two sites: Hill of Danestone, which is briefly described in the introduction, and Lavercockbraes, which is the subject of this study.

Manganese oxide was being mined by 1802 (Nicholson, 1989), when there was also an advertisement in the Aberdeen Press and Journal for contractors to lay out bleaching lines on “the Haugh near Grandholm”. The workings were well known by 1804, when William Dyce, the driving force behind early operations, was awarded a gold medal in chemistry by the London-based Society of Arts for developing a “mine of manganese” (Lancaster Gazette, 1804).

The first volume of James Sowerby’s classic British Mineralogy provides an early reference to the discovery (Sowerby 1804: p. 179):

“We are glad to be possessed of British specimens from the works near Aberdeen, which I have been given to understand were first discovered by the Rev. Mr. Smith”.

Sowerby’s claim that the works near Aberdeen were discovered by the Rev. Smith may be mistaken as there is no corroboration in the Paton family archives. Sowerby was often advised by others as to the specifics of his specimens and did not visit many of the localities described in his books (Henderson, 2015; Paul Henderson, personal communication, 2017).

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1 David Romer Paton, the ninth Baron of Granhome, head of the family, died on 4 February 2019 at Grandhome in Aberdeenshire (The Scotsman, 2019).

2 Early spellings of Granhome include the phonetic Granham or Granam; Grandholm, which was the preferred spelling on Ordnance Survey maps until the beginning of the twentieth century, and Grandholme, which appears in early letters. Grandhome is used herein unless the text is part of a quotation as it is the spelling used on modern maps produced by the Ordnance Survey and in the Memoirs of the British Geological Survey.
The mine was working in 1806, when Donald Sage, a student at Marischal College in Aberdeen, made a visit to "a manganese mine, near Grandholm" (Sage, 1889: p. 200).

A letter dated 4 August 1808 from John Paton, who was in Dublin, to Dr Alexander Dauney of Aberdeen (Paton, 1808), deals with the terms of a contract between the shareholders and Paton and Milne Cruden and Company who were responsible for mining the deposit. The operation was profitable at the time. In 1809 the shareholders are listed as Mr Paton, Dr Dyce, Mr D. Chalmers and Mr Al Brown (Fig. 1). In January of that year they were each paid just over £258; and in 1809 the total wrought from workings was £1466 (National Records of Scotland, 1809). This equates to 1955 tons of ore, which would require a larger operation than current exposures suggest. The workings were doing well in 1811, when an advertisement in the Royal Cornwall Gazette requested a person to superintend the working of a "Vein of Manganese lately discovered near Aberdeen". Applicants were asked to correspond with William Dyce and Company. In 1816, manganese from Aberdeen was listed for sale in the Durham County Advertiser; operations appear to have continued well into that decade.

The workings appear to have been abandoned at some time thereafter, but demand for manganese was considerable in the first half of the nineteenth century and the Laverockbraes workings were reopened in the late 1830s by the Cookson family, an industrial dynasty from Tyneside which can be traced to Isaac Cookson (1679—1743). Cookson’s great grandson, also Isaac Cookson (1776—1851) of Gateshead Park, had considerable interests in manganese mining; in addition to the workings at Laverockbraes, he was involved in the reopening of the Lecht Mine near Tomintoul in the 1840s. The principal use of the ore appears, once again, to be to have been in bleach making. Cookson also had iron and steel foundries, chemical works and extensive glass-making interests including a bottle works and plate and optical glass manufactory. Any or all of these might also have required manganese oxides. In 1838, Cookson leased:

"all and whole the Manganese Mine Grandhome situated at Laverock Braes with the sole privilege and liberty to the said Isaac Cookson and his foresaid to search for and work out and dispose of the mineral substance known by the name Manganese, or Magnesia Nigra wherever the same may found on Grandhome in the grounds in the natural possession of the Trustees".

He was to "make shafts, set down pits, and to build and erect, engines" and was granted "all lands which may be necessary and proper for carrying of the said works". The ground rent was set at twenty pounds sterling per annum to be paid on Whitsunday, plus fifteen shillings for every ton of twenty hundred weight of manganese in a picked and prepared state. If no ore was found in the first year then no rent was due, Cookson’s men merely had to pay for surface works and fill in any excavations (National Records of Scotland, 1838; 1840). All ores were to be transported to the Cookson foundry at Pipewellgate in Gateshead (Cookson Family Papers, n.d.).

An article of 'scientific intelligence' in the Edinburgh New Philosophical Journal (Anon., 1838) of the time records:

"We are informed by Dr Fleming that the ore occurs in a rock of mica-slate, which stretches in a northerly direction, and has an easterly dip, varying from 30º to 50º and upwards. In some places it is thin slaty, even, or waved, while at other parts thin beds of gneiss and granite make their appearance. When the mine was opened upwards of twenty years ago, an excavation, or opencast, was made across the stretch of the strata, at the eastern termination of which a mass of felspar porphyry

3 In today’s (2018) terms this is the equivalent of more than £124,000 (Morley, 2019).

4 Numerous foundries and glass works are noted at Pipewellgate in the first half of the nineteenth century (English Heritage, 2005).
makes its appearance, the relations of which are not seen at present. The ore, which is the “grey Manganese ore,” or “Hydrous Binoxide of Manganese,” occurs in irregular thin beds, rounded concretions or anastomosing films in the rock, accompanied by small quantities of sulphate of barytes. As the working has but recently commenced, little more than a dozen of tons of the ore have been obtained. But as the undertaking is in hands possessing abundance of capital and enterprise, Messrs Cookson of Newcastle, the mine will now have a fair trial, and it is hoped that a new branch of trade will thus be added to those already so successfully carried on at Aberdeen”.

Work carried on into the 1840s. In July 1844, thirty tons of manganese ore was ready to be sold, with a further regular supply from Mr Paton’s estate at “Grand home” (Gore’s Liverpool General Advertiser, 1844). A year later, the Aberdeen Press and Journal included an advertisement for contractors to make a cut across the Moss of Deanstone [Danestone] to convey water from the “manganese quarry” on the Grandhome Estate. The workings may have closed in the late 1840s when Messrs Cookson of Newcastle abandoned their manganese mining operations at Lecht near Tomintoul. This coincides with the failure of Messrs Leys, Masson and Company, who had run the Grandholm Works for more than half a century (Aberdeen Press and Journal, 1848). A year later, the manganese quarry at Laverockbraes was profitably let in the time of his grandfather.

There may have been further workings later in the nineteenth century. An archaeological survey of the site (CANMORE, 1997) dated 26 March 1997, reports:

“The remains of this quarry comprise a broad water-filled trench, measuring up to 65m in length from E to W by 18–20m in breadth, which has been excavated into the foot of a S-facing slope; the spoil has been spread to the S to form a broad terrace. To the N of the W end of the quarry there is evidence for further quarrying, but on the date of visit the area was heavily overgrown with whins and no other features could be discerned. The 1st edition of the OS 6-inch map (Aberdeenshire 1869, sheet lxvi) depicts only small-scale quarrying, and this would correspond with the heavily overgrown remains N of the W end of the main trench. The main trench was evidently dug between 1869 and 1901, since it is depicted water-filled on the 2nd edition map (Aberdeenshire 1901, sheet lxvi. SW)”. And John Paton (see below) writing in 1942 recalled that the manganese quarry at Laverockbraes was profitably let in the time of his grandfather.

Manganese was of strategic importance by the late Victorian period. Surveys of manganese deposits in the British Isles were published during and shortly after the First World War (Dewey et al., 1915; 1923; Dewey and Bromhead, 1916). According to Dewey et al. (1923: p. 73), manganese ores were worked on a small scale in Scotland and the finest specimens were said, on the authority of Matthew Forster Heddle, to be from:

“St. John’s Head, Hoy, Orkney Islands (mainly psilomelane) the Laoch [Lecht] Mines near Tomintoul (psilomelane), Lavock Braes, Granham (Grandholm), Aberdeenshire (manganese), Oa Peninsula, Islay (manganese)”.

There is no mention of Laverockbraes or any other site near Aberdeen in the manganese memoir compiled by Arthur Groves during the Second World War (Groves, 1952). The locality seems to have been too small and remote to be worthy of description. However, records held by the British Geological Survey reveal correspondence about the economic potential of the deposit. In reply to an enquiry written on behalf of John D. Paton by Messrs Burnett and Reid, of Aberdeen (British Geological Survey, 1942), the Assistant Director of the Scottish Branch of the Geological Survey, Murray MacGregor, noted:

“The occurrence of manganese … has been recorded at Lavock Braes near Grandhome, north of Persley and from the same locality the form psilomelane which contains a little barytes has also been noted as of rare occurrence”.

“I should be extremely glad to learn if you have any further information regarding the occurrence of manganese ore at this locality as it does not appear so far to have attracted any attention. If you have any further information to suggest that it may exist in workable quantities I should be only too glad to arrange for a visit to be paid by one of our staff”.

Paton replied on 10 May 1942:

“In my grandfather’s time from what I have been able to gather from ledgers and accounts, the Manganese Quarry below Lavockbraes Farm was very profitably let. I do not think the quarry was exhausted but it became unprofitable owing to cheaper sources from overseas & if this is the case, is it not possible that the reopening of the Quarry might contribute towards a larger supply of this ore which I understand is of great importance at the present?”

MacGregor was unable to find anything in the Geological Survey’s files to suggest that the deposit would be economic, but he wrote to Prof. T. C. Phemister (1902–1982) of Aberdeen University asking him to have a look. Phemister replied:

“I have your letter regarding the manganese deposits at Grandhome. At the beginning of the war I looked over the old workings very thoroughly and I was actually in touch with Paton to get any data regarding the former production etc. He was not at the time very interested and so I let the matter drop.

5 A recent biography of Heddle (1828–1897) is provided by his great-grandson Hamish Johnston (2015).
If he is now interested sufficiently to speak to me about it I will do what I can”.

“The old quarry is quite a big one and is now, of course, filled with water. The size of the quarry, however, is not necessarily an indication of a large deposit for the ore occurs in thin elongated lenses, so I suppose they had to work the whole zone in order to get a sufficient production”.

The Assistant Director and Prof. Phemister visited Laverockbraes with John Paton on 4 July 1942. Specimens were collected, two of which were crushed, analysed and found to contain 12.96% MnO. It seems likely that the deposit was too small and remote to be of interest and nothing further was done.

GEOLOGY

The geology of the Aberdeen area is summarised in Munro (1986). The country rock to the northeast of Laverockbraes consists of migmatised psammitic and semipelitic metasediment of the Aberdeen Formation, part of the Dalradian Supergroup. The site lies close to the contact with foliated muscovite-biotite granite of the Ordovician Aberdeen Pluton. The granite is late-tectonic with respect to Caledonian Orogeny and was emplaced shortly after the upper amphibolite facies metamorphic climax [the age given by Kneller and Aftalion (1987) is 470±1 Ma]. The boundary between the granite and metasediment is marked about 150 m to the southwest of manganese quarry on the modern geological map (British Geological Survey, 1982). However, the late nineteenth century survey marks what appears to be a granitic intrusion much nearer to the site lay on a south-facing slope to the east of Monument Wood, south of Whitestripes Road. Glacial action had sculpted the land into a tilted bowl shape with steep northern slopes. The water-filled excavation was bounded on the north side by a rock face, and tapered to the east and west. A vegetated area of tailings or spoil, about 65 m in extent, formed a broad terrace around the southern margin, and there was a trench dug at right angles, extending about 30 m into the northern slope (Fig. 5).

During site excavations, muscovite-biotite granite and migmatised metasediment were encountered, corroborating Dr Fleming’s account of “beds of gneiss and granite” among the country rock (Anon., 1838). Some manganese veins are within an equigranular granitic matrix, others are in migmatite or metasediment. The landscaping work did not expose sufficient of the bedrock to add much useful information to the solid geology. However, it is clear that the edge of the intrusion is more geologically complex than modern maps suggest.

LOCALITY

Until recent development removed it, the manganese working at Laverockbraes [NJ9168 1110], consisted of a water-filled trench, oriented in an east–west direction with an area of disturbed ground and spoil to the south, and a trench or platform to the north (Figs 3 and 4). The site lay on a south-facing slope to the east of Monument Wood, south of Whitestripes Road. Glacial action had sculpted the land into a tilted bowl shape with steep northern slopes. The workings cut obliquely into a south-facing escarpment. The water-filled excavation was bounded on the north side by a rock face, and tapered to the east and west. A vegetated area of tailings or spoil, about 65 × 20 m in extent, formed a broad terrace around the southern margin, and there was a trench dug at right angles, extending about 30 m into the northern slope (Fig. 5).

In 2008, the Grandhome Trust (Paton family trust) presented plans in response to the Scottish Government’s ‘Sustainable Communities Initiative’, which sought proposals for housing developments. Approximately 320 hectares of land, six miles to the northwest of Aberdeen, were to be developed into a new suburb of six to seven thousand homes, which was to be called Grandhome (Aberdeen City Council, 2013).

The development encompassed the Laverockbraes manganese workings, presenting a unique opportunity to survey the site and rescue specimens. The development plans retained the water-filled manganese trench as a ‘green feature’ but the area was to be landscaped with the removal of tailings and spoil and contoured to produce a safe and family friendly environment. Permission to

Figure 2. White fine-grained diatomite, a recent lake-bed deposit, 190 × 110 × 80 mm. Michael McMullen Collection, photo Roy Starkey.
Figure 3. Extract from the twenty-five inch Ordnance Survey map showing Laverockbraes. The survey was completed in 1864 and the map published in 1868. Reproduced with permission of the National Library of Scotland.

Figure 4. The Laverockbraes opencut as it stood in 1989, heavily overgrown and with little exposed mineralisation; at the time it was possible to collect small amounts of manganite in loose blocks as the inset shows. Reproduced by kind permission of Pamela and the late Gordon Todd.
Figure 5. Drone-derived 3D computer model imagery of the site. Reproduced with permission of William Donald Ltd, Civil Engineering Contractors. Note extensive earth clearance south of manganese workings and the areas of heavily mineralised soil.

Figure 6. View of the site looking northeast on 11 October 2016, during excavations to profile the slope near the manganese workings. The operators loaned a digger and driver to retrieve mineral specimens. Note the iron-stained bedrock exposures of muscovite-biotite granite. Photo Michael McMullen.
collect at the site was obtained from the developers, landowners and conservation bodies. Visits were made on numerous occasions over a two-month period in late 2016 while the excavation and landscaping was carried out (Figs 6 and 7).

The locality has been variously described as a ‘mine’, ‘quarry’ and ‘workings’ (Nicholson, 1989). Considerable excavation on the hill slope (Fig. 7) revealed no evidence of underground operations and the author concurs with the observation made during a visit by staff of the British Geological Survey in 1942, who suggested that the trench at right angles to the main face (Fig. 8) was probably cut to make a platform or bench onto which the ore would be placed before it was carted away.

The site is now ‘lost to collecting’, it has been landscaped and grassed and there are no visible rock outcrops. It is surrounded by private housing and forms part of an attractive recreational area.

MINERALS

Manganite is the principal species of collector interest at Laverockbraes. Specimens with attractive crystal sprays up to about 10 mm in length, were found during recent rescue collecting at the site. Baryte, kaolinite, pyrolusite, quartz and a mica-group mineral with a best-fit to powder X-ray diffraction data suggesting paragonite were also identified (Tom Cotterell, personal communication, 2019). The principal iron oxide present is goethite. The minerals occur as veins in granite and coarse-grained mica-rich metasediment and as loose masses in the overlying till.

BARYTE, \( \text{BaSO}_4 \)

Baryte occurs as discontinuous layers which lie approximately parallel to the edges of manganite veins (Fig. 9). In some specimens it forms a white selvedge to the veins. It occurs commonly as white blocky to bladed crystals in cavities (Figs 10 and 11). Although it is less abundant than goethite and manganite, baryte is common and widespread and occurs at all stages in the primary paragenesis. It infills cavities in goethite where it may take on a red colour, which is almost certainly due to finely divided hematite.
A specimen of a dark grey-black crystalline manganese oxide intergrown with a massive white phase was identified by powder X-ray diffraction as manganite with minor baryte (X-ray number NMW X-3544) at National Museum Wales.

GOETHITE, FeO(OH)

Massive dark brown goethite is abundant in the Banchory Till at Laverockbraes (Fig. 12). Specimens commonly contain cavities lined by distinctive chocolate-brown botryoidal crusts, with a characteristic radiating structure (Fig. 13). Goethite forms along the edges of some iron- and manganese-bearing veins, where it may be shattered and criss-crossed by later manganite veinlets. Powdery brown limonite, which may be recent in origin, coats some specimens found loose in the till. Cavities in massive goethite are commonly infilled with white to red-stained baryte (Figs 12 and 14).

HEMATITE, Fe₂O₃

Hematite occurs with goethite. It is less abundant, typically later in the paragenesis, and gives a distinctive red colouration to some baryte

MANGANITE, MnO(OH)

The account of “MANGANESIUM oxygenizatum, var. Primitivum” provided by James Sowerby (1804: pp. 178–180) appears to be one of the earliest that specifically differentiates specimens of the mineral which would become known as manganite in the British Isles. Sowerby notes:

“Not knowing of its being found hitherto in Great Britain, we give this short account of it, and shall be glad to be favoured with any specimens which may be met with hereafter. We describe with much pleasure the present specimen of crystallized oxide, as propitious to an expectation that Great Britan [sic] nearly includes all that is essential to a knowledge of mineralogy, very few genera being excepted”.

Figure 10. Manganite crystals up to 7 mm long, some with a slight iridescence, associated with white baryte in manganite veinstone. Michael McMullen Collection, photo Roy Starkey.

Figure 11. Coarse white baryte blades in a cavity with well crystallised manganite on a 65 × 50 × 35 mm specimen. Michael McMullen Collection, photo Roy Starkey.

Figure 12. A 50 × 45 × 25 mm specimen of massive to botryoidal goethite with white platy baryte and minor hematite. Michael McMullen Collection, photo Roy Starkey.
Figure 13. A typical cavity in massive goethite lined with botryoidal goethite crusts. Field width 16.6 mm. Michael McMullen Collection, photo John Chapman.

Figure 14. Close-up image of the specimen in Figure 12. Botryoidal chocolate-brown goethite as a crust about 0.75 mm thick lines a cavity in massive goethite. Red hematite-stained baryte (top right) partly infills the cavity. Image assembled from 147 individual photos stacked at 20 μm intervals using a Zeiss 25 mm Luminar lens mounted on bellows. Michael McMullen Collection, photo John Chapman.
He goes on to describe plate 86, which is dated 1 August 1804 (Fig. 15) as follows:

"The upper right hand figure is nearly the natural appearance and size of the specimen; the prisms standing irregularly and joining near the base, where they stand upon sulphate of barytes, &c. The gangue is a sort of stratified micaceous grit, through a stratum of which it runs in veins. In a mass sent me from Aberdeen, the manganese includes crystallized sulphate of barytes, &c. as trap sometimes does other stones”.

The specimens seem to have been supplied by:

"My friend, Mr. James Reid, among other similar favours, procured me the specimen figured, some time in the year 1803”.

As is common in British Mineralogy, Sowerby is not absolutely clear about where his figured specimens originated, however his description of a matrix made up of "a sort of stratified micaceous grit” together with the notes about Aberdeen is similar to specimens from Laverockbraes, which commonly contain an abundance of mica.

There are a number of specimens from Greenam or Granam at the Natural History Museum which predate 1837, when specimens began to be documented in registers (Robin Hansen, personal communication, 2017). A specimen from the Greville Collection, which was purchased in 1810, but not labelled and catalogued until 1883, is shown as Figure 16.

Many nineteenth century textbooks note the occurrence, although they are commonly vague. Jameson (1816: p. 319) describes “Radiated Grey Manganese-Ore” in the vicinity of Aberdeen. The locality is noted without description in various editions of William Phillips’ Elementary Introduction to Mineralogy and by the time the second edition of Dana’s Manual of Mineralogy was published in 1860, the details had become somewhat confused: pyrolusite and manganite were claimed from “Aberdeenshire, in England” (Dana, 1860: p. 259).

Greg and Lettsom (1858), who owed much of their information about Scottish mineral localities to Matthew Forster Heddle, describe manganite:

“formerly at Granam, in the parish of Towie, beyond the Don, in crystals in the form of the figure; and also that of the primary form. Acicular, compact and earthy at the same mine”.

Granam is a phonetic spelling of Grandhome, but the reference to the parish of Towie is incorrect; Laverockbraes is in the parish of Old Machar. Towie lies 36 miles to the west, about 4½ miles southwest of Kildrummy Church, in the district of Alford. The original entry in Heddle’s catalogue at the National Museum of Scotland is written “Granham Tower”, with the word “Towie” above it in a different hand (Peter Davidson, personal communication, 2018). The word tower may refer to a nearby landmark, perhaps associated with a local linen mill or foundry. It seems most probable that the specimen arrived as a donation early in Heddle’s career and by the time the information for the Manual of the Mineralogy of Great Britain and Ireland was being compiled in the mid-1850s the words Tower and Towie had somehow become confused. It is easy to see how the error might have been perpetuated in 1883 when the NHM specimen from the Greville Collection was labelled (Fig. 16). The then curator would have had a copy of Greg and Lettsom (1858) on hand to consult for locality information.
Heddle was certainly aware of the error in later life. By the time his works on the county geognosy and mineralogy of Scotland were being published (Heddle, 1878: p. 9) he had:

“attempted to visit every known mineral locality to the north of the Forth and Clyde, and having succeeded in this attempt with less than half-a-dozen exceptions, [was] able in most cases to authenticate, or the opposite, as the case may be, the statements of previous observers”.

Five years later, he noted: “I have verified the occurrence of manganite at Laverock-braes Farm, Grandholm, Aberdeenshire” (Heddle, 1883: p. 427).

Specimens with manganite crystals up to about 10 mm in length, in cavities in manganese oxide, were collected during landscaping work in 2016 (Figs 17–22). The crystal vary from acicular to equant or flattened prismatic, they are typically striated, along the prism, and some have developed a colourful iridescence.

Satisfactory images of lustrous black minerals are difficult to obtain as the contrast typically exceeds the dynamic range of printed media. As a result, the crystal habits are not always easy to discern. Manganite crystals coated by an unidentified chocolate-brown crust were found in one small cavity (Fig. 23). The reduction in

Figure 17. A nodular manganite specimen, 80 × 40 × 20 mm, with a central cavity containing iridescent crystals up to 5 mm long and an outer surface coated in goethite, altering to finely divided limonite. Michael McMullen Collection, photo Roy Starkey.

Figure 18. An irregular manganite vein, 80 × 40 × 20 mm, with a roughly symmetrical central cavity containing interlocking crystals up to 7 mm in length. Michael McMullen Collection, photo Roy Starkey.

Figure 19. Lustrous striated manganite crystals up to 10 mm long on a 25 × 30 × 15 mm specimen. Michael McMullen Collection, photo Roy Starkey.
contrast this coating produces gives perhaps the best visual impression of the typical prismatic crystal habit of manganite from Laverockbraes.

All of the coarsely crystalline material that was examined by powder X-ray diffraction at the National Museum Wales (NMW) proved to be manganite (NMW X-ray numbers X-3544; X-3545; X-3546); though a fine-grained layer on one specimen also contains pyrolusite (NMW: X-3543). Manganite occurs as relatively pure vein-like masses, which commonly contain crystal-lined cavities. Some specimens have weathered surfaces and are matrix free, others show manganite as veins in fractures in migmatised or equigranular granite.

**PYROLUSITE, MnO₂**

Pyrolusite was identified by powder X-ray diffraction (PXRD) as a component of a fine-grained crystalline layer with manganite (NMW X-3543). Dendrites found in fractures were initially labelled pyrolusite, but are likely to be another manganese-bearing phase.

**QUARTZ, SiO₂**

Quartz occurs rarely as small transparent crystals with well developed pyramid faces in cavities in manganite. The rock which forms the edges of some manganite veins contains micro-fractures lined with drusy pyramidal quartz. A few specimens of coarse (migmatic) quartz segregations with thin fractures containing manganite and baryte were found, but they are relatively uncommon.

**DISCUSSION**

Recent rescue collecting at Laverockbraes has produced some of the finest crystallised specimens of manganite known from the British Isles. The mineralisation at the now-landscaped site has been recorded, its history summarised, and representative specimens analysed and added to museum collections. The project demonstrates the value of working cooperatively and responsibly. Permissions were sought from all interested
parties including, landowners, developers and Scottish Natural Heritage, which has a statutory responsibility for sites of mineralogical interest in Scotland. From a landowner’s perspective, fear of litigation resulting from an unforeseen accident is a major barrier to access. Professional conduct and strict compliance with site rules and safety procedures is usually all that is needed to alleviate this concern.

Manganese has an unusually complex geochemistry (Williams, 1990; Post, 1999). Three different oxidation states: Mn(II), Mn(III) and Mn(IV) are common in nature. Manganese unites with oxygen in \([\text{MnO}_6]\) polyhedra, which can combine to produce startlingly complex structures. This unusual flexibility in oxidation state and topology is reflected in the number of manganese oxide minerals that have been discovered. Manganese oxides are commonly precipitated by biological processes, and recycled by microbial activity. They provide a ready source of energy for chemotropic bacteria. As a result, the geochemistry of near-surface manganese deposits is a complex and specialised field of study. To complicate matters further, the mineralogy of manganese oxide mineral assemblages is strongly influenced by the presence of certain other ions in solution.

Figure 23. Manganite crystals up to 1 mm in length with a striated prismatic habit coated in thin films of an unknown chocolate-brown manganese oxide. Image assembled from 242 individual photos stacked at 10 μm intervals using a Zeiss 25 mm Luminar lens mounted on bellows. Michael McMullen Collection, photo John Chapman.

Manganite is the most abundant natural polymorph of MnO(OH). Crystallisation is catalysed by the presence of sulphate ions in solution (Williams, 1990: p. 136). Manganite is metastable with respect to pyrolusite in strongly oxidising surface conditions (Ramstedt and Sjöberg, 2005) and specimens labelled manganite are sometimes found to be pseudomorphed by pyrolusite. This is not the case at Laverockbraes, a number of crystals analysed by powder X-ray diffraction are manganite. However, pyrolusite was found as a minor component of a fine-grained manganite layer on a single specimen (Tom Cotterell, personal communication, 2019).

Specimens of manganite from Laverockbraes began to appear in collections at the start of the nineteenth century. As well as the common and vague ‘Aberdeen’, labels may describe specimens from Laverockbraes, Laverock-Braes, Laverock Braes, Grandhome (see below), Danestone, Middleton and may use the parish name of Old Machar as well as the erroneous Towie. Only Laverockbraes or its variants are sufficiently specific for there to be reasonable certainty that the location is the site described in the foregoing text. Danestone lies to the south of Laverockbraes and might equally describe specimens from the manganese workings near Hill of Danestone. Middleton is about 500 m east of the former site of
Laverockbraes Farm. Grandhome House is a little nearer to Laverockbraes than Hill of Danestone but it is impossible to be sure which deposit such a label might describe; to complicate matters further, Grandhome might also refer to the former site of Grandhome Mills, near to Hill of Danestone. Early mineralogical spellings of Grandhome include the phonetic Granham, Granam or Greenam; Grandholm and Grandholme, which appear in the Lanfine Collection catalogue at the Hunterian Museum; and Grandholm, which was the favoured spelling on Ordnance Survey maps until the beginning of the twentieth century when it was replaced by Grandhome.

The current Ordnance Survey spelling of Grandhome is preferred for modern labels, and it is suggested that the locality should be recorded as: “Manganese workings, NJ 917 111, Laverockbraes, Grandhome, Grandhome Estate, Aberdeen”. For collectors and institutions lucky enough to have a nineteenth-century specimen, all previous labels should, of course, be retained.

A fine specimen of manganite from the Heddle Collection at the National Museum of Scotland is illustrated in Livingstone (2002: p. 149). The locality is given as “Granham Towie, Aberdeenshire”. This is not sufficiently precise to be sure that it came from Laverockbraes, especially in the absence of modern specimens from the nearby deposit at Danestone with which to make comparison. Grandhome might conceivably refer to either deposit. In the appendix of Scottish mineral species, Livingstone (2002: p. 174) also describes “crystals (<2 mm) in cavities throughout massive pyrolusite [from] Bridge of Don”. This refers to the locality at Bridge of Don Industrial Estate (Chew, 1978).

The Laverockbraes deposit is not an isolated occurrence. Small deposits of manganese ore were discovered on the Haugh, a flat section of land near the River Don, during canal building and there are two other nearby occurrences: the deposit at Bridge of Don Industrial Estate overlies semipelitic rock of the Aberdeen Formation and the Hill of Danestone manganese mine lies near the outer edge of the Aberdeen Pluton.

A mineral reconnaissance assessment, which describes the occurrence of manganese in the Highlands of Scotland, notes the mode of occurrence at Laverockbraes as “Unknown” (British Geological Survey, n.d.). Contemporary sources mention veins (Sowerby, 1804); “irregular thin beds, rounded concretions or anastomosing films in the rock” (Anon., 1838); and ‘elongated lenses’ (T. C. Phemister’s interpretation in a letter to Murray MacGregor). Most recent specimens were extracted from a manganese-bearing vein plexus exposed in the wall rock at the side of the water-filled quarry. Although the rock-head was usually obscured by the overlying Banchory Till (Fig. 24) there was sufficient exposure to show that a network of veins cuts across the cleavage of the country rock, and post-dates the intrusion of the Ordovician Aberdeen Granite (Figs 25 and 26). Isolated masses of manganese and iron oxides were found in the till, but it is unlikely that they formed in situ (cf. Chew, 1978). They probably represent plumes of mineralised debris extending in the direction of the ice flow, which are common in glaciated terrain.

The east–west orientation of the relatively shallow workings, the presence of vein breccias and kaolination of the feldspars are consistent with mineralisation which was deposited from highly oxidising epithermal fluids in a fault zone. It seems most likely that the Laverockbraes deposit represents either a vein plexus associated with a fault zone, or an elongated stockwork with veins which locally coalesced to produce ore-grade sections.

Figure 24. During the excavations the rock head was usually somewhat obscured by loose heterogeneous iron- and manganese-rich deposits of the Banchory Till Formation.

Figure 25. Millimetre-scale manganese oxide veins surrounding clasts of coarse foliated granite. Specimen 9040 in the collection of Aberdeen University Geological Collection. Photo courtesy of the University of Aberdeen.
Recently collected specimens suggest that goethite was the first major mineral to form. The presence of manganite veinlets in fractures in goethite shows that the main-stage manganese mineralisation is later than the iron mineralisation. Baryte crystallised throughout, early baryte forms thin selvedges to the vein and coarse late-stage baryte is usually the last major primary mineral to be deposited as white bladed masses in cavities in goethite and manganite. Coarse fragments of mica and angular clasts of altered country rock are common in the veins. Feldspar in the selvedges usually show signs of alteration to white powdery kaolinite, and in some cases has been completely replaced.

Whole-rock analyses of pelitic metasediment from the Aberdeen area (e.g. Munro, 1986: p. 24) reveal manganese concentrations of about a tenth of a percent, a level which is typical of crustal rocks. Similar concentrations are present in amphibolite bodies in the Aberdeen Formation (Munro, 1986: pp. 29–30). Leaching of a relatively small volume of metasediment would be sufficient to supply the manganese required to form the Laverockbraes deposit.

Although recent remobilisation has deposited some limonite (Fig. 17) and fine-grained manganese oxides in the till, the major primary mineralisation at Laverockbraes is probably not recent. Bog manganese oxide deposits and bog iron ores tend to be fine grained and poorly crystalline. Vein fillings, coarsening toward the centre, with cavities containing large euhedral crystals of baryte, quartz and manganite, suggest crystallisation in a hydrothermal setting (Fig. 27). There are mineralogical similarities with the deposits that formed across the British Isles from oxidising iron-manganese- and barium-rich fluids during the Permian and Triassic periods.

Unfortunately the exhumation history of the Aberdeen Formation is not well constrained (Munro, 1986: p. 100). Burial depths are estimated at between 17 and 20 km during Caledonian metamorphism (Kneller and Aftalion, 1987) and although it is clear that a considerable amount of the superincumbent rock had been removed by the end of the Palaeozoic, the depth of burial during the Permian and Triassic is unknown (Cope et al., 1992). It is not possible, with the evidence currently available, to suggest an affinity with Permian and Triassic iron and manganese deposits with any certainty.

Another genetic possibility is deep weathering, with deposition of iron and manganese minerals in fault zones. In the Aberdeen area, zones of highly altered rock, which are interpreted as products of sub-tropical weathering during the Cenozoic (prior to Pleistocene glaciations), have been identified (Munro, 1986: p. 100). They commonly contain highly oxidised mineral assemblages and bear little or no relationship to the current periglacial topography.

In contrast to the vein plexus at Laverockbraes, manganite and goethite cement rounded cobbles of granitic rock at the Bridge of Don Industrial Site. Cavities within the conglomerate are commonly lined with euhedral manganese crystals and cockscomb baryte (Fig. 28). The Bridge of Don deposit is interpreted by Chew (1978) as of relatively recent origin. However, the presence of coarse baryte leaves this open to question. Could such large and coarse aggregates of baryte and manganite, without obvious admixed clay, have formed in periglacial conditions in the recent past? It seems unlikely.

Despite careful research and fieldwork, many questions remain unanswered. The age and genesis of the Laverockbraes deposit are not well constrained. There have been significant advances in isotopic age determination of oxidised assemblages in recent years. The decay of U and Th in goethite (Lippolt et al., 1998) produces $^4$He, and this can be used to date mineral formation if the $^4$He is retained. The retention of $^4$He can now be quantified reliably (Shuster et al., 2005; Heim et al., 2006; Monteiro et al., 2014). Thus, reliable dating of goethite from Laverockbraes is a real possibility. In addition, a few manganese oxide deposits have been dated using the $^{40}$Ar/$^{39}$Ar method (Vasconcelas et al., 2015). This technique relies on the presence of potassium-bearing species such as cryptomelane and hollandite. A more thorough analytical survey might reveal potassium-bearing species.

Figure 26. A manganite vein in foliated granite showing conspicuous flakes of silvery mica. The vein post-dates the development of the rock fabric and appears to be a relatively simple symmetrical fracture fill. Specimen size $80 \times 65 \times 40$ mm. Michael McMullen Collection, photo Roy Starkey.
No definitive record of working in the last half of the nineteenth century has been uncovered. The author would be pleased to hear from any reader with further information. The mineral coating prismatic manganite (Fig. 23) remains to be identified and the dendritic fern-like fracture fills in some specimens (Fig. 29) are also

Figure 27. A manganite vein with crystal-lined central cavities in migmatic matrix. The mineralisation extends into surrounding hairline fractures. Michael McMullen Collection, photo John Chapman.

Figure 28. Manganite with a crystal-lined cavity containing cockscomb baryte cementing rounded granitic cobbles, 180 × 145 mm specimen, from the Bridge of Don Industrial Site. Note that the ellipsoidal shape of the cobbles is not typical of glacial action. Philip G. Taylor specimen and photograph.

Figure 29. Bright metallic fern-like fracture fills of an unknown manganese oxide on quartz. A 110 × 100 × 40 mm specimen. Michael McMullen Collection, photo Roy Starkey.
uncharacterised. Manganese dendrites are commonly labelled ‘pyrolusite’, but undoubted pyrolusite dendrites of any kind are yet to be identified (Potter and Rossman, 1979). Given the abundance of baryte and manganese oxides, it is surprising that romanéchite has not been identified. It occurs at the nearby Bridge of Don deposit (Chew, 1978).

Further analyses and research would undoubtedly add to our understanding of the deposit; any such research requires a collection well curated and provenanced specimens. It is fortunate that rescue collecting in 2016 produced such a collection.

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WULFENITE FROM ROAR HILL, BALLATER, ABERDEENSHIRE:
A NEW SCOTTISH LOCALITY

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Recent groundwork at Roar Hill, on the eastern edge of the Cairngorms National Park in Aberdeenshire, has exposed veins containing baryte, cerussite, fluorite, galena, mimetite, pyromorphite and sphalerite. Wulfenite occurs as orange-red crystals ranging from sharply pointed ‘spires’ and equant bipyramids to rare octagonal tablets. The mineralisation is the product of supergene alteration of sparse base-metal sulphides associated with quartz-fluorite veins in the Ballater Granite.

INTRODUCTION

Although it was first reported in the nineteenth century, wulfenite was noted from few Scottish locations until relatively recently. It is now known to be widespread as small, sparse, inconspicuous crystals, which typically develop during the supergene alteration of lead-bearing mineral assemblages.

Surveys of Scottish wulfenite occurrences are provided in Rothwell and Mason (1992), Livingstone (2002) and Tindle (2008: p. 540). The first definite report appears to be from Lauchentyre Mine near Gatehouse of Fleet in southwest Scotland. It is described in Heddle (1901: p. 182) as follows:

“Lauchentyre in veins traversing rocks of Silurian Age, chiefly in cavities within quartz veins, and associated with Galena, Chalcopyrites; Malachite, Pyromorphite, Limonite, Chrysocolla”.

“In interpenetrating groups of small translucent, tabular crystals of a chrome yellow colour, some with a darker border and with a bright resinous lustre. A few shew [sic] the hemihedrism characteristic of the species”.

On the same page, Heddle notes “Reinite var. Eosite”, a ‘vanado-molybdate of lead’, in minute red octahedral crystals on pyromorphite and cerussite at Leadhills. This mineral was included in The Mineralogy of Scotland on the basis of a study by Albrecht Schrauf (1837–1897) curator of the Imperial Mineral Collection and later Professor at the University of Vienna (Schrauf, 1871; Veselovsky et al., 1997). The now obsolete name reinite has several connotations: modern glossaries tend to regard it as a synonym for ferberite pseudomorphs after scheelite, but this is a poor fit for the mineral described by Schrauf. In a review of the natural chromates of lead, Williams (1974: p. 400) noted:

“Schrauf (1871) described a new mineral from Leadhills in Scotland as eosite. His morphological data are exhaustively complete, and the crystals are clearly close to wulfenite, both in angles and habit”.

To complicate matters, an ‘eosite’ specimen from Leadhills, which Williams located in a collection of poorly characterised species at the Natural History Museum, proved to be phoenicochroite, and to add further to the confusion, Livingstone (1992) records that much of the so-called eosite from Leadhills in the collection of the National Museum of Scotland is vanadinite. The puzzle remained until relatively recently when some of Schrauf’s original material was located at the Natural History Museum. Analysis by energy-dispersive spectrometry conclusively shows that the original ‘reinite var. eosite’ from Leadhills is chromium-bearing wulfenite (Rumsey, 2019).

Sir Arthur Russell reported the next Scottish wulfenite locality (which he considered to be the fifth British occurrence), at Loch na Meine near Struy in Strath Glass (Russell, 1946). Small orange crystals occur with pyromorphite and cerussite in quartz-baryte veins in ancient metamorphosed sediments of the Tarvie Psammit Formation.

More recent finds can be divided into two categories: those encountered incidentally during the analysis of stream sediment samples; and discoveries made by amateur collectors after careful examination of lead-bearing supergene assemblages using stereomicroscopes.

The first category includes identifications from panned concentrate from the southeastern edge of the Grudie Granite, near Lairg in Sutherland; Bail Hill near Sanquhar in southern Scotland; and the Etive Granite Complex in Argyll (Tindle, 2008).

Reports of wulfenite in the Leadhills–Wanlockhead district of southern Scotland are summarised in Tindle (2008). The largely visual identifications must be treated with caution as Livingstone (1992) showed that a specimen from Whyte’s Cleuch was “molybdenian stolzite with a compositional range Pb(W0.75Mo0.25)O4 to Pb(W0.52Mo0.46)O4” and that another specimen from nearby Margaret’s Vein also contained significant amounts of tungsten. Specimens have been identified from about a dozen localities, typically as orange-red bipyramidal crystals, less than a millimetre in size, sparsely scattered on yellow-green drusy pyromorphite.

Wulfenite localities in southwest Scotland include Clatteringshaws Reservoir, Drumruck Mine, Kings Laggan Mine, Lauchentyre Mine, Pibble Mine and the
uranium-bearing veins which crop out around Needle’s Eye on the Solway Coast (Rothwell and Mason, 1992). Analyses from southwestern Scotland reported in Livingstone (1992) are all near to molybdate end-member composition, although there was a tentative identification of stolzite from Girthon in Dumfries and Galloway in the nineteenth century (Dudgeon, 1890).

Wulfenite occurs at Abergairn Mine near Ballater in the Cairngorm National Park as elongated orange to yellow bipyramids and thin yellow tabular crystals, in galena-bearing quartz veins with low-temperature feldspar and fluorite (Tindle, 2008). It occurs as colourless to buff bipyramids and unusual purplish grey blocky crystals in the Ag-Bi-Mo-Sn-W zinnwaldite greisen near Gairnshiel Bridge in Glen Gairn northwest of Ballater (Meikle, 1990; Livingstone, 1992; Webb et al., 1992). It has also been found in cavities in granite at Creag an t-Seabhaig on the north side of the Pass of Ballater (Livingstone, 1992). Analyses reported in Livingstone (1992) from this area are all near to the molybdate end-member composition, although tungsten was found in an elongated prismatic yellow crystal from Abergairn Mine examined by energy dispersive X-ray analysis at Manchester University (David Green, personal communication, 2019).

Other wulfenite occurrences in the Highlands of Scotland include inconspicuous pale buff crystals on galena in the lead veins near Tyndrum (Wolfe, 2006) and a single specimen with a few minute pale brown elongated bipyramids from the dumps of Whitesmith Mine near Strontian (Richard Bell, personal communication, 2018).

**LOCATION AND GEOLOGY**

Roar Hill rises to a little over 530 m about 7.5 km NNE of Ballater on the eastern edge of the Cairngorm National Park. The surrounding country is mountainous, reaching 872 m at Morven a little more than 2 km to the WNW and 604 m at Culblean Hill about the same distance to the south. The area is dominated by heather moorland and is part of the Dinnet Estate.

Lead-bearing vein mineralisation was exposed during recent work carried out on an unmetalled vehicle track. A small temporary quarry (Fig. 1) at NJ 4094 0207 exposed fluorite-bearing quartz veins and minor wulfenite. At a second site, a little further to the west [NJ 4032 0198] track-making activities exposed an oxidised galena-bearing quartz vein (Fig. 2).

The veins lie within pale Silurian leucogranite of the Ballater Pluton, which was intruded into rocks of the Dalradian Supergroup during Caledonian mountain building. The Ballater Granite is a rather variable
intrusion which extends over an area of about thirty square kilometres around Ballater and Cambus O’ May. It is described in Smith et al. (2002: pp. 98–100), who note a high volatile content and an abundance of late-stage fluids.

On the geological map of the area, the quarry is located near the edge of a small undifferentiated ultramafic body of the Ordovician Morven-Cabragh Pluton (British Geological Survey, 1995). The hillside in this area was densely vegetated heather moorland until the underlying rock was exposed during recent track-building activity. The primary survey was probably based on exposed boulders, which do not, at this point, reflect the underlying geology.

MINERALS

Identifications were made at the National Museum of Scotland in Edinburgh and the Hunterian Museum in Glasgow. Mineralisation at the quarry site is relatively simple with quartz-fluorite veins containing minor wulfenite. Minor baryte is present in the nearby lead vein which was exposed during track-making. The supergene assemblage at this second site is more varied, including cerussite, mimetite, pyromorphite and wulfenite. The sites are described as ‘quarry’ and ‘track’, respectively, in the following text.

BARYTE, BaSO₄

Baryte was found as blocky white crystals and cleavages in vein quartz at the exposure on the estate track.

CERUSSITE, PbCO₃

Cerussite occurs as a white overgrowth on partly corroded galena crystals in vein quartz at the track exposure. On some specimens a phase with a visual similarity to anglesite is also present, but no analysis has been undertaken.

FLUORITE, CaF₂

Cavities lined with pyramidal quartz crystals, low-temperature potassium feldspar and fluorite were common in veins exposed at the former quarry site. Most of the cavities are narrow and although crystal sections up to 25 mm across were found, complete fluorite crystals rarely exceed 5 mm on edge. Many crystals have distinct blue to purple colour zones, and in a few crystals a dark purple corner is present (Fig. 3). The intensity of the colour zones is particularly evident in broken crystal sections (Fig. 4). Although fluorite appears to be absent at the track locality its former presence is betrayed by the presence of cubic epimorphs. Similar epimorphs occur at the quarry site.

Figure 3. Translucent matt fluorite cubes with conspicuous dark purple corners in a quartz-lined cavity from the quarry exposure on Roar Hill. Field width 6.5 mm. Michael McMullen Collection; photo John Chapman.

GALENA, PbS

Galena occurs as altered crystals in vein quartz at the track exposure. It is commonly overgrown by cerussite and possibly anglesite and may be associated with lime-green crustose pyromorphite, brown spheroidal mimetite and drusy orange wulfenite.

QUARTZ, SiO₂

Quartz is the principal vein mineral at both localities on Roar Hill. It occurs as small clear to smoky single crystals and drusy crystal groups with pyramidal terminations lining thin planar cavities up to 25 cm long at the quarry exposure. Similar specimens up to about 15 cm were found at the track exposure.

MIMETITE, Pb₅(AsO₄)₃Cl

Shiny brown spherules with green pyromorphite, on pyramidal quartz (Fig. 5) were identified by energy-dispersive X-ray analysis as mimetite (John Faithfull, personal communication, 2018). The presence of mimetite suggests that a primary arsenic-bearing mineral was present in the vein assemblage.

PYRITE, FeS₂

Fine grains of a silvery metallic mineral are tentatively identified as pyrite.

PYROMORPHITE, Pb₅(PO₄)₃Cl

Pyromorphite occurs as lime-green to yellow crusts and thin coatings in quartz-lined cavities at the track location (Fig. 5). Analyses suggest that minor OH is present in substitution for Cl in some specimens (Brian Jackson, personal communication).

SPHALERITE, ZnS

Sphalerite occurs as honey-brown crystals and cleavages in partly corroded galena at the track exposure. It is much less common than galena. No zinc-bearing supergene minerals have been found at either site.

WULFENITE, PbMoO₄

Wulfenite was identified by X-ray diffraction in vein quartz at the quarry and track exposures. Analyses show that it is close to the molybdate end member. At the quarry exposure it occurs as bright orange to red tabular to bipyramidal crystals, easily visible to the naked eye, covering areas of colourless to smoky quartz matrix up to about 6 mm across. Similar specimens were found at the track exposure, where wulfenite is commonly associated with pyromorphite. Crystal habits are variable (Figs 6—9).
DISCUSSION

The discovery of wulfenite and other lead-bearing supergene minerals at Roar Hill adds to a small suite of similar occurrences along the eastern margin of the Cairngorms. Wulfenite has been identified in cavities in granite on the cliffs of Creag an t-Seabhaig, and it occurs in quartz-fluorite veins with low-temperature feldspars at Abergairn Mine, about 500 m to the west of the exposed edge of the Ballater Granite (Smith et al., 2002).

It is also present in veins in greisen on the edge of the Glen Gairn Pluton at Gairnshiel Bridge, northwest of Ballater (Tindle, 2008).

Reports of the presence of wulfenite in stream sediments in Scotland reveal its chemical stability and persistence in near-surface conditions. It has been noted in other mineralised areas around the edges of granitic plutons and is likely to be more widespread than records currently suggest.

Figure 5. Dark brown resinous globular mimetite with thin green pyromorphite crusts on pyramidal quartz from the trackside exposure on Roar Hill. Michael McMullen Collection; photo John Chapman.

Figure 6. Blocky orange wulfenite crystals up to about 0.4 mm across on pale smoky quartz, from the trackside exposure on Roar Hill. Michael McMullen Collection; photo John Chapman.

Figure 7. Elongated wulfenite spires up to about 0.6 mm in length with slightly curved prism faces terminating at a sharp point, from the trackside exposure on Roar Hill. Michael McMullen Collection; photo John Chapman.
Figure 8. Elongated orange wulfenite, 0.9 mm in length, with horizontally striated curved prism faces terminated by a well formed pinacoid, overgrown by minutely drusy pyromorphite, from the trackside exposure on Roar Hill. Michael McMullen Collection; photo John Chapman.

Figure 9. Blocky orange wulfenite crystals up to 0.3 mm on edge with rather matt, pitted surfaces, the principal forms appear to be the pyramid \{112\} and pinacoid \{001\}; the corners of some of the crystals are probably truncated by \{201\}. A few of the crystals show a degree of hemihedral development not unlike that reported at Loch na Méine near Struy (Russell, 1946: p. 151). From the trackside exposure on Roar Hill. Michael McMullen Collection; photo John Chapman.
The variation in the crystal habit at Roar Hill is considerable. It bears comparison with Loch na Méine near Struy in Strath Glass where Sir Arthur Russell measured a number of crystals and commented on their unusual habits. His description (Russell, 1946: p. 151) bears repetition:

"Wulfenite occurs ... as very small, not exceeding 2 mm., crystals, which, minute as they are, appear both beautiful and interesting when viewed under the microscope. Their colour is orange-red, rarely golden yellow with blotches of red; and their habit, except in the case of one crystal, is acute pyramidal, which is distinctly rare for this species and has not previously been observed at the four other British localities, where the crystals are always tabular in habit. ... Sometimes as many as 25 minute crystals are present on a square inch of the pyromorphite-covered surface. The wulfenite appears to have been the last mineral formed. In a few cases wulfenite crystals are penetrated by and have grown round prisms of pyromorphite. The crystals are sharp and well defined and consist of the acute pyramid (111) either alone ... or usually in combination with (221), the prism (110), and base (001). The faces (111) are slightly curved except at the apex and merge by repetition into those of (221) and (110), giving the whole crystal a curved outline, some in fact being almost barrel-shaped ... The apparent hemihedral development is shown ... The basal plane (001) is never smooth, the surface being either square-pitted or studded with innumerable extremely minute (111) pyramids. The faces of (110) are horizontally striated from repetition with the adjoining pyramids, while on most of the crystals the surfaces of (110), (221), and (111) are covered with raised and overlapping outlines of acute pyramids giving them a scaly appearance".

Improvements in photography since Russell’s time, particularly the use of focus stacking techniques, which allow small crystals to be recorded with good resolution and depth of field (Savazzi, 2011), mean that crystal drawings are less common as accompaniments to descriptive papers. Russell’s nuanced descriptions of curved or scaly faces would, nowadays, almost certainly be accompanied by a photograph. At Roar Hill wulfenite occurs in a variety of crystal habits, these include:

1) minute sharply pointed almost acicular pyramids with faces that appear slightly curved under the optical microscope (Fig. 7);
2) steeply pyramidal crystals with reasonably plane d (201) faces terminated by small a {001} (sketch 1 in Fig. 10);
3) pyramidal crystals with steep curved pyramid faces and flat pinacoidal terminations (Fig. 8);
4) equant blocky crystals with about equally developed prism m {101} and pinacoid a {001} forms (sketch 2 in Fig. 10);
5) equant crystals with matt surfaces and varying development of the pyramid s {112} and pinacoid a {001}, some showing hemihedral development (Fig. 9 and sketch 3 in Fig. 10);
6) tiny bipyramidal crystals dominated by {112} with a pseudo-octahedral habit;
7) rare tabular crystals, some with an octagonal outline, bounded by steep pyramids with the forms {h0l} and {hkl} with h = k which are too small to measure.

Similarities between Roar Hill wulfenite and the crystals from Loch na Méine (Russell, 1946: p. 152) are striking. At both localities steeply pyramidal forms with slightly curved faces predominate. Little is known about the influence of chemical conditions on the crystal habit and colour of wulfenite. However, it seems likely that the two sites experienced similar supergene environments, with cerussite, pyromorphite and wulfenite being the most abundant secondary minerals in both cases.

Fluorite is not uncommon in vein quartz in and around the Ballater Pluton (Smith et al., 2002). The dark purple colour zones in fluorite from Roar Hill (Fig. 11) are visually similar to those found in Derbyshire Blue John (Ford, 2019). They are caused by a type of colour centre (F-centre) which is associated with defects in the crystal lattice. Sites in the crystal lattice where a fluoride ion is missing are typically present at a level of about 0.01% in natural fluorite crystals. They do not in themselves, produce colour, but in certain circumstances can trap an electron to produce a colour centre. This may occur if the crystal lattice is exposed to ionising radiation. A defect containing a trapped electron is very effective at absorbing specific wavelengths of visible light. It produces a characteristic blue colour (Nassau, 1983: pp. 184–203).

It is clear from the sharpness of the banding that the process that produced the colour zones in fluorite from Roar Hill was localised. Radiation damage seems the most likely
cause. Alpha or beta particles, which typically penetrate just a few tens of micrometres into solid matter, are a possibility (Nassau, 1983: p. 197). Gamma rays are less likely as they can traverse considerable thicknesses of solid material, producing a more uniform colouration. The banding may reflect changes in solution chemistry during crystallisation (perhaps an episodic increase in the concentration of radioactive elements) or the accumulation of colour centres at surfaces exposed to slightly radioactive hydrothermal solutions over a long period of time. The banding patterns and sharpness of the blue to colourless transitions deserves further research, but such investigations are beyond the scope of this descriptive note.

The dark purple corners (Fig. 3) to some cubes are intriguing. Complex colour zonation is well known in fluorite, but vertex-specific effects are unusual.

There is little chance of finding further specimens at the sites. The quarry exposure has been landscaped and the moorland restored at the request of Scottish Natural Heritage. However, such sites may be more common on the eastern flanks of the Cairngorms than current records suggest, much of the rock in the area is obscured by vegetation and collectors are few.

ACKNOWLEDGEMENTS

Thanks go to John Hay, Head Keeper for the Dinnet Estate for his advice about the site and allowing access; Brian Jackson, formerly of the National Museum of Scotland for initial analysis of specimens; John Faithfull, Curator (Mineralogy/Petrology) at The Hunterian, University of Glasgow for additional mineral analysis and general guidance. David Green helped with a literature search and John Chapman is thanked for his excellent images of small areas of the specimens. Alec Livingstone generously acted as referee.

REFERENCES


Lettermuckoo Quarry is a small abandoned working near the hamlet of Kinvarra in Co. Galway. It is situated near the faulted eastern edge of the Errisbeg Townland Granite, a megacrystic pink to grey monzogranite which forms part of the Galway Batholith. A roughly east–west striking vein which cuts across the quarry produced octahedral purple fluorite crystals up to about 20 mm on edge. The vein assemblage also includes tabular baryte, lamellar to prismatic calcite, sphenoidal chalcopyrite, galena, prismatic quartz and resinous green sphalerite. Supergene alteration is minimal, but wulfenite has been identified as poorly formed yellow to orange blocky bipyramidal to tabular crystals up to about 1 mm on edge.

INTRODUCTION

The granitic intrusions of Connemara and Galway Bay, and the surrounding metamorphic rocks, host numerous minor fluorite occurrences (O’Raghallaigh et al., 1997; Reynolds et al., 1990). Some of the localities, such as the Inveran and Glengowla East mines, have been known since the nineteenth century for fluorite specimens. Although little now remains at Inveran, Greg and Lettsom (1858) record fluorite as “fine octahedral crystals, ... with blende and calamine”. Glengowla East Mine produced lead and zinc ore and baryte from a vein in marble host rock. It is currently operated as a ‘show mine’ and a few specimens are on display at the site museum. Its history, geology and minerals are described by Moreton (2019). A pale green octahedral fluorite crystal, 70 mm across, from Glengowla and now in the Russell Collection at the Natural History Museum, is figured on the front cover of volume 5, part 2 of this journal.

There are a number of granite quarries, which are either working or have been worked until relatively recently, in the southern part of the region. Fluorite occurs in most of them, specifically at the quarry at Toombeola; at quarries along the roadside at Tully (Walsh’s Quarry now disused, the neighbouring Flaherty’s Quarry just to the south and currently active, and a tiny disused working opposite); at a quarry by the roadside 1.2 km northeast of Bovroughaun Hill (Larkins’ disused quarry); at quarries along the roadside at Tully (Walsh’s Quarry now disused, the neighbouring Flaherty’s Quarry just to the south and currently active, and a tiny disused working opposite); at a quarry by the roadside 3 km north of Kinvarra; at a disused quarry by the roadside 3 km north of Kinvarra; at a disused quarry at Rossaveel (Barr Flannery, personal communication, 2016); and at Lettermuckoo Quarry, 1.5 km southeast of Kinvarra. Traces of fluorite are also present in quarries in the surrounding metamorphic rocks at Ardragh, just south of Maam Cross, and at Recess.

Most of the fluorite from these locations is of little interest from a specimen point of view. It typically occurs as thin veneers on joint surfaces and is usually massive, or crystallised but shattered. However, in 2015, a spectacular discovery was made at Shannapheasteen Quarry (Parkes, 2017). The quarry, which is worked by its owners, the Larkin brothers, has attracted considerable interest among collectors for the size and perfection of its fluorite specimens. It is currently the subject of a study by staff at the National University of Ireland, Co. Galway (Martin Feely, personal communication, 2019) and is not discussed further here.

Prior to the discovery at Shannapheasteen Quarry, Lettermuckoo Quarry (Fig. 1) was the principal modern producer of crystallised fluorite specimens in the district (followed by Walsh’s Quarry). The quarry is situated along a track off the east side of the Maam Cross to Costelloe road, at Irish grid reference L 9824 3229, near the hamlet of Kinvarra (not to be confused with the town of the same name south of the city of Galway, in Co. Clare).

Lettermuckoo Quarry’s specimen potential was first recognised by John Fisher. Nick Peters subsequently recovered many fine specimens. The locality is commonly described on specimen labels as ‘Tess’ Quarry’, after its (now deceased) owner Mickey Tess, or occasionally as ‘Lough Naskeha Quarry’ after a nearby lough. As it is located in Lettermuckoo townland, it is more properly called Lettermuckoo Quarry. This name is adopted here and is used in most recent descriptions (e.g. Mindat, 2019).

The minerals at Lettermuckoo Quarry are hosted by the Errisbeg Townland Granite, a megacrystic pink to grey monzogranite, with occasional pegmatic segregations. Further information about the petrology of the Caledonian granites in the area is provided in Feely et al. (2006) and Morris et al. (1996).

MINERALS

The fluorite and associated minerals from Lettermuckoo Quarry, listed alphabetically in the
following text, are confined to joints in the granite, and a narrow east–west trending vein, rarely more than a few centimetres wide, which crosses the working near its mid-point. Two smaller veins are reported as present by other collectors (Nick Peters, personal communication, 2019) but were not seen by the authors. The rock-forming minerals are not discussed further.

BARYTE, $\text{BaSO}_4$

Platy white baryte is one of the principal minerals in the vein assemblage. It commonly overgrows fluorite, a paragenetic sequence which is typical of other similar localities. The crystals occur as delicate lath-like aggregates and thin tabular plates up to about 20 mm across (Fig. 2).

Figure 1. The relatively shallow workings of Lettermuckoo Quarry as they stood in 2003. The quarry is developed in Caledonian Granite of the Galway Batholith and extends for about 50 m from east to west (left to right in the photo) and about 150 m south from an unmetalled track. Photo Stephen Moreton.

Figure 2. Platy white to pale pinkish brown baryte overgrowing dark purple fluorite with green resinous sphalerite. Specimen is 140 mm across; enclosing carbonate has been removed using dilute orthophosphoric acid. Collection and photo Stephen Moreton.
 CALCITE, CaCO₃

White calcite is a common vein filling, and was the last major primary phase to be deposited. On many specimens from Lettermuckoo Quarry, calcite has been removed using dilute acid to expose crystals of the paragenetically earlier phases. As the space in which calcite formed is usually very restricted, it rarely forms euhedral crystals. Those that do occur are typically lamellar to short prismatic in habit and up to about 10 mm across (Fig. 3). Rarely, small (<2 mm) acicular crystals occur.

CHALCOPYRITE, CuFeS₂

Tiny (<1 mm) golden crystals of chalcopyrite occasionally overgrow fluorite and baryte. Rarely, isolated sphenoidal crystals and crystal groups, which may reach several millimetres across, occur.

CHLORITE GROUP,
(Mg,Fe)₃(Si,Al)₄O₁₀(OH)₂·(Mg,Fe)₃(OH)₆

Patches of a powdery green chlorite-group mineral are present on a few specimens. One analysis by energy-dispersive X-ray spectrometry revealed that iron was present in much greater amounts than magnesium, and the species is therefore chamosite. Another analysis of a fluorite-contaminated sample revealed that molar iron and magnesium were about equal, corresponding to a composition near the boundary between chamosite and clinochlore.

FLUORITE, CaF₂

Fluorite and quartz are the principal early phases in the paragenetic sequence. Fluorite was occasionally found as free grown crystals, but on most specimens calcite was removed using dilute orthophosphoric acid to reveal earlier fluorite. Crystals vary from medium to very dark purple, and are invariably octahedral. The largest crystals are up to about 20 mm on edge, but tend to be crude and may be somewhat shattered; smaller examples, up to about 5 mm or so, can be better developed (Figs 4–6).

GALENA, PbS

Small masses of galena, up to around 20 mm across were occasionally found, but euhedral crystals are very rare.

Figure 3. Squat prismatic hexagonal calcite overgrowing dark purple fluorite on an 80 × 50 mm specimen. Robert Lawson Collection, photo Stephen Moreton.
QUARTZ, SiO$_2$

Colourless to translucent white slender quartz prisms formed early in the sequence. They rarely exceed 30 mm in length.

SPHALERITE, ZnS

Sphalerite occurs occasionally as resinous green masses up to about 20 mm across, and rarely as complex crystals typically no more than a few millimetres in size (Fig. 7).
WULFENITE, PbMoO₄

Poorly formed yellow blocky to tabular wulfenite crystals up to about 1 mm on edge were found by Nick Peters and identified at Manchester Museum (Nick Peters, personal communication). Minute orange bipyramidal crystals were subsequently found by Richard Bell, in the interstices between octahedral fluorite crystals.

**DISCUSSION**

Lead, zinc and copper mineralisation in quartz-fluorite-baryte-calcite gangue is widely developed in the Galway Batholith and surrounding metamorphic rocks (O’Raghallaigh et al., 1997; Reynolds et al., 1990). It may be Mid to Late Triassic, making it much younger than the granite, which is Caledonian (Devonian) in age (Feely et al., 2006).

The occurrence at Lettermuckoo Quarry is noteworthy for the quality of the octahedral fluorite crystals which, although not large, are often perfectly formed, with an intense dark purple colour. Baryte, calcite, chalcopyrite and sphalerite also occur as well crystallised specimens, although much less commonly than fluorite.

Although some of the vein minerals were collected from just a few metres below the current land surface, supergene alteration of the lead, copper and zinc sulphides is minimal. The only supergene species recorded in this study is wulfenite.

In view of the widespread nature of this style of mineralisation in and around the Galway Batholith, and the recent spectacular fluorite find at Shannapheasteen, other similar occurrences must surely await discovery. Readers should note that Lettermuckoo Quarry is now abandoned and flooded. The specimens described and figured herein were collected in the early to mid-2000s while active quarrying was taking place. If quarrying is resumed further material may become available, but there is little to be seen at the locality as it currently stands.

**ACKNOWLEDGEMENTS**

The authors are grateful to the late Mickey Tess of Carraroe for permission to collect specimens at Lettermuckoo. Thanks go to Nick Peters and David Green for useful comments and information, and to the referees who made suggestions which improved the manuscript.

**REFERENCES**


Distinctive pale amethyst-purple muscovite occurs with hyalophane, albite and baryte in veinlets in Ba-feldspar-hematite matrix at Benallt Mine, near Rhiw, Pen Llyên, Gwynedd, Wales. It contains between 3.70 and 5.24 wt% BaO and has an empirical formula \( (\text{Ba}_{0.12}\text{Na}_{0.01}\text{K}_{0.83})(\text{Al}_{1.95}\text{Mn}_{0.05}\text{Mg}_{0.01})[(\text{Si}_{2.96}\text{Al}_{1.04})\text{O}_{10}](\text{OH})_{2} \). The purple colour reflects the relatively high manganese content and low iron content of the mica. Hyalophane, a barium-rich microcline feldspar with a mean empirical formula \( (\text{K}_{0.59}\text{Ba}_{0.39}\text{Na}_{0.04})(\text{Si}_{2.63}\text{Al}_{1.37})\text{O}_{8.3} \), occurs in intimate association with muscovite and albite. Its mean composition can be written 4 mol.% albite, 38 mol.% celsian and 58 mol.% K-feldspar. Hyalophane-albite geothermometry shows that the mineral assemblage formed in low-grade metamorphic conditions.

INTRODUCTION

Benallt Mine, near the village of Rhiw at the southwestern end of Pen Llyên in Gwynedd, is one of the most important and diverse mineralogical sites in Britain. It is the type locality for three mineral species, banalsite, pennantite and cymrite, and is host to a number of uncommon manganese-bearing minerals, including bannisterite, eggletonite, feitknechtite, ganophyllite, kinoshitalite, piemontite-(Sr) and tamaite (Campbell Smith et al., 1944a,b, 1946, 1949; Cotterell, 2008, 2012; Tindle, 2008; Cotterell and Tayler, 2012; Dyer et al., 2014). The locality is noted for uncommon barium minerals, some of which are uniquely well crystallised (Russell, 1911; Spencer, 1942; Campbell Smith et al., 1944a,b, 1949; Campbell Smith, 1945).

Benallt Mine worked a series of metamorphosed exhalative manganese deposits in marine mudstones of Lower Ordovician age (Gibbons and McCarroll, 1993). Structurally complex lenticular barium- and manganese-bearing orebodies, affected by later faulting and alteration, lie between high-level basic intrusions (Brown and Evans, 1989). Geological résumés are provided in Bevins and Mason (2010) and Cotterell (2012). Much useful information is also included in a report produced by Arthur Groves (1952), who oversaw the final phase of mining during the Second World War.

This note describes veinlets of pale amethyst-purple muscovite, containing baryte, albite and barium-rich feldspar, collected by staff at Amgueddfa Cymru – National Museum Wales (AC—NMW) and members of the Russell Society from the dumps at Benallt Mine. Permission to collect was obtained from the landowner and Natural Resources Wales.

SPECIMENS

In 2006 one of the authors (TFC) collected a distinctive pale amethyst-purple micaceous mineral, as millimetre-wide veinlets, cutting rather decomposed iron-rich rock on the dumps at Benallt Mine (Figs 1 and 2). Powder X-ray diffraction (PXRD) (analysis numbers NMW X-1618 and NMW X-1749) produced a good match for muscovite, with minor celsian\(^2\) presumed to be derived from the groundmass (NMW X-1749).

In 2010, another of the authors (ID) collected a similar micaceous mineral on a Russell Society field visit. A small fragment (NMW 2018.19G.M.1) was submitted for identification. Powder X-ray diffraction (PXRD) (analysis numbers NMW X-1618 and NMW X-1749) produced a good match for muscovite, with minor celsian\(^2\) presumed to be derived from the groundmass (NMW X-1749).

\(^1\) Formerly Amgueddfa Cymru – National Museum Wales, Cathays Park, Cardiff, CF10 3NP

\(^2\) Quantitative chemical analysis by wavelength-dispersive X-ray spectrometry has subsequently shown that the feldspar is barium-rich microcline rather than celsian.
ANALYSIS

Preliminary analyses by energy-dispersive spectrometry (EDS) on a scanning electron microscope, were conducted by HK at AC—NMW on a polished block (NMW 2018.19G.M.1a). They showed that the muscovite contained a significant amount of barium. Subsequent electron probe microanalysis (EPMA) by wavelength-dispersive spectrometry (WDS) conducted by AGT on the same polished block confirmed the presence of barium, in the range 3.70–5.24 wt% BaO, and also identified manganese. Twenty spot analyses (Table 1) taken in a traverse (AA) across the muscovite (Fig. 3) reveal a mean BaO content of 4.25 wt%. The manganese content varies between 0.68 and 0.99 wt% MnO, with a mean value of 0.81 wt%.

Electron probe microanalyses of mineral grains with obvious atomic number contrast in the muscovite veinlets showed that albite, hyalophane (Table 2) and baryte were also present (Figs 3 and 4). Further investigations of sample NMW 2018.16G.M.1a, using PXRD, revealed that the central portion of the muscovite veinlets contain white baryte (NMW X-3381) which has, in places, corroded (see Fig. 4, which shows specimen NMW 2018.16G.M.1a). The red groundmass consists of hematite, Ba-feldspar and muscovite (NMW X-3383). A number of minute blocky colourless crystals have not been identified.

A polished thin section (NMW 2018.19G.M.1b) prepared from the material collected by ID revealed that in transmitted light the barium-rich muscovite is optically indistinguishable from end-member muscovite.

Table 1. Analyses of barium-rich muscovite (specimen NMW 2018.19G.M.1a) from Benallt Mine (traverse AA in Fig. 3), by wavelength-dispersive spectrometry using an accelerating voltage of 20 kV, beam current of 20 nA and a 10 μm defocused beam. Only those element that make a significant contribution to the empirical formula (>0.01 atoms per formula unit) are listed. Elements analysed but not reported (column 8) include Ti, Mg, Ca, Fe and Zn. The low totals are due to the inability of microprobe techniques to measure OH.

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Figure 1. Pale amethyst-purple barium-rich muscovite veinlet from Benallt Mine. Specimen NMW 2018.16G.M.1b. Photo Tom Cotterell.

Figure 2. Pale amethyst-purple barium-rich muscovite veinlet from Benallt Mine. Specimen no. NMW 2018.16G.M.1a. Photo Tom Cotterell.

DISCUSSION

The distinctive colour of muscovite from Benallt Mine is almost certainly due to manganese. Octahedrally coordinated manganese is a common cause of pink to purple colouration (Nassau, 1978) and its role as a chromophore in mica is noted in Deer et al. (2013). The analytical data (Table 1) show that barium-rich muscovite from Benallt Mine contains up to 0.99 wt% MnO, with an average of 0.81 wt%. Muscovite of a similar colour from Franklin, New Jersey contains about 0.8 wt% MnO (Dunn, 1984). Neither of these muscovites contain much iron (the mean value for the Benallt sample is just 0.05 wt% FeO). Iron is a strong chromophore and masks the colour produced by manganese if it is present in more than trace quantities. The distinctive purple colour appears to be a reflection of the relatively high manganese content and low iron content of the specimens from Benallt Mine.

Barium is an uncommon substituent in muscovite on a worldwide basis (Tischendorf et al., 2007), but is not obviously related to the unusual colour. Neither barium-rich muscovite from Aberfeldy in Scotland (Fortey and Beddoo-Stephens, 1982) nor the even more barium-rich mica ganterite3 from the Berisal Complex, Simplon Region, Switzerland (Graeser et al., 2003; Hetherington

![Figure 3. Back scattered electron image showing barium-rich muscovite (dark grey), hyalophane (pale grey) and baryte (white) from Benallt Mine. The analyses listed in Table 1 were made along the traverse AA. The other letters show where various grains of hyalophane were analysed (listed in Table 2). The black areas are holes in the specimen infilled with resin. Specimen no. NMW 2018.19G.M.1a. Photo Andy Tindle.](image)

![Figure 4. Back scattered electron image showing barium-rich muscovite (grey), hyalophane (pale grey), albite (dark grey) and baryte (white) from Benallt Mine with spot analyses of hyalophane and albite marked (listed in Table 2). The large grain of baryte (lower right) has a particularly irregular outline suggesting some remobilisation. The black areas are holes in the specimen infilled with resin. Specimen no. NMW 2018.19G.M.1a. Photo Andy Tindle.](image)

3 Ganterite, the barium analogue of muscovite, is discussed in Green et al. (2019).
et al., 2003) or the Lincoln Hill dumortierite deposit near Oreana, Nevada (Ma and Rossman, 2006) is pink or purple.

The muscovite and feldspars (Figs 3 and 4) are intergrown in what appears to be an equilibrium assemblage at Benallt Mine. As muscovite-plagioclase and various barium feldspar geothermometers have been proposed (Green and Usdansky, 1986; Essene et al., 2005) it is reasonable to ask whether the way in which barium, sodium and potassium partition into the minerals reveals anything about the conditions of formation. Substitution in micas is relatively complex (Rieder et al., 1998). A review is provided in a companion paper (Green et al., 2019).

The data listed in Table 1 produce a mean empirical formula, on the basis of an idealised \([O_{10}(OH)_2]\) anion group, of:

\[(B_0.12N_0.01K_0.83)_{2.00}\text{Na}_{1.00}\text{Mg}_{0.01}\text{Al}_{1.00}O_{10}(OH)_2,\]

There is significant substitution of barium for potassium in the interlayer and of manganese for aluminium in the central octahedrally coordinated layer. The occupancy of the interlayer, which is represented by the first bracket in the formula, is low and variable. The calculations are discussed in more detail in a companion paper (Green et al., 2019), which concludes that the mica is strictly dioctahedral, and that the low and variable interlayer occupancy probably reflects some form of illitic alteration.

The Ba:Na:K ratio in the interlayer is an important parameter in thermodynamic models which involve mica-feldspar equilibria. Simple muscovite-plagioclase geothermometers have been proposed (e.g. Green and Usdansky, 1986), but the possible illitic alteration and abundance of barium at Benallt Mine (Green et al., 2019) make any interpretation problematic.

A more promising way to characterise the conditions of formation involves coexisting albite-hyalophane pairs. Essene et al. (2005: p. 529) note:

“The amount of Na in hyalophane progressively increases with metamorphic grade when buffered in the presence of albite ... In diagenetic associations, hyalophane has 3-7 % Ab\(^{13}\). In the blueschist and greenschist facies, hyalophane takes up 7-11 % Ab ... in the presence of albite, and 14-18 % in the lower to mid-amphibolite facies ... Hyalophane in the upper amphibolite to granulite facies may have 30 % Ab ... even when unbuffered with a separate albite phase”.

Hyalophane\(^5\) was originally identified at Benallt Mine at the beginning of the twenty-first century (Richard Tayler, personal communication, 2002), but the data listed in Table 2 appear to be the first quantitative analyses. The mean composition, \((K_{0.59}Ba_{0.39}Na_{0.04})(Si_{2.63}Al_{1.37})O_{8.00}\), should strictly be described as a barium-rich microcline (as K>Ba). However, the term hyalophane is useful in discussions of barium feldspars as it provides an easy way to differentiate end-member celsian, albite and microcline from barium-rich intermediate compositions.

Two grains of albite are labelled in Figure 4. One grain (BH) is very close to the ideal end-member composition; on the basis of eight oxygen atoms, its formula is \(Na_{1.01}Si_{3.00}Al_{1.00}O_{8.00}\). A second grain (BI) contains potassium and a small amount of barium, its formula is:

\((K_{0.12}Ba_{0.02}Na_{0.83})(Si_{2.96}Al_{1.03})O_{8.00}\).

Assuming that the albite and hyalophane are in an equilibrium assemblage\(^6\) an estimate of the conditions of formation can be made from the sodium content of the hyalophane. The mean composition of the four hyalophane analysis points (labelled BK – BN) nearest to the albite grains (on the basis of eight oxygen atoms) is:

\((K_{0.62}Ba_{0.34}Na_{0.04})(Si_{2.68}Al_{1.31})O_{8.00}\).

This can be written 4 mol% albite, 34 mol% celsian and 62 mol% K-feldspar and is consistent with mineralisation in low-grade metamorphic conditions (zeolite to prehnite-pumpellyite facies) (Essene et al., 2005: p. 529).

A compilation of celsian—K-feldspar—albite phase diagrams for different metamorphic grades (Essene et al., 2005: p. 528) shows that there is a complete solid solution between K-feldspar and celsian at temperatures exceeding about 650ºC. At lower metamorphic grades an asymmetric miscibility gap centred at about 75 mol.% celsian opens and widens, and at low metamorphic grades hyalophane always contains less than about 50 mol.% celsian. The barium content was used by Raith et al. (2014) to characterise the conditions of formation of hyalophane in the Mesoarchaean Ghatthiosahalli Belt of southern India. This technique cannot be used to corroborate the albite-hyalophane geothermometer at Benallt Mine as it requires celsian and hyalophane to be present in an equilibrium assemblage. Although end-member celsian is well known at Benallt Mine (e.g. Spencer, 1942; Gay and Roy, 1968), it has not been identified in the muscovite veinlets. The most that can be concluded is that the barium content of hyalophane from Benallt Mine is consistent with a low metamorphic grade (as none of the analyses listed in Table 2 contains more than 50 mol.% celsian).

4 The abbreviation Ab is used in petrology to represent albite.

5 Hyalophane is not a valid species name, however, it is in common use in petrology to describe barium-rich feldspars containing between 15 and 75 mol.% of the celsian molecule (e.g. Deer et al., 2013).

6 The SEM photos suggest the mica and feldspars are in an equilibrium assemblage, however the baryte grain (Fig. 4) has an indented outline which suggests remobilisation.
CONCLUSION

Muscovite from Benallt Mine is barium rich, with an empirical formula \((\text{Ba}_{0.127}\text{Na}_{0.010}\text{K}_{0.003})\text{(Al}_{1.95}\text{Mg}_{0.05})\text{(Si}_{2.96}\text{Al}_{0.04})\text{O}_{10}[(\text{OH})_{2}]\). It owes its distinctive pale amethyst-purple colour to a relatively high manganese content and unusually low iron content. It occurs in veinlets with hyalophane, albite and minor baryte in a Ba-feldspar and hematite matrix. Geothermometry, based upon equilibrated hyalophane-albite pairs, shows that the assemblage formed in low-grade metamorphic conditions, a conclusion which is consistent with the barium content of the hyalophane. The way in which barium, sodium and potassium partition into mica and feldspar ought to provide further information about the conditions of formation, but the detailed thermodynamic modelling required is beyond the scope of this research. Quantitative data on both muscovite and hyalophane is

ACKNOWLEDGEMENTS

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REFERENCES


Ma, C. and Rossman, G.R. (2006). Gannerite, the barium mica \(\text{Ba}_{8}\text{Si}_{2}\text{Al}_{2}\text{Si}_{2}\text{O}_{10}[(\text{OH})_{2}]\) from Oreana, Nevada. American Mineralogist, 91, 702–705.


The composition of barium-rich muscovite from Benallt Mine, Gwynedd is explored with the aid of a simple model. The central composite layer is dioctahedral with a combined $M$- and $T$-sheet cation sum which is very close to six. The $M$- and $T$-sheet occupancies can be modelled using the equations $^T Si^{4+} + ^T Al^{3+} = 4$ and $^M M^{2+} + ^M Al^{3+} = 2$, with simple charge-balancing one for one exchanges. The $I$-sheet, which is made up of large charge-balancing cations is less well behaved. It has a low and variable cation sum and cannot be modelled on the basis of one for one exchanges. Pearson product moment correlations and least-squares regressions are used to examine the relationships between microprobe datasets. A plot of $^{1}Ba^{2+}$ vs $^{1}K^{+}$ furnishes an interesting example of a dataset in which the results of regressing $y$ on $x$ and $x$ on $y$ are significantly different. Such data can be explored by the method of ‘total least squares’, which considers errors in both quantities.

INTRODUCTION

This study began as an exploration of the composition of the barium-rich pale amethyst-purple muscovite from Benallt Mine, Gwynedd, described in Cotterell et al. (2019). It was initially intended as an appendix which discussed empirical formulae and how they are calculated. The analysis proved less straightforward than anticipated and it was decided that a companion paper which focussed on the composition of the mica and the way in which barium was accommodated in the structure was more appropriate. This allows a discussion of the rare barium analogue of muscovite: ganterite.

The minerals of the mica group occur in a wide variety of geological situations (Bailey, 1984; Mottana et al., 2002). They have a common structural motif (Deer et al., 2013). A central sheet of octahedrally coordinated cations ($M$) is sandwiched between inward pointing tetrahedrally coordinated sheets ($T$). Each of these composite layers is separated by charge-balancing cations (Figs 1 and 2). The tetrahedral sheets are made up of $TO_4$ units, which link at three vertices to form an approximately hexagonal net. The oxygen atoms at the unattached vertices point inward toward the central $M$-sheet. Each of the cations in the $M$-sheet, is surrounded by four inward pointing oxygen atoms and two anions, labelled $A$, in broadly six-fold octahedral coordination. The central composite layer has an overall negative charge which is balanced by positively charged interlayer cations. These interlayer cations ($I$) sit in approximately twelve-fold coordination in the hexagonal ‘holes’ in the $T$-sheet.

Mica-group minerals can be represented by the general formula:

$I_1M_2-3\square_1-6TdO_{10}A_2$.
celadonite, 3:1 as in muscovite, 2:2 as in eastonite, and 1:3 as in clintonite.

Although most compositions lie in the complex composition space between species, there is no easy way of expressing a particular point in composition-space in terms of a unique sum of ideal formulae. In addition some compositions, notably micas with interlayer deficiencies, lie outside the network of currently approved species. Attempts to provide schemes to systematise and simplify chemical studies are summarised in Tischendorf et al. (2007). Discussions of chemical composition commonly include hypothetical formulae which lie beyond the currently approved species framework. Some graphical interpretations have proved useful, but there are not enough spatial dimensions to produce plots that show the true complexity of relationships.

Micas are described as ‘true micas’ if more than 50% of the I-sheet cations are monovalent, and ‘brittle micas’ if more than 50% of the I-sheet cations are divalent. They are dioctahedral if there are less than 2.5 M-sheet cations per formula unit; and trioctahedral if there are more than 2.5 M-sheet cations per formula unit. Interlayer deficient varieties which have less than one cation per formula unit in the I-sheet are well known. Micas with a substantial proportion of divalent cations in the interlayer, such as the barium-rich muscovite from Benallt Mine discussed here, form a relatively small group to which 3.2% of a total of 6750 analyses surveyed in Tischendorf et al. (2007) belong.

Muscovite

Muscovite is probably the best known member of the mica group. It is a dioctahedral true mica. The ideal formula is usually written $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, without the $M$-sheet structural vacancy (CNMNC, 2019). With the structural vacancy the formula is $\text{KAl}_2(\cdot)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$. Deconstructing the formula illustrates the relationship between ideal and general formulae. The large positively charged interlayer ions, symbol $I$, are represented by the element potassium [K]. The octahedrally coordinated $M$-sheet cations are represented as $[\text{Al}_2]$ (or $[\text{Al}_2\square]$ if the vacancy is included). The tetrahedrally coordinated elements in the $T$-sheet are $[(\text{Si}_3\text{Al})]$. In muscovite and many other micas the $M$- and $T$-sheets contain two components in simple whole-number ratios. The $T$-sheet elements are linked by bridging oxygen atoms, to form $(\text{Si}_3\text{Al})\text{O}_{10}$ units. The anion group, which provides a charge balanced formula, is $[\text{O}_{10}(\text{OH})_2]$.

In a meta-study of more than 1500 analyses, Tischendorf et al. (2007) found that most muscovite (55%) has a composition that is very close to the ideal formula. The next most common compositions are Fe-rich muscovite and Mg-rich muscovite (16% each). Other substitutions are uncommon. Nonetheless, barium-rich muscovite has been reported at a few localities worldwide (Fortey et al., 1982; Dunn, 1984; Moles, 1985; Tracy, 1991; Grapes, 1993; Harlow, 1995; Jiang et al., 1996; Bocchio, 2007; Raith et al., 2014). In 2003, ganterite, a barium analogue of muscovite, was described as a new species from metamorphosed basement rocks of the Berisal Complex, Simplon Region, Switzerland (Graeser et al., 2003; Hetherington et al., 2003). A slightly more barium-rich
The method of converting data expressed as wt% oxides into an empirical formula is well known (Deer et al., 2013). Data are converted to molar ratios and for mica group minerals they are then scaled so that the sum of the cation charges (minus any fluorine) adds to 22. This is equivalent to an idealised $O_{10}(OH)_2$ anion group. The results are listed in Table 1.

Taking the mean values of each of the major constituents produces an average empirical formula:

$$(Ba_{0.12}Na_{0.01}K_{0.83})_{22}(Al_{1.76}Mn_{0.05}Mg_{0.01})_{22}O_{10}[(Si_{2.87}Al_{1.13}O_{3.33})]_{18}OH_2.$$  

Elements present at less than 0.01 atoms per formula unit are not included. Empirical formulae typically include minor substituents at structural sites, but omit trace elements. A cut-off of 0.01 atoms per formula unit is convenient.

Water by Difference

An alternative method of calculating the formula is to assume ‘water by difference’. This is not recommended by Rieder et al. (1998) and it is worthwhile exploring why this is so. If the remainder in the microprobe data is assigned as water and (in muscovite) calculations are then based on twelve atoms of oxygen, the empirical formula becomes:

$$(Ba_{0.11}Na_{0.01}K_{0.81})_{22}(Al_{1.76}Mn_{0.05}Mg_{0.01})_{22}O_{10}[(Si_{2.87}Al_{1.13}O_{3.33})]_{18}OH_2,$$

if all of the H is assumed to be hydroxyl. Some H might be water, in which case another possible formula has an anion

Table 1. Twenty barium-rich muscovite compositions from Benallt Mine, Gwynedd, calculated as atoms per formula unit, on the basis of 22 positive charges, as suggested by Rieder et al. (1998). The mean values, standard deviations of the distributions (at 1σ) and standard errors in the means (also at 1σ) are listed in the three lower rows.
group $O_{9.66}(OH)_{2}$:0.33$H_2O$, or the $I$-site might have $[H_2O_{0.07}]$ with further adjustments elsewhere.

It is worthwhile considering what has happened in these calculations. By forcing the analytical total to 100.0 wt% and assuming the remainder is entirely $H_2O$, an anion group on the basis of twelve atoms of oxygen, represented as $[O_{9.33}(OH)_{2.67}]$, has emerged. The number of atoms per formula unit for everything except ‘hydrogen’ has reduced. As aluminium is apportioned between two possible sites on the basis that $Si + ^7Al = 4$, there is a particularly large effect on the calculated composition of the $M$-sheet, and the cation sum for the central layer, at 5.82, is unreasonably low.

**EXAMINING COMPOSITION**

The complexity of substitution in micas is such that any sort of simplifying model may seem to be a lost cause. However, Tischendorf et al. (2007) note:

“...solid-solution series between common true K micas ... and brittle micas are characterized by simpler, element-for-element, binary substitutions”.

The data listed in Table 1, with the general formula outlined in the introduction as a guide, indicate that the only significant substitutions in muscovite from Benallt Mine are barium for potassium in the interlayer; divalent ions (described hereafter as $^{4+}M^2+$) such as manganese and magnesium for aluminium in the $M$-sheet; and aluminium for silicon in the $T$-sheet. Small quantities of fluorine and chlorine are of no significance and can be disregarded, as can titanium, which is present in tiny quantities.

The sum of the $M$- and $T$-sheet cations has a mean$^1$ of 6.007 ± 0.01, which is very close to the value of six for dioctahedral micas. This suggests that the central composite sheet is dioctahedral, with full sites, and that the substitutions are one for one on an atomic basis. This is not true for the interlayer, where the cation sum has a low and variable total, but a model with well defined one for one substitutions in full sheets makes a useful starting point from which deviations can be explored. The system under study can therefore be simplified to the following six variables: $^1Ba^{2+}$ and $^1K^+$ for barium and potassium in the interlayer ($I$); $^1Si^{4+}$ and $^1Al^{3+}$ for aluminium and silicon in the tetrahedral sheets ($T$); and $^{4+}M^2+$ and $^{3+}M^3+$ for divalent metal ions and aluminium in the octahedral sheet ($M$).

For sites with simple one for one substitution and with sums in the $I$-, $T$- and $M$-sheets of 1, 4 and 2, respectively:

$^1Ba^{2+} + ^1K^+ = 1$;
$^1Si^{4+} + ^1Al^{3+} = 4$;
$^{4+}M^2+ + ^{3+}M^3+ = 2$.

To maintain charge balance, any substitution that increases the partial charge at a particular site must be compensated by a substitution which reduces the partial charge at another site. With the constraints imposed by full sites and one for one substitution, three exchanges between cation pairs with different charges are possible:

$^1K^+ + ^1Si^{4+} \leftrightarrow ^1Ba^{2+} + ^1Al^{3+}$;
$^{4+}M^2+ + ^{3+}M^3+ \leftrightarrow ^1MAl^{3+} + ^1TAl^{3+}$;
$^1K^+ + ^3Al^{3+} \leftrightarrow ^1Ba^{2+} + ^4MAl^{2+}$.

The extent of these coupled heterovalent substitutions is limited by the capacity of the respective sheets.

The first and second substitutions, which involve exchanges between adjacent sheets, are well known (e.g. Tischendorf, 2007); the third is not commonly discussed as for most practical purposes it can be modelled using linear combinations of the first two. The exchanges act to move the formula from muscovite toward one of three compositions:

1. Muscovite to barium brittle mica
   $KAl_2(Si_3Al)O_{10}(OH)_{2}$
   $^1K^+ + ^1Si^{4+} \leftrightarrow ^1Ba^{2+} + ^1Al^{3+}$
   $BaAl_2(Si_2Al)O_{10}(OH)_{2}$

2. Muscovite to aluminoceladonite
   $KAl_2(Si_3Al)O_{10}(OH)_{2}$
   $^{4+}Al^2+ + ^3Al^{3+} \leftrightarrow ^1MAl^{3+} + ^1TAl^{3+}$
   $KAl_2(Si_2Al)O_{10}(OH)_{2}$

3. Muscovite to barium celadonite
   $KAl_2(Si_3Al)O_{10}(OH)_{2}$
   $^1K^+ + ^3Al^{3+} \leftrightarrow ^1Ba^{2+} + ^4MAl^{2+}$
   $BaAl_2(Si_2Al)O_{10}(OH)_{2}$

Of these, ‘barium brittle mica’ and ‘barium celadonite’ are hypothetical compositions; only aluminoceladonite (with $M^{2+} = Mg,Fe^{2+}$) is an accepted species.

All of these compositions has a unique $I$-, $M$- and $T$-sheet signature. They are the nearest ‘whole number’ formulae to muscovite in the simplified composition space explored by the model. Although they do not represent independent vectors in composition space$^2$.

---

$^1$ The error value quoted here is the standard error in the mean, which is a measure of the confidence that the mean lies within quoted error bounds. This is obtained from the standard deviation of the distribution (at 95% confidence level i.e. 2σ), using the formula:

\[
\text{Std Error} = \frac{\text{Std Dev}}{\sqrt{n-1}}
\]

where $n$ is the total number of measurements. Note that the standard error in the mean becomes more accurate as more measurements are included, whereas the standard deviation of the distribution remains about the same.

$^2$ The way that mica-group species are defined, with ‘whole-number occupancy’ in the $M$- and $T$-sheets (Rieder et al., 1998) means that although the hypothetical formulae would represent new species if found in nature they are not independent in a mathematical sense. A composition halfway between muscovite and ‘barium celadonite’ can, for example, be obtained by adding 50% of the formula for ‘barium brittle mica’ to 50% of the formula for ‘aluminoceladonite’ (see also Table 5).
they can be used in a limited way to characterise chemical trends. Ganterite, which is commonly described as the barium analogue of muscovite, lies halfway between muscovite and barium brittle mica; its unusual ideal formula, with fractional occupancy in the I- and T-sheets, make it unsuitable for use as a model composition.

A scheme which only considers charge balance and site occupancy is about the simplest that can be imagined. Its limitations include an inability to deal with deficiencies in the I-sheet or with trioctahedral tendencies. Many other factors impose constraints on substitution include differences in ionic radius and incompatibilities such as the Al—O—Al bond avoidance encapsulated in ‘Lowenstein’s rule’ (Tischendorf et al., 2004; 2007). It is also worth noting that the datasets are normalised to a cation sum to 22; thus any tendency toward an oxy-mica composition, oxidation of a redox-sensitive element, or contribution from a species of low atomic number (e.g. lithium or hydronium) is not taken into account. Such factors can be explored using more complex models, but are beyond the compass of this simple note.

**DISCUSSION**

Empirical formulae commonly appear in research that discusses chemical variation in minerals and are often included in species descriptions. They can be cumbersome and awkward to interpret. The empirical formula for muscovite from Benallt Mine is a case in point:

\[(Ba_{0.12}Na_{0.01}K_{0.83})_{22.96}(Al_{1.93}Mn_{0.03}Mg_{0.01})_{22.00}\]

\[\times[(Si_{2.96}Al_{1.04})O_{10}](OH)_{2}\]

The calculated coefficients, in atoms per formula unit, with their associated standard deviations, are listed in Table 2. Although the formula is relatively close to muscovite, it is not instantly apparent what it communicates. The presence of barium in the interlayer is of particular interest. A substitution of the form \(1^\text{Ba}^2+ + 3^\text{Si}^4+ \leftrightarrow 1^\text{Ba}^2+ + 1^\text{Si}^4+\) which is advanced to account for barium substitution in ganterite (Graeser et al., 2003; Hetherington et al., 2003; Ma and Rossman, 2006) is not at all obvious. However, with the model outlined in the foregoing text as a guide, and the datasets in Table 1, substitutions can be explored.

If there are two substituents in a particular sheet, and the sites are full, one for one replacement should produce a negative correlation. Strong negative correlations are expected between \(1^\text{Ba}^2+ + 1^\text{K}^+ + 1^\text{Na}^+\) in the I-sheet; \(1^\text{M}^{2+} + 1^\text{Al}^{3+}\) in the M-sheet; and \(1^\text{Si}^{4+} + 1^\text{Al}^{3+}\) in the T-sheet. These relationships can be tested using Pearson functions which return a number that quantifies the strength of linear correlation (Table 3).

The correlation analysis is complicated by the fact that aluminium is present in both the M- and T-sheets, and can only be assigned by calculation. The Pearson correlation between \(1^\text{TAl}^{3+} + 1^\text{Si}^{4+}\) in the T-sheet is perfect and negative because the sheet occupancy is calculated on the basis that \(1^\text{TAl}^{3+} + 1^\text{Si}^{4+} = 4\). In the M-sheet, the correlation between the remaining \(1^\text{M}^{2+}\) and the sum of the minor divalent cations is excellent and negative, with a Pearson coefficient of \(-0.80\); but neither represents a ‘fair test’. However, the fact that the M- and T-sheet cation sum has a mean value of \(6.007 \pm 0.01\), suggests that the assumption of one for one substitution in a dioctahedral mica with full M- and T-sheets is robust. Although the within-site correlations cannot be tested, the substitution \(1^\text{M}^{2+} + 1^\text{Al}^{3+} \leftrightarrow 1^\text{Si}^{4+} + 1^\text{Al}^{3+}\) can be examined (as all of the Al in this exchange is on the right hand side). A regression analysis and plot are discussed in the appendix. This reveals a well-behaved central composite sheet.

Further investigation, with a focus on I-sheet substitution, provides a more interesting challenge. The relatively poor correlation \((-0.58)\) between \(1^\text{Ba}^2+\) and \((1^\text{Na}^+ + 1^\text{K}^+)\) which results from a low and variable I-

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>(1^\text{Al}^{3+})</th>
<th>(1^\text{M}^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1^\text{Si})</td>
<td>(-0.38)</td>
<td>(-0.27)</td>
<td>(0.68)</td>
<td>(-0.58)</td>
</tr>
<tr>
<td>(1^\text{Al})</td>
<td>(-0.77)</td>
<td>(0.29)</td>
<td>(-0.80)</td>
<td>(0.43)</td>
</tr>
<tr>
<td>(1^\text{M}^{2+})</td>
<td>(-0.80)</td>
<td>(-0.14)</td>
<td>(-0.29)</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Calculated coefficients in the empirical formulae (based on an idealised \([O_{10}(OH)_2]\) anion group) with the associated standard deviation on the basis of 20 measurements of barium-rich muscovite from Benallt Mine. The standard deviation, quoted here at 95% confidence level (2\(\sigma\)), represents the spread of the distribution due mostly to natural chemical variability, and is not an indication of ‘random instrumental error’ associated with individual values. The measured value of Al is the sum of M- and T-sheet aluminium. Assigning aluminium into these sheets on the basis Si + \(1^\text{TAl} = 4\), gives the values for tetrahedrally coordinated and octahedrally coordinated aluminium, \(1^\text{TAl}\) and \(1^\text{MAl}\), respectively.

**Table 3.** Pearson product moment correlation coefficients between datasets for 20 independent microprobe measurements of the principal components of the muscovite structure. A general ‘rule of thumb’ is that a strong positive correlation is indicated by a Pearson value between 1.0 and 0.5, a weak positive between 0.3 and 0.5, no correlation between 0.3 and -0.3, a weak negative correlation between -0.3 and -0.5, and a strong negative correlation between -0.5 and -1.0.
Recalculating the empirical formula with this assumption results in the 2+ sheet occupancy so that $\text{Barium Celadonite'}. The path from muscovite to ‘barium celadonite’ involves the substitution $I_2K^+ + MAl^{2+} \leftrightarrow IBa^{2+} + M^{2+}$. This is not discussed in surveys of mica composition (e.g. Tischendorf, 2007), perhaps because the I- and M-sheets are physically separated by the T-sheet. Exchanges toward barium brittle mica and aluminoceladonite are all that are required to model any of the known barium-rich dioctahedral micas. However.  

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>$T_{\text{Al}}$</th>
<th>$M_{\text{Al}}$</th>
<th>Mg</th>
<th>Mn</th>
<th>Ba</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>2.958</td>
<td>2.979</td>
<td>1.041</td>
<td>1.937</td>
<td>0.006</td>
<td>0.047</td>
<td>0.115</td>
<td>0.009</td>
<td>0.876</td>
</tr>
<tr>
<td>SD (2σ)</td>
<td>0.025</td>
<td>0.043</td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.011</td>
<td>0.023</td>
<td>0.006</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Table 4. Calculated coefficients (based on an idealised [O10(OH)2] anion group) as in Table 2, using an iterative modification to add K into the I-sheet so that $'Ba^2+ + K^+' = 1$. This effectively models the effect of leaching. The equation Si + $T_{\text{Al}}$ = 4, gives the values for $T_{\text{Al}}$ and $M_{\text{Al}}$.

<table>
<thead>
<tr>
<th>End Member</th>
<th>Formula</th>
<th>Mole Fraction</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite</td>
<td>KAl$<em>2$(Si$</em>{3.96}$Al$<em>{1.04}$)O$</em>{10}$(OH)$_2$</td>
<td>82.5%</td>
<td>88.9%</td>
</tr>
<tr>
<td>‘Barium Brittle Mica’</td>
<td>BaAl$<em>2$(Si$</em>{2.96}$Al$<em>{1.04}$)O$</em>{10}$(OH)$_2$</td>
<td>11.1%</td>
<td>4.7%</td>
</tr>
<tr>
<td>‘Aluminoceladonite’</td>
<td>KAlM$<em>2$($Si</em>{2.96}$Al$<em>{1.04}$)O$</em>{10}$(OH)$_2$</td>
<td>6.4%</td>
<td>0.0%</td>
</tr>
<tr>
<td>‘Barium Celadonite’</td>
<td>BaAlM$<em>2$($Si</em>{2.96}$Al$<em>{1.04}$)O$</em>{10}$(OH)$_2$</td>
<td>0.0%</td>
<td>6.4%</td>
</tr>
</tbody>
</table>

Table 5. The composition of barium-rich muscovite (with the I-sheet adjusted to full occupancy) expressed in terms of the ideal formulae suggested by the simple model. The formulae are not linearly independent and the best fit can be expressed in a variety of ways. The first column provides the simplest interpretation with no ‘barium celadonite’, the second offers an identical alternative.

It may seem that the low I-sheet occupancy could be addressed by using an interlayer deficient composition as an ideal formula. Although this may seem to be an attractive option, choosing an appropriate composition is difficult. Replacing ideal muscovite with K$_{0.96}$Al$_{0.04}$Si$_{3.96}$O$_{10}$(OH)$_2$, adds the implication that the interlayer deficiency is due to structural vacancy. This may not be the case. Using an interlayer deficient variety of muscovite, such as ‘ideal illite’, is even more problematic as the formula is poorly defined and it produces a system which is catastrophically overdetermined.

A different way to attack the ‘I-sheet problem’ is to assume that some cations have leached from the structure, and to add them back into the original datasets to produce a sheet occupancy of 1. It seems likely that univalent cations are the more mobile, and as potassium is the dominant species it is the obvious choice. Recalculating the empirical formula with this assumption (Table 4) yields:

$$\text{(Ba}_{0.11}\text{Na}_{0.06}\text{K}_{0.88})\text{Si}_{2.96}\text{Al}_{1.04}\text{O}_{10}\text{O}_{10}(\text{OH})_2.$$ 

This mathematical slight-of-hand$^4$ removes the principal impediment to a good fit. Minimising the differences between site occupancies produces a composition that can be represented by a linear combination of three ideal formulae (Table 5). Adding the contributions from each formula in the proportions listed reproduces the modified empirical formula to better than two decimal places.

This partial solution is useful as an aid to interpreting the empirical formula. In the T-sheet, an 11.1% substitution from muscovite, ideally [(Si$_3$Al)$_{10}$O$_{20}$], toward ‘barium brittle mica’, ideally [(Si$_2$Al)$_{10}$O$_{20}$], is opposed by an antithetic 6.4% substitution toward ‘aluminoceladonite’, ideally [(Si$_4$)O$_{10}$]; the resulting sheet occupancy [(Si$_{2.96}$Al$_{1.04}$)O$_{10}$] is little different from ideal muscovite. Barium, on the other hand, is only affected by the first of these substitutions and the best fit I-site occupancy of 11.1% is close to the measured value of 11.5%.

The best fit does not require any contribution from ‘barium celadonite’, BaAlM$_2$($Si_{2.96}$Al$_{1.04}$)O$_{10}$(OH)$_2$. As noted in the foregoing text, the model formulae are not mathematically independent (see Table 5 for an alternative and equally valid set of compositions including ‘barium celadonite’). The path from muscovite to ‘barium celadonite’ involves the substitution $I_2K^+ + MAl^{2+} \leftrightarrow IBa^{2+} + M^{2+}$. This is not discussed in surveys of mica composition (e.g. Tischendorf, 2007), perhaps because the I- and M-sheets are physically separated by the T-sheet. Exchanges toward barium brittle mica and aluminoceladonite are all that are required to model any of the known barium-rich dioctahedral micas. However.

$^3$ In the absence of a direct measurement of $T_{Al}^{2+}$, there is no way to test the substitution $I_2K^+ + 3Si^{4+} \leftrightarrow IBa^{2+} + 3Al^{3+}$, directly. Using the calculated value simply has the effect of introducing pairs of numbers, $3Si^{4+}$ and $3Al^{3+}$, which are much larger than $I_2K^+$ and $IBa^{2+}$, with perfect negative covariance.

$^4$ The changes produce a modified dataset in which the sum of the M- and T-sheet cations has a mean of 5.995 ± 0.01, which is close enough to the value of six, characteristic of dioctahedral micas, not to ring any alarm bells.
in theory, these could ‘run out of capacity’ and in a full exploration of composition space a substitution toward ‘barium celadonite’ should to be considered, if only to rule it out.

Removing the constraint that $^{I}Ba^{2+} + ^{I}K^{+} = 1$ (and replacing with $^{I}Ba^{2+} + ^{I}K^{+} < 1$) leaves charge balance as the only control on I-sheet composition. Put simply, unit charge on the I-sheet could result from $\frac{1}{2}^{I}Ba^{2+}$ as easily as $^{I}K^{+}$ per formula unit. A significant variation in cation sum is all that is required to remove evidence of one for one exchange in a regression analysis. Such evidence could reappear with a suitable soft constraint on site occupancy, even though the composition could not be modelled in terms of whole-number formulae. The variation in the I-sheet cation sum (0.011 in 0.959) is significantly larger than the M- and T-sheet value (0.005 in 6.007), and this appears to be the cause of the rather poor correlation and regression statistics. The variation in cation sum is not much smaller than the total range of compositions explored in the data.

The composition of the I-sheet invites discussion. Electron-beam interactions during microprobe analysis affecting volatile interlayer ions ($K^+$ is less massive and has a lower charge than $Ba^{2+}$) might have some effect on the measured composition. However, systematic errors seem unlikely to be a major factor as similar effects would surely be reported in other studies using similar methodologies (Graeser et al., 2003; Hetherington et al., 2003; Ma and Rossman, 2006; Tischendorf et al., 2004, 2007). It may be that the interlayer composition reflects unusual P-T-X conditions during crystallisation, however a comparison with more barium-rich compositions at worldwide locations suggests that this is unlikely. If high Ba/K ratios during crystallisation resulted in K-deficient localities suggests that this is unlikely. If high Ba/K ratios during crystallisation resulted in K-deficient interlayers, the most Ba-rich compositions would be expected to show the most pronounced deficiencies. The metamorphic history of the deposits at Benallt Mine is complex (Brown and Evans, 1989). Barium metasomatism might alter the interlayer composition and could be modelled as a within-site charge-balanced exchange of the form $^{I}Ba^{2+} + \square \leftrightarrow 2^{I}K^+$. Relaxing the constraint that the cation charges must add to 22 would add further flexibility to such a model, although there is no supporting evidence. The presence of an undetected light element such as lithium would affect the calculated formulae, but unfortunately there is no easy way estimate lithium content in dioctahedral micas using microprobe data (Tindle and Webb, 1990), and suggestions that it may substitute for $K^+$ in the I-sheet, in addition to the well known M-sheet substitution (e.g. Brigatti et al., 2001) further complicate the picture.

Some form of broadly illitic alteration has altered the I-site occupancy, there is at least some merit in replacing potassium to produce the formula in Table 4. If this is the case, the two heterovalent substitutions:

$$^{I}K^{+} + ^{T}Si^{4+} \leftrightarrow ^{I}Ba^{2+} + ^{T}Al^{3+};$$
$$^{M}Al^{3+} + ^{T}Al^{3+} \leftrightarrow ^{M}Fe^{2+} + ^{T}Si^{4+};$$

with an 11.1% substitution toward ‘barium brittle mica’ and a 6.4% substitution toward ‘aluminoceladonite’, are all that is required to generate the original unaltered composition.

Ganterite, a comment

This study began as an attempt to reconcile the empirical formula of barium-rich muscovite from Benallt Mine with possible substitution mechanisms. In the early stages of the research the mineral ganterite, which is commonly described as the barium analogue of muscovite, was encountered. After some consideration, ganterite, with an ideal formula $[Ba_{0.5}(Na,K)_{0.5}Al_{4}(Si_{1.5}Al_{1.5}O_{10})(OH)_{2}]$ (Graeser et al., 2003; CNMNC, 2019) was abandoned in favour of the hypothetical ‘barium brittle mica’, $BaAl_{2}Si_{12}Al_{1}O_{30}(OH)_{2}$. There are inconsistencies in the ideal formula, primarily the fractional occupancy of the I- and T-sites and the interchangeable (Na,K), which make ganterite a difficult species to conjure with as currently described.

Barium is the dominant cation in the interlayer sites in ganterite, however, the mineral was described before the IMA–CNMNC dominant-constituent rule was revised and extended by Hatert and Burke (2008). This states that a group of atoms with the same valency at a particular
crystallographic site must be considered as a single constituent. Graeser et al. (2003) give the empirical formula\(^6\) for ganterite as:

\[
(Ba_{0.44}K_{0.28}Na_{0.27})_{2+}^{2+}(Al_{1.44}Mg_{0.09}Fe_{0.06}Ti_{0.04})_{3+}^{3+}(Si_{2.3}Al_{2.5}O_{10})(OH)_{1.89}
\]

Under the revised IMA–CNMNC rules, this formula is barium-rich muscovite (Bayliss et al., 2005; Hatert and Burke, 2008). Univalent cations are dominant in the interlayer (as 0.28±0.27 > 0.44) and the dominant cation (by a very small margin) is potassium. However, one of the analyses of barium-rich mica [Table 6 of Graeser et al. (2003)] has 0.5 atoms per formula unit of Ba. This exceeds the sum of K + Na and qualifies as a new species under the revised dominant-valency rule.

In constructing their ideal formula, [Bar0.5(Na,K)0.5]

\[
Al_2(Si_{2.5}Al_{1.5}O_{10})(OH)_2,
\]

Graeser et al. (2003) note that:

"The high concentrations of Ba atoms are compensated for by higher concentrations of Al and lower concentrations of Si than is normally expected in muscovite ... Thus, the increase in partial charge in the interlayer site by the substitution of K by Ba in the white mica is being totally compensated for by an exchange of Al\(^3+\) for Si\(^2+\) at the tetrahedral site (Fig. 2)".

If the only charge compensation mechanism in operation is the exchange of Al\(^3+\) for Si\(^2+\) at the tetrahedral site, a formula with Bar0.44 would be expected to have a tetrahedral site close to [Si2.6Al1.4O10]. Even allowing for an antithetic substitution toward ‘aluminoceladonite’ does not reproduce a T-sheet with [Si2.72Al1.35O10], as quoted in the empirical formula. It is hard to see how the regression analysis presented in Figure 2 of Graeser et al. (2003), which plots total Al vs Si, other enalyses of barium-rich muscovite from Benallt Mine, Gwynedd suggests the following.

The ideal formula for ganterite is unusual in that it represents a composition in which only half of the univalent ions in a formula unit are replaced by barium. This composition would be considered to be on the boundary between species in other minerals of the mica group. There may be an implicit assumption that a hypothetical barium-dominant dioctahedral mica, with a formula BaAl12(Si2Al2O10)(OH)\(_2\), is unreasonable\(^7\), or that there is some kind of I-sheet cation ordering in ganterite\(^8\), but no compelling evidence for these or other possibilities is presented.

The original interpretation of ganterite is complicated by the presence of almost as much Na as K (Hetherington et al., 2003), which is reflected in the ideal formula as (Na,K)0.5. Ma and Rossman (2006) show that Na is not essential, and that nearly pure K for Ba replacement in the solid solution KA12(Si3Al)O10(OH)\(_2\) - BaAl12(Si2Al3)O10(OH)\(_2\) extends slightly beyond the halfway point. Unlike Graeser et al. (2003), Ma and Rossman (2007) do not note any changes in the Raman spectra which might be interpreted as structural in this composition range.

It seems probable that the original authors considered their ideal formula to be the best representation of the available data, but it is not in accord with other members of the mica group; BaAl12(Si2Al3)O10(OH)\(_2\) has its advantages even if (as is the case for example with ankerite) it does not represent a composition which occurs in nature.

CONCLUSIONS

The limitations of electron probe micro-analysis, which is unable to detect light and volatile elements are shown. The benefits and drawbacks of normalising data to a particular cation sum are also explored. An analysis of twenty electron probe micro-analyses of barium-rich muscovite from Benallt Mine, Gwynedd suggests the following.

1) Formulae are best computed and compared on the basis of 22 cation charges (the equivalent of an idealised [O10(OH)\(_2\)] anion group). Calculations involving ‘water by difference’ produce unrealistic results. However, the potential presence of light and volatile elements and any chemical variation that might affect the charge of the anion groups must be factored into discussions of chemical composition.

2) The compositions are strictly dioctahedral with an M- and T-sheet cation sum which is very close to six.

3) The M- and T-sheet occupancies can be modelled using \(7Si^{4+} + 2Al^{3+} = 4\) and \(4M^{2+} + 2Al^{3+} = 2\), with simple one for one substitutions.

\(7\) Substitutions beyond $[Ba_{0.4}K_{0.6}]$ might be impeded by an increasing octahedral–tetrahedral sheet misfit according to Armbuster et al. (2002). However, the IMA-approved ideal formula for the equivalent trioctahedral barium mica, kinoshitalite, is $BaMg_3(Si_3Al_2O_{10})(OH)_2$ (CNMNC, 2019).

\(8\) Ma and Rossman (2006) suggested this possibility, but found no evidence to support it.
4) There is a coupled heterovalent substitution of the form \( M^3+ Al^3+ \leftrightarrow M^2+ Si^4+ \) among the elements of the \( M \)- and \( T \)-sheets. A regression analysis reveals an excellent linear correlation with a slope that is not statistically different from the predicted value of \(-1\).

5) The correlation between the univalent and divalent substituents in the \( I \)-sheet, \( K^+ + \) and \( Ba^2+ \), is relatively poor with a Pearson coefficient of \(-0.58\). This is due to the variable \( I \)-sheet occupancy, with \( Ba^2+ + K^+ + Na^+ = 0.959 \pm 0.011 \), and the relatively small composition range explored in the dataset.

6) A model based on one for one exchange cannot fully reproduce the variation in \( I \)-sheet composition. The only constraint on the \( I \)-sheet composition is that its partial positive charge balances the excess negative charge on the \( M \)- and \( T \)-sheets.

7) A survey of possible reasons for the \( I \)-sheet deficiency suggests that some form of illitic alteration as the most likely candidate.

8) If potassium is added back into the dataset in a mathematical ‘slight of hand’ such that \( Ba^2+ + K^+ + Na^+ = 1 \) a composition which can be represented as 82.5% muscovite, ideally \( KAl_2(Si_3Al)O_{10}(OH)_2; \) 11.1% ‘barium brittle mica’, ideally \( BaAl_2(Si_2Al)O_{10}(OH)_2; \) and 6.4% ‘aluminoceladonite’, ideally \( KAl_2Si_4O_{10}(OH)_2 \) is obtained. These three formulae are all that is required to model the composition.

9) Least-squares regression should not be used as a mathematical block box. Regressions which only minimise errors in the \( y \)-values may produce best-fit lines that are not appropriate, especially if correlation is relatively poor and there are significant errors in both \( x \) and \( y \). Such data can be explored by the method of ‘total least squares’, which considers errors in both quantities. A plot of \( Ba^2+ \) vs \( K^+ + Na^+ \) furnishes an interesting example of a situation in which the results of regressing \( y \) on \( x \) and \( x \) on \( y \) are significantly different.

10) The ideal formula for ganterite is inconsistent. It is the only mica with an ideal formula that is halfway between what would normally be considered to be species compositions. It is unsuitable in modelling the composition of mica-group minerals.

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REFERENCES


**APPENDIX — REGRESSION ANALYSIS**

Modern mathematical textbooks and websites tend to describe regression in the language of matrices. This is convenient and succinct, but used with clever software and attractive graphics it can result in a ‘black box’ approach to analysis. It is important to understand how the software functions and what the analysis does.

Science students are usually introduced to regression in carefully thought out experiments in which a parameter which can be described by a variable, \( x \), is changed in a precise way and another parameter, \( y \), in which there are small errors, is recorded. The values are plotted as a graph, and the relationship between the two quantities determined. If there is a linear relationship, the slope, intercepts and various error parameters can be calculated with relative ease. This is such a common and useful procedure that most spreadsheets have functions which automate the calculations (e.g. the LINEST function in MS Excel). Dedicated software allows more complex equations to be fitted, but at the heart of these routines there is usually a calculation that minimises the sums of the squares of differences between a desired functional form and measured \( y \)-values (perhaps weighted by their associated errors). The result is a ‘best fit curve’.

As an illustration, the data for \( ^{7}Al^{3+} + ^{4}Al^{3+} \) vs \( ^{2}M^{2+} + ^{7}S^{4+} \) are plotted in Figure 3. An inspection of the graph immediately suggests a linear relationship. A least squares regression using the LINEST function in MS Excel suggests a straight line with a slope of \(-0.93 \pm 0.1\). This is close (identical within the relatively small errors) to the value of \(-1\), predicted on the basis of coupled heterovalent substitution with full site occupancy and one for one exchanges. The best fit line calculated by the LINEST regression is the line that minimises the sum of the squares of the vertical distances (along the \( y \)-axis) from the individual data points. The answer is the best that can be obtained if all of the errors are in \( y \).

This procedure is ingrained in science and it almost always produces a ‘credible answer’. However, if there are comparable errors in \( x \), the results can be misleading. If errors in both \( x \) and \( y \) are assumed to be the same, and a regression is made which minimises both with an equal weighting, a line with a slope of \(-0.95\) emerges. In this case, the two lines are identical within errors and from a purely pragmatic viewpoint, (as is often the case if there is a clear relationship), the simple regression appears to work well. This is not always the case, and it is important to understand the limitations of the technique.

Consider the plot of \( ^{1}Ba^{2+} \) vs \( ^{1}K^{+} + ^{1}Na^{+} \) (Fig. 4), which is a useful way to look for potential exchange mechanisms in the \( I \)-sheet. Analysis shows (Pearson function value \(-0.58\)) that there is a negative correlation between the variables. The data points swarm around a central square (highlighted in pink) but the relationship is less obviously linear. A regression which minimises errors in \( y \) (i.e. the variable \(^{1}Ba^{2+}\)), produces a line with a slope \(-0.58\), and this looks reasonably credible on a plot. However, if the procedure is reversed, minimising the errors in \( x \) (the variable \(^{1}K^{+}\)) the slope is \(-1.77\): in isolation this also looks reasonable. In this case, the two regression values (with their associated errors of ca. \( \pm 0.38\)) are significantly different and could be used to argue for different exchange mechanisms.

![Figure 3](image-url) A plot of \( ^{7}Al^{3+} + ^{4}Al^{3+} \) vs \( ^{2}M^{2+} + ^{7}S^{4+} \). An inspection of the graph immediately suggests there is a linear relationship. If errors in both \( x \) and \( y \) are assumed to be the same, and a regression is made which minimises both with equal weighting, a line with a slope of \(-0.95\) emerges (the dotted line on the diagram).
As in the first case, there is no reason to assume that the errors are all in $x$ or all in $y$ and a more satisfactory analysis can be made using a regression that minimises the errors in both quantities. Few software packages offer this method, or the more general ‘total least squares’, which allows for a more realistic and complicated error structure (Linnet, 1993). For a simple straight-line fit, it is relatively simple to determine the slope and intercept assuming the errors in $x$ and $y$ are equal, and to add a parameter, $d$, which models unequal error variance in $x$ and $y$. The following values, for $n$ data points with values $x_i$ and $y_i$, are required:

$$
\bar{x} = \frac{1}{n} \sum x_i;
$$

$$
\bar{y} = \frac{1}{n} \sum y_i;
$$

$$
s_{xx} = \frac{1}{n-1} \sum (x_i - \bar{x})^2;
$$

$$
s_{xy} = \frac{1}{n-1} \sum (x_i - \bar{x})(y_i - \bar{y});
$$

$$
s_{yy} = \frac{1}{n-1} \sum (y_i - \bar{y})^2.
$$

These are easy to calculate using a spreadsheet. The best fit line to the data has a slope $m$ and intercept $c$, which can be calculated as follows:

$$
m = \frac{s_{yy} - \delta s_{xx} + \sqrt{(s_{yy} - \delta s_{xx})^2 + 4\delta^2 s_{xy}^2}}{2 s_{xy}};
$$

$$
c = \bar{y} - m \bar{x}.
$$

The weighting parameter $\delta$, adjusts the model to allow for different variances of the errors in $x$ and $y$. If $\delta = 1$, the variances are equal and the analysis returns values which minimise $x$ and $y$ equally.

For the dataset in Figure 4 setting $\delta = 1$ produces a slope of $-0.99$. As $\delta$ tends toward zero and infinity the regressions of $y$ on $x$ or $x$ on $y$ dominate and the best fit slopes, which only take account of errors in $y$ or $x$, respectively, tend toward $-0.58$ and $-1.77$. These results show that in this dataset, widely different conclusions could be drawn from apparently sound regression techniques. Extending the argument to the complex modelling scenarios that are in common use in research, shows the need for a sceptical approach to ‘black box analysis’.

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**Figure 4.** The relationship between Ba and Na + K, the major substituents in the $\beta$-sheet in barium-rich mica from Benallt Mine. A regression which minimises errors in $y$ (the variable 'Ba$^{2+}$'), produces a best fit line which minimises the sum of the squares of the length of the vertical red lines (shown for the five data points on the right hand side, and understood for the rest). This dotted line is what a 'standard regression' would produce. A regression which minimises the errors in $x$ (i.e. the variable 'Na$^{+}$ + $\mathcal{K}^+$') produces a best fit line which minimises the sum squares of the length of the green horizontal lines (shown for the five data points on the left hand side, and understood for the rest). The full line (slope = $-0.99$) is the result of a regression which minimises errors in both $x$ and $y$ with equal weighting.
Amazonite (a green variety of microcline feldspar) has long been known from Sutherland. In the late nineteenth century, Matthew Forster Heddle described the mineralogy of a large amazonite-bearing glacial erratic, which he assumed to have originated from Ben Loyal. The history and occurrence of this ‘amazonstone’ is reviewed and discussed. Specimens of amazonite from Sutherland are preserved in the collections of the National Museum of Scotland, Edinburgh; the Hunterian Museum, Glasgow; the Natural History Museum, London; and at Dunrobin Castle, Golspie. The recent discovery of a large block of Ben Loyal syenite, traversed by an amazonite-bearing pegmatite, below the north face of Sgor Chaonasaid on Ben Loyal is reported. Modern specimens are comparable with the best that were collected in the nineteenth century.

INTRODUCTION

Amazonite from the area around Ben Loyal in Sutherland (Fig. 1) is among the most elusive and desirable of Scottish minerals. The best known source is ‘Hedde’s boulder’, a large erratic block discovered on Beinn Bhreac, which contained a vein of amazonite with individual crystals to almost 40 cm (Heddle, 1877; 1883a; 1883b; 1901). Historical accounts also describe specimens from the north face of Sgor Chaonasaid (712 m), one of the four peaks making up the ‘Queen of Scottish Mountains’, Ben Loyal (Fig. 2).

GEOLOGY

The Loch Loyal intrusions form the largest area of alkaline rocks in Britain, and contain the only extensive body of the quartz-bearing syenite rock ‘nordmarkite’ (Parsons, 1999). They are part of a suite of Silurian, high Ba-Sr syenitic to granitic plutons which extends across the Northern Highlands (Walters et al., 2013). The complex is commonly divided into three parts: the largest intrusion, Ben Loyal itself which forms the highest ground; a smaller body to the south, known as Cnoc nan Cuilean; and Ben Stumanadh which lies to the east beyond Loch Loyal. The Ben Loyal Syenite is intruded into Moine and Lewisian metamorphic rocks and has the form of a semicircle with a circular boundary in the northwest and a linear boundary in the southeast, which has been interpreted as a major fault (Holdsworth et al., 1999).

The area has been studied by generations of geologists, with important contributions by Read (1931), King (1942), Von Knorring and Dearnley (1959), Parsons (1972), Robertson and Parsons (1974), Gallon (1974), Holdsworth et al. (1999), Holdsworth et al. (2001) and Fowler et al. (2008). The petrography of the complex has been described in detail by Parsons (1972) and Robertson and Parsons (1974). The Ben Loyal mass has a distinctive zonation with a hypersolvus (higher crystallisation temperature) central core unit with only one perthitic feldspar present, and a surrounding foliated marginal subsolvus (lower temperature) syenite, containing both alkali feldspar and albite.1

Recent work by Hughes et al. (2013) and Walters et al. (2013) has focused on the enrichment of rare-earth elements during magmatic and post-magmatic processes with particular reference to the Cnoc nan Cuilean intrusion.

The Ben Loyal syenite is well exposed in the steep ground on the northwest flank of the mountain although the precipitous nature of the terrain means that much of it is rather inaccessible to the non-climber. The rock is generally of a fairly uniform white or cream colour and both syenite units, but particularly the foliated marginal variant, contain cavities lined by a yellow, powdery material identified by von Knorring and Dearnley (1959) as a monazite-group mineral. This is particularly well seen at the Lettermore Quarry on the eastern side of the

1 The terminology of potassium feldspars can be confusing, especially as historical usage may differ from current approved usage. Magmatic K-feldspars usually crystallise as monoclinic orthoclase, anorthoclase or sanidine, and contain significant quantities of sodium in their crystal structures. Unless they cool quickly (e.g. surface volcanic rocks), such feldspars tend to ‘unmix’ on cooling, with the Na coming out of the K-feldspar, to form areas of albite. This texture is known as a ‘perthitic intergrowth’, or ‘perthite’. The remaining K-feldspar is enriched in K, and often changes crystal structure to triclinic microcline as it cools. In low-temperature igneous rocks (e.g. pegmatites), K-feldspar commonly crystallises directly as microcline, although it may still contain Na, and exsolve albite to form a perthitic intergrowth. In Heddle’s time external crystal morphology was sometimes used to indicate whether a feldspar had originally crystallised as microcline or orthoclase, but this would not indicate whether the feldspar was now microcline, or orthoclase perthite. A useful review of feldspar terminology is provided in Smith (1974).
massif. These cavities also contain montmorillonite, harmotome and stilbite, although none of these minerals was noted during the present investigation.

**HISTORY**

Amazonite was first cited in French as ‘Pierre des Amazones’, meaning ‘stone of the Amazon’ [river] by Nicholas Venette in his *Traité des Pierre* [Treatise on Stones] (Venette, 1701), and the name was modified to ‘amazonite’ in 1847 by Johann Friedrich August Breithaupt on the basis of material from an unspecified ‘type locality’ area near the River Amazon (Breithaupt, 1847).

The occurrence of amazonite in Sutherland first came to the attention of the mineralogical community in 1875
when a few crystals of it were sent to Rev. Dr James Maxwell Joass (1830–1914), minister of Golspie and also librarian at Dunrobin Castle as “a pretty green stone from a boulder” (Heddle, 1883a). These specimens were deposited by Joass in the museum of the Duke of Sutherland at Dunrobin Castle. Fragments of amazonite were subsequently provided by Dr Joass, and Professor Nicol (1810–1879) of the University of Aberdeen, to the legendary Scottish mineralogist Professor Matthew Forster Heddle (1828–1897) who undertook a chemical analysis (Heddle, 1877). A later report states that the analysis of the amazonite was made shortly after the discovery of the stone in 1875 (Heddle, 1883a).

The source of the specimens was a large erratic boulder of syenite, later to become known as ‘Heddle’s Boulder’, that had been discovered on the west slope of Beinn Bhreac about 1.5 km ESE of Tongue. The boulder was considered by Heddle to have been derived from Ben Loyal, 7 km to the SSW.

In his first account [see Fig. 3], Heddle (1877) describes the boulder as follows:

“Having been broken up by the author for the Duke of Sutherland in the interests of science, it proved to be quite a mineral casket. Specimens of amazonite of unparalleled magnificence were profusely distributed among an assemblage of minerals occurring, within the same space, certainly nowhere else in Scotland”.

Figure 2. The magnificent profile of Ben Loyal viewed from the north across the Kyle of Tongue, a distance of 11 km. Roy Starkey photo.

Figure 3. Plate XVII from Heddle (1877). The original caption reads: “In the centre is figured one of the crystals of amazonite from Tongue. [This specimen is almost certainly Hunterian Museum specimen no. GLAHM:106664 transferred from Dundee University Geology Department (1988–1989), and formerly in the collection of Alexander Thoms]. The figure on the left side thereof shows the appearance, with polarised light, of a slice of the same, cut parallel to c; magnified about 25 diameters; the undulating “corded structure” runs parallel to a, and exhibits gradations of colour on account of a difference in the thickness of the slice at its two edges: the twinned and dovetailed linear structure, which is at right angles to the other, is parallel to b. The figure on the right shows the appearance of the “corded structure” in a slice cut parallel to b.”
The assertion that the boulder weighed in the region of 100 tons suggests that if roughly cuboidal it would have been about 3.4 m on edge, or if spheroidal about 4.2 m in diameter. The amazonite-containing vein traversing the boulder is reported as having been about two feet in width (0.6 m). The occurrence was considered sufficiently newsworthy to be reported in *Nature* (Anon., 1877).

Heddle (1877) describes two particularly impressive crystals that measured 15.5 × 10 × 8 inches (39 × 25 × 20 cm) and 12.5 × 8 × 6 inches (32 × 20 × 15 cm), respectively; both were "unavoidably broken in the extraction".

Some years later, seemingly at variance with his original report, Heddle (1883a: p. 178) wrote that:

"Amazonstone was first stated to have been found in breaking up a boulder at Ribigill at the foot of the great north precipice of Ben Loyal. This was thought to be an error, but in the year 1882 I was presented by Mr. Wisdom with a portion of a crystal of amazonstone, which he broke out of a wall about 60 yards from Ribigill; and he stated that he thought he could see a vein running up the face of the cliff. Dr. Joass, in a letter of date March 20th, 1883, writes:- "The other day a good specimen of amazonstone, containing part of a large crystal of tourmaline[2], was brought to me as found in the burn running out of Lochan Hacon [Lochan Hakel of the current 1:25,000 Ordnance Survey map], where the rolled specimen was got which contained small flakes of talc, and which you thought curious. It is of interest to know that the vein with the amazonstone comes to the surface somewhere on the Ben Loyal side of the Tongue strath, either in this burn or on some of the slopes overhanging it".

"This crystal of tourmaline is the first found in Sutherland. The absence of that mineral from the red granite and other veins of the Hebridian rock is a fact worthy of note".

Confusion appears to exist as to the location of ‘Heddle’s boulder’ because in the same paper (Heddle, 1883a) it is reported that:

"Upon the eastern slope of Ben Bhreck – a hill formed of Old Red Sandstone Conglomerate, which lies to the south-east of Tongue – two large syenite boulders, probably from the crags of Loyal, are imbedded in till."

"These were partly cut up for lintels and fragments of what was designated a "pretty green stone," which came out of one of them, found their way into Dr. Joass’s hands. This at once led to an examination,

2 This is almost certainly a misidentification. Tourmaline is very unlikely to occur in the syenite; it is more or less restricted to peraluminous, boron-rich melts derived from sedimentary protoliths (John Faithfull, personal communication, 2019).
and ultimately to the larger part of the boulder being broken up by the writer in the interests of science”.

Clearly impressed by the calibre of the material Heddle (1883a) notes that:

“Many of the crystals are of so fine a colour that, when first seen, the effect, merely as a coloured stone sticking out of the side of the hill, was quite startling. From the centre of this mass specimens of unparalleled magnificence were obtained”.

“Plate V. gives portraits of some of the crystals, - by no means the finest. Those figured varied from 8 to 18 lbs in weight”.

According to Heddle (1877) a “magnificent museum specimen” in the possession of the Duke of Sutherland “showed on its surface of some three square feet, eight perfect and some half dozen imperfect crystals of amazonstone, of the size of the fist”. Visits to Dunrobin Castle in 2003 and 2015, and enquiries there, failed to generate any information as to the present whereabouts of this specimen, nor indeed is there any recollection by the present and immediately previous curators of ever having seen it (Starkey, 2015). It is not on display in the museum (Fig. 4), and there appears to be no record of its disposal. There are, however, two

Figure 6. A fractured bright bluish green crystal of ‘microcline var. amazonstone’ about 11 × 8 × 4 cm, from Beinn Bhreac. Roy Starkey photo reproduced by courtesy of Dunrobin Castle.

Figure 7. A 70 × 43 × 56 cm [230 kg] specimen of amazonite in pegmatite from Beinn Bhreac, Tongue, Sutherland collected by Professor M. F. Heddle and deposited in the museum at Dunrobin Castle. The specimen was subsequently presented to National Museums Scotland by the Countess of Sutherland in 1966. Reg. No. NMS G.1966.41. Image reproduced courtesy of National Museums Scotland.
specimens on display in the unlit cabinets on the upstairs balcony of the museum: a block of amazonite-bearing pegmatite from Ben Loyal (Fig. 5); and a smaller, fractured, bright bluish green crystal of ‘microcline var. amazonite’, from Beinn Bhreac (Fig. 6).

Further enquiries revealed that the specimen referred to by Heddle (Fig. 7) had been presented to the National Museum of Scotland (now National Museums Scotland) by the Countess of Sutherland in 1966. The specimen was mentioned, and figured, in The Royal Scottish Museum Annual Report for 1966 (Anon., 1966), and is also noted in Livingstone (2002). The entry in the museum register reads:

“Presented by the RT. HON. THE COUNTNESS OF SUTHERLAND, Uppat House, Golspie, Sutherland”.

“Magnificent mineralogical specimen consisting of fist-sized felspar [sic] crystals (amazonite) stud-ding surface of granitic vein which cuts syenitic granite. The size of the specimen is 2½ x 2 x 1½ feet and is a perfect mineral casket containing many minerals, some of which are rare or peculiar to Scotland. The specimen was obtained about 1873, from the eastern slopes of Ben Bhreck [sic], Sutherland. See Min. Mag. for 1884, pp. 133–189 “The Geognosy and Mineralogy of Scotland, Part IV” by Professor M. F. Heddle. Many cracks in microcline crystals and matrix surrounding crystals. Cracks injected by syringe with polyvinyl acetate, several times.” [Note the reference is cited incorrectly and refers to (Heddle, 1883a)].

Victorian Specimens

A surprising number of nineteenth-century specimens of Sutherland amazonite have been located in museum collections in the course of this research. They are almost all traceable to Heddle or his collecting partner Patrick Dudgeon. The following paragraphs provide an overview of the material.

National Museums Scotland, Edinburgh

Unsurprisingly, the collections of National Museums Scotland contain the greatest number of specimens of amazonite from Sutherland. A total of sixty-one specimens were examined in this research and of these forty-one originated from the boulder (or boulders) on Beinn Bhreac near Tongue (variously spelled Beinn Bhreck, Ben Bhreck, Ben Bhreac and Ben Bhreck); three are stated to be from Ben Loyal (Ben Laoghal) but of these possibly two are also from Beinn Bhreac; five are listed as Sutherland, five are from Sgo`r Chaonasaid on Ben Loyal (Sgo`r-a Chonais-aite of Heddle); one is from a wall at Ribigill; and one is from Taransay in the Outer Hebrides. Thirty-two of the specimens are from the Heddle Collection and a further twenty from that of Heddle’s collecting partner and friend Patrick Dudgeon.

Most of the specimens are anhedral fragments and part-crystals of various sizes ranging from about 1 x 5 cm or so, up to about 60 x 50 cm, but there are several fairly complete euhedral crystals up to about 100 x 50 cm, and a couple of exceptionally large, fractured crystals, most notably NMS G.1952.5.266 which is split in two, but when re-assembled forms a blocky composite crystal of about 180 x 110 x 110 mm. The colour of the amazonite varies from very pale green to an intense blue-green. The specimens commonly exhibit a pronounced perthitic intergrowth.

A number of well defined crystals have faces annotated with the various crystallographic forms and several were

3 The specimen had not been seen for many years, and the authors are grateful to Peter Davidson of NMS for the considerable effort which he expended in locating the crate in which it is stored and for arranging a viewing in May 2019.
exhibited as part of a display of the ‘Annotated Mineral Specimens of Professor Matthew Heddle’ at the Tucson Mineral Show in Arizona, USA in February 2018, bringing this interesting historical occurrence to the attention of a global audience (Figs 8 and 9).

The Hunterian Museum, Glasgow
Ten specimens of Sutherland amazonite are preserved in the collections of the Hunterian Museum, University of Glasgow. Several of these are from the collection of the former Department of Geology at the

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**Figure 10.** A tray of thin sections from Matthew Forster Heddle’s thin section collection. Roy Starkey photo reproduced courtesy of the Hunterian Museum, University of Glasgow.

**Figure 11.** Thin sections of Sutherland amazonite from Matthew Forster Heddle’s collection. Roy Starkey photo reproduced courtesy of the Hunterian Museum, University of Glasgow.
University of Dundee: some are labelled as from Ben Loyal and others from ‘Ben Breck’. One sawn slab presented by Heddle in 1883 bears a handwritten label:

“Amazonstone Ben Loyal. Mr John Young from Dr. Heddle”.

The most impressive specimen is a blocky euhedral crystal from the Alexander Thoms Collection, formerly at the University of Dundee, which measures $122 \times 97 \times 70$ mm (Fig. 3). Two specimens showing very faintly green crystal sections in a slightly smoky quartz matrix are from the collection of the late Trevor

Figure 12. Photomicrograph of a thin section of amazonite showing exsolved laths of albite in a pale green groundmass of K-feldspar, from the collection of Matthew Forster Heddle (his number 1.8.a.5). The microcline exhibits pleochroism (left), and bright birefringence colours (right) due to the excessive thickness of the old slide, something almost never seen in modern feldspar thin sections of standard 30 μm thickness. Hunterian Museum Reg. No. GLAHM 156210. Field of view approximately 2 mm. John Faithfull image, reproduced courtesy of the Hunterian Museum, University of Glasgow.

Figure 13. The steep and inaccessible face of Sgor Chaonasaid viewed from the north. The crag is about 260 m from bottom to top. Roy Starkey photo.
Bridges, collected by him high up on Sgór Chaonasaid.

In addition to the above hand specimens, the Hunterian Collection includes Matthew Forster Heddle’s thin section collection, which passed to Alexander Thoms (Figs 10–12). This beautifully curated collection contains more than a dozen thin sections of amazonite from Sutherland.

Natural History Museum, London

The collections of the Natural History Museum (London) include sixteen specimens of amazonite from Sutherland. Of these, nine have early British Museum style numbers e.g. BM.53783; four were presented by Patrick Dudgeon in 1881, and a further three specimens (one of which is actually five separate fragments accessioned as BM.71582) were presented in 1893. Notable specimens include:

BM.53783, a large incomplete single crystal 100 × 65 × 60 mm with a label affixed “Amazonstone, near Tongue, Sutherland. P.D.” [presumably Patrick

Figure 14. Pegmatite boulder 30 cm across showing crystal sections of bleached amazonite. Photo copyright and courtesy of Mike Wood.

Figure 15. Amazonite-bearing pegmatite vein in a large boulder of syenite. The exposed surface is about 40 cm wide. Chris Finch photo.

Figure 16. Detail of the amazonite-bearing pegmatite vein (35 cm wide). The black grains are magnetite. Roy Starkey photo.

Figure 17. Typical example of amazonite-bearing pegmatite, 110 × 80 × 60 mm, showing clean white sprays of platy albite variety cleavelandite. Roy Starkey specimen and photo. Reg. No. RES 0080-017.
BM.55730, a portion of a crystal cut into two sections with the surfaces polished to show the perthitic texture 75 × 50 × 50 mm. Tongue, Sutherland, Scotland. Presented by Professor J. W. Judd FRS in 1884.

A further five examples are from the collection of C. R. Lindsey, accessioned in 1985, but acquired by the Museum in the early years of the twentieth century. Lindsey’s specimens include a large and well formed, cracked and possibly repaired, green prismatic crystal 165 × 70 × 60 mm stated as being from Tongue, Sutherland, which was acquired by him in 1909; its original source is not stated.

British Geological Survey, Edinburgh

The Scottish mineral collection at BGS Edinburgh contains eight small fragments of amazonite from Tongue, Sutherland, typically up to about 50 × 50 mm, accessioned as MC2027 - MC2033. Specimen MC4188, also from Tongue, Sutherland, shows pale bluish green amazonite in syenitic matrix, is 12 × 10 × 8 cm and contains a black grain possibly of magnetite. Unfortunately there is no additional data concerning the date of collection, nor the source of the specimens.

In addition to the hand specimens S274 is a thin section prepared from material presented by Archibald Geikie (from a boulder containing amazonstone).

Heddle’s Boulder

‘Heddle’s boulder’ was ‘rediscovered’ by the late Gordon Sutherland of Abriachan in 1975. Specimens collected by him passed to one of us (RES) via the late Kemp Meikle and Max Wirth (Roy Starkey Collection registered nos. 0043-009, 0080-002, 0080-003 and 0080-004). The remaining portion was reportedly about “half the size of a family car, and around it were lying fragments which had either been chipped or blown off with explosives by the great man himself”; although initially overjoyed at his find, Gordon Sutherland later told Garry McKay of the Glasgow Herald of his disappointment when he returned to the spot some weeks later only to find that the boulder had been broken up and removed wholesale by person or persons unknown, with only a few fragments remaining (McKay, 1984). The circumstances surrounding this episode are unclear and the whereabouts of the bulk of the material remain a mystery (Johnston, 2019).

The situation regarding the supposed source of the boulder, Sgor Chaonasaid, is equally intriguing. Although Heddle (1877) clearly considered the boulder to be derived from Ben Loyal, he notes (Heddle, 1883b) that:

“In the description of the great boulder which lay upon the west slopes of Ben Bhreck, it was pointed out that in all probability it had been ice carried from the opposite cliffs of Ben Loyal; – an inference exceedingly repulsive, to the views of those geologists who hold that the ice swept over the north of Scotland from the Baltic, the North Sea, and the South-east. The finding by Mr. Mitchell of the piece of amazonstone which he sent to Dr. Joass, ... was a step in determining this question, and in order to ascertain the circumstances of that find, the writer was induced with all haste to return to the locality”.

“A summer’s shower of but two hours’ duration, but of unprecedented violence, had burst with concentrated force upon the northern frontlet of Ben Loyal, (in fact it burst nowhere else). The deluge had, by the action of a water-wedge, torn slabs of rock from the great cliffs, and had cut great trenches in the talus at their foot; which talus had lain undisturbed so long that it was everywhere turf-covered and swathed in birch”.

Figure 18. Specimen showing the contact between the amazonite-bearing pegmatite and ‘normal’ syenite. Chris Finch specimen Reg. No. 2013/69. Dimensions 150 × 150 × 100 mm. Mica plate is 25 mm across. Amazonite crystal 60 × 20 mm. Roy Starkey photo.

Figure 19. Markedly perthitic amazonite, 40 × 30 mm, showing white lamellae of albite in a groundmass of green microcline. Roy Starkey specimen and photo. Reg. No. RES 0080-018.
Here was a rare opportunity for the mineralogist.

Masses of rock which had hammered themselves against each other after plunging through the air for some hundred feet, and gashes out of which the torrent had tossed up the debris of former falls, to a depth of fifteen feet and for a length of half-a-mile.

“I have described the section laid bare in more than one of these gashes; the minerals found were got

Figure 20. Crystal sketches illustrating the morphology of Sutherland amazonite, reproduced from Heddle (1877). The original caption reads:
“Some of the forms of the Tongue crystals. No. 1 is in the possession of Professor Nicol of Aberdeen. Nos. 6 and 7 (Murchisonites from Arran) belong to Mr Dudgeon of Cargen. The others are in the collection of Mr Dudgeon and the Author.”
almost entirely from that which scars the great cliff on its western fringes.

“While desirous to find amazonite in situ, and so definitely to connect the Ben Bhreck boulder with the hill, the writer was above all anxious to find the thorite in quantity sufficient to enable him to analyse it”.

“Three blocks only were found which contained veins with amazonite. One appeared to be an old block disinterred, a second was a fresh new-fallen mass, – the third was doubtful. Though only three blocks showed veins with green felspar, several others carried veins in which the felspar showed the
same structure as does the amazonstone, but from which the green colour seemed to have been bleached”.

“It has in this connection to be remembered that exposure to light exalts the colour of amazonstone; and that a mantle of peat bleaches almost all rocks, and that turf, to a certain extent, effects the same change. The cliffs of Ben Loyal “weather” purple; those portions from which the mantle of turf has lately been skinned off, are as white as paper”.

It appears that Heddle did not actually observe or collect amazonite in situ from the face of Ben Loyal, and that the veins which he discovered in the boulders at the foot of the mountain were narrower than the one here described as they were “never above three inches in width” (Heddle, 1883b).
Other Reports

Gallon (1974) discusses the occurrence of amazonite and notes that:

"Its presence at [Ben] Loyal was first brought to light by Heddle (1879 [actually 1877]) who showed its occurrence in pegmatitic veins in the cliffs of Sgòr Chaonasaid".

It is unclear whether or not Gallon actually observed amazonite occurring in situ. Enquiries at the University of Leeds failed to locate any of Gallon’s research specimens and attempts to contact him via his last known employer in Canada have proved unsuccessful.

Livingstone (2002: pp. 58–59) reported that:

"The Scroll Register of Minerals and Exchange Schedules in the Australian Museum, Sydney, reveals that Professor Anderson-Stuart at the University of Sydney participated in exchange arrangements with the Observatory Museum, Maxwelltown, Dumfries. Most of the 52 specimens sent from the latter originate from Leadhills-Wanlockhead, Tongue, Sutherland (amazonite) ... (R. Pogson, pers. comm., 1997)".

The existence of three amazonite specimens from Scotland (locality variously written as Sutherland or Sutherlandshire) was confirmed in February 2019 as part of this investigation. Specimens D3057 and D3061 are amazonite feldspar from Tongue, Sutherlandshire, Scotland, exchanged from Dumfries Museum, Scotland [Registered 6 August 1890]; and D11370 is a large single crystal of amazonite feldspar, Ben Loyal, Sutherlandshire, Scotland, from Kelvingrove Museum, Glasgow, Scotland [Registered 1 December 1896].

The collector and rock climber Mike Wood, who has visited the area on several occasions, described a steep ascent of Sgòr Chaonasaid (Fig. 13), and the finding of a loose block of amazonite-bearing pegmatite, although this was not of a good colour nor productive of specimens (Wood, 2014). This loose block (Fig. 14) was found on the crest of the precipitous arête of Sgòr a’ Cheirich.

More recently, one of us (CF) discovered a large boulder of syenite traversed by a vein of amazonite-bearing pegmatite whilst exploring Ben Loyal (Figs 15 and 16). Formal permission was sought from the Ben Loyal Estate to undertake field work and collect specimens and we returned independently in 2017 and 2018 to record the occurrence and recover specimens.

Field Description

A large, partially buried, boulder of amazonite-bearing pegmatite was found on steep ground in a gulley below Sgòr Chaonasaid [NC 582 501] at an altitude of about 380 m. The dimensions of the boulder were $85 \times 70 \times 65\text{ cm}$ with an estimated weight of about 1000 kg. It was initially unclear whether the boulder was in situ or not, but excavation around the sides and back of the block has established that it is indeed a loose boulder and that the vein continues through to the underside.

The syenite on either side of the vein is typical, equigranular, pale coloured Ben Loyal syenite and the boundary with the pegmatite is well defined and extremely sharp. The vein is dominated by milky...
quartz with radiating sheaves of platy albite, variety cleavelandite, about 10–20 mm long (Fig. 17).

Crystals and ‘clots’ of blue-green amazonite range from about 10 mm up to 90 mm in length, and typically are surrounded by quartz and show a close association with platy albite, corroborating the observations made by Heddle (1883a). Black grains of strongly magnetic magnetite to about 10 mm across are scattered throughout the vein, and an uncharacterised black mica (the lepidomelane of Heddle) forms thin plates up to about 30 mm in maximum dimension which are sparsely distributed within the vein (Fig. 18). Microscopic rosettes of specular hematite occur here and there in miarolitic cavities. Large masses of cream feldspar, described as orthoclase by Heddle (1883a), are also a significant constituent of the outer part of the vein and in places appear to grade into amazonite.

The amazonite is strikingly perthitic in hand specimen showing white lamellae of albite intergrown with green microcline. This distinctive texture, an intimate intergrowth of sodic and potassic feldspar, results from subsolidus exsolution (the unmixing of two minerals) (Fig. 19).

Many of the crystals and crystal fragments are discoloured due to attack by organic acids and weathering, but deeper within the mass of the boulder fresh bright blue-green crystals occur. Due to the inherent

Figure 30. The finest recent amazonite specimen, in pegmatite on syenite, 170 × 150 × 120 mm in size, with a euhedral crystal of bluish green amazonite measuring 90 × 65 × 60 mm. Roy Starkey specimen and photo; Reg. No. RES 0080-016.
toughness of the pegmatite, the intimate contact between the amazonite and the encasing quartz and the highly pronounced cleavages of the feldspar, it proved extremely difficult to extract intact crystals. However, great care was taken to cause the minimum of damage and several good specimens exhibiting a variety of habits and crystal faces were obtained.

The specimens recovered during the course of this investigation are on a par with the best surviving examples in museum collections. The general morphology of the amazonite crystals is in excellent agreement with the crystal sketches reproduced by Heddle (1877) (Fig. 20). The principal focus of the collecting was to extract intact euhedral crystals of amazonite, but representative matrix specimens to illustrate the mode of occurrence were also secured (Figs 21–30).

DISCUSSION

Amazonite from Sutherland is perhaps one of the most elusive of Scottish minerals, the best known source being ‘Heddle’s boulder’, of which little survives. Convincing evidence of the reported veins in the face of Sgor Chaonasaid is lacking, but new technology in the shape of remote controlled drones with high resolution photographic capabilities, raises the intriguing possibility that one day a project to compile an airborne survey of the inaccessible portions of the crags might be feasible.

Specimens of amazonite have been collected by several individuals from boulders around the foot of Sgor Chaonasaid. The close similarity in textural appearance and mineralogy of ‘Heddle’s boulder’ and that of material from directly below Sgor Chaonasaid lends support to Heddle’s assertion that the large boulder (or boulders) on Beinn Bhreac were derived from Ben Loyal. It is therefore possible that similar boulders of amazonite-bearing pegmatite may yet be uncovered from the rather featureless and boggy tract of peat-covered ground to the north of the mountain.

Colour in Amazonite

The cause of the colour in amazonite has attracted the attention of mineralogists and geologists for more than 200 years. A summary of the various competing theories and explanations is provided in Gallon (1974).

These include the incorporation of chromophore elements such as copper, ferrous iron and manganese; the amount of rubidium in the feldspar; the presence of traces of organic matter; the thallium content; the effect of radioactivity on thallium ions; release of free rubidium ions by irradiation; the substitution of fluoride for oxygen in microcline; physical differences such as lattice defects or strain and the formation of X-type colour centres caused by the replacement of potassium ions by lead.

More recently, an exhaustive review of the history of research has been published by Ostrooumov (2016) in which attention is drawn to the failure of past workers to take into account the crystal chemical features of amazonitic K-feldspar. It is concluded that the colour of amazonite is affected by a number of parameters which reflect the great variation in the chemical and structural peculiarities of this variety of potassium feldspar.

There now appears to be general agreement that there is a direct correlation between the intensity of amazonite colour and its lead content, although this is not the only factor (Ostrooumov, 2016). The cause of the amazonite colour is complex in nature and results from the aggregate effect of several factors, each of them necessary components in the ‘amazonitisation process’.

A specimen of amazonite from the boulder here described was subjected to analysis by laser ablation inductively coupled plasma mass spectrometry at the University of Aberdeen. This yielded a result of 39 ppm lead, which is broadly in line with the data reported for Ben Loyal samples by Gallon (1974).

Dr J. Faithfull of The Hunterian, University of Glasgow, kindly analysed their specimen number DM2873, using a hand-held X-ray fluorescence analyser to examine deep green, pale green, and cream areas on the polished face of this specimen (Fig. 31). This provided a clear demonstration that the green colour...
intensity is related to lead abundance (Fig. 32). Lead abundance correlates with rubidium content, which is a general index of fractionation in granitic feldspars, suggesting that the greenest feldspars crystallised later than buff and pale-coloured ones. This is consistent with the darkest green zone being at the exterior of this cleaved crystal, and the cream zone in the early formed core.

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In the nineteenth century, several trials were driven to test lead- and copper-bearing quartz-baryte-dolomite veins in the Smale Gills, two steeply incised ravines between Brae Fell Mine and Red Gill Mine, in the Caldbeck Fells, Cumbria. Dry Smale Gill Low Level, the most extensive trial, was driven from the north bank of Swinburn Gill. Three distinctive assemblages occur in the spoil: unoxidised primary galena, chalcopyrite and minor sphalerite in quartz-baryte-dolomite veinstone; slightly oxidised ore containing black copper sulphides, bornite and covellite, which is characteristic of enrichment at the base of the supergene zone; and oxidised ore with conspicuous cerussite, ‘chrysocolla’, goethite, malachite and pyromorphite. At the Middle Trial in Dry Smale Gill, poorly mineralised quartz-baryte veinstone contains a ‘Leadhills-type’ supergene assemblage including calcedonite, cerussite, lanarkite, leadhillite, mattheddleite, scotlandite and susannite. At the Upper Eastern Trial in Wet Smale Gill, galena and chalcopyrite have altered to produce a supergene assemblage including anglesite, cerussite, goethite, pyromorphite, malachite and rare mottramite. Other trials in the area appear to have intersected similar mineralisation, but are so overgrown that meaningful sampling is not possible without significant excavation.

INTRODUCTION

Revisions of the principal sites of mineralogical interest in the Dale Beck valley, including Braefell Mine, Red Gill Mine, Silver Gill, the Roughton Gill mines, Hay Gill Mine, Short Grain and Ingray Gill, appeared in the Journal of the Russell Society between 2005 and 2011 (Bridges et al., 2006, 2008, 2011; Green et al., 2005, 2006; Neall and Green, 2009). A few minor localities remain to be described, including the Smale Gill trials, which are the subject of this note.

The Smale Gill trials were made by the Red Gill Company in the late 1860s and early 1870s according to Adams (1988), although an earlier date is implied for the Upper Western Trial in Wet Smale Gill in Shaw (1970). In spite of their proximity to Red Gill Mine, a site which is of international importance for its ‘Leadhills-type’ supergene mineral suite (Cooper and Stanley, 1990; Bridges et al., 2008; Young, 2010), little has been recorded of the minerals that are present.

This account is based on specimens collected in the 1990s by two of the authors (CML and TN) at the Middle Trial in Dry Smale Gill; on specimens collected at the Upper Eastern Trial in Wet Smale Gill by Norman Thomson (NT) during excavations organised by the Mines of Lakeland Exploration Society (MOLES); and on material gathered by David Green (DG) during a field survey with permission of the Lake District National Park Authority (LDNPA) in 2012.

Collections and their associated data inevitably degrade over time. There has been a virtual moratorium on collecting in the Dale Beck valley since the beginning of the twenty-first century. In the current climate few public institutions have the resources to preserve specimens and access to the analytical equipment required to characterise material is extremely limited. A small suite of specimens from the Middle Trial in Dry Smale Gill was donated to the Manchester Museum while that institution was able to accept specimens and actively participate in mineralogical research. Specimens collected by Norman Thomson at Wet Smale Gill were donated to the Oxford University Museum of Natural History (Green et al., 2012) where they are currently being accessioned (Chris Finch, personal communication, 2019). Despite these donations, the most important suites from the Smale Gill trials remain in private hands. One way to safeguard the information is to describe the specimens while they remain available for study.

THE SMALE GILL TRIALS

Two steep ravines cut the eastern flank of Brae Fell between Braefell Mine and Red Gill Mine on the western side of the Dale Beck valley in the Caldbeck Fells (Fig. 1). The southern ravine, Wet Smale Gill, is the larger of the two and it usually contains a small stream. It drops about 170 m in a 650 m course from boggy headwaters around
NY 2915 3503 to NY 2970 3518 where it joins Swinburn Gill. The northern ravine, Dry Smale Gill, only contains an active watercourse after heavy rain. It drops a little more than 100 m in a 350 m course from NY 2947 3538 to NY 2979 3525. The trials are described in two groups, starting in Dry Smale Gill and ending in Wet Smale Gill.

Dry Smale Gill

Dry Smale Gill Low Level (Fig. 2) is driven into the flank of Braefell in an approximately WNW direction from NY 2979 3526 on the north bank of Swinburn Gill. A considerable flow of water issues from the level mouth and together with the relatively large spoil heap this suggests it is more extensive than any of the upper trials. The total drivage is probably a few hundred metres. It may be that Dry Smale Gill is almost completely dry where it discharges into Swinburn Gill because water which previously flowed in the ravine has found a way into the mine workings.

Dumps and other features extend over approximately 40 × 20 m to the northeast of the level mouth. The site is described as considerably degraded by motorcyclists in Tyler (2006), but some restoration may have gone on since then as there were no obvious signs of damage in 2012. The fact that the spoil is relatively unvegetated (unlike any of the other trials in the Smale Gills) suggests the presence of relatively high concentrations of toxic heavy metals; Shaw (1970: p. 60) describes “a hand-washing and sorting floor and the remains of the ore bin”.

The remains of a collapsed shaft or run-in rise can be seen 40 m WNW of the level entrance, below the path that leads to Red Gill, [NY 2976 3527]. This suggests that the low level was driven WNW to undercut the course of Dry Smale Gill. Shaw (1970: p. 70) notes:

“a strong quartz vein carrying lead and copper was discovered by the ancients ... and for much of its course follows [Dry Smale Gill], but at no place can it actually be seen in situ”.

On the north side of the gulley, about 40 m above the path, two trials or pits lie close together at NY 2971 3531 and NY 2972 3531. The associated dumps are very small (about 5 × 5 m) and completely grassed over, suggesting that little mineralised material was found. Traces of supergene minerals including brochantite, cerussite, chalcopyrite, galena, goethite, linarite and pyromorphite were found in an isolated quartz block about 10 m southeast of the dumps [NY 2971 3530] in 2012, but it is impossible to be certain that it was from these trials. About 40 m west of the trials a small trench with a north–south orientation may be related to mining. A possible interpretation is that these features were cut in search for the vein in situ in areas where float quartz was found, and that they were abandoned when it became clear that there was little or no ore to be won.
The majority of specimens labelled ‘Dry Smale Gill’ in modern collections [mostly micromount-size specimens found by CML] are from the Middle Trial. It was driven in a WNW direction from the gill bed at NY 2966 3532 (Fig. 3). The dump is 15 x 10 m in extent; sparse quartz blocks with traces of cerussite, chalcopyrite, galena, goethite and pyromorphite were noted in 2012. About 25 m further up the ravine [NY 2964 3533] a depression surrounded by an area of mineralised scree might represent the remains of an air shaft, a collapse in the level, or float quartz from the vein outcrop.

The Upper Trial in Dry Smale Gill is at NY 2958 3535. The subsidence crater at the level entrance suggests the drivage is in a WSW direction. It may be a cross-cut, driven from the gill bed to intersect WNW trending veins. A WNW trending vein, which is probably a continuation of the poorly exposed mineralised structures found lower in the Dry Smale Gill is exposed above the level entrance. The mine dump, which covers an area of about 15 x 12 m, is grassed over. Sparse bindheimite, cerussite, galena, goethite and pyromorphite occur in vein quartz, some of which has an unusual stalactitic morphology.

Wet Smale Gill

The vein in Wet Smale Gill is described as “a strong quartz lode which runs in a north-westerly direction” in Shaw (1970: p. 60). There are two obvious trials in the headwaters of the ravine. Both are near the point where a leat, which contours around the hillside to supply water to the dressing floor at Red Gill Mine, crosses the ravine. The Upper Eastern Trial [NY 2951 3527] is driven directly on a steeply dipping quartz vein which is about 0.3 m wide (Fig. 4). The level has been surveyed by Ian Tyler and Warren Allison of the Mines of Lakeland Exploration Society (MOLES) who record a total drivage of “about 140 yards”, but little of mineralogical interest (Tyler, 1995; Tyler and Allison, 1996). An unusual feature of the Upper Eastern Trial is the presence of two entrances within a few metres of each other, perhaps reflecting different periods of working. The extent of the level is indicated on the accompanying sketch map (Fig. 1). Loose blocks of vein quartz from the trial contain anglesite, cerussite, ‘chrysocolla’, galena, goethite, malachite, pyromorphite and mottramite in cavities and on joint planes.

A WNW – ENE trending quartz vein is exposed along a strike length of about 20 m on the hillside above the Upper Eastern Trial (Fig. 5). Several small pits have been cut directly on the vein. The principal gangue
mineral is compact to saccharoidal quartz; baryte is also present. Primary base-metal mineralisation includes galena, sphalerite and chalcopyrite. The principal supergene minerals are cerussite, goethite and pyromorphite with traces of bindheimite, brochantite, hemimorphite, linarite, malachite and mottramite.

About 40 m southwest of the Upper Eastern Trial a level has been driven south from NY 2948 3521, perhaps as a cross-cut. Shaw (1970: p. 60) describes it as ‘a very old level’, and records small amounts of baryte and malachite. Sparse vein quartz containing pyromorphite and a little malachite were noted in 2012. The size of the spoil heap suggests a drivage of about 100 m, however it is almost entirely grassed over and little of mineralogical interest is visible.

Loose blocks of mineralised quartz are present in alluvium just above the point where the track to Red Gill Mine crosses Wet Smale Gill. They may be from the Upper Eastern Trial as the spoil heap has been entirely washed away, but the presence of a hidden lower trial (hinted at in Shaw, 1970) cannot be ruled out. Alternatively, the blocks, which appear relatively fresh and do not appear to have moved far, may be from the top of a vein. Projecting the course of the vein exposed above the Upper Eastern Trial to the ESE suggests that mineralised structures are coincident with the lower course of Wet Smale Gill, but significant excavation would be required to test this hypothesis. Minerals present include malachite, cerussite and pyromorphite with minor baryte in vein quartz.

Figure 4. The Upper Eastern Trial at about NY 2951 3526 in Wet Smale Gill in April 2012. Excavations were carried out here by the Mines of Lakeland Exploration Society; they revealed two entrances, one above the other and “about 140 yards of level” (Warren Allison, personal communication, 2012). Photo Julie Green.

Figure 5. Looking east along the vein from about NY 2945 3526 above the Upper Eastern Trial in Wet Smale Gill, with the Dale Beck valley and part of Roughton Gill Mine in the distance. Quartz blocks are conspicuous in the grass. Photo Julie Green.

MINERALS

The common and characteristic species described in the following text, particularly those recorded during the field survey in 2012, were identified visually, or with the aid of simple chemical and optical tests. Collection specimens were subjected to more rigorous analysis. In cases where there was doubt about an identification, tiny fragments were detached and analysed by energy dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM) in the School of Earth, Atmospheric and Environmental Sciences (SAEAS) at the University of Manchester. If the results proved interesting and sufficient material was available, powder X-ray diffractometry (PXRD) was used in combination with the chemical data to provide an identification.

Minerals such as quartz, baryte, galena and chalcopyrite, which the authors consider to be sufficiently characteristic for visual identification to be appropriate, and those which have been confirmed by PXRD (lanarkite, leadhillite, scotlandite), or EDS (brochantite, malachite, mattheddleite, mottramite and pyromorphite), are listed with their names in the respective subheadings in upper case. Species such as bindheimite which are regarded as questionable by the International
Mineralogical Association are listed in upper case italics. If there is doubt about an identification and further determinative work is required the names are listed in lower case. If a mineral is not considered to be a valid part of the assemblage, or is the subject of a fraudulent or mistaken claim, the names are listed in lower case italics.

A number of species which are present in such small quantities that analysis would either destroy or seriously damage the specimens are excluded from the list. They are briefly noted in the discussion and remain available for study if access to appropriate instrumentation becomes available.

Acanthite, Ag$_2$S

Minute spiky acanthite crystals are present on a few specimens from the Middle Trial in Dry Smale Gill in the Mike Leppington Collection. In common with other localities in the Caldbeck Fells, the acanthite appears to have formed after the specimens were collected and cannot be regarded as a valid part of the supergene assemblage (Bridges et al., 2006, 2008; Green et al., 2006, 2008). It seems likely that the acanthite is produced by the oxidation of native silver, as is the case at Red Gill Mine (Wirth, 1989; Max Wirth, personal communication, 1995), possibly in an electrochemical reaction. Silver was not located on any of the specimens from Dry Smale Gill.

ANGLESITE, PbSO$_4$

Anglesite can be expected wherever galena is subject to supergene oxidation in acid conditions. It occurs rarely on partly oxidised galena as colourless blocky to prismat crystals up to 0.5 mm long at the Middle Trial in Dry Smale Gill. Colourless transparent prismatic to blocky anglesite crystals up to 1.0 mm in length occur in drusy cavities in vein quartz at the Upper Eastern Trial in Wet Smale Gill (Fig. 6).

Ankerite, Ca(Fe,Mg,Mn)(CO$_3$)$_2$

Ankerite is recorded on the “highest tip” (presumably the Upper Trial at NY 2958 3535) in Dry Smale Gill by Shaw (1970). It was not found at this locality on a field survey in 2012. Dolomite-group minerals are common in lead-zinc-copper veins in the Caldbeck Fells, but quantitative analyses are required to distinguish dolomite from ankerite. Most claimed ankerite occurrences across a wide area of northern England have proved to be iron-rich dolomite (e.g. Bridges et al., 2014; Bateman et al., 2018).

BARYTE, BaSO$_4$

Primary baryte occurs as white laminar masses which are relatively late in the primary paragenesis at all of the Smale Gill trials. Casts after a bladed mineral, probably baryte, in vein quartz, rarely contain galena and may be lined with later drusy quartz. This suggests that early baryte was remobilised in the primary paragenesis, prior to the deposition of the late laminar masses.

Supergene baryte occurs rarely as small white rhombic to tabular crystals and colourless to white lozenge-shaped tablets, up to about 1 mm on edge and 0.5 mm in thickness, with cerussite, malachite or ‘chrysocolla’ at the Middle Trial in Dry Smale Gill.

BINDHEIMITE, Pb$_2$Sb$_2$O$_6$(O,OH)

In a standardisation of pyrochlore-supergroup nomenclature Atencio et al. (2010) discredited bindheimite, which was renamed oxyplumboromite using a site-specific chemical scheme. It proved impossible to find the type specimen of bindheimite and in a clarification Christy and Atencio (2013) decided that the status of bindheimite should be changed from ‘discredited’ to ‘questionable’ pending further research. Until this issue is resolved it seems prudent to retain the original name.

Pale yellow earthy bindheimite coatings are common in cavities in quartz containing partly oxidised galena. Bindheimite occurs on the dumps of Dry Smale Gill Low Level and all of the significant trials in Dry Smale Gill and at the Upper Eastern Trial in Wet Smale Gill. Pale yellow pulverulent coatings are particularly common in cavities containing the ‘Leadhills-type’ assemblage at the Middle Trial in Dry Smale Gill, where bindheimite appears to have been one of the last minerals to form. The loose powdery aggregates are particularly vulnerable to washing in water and bindheimite is probably more abundant than a casual inspection of the relatively clean specimens preserved in collections suggests.
Bornite, Cu$_5$FeS$_4$

Typical metallic pinchbeck-brown bornite was visually identified on broken fragments of copper ore at Dry Smale Gill Low Level in 2012.

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

Although it is less common than malachite, brochantite is widespread. It occurs as drusy crusts of minute emerald-green blocky to tabular crystals in cavities in dark brown goethite at the Lower and Middle trials in Dry Smale Gill and drusy crusts of rather rounded poorly developed crystals in granular quartz at the Upper Eastern Trial in Wet Smale Gill. Brochantite rarely overgrows caledonite and linarite at the Middle Trial in Dry Smale Gill.

CALCITE, CaCO$_3$

Calcite occurs as white masses with characteristic rhombohedral cleavage in relatively unaltered vein material on the dumps at Dry Smale Gill Low Level. It is absent or very rare in the oxidised vein material found higher in the Smale Gills.

CALEDONITE, Pb$_5$Cu$_2$(CO$_3$)(SO$_4$)$_3$(OH)$_6$

Euhedral, transparent to translucent, blocky to elongated-prismatic and tabular caledonite crystals of a rich turquoise-blue to blue-green, up to about 1.5 mm in length, were found in a few blocks of vein quartz at the Middle Trial in Dry Smale Gill in the mid-1990s (Fig. 7). The crystals are typically associated with the minerals of the ‘Leadhills-type’ supergene assemblage including bindheimite, cerussite, ‘hydrocerussite’, leadhillite, linarite, mattheddleite and susannite.

Small blue blocky crystals occur rarely on partly oxidised galena with platy hydrocerussite. Some are slightly corroded and may be overgrown by minute acicular mattheddleite. Although they are not as large or rich as the best from nearby Red Gill Mine, caledonite specimens from the Middle Trial in Dry Smale Gill are closely comparable in their morphology and associations.

A reference to caledonite in the collection of the Natural History Museum from Wet Smale Gill in Young (1987) appears to refer to questionable material collected by Arthur Kingsbury at a bell pit on the west side of Swinburn Gill near NY 2965 3508. Specimens from this locality, which include claimed gold, are described in detail in Bridges et al. (2008).

CERUSSITE, PbCO$_3$

Cerussite is common at the Smale Gill trials, it occurs as thin films and minutely drusy crusts wherever galena is subject the supergene oxidation, and was noted at all of the localities surveyed in 2012.

CHALCOPYRITE, CuFeS$_2$

Chalcopyrite is the most abundant primary copper mineral at the Smale Gill trials. Large masses of chalcopyrite occur rarely on the dumps to the north and east of Dry Smale Gill Low Level where Shaw (1970) noted “some fair pieces of mixed lead-copper ore”. More commonly, chalcopyrite occurs as small anhedral to idiomorphic masses, some crudely sphenoidal, in quartz veinstone. Some are relatively unaltered and reveal bright brassy yellow chalcopyrite on broken surfaces, but most are partially to completely replaced by dark brown goethite.
Chrysocolla, (Cu,Al)$_2$H$_2$Si$_2$O$_5$(OH)$_4$.nH$_2$O

‘Chrysocolla’ has been reported at numerous localities in the Caldbeck Fells (Cooper and Stanley, 1990), but to the authors’ knowledge, none of the specimens have been confirmed by PXRD. Indeed powder patterns that are supposed to be characteristic of chrysocolla (published by the Joint Commission on Powder Diffraction Standards) are widely variable. Copper-bearing silica gels from Tankardstown Mine in Co. Waterford were investigated by Moreton (2007) and compared with material from the Caldbeck Fells. It was concluded that material which is widely labelled as chrysocolla might be better described as a ‘copper-bearing silica gel’. In the absence of detailed structural data this seems to be a reasonable recommendation, however the term ‘chrysocolla’ is retained in this description for convenience and continuity.

Chrysocolla, *sensu lato*, is relatively common at the Smale Gill trials. It occurs as bright blue masses on the dumps of Dry Smale Gill Low Level (Shaw, 1970: p. 60). At the Middle Trial in Dry Smale Gill, blue to green coatings of ‘chrysocolla’ on radiating acicular malachite crystals to about 6 mm long are relatively common. In some cases, the malachite has been completely replaced to produce pale blue to blue-green pseudomorphs.

Blue to blue-green masses up to 5 mm across, which developed characteristic syneresis cracks in storage, were collected at the Upper Eastern Trail in Wet Smale Gill in 2012.

Covellite, CuS

Metallic blue rims, which may develop an iridescent tarnish, commonly surround primary sulphides, especially galena, at the Smale Gill trials. This material is commonly described as covellite, although, as with chrysocolla, the term must be used *sensu lato*, as the rims probably contain intergrown yarrowite and spionkopite and other compositionally similar intermediate copper sulphides which can only be distinguished to species level using reflected light microscopy.

**CUPRITE, Cu$_2$O**

Minute red cuprite cleavages in oxidised copper-rich vein quartz are present on two specimens from the Middle Trial in Dry Smale Gill in the Mike Leppington Collection. Cuprite is uncommon but widespread in the Caldbeck Fells in this type of oxidised assemblage and is sufficiently characteristic for there to be little doubt about the visual identification.

**DOLOMITE, CaMg(CO$_3$)$_2$**

Massive white to beige dolomite occurs with base-metal sulphides in vein quartz on the dumps of Dry Smale Gill Low Level. Pale to dark brown cellular rhombohedral pseudomorphs of clay minerals and limonitic iron oxides after dolomite (or possibly ankerite) occur at the Middle Trial in Dry Smale Gill, and the Upper Eastern Trial in Wet Smale Gill, suggesting that dolomite-group minerals were formerly abundant in the oxidised veins. The absence of abundant goethite, which is commonly formed where ankerite undergoes supergene alteration, strongly suggests dolomite rather than ankerite is the dominant mineral at the Smale Gill trials.

**GALENA, PbS**

The Smale Gill trials were made in the nineteenth century for lead and copper ores. Although it does not appear to have been found in commercially viable quantities, galena was noted at all of the localities surveyed in 2012. It occurs as anhedral to idiomorphic masses in quartz-baryte-carbonate veinstone and is concentrated between early primary quartz and later baryte on some specimens. Masses of mixed galena-chalcopyrite in vein quartz up to 10 cm across occur rarely on the poorly vegetated dumps of Dry Smale Gill Low Level; these are the ‘fair pieces of mixed lead-copper ore’ described in Shaw (1970). Cubic to cuboctahedral galena crystals, up to a few millimetres on edge, occur rarely in cavities lined with drusy quartz crystals at the Middle Trial in Dry Smale Gill and the Upper Eastern Trial in Wet Smale Gill.

**GOETHITE, FeO(OH)**

Goethite and hematite are the most common and stable iron oxide minerals in the conditions at the surface of the earth and are end-points of most alteration sequences involving iron minerals (Cornell and Schwertmann, 2003). Goethite tends to be the dominant phase in gossans.

Iron-stained quartz veinstone is conspicuous at all of the Smale Gill trials, but goethite and ‘limonite’ are not especially abundant. Partial to complete goethite
Pseudomorphs after chalcopyrite are fairly common at the Upper Eastern Trial in Wet Smale Gill. Goethite also occurs as dark brown crusts with a radiating structure on broken edges, associated with pyromorphite and cerussite. Goethite is likely to be a component of brown cellular material which replaces iron-bearing dolomite at most of the trials.

**HEMIMORPHITE, Zn₄Si₂O₇(OH)₂·H₂O**

Zinc-bearing supergene minerals are rare at the Smale Gill trials. Grey to white drusy crusts with minor sphalerite from quartz blocks in the vein exposure above the Upper Eastern Trial in Wet Smale Gill are almost certainly hemimorphite; they gelatinise in dilute mineral acid.

**Hydrocerussite, Pb₃(CO₃)₂(OH)₂**

The revalidation of plumbonacrite (CNMNC, 2012), and recent description of the pale green hydrocerussite-like mineral somersetite (Sidra et al., 2018a,b) makes many descriptions of ‘hydrocerussite’ from the Caldbeck Fells and other areas unreliable. Visual identifications aided by simple chemical or optical tests are no longer sufficient to be sure an unknown phase is hydrocerussite; analysis by PXRD is required to characterise specimens. In the Caldbeck Fells, the problem is further complicated by Arthur Kingsbury’s potentially fraudulent claims, based on specimens that cannot be located (Bridges, 2009).

White to pale blue crystalline patches and pearly cavity linings, typically covering areas up to about 1 mm², but rarely with crystals up to about 2 mm across covering larger areas (Fig. 9) associated with caledonite or cerussite occur at the Middle Trial in Dry Smale Gill. Analyses by wet chemistry shows the material is a basic lead carbonate. It may be hydrocerussite, plumbonacrite or, as the minerals may intergrow, both. A faint green tinge which is evident on some specimens is not dissimilar in colour to somersetite, which also occurs as intergrowths with hydrocerussite.

Hydrocerussite listed in good faith from an “old bell pit” in Wet Smale Gill in Young (1987) on the basis of specimens at the Natural History Museum in London appears to refer to questionable material collected by Arthur Kingsbury on the west side of Swinburn Gill near NY 2965 3508 (Bridges et al., 2008).

**Lanarkite, Pb₂(SO₄)O**

Lanarkite is relatively rare in the Caldbeck Fells. Fraudulent specimens in the Kingsbury Collection are summarised in Bridges (2009). Genuine specimens are restricted to ‘Leadhills-type’ assemblages at Braefell Mine (Bridges et al., 2006); Driggith Mine (Green et al., 2006); Red Gill Mine (Bridges et al., 2008); Silver Gill (Green et al., 2005); the outcrop of the South Vein in higher Roughton Gill (Green et al., 2008); and Short Grain Low Level (Neall and Green, 2009). Lanarkite is very rare as millimetre-size or smaller crystals at all of these localities except the outcrop of the South Lode in higher Roughton Gill, where crystals up to about 5 mm have been collected with other lead-bearing supergene minerals on specimens to small hand size.

At the Middle Trial in Dry Smale Gill, lanarkite occurs rarely as bladed crystals up to about 3 mm in length in cavities associated with galena, leadhillite-group minerals, mattheddleite and scotlandite (Fig. 10). Lanarkite occurs rarely in well-sealed cavities containing slightly oxidised galena between quartz and massive white baryte. Although rare, the crystals from Dry Smale Gill are comparable in size and quality to those from higher Roughton Gill.

**Leadhillite, Pb₄(SO₄)(CO₃)₂(OH)₂**

Leadhillite is noted without description at the Middle Trial in Dry Smale Gill in Neall et al. (2006). Pseudohexagonal white to colourless leadhillite crystals, up to 4 mm across, some with characteristic offset chamfers, occur in cavities in quartz-baryte veinstone (Fig. 11). Although it occurs with other supergene minerals of the ‘Leadhills-type’ assemblage, including bindheimite, caledonite, mattheddleite, scotlandite and susannite, leadhillite is commonly found in isolation as relatively large crystals in cavities in quartz veinstone.
LINARITE, PbCu(SO₄)(OH)₂

Linarite is conspicuous due to its dark royal blue colour and is noted on the dumps of Dry Smale Gill Low Level in Shaw (1970), which notes:

"Some fair pieces of mixed lead-copper ore can be picked up and specimens show small quantities of linarite and chrysocolla."

No specimens were located at the site on a field survey in 2012, collector activity perhaps removing all of the obvious material in the intervening years.

Dark blue prismatic, bladed, and lath-like linarite crystals up to 2.5 mm long occur with caledonite in cavities in vein quartz at the Middle Trial in Dry Smale Gill (Fig. 12). Thin blue to blue-green flowstone crusts found at the same site may be the result of post-mining oxidation and appear to be mixtures of poorly crystalised linarite, malachite, cerussite and possibly brochantite. Similar crusts containing dark blue linarite occur in float quartz above the Upper Eastern Trial in Wet Smale Gill.

Figure 10. Typical flattened colourless lanarkite blades bridging a cavity around partly oxidised galena with abundant minutely drusy mattheddleite overgrowing the left hand crystal and the matrix in the bottom third of the image. Field width 3.5 mm. From the Middle Trial in Dry Smale Gill. Tim Neall Collection; photo David Green.

Figure 11. A group of pseudo-hexagonal white leadhillite crystals, 5 mm across, on iron-stained quartz from the Middle Trial in Dry Smale Gill. Specimen No. 3791 in the Tim Neall Collection; photo David Green.
MALACHITE, Cu₂(CO₃)(OH)₂

Malachite is the most abundant supergene copper mineral at the Smale Gill trials. It is widespread and conspicuous at Dry Smale Gill Low Level. Shaw (1970: p. 60) notes its occurrence at the Upper Western Trial in Wet Smale Gill. Traces of malachite and pyromorphite were noted at this locality in 2012, but the spoil heap was so heavily vegetated that little could be located.

Radiating sprays of dark green malachite up to about 6 mm across, some with tabular supergene baryte, occur in cavities in vein quartz at the Middle Trial in Dry Smale Gill (Fig. 13). They are commonly coated by a thin pale grey to blue ‘haze’ which is probably an amorphous copper-bearing silicate.

Malachite is relatively common at the Upper Western Trial in Wet Smale Gill. Rich dark green botryoidal sprays with white prismatic to tabular cerussite, were found in float quartz (which may have been washed down from one of the upper trials or may represent a vein exposure in the gill bed), just above the point where the track to Red Gill crosses Wet Smale Gill on a field survey in 2012 (Fig. 14).

MATTHEDDLEITE, Pb₂₀(SiO₄)₇(SO₄)₄Cl₄

Mattheedleite occurs in ‘Leadhills-type’ supergene assemblages at a number of localities in the Caldbeck
Fells (Cooper et al., 1988; Cooper and Stanley, 1990; Bridges et al., 2008; Green et al., 2008). It is noted without description at the Middle Trial in Dry Smale Gill in Neall et al. (2006). At this locality, mattheddleite occurs in cavities in quartz-baryte veinstone with caledonite, leadhillite, scotlandite and susanite, as minutely drusy crusts and radiating sprays of colourless to white hexagonal crystals terminated by a sharp ‘pencil point’ (Fig. 15). Most crystals are less than 0.1 mm in length, although a few reach 0.25 mm.

MOTTRAMITE, PbCu(VO₄)(OH)

Mottramite occurs as inconspicuous brown bipyramidal crystals on specimens from the Upper Eastern Trial in Wet Smale Gill. Minute brown crystals occur on a black botryoidal barium manganese oxide, probably romanèchite. Blocky brown mottramite bipyramids up to about 0.2 mm across occur with white to pale green pyromorphite on iron-stained quartz veinstone (Fig. 16).

PYROMORPHITE, Pb₅(PO₄)₃Cl

Although the specimens are generally small, pyromorphite from the Smale Gill trials displays in miniature many of the features that make it such a desirable collector species at more famous localities in the Caldbeck Fells (Cooper and Stanley, 1991). Colours vary from white to yellow, green and brown; and multicoloured zonation is commonplace. Crystals may be elongated to squat prismatic and tabular and commonly display the curved rice-grain morphology that is well known at other localities in the area. Curved prism faces and concave pinacoids are common. All of the handful of specimens examined by EDS during this study proved to be pyromorphite; no arsenic or vanadium were detected. Unlike other recent studies however, the sample size (5 specimens) is relatively small. The possibility that some crystals might have compositions tending toward mimetite or vanadinite remains.

Pyromorphite is the most abundant and conspicuous lead-bearing supergene mineral at the Smale Gill trials. It was visually identified at all of the localities surveyed in 2012, as yellow to green minutely drusy crusts in cavities and fractures in vein quartz, and rarely in fractures in the associated country rock. Well crystalised specimens, with millimetre-size colour-zoned rice-grain crystals in fractures in vein quartz were...
collected in the mid-1990s at the Middle Trial in Dry Smale Gill (Figs 17 and 18). Blocky white, yellow, brown and olive-green crystals up to about 3 mm on edge were found on iron-stained vein quartz at the Upper Eastern Trial at Wet Smale Gill at about the same time (Fig. 19).

Figure 17. Colour zoned lenticular to squat prismatic pyromorphite crystals, the largest about 0.6 mm long, on iron-stained quartz from the Middle Trial in Dry Smale Gill. Mike Leppington Collection; photo David Green.
QUARTZ, SiO₂

Quartz is the principal primary mineral in all of the veins tested by the Smale Gill trials. It occurs intergrown with carbonates, baryte and base-metal sulphides in relatively unaltered veinstone on the dumps of Dry Smale Gill Low Level. Quartz with a hacked texture,
containing planar voids, suggesting the former presence of platy baryte is present on some of the dumps in Dry Smale Gill. Some voids are lined by drusy pyramidal quartz crystals, which clearly post-date the dissolution. Quartz crystals with prominent pyramidal terminations and prism faces that are either very small or absent are common in cavities; they do not generally exceed 10 mm on edge. Minutely drusy crusts overgrowing rounded stalactites were noted at the Upper Trial in Dry Smale Gill in 2012.

Weathered veinstone is present as blocks in the till in the Smale Gills and is particularly abundant at the vein exposure above the Upper Eastern Trial in Wet Smale Gill; it varies from tough and compact to cavernous and locally minutely crystalline and saccharoidal in texture depending on the quantity of carbonate and sulphide minerals that have leached away.

Sphalerite, ZnS

Sphalerite is the least common of the major base-metal sulphides at the Smale Gill Trials. It occurs as resinous brown cleavages in relatively unaltered veinstone on the dumps of Dry Smale Gill Low Level. No specimens are known from the upper trials in Dry Smale Gill. Idiomorphic crystals up to about 1 mm on edge, embedded in vein quartz and small red to brown resinous masses occur at the Upper Eastern Trial in Wet Smale Gill.

Scotlandite, PbSO₃

Scotlandite is the only species from the Smale Gill trials which has been described in any detail. It is noted from the Middle Trial in Dry Smale Gill in Neall et al. (2006: p. 86) as follows:

“Scotlandite occurs with leadhillite and mattheddeite in cavities and thin fractures in the centre of poorly-mineralised veinstone blocks, sometimes with partly corroded galena. It is the first supergene mineral to have formed on all of the specimens that were examined. Prismatic to blocky Type 2 crystals and Type 4 prisms are the predominant habits. The scotlandite from Dry Smale Gill was identified by XRD (reference number MANCH: XRD765). A specimen [is] preserved in the Manchester Museum collection under accession number N16035”.

Four distinctive scotlandite crystal habits are recorded in Neall et al. (2006: pp. 83–84); the first two are commonly present at sites in the British Isles where scotlandite occurs, the others are more site specific, with type 4 having a particular association with Dry Smale Gill:

“Most scotlandite crystals on the specimens we have examined are variants of two distinct habits labelled here as types 1 and 2. ... Type 1 crystals comprise elongated needles bounded by four gently curved faces that terminate at a point, they often occur in radiating clusters. Type 2 crystals are made up of elongated prismatic {100} and {010} forms terminated by various pinacoids to produce acute chisel-shaped crystals ...”

“There is another morphology, described here as Type 4, in which the crystals are elongated parallel to the a-axis. At Dry Smale Gill, the Type 4 morphology is relatively common and the crystals are often twinned, sometimes repeatedly, producing low angle V-shaped or W-shaped crystals. In some scotlandite from Dry Smale Gill, prisms which are highly elongated parallel to the a-axis are terminated by a small rhomb or canoe shaped {100} pinacoid”.

In addition to the type 2 and type 4 crystals, crystals with a type 1 crystal habit up to about 0.3 mm long occur with susannite, minor covellite and bindheimite on slightly corroded galena. Flattened prismatic crystals up to about 0.3 mm in length with characteristic type 2 terminations, associated with minor mattheddleite and leadhillite, in quartz-baryte matrix with slightly oxidised galena are shown in Figure 20.

Sulphur, S

Sulphur is rare. It occurs as minute resinous crystals along fractures and in cavities in slightly oxidised galena.

Susannite, Pb₄(SO₄)(CO₃)₂(OH)₂

Susannite is difficult to separate from leadhillite by PXRD as the powder patterns are very similar, however it can be identified optically in basal sections by its strictly uniaxial interference figure.
DISCUSSION

The Smale Gill trials tested ESE–WNW trending quartz-baryte-carbonate veins, typically a few tens of centimetres in width, containing primary copper, lead and (less commonly) zinc sulphides in lavas of the Ordovician Eycott Volcanic Group. Wet and Dry Smale gills almost certainly follow the course of the veins in their lower reaches, suggesting the presence of shatter zones which are more amenable to erosion than the surrounding rocks.

Most recent reviews of the mineralogy of sites in the Caldbeck Fells are based on significant bodies of published work, supported by ‘old-time’ specimens in museum collections. This is not the case for the Smale Gill trials. The literature is sparse and occasionally contradictory and their mineralogical significance was not recognised until the mid-1990s. The key reference to the mineralogy of the area: *Minerals of the English Lake District: Caldbeck Fells*, simply notes “several small dumps...[which] consist almost entirely of barren quartz or rock deeds” (Cooper and Stanley, 1990: p. 55) and does not record the upper trials in Wet Smale Gill on an otherwise comprehensive plan of localities in the Dale Beck valley (Cooper and Stanley, 1990: p. 56). A plan of the Red Gill Sett in Adams (1988: p. 76) also omits the trials in Wet Smale Gill. This is surprising as Adams (1988) notes that the Red Gill Company reopened the trials in the Smale Gills and drove a new level in Wet Smale Gill in the 1860s.

About thirty species have been identified in this research. Chalcopyrite and galena are the most common primary sulphides. Sphalerite is comparatively rare. The presence of bornite, covellite and fragments of an unidentified black copper sulphide on the spoil heaps north and east of Dry Smale Gill Low Level suggest the working cut the base of the oxidation zone in an area where primary chalcopyrite had undergone supergene enrichment. The level clearly penetrated into unaltered primary mineralisation as compact blocks of quartz veinstone containing fresh baryte, calcite and dolomite are present in the spoil.

Extensive supergene alteration is evident at the upper trials in the Smale Gills. The primary carbonate minerals have been leached away and the relatively mobile zinc sulphide, sphalerite, is rare or absent. Two distinct supergene suites have been identified: a Leadhills-type assemblage found at the Middle Trial in Dry Smale Gill includes the minerals for which Red Gill Mine is famous except macphersonite and chenite (Bridges et al., 2008). A simpler assemblage dominated by the common supergene minerals cerussite, ‘chrysocolla’, goethite, malachite and pyromorphite is present at Dry Smale Gill Low Level, the Middle Trial in Dry Smale Gill and the Upper Eastern Trial in Wet Smale Gill.

An introduction to the formation of supergene minerals in lead-zinc-copper veins is provided in Bridges (2015) and a discussion specific to the formation of the Leadhills-type assemblage at Red Gill Mine in Bridges et al. (2008). Scotlandite forms at intermediate oxidation potentials in solutions in which sulphite rather than sulphate ions are stable. It is associated with slightly oxidised galena and is restricted to isolated sealed cavities, in which, presumably, a relatively low oxidation potential was maintained for sufficient time for a small amount of galena to dissolve. Lanarkite, another product of the early alteration of galena, requires a very low carbonate activity to form [described using $pCO_2$; Bridges et al. (2008); Bridges (2015)]. It also favours cavities in the interior of veinstone blocks. Caledonite, leadhillite, mattheddleite and susannite are common associates and are also found in cavities in the interior of quartz-baryte veinstone blocks from which all traces of carbonate minerals have been leached. Mattheddleite is a very rare species on a worldwide basis and a remarkable number of occurrences are in ‘Leadhills-type’ assemblages in the British Isles.

Cerussite, ‘chrysocolla’, goethite, malachite and pyromorphite dominate in more permeable matrices and in fractures and joints in the vein, where the assemblage is exposed to oxygenated groundwater with a higher $pCO_2$ and phosphate ion activity.

There can be no doubt that further exploration and study would add to the mineralogy of the Smale Gill trials. Black copper sulphides from Dry Smale Gill Low Level require analysis by PXRD to characterise the species present. Tiny green to blue green spherulitic aggregates from Wet and Dry Smale Gills have a visual
similarity to rosasite, but zinc, copper and carbonate would need to be confirmed before listing them as such. Rare blue platy crystals with a pointed termination are clearly one of the hydrated copper sulphates, and look like posnjakite, but cannot be listed without analytical data. Material described as ‘hydrocerussite’ needs to be re-evaluated in the light of recent research on similar species (CNMNC, 2012; Siidra et al., 2018a,b). Pearly scales from the Middle Trial in Dry Smale Gill, in particular, are a ‘good fit’ to plumboanocrite. A blocky leadhillite-like mineral from the Middle Trial in Dry Smale Gill in the Mike Leppington Collection has a strong similarity to the macphersonite described in Neall and Green (2009) from Short Gill. A dark botryoidal barium manganese oxide associated with mottramite from the Upper Eastern Trial in Wet Smale Gill is tentatively described as romanèchite, but requires PXRD to be sure. A few buff to yellow plates with pyromorphite from the same locality may be wulfenite. More of the cream coloured ‘pyromorphite’ associated with mottramite needs to be analysed to determine whether it contains vanadium as vanadinite of near end-member composition has been identified at nearby Red Gill Mine (Bridges et al., 2008). None of the minerals described in this paragraph would be particularly surprising; all have been identified in similar situations at nearby localities in the Caldbeck Fells. They are currently available for study, and would make interesting additions to the mineralogy if a revision of Cooper and Stanley (1990) is ever attempted.

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**INTRODUCTION**

Replacements of rugose corals by hemimorphite were reported and figured by Young (2013) from Grovebeck Mine, Swaledale [SE 0275 9675] in the Askrigg Block portion of the Northern Pennine Orefield. These were interpreted as direct replacements of limestone host-rock by interaction of zinc- and silica-rich fluids during supergene alteration of primary sphalerite. Recent field work has revealed the presence of comparable replacements of rugose corals by smithsonite from the zinc deposits worked in the Middle Fell area, southeast of Alston, in the Alston Block portion of the orefield.

In the Middle Fell area of the Alston Pennines, the cyclothem succession of rocks of the Alston and overlying Stainmore formations of the Carboniferous Yoredale Group host numerous mineralised veins and, in limestone units, locally extensive associated replacement deposits. This part of the orefield is notable both for the great abundance of sphalerite, with galena, other sulphides and both fluorite and barium gangue minerals, typically in subordinate amounts (Dunham, 1990). The deposits of the area are also characterised by the preservation of much more intense supergene alteration of the ore minerals than seen in most other parts of the orefield (Wallace, 1861: p. 199; Dunham, 1990: p. 124). Indeed, at several mines, supergene cerussite and smithsonite have been the principal or only ores of lead and zinc, respectively.

Deposits of supergene smithsonite (described as ‘calamine’) were worked at Farnberry [NY 7319 4493], Holyfield [NY 7320 4491] and the Bayle Hill [NY1728514565] mines, though no reliable records of the tonnages raised are known (Dunham, 1990). Although none of the underground workings are accessible, and the opencast workings at Bayle Hill are today almost wholly overgrown, mineralised material remaining on the dumps provides evidence of the deposits worked.

**LOCATIONS AND DESCRIPTIONS**

**Farnberry and Holyfield mines**

In his description of the Farnberry and Holyfield mines, Dunham (1990: p. 124) notes the development of extensive flat deposits in the Great Limestone containing galena, cerussite, smithsonite, aragonite and calcite within and associated with the Farnberry Old, Holyfield and Holyfield Sun veins, and highlights Wallace’s (1861: p. 199) comment with regard to the presence of smithsonite filling joints in the limestone. Although no dates are given for the workings, the nineteenth century was almost certainly the main period of activity.

The substantial dumps remaining at Farnberry and Holyfield [NY 7312 4484] contain the combined spoil from both mines. Dunham (1990: p. 124) noted that smithsonite remained common on the dumps even though the mines were worked for it and the dumps picked over between 1850 and 1870. Brown cellular ‘dry bone’ smithsonite, the most common form of this mineral in the orefield, is common here, and small masses of compact crystalline pale grey and more rarely, yellowish green smithsonite are also present. The mines are known to have yielded specimens of crystalline smithsonite, a fine yellow crystalline mass from Farnberry Mine is illustrated in Symes and Young (2008: p. 171). One of the writers (BY) recalls seeing cut and polished specimens of banded yellow and brown smithsonite said to have originated from here.

A single partially weathered specimen of a complete corallite of a rugose coral, preserved in smithsonite, has been recovered from these dumps. It consists of crusts of minute (>0.1 mm) globular aggregates of very pale buff crystalline smithsonite replacing the main anatomical features of the coral. The form of the corallite is well preserved, retaining clear traces of both the external septal grooves and internal septa (Fig. 1).
The preservation is significantly better than that recorded for the rugose corals replaced by hemimorphite reported from Swaledale by Young (2013) and is sufficient to identify it as belonging to the genus *Dibunophyllum* perhaps *D. bipartitum*, a common form in the Great Limestone, notably in the well-known ‘Frosterley Band’ or ‘Frosterley Marble’ (Johnson, 1958).

**Bayle Hill Mines**

The Bayle Hill and Middle Fell Cross veins within the Great Limestone were worked for supergene smithsonite between 1877 and 1890, both underground and from surface opencuts centred around NY 7285 4565. Mineralised limestone in the remaining spoil, together with the extent of the overgrown opencasts, suggests that replacement flats were associated with one or more of these veins and may have also been worked. The only other minerals recorded by Dunham (1990) are calcite and aragonite.

In recent years, partial development of the mine site by the workshops of the modern building stone company have obliterated most of the modest amount of spoil. However, specimens of typical pale brown ‘dry bone’ smithsonite have revealed traces of a solitary coral, preserved as crystalline crusts within the cellular ‘dry bone’ texture (Fig. 2). Although the preservation is much poorer than that of the specimen from Farnberry and Holyfield, sufficient detail remains to indicate that it is likely to be an example of *Dibunophyllum*, though it is impossible to suggest the individual species.

**DISCUSSION**

Dunham and Wilson (1985: p. 107) noted that during supergene alteration, groundwaters may transport zinc for some distance from the primary sphalerite before it is deposited. Young (2013) concluded that the hemimorphite replacements from Swaledale reflect such a mechanism and indicate replacement of the adjacent limestone by zinc-rich fluids during supergene alteration rather than by direct alteration of sphalerite replacements of these fossils. The smithsonite replacements reported here may reasonably be regarded as directly comparable with those hemimorphite replacements.

Whereas hemimorphite is a very widespread supergene zinc mineral in the Askrigg Pennines, where abundant chert wall-rocks produce silica-rich groundwaters, smithsonite dominates the supergene zinc assemblages of the Alston Pennines where chert wall-rocks are virtually absent and groundwaters are typically carbonate-rich.

Wallace (1861: p. 199) commented on the extensive alteration which had affected the zinc deposits at Farnberry and observed that calamine commonly filled joints in the limestone here. This too is consistent with the transport of zinc in solution in supergene groundwaters and may also hint at these smithsonite deposits filling, at least in part, some form of cave system, perhaps analogous to the Malham smithsonite deposits of the Askrigg Pennines (Raistrick, 1954, 1983; Dunham and Wilson, 1985; Arthurton et al., 1988).
An extensive maze cave system in the Great Limestone at Hudgill Burn Mine, approximately 1.5 km east of the Farnberry workings, where widespread supergene alteration of lead and zinc veins and associated flats are also well preserved, has recently been described by Dale et al. (2015). Cerussite was the main lead ore worked at this mine.

It may be that the unusually intense supergene alteration present in the deposits of the Middle Fell area is related to the widespread development of karstic features in this area during Quaternary interglacial and post glacial processes.

Whereas it is reasonable to suppose that well developed pre-Quaternary supergene alteration zones were widespread in the vein and associated deposits of the Northern Pennines, most of these were almost completely removed by erosion during glacial episodes. The Middle Fell area is almost unique within this orefield for the survival of such extensive supergene alteration. This may be attributable to the absence of significant glacial stripping here, and invites speculation that the Middle Fell area may have lain beneath a limited cover of static, ‘cold-based’ ice between the Nent and South Tyne valleys, when adjoining areas were being actively eroded.

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REFERENCES


EPIMORPHS AND PSEUDOMORPHS AFTER FLUORITE FROM THE NORTHERN PENNINE OREFIELD

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Epimorphs after fluorite cubes in quartz, ‘limonite’ and more rarely siderite, ankerite-dolomite, calcite or a combination of these carbonates are present at numerous localities across the Alston portion of the Northern Pennine Orefield. Where subsequent overgrowths of minerals typical of the orefield’s veins occur, dissolution of fluorite during the primary emplacement of these deposits is indicated. In other instances, epimorphs could equally be the result of the displacement of fluorite by more recent weathering processes. Two occurrences of siderite epimorphs after fluorite cubes have similarities to the well known ‘boxes’ from the Virtuous Lady Mine in Devon. In addition to the epimorphs, quartz pseudomorphs after fluorite are described from three locations.

INTRODUCTION

The marked zonal distribution of constituent minerals has long been recognised as one of the most distinctive features of the Northern Pennine Orefield of the Alston Pennines (Smythe, 1921; Dunham, 1934; 1948; 1990). Within most of the vein and associated deposits of the central zone, the principal sulphide minerals, galena, sphalerite and locally chalcopyrite, pyrite and pyrrhotite, occur within a gangue assemblage dominated by fluorite. This is typically associated with an abundance of quartz, both in a coarsely crystalline form and as fine-grained chalcedony, together with variable amounts of siderite, ankerite and locally calcite.

Successive encrusting or inter-banding of constituent minerals is a common feature of the Northern Pennine deposits (Dunham, 1948; 1990). Within vugs, euhedral fluorite crystals are frequently wholly or partially encrusted with other minerals, commonly quartz, both as coarse crystals and as fine-grained chalcedony, and also with siderite, ankerite-dolomite, calcite or a combination of these minerals. In compact vein sections, the cubic outline of fluorite crystals is commonly delineated by overgrown bands of these encrusting minerals. Epimorphs in these encrusting minerals, resulting from the removal of the underlying fluorite, occur at many locations.

The earliest description of epimorphs after fluorite in the Northern Pennines is that of Wallace (1861) who noted the abundance of cubic ‘casts’ (epimorphs) in quartz within the workings of Rampgill Mine, Nenthead, Cumbria [NY 782 435]. More recently Bridges and Wilkinson (2003; 2005) and Wolfe (2004) have described very similar specimens, clearly epimorphous after original fluorite, from this and other locations in the Nenthead area, and have commented very briefly on the presence of similar specimens from Weardale.

In this paper we describe and illustrate the more widespread occurrence within the orefield of such quartz epimorphs and describe hitherto unrecorded epimorphs after fluorite preserved in siderite, ankerite-dolomite and ‘limonite’ and quartz pseudomorphs after fluorite.

Whereas siderite and ankerite-dolomite are extremely abundant minerals within the veins and associated deposits of this orefield, and commonly encrust fluorite crystals in vein sections and in vugs, the precise nature (chemical composition and mineral species) of the iron-bearing carbonate mineral(s) and their subsequent supergene oxidation products has rarely been established (see Bridges et al. (2014) for a discussion of dolomite and ankerite). Accordingly, except where the true identity is known, for the purposes of this paper we refer to the iron-bearing carbonate encrustations and related epimorphs as ‘siderite/ankerite’ and the oxidation products as ‘limonite’.

EPIMORPHS IN QUARTZ

Nenthead and Alston Moor Mines

In his description of Rampgill Mine, Nenthead, Dunham (1990: p. 144) noted that whereas fluorite was abundant within the Rampgill Vein at the horizon of the Firestone Sill, Wallace (1861: p. 143) had observed that in the Great Limestone the mineral was rarely found in significant amounts, adding that:

“At some former period it must have been plentifully deposited in the veins of the district, since casts of its crystals in quartz are by no means uncommon, even in veins where not the smallest particle of the substance can now be found”.

These are plainly quartz epimorphs after fluorite. Wallace (1861) gave no more further descriptions of these, but following the re-establishment of access to workings in this part of the mine by mine explorers, Bridges and Wilkinson (2003; 2005) gave detailed descriptions of numerous specimens collected here together with examples from Smallcleugh Mine [NY 788 429] and Nentsberry Haggs Mine [NY 766 450].
They also noted the presence on some specimens of subsequent overgrowths of minerals including fluorite, ‘siderite/ankerite’ and sphalerite. A fine example from the former locality with overgrowths of sphalerite crystals was figured by Wolfe (2004: p. 5).

Examples of quartz epimorphs after fluorite from Smallcleugh Mine [NY 7870 4300] are sparingly present on that mine’s dumps. Recently collected specimens exhibit overgrowths of minute colourless pyramidal quartz crystals, and more rarely sphalerite and pyrite, on the inner surfaces of these epimorphs (Fig. 1).

Elsewhere on Alston Moor, sharp cubic quartz epimorphs after fluorite cubes up to 15 mm across, though without subsequent overgrowths of vein minerals, have been collected from the dumps of Bentyfield Mine, near Garrigill [NY 756 426].

**Weardale Mines**

In their description of epimorphs after fluorite from the Nenthead area, Bridges and Wilkinson (2003) referred briefly to the presence of similar epimorphs in quartz from Cambokeels Mine, Weardale [NY 935 383], Frazer’s Hush Mine, Rookhope [NY 890 444] and Redburn Mine, Rookhope [NY 928 432]. Although they gave no detailed descriptions of these Weardale specimens, they commented on the presence of later overgrowths of fluorite, ‘siderite/ankerite’ and sphalerite on some of these epimorphs.

Quartz epimorphs after fluorite are common at several other mines in Weardale. Well formed epimorphs after fluorite up to 7 mm across are conspicuous in massive white quartz in a surface exposure of the Slitt Vein. This quartz-rich portion of the vein is exposed within sandstone wall rocks of the Firestone Sill, on the southeastern side of Catterick Moss, at Hill End, near Frosterley in Weardale [NZ 008 356]. Only very small traces of pale purple fluorite remain in these epimorphs, both in the vein exposure and in the numerous loose blocks derived from it (Fig. 2).

Similar epimorphs in crystalline quartz are common in the spoil from a small trial working on Slitt Vein [NY 9850 3610] approximately 2 km west of the previous location (Fig. 3), and are conspicuous on the dumps of following Weardale mines: Yew Tree Mine,
Bollihope [NY 9935 3540]; old workings on Birch Vein, Hill End, Frosterley [NZ 0190 3600]. Specimen is 6 cm across. Brian Young specimen, No. BY9097. Photo Andy Hopkirk.

Figure 4. Bluish white chalcedony epimorphs after fluorite from the workings on Birch Vein, Hill End, Frosterley, Weardale [NZ 0190 3600]. Specimen is 6 cm across. Brian Young specimen, No. BY9097. Photo Andy Hopkirk.

Bollihope [NY 9935 3540]; old workings on Birch Vein, Hill End, Frosterley [NZ 0190 3600] (Fig. 4); and old surface workings on Groverake Vein, Rookhope [NY 8985 4412].

Figure 5. Siderite epimorph after fluorite, reminiscent of Virtuous Lady ‘boxes’. Boltsburn Mine, Rookhope, Weardale [NY 9366 4276]. Specimen is 22 cm across. Specimen in Russell Collection in Natural History Museum; BM 1964, R 1234. Photo © NHM, London.

**Figure 5.** Siderite epimorph after fluorite, reminiscent of Virtuous Lady ‘boxes’. Boltsburn Mine, Rookhope, Weardale [NY 9366 4276]. Specimen is 22 cm across. Specimen in Russell Collection in Natural History Museum; BM 1964, R 1234. Photo © NHM, London.

**EPIMORPHS IN ‘SIDERITE/ANKERITE’ AND ‘LIMONITE’**

Fluorite epimorphs in ‘siderite/ankerite’ and ‘limonite’ have been found at the following locations.

**Boltsburn Mine**

To date the only published description of fluorite epimorphs in siderite is an example from Boltsburn Mine, Rookhope [NY 9366 4276], illustrated and briefly described by Symes and Young (2008: p. 151) and reproduced here as Figure 5. In this specimen, now in the Russell Collection at the Natural History Museum, London, fine-grained dark brown partially oxidised curved rhombic crystals of siderite form hollow casts after former fluorite cubes up to about 8 cm across. Crystals of siderite of exactly similar colour and morphology coat the inner surfaces of the hollow casts and also form rather irregular crusts, of obviously later origin, within the epimorphs. Smaller pale purple fluorite cubes appear to have grown within the casts, indicating a later phase of fluorite deposition. The specimen is reminiscent of the so-called hollow siderite epimorphs known as ‘boxes’ formerly found at Virtuous Lady Mine in Devon (Russell, 1913), a spectacular example of which was illustrated by Embrey and Symes (1987: p. 122).
Beaumont Mine

During the re-opening of Allenheads Mine, Northumberland [NY 8596 4538] as a fluorspar prospect, known as Beaumont Mine, in the 1970s, box-like ‘siderite/ankerite’ epimorphs after fluorite were encountered in mineralised ground in Henry’s Vein, cut in the new inclined access drift at its intersection with the Knopley Level. Contemporary anecdotal reports (Charlie Cooper, personal communication, 2016) suggest that these, together with dull greyish purple fluorite cubes coated with dark brown ‘siderite/ankerite’, were rather common here, though remarkably few examples were either recovered or retained. The few surviving examples of these epimorphs consist of crusts up to about 2 mm thick composed of dark brown finely crystallised ‘siderite/ankerite’, in part altered to ‘limonite’ (Fig. 6).

The outer surfaces of the epimorphs, i.e. the surfaces distant from the underlying fluorite, exhibit sharp curved saddle-shaped rhombic crystals of ‘siderite/ankerite’. All of the specimens observed by the authors consist of broken fragments up to around 10 cm across, of what were plainly encrustations on interpenetrant fluorite cubes up to 4 cm across. No complete ‘boxes’ have been seen, suggesting that the epimorphous crusts were brittle and either fractured in situ after their formation or were broken during mining.

Thorn Green Quarry

The Great Limestone formerly exposed in the western wall of Thorngreen Quarry, near Middlehope in East Allendale, Northumberland [NY 8445 4670], locally exhibited patchy fluorite and ‘limonite’ mineralisation. This was associated with minor fractures within the eastern margin of the Burtleford Disturbance. Dull brownish yellow fluorite was here accompanied by, and in places encrusted with, an abundance of hard dark brown to rather earthy yellowish brown ‘limonite’, almost certainly derived from superficial alteration of original ‘siderite/ankerite’. A few blocks of this ‘limonite’ exhibited very clear cubic epimorphs after interpenetrant fluorite cubes up to about 4 mm across (Fig. 7).

Figure 6. Siderite crusts from a hollow box-like epimorphous cast of former interpenetrant fluorite cubes. Beaumont Mines, Allenheads [NY 8596 4538]: (a) front side; (b) detail of ‘siderite/ankerite’ crystals from front side surface; (c) back side. Specimen is 7 cm across. Brian Young specimen, No. BY9341. Photos Andy Hopkirk.

Figure 7. Epimorphs after fluorite in dense massive limonite. Thorn Green Quarry, East Allendale [NY 8445 4670]. Field of view 5 cm. Brian Young specimen, No. BY7520. Photo Andy Hopkirk.
In recent years this quarry has been abandoned, partially back-filled and the site extensively landscaped, leaving little exposed mineralisation.

**Swinhope Mine**

The mineral collection held at Nenthead Mines Conservation Society includes a specimen of epimorphous casts after fluorite crystals up to 8 mm across in dense dark brown ‘limonite’ (Fig. 8). No details of the specimen’s precise location in the workings is recorded, though fluorite is a rare mineral in the Swinhope veins: Dunham (1990: p. 166), notes that it was a minor constituent only of the southernmost veins worked here.

**Grasshill Common**

At the extensive set of old workings collectively known as the Grasshill mines in the Harwood Valley, Upper Teesdale (Dunham, 1990), several old spoil heaps from workings on the Coldberry Sun Vein [NY 8290 3574] contain an abundance of dense, dark brown, massive ‘limonite’. Epimorphs of interpenetrant twinned fluorite crystals up to 15 mm across are extremely abundant within fragments of this ‘limonite’ (Fig. 9). The surfaces of the epimorphs are invariably smooth with many exhibiting lustrous surfaces. None of the many examples examined display overgrowth of any subsequent minerals. Lustrous dark brown ‘limonite’ pseudomorphs after curved saddle-shaped rhombs up to 1 mm across of ‘siderite/ankerite’ are also abundant, though fluorite is extremely scarce within these dumps.

Exactly similar cubic epimorphs in dense ‘limonite’ are also sparingly present on the dumps from old workings on the Grasshill North Vein at the southern end of the old workings known as Highfield Hushes, Teesdale [NY 8178 3564]. No sign of fluorite is present on any of the specimens seen here or in the associated spoil.

**Queensberry Ironstone Workings**

Extensive flat deposits of ‘limonite’ within the Great Limestone between the Burtreeford Disturbance and the Breckonsike Vein [NY 8565 4135], immediately north of Cowshill in Weardale, have been worked opencast for

![Figure 8. Epimorphs after fluorite crystals up to 8 mm across in dense dark brown 'limonite'. Swinhope Mine, East Allendale. Nenthead Mines Conservation Society, specimen No. 341. Photo Andy Hopkirk.](image)

![Figure 9. 'Limonite' epimorphs after fluorite, with pale blue silicone cast of the original crystals. Grasshill Common, Teesdale [NY 8290 3574]. Specimen is 8 cm across. Brian Young specimen, No. BY8761. Photo Andy Hopkirk.](image)
iron ore (Dunham, 1990). Specimens of dark brown ‘limonite’ pseudomorphous after typical saddle-shaped ‘siderite/ankerite’ rhombs are locally common and, as at other locations described here, are consistent with the origins of the ‘limonite’ by supergene alteration of this carbonate. A few specimens of the typically dense, dark brown, massive ‘limonite’ worked here exhibit epimorphs after interpenetrant fluorite cubes up to 3 mm across. Whereas the inner surfaces of many of these casts display very thin uneven overgrowths, up to >0.5 mm thick, composed of paler brown massive ‘limonite’, no example of ‘siderite/ankerite’ or any other mineral has been observed coating these surfaces.

**PSEUDOMORPHS IN QUARTZ**

Pseudomorphs of fluorite crystals are much less common than the epimorphs already described. However, good examples occur at the following locations, all from mine spoil heaps: none has been seen in situ.

**Shildon Mines**

The veins worked for lead ore at the Shildon mines, north of Blanchland, all carried significant amounts of fluorite (Smith, 1923; Dunham, 1990), accompanied by quartz. The latter mineral occurs both as coarse colourless to white pyramidal crystals and more abundantly as fine-grained chalcedony (Smith, 1923: p. 43; Dunham, 1990: p. 223). From the material remaining on the spoil heaps it seems that chalcedony was a major component of the gangue assemblage. The chalcedony here includes varieties displaying beautiful banding in shades of grey, pale blue and white agate-like forms, and more rarely, well formed botryoidal aggregates. Symes and Young (2008: p. 69) illustrate a fine example typical of the location. Specimens recovered from the dumps display fluorite cubes encrusted with layers of fine-grained banded chalcedony.

A very few specimens collected from the adit spoil heap [NY 9625 5080] in the 1960s exhibit white to very pale blue chalcedony pseudomorphing interpenetrant fluorite cubes up to 4 cm across (Fig. 10). The pseudomorphs consist of crusts composed of an outer layer, up to 1 mm thick, of botryoidal pale bluish grey chalcedony which coats a layer of coarsely crystalline colourless quartz up to 2 mm thick, on the inner surface of which is a further 1 mm thick crust of botryoidal chalcedony, identical to that on the outer face. The inner quartz layer locally includes small concentrations of dark brown crystalline sphalerite up to 1 cm across. The internal portions of the former fluorite cubes are occupied by confused masses of interfering crusts of botryoidal chalcedony, identical to that already described, together with crusts of colourless pyramidal quartz crystals individually up to about 2 mm long. Between these internal quartz and chalcedony layers, open voids up to 3 mm wide, locally lie parallel the former cube faces. No remnants of original fluorite are present. The botryoidal chalcedony crusts which form the external faces of the former cubes are cut in several places by open cracks up to about 0.5 mm wide which appear locally to have been ‘healed’ by further chalcedony mineralisation (Fig. 10).

A second specimen (Fig. 11), appears to consist of a cross section through a former fluorite cube now wholly replaced by pale blue and white banded chalcedony. The arrowed chalcedony layer plainly outlines an original fluorite cube. Roughly parallel layers of similar colour-banded chalcedony encrust this layer. The inner portions of the original fluorite cube are now occupied by convoluted bands of exactly similar chalcedony, with a small central void up to 10 mm across lined with minute colourless pyramidal quartz crystals. Small amounts of pale purple fluorite are present locally beneath a chalcedony crust on the reverse of this specimen, though the relationship of this to the replaced cube illustrated cannot be seen.

Since the specimens described were collected, this spoil heap has been severely eroded by the adjoining stream and the remaining portions of it are today heavily overgrown.

**Rotherhope Fell Mine**

A single specimen, collected from the dumps at the Middle Level of Rotherhope Fell Mine [NY 697 422], in 1984, exhibits sharp white quartz pseudomorphs after interpenetrant fluorite cubes up to 12 mm across (Fig. 12). Broken corners on some of these reveal...
hollow interiors lined with colourless pyramidal quartz crystals up to 1 mm across. All of these pseudomorphs are overgrown by coarsely crystalline colourless pyramidal quartz crystals up to 5 mm across.

**Hard Rigg Edge**

Pale grey quartz pseudomorphs after interpenetrant fluorite cubes up to 4 mm across have been found in the small amounts of spoil remaining from old workings on the west side of Hard Rigg Edge on Melmerby Fell [NY 658 390]. This location was formerly a source of fine specimens of well crystallised green pyromorphite, minute crystals of which locally encrust the quartz pseudomorphs (Fig. 13). At this same location several very striking examples of quartz pseudomorphs after typical rounded ‘cockscomb’ aggregates of baryte up to 25 mm across have also been found (Fig. 14).

**DISCUSSION**

At all of the occurrences described by Bridges and Wilkinson (2003) the quartz epimorphs after fluorite were encountered either *in situ* or as detached blocks...
within old workings far beneath the present ground surface and well below the levels affected by present or recent surface waters. In these instances it seems clear that, as these authors suggest, removal of the original fluorite occurred at some stage during the main mineralising episode and that this was followed by further deposition of small amounts of other minerals typical of the Northern Pennine mineralisation.

However, with the exception of those from the Catterick Moss exposure of Slitt Vein, all of the quartz epimorphs after fluorite described here were collected from mine spoil heaps. It is therefore impossible to establish their original positions in the parent deposits and thus to know whether they result from dissolution events during the original mineralising processes or whether they are the products of recent, post-mining, disintegration or dissolution of fluorite within the present day surface environment. Recent weathering of fluorite commonly results in fragmentation and Dunham (1990: p. 88) has noted that dissolution of fluorite may occur in the presence of sulphate-rich groundwaters, as evidenced by the common occurrence of deeply etched crystal faces seen in fluorite crystals in old spoil heaps or in long-exposed natural outcrops. Unlike the specimens described by Bridges and Wilkinson (2003; 2005) and illustrated by Wolfe (2004), and with the single exception of the specimen from the Smallecleugh Level dump (Fig. 1), none of the quartz epimorphs described here exhibit any later overgrowth of vein minerals. It is therefore possible that many, perhaps most, of the epimorphs found today in spoil heaps are likely to reflect the effects of simple disintegration, augmented in places by dissolution.

The Catterick Moss exposure invites consideration. Whereas fluorite commonly disintegrates relatively easily in the near surface environment and as has been noted, may undergo some limited dissolution, it is difficult to account for its almost total elimination from a portion of vein in which the numerous epimorphs indicate its former abundance. It is therefore possible that some displacement of fluorite may have occurred here during similar mineralising processes to those responsible for creating the epimorphs commonly encountered in the Nenthead area.

With regard to epimorphs in ‘siderite/ankerite’ and ‘limonite’, it is important to note that those described from both Boltsburn and Beaumont mines were, like the quartz epimorphs from the Nenthead area, collected in situ from situations far beneath the level of present or recent surface waters. These occurrences bear considerable similarities to the so-called siderite ‘boxes’ formerly recovered from the Virtuous Lady Mine in Devon (Russell, 1913). Both these and the Northern Pennine epimorphs described here exhibit subsequent overgrowth of later minerals. Clearly, these must have resulted from remobilisation and displacement of fluorite at some stage during the emplacement of the host deposits, followed by overgrowth with minerals characteristic of the parent deposits.

The ‘limonite’ epimorphs after fluorite from the other locations described above show no overgrowth of later minerals. Although the abundance of fluorite in the remaining mineralised material at Queensberry is consistent with the origin of the ‘limonite’ epimorphs by recent weathering of fluorite, the almost complete absence of that mineral from much of the epimorph-rich spoil at Grasshill is rather curious. Had these epimorphs resulted simply from weathering, either in situ in the worked veins, or since incorporation of the mineralised material into these dumps, it might be expected that fluorite would be very much more obvious than is the case. From the limited field evidence at this site, the origin of these epimorphs must be regarded as ambiguous.

It thus seems reasonable to suppose that epimorphs after fluorite in quartz, ‘siderite/ankerite’ and ‘limonite’ result from two separate processes:

1. Epimorphs after fluorite formed during an early episode of fluorite dissolution and displacement during the main phase of emplacement of these deposits;
2. Epimorphs resulting from recent weathering and dissolution of fluorite in the near surface environment.

With regard to (1) above, these are the epimorphs found far below current surface water levels and which commonly exhibit later overgrowths of minerals typical of the orefield. The chemical and physical conditions required to effect the preferential removal of fluorite to leave unaltered overgrowths of both quartz and ‘siderite/ankerite’ are difficult to envisage and we make no attempt to explain them here. They invite further investigation.

Insufficient evidence has been found to suggest a reliable date or mechanism for the formation of the quartz pseudomorphs described here, though it must be considered likely that, like the epimorphs, they were also the product of changing physical and chemical conditions during the original emplacement of the parent deposits.

ACKNOWLEDGEMENTS

We are grateful to Charlie Cooper for providing specimens of the epimorphs from Beaumont Mine and for information on their occurrence within the workings. Adam Pacey is thanked for useful discussions on possible mechanisms of fluorite dissolution and remobilisation. We also thank the volunteers of the Nenthead Mines Heritage Trust for giving access to their collections, the Trustees of the Natural History Museum for allowing the use of Figure 5 and Peter Young for preparing silicone casts of epimorphs examined in this study.

REFERENCES


This beautifully produced and illustrated book is a delight to hold. From the very first page it is clear that this is a quality product with images and text assembled by a veritable army of contributors. Many of the authors will be unknown to JRS readers, hardly surprising for a French publication, but let this not deter you. The images come from Louis-Dominique Bayle, Joaquim Callén, Julien Lebocey, Jeffrey Scovil and Eddy Van Der Meersche.

A preface by Pierre-Jacques Chiappero sets the scene and explains the rationale behind the book. He notes that this is not a classical mineralogical tome, but rather a philosophical essay that showcases the beauty of fluorite and explores its attractions to the collector.

A six page introduction by Christophe himself (in French) is followed by an English version of the same text, but with a different selection of superb images. Here, the author discusses why fluorite holds such a fascination for mineral collectors, reviews the fifty localities selected for inclusion and acknowledges the collectors, photographers and co-authors who have helped to bring this project to fruition.

Next we are treated to six pages putting fluorite into a mineralogical and historical context by Julien Lebocey (in French), followed by an English version of the same text, again with superb, but different, illustrative photos.

A double page spread of an index map of the featured localities together with an index listing them, in order from north to south, concludes the introductory sections. From here it is straight into the locality descriptions.

First up is Bois-le-Duc (known to collectors also as ‘Foisches’ or ‘Givet’). Three beautifully photgraphed specimens are featured, together with a deeply personal narrative from the well-known Catalan dealer Jordi Fabre. Next we have Rancennes in the Ardennes, followed by Glageon in the Nord – Pas-de-Calais Region. Eddy van der Meersche, author of ‘Crystal Forms of Fluorite’ and an accomplished photographer in his own right, provides descriptive text to accompany his chosen specimen.

A rather different locality and one hardly in the same league as most of the others in the book is Les Halle, in the 1st arrondissement of Paris. Here, small crystals of fluorite were discovered in rock excavated in the nineteenth century from the foundations of the Sorbonne and the Horse Market. Given the difficulty of mineral collecting in the centre of Paris today specimens from this locality are considered a real rarity. How many other capital cities can boast a fluorite locality?

Bergheim in the Haut-Rhin provides superb specimens of fluorite hosted in the silicified limestones of the “Muschelkalk” outcrop on the flanks of the Vosges, about 25 km east of Sainte-Marie-aux-Mines, a part of France that will be familiar to many readers.

Pink fluorite from the Massif Du Mont Blanc, Chamonix in the Haute-Savoie probably needs little introduction for JRS readers, even those who collect only British minerals! Ten pages are devoted to this locality and the accompanying images certainly do justice to the specimens.

The 50 featured localities and accompanying text by 45 authors draw together a diverse range of crystal forms, colours and associations. It would be invidious of me to single out a contributor or specimen as a ‘favourite’ so I leave that to purchasers of the book.

A French and English glossary, index of deposits, index of contributors and a list of 48 references conclude the work.

Finally I should like to pay tribute to Tim Greenland who took on the onerous task of providing an English translation of the text whilst retaining the individual styles of the contributors. His efforts will surely broaden the appeal of the book far beyond the borders of France and bring these wonders of the mineral world to the attention not only of serious collectors but also lovers of beautiful natural objects, enjoy! If you have any interest in fluorite, especially from French localities, you really should consider purchasing this book.

Roy Starkey
This book is a completely new edition, with a new publisher, of the classic and definitive work on Blue John fluorite, which Trevor Ford first published in 2000. It has been completely revised, much updated and somewhat expanded by Tony Waltham and Noel Worley. Sadly, Trevor died during the early stages of its preparation. It covers the discovery and mining of the mineral, describes its geology, provides an explanation of the distinctive colour, and records the past and present production of ornaments and decorative items.

The overall content broadly mirrors the first edition starting with ‘The Origin of Blue John’ and continuing through to ‘Notable Blue John Collections’. As one might expect the chapters have been revised to reflect recent discoveries. For example the supposed Roman connection with Blue John is more forcefully discounted, a fact that many Castleton cave guides should take on board, albeit with a heavy heart. The chapter on ‘Blue John look-alikes’ warns caveat emptor. There are many areas of the world with fluorite which bears a passing resemblance to that found at Castleton. Genuine Blue John is highly prized, but it has its imitations. There are similar specimens from other British mines included banded blue fluorite from Matlock and little known specimens from the area around Clitheroe in Lancashire. Similar banding has even been recorded in Scottish fluorite as one of the articles in this journal notes.

Readers familiar with the first edition will notice a larger page and font size. This is key to a successful update. Each page can accommodate larger diagrams and photographs, and can deliver information more clearly. The addition of colour to the maps, sections, profiles and tables is helpful in engaging a wider audience.

The number and quality of photographs in a popular volume such as this is important if it is to be successful and attract the casual reader or tourist who will quickly flick through looking for an arresting feature: in this, the third edition is a considerable improvement. In particular the editors have addressed a problem with the first edition in that they have included photographs of all the fifteen named veins of Blue John. The reader can now compare and contrast the different patterns and attempt to assign specimens to a particular vein; although the natural variation can still provoke discussion!

The question ‘how does Blue John get its colour?’ is frequently asked and has an answer that can run to many paragraphs. In the new edition the chapter that deals with this, ‘The Mineralogy of Blue John’, is less technical than the first edition. The basics are there to guide the reader and present the more refined ideas, with the section ‘Further Reading’ giving more detailed references if required.

It is clear that much thought and effort have gone into this edition. Taking a successful and definitive book and reshaping its contents is not a matter to be taken lightly. This volume is thirty pages shorter than the original but it deals with all the topics covered in the first edition without any obvious loss of data. It appears to be a case of ‘less is more’. Seemingly minor points can make a difference, for example there are no double pages of text without a photograph, chart or table to break up the rubric; there were twelve in the first edition. Even in the section ‘The Discovery of Blue John’ for which there is little primary source material, a carefully placed advertisement from 1769 appears.

A minor point, if there is a reprint of this edition, is that there are a few photographs, in particular of vases and bowls, that have no scale. Some objects on the same page are of very different dimensions.

Many of the chapters, in particular ‘Notable Collections of Blue John’, cite castles, houses and museums where collections of Blue John in all its forms may be found. Given that most have a presence on the internet in one form or another it would be quite easy to organise days out looking at the range of items that have been crafted from the stone.

The comprehensive pages of ‘Further Reading’ and ‘Acknowledgements’ provide useful leads for anyone wanting to dig a little deeper into the subject. This book covers a diverse range of topics in its eighty pages at a depth that anyone interested in Blue John will find rewarding. The editors, Tony Waltham and Noel Worley, are to be congratulated on a guide which has something for everyone. The new edition continues to stand as the finest single volume on Blue John. I’m sure that the late Trevor Ford would approve.

Richard Bateman
NOTES FOR CONTRIBUTORS

The Journal of the Russell Society publishes articles by amateur and professional mineralogists dealing with all aspects of the mineralogy of Britain and Ireland. A detailed Guide for Authors is available on the Russell Society website at: http://russellsoc.org/wp-content/uploads/2019/09/GUIDELINES-FOR-AUTHORS-SUBMITTING-MANUSCRIPTS-FOR-PUBLICATION-IN-THE-JOURNAL-OF-THE-RUSSELL-SOCIETY-2.pdf. Authors are encouraged to prepare papers in electronic format using Microsoft Word and to send file(s) as e-mail attachment(s). All articles should begin with an abstract summarising the significant points of the paper. The body of the text should be divided into appropriate sections and subsections. Results and discussion are not normally intermingled. Figures should be supplied as separate files, with an indication of where they should be inserted in the text. Articles will normally be reviewed by two referees. Submission of a paper to the Journal is taken to imply that all necessary permissions have been obtained and, where appropriate, acknowledged by the authors.

National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST 40 71 and enclosed in square brackets where necessary, e.g.: [ST 4015 7185], [ST 401 718], [ST 40 71]). Claims of less common minerals should be supported by sufficient proof (e.g. X-ray diffraction, electron beam analysis). 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) authors are encouraged to donate to a public museum and record the specimen’s accession number.

All figures must be cited in the article text [e.g.: Figure 1, or (Fig. 1)] and numbered with consecutive Arabic numerals. They should have descriptive captions which record specimen sizes and other relevant data. Tables should be numbered consecutively and referred to in the text as Table 1, etc. Each table should have a caption. Horizontal lines should mark the top and base of tabulated data.

Authors are requested to adhere to the nomenclature and terminology of the International Mineralogical Association. The official list of mineral names and formulae is regularly updated and available at: http://ima-cnmnc.nrm.se/imalist.htm.

Except for common non-scientific abbreviations and those for standard units of measurement, abbreviations should be spelt out in full at their first mention in the article, e.g. platinum group mineral (PGM). If used, ‘n.d.’ in tables must be defined (as ‘not determined’ or ‘not detected’). The following abbreviations are commonly used in journal articles: XRD = X-ray diffraction; PXRD = powder X-ray diffraction; XRF = X-ray fluorescence; EPMA = electron probe microanalysis; EDS = energy-dispersive X-ray spectrometry; WDS = wavelength-dispersive X-ray spectrometry; SEM = scanning electron microscope or microscopy; IR = infrared; UV = ultraviolet.

References should be indicated in the text thus: (Heddle, 1901) or ‘as stated by Heddle (1901)’ or ‘as stated in Heddle (1901)’. Extending the protocol, two authors are cited as (Kneller and Aftalion, 1987) and three or more authors as (Bannister et al., 1950). Personal communications should be cited in the text: (Ann Brown, personal communication) or (Ann Brown, personal communication, 1992). A list of references in alphabetical order should form the last section of each paper. Some examples of the style are given below.

References


