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A Journal of the Topographic Mineralogy of Britain and Ireland

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FRONT COVER: Blocky dark blue azurite crystals with green malachite spherules on white baryte, collected in February 1982 at Tynagh Mine, Tynagh, Co. Galway, by Jean Spence. The field of view in 2.0 mm across. Photo John Chapman.

BACK COVER: A 40 × 40 mm axe-head calcite twin from Moor Farm Opencut, Bonsall Moor, Derbyshire, found in 1981 by Jean Spence and now in the Roy Starkey collection. Photo Roy Starkey.

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EDITORIAL

THERE'S TREASURE EVERYWHERE

Treasure is hidden in all sorts of unlikely places: dusty museum drawers, private collections and even more of it in member's heads. But like treasure everywhere, it's what you do with it that makes the difference. Sitting like Smaug atop a pile of gold may appeal to some. Writing a report for the Newsletter or Journal makes a permanent record and shares some of the excitement with others.

In *JRS* 23, fourteen authors have taken the time to share their discoveries. We begin with a collection focussed biography of Jean Spence. The current 'History of Mineral Collections' in the UK is not even a 'History of Kings and Queens'. A small number of British collections have been described, but even Sir Arthur Russell has no collection focussed biography more than half-a-century after his death. Although it is unusual for a 'typical' amateur collection to be recorded in this way, there can be few Society members who do not own noteworthy specimens. And Jean's material from localities such as Tynagh Mine in Co. Galway and Pendarves Mine in Cornwall (Figs 1 and 2) serves as a reminder of the many similar localities that are crying out for a detailed modern topographic description.

Museum collections play an important role in topographic mineralogy. The first Derbyshire strontianite is noted on specimens from the two-hundred-year-old Joseph Dawson collection, which is preserved at Cliffe Castle, Keighley, West Yorkshire. Museums, especially local museums, have had a tough time in recent years. Cliffe Castle has an eclectic display which includes one of the largest remaining mineral galleries in northern England. Strontianite was discovered by chance while volunteers were making an audit of fluorite specimens. It was subsequently confirmed by XRD at Amgueddfa Cymru – National Museum Wales. It may be of interest to potential authors to note that the Society has set some funds aside to support identifications with a view to publication in the Journal. The report of strontianite also adds 'value' to the specimens entrusted to the care of Bradford Museums and Galleries. It is one of many stories waiting to be told by collections in local museums across the British Isles.

First occurrences are always cause for celebration and several are revealed in *JRS* 23. The first British richelsdorfite is reported on specimens collected by Neil Hubbard at Dolyhir Quarry, one of the most diverse localities in the British Isles and a regular venue for Society field visits (Cotterell *et al*., 2011). The discovery dates from the mid-1990s, when a substantial lead-copper vein was exposed in the Silurian Dolyhir Limestone. Richelsdorfite occurs as attractive turquoise-blue micro-crystals which appear to be an alteration product of antimony-bearing tennantite-(Zn). A recent revision of the minerals of the tetrahedrite group (Biagoni *et al*., 2020) provides an opportunity to examine the composition of 'tennantite' from Dolyhir Quarry. The new species tennantite-(Fe) and tennantite-(Zn), and an unidentified sulphosalt with a composition which suggests it belongs to the stannite group, are reported in a second article.

Although the mineralisation is well understood at a regional scale, many interesting localities remain to be described in the Pennine orefields. Brian Young and colleagues record grains of supergene silver in a diverse assemblage of sulphide, sulphosalt and sulpharsenide minerals from remote workings at Clargillhead in Cumbria. Galena from the area around Clargillhead has an unusually high silver content in comparison to most Pennine localities. The report realises a prediction made by Dunham *et al*. (2001) that a discovery of silver in the Northern Pennines was "only a matter of time".

John Mason, a regular contributor to this Journal, is well known for his studies of mineralisation and metallogeny in Wales. A detailed analysis of deformed pre-Acadian lodes in north Wales, copiously illustrated with reflected light micrographs, concludes that four seemingly disparate groups of workings are part of a single late Ordovician metallogenic province. The study is the product of many years of careful fieldwork, in collaboration with Department of Natural Science at Amgueddfa Cymru – National Museum Wales, where John is an honorary research associate.

Figure 1. Cuprite variety chalcotrichite from a stope between 4 and 5 levels on Tryphena Lode, Pendarves Mine, Cornwall. The field of view is 2.7 mm across. Jean Spence collection. Photo John Chapman.

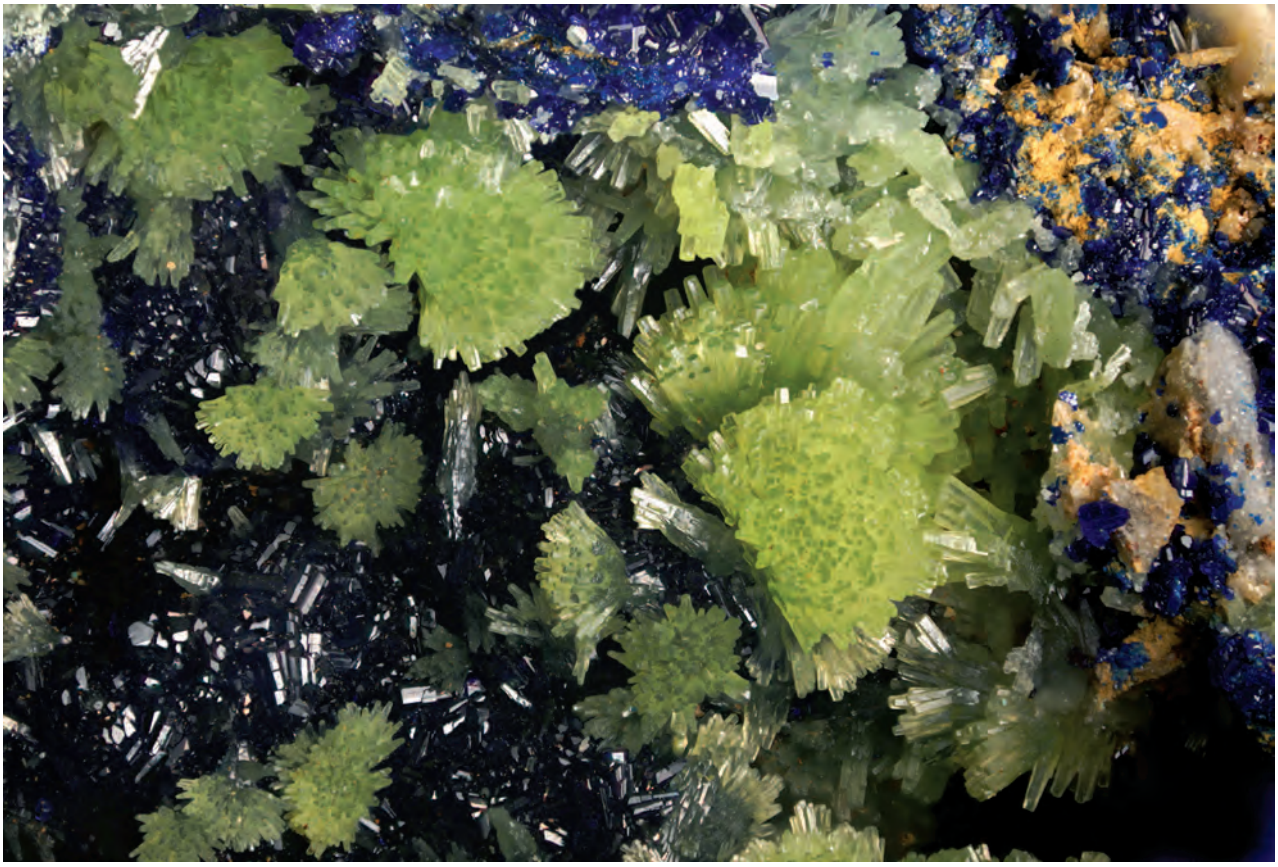

Figure 2. Radiating clusters of prismatic lime-green mimetite, up to 2.2 mm across, on deep blue azurite from Tynagh Mine, Co. Galway. Jean Spence collection. Photo John Chapman.

Two articles in *JRS 23* focus on isolated base-metal deposits on the periphery of the Pennine orefields. Brian Young and colleagues describe lead mineralisation in the Stublick Fault Zone at Church Burn and Wolf Hills in Northumberland. Long regarded as an outlying portion of the Northern Pennine Orefield, these deposits are

separated by approximately 15 km of barren ground from the nearest similar mineralisation. Galena is the principal primary sulphide in the veins, gangue minerals are rare, and supergene oxidation has produced malachite, linarite and rare plumbojarosite.

Zeolites and related minerals from gas cavities in the Tertiary basalts of the Isle of Skye have long been of interest to British mineralogists. Mordenite, an otherwise rare species, is recorded as compact masses of acicular crystals in basalt of the Skye Lava Group at a trackside exposure in Glen Brittle Forest.

The second article in *JRS* 23 to feature an outlying Pennine locality records linarite on an old specimen from Cononley Mine near Skipton in North Yorkshire. Cononley, the largest lead mine in the Craven Basin, has well preserved archaeological remains, but little of mineralogical interest remains on the dumps. The authors had originally intended to produce a more comprehensive account of the site, but difficulties accessing museum collections in 2020 restricted the report to linarite and associated species. The editor would be interested to hear from any readers with old-time specimens as a more complete description may appear at a future date.

Previous editions of this Journal have occasionally featured minerals in an archaeological context. An unusual magnesium-bearing vivianite in a sandstone hone, which was excavated near Canterbury in Kent, takes the reader to the southeast of England. Anthropogenic vivianite is probably more widespread than the relatively few published records suggest. It is commonly betrayed by a powder blue colour, though this alters over time to dark brown. Broad-minded readers might enjoy Alfredo Petrov's humorous and educational account of colour change in vivianite, which is caused by photon-induced deprotonation (Petrov, 2006).

Topographic surveys are of interest to most readers of the *JRS* and there are two in this edition. Tom Cotterell and colleagues delve into the fascinating and complex world of manganese oxides, describing numerous occurrences across the Northern Pennines.

In a similar vein, Mike Rumsey surveys occurrences of the rare calcium molybdate powellite across the British Isles. A number of new discoveries, including the first three Irish occurrences, are described. The first British powellite was identified in the 1950s on specimens collected by Arthur Kingsbury at Carrock Mine in Cumbria. Kingsbury part prepared a manuscript which would have added powellite to the British list, but it was never published. His specimens are entirely genuine. Powellite commonly forms inconspicuous micrometre-thick crusts in cracks around partly oxidised molybdenite. In this setting, its distinctive pale yellow fluorescence in shortwave ultraviolet light provides a valuable clue to its identity. As the nights draw in, half an hour spent with a ultraviolet lamp and any handy molybdenite specimen may reveal further potential localities. And perhaps add a rather rare species to collectors' personal 'British lists'.

Figure 3. A 22 × 17 mm vanadinite specimen on Cadeby Formation dolostone from Whitwell Quarry, Whitwell, Derbyshire. Collected in 1986 by David McCallum and registered as specimen E089 in his collection. Photo David Green.

Looking ahead, it is hoped that localities in the Permian rocks which stretch from Nottingham to the mouth of the Tyne will feature in *JRS* 24. A description of the diverse lead mineralisation at Whitwell Quarry (Fig. 3) is in the final stages of the preparation and shorter notes on several lesser known localities are nearing completion.

If any member has an interest in contributing to an issue which will include articles about this area, or mineralisation in the British Permian in general, the editor would be pleased to hear from them.

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JEAN SPENCE (1934–2019): HER COLLECTION AND CONTRIBUTION TO MINERALOGY

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Jean Carr Spence (18 July 1934 – 21 January 2019) was a well known member of the British mineral community. An interest in geology, fostered by an adult education class, gradually developed into a passion for minerals. Jean was a mainstay of the quarterly meetings of the northern branch of the British Micromount Society and, with her husband Derek, a key member of the team that produced the *UK Journal of Mines & Minerals*. She amassed a fine personal collection in the last quarter of the twentieth century. It included a suite of copper and lead secondary minerals from Tynagh Mine in Co. Galway; fluorite from northern England (with a selection of cut stones); a comprehensive collection from Fall Hill Quarry in Derbyshire; rare micro-minerals from the Caldbeck Fells; cabinet specimens from the iron mines of west Cumbria; and a unique collection from Vale Road Quarry in Nottinghamshire.

INTRODUCTION

Few descriptions of contemporary collections have appeared in the *Journal of the Russell Society*. Yet most society members are themselves collectors, with a more than passing interest in mineral specimens and the people who collect them. Obituaries appear in the *Newsletter of the Russell Society* with disquieting frequency. Such summaries often include a list of publications, but not much about the associated collections. This is unfortunate. In addition to providing a narrative structure, a collection can reveal something of a person's life and personality.

The current authors have described a number of contemporary collections in recent years (Green *et al*., 2012; Barnes *et al*., 2017; Bateman *et al*., 2018), outlining their size and scope, with photographs of important specimens, associated labels and catalogue pages. These are the tip of a very large iceberg. In the third decade of the twenty-first century few public institutions in the British Isles have the resources required to preserve a typical amateur collection. Most are dispersed without record and an unfortunate few are consigned to the dustbin. As a collection is dispersed a picture of what was assembled, and the inter-relationship of the specimens, is lost. Catalogues and databases are almost inevitably separated from the specimens to which they refer, and the opportunity to record a chapter in the history of mineralogy vanishes.

The recent development of internet sites with collector biographies and label archives reflects a desire to record the history [and personality] of mineral collecting. A small number of important British collections have been described (e.g. Livingstone, 2002; Cooper, 2006; Starkey and Cooper, 2010; Wilson, 2010) but more typical collections are rarely recorded. Yet such collections almost always contain noteworthy specimens and specimen suites.

It is not easy to write about a friend who has been an important part of one's life, but in an analysis of material in the collection of the National Museums of Scotland, Alec Livingstone (2002: p. 68) observes:

> "A disquieting feature of both the Scottish and General Mineral Collections is a virtual absence of archival records, thus complex collection and personality histories have vanished with time".

This article, written eighteen months after Jean passed away, records a small element of that history.

A PASSION FOR MINERALS

Jean spent most of her working life as a teacher. She was energetic, a good organiser, and had a strong interest in the natural world. In mineralogy she was motivated by curiosity, the colour and beauty of crystals, and the sheer joy of getting out into the field (Fig. 1). Her principal interest was in British specimens, with a particular focus on northern England. She was a keen micromounter and a member of the British Micromount Society from its foundation in 1983. An obituary summarising her life and extensive interests outside mineralogy was published shortly after her death (Green, 2019). This article does not repeat that biographical detail but extends the text to describe her mineral collection and some of the stories that cluster around it.

Mineral collecting had a strong recreational focus in the mid-1970s. The introduction to Peter Rodger's *Yorkshire Minerals* gives a flavour of the times (Rodgers, 1975: p. 8):

> "Collecting rocks, minerals and gemstones is probably the fastest growing hobby in Britain today, and every weekend scores of people make their way to the mineral-rich areas of our country to search for beautiful specimens".

Figure 1. Jean Spence (front), hammer in hand, with her friend and collecting companion Muriel Tissington, on the track to Red Gill Mine in the Caldbeck Fells in June 1987. Photo David Green.

Lapidary had become popular and Rodgers went on to list eight amateur societies in Yorkshire alone. Coal mining was part of the fabric of northern England and there were hard-rock mines in Derbyshire, Durham, Cornwall and Ireland (Colman, 2019). Many schools and universities offered geology courses, and these spilled over into adult education. A wide range of sites were accessible for field visits. Health and safety legislation was less prescriptive and quarry operators would often allow collectors to look around if asked. It is through this prism that Jean's nascent interest should be viewed.

Every collection begins with a first specimen. In Jean's case it was an Australian selenite, purchased from Tideswell Dale Rockshop (Fig. 2). There were a number of small geological shops in northern England and they played a key role in encouraging people into mineralogy. Jean became friends with the proprietor, Don Edwards, and made regular visits.

In 1976, Jean enrolled in an adult geology class at Worksop Technical College. There she met Muriel Swindell (formerly Tissington) and the two became friends. A wide ranging curiosity about rocks, fossils, minerals and landforms gradually morphed into a fascination for minerals. Mineral collecting combined an enjoyment of exploration and the outdoors with an appreciation of aesthetically beautiful objects and the opportunity to learn about them. It led to weekend field trips into Derbyshire, notably to Fall Hill Quarry near

Figure 2. Gypsum var. selenite, 120 mm across, from near Whyalla, Eyre Peninsula, South Australia. Jean's first purchase (£10 from Don Edwards at the Tideswell Dale Rock Shop) in 1975, listed as specimen 123 in the display collection catalogue. Jean was essentially a British Isles collector and this was the only foreign specimen in her display collection when she died. A few Cave-In-Rock fluorites acquired from her friend Janet Schmitt, a part time mineral dealer who lived near her daughter Judy in Wisconsin, occupied a glass shelf in her display until about 2014, when they were sold. Photo Peter Briscoe.

Ashover, where Jean and Muriel were often accompanied by John Morgan, an audio-visual technician with an interest in natural history. Visits were time-limited by the demands of family life, but the nucleus of a mineral collection was gradually amassed. Jean had a particular fondness for the delicate sprays of millerite that lined cavities in calcite veins in the tuff. It may have been these that ignited her interest in micro-minerals.

When one of the schoolchildren at Mansfield Woodhouse in Nottinghamshire brought a 'necklace of pyrite balls' to show her teacher, Jean arranged to visit the locality. Vale Road Quarry worked Permian dolomite and marl. Remarkable specimens were occasionally encountered, one quarryman recalling a cavity 'the size of a shed' lined with pyrite crystals. More specimens accrued.

The nearest collecting locations to Jean's house at Carlton in Lindrick were in Derbyshire and they were the focus for many early field trips. It was on a visit to Watts Shaft at Old Millclose Mine that Jean and Muriel met George Fletcher and his friend Nick Bartlett. The two would often call in to see George and his extensive collection during their forays into the county. It was at about this time that the now-famous axe-head calcites were found on Bonsall Moor; several trips were made and a few fine examples collected in the process (Fig. 3).

Figure 3. A 40 × 40 mm 'axe-head' calcite twin from Moor Farm, Bonsall, Derbyshire, collected by Jean Spence in 1981. These unique specimens were discovered at a shallow fluorite opencast which was being worked by the Slinter Mining Company on Bonsall Moor (Starkey, 2018: p. 75). Crystals are always off matrix, and very few complete, undamaged examples were found. This specimen is figured in *Minerals of the Peak District* (Ford *et al*., 1993: p. 34). Specimen 126 in the display collection catalogue, subsequently acquired by Roy Starkey and now registered as RES-0445-416 in his collection. Photo Roy Starkey.

As their contact with the collector community developed, Jean and Muriel realised that a whole world of geology was concealed beneath their feet. A first underground foray was made to Nenthead with the Tideswell Mineral Society in 1980. Many more would follow. Small collector groups were common in the late 1970s, and Jean and Muriel joined the Doncaster Mines Research Group (DMRG). The members soon learned that Jean wasn't prepared to accept a traditional female role. As far as collecting went she preferred to be at the sharp end of the shovel! Field trips to the North Pennines (Fig. 4), the Lake District and the quarries around Cardiff were arranged, and Jean collected a few top-drawer specimens (Fig. 5).

The DMRG had a journal, which included articles about British mineral localities and mining history and made records of the group's field excursions. Its tongue-in-cheek title was *Rockbottom*, and Jean became circulation manager. With hindsight it seems remarkable that a local society with a couple of dozen members had the ambition and energy to produce a good-sized printed journal twice a year.

Figure 4. Exploring in the north Pennines with the Doncaster Mines Research Group on 28 August 1982. The group are at the adit entrance to Howgillsyke Mine near Garrigill. From left to right: Jean Spence, Peter Briscoe (hidden in the entrance), Muriel Tissington (now Swindell), Rick Roberts and Ray Richardson. Ray's diary entry for the day records that the water was three feet deep in the level and little of mineralogical interest was located underground, though quartz and barytocalcite were present on the mine dump.

Figure 5. A yellow fluorite twin, 15 mm on edge, from Hilton Mine, Scordale, Cumbria. Collected on a field trip by Jean Spence in 1981 and listed as specimen 60 in her display collection catalogue. Photo John Chapman.

In February 1982 Jean, Muriel and John Morgan embarked on what would be their most memorable collecting trip. Inspired by a magazine article, Jean and John made a mineralogical tour of Ireland in 1981. They visited Silvermines just after the remarkable sulphide minerals had been found (Moreton, 1999) (Fig. 6). The geologist told them about the massive but almost unknown copper deposit at Tynagh Mine in Co. Galway. Originally planned for Easter, the Tynagh trip had to be brought forward when the mine's imminent closure was announced. The group set off in February half-term arriving on the day the pumps were switched off. Four days were spent in the open pit, filling tomato trays with rich crystalline azurite, plush malachite and mimetite, from 'a wall of blue and green'. Driving off the ferry on the way back, the car was followed by the police for more than two hours. It was stopped on the way through Derbyshire. The authorities wanted to know what the tomato trays piled on the roof-rack contained. They were relieved to find 'crystals not pistols'.

Jean and Muriel joined the British Micromount Society (BMS) at its inaugural meeting in 1983. They attended early society symposia and decided that a local group would be a good idea. A meeting place was found at Bircotes Library (it was made available free of charge as Muriel was the librarian) and members living in the north of England were invited. Early meetings were attended by Mike Rothwell, John Dickinson and Richard Bell from the northwest; Avril Woodburn, Eric Otty and Nigel Hoppé from Manchester; David Green and John

Figure 6. Galena on dolomite, 48 × 30 mm, from Mogul Mine, Silvermines, Co. Tipperary. Specimen 119 in Jean's catalogue with her handwritten label and a catalogue entry which reads "Presented to me by the geologist. Aug 1981. In return for mineralogical information! R. Barstow had just made his infamous buying trip there. We followed his visit by a few weeks and were not immediately popular". Photo Peter Briscoe.

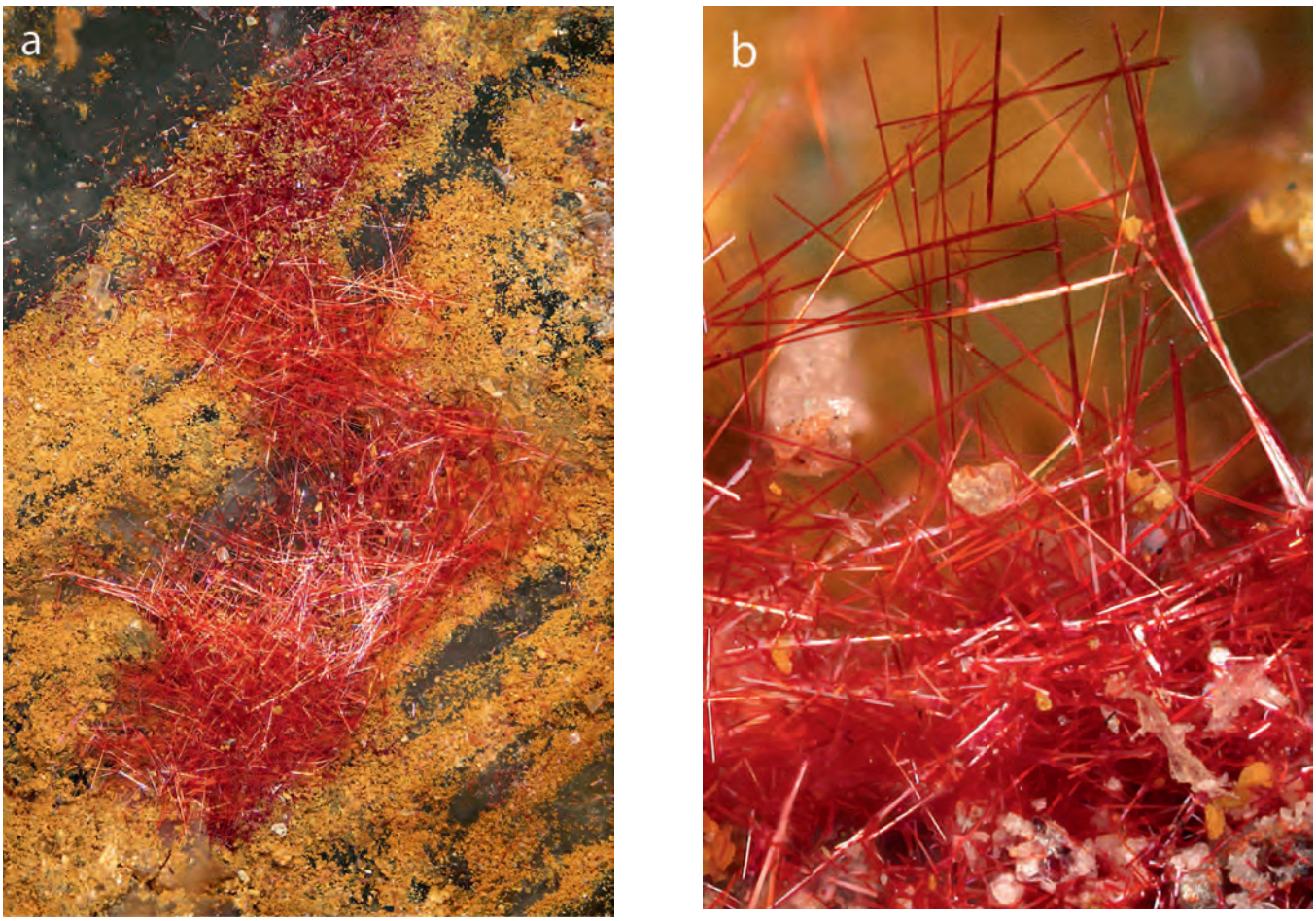


Figure 7. Cuprite variety chalcotrichite from a stope between 4 and 5 levels on Tryphena Lode, Pendarves Mine, Cornwall: a). 12 × 9 mm area of a large hand specimen richly covered in similar material; b). 1 × 1.3 mm area showing individual crystal aggregates. Specimen 121 in the display collection catalogue, with an accompanying note: "Russell trip. 2 pieces each presented to us by the Geologist who literally risked life and limb to go into the crumbling part of the mine to collect these for us. The mine closed nearly immediately after our visit". Acquired by Nigel Hoppé, who led Northern Branch members on collecting trips to Cornwall in the mid-1980s. Photo John Chapman.

Figure 8. Nant-y-Cagl (Eaglebrook) Mine became something of a mecca for micromounters in the mid-1980s. Although she enjoyed driving, Jean found the mountain road from Talybont to the site challenging. It usually proved worthwhile as this photo of prismatic linarite crystals up to 2 mm in length, overgrowing thin iron-stained shells with a few minute blocky anglesite crystals, shows. Photo John Chapman.

Bottomley from West Yorkshire; Peter Braithwaite and later Mick Cooper from the north Midlands; and Chris Jewson and Ivan Peak from Hull. There were occasional visits from Peter Briscoe, Neil Hubbard and Trevor Wolloxall. Richard Belson, Bob Snowball and other members of the 'Norfolk Mineral Mafia' made appearances on their way to and from collecting forays. The meetings were a great success. If you want something doing, ask a busy woman.

Jean attended most of the early BMS field weekends and particularly enjoyed visits to the Caldbeck Fells, Leadhills–Wanlockhead and southern Scotland. The northern branch soon began to organise their own excursions. A trip to the Isolation Mine near Snelston provided a blueprint for subsequent forays. George Fletcher showed the party where to look. The minerals, notably wulfenite, (for which the site is known) were soon located. Jean wanted to spend the time collecting: sandwiches were packed but not always eaten, and two hours for a pub lunch wasn't an option!

Cornwall was something of a mecca for collectors in the 1980s. It offered a variety of minerals, especially in micromount size, not available anywhere else in the British Isles. An excursion with the Russell Society in 1985 yielded well crystallised phosphates from Gunheath Pit and a lovely chalcotrichite from Pendarves Mine, of which Jean was particularly proud

Figure 9. Dark blue euhedral veszelyite on colourless minutely drusy hemimorphite from the old Waygate Shaft Dump on Straitstep Vein, Wanlockhead, Dumfries and Galloway. Collected by Jean Spence on a BMS field trip to Leadhills–Wanlockhead in southern Scotland in 1988 and figured in Tindle (2008: p. 526). Photo David Green.

Figure 10. The UKJMM stand at the Bakewell Show in the early 1990s. Jean Spence (on the left) and Kathryn Moore with the most recent editions of the journal and the first cumulative index set out on the table. Photo Peter Briscoe.

(Fig. 7). There were a number of dealers with stocks of local minerals. Jean particularly looked forward to visits to Maurice Grigg's house at Indian Queens. On several occasions, Maurice was kind enough to lead field trips to Gunheath Pit and Greystone Quarry.

In the mid-1980s the old mines in mid-Wales were becoming popular with micromount collectors. For a time they rivalled Cornwall and the Caldbeck Fells as the premiere source of unusual species. Field trips were arranged to the well known Esgair Hir, Nant-y-Cagl and Frongoch mines, which were rich in well crystallised supergene minerals (Fig. 8). Jean was particularly inspired by a minute crystal group which Mike Rothwell brought to a BMS meeting. It was mounted on the head of a pin and had five colourful perfectly crystallised copper secondaries. The whole specimen covered no more than a square millimetre.

In 1987, a BMS field trip which Jean led to the Leadhills–Wanlockhead district produced an abundance of slag-minerals from Meadowfoot Smelter and the first British veszelyite (Fig. 9). She would later be awarded the BMS Founder's Cup for her tireless work organising field trips and hosting Northern Branch meetings.

Jean was a key member of the team that produced the *UK Journal of Mines and Minerals* (Fig. 10). In fact, as far as most readers were concerned, Jean **was** the *UKJMM*. She served as circulation manager for almost the whole of the time the journal was published. Her husband Derek took on the role of treasurer when Muriel married Russell Society president Bill Swindell and moved to Leicester.

Jean anchored the journal firmly in the real world, dismissing ideas that were wasteful, impractical or beyond limited financial resources. Contacts were developed in many countries, particularly with Joop and Anneke Wolters in Europe, Bernie Day in Australia, Horst Windisch in South Africa and Janet Schmitt in the USA.

MINERAL COLLECTION

Jean supplemented self-collected specimens (always her favourite) with thoughtful purchases. She did not catalogue the micromount to hand-size material in the 'drawer collection', which at one time numbered about 2000 specimens, but described 125 pieces arranged inside a glass-fronted display cabinet in the sitting room in a handwritten catalogue (Fig. 11). Jean disposed of most of her micromount and thumbnail specimens before she died, leaving her display collection and three small drawer cabinets, which evoked memories of a lifetime in the field.

Derek passed the display specimens and remaining drawer cabinets to Peter Briscoe and David Green when Jean died. They distributed pieces to her friends (in exchange for donations to the British Heart Foundation) and the wider mineral community.

The more important specimen suites are described, roughly in the order in which they were collected, in the following text.

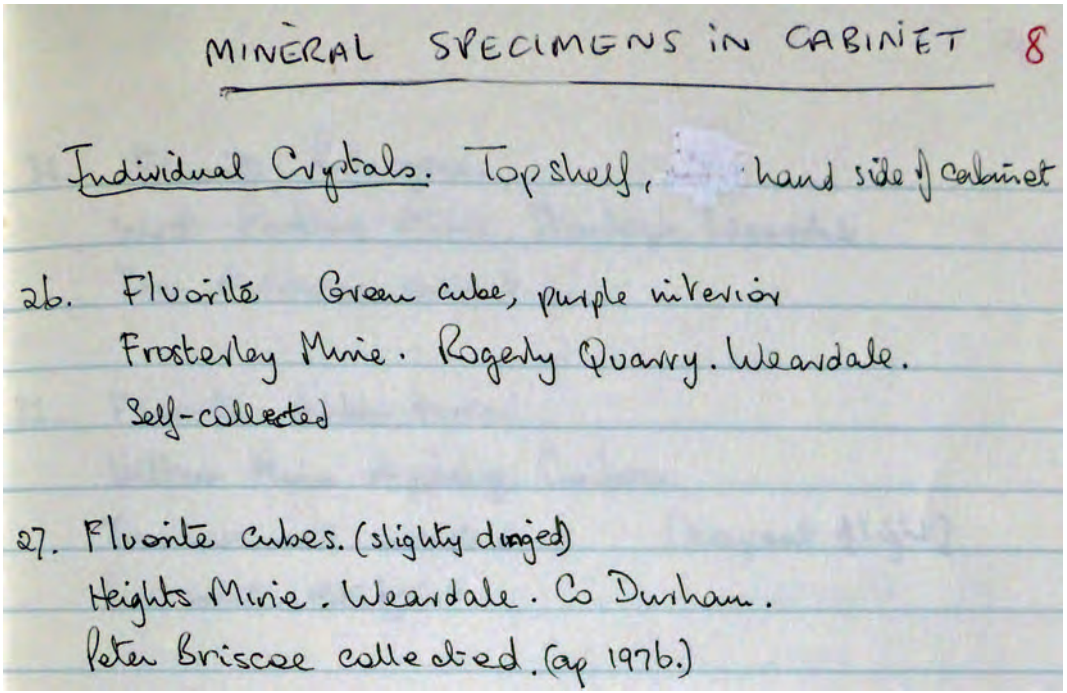
Vale Road Quarry, Nottinghamshire

Jean collected a suite of specimens, including well crystallised calcite, pyrite and sphalerite, from cavities in late Permian Cadeby Formation dolostone and the underlying Marl Slate at Vale Road Quarry, north of Mansfield Woodhouse, in Nottinghamshire (Green and Spence, 1988) (Figs 12 and 13). The site was productive, but the minerals did not attract much collector interest. A few specimens were donated to friends. Jean retained fifteen in her personal collection, three of which were on display. The quarry closed in the early 1980s and on a visit made with David Green in 1986 few productive exposures remained. It has subsequently been filled and landscaped (Starkey, 2018).

Mineralisation is widespread at the base of the Permian in northern England but it is generally unremarkable and relatively little has been preserved. Most exposures have been restored adding to the value of the few specimens that survive in collections. From a scientific viewpoint the minerals from Vale Road Quarry are among the most important in Jean's collection.

Fall Hill Quarry, Derbyshire

Between 1978 and 1981, Sunday morning visits to Fall Hill Quarry near Ashover were frequent. It was an easy drive from Carlton in Lindrick and offered fresh exposures and well crystallised specimens (Fig. 14). The quarry was unusually deep for its size and when


MINERAL SPECIMENS IN CABINET 8

Individual Crystals. Top shelf, hand side of cabinet

26. Fluorite Green cube, purple interior
Frosterley Mine. Rogerly Quarry. Weardale.
Self-collected

27. Fluorite cubes. (slightly dinged)
Heights Mine. Weardale. Co Durham.
Peter Briscoe collected. (ap 1976.)

Figure 11. Page eight from Jean's display collection catalogue is the first to list mineral specimens rather than cut stones. The catalogue has thirty-seven numbered, handwritten, A5 pages, describing the minerals in a glass fronted cabinet in the living room. It is undated but was written retrospectively in the 1990s. Jean's handwriting style varied little through the years. For clarity some of her specimen labels were written in block capitals, but this page is typical. Note the use of the term 'slightly dinged' to describe damage on a Heights fluorite specimen which had been given by Peter Briscoe in 1976. Dings and wilbers [tiny dings visible only under a hand lens] were frowned upon, but could be tolerated if a specimen was donated by a friend.

Figure 12. Calcite-lined cavity in grey marl from Vale Road Quarry, Mansfield Woodhouse, Nottinghamshire, with interlocking groups of brown-tarnished cubic pyrite up to 3 mm on edge. Photo John Chapman.

extraction ceased in 1981 it was partially backfilled and allowed to flood (Smith, 1982).

Jean collected excellent examples of the principal primary minerals calcite, fluorite, galena, marcasite, millerite, pyrite, quartz and sphalerite. There were small

Figure 13. Complex cuboctahedral pyrite crystal, 20 mm across, with cubic overgrowths, from a marl band in dolostone of the Cadeby Formation at Vale Road Quarry, Mansfield Woodhouse, Nottinghamshire. Photo John Chapman.

Figure 14. An unusually sharp double terminated scalenohedral calcite crystal, 40 mm tall, on quartz from Fall Hill Quarry, Ashover, Derbyshire. Found by George Batey in 1980 and later acquired by Jean Spence. The specimen is figured by Quirk (1993: p. 9). Photo David Green.

but spectacular specimens of iridescent sphalerite, fluorite overgrown by a dark brown to black hydrocarbon labelled 'thucolite', and a suite of supergene minerals, mostly of micromount- to thumbnail-size, including cerussite, gypsum, yellow cadmium sulphide crusts which were labelled 'hawleyite' and smithsonite.

Jean was particularly fond of the delicate sprays of millerite found in calcite veins in the tuff. She often recounted the story of a collector who found an outstanding specimen and lovingly carried it back to the car. His wife, who was waiting, looked for a moment, saw 'hairs' all over the calcite, and quickly brushed them all away.

Tynagh Mine, Co. Galway

The specimens from Tynagh Mine in Co. Galway are among the best Jean collected (Figs 15–17). She was fortunate to visit in February 1982, just as the mine

Figure 15. Radiating clusters of rounded white prismatic mimetite up to about 2 mm with minor spherulitic malachite in a cavity lined with dark blue blocky azurite from Tynagh Mine in Co. Galway. Photo John Chapman.

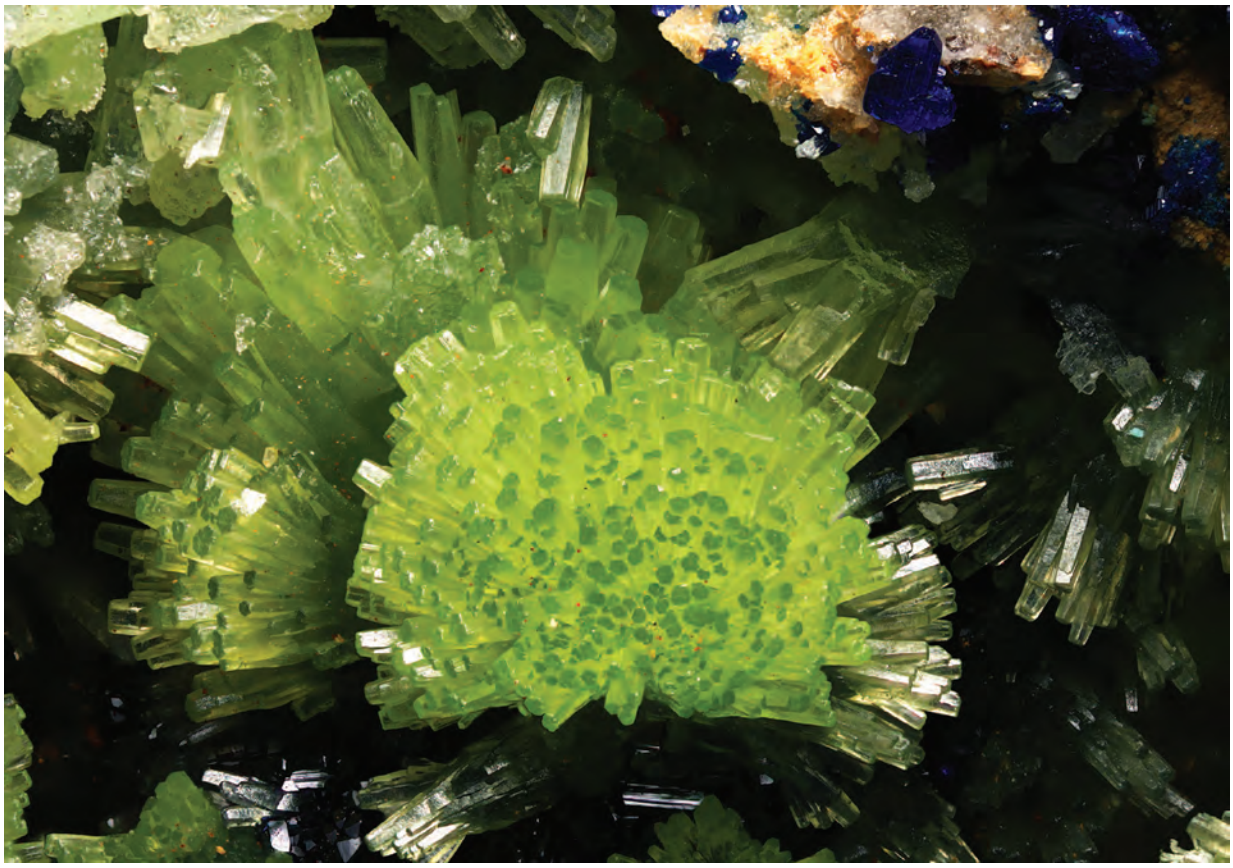


Figure 16. Radiating cluster made up of prismatic lime-green mimetite, 2.2 mm across, with a little deep blue azurite from Tynagh Mine, Co. Galway. Photo John Chapman.

Figure 17. The collecting area in the open pit at Tynagh showed metre-scale zonation. The best malachite was collected at one end of the exposure by Muriel Tissington; John Morgan found excellent mimetite at the other end; Jean did most of her collecting in the middle and occasionally found specimens with all three of the common supergene minerals. The malachite balls are 1.6 mm in diameter. Photo John Chapman.

closed. After four days of collecting in the open pit, selecting specimens for transport proved difficult. The car was filled to overflowing, and a pile of 'sparkling blue and green' had to be abandoned. The water level rose in the following months and the pit flooded. Jean joked that she needed to make a return trip with a diving bell. Tynagh Mine fell into dereliction until 2004 when the remaining buildings were bulldozed and it was redeveloped for industrial use. Interesting specimens could be found around the flooded open pit until that time, but little of mineralogical interest now remains.

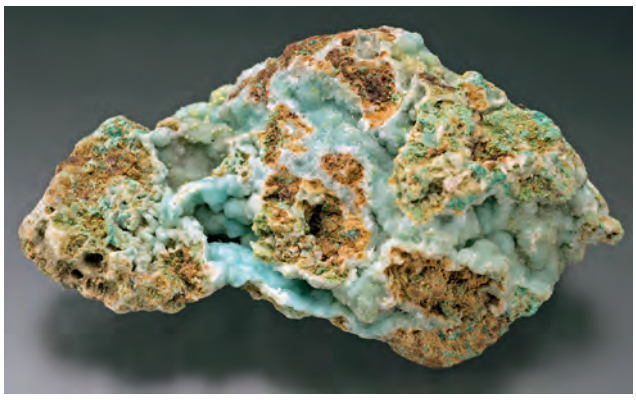
Jean's specimens are typical of the oxidised zone of the orebody, with azurite crystals up to 2 mm on edge scattered on iron-stained baryte-rich matrix to large cabinet size. Malachite is common as green spherulites and was also found as thick 'plush' botryoidal crusts to small hand size. Many of the azurite specimens are overgrown by prismatic white to pale green mimetite up to about 2 mm in length. Less common species in the micromount collection include beudantite, linarite, olivenite, pharmacosiderite and strashimirite.

Tynagh Mine is one of the few localities in the British Isles where more than a hundred mineral species have been recorded (Stephen Moreton, *personal communication*, 2020). Despite the abundance of rare and colourful supergene minerals, no topographic description has ever been published. Collectors were few and far between in rural Ireland while the deposit was being worked. There was no tradition of mineral collecting in the local area. It is only as a result of chance visits that any specimens were preserved.

Caldbeck Fells

Jean made her first visit to the Caldbeck Fells in 1983. At the time, excitement about the rare micro-minerals that could be found was building and new discoveries seemed to be made on almost every visit. It was easy to find specimens with attractive micro-crystals at classic localities such as Brandy Gill, Carrock, Dry Gill, Red Gill and Roughton Gill mines (Figs 18–20), and 'new' sites were still being discovered in the Dale Beck valley. Mick Cooper regularly attended BMS meetings and infected many of the participants with the 'Caldbeck bug'. Mike Rothwell had access to EDS analysis and David Green to XRD. As a result, most members of the BMS Northern Branch had some involvement in data gathering for the Caldbeck Fells book (Cooper and Stanley, 1990).

Figure 18. Tabular pseudohexagonal leadhillite, the main crystal 1.5 mm across, with yellow powdery bindheimite. Collected from the No. 2 Level Dump at Red Gill Mine with David Green and Muriel Tissington in June 1987 (see Fig. 1). Photo John Chapman.



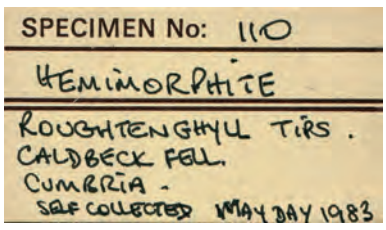


Figure 19. On early visits to the Caldbeck Fells, it was relatively easy to find hand specimens. This 65 × 40 mm pale blue hemimorphite was collected from a hole dug "by Mike Rothwell & self" on the 90-Fathom Level dumps at Roughton Gill Mine on a BMS field trip in 1983. Specimen 110 in the display collection. Photo Peter Briscoe.

Figure 20. Red Gill Mine was undoubtedly Jean's favourite Caldbeck Fells locality and caledonite its most desirable species. This blocky striated caledonite crystal, 2 mm in length, is typical of a number of self-collected pieces in her 'small specimen' collection. Photo Richard Bell.

Excellent lodgings were offered by Mrs Stott at Nether Row Farm. From there it was an easy walk (or short drive) onto the fells. Red Gill Mine (Fig. 1) was probably Jean's favourite because of the wonderful deep blue micro-crystals of caledonite found on the old No. 2 Level Dump. A focus on the micro-minerals at the site led to the discovery of unusual species, notably elyite, macphersonite, mattheddleite and queitite, by BMS members (Bridges *et al*., 2008).

West Cumbria

Jean had a particular fondness for the iron mines of west Cumbria. She had collected good specimens of aragonite from Eskett Quarry near Rowrah in the early 1980s and calcite when a small area of the old Pallaflat Mine dumps was exposed in 1985. Florence Mine was a particular favourite. Specimens could be purchased for a few pounds directly from the mine and hematite 'bought by weight off the shed floor'.

Dealers offered better material and Jean got to know Bill Creighton, who had a shop in Keswick, and George Wilson, who lived in nearby Workington. She eventually acquired good hand specimens of almost all of the 'classic species' including aragonite, baryte, calcite,

Figure 21. An attractive old-time baryte from Frizington, Egremont, Cumbria, 70 mm from point to point, purchased in the mid-1990s from Don Edwards at Tideswell Dale Rockshop for £79. Jean 'hung her nose' over this piece for some time, the price seeming high, but later she was very pleased to have acquired it. Specimen 95 in the display collection. Photo Peter Briscoe.

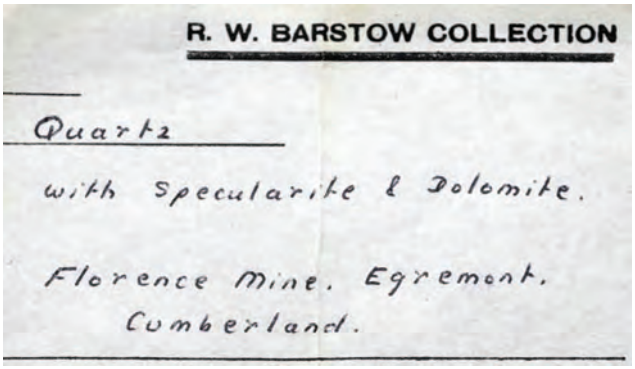


Figure 22. Smoky quartz with specular hematite, 100 mm across, from Florence Mine, Egremont, Cumbria. Don Alderson of Isis Minerals exchanged this specimen with Richard Barstow in 1980. It has a white label (inset) indicating that it was part of Barstow's personal collection (Starkey and Cooper, 2010). Cornish dealer Nick Carruth acquired the specimen sometime after Don decided to specialise only in baryte. Jean purchased it from Nick and it is specimen 106 in her display collection catalogue. Photo Peter Briscoe.

fluorite, hematite and quartz, at prices which now seem ridiculously reasonable (Figs 21–22).

North Pennine Fluorite

To collectors, the mines of the North Pennine Orefield are famous, above all else, for fluorite specimens, and penetration twins in particular. When Jean started collecting in the early 1980s it was possible to obtain permission to collect underground at Hilton Mine. Keys were collected from the Camp Commandant at Warcop and returned at the end of the day. On a trip in 1981 she collected one of the fine yellow twins for which the locality is famed (Fig. 5). She subsequently persuaded Trevor Wolloxall to sell her a transparent matrixless crystal found at about the same time. It became one of her favourite pieces (Fig. 23).

Blackdene Mine was in operation and a few specimens were acquired from miners including an interesting matrixless twin with very unusual surface ornamentation (Fig. 24): Jean always had an eye for detail. It was still possible to find green fluorite in 'cavity mud' on the dumps at Heights Pastures, and several good pieces were collected there in 1985. Fluorite from Heights Quarry and the Cement Quarry was purchased

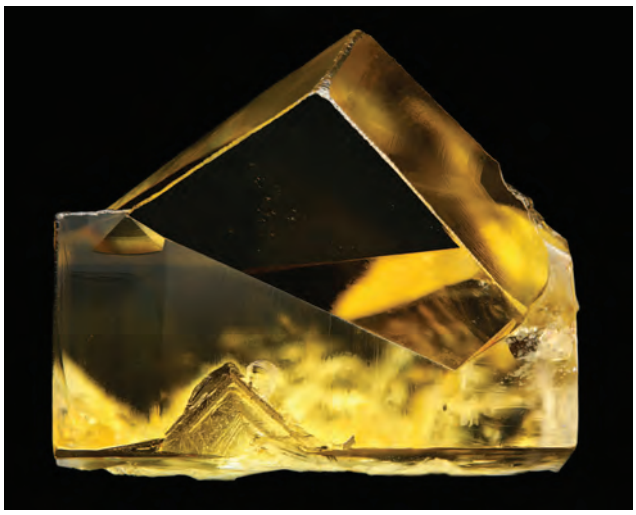


Figure 23. Flawless amber fluorite twin, 25 mm on edge, from Hilton Mine, Scordale, Cumbria. Collected in the early 1980s by Trevor Wolloxall, who [reluctantly] sold it to Jean. Specimen 32 in the collection catalogue and one of her favourite pieces. Photo John Chapman.

Figure 24. Matrixless purple fluorite twin, 28 mm across, from Blackdene Mine, Ireshopeburn, Weardale, Durham. It is extremely unusual to find penetration twins with a mosaic structure on the crystal surface. They almost invariably have stepped growth hillocks (compare Fig. 25). Photo Peter Briscoe.

from local dealers and collectors, notably a Mr Blackburn who Jean visited in 1989 with her American friend Janet Schmitt. He had a 'cellar full of Cement Quarry green'.

Specimens from Frazer's Hush Mine (Fig. 25), Cambokeels Mine (Fig. 26) and Rogerley Mine were added while they were in production. Lindsay Greenbank gave permission for a dig at Rogerley Quarry in 1988 and an excellent deep purple twin was recovered from the Sutcliffe Vein. In about 1990, Jean began to collect cut Weardale fluorite. Doug Morgan worked miracles, producing cut stones from 'dinged' crystals found on fieldtrips, he often kept one for himself, but always gave the finest to Jean. The best piece in the gem collection is a flawless 20 ct amber stone from Hilton Mine, cut by Dennis Durham. At £125, this was one of Jean's more expensive acquisitions and she loved to show it off to visitors.

CONCLUSION

Jean Spence had a pivotal role in mineralogy in the north of England from the mid-1980s onward, organising meetings and field trips and managing the *UK Journal of Mines and Minerals*. Her collection contained important self-collected suites from Tynagh Mine, Vale Road Quarry and Fall Hill Quarry, attractive display specimens from west Cumbria and the north Pennines, and rare and unusual micromounts from the Caldbeck Fells, Cornwall, southern Scotland and mid-Wales. It reflected locations that were productive at the time and specimens that could be acquired relatively inexpensively with patience and a good eye. Very few specimens in her collection cost more than a hundred pounds, but in its entirety her display was a 'sight to see'.

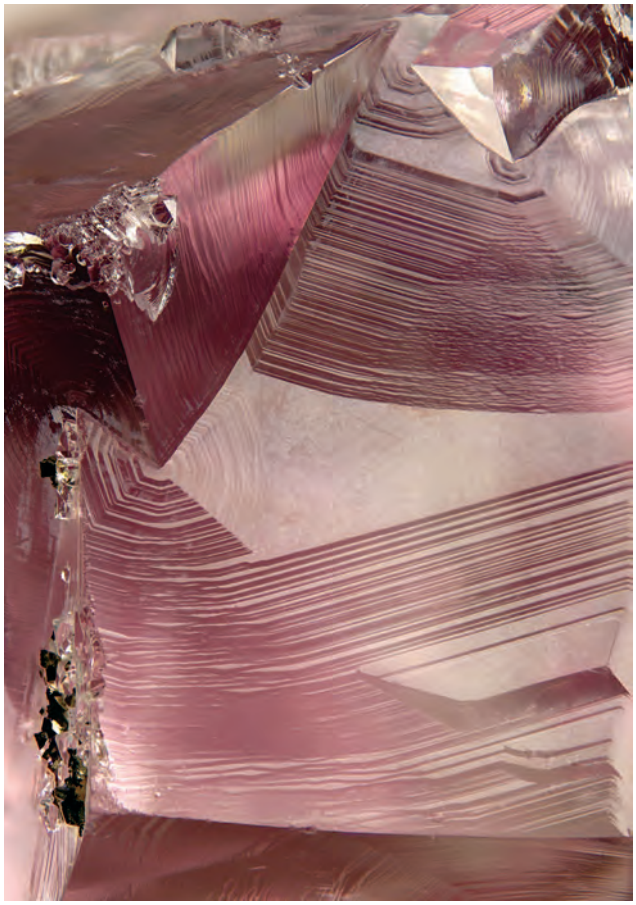


Figure 25. Typical surface patterning on a fluorite twin with minor quartz and pyrite from Frazer's Hush Mine, Rookhope, Durham. Field of view is 10 mm across. Twin crystals almost invariably have stepped growth hillocks such as these (compare with Fig. 24). Photo John Chapman.

Mineralogy, like most other pastimes, is a social construct. To be successful it needs people who can organise meetings, enthuse newcomers and record data. Jean was one such. She was a pleasure to work with and is sadly missed. It is hoped that this article will encourage similar biographies of collectors and their collections. In the absence of much engagement from local museums or

Figure 26. Fluorite cubes coated in a thin layer of berthierine-chamosite with a scattering of pyrite, on a 70 × 50 mm specimen from Cambokeels Mine, Weardale, Durham. Specimen 72 in the display collection catalogue. Photo Peter Briscoe.

Figure 27. Jean had a passion for the natural world and a good eye for colour, composition and light. This image of a classic English bluebell wood was one of her favourites. Photo Jean Spence.

archives some kind of permanent record is becoming more important than ever.

Jean had an appreciation of colour and light and a real love of the outdoors. It seems appropriate to end with a photograph (one of her favourites), not of a mineral, but of a bluebell wood near to her home in Bawtry (Fig. 27).

ACKNOWLEDGEMENTS

Thanks are due to Jean's friends particularly Richard Bell, George Fletcher, Muriel Swindell and Michael Wolfe for providing information and to her husband Derek who passed Jean's collection to the authors following her death in 2019. John Chapman spent many hours recording the better specimens and proof-reading. Without his tireless work the article would be much the poorer. The referees, Susan Tyzack and Steve Warren, are thanked for reading the article at relatively short notice and making incisive comments and corrections.

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STRONTIANITE FROM CASTLETON, DERBYSHIRE IN THE JOSEPH DAWSON COLLECTION

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Strontianite occurs as white millimetre-size tapering prismatic crystals with colourless to white calcite, pale to dark purple fluorite, curved white baryte, dark resinous sphalerite and sphenoidal chalcopyrite on two specimens in the Joseph Dawson collection. Although Dawson's collection is somewhat disorganised, a careful analysis of his catalogue and labels, and a comparison with reliably provenanced material, leaves little doubt that the specimens are from lead veins around Castleton. This is the first report of strontianite from Derbyshire. In common with other occurrences in the Pennine orefields, strontianite is late in the primary paragenesis. Its composition, calculated on the basis of inter-plane spacing, is $Sr_{0.8}Ca_{0.2}CO_3$.

INTRODUCTION

Joseph Dawson (1740–1813) was a leading industrialist who pioneered a scientific approach to manufacturing and production. He was one of the founders of the famous Low Moor Ironworks near Bradford and the driving force behind its successful early development (Pacey, 2003). Dawson accumulated a mineral collection as an adjunct to his scientific endeavours. It is now part of the collections cared for by Bradford Museums and Galleries at Cliffe Castle Museum in Keighley, West Yorkshire. The specimens are accompanied by a handwritten manuscript catalogue, which was begun in 1810 and lists the collection as it stood in 1813 (Dawson, 1810–1813). It provides a unique and fascinating window into the development of mineralogy in northern England in the late eighteenth and early nineteenth centuries.

Dawson's collection was unpacked in 1973 in a somewhat jumbled condition after many decades in storage. A handwritten note by Margaret Hartley, the curator at the time, is taped into the inside front cover of the manuscript catalogue and reads:

> "These minerals - identifiable by rectangular labels bearing the numbers given here & name & locality in similar handwriting to this catalogue are now in the Bradford Museums. Some were unpacked from a wooden packing case & 1920/21 newspaper in 1973; the specimens being filthy and many labels lying loose, or several with 1 [one] specimen. There were also fossils mounted on Bfd. Phil. Soc. cards with them.
>
> "Did they go from Joseph Dawson (1810) to the Bfd. Phil. Soc. and hence to the museum; or did they come direct to the museum? No Accession has yet been traced. As this catalogue has a Bfd. Phil. Soc. library label, presumably they went to the Phil. Soc. & hence came to the museum.
> Margaret H. Hartley 8th Nov. 1973".

Preliminary research suggests that the story may be more complicated. Dawson's family appear to have donated the collection to the Leeds Philosophical and Literary Society in 1865. The annual report for 1865–1866 (Leeds Philosophical and Literary Society, 1866: p. 13) records:

> "A valuable Cabinet of Minerals; a Series of Plants from the Yorkshire Coalfield; and an extensive collection of Minerals and Fossils from various parts of the United Kingdom ... [from] ... The Family of the late Christopher Holdsworth Dawson and Joseph Dawson, Esqrs, of Royds Hall".

In the same year the family donated some scientific instruments which had belonged to Joseph Dawson and a copy of William Smith's geological map of England and Wales. Leeds Museum retained the scientific instruments (Pacey, 2003) but the mineral collection seems to have passed to the re-formed Bradford Philosophical Society (BPS). A note in an unknown hand records: "Dawson Coll^{n} given to B.P.S. in 1865" and a BPS bookplate pasted into the inside front cover indicates that the manuscript catalogue was item number 575 in their library.

In about 1871 part of the collection was loaned to Bradford Grammar School, but no specimens remain there now. It was was subsequently loaned for display at the public library in Darley Street. When Cartwright Memorial Hall (CMH) in Lister Park opened in 1904, the collection was housed there. In 1974, when CMH became a dedicated art gallery, all of the stored natural science collections were removed. Joseph Dawson's specimens found a home at Cliffe Castle in Keighley.

A transcript of the catalogue was completed by the authors in 2018 and a comparison of the catalogue entries, labels and specimens has begun. Early curatorial work concentrated on quartz, but the descriptions are not

particularly detailed and few of the specimens are sufficiently characteristic to be sure of provenance.

A preliminary examination of Dawson's fluorite specimens was made in October 2019. Unlike quartz, the catalogue entries are relatively detailed, describing the colour and associated minerals. A critical comparison suggests that a significant number of errors have accumulated since Dawson's death in 1813 as a result of labels and specimens being mixed up (e.g. Fig. 1). In the absence of permanent accession numbers it is easy to see how this has happened.

Every specimen was examined during the 'fluorite survey' and as an unexpected bonus, strontianite was identified with baryte, calcite and minor sulphides on specimens 783 and 806, which have labels that indicate they are from Castleton in Derbyshire (Figs 2 and 3).

One of the aims of the curatorial work is to highlight the importance of the collection and raise its profile among mineralogists and historians. A few of Dawson's Coal Measures specimens are figured in a recent account of the minerals of the Yorkshire Coalfield (Bateman *et al*., 2018) and two manganite specimens from Aberdeen are described by Chapman and Green (2020). The discovery of early and apparently unique strontianite specimens from Castleton in Derbyshire underlines its scientific value.

Figure 1. One of the mismatched specimen-label pairs found during the survey of Dawson's fluorite collection (accessioned as BRFMS: 8.4.15/62). The purple fluorite with dark green chlorite on killas matrix is characteristic of St Agnes in Cornwall. Several St Agnes specimens are listed in Dawson's catalogue. The label records "Rose coloured Fluor with Calc or Pearl Spar from Cumberland" and clearly belongs to a different specimen: neither calcite nor dolomite is present. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Figure 2. The original fluorite-survey 'record image' of specimen 783 [accessioned as BRFMS: 8.4.15/119] with its accompanying labels. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

THE JOSEPH DAWSON COLLECTION

The available records suggest that Joseph Dawson's collection originally contained between 2400 and 2500 geological specimens, a substantial number for the period in which it was assembled. The main catalogue lists 2220 specimens (Dawson, 1810–1813). It begins following an unnumbered title page on page 125 and ends on page 196 (with two consecutive pages numbered 167). It is supplemented by an unpaginated four-page index and a five-page list which describes 166 specimens that were "on display in the upper part of a cabinet in the parlour".

The catalogue is almost certainly the second part of a more extensive manuscript as the missing pages (1 to 124) are referred to in the index. Most of the entries are listed on the right-hand leaves of the bound folio, which seem to have been completed in 1810. The left-hand leaves were originally left blank so that further specimens and information could be added.

Dawson organised his specimens systematically, using a Linnaean system, into orders, families, genera,

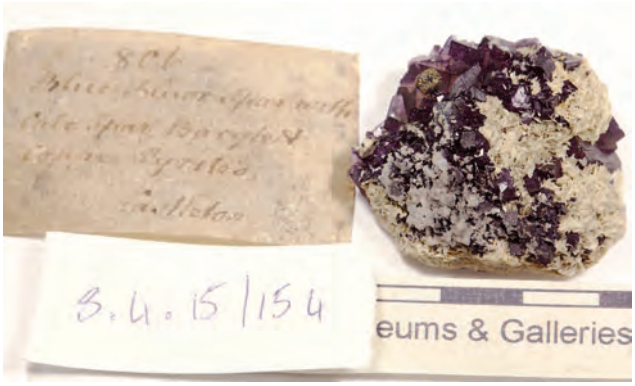


Figure 3. The original fluorite-survey 'record image' of specimen 806 [accessioned as BRFMS: 8.4.15/154] with its accompanying labels. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

species, subspecies and varieties. He based the classification on "Dr Thompson's [*sic*] Arrangement in the 3d: Ed. of his System of Mineralogy" (Dawson, 1810–1813: p. 125). This refers to the third edition of Thomas Thomson's *A System of Chemistry* which was published in 1807 and contains a very early account of John Dalton's atomic theory (Partington, 1949).

Dawson made a few numerical errors in the course of cataloguing: some numbers are used twice (and one three times) and two blocks of numbers (ten numbers between 645 and 656 and one hundred between 834 and 935) are missing from the sequence. Additional specimens, listed on the left-hand leaves of the catalogue, are interposed into the numerical sequence using a letter code: thus ten calcite specimens with numbers 677a–k are listed on the left-hand side of page 167. The final number in the catalogue is 2206; seven specimens near the end are listed without numbers, and 21 specimens with Dawson labels which are not listed in the catalogue have been found in the course of curatorial work.

There are more minerals from Derbyshire in Dawson's collection than any other British county. Of the 311 catalogued specimens from the county, 81 are from Castleton (both of these numbers are probably underestimates as many specimens are listed without any locality data). Most of the specimens from Castleton are fluorite: out of a total of 114 fluorite specimens, 76 are from Castleton. This concentration on a particular area is probably a reflection of the geological tourist trade which developed in the second half of the eighteenth century around the Blue John mines (Starkey, 2018; Ford, 2019). According to Pacey (2003), Dawson purchased specimens from the dealer John Mawe (1766–1829) who had premises in Derby, Matlock Bath and Castleton (Cooper, 2006: pp. 208–215).

A total of 730 Dawson specimens with labels (not all of which are correctly paired) and 201 labels that had become separated from specimens were identified in the early 1990s by Helen Fothergill (Fothergill, 1993). Thus, rather less than half of the original collection survives at Cliff Castle. The 'fluorite survey' identified 47 fluorite specimens with Dawson labels and 21 loose fluorite labels.

Strontianite Specimens

The two fluorite specimens with strontianite, which are the subject of this study, are catalogued as "fluate of lime", an early and now obsolete name for fluorite.

Specimen 783 (Fig. 4) is included in a category "Subspecies of Fluates of Lime. Crystallized" in subsection 1: "Crystallized Fluor of a Water Colour", and is described:

> "8. Variety covered with Baryte & Calamine Castleton."

Specimen 806 (Fig. 5) is included in the same category "Subspecies of Fluates of Lime. Crystallized" but in subsection 2: "Crystallized Fluor of a Blue Colour", and is described:

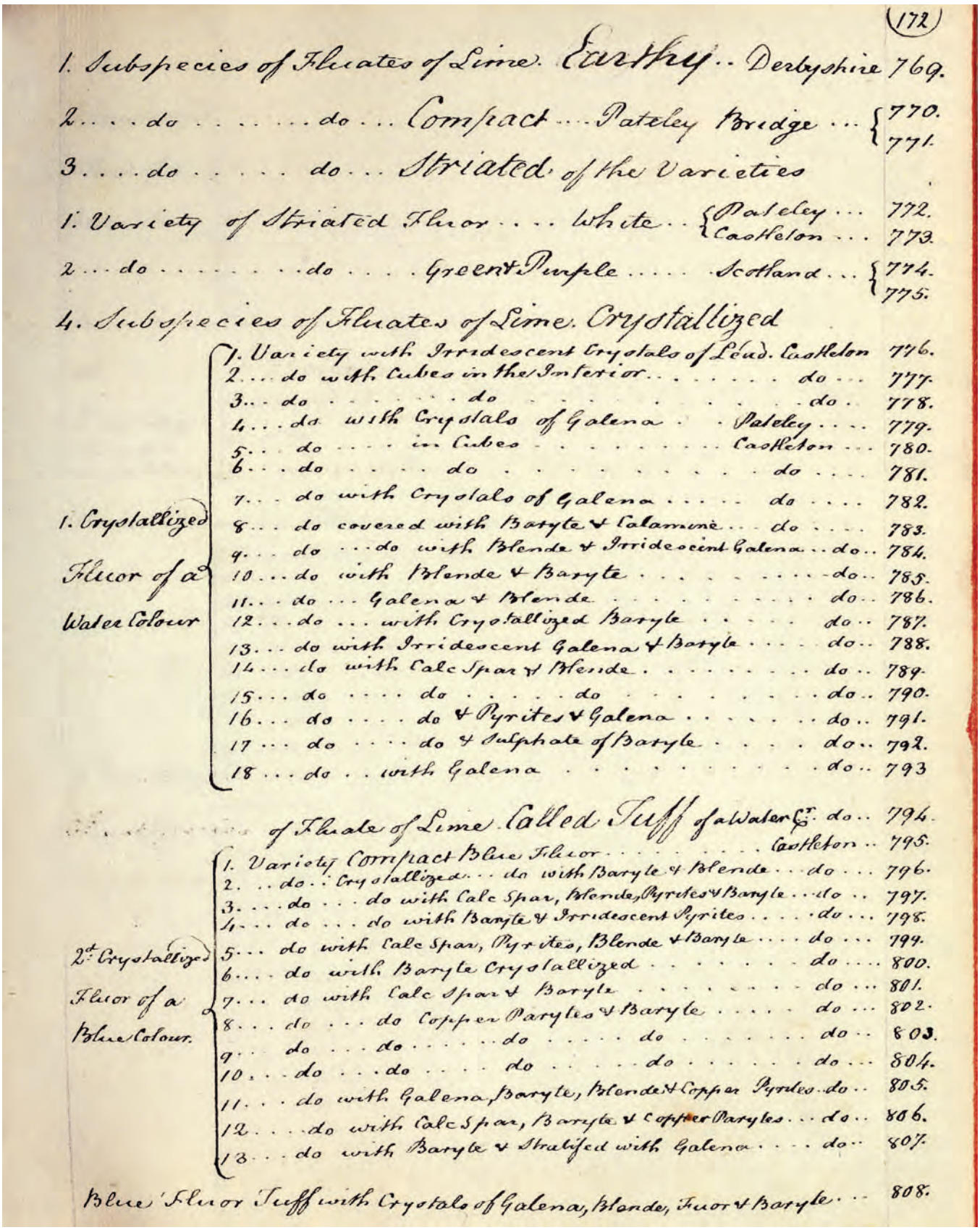
> "2. Variety Crystalline Blue Fluor with Calc Spar, Baryte & Copper Parytes [*sic*] Castleton".

The accompanying labels are shown beside the specimens in Figures 2 and 3. The page from the manuscript catalogue on which they are described is reproduced as Figure 6.

Figure 4. Specimen 783 [BRFMS: 8.4.15/119] a 57 × 47 × 37 mm fragment of brecciated veinstone. White calcite clasts showing specular reflections from crystals in parallel growth (middle right) are overgrown by colourless to pale purple fluorite which is common on this [originally upward-facing] side of the specimen. The fluorite-covered fragments are overgrown by curved baryte and minor strontianite. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Specimen 783 is an open-textured collapse breccia in which angular fragments of calcite are cemented by later

Figure 5. Specimen 806 [BRFMS: 8.4.15/154] a 36 × 32 × 16 mm fragment of massive fluorite and baryte with dark blue-purple fluorite cubes, curved baryte rosettes and a single large sphalerite (top centre-left) overgrown by minute brassy-yellow sphenoidal chalcopyrite. White drusy strontianite richly encrusts an area of about 10 × 20 mm on the lower left. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.



(172)

1. Subspecies of Fluates of Lime. Earthy .. Derbyshire 769.

2. ... do ... do ... Compact ... Pateley Bridge ... {770. 771.

3. ... do ... do ... Striated of the Varieties

1. Variety of Striated Fluor ... White .. {Pateley ... 772. Castleton ... 773.

2 ... do ... do ... Green & Purple ... Scotland ... {774. 775.

4. Subspecies of Fluates of Lime. Crystallized

1. Crystallized Fluor of a Water Colour

1. Variety with Irridescent Crystals of Loud. Castleton 776.
2. ... do with Cubes in the Interior ... do ... 777.
3. .. do ... do ... do. 778.
4. ... do with Crystals of Galena . Pateley .... 779.
5. .. do .... in Cubes ... Castleton ... 780.
6. .. do .... do ... do .... 781.
7. .. do with Crystals of Galena ..... do .... 782.
8. .. do covered with Baryte & Calamine ... do .... 783.
9. .. do ... do with Blende & Irridescent Galena .. do .. 784.
10. .. do with Blende & Baryte ... do .. 785.
11. .. do ... Galena & Blende ... do .. 786.
12. .. do ... with Crystallized Baryte ... do .. 787.
13. .. do with Irridescent Galena & Baryte ... do .. 788.
14. .. do with Calc Spar & Blende ... do .. 789.
15. .. do .... do ... do ... do .. 790.
16. .. do .... do & Pyrites & Galena ... do .. 791.
17. .. do .... do & Sulphate of Baryte ... do .. 792.
18. .. do .. with Galena ... do .. 793

... of Fluate of Lime called Tuff of a Water Cr. do .. 794.

Castleton .. 795.

2d Crystallized Fluor of a Blue Colour.

1. Variety Compact Blue Fluor ... do ... 796.
2. .. do .. Crystallized .. do with Baryte & Blende .. do ... 796.
3. .. do ... do with Calc Spar, Blende, Pyrites & Baryte .. do .. 797.
4. .. do ... do with Baryte & Irridescent Pyrites ... do ... 798.
5. .. do with Calc Spar, Pyrites, Blende & Baryte ... do ... 799.
6. .. do with Baryte Crystallized ... do .... 800.
7. .. do with Calc Spar & Baryte ... do ... 801.
8. .. do ... do Copper Pyrites & Baryte ... do ... 802.
9. .. do ... do ... do ... do ... do .. 803.
10. .. do ... do ... do ... do ... do ... 804.
11. .. do with Galena, Baryte, Blende & Copper Pyrites .. do .. 805.
12. .. do with Calc Spar, Baryte & Copper Pyrites ... do .. 806.
13. .. do with Baryte & Stratified with Galena ... do .. 807.

Blue Fluor Tuff with Crystals of Galena, Blende, Fluor & Baryte .. 808.

Figure 6. Page 172 of Dawson's manuscript catalogue is entirely devoted to fluorite and includes his handwritten descriptions of specimens 793 and 806. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

fluorite, baryte and strontianite. The clasts are overgrown by colourless transparent nail-head and scalenohedral calcite crystals which reach 5 mm in length, but are typically much smaller. All of the broken fragments are coated by a thin veneer of calcite, suggesting that brecciation was followed by rapid carbonate deposition. Fluorite occurs as colourless to purple cubic crystals up to about 3 mm on edge, which encrust one side of the

Figure 7. The reverse side of specimen 783 [BRFMS: 8.4.15/119], showing spheroidal drusy strontianite aggregates on calcite with minor fluorite and numerous minute tarnished sphenoidal chalcopyrite crystals (black dots on calcite). Many years of handling have damaged the terminations of the exposed strontianite crystals. Euhedral crystals are almost entirely restricted to protected fractures. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

clasts (a possible result of geopetal deposition in an open cavity). Rosettes of creamy white baryte overgrow the fluorite. Strontianite, which overgrows all of the major primary minerals, is particularly conspicuous on the 'reverse' of the specimen (Fig. 7).

A few subhedral silvery marcasite inclusions are visible in the baryte under a stereomicroscope. Chalcopyrite occurs as irregular inclusions near the edges of the fluorite crystals (Fig. 8) and as minute tarnished sphenoidal crystals which are particularly common on exposed calcite surfaces. Rosettes of creamy white baryte with minor late-stage strontianite overgrow calcite and fluorite on the 'upper' surfaces of the clasts (Fig. 9). Spheroidal masses of tapering prismatic strontianite up to 32 mm in diameter and scattered radiating fan-like and bow-tie groups of acicular crystals (Fig. 10) invest the other surfaces.

The strontianite crystals are typically less than 3 mm in length, elongated along their *c*-axes and gently curved along their growth direction (Fig. 11). They have flattened six-sided cross-sections, and taper to sharp blade-like or ragged lath-like terminations (Figs 10–12).

Exposure to long-wave ultraviolet radiation produces very weak blue-violet fluorescence in the fluorite, a weak

Figure 8. A pale purple fluorite cube, 3 mm on edge, with a mosaic structure and a suggestion of tetrahexahedral modification on the upper face, on specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. Chalcopyrite forms irregular inclusions in the fluorite and occasional sphenoidal crystals where it has grown freely. Curved white baryte plates, which are later than the fluorite, are present at top left. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Figure 9. An area of the 'upward-facing' surface of specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection, showing groups of curved lamellar baryte on colourless to pale-purple fluorite, with a few white late-stage pointed prismatic strontianite crystals just visible on the right-hand side. Chalcopyrite occurs as irregular inclusions in the fluorite and as tiny tarnished sphenoidal crystals on the baryte. Strontianite is later than fluorite, baryte and chalcopyrite. The field width is 15 mm. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

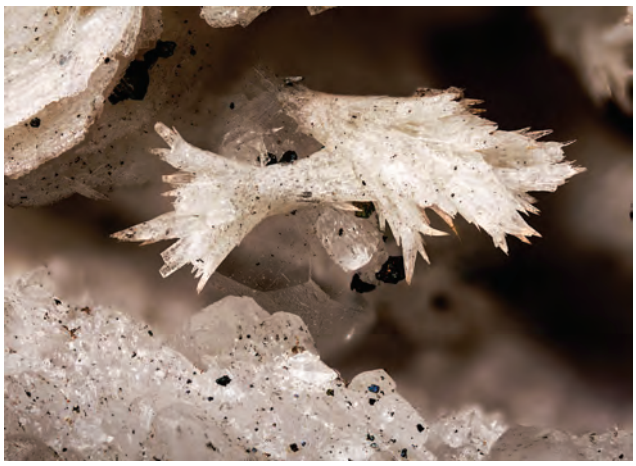


Figure 10. Bow-tie aggregates of curved white strontianite on nail-head calcite with a few tarnished sphenoidal chalcopyrite crystals (the field of view is 2.8 mm across). One of a number of similar crystal aggregates on specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. The direction of curvature is generally away from the growth vector of the crystal bundle. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

rose-red to mauve fluorescence in the calcite (and a distinct brick-red fluorescence in some of the clasts) and intense creamy white fluorescence in the strontianite (Fig. 13). The strontianite is strongly phosphorescent with a glow that is visible for more than a second after the incident illumination is terminated.

Specimen 806 is smaller and less complex than specimen 783. Dark blue-purple fluorite is intergrown

Figure 11. Curved strontianite crystals with flattened six-sided cross-sections and sharp blade-like terminations on specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. The field of view is 6 mm across. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Figure 12. Aggregates of curved pointed white strontianite on pale purple fluorite (bottom) and white calcite (top) with minute tarnished chalcopyrite crystals on specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. The strontianite crystals have sharp blade-like to ragged lath-like terminations. The field of view is 6.7 mm across. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

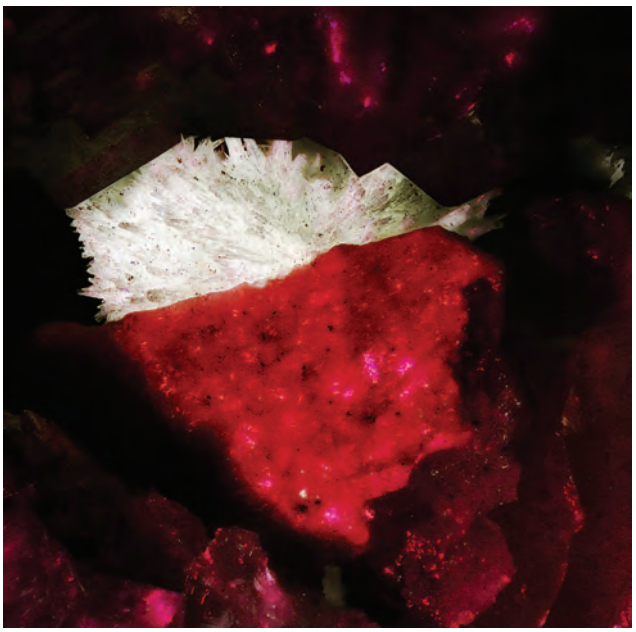


Figure 13. A fluorescence image of strontianite and fluorite on specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. Tapering prismatic strontianite crystals with white fluorescence (the colour is not entirely in accord with the creamy white colour which is perceived visually) infill a fracture between an irregular clast (brick-red fluorescence) with a thin calcite veneer (weak mauve fluorescence), and cubic fluorite crystals (violet fluorescence). The fluorescence is produced by long-wave ultraviolet, centred at 370 nm, with negligible intensity at 400 nm and above. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

with baryte, which reveals rare minute silvery marcasite inclusions on broken surfaces. Fluorite crystals up to 8 mm on edge are associated with curved fan-like baryte rosettes up to 2 mm across on the display surface of the specimen (Fig. 14). A dark opaque sphalerite crystal 3 mm across and several smaller crystals (one resinous with a yellow colour and a degree of translucency) overgrow the fluorite and baryte. Minute sphenoidal chalcopyrite crystals are sparsely scattered on the calcite and fluorite and are common on the large sphalerite. Clusters of pointed white strontianite crystals, typically less than 1 mm long, overgrow the fluorite (and rarely baryte) covering an area of about 10 × 20 mm (Fig. 15).

In common with specimen 783, the fluorite on specimen 806 has a weak blue-violet fluorescence and the strontianite has an intense creamy white fluorescence. Some of the baryte on the broken back surface has a distinct brick-red fluorescence.

ANALYSIS

Facilities for identification at Cliffe Castle Museum are limited. The initial visual identification was confirmed by powder X-ray diffraction at Amgueddfa Cymru – National Museum Wales (X-ray reference number: NMW X-3761) (Tom Cotterell, *personal communication*, 2019). The powder diffraction pattern (Fig. 16) is an excellent match to the reference pattern for strontianite, which is distinct

Figure 14. Dark purple fluorite cubes, up to 8 mm on edge, with a mosaic structure, minor brassy yellow chalcopyrite and curved white baryte rosettes, on specimen 806 [BRFMS: 8.4.15/154] from the Joseph Dawson collection. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Figure 15. Minute radiating sprays of white strontianite on dark purple fluorite with abundant creamy curved baryte on a small area of specimen 806 [BRFMS: 8.4.15/154]. The field is 6.7 mm across. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

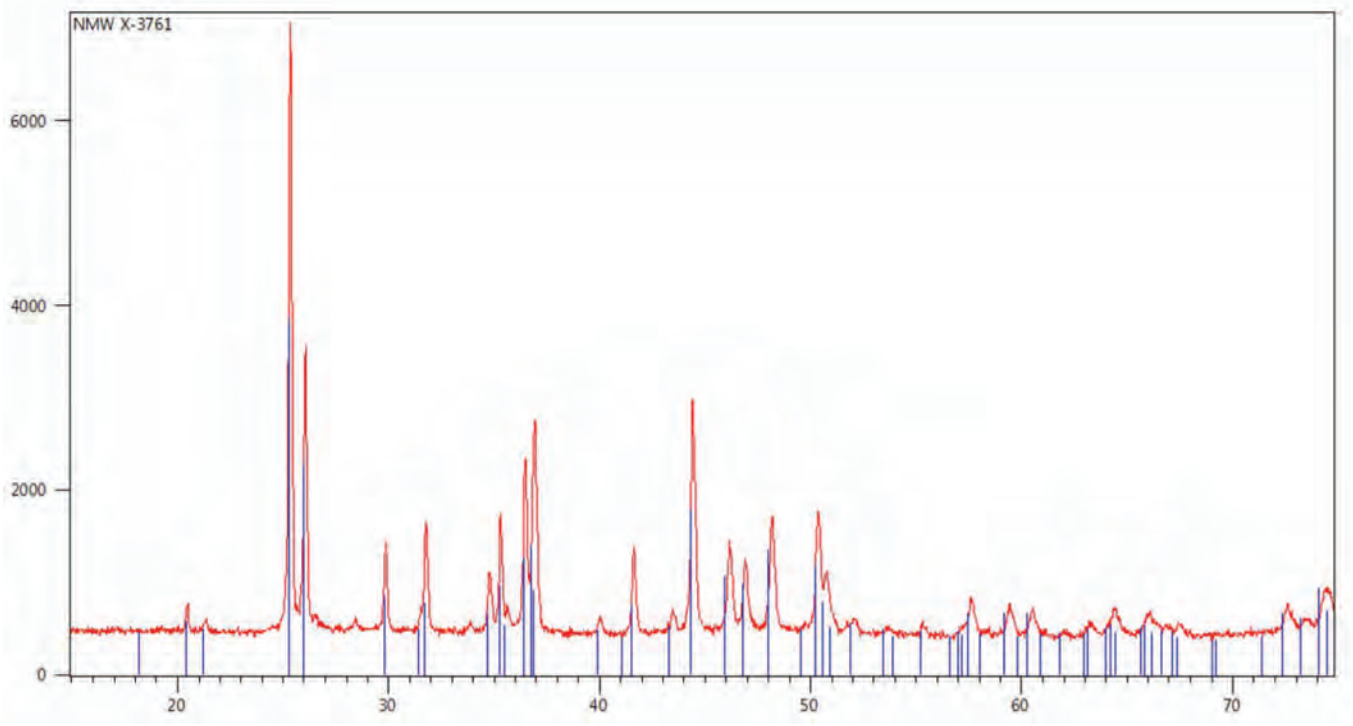


Figure 16. The X-ray powder diffraction pattern (red line) from a tiny fragment of the white unknown on Dawson's specimen 783 [BRFMS: 8.4.15/119]. The vertical blue lines represent the positions and intensities of peaks in the strontianite diffraction pattern. The position of the $d_{(132)}$ peak is about 48.17º(2θ) which with Cu Kα radiation with a mean wavelength of 1.541838 Å corresponds to a *d*-spacing of 1.8891(8) Å.

from the other isomorphous carbonates of the aragonite group (de Villiers, 1971).

Strontianite commonly contains calcium in solid solution. The differing ionic radii of Ca and Sr atoms allow the composition to be estimated from the spacing of the <132> planes in the crystal lattice (Fig. 17). The equation derived by Speer and Hensley-Dunn (1976):

$$Sr_{(Mol\%)} = 1162.84 d_{(132)} - 2116.24,$$

with a value of $d_{(132)}$ of 1.8891 Å, provides an estimated composition for the sample of $Sr_{0.8}Ca_{0.2}CO_3$ with random errors of about 1 mol% Ca. This is well within the range for natural strontianite (Chang *et al*., 1998: p. 255).

DISCUSSION

Any report of strontianite from Derbyshire, particularly one that is based on specimens from an old and somewhat disorganised collection, demands careful substantiation, especially as there are no reliable records of the mineral from the county (Ford *et al*., 1993; Tindle, 2008; Starkey, 2018). However, such discoveries are not without precedent. The first enargite from Derbyshire was found on an old (1804 catalogue date) specimen in the collection of Georgiana, Duchess of Devonshire (1757–1806), a near contemporary of Joseph Dawson (Cooper, 1995).

The only previous claim of strontianite from any locality in the South Pennine Orefield is in Joseph J. W. Watson's account of the mineralisation at the Ecton mines in Staffordshire (Watson, 1860: p. 364). It appears in a list of the gangue minerals which include:

> "carbonate of lime, barytes-calcite, (carbonate of lime and baryta), cawk, or the massive variety of sulphate of baryta, dreelite (sulphate of baryta and lime) and strontianite".

In a review of the minerals of the Peak District, Ford *et al*. (1993: p. 41) suggest Watson's claim may be a mistake for celestine, which occurs at Clayton Adit. Strontianite is not noted in a recent description of the minerals of the Ecton mines based on a thorough survey of museum specimens (Starkey, 2018: pp. 300–308).

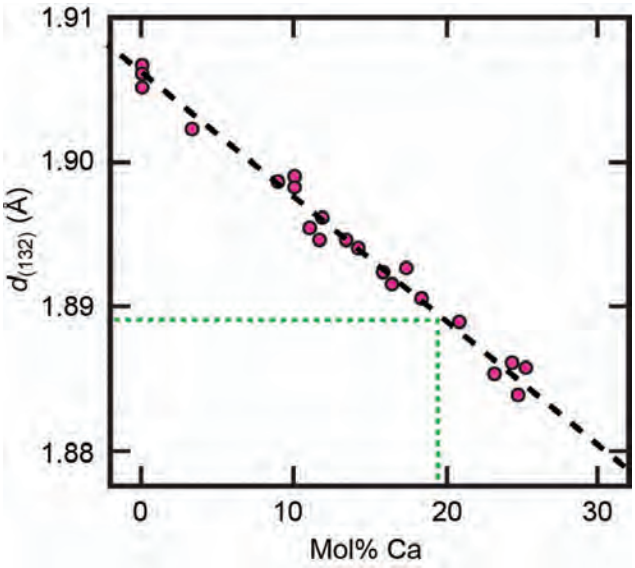


Figure 17. Graph showing the relationship between the position of the $d_{(132)}$ peak (in Å) and calcium substitution in the strontianite lattice. The pink circles are from Reeder (1983), the dashed black line is the best fit to these data and the *d*-value (where the dotted green line meets the *x*-axis) is the spacing of the $d_{(132)}$ peak measured for Dawson's specimen 783 [BRFMS: 8.4.15/119], which corresponds to 20 ± 1 mol% Ca.

The single-word mention in Watson's account and lack of modern corroboration render the record questionable.

There is no doubt that specimens 783 and 806 are from the Joseph Dawson collection and contain hitherto unrecognised strontianite. The disorganised nature of the collection raises two questions: 'could the labels have been mixed up?' and given the species that are present and their paragenesis 'is the location credible?'

The transcription of Dawson's manuscript catalogue into a spreadsheet[1] helped to answer the first question. The possibility of confusion resulting from accidental re-ordering of labels is considerably reduced by the fact that two similar specimens are accompanied by labels which state they are from Castleton. Dawson's label and catalogue describe specimen 783 as "covered with Baryte & Calamine". Baryte is conspicuous, but specimen 783 is the only fluorite specimen on which 'calamine', which Dawson used as a catch-all term for white late-stage overgrowths, is noted[2]. If the label and specimen are correctly matched it seems he mistook strontianite for 'calamine'.

Most of the important facts about strontianite had been established by the time Dawson began his mineral catalogue in 1810. The first indication that strontianite contained a hitherto undiscovered chemical element is usually traced to the late 1780s when specimens from Strontian in Scotland were examined by Adair Crawford and William Cruickshank (Crawford, 1790). The 'new earth' that they found was investigated by many chemists of the day and by the turn of the century the properties of strontium were reasonably well established. The metallic element was isolated by Sir Humphry Davy using newly devised electrolytic methods in 1808 (Partington, 1942; 1951; Moreton and Green, 2018).

Strontianite and celestine are included as a distinct chemical grouping in most systematic textbooks of mineralogy from the beginning of the nineteenth century onward. Thomas Thomson grouped these species as "Genus III. Strontian Salts" in volume four of the third edition of *A System of Chemistry*, which Dawson used as the basis for his classification system (Thomson, 1807: pp. 402–404).

Dawson's catalogue lists three specimens of strontianite from Strontian in Scotland (numbers 1128 to 1130) and twelve specimens of celestine from Bristol (numbers 1131 to 1142, with two additional specimens, 1141a and 1141b, interposed[3]). The single surviving strontianite from Strontian in Dawson's collection is a typical coarsely crystallised pale green mass (Fig. 18). It is unlike the white drusy strontianite on specimen 783 (Fig. 7) and it is easy to see how the latter might be mislabelled as 'calamine'.

Figure 18. Joseph Dawson's specimen of strontianite from Strontian in Scotland (his catalogue number 1128; now BRFMS: 11.5.1/3). A typical coarsely crystallised pale green mass, $65 \times 35 \times 20$ mm, showing the difference in appearance from specimens 783 and 806. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

Strontianite is present as an inconspicuous crust on specimen 806. It was only recognised in the 'fluorite survey' due to its intense creamy white fluorescence. Specimen 806 is described as "Blue Fluor with Calc Spar, Baryte & Copper Parytes [*sic*]" in Dawson's catalogue. The text on his label is similar but with the correct spelling of "pyrites". The fluorite is a deep blue-purple, the baryte is conspicuous as white platy crystals and there is a little scattered chalcopyrite. All of these species match the specimen label and catalogue description. If the label is correctly matched to the specimen, the strontianite must, in this case, have been misidentified as calcite.

The strontianite crystals on specimen 806 are mostly much less than 1 mm in size. Dawson began his catalogue when he was seventy years old. His visual acuity is unlikely to have been good, and at the time stereomicroscopes (or compound microscopes of any worth) had not been developed. He would, at best, have relied on a simple hand magnifier to examine fine details. Calcite commonly occurs as a white encrustation on fluorite from Castleton. As the strontianite forms a crust made up of minute white crystals, it is easy to see how the two species might be confused.

[1] The spreadsheet, which was part of a volunteer project, includes historical information about early mineral collecting in the British Isles and is available on request from the curator at Cliffe Castle.

[2] Although calamine is not recorded on any other fluorite specimen in the main catalogue, specimen 164 in an unpaginated list of 'a display collection in the parlour', which is bound at the end of the catalogue, is described as "Fluor covered with Hydrate of Calamine" (Dawson, 1810–1813). "Hydrate of Calamine" is an obsolete name for the mineral hydrozincite. The specimen has not been located.

[3] Specimens 1141a and 1141b are assumed to be from Bristol although the catalogue does not make the locality absolutely clear. The first Yorkshire celestine was reported by Dr Peter Murray of Knaresborough in 1811, and as these two specimens were added into Dawson's collection after 1810 there is a chance they are from there (Briscoe *et al*., 2020).

The foregoing arguments show that the label and catalogue data for specimens 783 and 806 are consistent and credible. In the context of early nineteenth century mineralogy, the mistaken identifications of strontianite for 'calamine' and calcite are entirely reasonable.

The possibility that the localities might have been mixed up remains to be addressed. It is clear that the specimens are not from Strontian in Scotland, the only British locality that was known in 1810. Fluorite is restricted to a small area of Whitesmith Mine at Strontian and Dawson's specimens are unlike any that have ever been found there (David McCallum, *personal communication*, 2019).

The mineral assemblage is typical of the Pennine orefields. Strontianite occurs at a few mines in the northern part of the North Pennine Orefield (Young, 1985; Tindle, 2008) but the character of the mineralisation is different and Dawson had few specimens from that area. The possibility of confusion with any location in the northern part of the North Pennine Orefield (effectively the Alston Block) is negligible.

Strontianite has been identified at two mining districts in the Yorkshire Pennines. Fine specimens (the first English strontianite to be recognised as such) were described by the Knaresborough physician Peter Murray from Merryfield Mine near Pateley Bridge in the mid 1820s (Symes and Young, 2008). They typically occur as coarse white crystal aggregates with baryte, fluorite, galena, pyrite and sphalerite. Strontianite has also been recorded at a number of localities in the North Swaledale Mineral Belt (Dunham and Wilson, 1985; Young, 1987; Wood, 1993; Tindle, 2008) where typical associates include baryte, fluorite and sphalerite.

Dawson had specimens from both areas of the Yorkshire Pennines where strontianite is now known to occur. His catalogue lists six specimens from Pateley Bridge and twenty-three from 'Arkendale'[4] [i.e. Arkengarthdale] in the North Swaledale Mineral Belt. Of the five fluorite specimens from Pateley Bridge, only one, specimen 817, which is described as "Variety Rose Coulered [*sic*] & Pink" (Dawson, 1810–1813: p. 173) is a possible match with the fluorite on specimens 783 or 806. Even then the match is poor, as the respective colours are pale purple (783) and very dark blue-purple (806). A fluorite in the collection at Cliffe Castle [accessioned as BRFMS: 8.4.15/43] is currently associated with Dawson's label for specimen 817 and it is an excellent match for the label. This eliminates any possible confusion with specimens from Pateley Bridge. Fluorite is not recorded on any of Dawson's specimens from Arkengarthdale and as it is conspicuous on specimens 783 and 806 any possible confusion with the specimens that Dawson catalogued from there can also be discounted.

Figure 19. Specimen 804 in the Dawson collection (BRFMS: 8.4.15/83) a 65 × 50 × 35 mm purple fluorite with platy baryte, calcite and chalcopyrite from Castleton in Derbyshire. The accompanying label describes "Blue Fluor Spar with Calc Spar and Barytes". The similarity with the strontianite-bearing specimens is striking. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

The combination of dark blue-purple fluorite, curved white platy baryte, highly fluorescent strontianite and chalcopyrite on specimens 783 and 806 is unlike any reliably provenanced specimen from Merryfield Mine[5], where fluorite is typically colourless to amber, baryte is typically massive and strontianite is coarsely crystalline and not particularly fluorescent. It is also unlike any of the strontianite specimens that have been found in northern Swaledale, none of which are associated with dark blue-purple fluorite (David McCallum, *personal communication*, 2019).

Figure 20. Specimen 937 in the Joseph Dawson collection (BRFMS: 8.4.15/58) a 65 × 50 × 30 mm pale purple-edged fluorite with curved platy baryte from Castleton in Derbyshire. The baryte is very similar to specimens 783 and 806. The accompanying label describes "Purple Fluor Spar". John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

[4] Arkendale refers to Arkengarthdale, not the village of that name to the northeast of the market town of Knaresborough. Dawson was acquainted with the flamboyant entrepreneur Frederick Hall who lived at Scar House near Langthwaite in Arkengarthdale and had interests in many of the mines of the area (Pirt and Dodds, 2002).

[5] Excellent specimens from Merryfield Mine are preserved at a number of local institutions, notably the Yorkshire Museum in York, and at the Natural History Museum in London.

Specimens 783 and 806 are similar to many of Dawson's other specimens from Castleton (e.g. Figs 19 and 20) and (with the exception of the strontianite) to contemporary specimens from mines in that part of the South Pennine Orefield. Curved fan-like to cockscomb baryte crystal aggregates with dark blue-purple fluorite are well known from the Castleton mines. Very similar combinations of fluorite and baryte have been found at Odin Mine, and at some of the abandoned workings in Pindale and towards Bradwell; chalcopyrite occurs with both of these minerals in overgrown scrins around Cow Low to the southwest of the village. John Mawe, who supplied specimens to Dawson, would certainly have had access to these locations (Pacey, 2003; Cooper, 2006).

If there is one lesson to be learned from this study it is this: specimens should have a locality label permanently glued to them. It does not have to be large or obtrusive, but should include as much information as possible about where the specimen is from (Cotterell, 2018). Dawson failed to realise this and as a result the scientific value of his specimens is diminished. He did fix numbered circular labels to some specimens (e.g. Fig. 21) but (as noted in the foregoing text) the part of his catalogue containing the corresponding information has been lost.

In the not too distant future it may be that 'forensic techniques in mineralogy' will develop to a point where provenance can be determined. In archaeology, a variety of analytical techniques are routinely deployed to answer the question: 'where is it from?' (e.g. Kolb, 2014; Pernika, 2014; Longman *et al*., 2018). Trace-element and isotopic analysis is already used to fingerprint high-value minerals and gemstones (Shabaga *et al*., 2010; Cal Graeber, *personal communication*), and numerous studies show that minerals from different locations have distinctive signatures (e.g. Kemp *et al*., 2018; Boni *et al*., 2019; Canals *et al*., 2019). Unfortunately, the calcium content of the strontianite does not provide any useful information as far as provenance is concerned. Calcium contents vary widely in specimens from the Pennine orefields, even in material collected from the same vein system (Stephen Moreton, *personal communication*, 2020).

Figure 21. Dawson's stuck-on circular label for specimen 798 (fluorite from Castleton in Derbyshire) uses the letter code F, presumably for 'Fluor' and a number code which is either 82 or 83 (or possibly one of these digits over-writing the other). The corresponding catalogue (if one existed) is lost. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

An analysis such as this cannot prove the presence of strontianite at Castleton with absolute mathematical certainty, but we believe it establishes the first occurrence in Derbyshire beyond reasonable doubt.

This study leaves interesting questions unanswered. In a general sense, much remains to be discovered about Joseph Dawson and the history and disposition of his collection. Fewer than half of his specimens are currently accounted for. Missing specimens may lurk unrecognised in other collections or in the wider geology collection at Bradford Museums and Galleries. The team at Cliffe Castle would be delighted to learn of anyone who has specimens with labels similar to those figured herein. It would be easy to check the numbers against Dawson's manuscript catalogue.

More specifically, the fluorescence and curvature of the strontianite crystals invite further study (Fig. 22). Ultraviolet radiation produces fluorescence in strontianite from most worldwide localities, but the reason for the unusually intense response of the specimens from Castleton is unknown. Luminescence in strontianite is commonly produced by broad emissions from water-organic complexes (Gaft *et al*., 2015). It may be that the Castleton specimens formed in an environment that was unusually rich in appropriate organic molecules. Abundant late-stage bituminous hydrocarbons certainly occur with fluorite at Windy Knoll to the west of the village. However, without

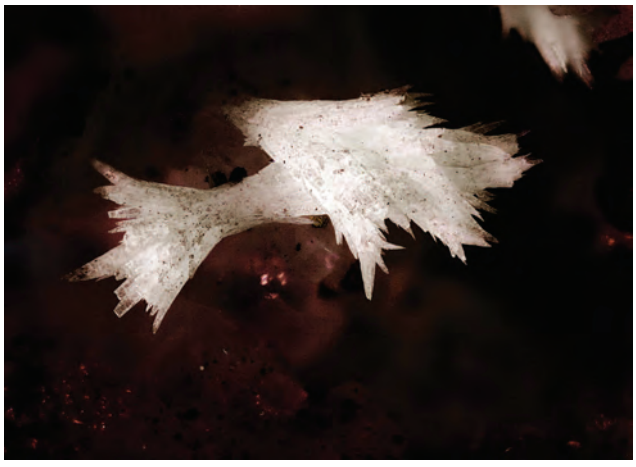


Figure 22. Fluorescence image of the bow-tie aggregates of strontianite illustrated in Figure 10, showing remarkably intense fluorescence and emphasising the crystal curvature (the field of view is 2.6 mm across). Specimen 783 [BRFMS: 8.4.15/119] from the Joseph Dawson collection. John Chapman photo, reproduced by courtesy of Bradford Museums and Galleries.

access to spectrofluorimetry it has not been possible to make a quantitative assessment of the fluorescence spectra. An examination of the fluorescence produced by long-wave ultraviolet radiation (with a peak at 370 nm) using a simple hand spectroscope revealed no obvious structure in the visible range.

It may be that the Ca:Sr cation disorder, which is reported in strontianite by de Villiers (1971: p. 759), has some influence on the curvature of the crystals, or that it is related to the presence of inhibiting impurities on growing faces as noted in aragonite-group minerals by García-Ruiz and Otálora (2015: pp. 33–34). The observation that individual crystals tend to curve away from a central axis to produce bow-tie aggregates suggests some form of competitive crystallisation.

In common with localities in the North Pennine Orefield, strontianite post-dates the major primary minerals at Castleton. The chemistry of ore-bearing solutions is complex, but the observation that strontianite occupies a late-stage paragenetic position across a wide area suggests that similar geochemical processes are at play.

The sulphate in the late-stage baryte in the South Pennine Orefield is thought to have originated in fluids expelled from near contemporary calcium sulphate evaporites (Ford and Worley, 2016). Such fluids would undoubtedly contain strontium, which partitions into calcium sulphates as they form (Warren, 2006). The relative solubility means that strontium is removed in solid solution in baryte if significant barium is present in solution. Thus, in low-temperature hydrothermal veins in the Pennine orefields, sulphate activities control the availability of strontium in solution and discrete strontium minerals do not usually precipitate until all of the solution sulphate has precipitated as baryte.

In recent decades, an extensive database of $^{87}Sr/^{86}Sr$ ratios in different geological environments has been assembled. It is widely used to trace geochemical pathways (Hoefs, 2015). Isotopic fingerprinting would probably provide useful insights into the origin of the Castleton strontianite, especially if it were compared with other Pennine strontianite and with the isotopic signature of strontium in coexisting baryte. Sufficient material is available on the specimens at Cliffe Castle for such a study. The authors would be able to supply well provenanced specimens from other parts of the Pennine Orefields for comparison if such research was considered worthwhile.

Regardless of the way in which it formed, the occurrence of strontianite as a late-stage primary mineral at Castleton is of significant mineralogical interest. It may have been overlooked on other specimens from the area. The unusually bright fluorescence is helpful in making identifications. The authors (and Newsletter Editor) would be interested to learn of any further examples in collections, especially if more detailed locality information was available.

CONCLUSION

This article demonstrates the value of volunteer projects. Many museums have collections that could benefit from such input. Collections in provincial museums often have a reach that extends far beyond their local area. Years of underinvestment following the financial crash of 2008 and austerity in the years that followed has left most of these collections under threat. The discovery of strontianite specimens in the Joseph Dawson collection at Cliffe Castle Museum may seem trivial when considered in isolation, yet just two specimens from a large and historically important collection have made a useful contribution to our knowledge of mineralisation in the British Isles. Although these specimens have been available for study for more than two centuries it is clear that much still remains to be discovered. Surely such collections are worthy of care and preservation.

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RICHELSDORFITE FROM DOLYHIR QUARRY, OLD RADNOR, POWYS: THE FIRST BRITISH OCCURRENCE

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Richelsdorfite has been identified as turquoise to sky-blue spheroidal masses with azurite, malachite, 'tyrolite', zincolivenite and an amorphous copper iron arsenate in thin calcite-filled fractures adjacent to a vein which was exposed in the Silurian Dolyhir Limestone in the northwest corner of Dolyhir Quarry, Old Radnor, Powys in the mid-1990s. It appears to have formed as a result of the oxidation of antimony-bearing tennantite-(Zn). This is the first record of the mineral in the British Isles. A similar but as yet uncharacterised lavendulan-like mineral which is present in the same assemblage is described and tyrolite and tangdanite are briefly discussed.

INTRODUCTION

Richelsdorfite, ideally $Ca_2Cu_5^{2+}Sb^{5+}(AsO_4)_4Cl(OH)_6{\cdot}6H_2O$, is an uncommon mineral which was identified and described on specimens from the Wilhelm Mine, about 2 km northwest of Richelsdorf, Hessen, Germany (Süsse and Schnorrer-Köhler, 1983). At the type locality it occurs in a supergene assemblage formed by the oxidation of primary tetrahedrite-group minerals as turquoise-blue spherulites and crusts made up of thin platy crystals. Richelsdorfite is currently recorded at more than fifty worldwide localities, the vast majority in Europe (Mindat, 2020), but this is the first report from the British Isles.

LOCATION

Dolyhir Quarry is one of the most diverse mineral localities in Britain (Cotterell *et al.*, 2011). In the mid-1990s, a substantial lead-copper vein was uncovered in the Silurian Dolyhir Limestone in the northwest corner the quarry [SO 2445 5861]. The locality is briefly described by Cotterell *et al.*, (2000: pp. 6–7), and a sketch plan showing its position is included in a description of tetrahedrite-group minerals published elsewhere in this journal (Green *et al.*, 2020).

Thin calcite-filled fractures in limestone adjacent to the lead-copper vein contained abundant tennantite-(Zn), with baryte, chalcopyrite, enargite, galena and minor relict sphalerite. The top of the vein exposure was very close to the original land surface and oxidation had produced a diverse assemblage of secondary minerals including azurite, copper, cuprite, malachite, mimetite, 'tyrolite' and zincolivenite (Fig. 1). The last two of these are uncommon arsenates with ideal formulae $Ca_2Cu_9(AsO_4)_4(CO_3)(OH)_8{\cdot}11H_2O$ and $CuZn(AsO_4)(OH)$, respectively.

Turquoise to sky-blue crystal aggregates were found on a small number of specimens (Cotterell *et al.*, 2011: p. 53). Identifications were hampered by the small amount of material and the thin platy crystal morphology. Analyses suggested that at least two similar phases were present. One of these is identified here as richelsdorfite and the available data on the second uncharacterised phase is included for comparison.

Representative specimens collected by the authors before the vein was quarried away are preserved at Manchester Museum (accession numbers MANCH: N14518 to N4623) and in the collection of Amgueddfa Cymru – National Museum Wales.

ANALYSIS

Analyses by powder X-ray diffraction at the University of Manitoba, Canada and the Natural History Museum, London show that one of the lavendulan-like minerals from Dolyhir Quarry is richelsdorfite. Semi-quantitative energy-dispersive X-ray analyses on a scanning electron microscope at the University of Cardiff confirm the presence of antimony, arsenic, calcium, chlorine, copper and oxygen (Fig. 2) (Tom Cotterell*, personal communication*, 2018). The calculated molar proportions are not in precise accord with richelsdorfite, but this is almost certainly due to the effects of crystal morphology and orientation under the electron beam (Newbury and Ritchie, 2013).

The identification of richelsdorfite prompted a re-examination of the data obtained from similar looking unidentified material (Cotterell *et al.*, 2011: p. 53). This includes powder diffraction patterns acquired from crushed fragments in reflection geometry on a Phillips diffractometer (Table 1) and wavelength-dispersive X-ray analyses of a polished crystallite.

The wavelength-dispersive X-ray analyses could not be linked to the original unidentified mineral with absolute certainty and the analytical totals are sufficiently low that antimony might have been present but

Unknown Lavendulan-like		Richelsdorfite		Lavendulan	
d-value (Å)	Relative intensity	*d*-value (Å)	Relative intensity	*d*-value (Å)	Relative intensity
12.99	10	6.8	3	9.72	10
6.58	2	4.91	7	5.00	1
4.38	4	4.39	6	4.86	2
3.29	1	3.05	10	4.45	1
3.02	6	2.67	5	3.11	1
2.63	1	1.753	6	2.97	1
1.648	1	0.795	5	2.75	1

Table 1. Comparison of the positions of the seven most intense lines in the powder diffraction patterns of the uncharacterised lavendulan-like phase from Dolyhir Quarry and the accepted values for richelsdorfite and lavendulan. Note the differences in the last two patterns despite the similarity of the layer structures.

not measured. Therefore, they might equally apply to richelsdorfite. This calls the formula suggested in Cotterell *et al*. (2011: p. 53) into question. Regardless of this unforeseen complication, the X-ray powder diffraction data indicate that an as yet unidentified lavendulan-like mineral is present.

DESCRIPTION

Richelsdorfite occurs as turquoise to sky-blue spheroidal masses (Fig. 3) up to about 0.75 mm in diameter, which rarely aggregate to form minutely botryoidal crusts (Fig. 4). The crystals range up to about 0.3 mm on edge, but are typically smaller. They are never more than a few micrometres in thickness (Fig. 5).

Figure 1. The 'main vein' in the Dolyhir Limestone in June 1996. Overburden (quarry debris and loose shaly mudstone) covering the calcite-bearing mineralised fractures beside the vein has been dug away and white calcite with rich blue-green supergene mineralisation is visible on a block (1.4 × 0.7 m) at the centre of the frame. The vein occupies the steeply dipping fissure in front of the mineralised block.

Very few undoubted richelsdorfite specimens have been identified to date. They were all collected from cavities in thin calcite-filled fractures surrounding the main vein. Richelsdorfite is always closely associated with tennantite-(Zn) (Green *et al*., 2020), which commonly has surface alteration to an unidentified amorphous sage-green copper-iron arsenate (Figs 3 and 4). Azurite, malachite, 'tyrolite' and zincolivenite are common in the same fractures but are rarely found in close association.

DISCUSSION

The presence of two similar platy turquoise-blue minerals in the supergene assemblage makes visual identifications problematic and as yet no detailed systematic study of specimens has been possible. The simplest way to distinguish the two phases is probably energy-dispersive X-ray analysis, which would reveal antimony. The overlap of the CaKα and SbLα peaks, which are centred at 3.691 keV and 3.605 keV (Newbury, 2007) is well known, and modern software has little difficulty differentiating them. The satellite CaKα and SbLα peaks are reasonably well separated and a visual inspection of the high-energy side of the main peak is all that is needed to determine whether antimony is present (Fig. 2).

The copper and arsenate ions required for the supergene minerals to form are likely to have been released by the oxidation of tennantite-(Zn). Calcium was almost certainly supplied by calcite, which is ubiquitous in the fractures and surrounding limestone. The antimony required for richelsdorfite was probably also supplied by tennantite-(Zn) as no other antimony-bearing primary phases are present[1]. There is sporadic substitution of antimony for arsenic in tennantite-(Zn)

[1] A small amount of antimony may be present in galena at Dolyhir Quarry, but none was detected in ten microprobe analyses in a recent study of the mineralisation (detection limit <0.1 wt%). Any antimony released by oxidising galena would almost certainly be locked into the common and stable lead mineral oxyplumboroméite (Deimar *et al*., 2009).

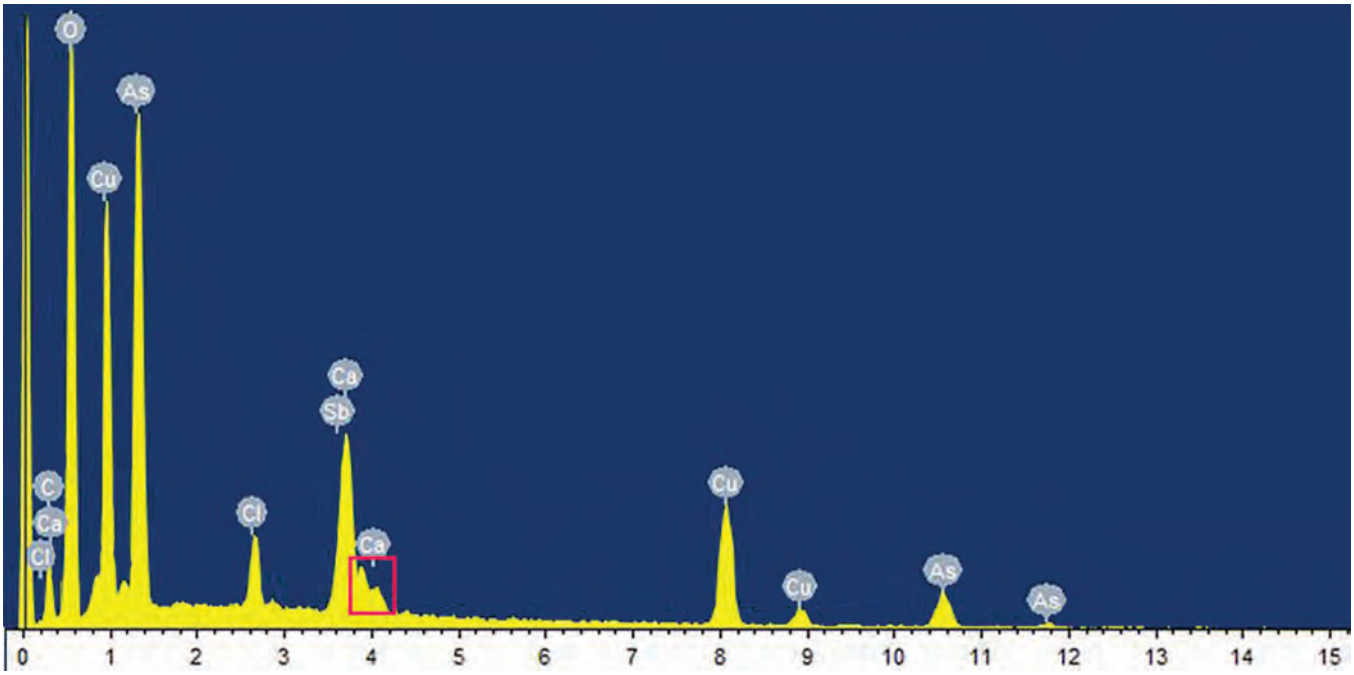

Figure 2. Energy-dispersive X-ray spectrum of richelsdorfite from Dolyhir Quarry. The main peaks for calcium and antimony (around 3.7 keV) overlap, but are both identified by the peak-search software. The two small satellite peaks, CaKα and SbLα, in the red box on the right-hand side of the composite peak confirm the presence of both elements.

from the 'main vein' and surrounding calcite-rich fractures (Green *et al*., 2020). The measured content varies from near zero to 9.32 wt% Sb. This extreme variation may have had a bearing on whether richelsdorfite or the uncharacterised lavendulan-like phase formed.

Figure 3. Turquoise-blue balls of richelsdorfite up to about 0.5 mm across with rhombohedral calcite, tabular colourless baryte and partly altered tennantite. Most of the tennantite has an amorphous sage-green copper-iron arsenate coating. Photo John Chapman.

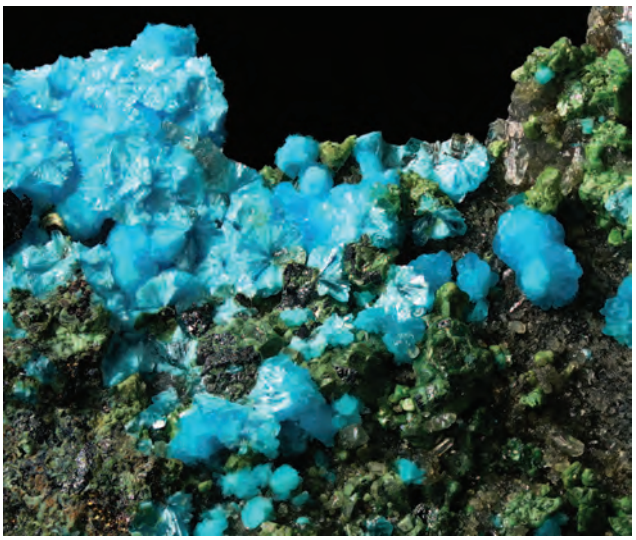

Figure 4. Turquoise-blue balls of richelsdorfite up to about 0.3 mm across with rhombohedral calcite and tennantite. Most of the tennantite has an amorphous sage-green copper-iron arsenate coating. Photo John Chapman.

Lead may also have acted as a control on the activity of antimony. At Dolyhir, richelsdorfite is never associated with lead-bearing supergene minerals; in the presence of lead, antimony in supergene solution is typically deposited as the common and highly insoluble mineral oxyplumboroméite (formerly known as bindheimite) (Diemar *et al*., 2009; Leverett *et al*., 2012).

The minerals of the lavendulan group, lavendulan, sampleite and zdeněkite (ideally $NaCaCu_5(AsO_4)_4Cl{\cdot}5H_2O$, $NaCaCu_5(PO_4)_4Cl{\cdot}5H_2O$ and $NaPbCu_5(AsO_4)_4Cl{\cdot}5H_2O$), respectively, have layer structures which are based on $Cu(O,H_2O,Cl)_5$ pyramids joined by arsenate or phosphate groups. The layers are linked by NaO_6 and CaO_7 (or PbO_7) polyhedra and the hydrogen bonds provided by interlayer water molecules (Fig. 6). As structural data has been refined in recent years (e.g. Ondruš *et al*., 2006; Giester *et al*., 2007; Zubkova *et al*., 2019) it has become clear that similar layers are present in other minerals. Lemanskiite, ideally $NaCaCu_5(AsO_4)_4Cl{\cdot}3H_2O$, has an almost identical layer structure but differs from lavendulan in having three rather than five interlayer water molecules (Zubkova *et al*., 2019). Layer structures based on $Cu(O,H_2O,Cl)_5$ pyramids linked by arsenate groups are also present in mahnertite, ideally $NaCu_3(AsO_4)_2Cl{\cdot}5H_2O$ (Pushcharovsky *et al*., 2004), and there are similar but chlorine-free layers in andyrobertsite and calcioandyrobertsite (Giester *et al*., 2007).

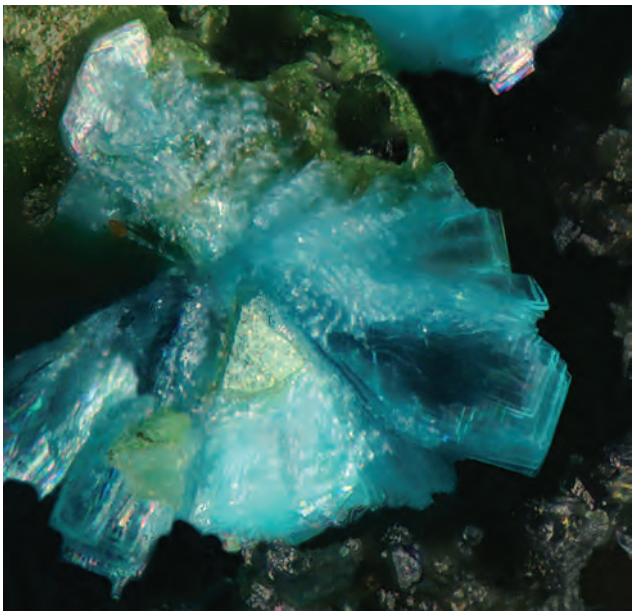

Figure 5. An ultra-high magnification image showing richelsdorfite as radiating aggregates of roughly rectangular plates up to about 0.07 mm across. The thickest plates in the crystal bundle at the right-hand side are between 1 and 2 μm, which is close to the limit of resolution for this type of stacking photography. Photo John Chapman.

Reports of several similar but as yet uncharacterised phases make richelsdorfite a problematic mineral to study (Mindat, 2020). It has a copper-arsenate layer which is similar to lavendulan but a more complex interlayer which contains $Sb(OH)_6^-$ (Süsse and Tillmann, 1987; Rruff, 2020). Richelsdorfite-like phases with hydroxyl replacing chlorine appear to be stable (Süsse and Tillmann, 1987); a 'carbonate richelsdorfite', in which a carbonate group replaces one of the arsenate groups in the copper-arsenate layer has been described from Austria (Drescher and Susse, 1997); and at least four different minerals with similarities to richelsdorfite are recorded from the Black Forest; some contain no antimony, others contain no chlorine (Walenta and Dunn, 1988; Walenta, 2000).

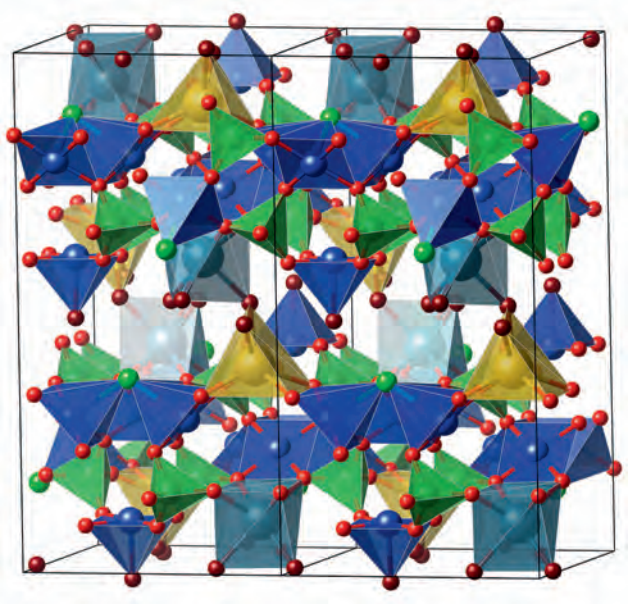

Figure 6. Polyhedral model of lavendulan, the *b*-axis is set vertical and copper arsenate layers extend in the *a*-*c* plane. Square-based CuO_5 and CuO_4Cl pyramids (deep blue) are linked by tetrahedral arsenate groups (green); CaO_7 polyhedra (pale blue) and NaO_6 polyhedra (pale yellow) are associated with water molecules (oxygen atoms dark red) between the layers. Remaining oxygen atoms are shown in red. Chlorine is bright green. Reproduced by courtesy of Dr Frank Hoffman, Department of Chemistry, University of Hamburg (Hoffman, 2017).

The foregoing paragraphs show that diverse molecular species and differing amounts of water can be accommodated by structures with lavendulan-like layers. Unfortunately, such structures are difficult to study, the crystals are typically thin and register between the layers is commonly poor. The diverse range of elements present in species that have been characterised to date suggests that many further combinations might exist.

A preliminary study of the uncharacterised lavendulan-like mineral by electron diffraction suggests a nearly rectilinear unit cell with two edges of ~9.9 Å (or ~14 Å if the base vectors lie along the diagonals). This has similarities to lavendulan, which has a layer structure with a = 10.011 Å and c = 10.056 Å (Fig. 6) and to richelsdorfite which has a = 14.08 Å, b = 14.21 Å and c = 13.49 Å. If the intense reflection at 12.99 Å (Table 1) is a basal spacing, which is probable in view of the effects of preferred orientation, it may be that the uncharacterised mineral has a similar layer structure to lavendulan with a more complex richelsdorfite-like interlayer.

Lavendulan has been reported at a significant number of localities where primary minerals containing copper and arsenic have been exposed to alteration (Tindle, 2008). In most cases the identifications are visual or by qualitative energy-dispersive X-ray analysis. More detailed studies including chemical and structural data are desirable. Other minerals, some as yet uncharacterised, may masquerade as lavendulan. It is not possible, for example, to differentiate lavendulan from lemanskiite by energy-dispersive X-ray analysis. Several uncharacterised richelsdorfite-like phases have also been claimed and therefore richelsdorfite might also be misidentified. It should be sought at localities where antimony-bearing tetrahedrite-group minerals (or luzonite–famatinite) are exposed to supergene oxidation.

As well as richelsdorfite and related minerals, tyrolite-like copper calcium arsenates from Dolyhir and other British localities would benefit from further study. In an analysis of two sets of 'tyrolite' powder diffraction data, Cotterell *et al*. (2011: p. 48) note:

> "neither set of peaks match published tyrolite, but they are similar to specimens from other locations including Alderley Edge, Cheshire and Tynagh Mine, Co. Galway".

Some of the so-called tyrolite is likely to be the recently described mineral tangdanite, ideally $Ca_2Cu_9(AsO_4)_4(SO_4)_{0.5}(OH)_9{\cdot}9H_2O$ (Ma *et al*., 2014). Tangdanite (formerly known as clinotyrolite) has a layer structure which is similar to tyrolite, with a unit cell that is very close to the 2*M*-polytype (Krivovichev *et al*., 2006). It differs from tyrolite in having interlayer sulphate rather than carbonate. Material from the type locality contains 1.6 wt% SO_3, which is very close to the 1.82 to 1.88 wt% SO_3 reported by Cotterell *et al*. (2011: p. 48) at Dolyhir. These values are similar to those reported for tangdanite from most worldwide localities, but are less than the 2.55 wt% SO_3 required by the ideal formula. Tangdanite with a close-to-ideal interlayer sulphate content has only been identified at Příbram in the Czech Republic (Škácha *et al*., 2019).

There appears to be a solid solution between tangdanite and tyrolite, but the unit-cell parameters are surprisingly unaffected by changes in sulphate content (Škácha *et al*., 2019: p. 209). Substitution does not, therefore, explain observed variations in the X-ray powder patterns of specimens from Dolyhir. Further research, perhaps including infra-red and Raman spectroscopy, is desirable. Measurements of the intensity of the Raman-active ν_1 symmetric sulphate-stretch at 997 cm^{-1} may be of use as a rapid and non-destructive method of mapping sulphate content.

In a recent study of old specimens from Murton Mine in Scordale, Cumbria, a hand specimen containing chalcopyrite, galena, goethite and quartz, with minor annabergite, fluorite and malachite, was broken up. It revealed a tiny cavity almost completely enclosed in goethite containing a blue lavendulan-like aggregate about 0.5 mm across. A microscopic fragment was separated for energy-dispersive X-ray analysis and antimony, calcium, arsenic, copper and chlorine were found in approximately the correct proportions for richelsdorfite (Christian Rewitzer, *personal communication*, 2019). This may be the second British occurrence, but unfortunately the amount of material available for study is too small for confirmation by X-ray powder diffraction.

CONCLUSION

This study reports the first British occurrence of the rare antimony-copper-calcium chlorarsenate richelsdorfite. It appears to have formed as a result of the oxidation of antimony-bearing tennantite-(Zn). A similar, but as yet uncharacterised, lavendulan-like mineral occurs in the same assemblage. Dolyhir Quarry is one of the most diverse and important mineral localities in Britain; fieldwork and analysis continue to reveal unusual species.

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TETRAHEDRITE-GROUP MINERALS FROM DOLYHIR QUARRY, OLD RADNOR, POWYS

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The compositions of tetrahedrite-group minerals from veins in Precambrian and Silurian wall-rocks at Dolyhir Quarry, Old Radnor, Powys are reported. They vary from near ideal end-member tennantite-(Fe) to tennantite-(Zn) with 14 mol% iron substituting for zinc. Up to 31 mol% of antimony substitutes for arsenic in tennantite-(Zn) from calcite-filled fractures associated with a substantial lead-copper vein in the Silurian Dolyhir Limestone. Silver-rich tennantite-(Fe), which contains no zinc and is depleted in iron, occurs in thin carbonate veins in Precambrian wall-rocks. The most argentiferous grain has an empirical formula $Cu_{8.36}Ag_{2.12}Fe_{1.55}As_{3.93}S_{13.04}$. An unidentified sulphosalt mantles one of the grains of tennantite-(Fe). Its empirical formula on the basis of four sulphur atoms is $Cu_{2.28}Fe_{1.00}As_{0.86}Sb_{0.06}S_4$. The composition suggests it may be an iron-bearing member of the stannite group, related to luzonite, but it does not correspond to any currently approved mineral species.

INTRODUCTION

Tetrahedrite and tennantite are widespread in low-temperature hydrothermal ore deposits in the British Isles (Tindle, 2008). Until the recent revision of tetrahedrite-group nomenclature, the two species were considered to be opposite ends of a solid solution series with formulae that were commonly written $Cu_{10}(Fe,Zn)_2Sb_4S_{13}$ and $Cu_{10}(Fe,Zn)_2As_4S_{13}$. Tetrahedrite was a 'grandfathered' species, without either a type locality or type specimen. Tennantite[1] was first described from Cornwall (Phillips, 1819a,b), but the precise locality and type specimens are lost.

Tetrahedrite and tennantite are now considered to be series names. The series are subdivided into species based on the chemical content of the M(1)-site in the crystal structure (Biagioni *et al*., 2020). The structure is relatively flexible and can accommodate a large number of different elements. Substitutions are complex and extensive and tetrahedrite-group minerals are sensitive indicators of conditions during the formation of ore deposits (George *et al*., 2017).

LOCALITY

Dolyhir Quarry is a large modern aggregate producer in the Welsh Borderlands near the village of Old Radnor [SO 244 584]. It came to the attention of mineralogists in the mid 1990s when a lead-copper vein with an unusual associated supergene assemblage was discovered in the Silurian Dolyhir Limestone Formation. Subsequent research has revealed one of the most diverse mineral assemblages in the British Isles (Cotterell *et al*., 2011).

The range of primary minerals found in the veins at Dolyhir Quarry is considerable. A sketch plan showing the positions of principal tennantite localities is reproduced as Figure 1. These are described by Cotterell *et al*. (2011: p. 48) as follows:

> "In the main vein [location 1], silvery metallic tennantite was abundant. It was commonly intergrown with galena and associated with chalcopyrite, baryte and calcite ... Although mostly massive, small crystals were found".
>
> "Rich tennantite was found in fractures in Strinds Formation sandstone beneath the limestone in the northwest of the quarry in 1998 and as distinct microcrystals with calcite and harmotome at location 6".
>
> "Elsewhere in the basement rocks, tennantite was found as small but bright tetrahedral crystals in the silver vein at location 15. It occurs as patches in calcite and baryte-containing veins and in narrow alpine-type fractures in the Yat Wood Formation [location 19]".

All of these identifications of tennantite are supported by wavelength-dispersive X-ray analysis, but none of the analytical data have been published. The recent revision of tetrahedrite-group nomenclature (Biagioni *et al*., 2020) provides a timely framework.

[1] Tennantite is named in honour of the Yorkshire-born chemist Smithson Tennant (1761–1815).

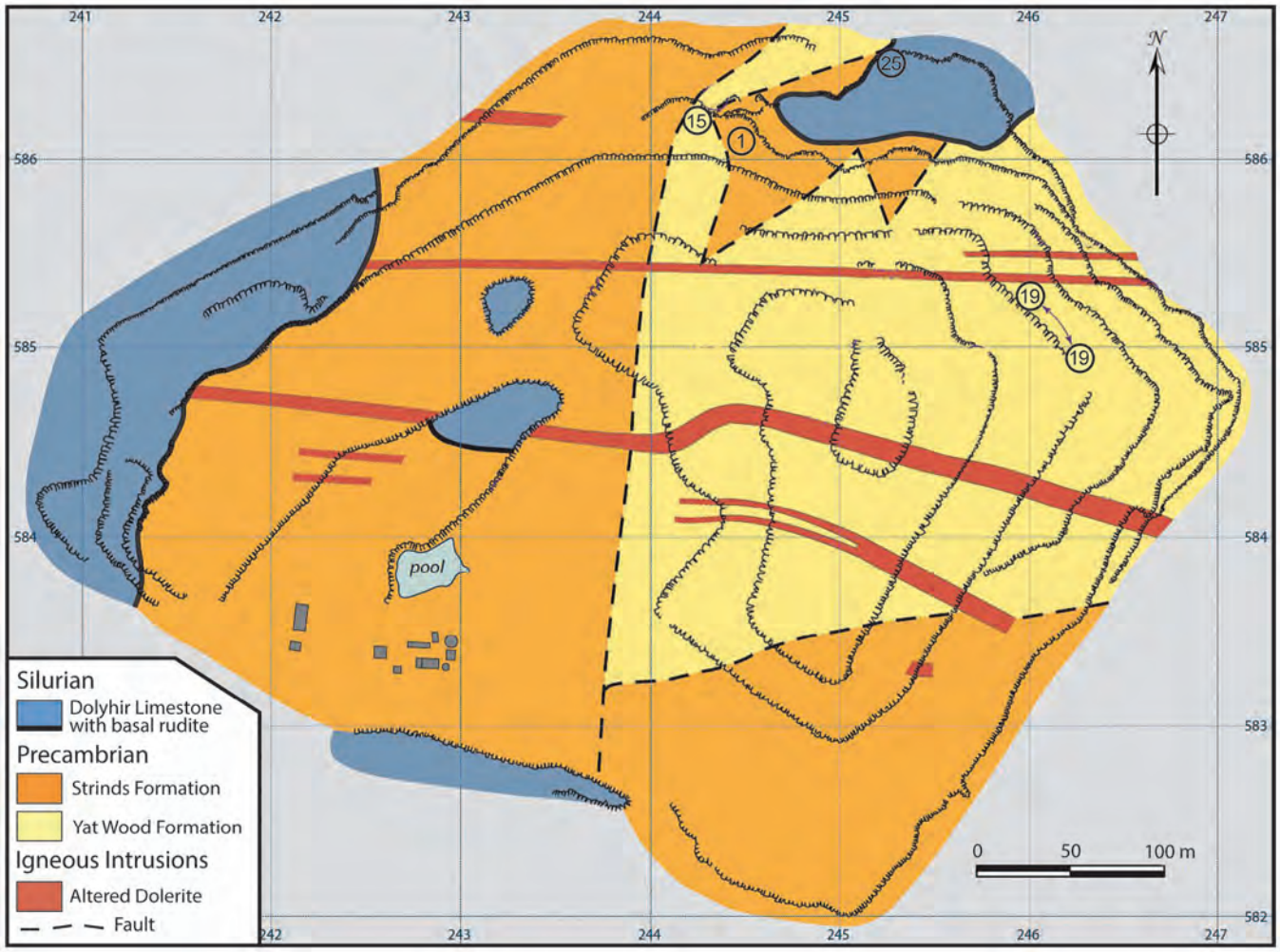

Figure 1. Sketch plan (modified from Cotterell *et al*., 2011: p. 6) showing the localities where the tennantite-series minerals described in this study were collected. The geological detail and quarry faces are based on the locality as it stood in about 2008; they do not correspond with the earlier (or later) discoveries. Locations described in the text are as follows:

Location 1: The 'main vein' [SO 2445 5861] trending northwest-southeast at the top of the Dolyhir Limestone. Tennantite, galena and baryte; lesser chalcopyrite and calcite; minor enargite and greenockite; and a diverse suite of supergene minerals were collected in the mid 1990s. Tennantite was the dominant ore mineral in thin calcite-filled fractures in the surrounding limestone. This locality is shown (erroneously) in the Strinds Formation because the Dolyhir Limestone in the area had been removed by quarrying by the time it was surveyed.
Location 15: The 'silver vein' [SO 2442 5863] a narrow (10 to 25 mm) calcite vein in the northwest corner of an upper level. Micro-crystals of proustite and xanthoconite along with realgar, chalcopyrite and tennantite were collected in October 2004.
Location 19: Thin fractures and shallow dipping carbonate veins in the northeast face on a lower level [between SO 2462 5849 and SO 2460 5852]. Witherite, alstonite and associated species were collected between 2005 and 2007.
Location 25: A large block of limestone fallen from a disused upper quarry face [SO 2453 5865] with fractures and pods containing intergrown tennantite, chalcopyrite and galena.

TETRAHEDRITE-GROUP NOMENCLATURE

The newly approved classification of tetrahedrite-group minerals is based on the dominant occupancy of specific sites in the crystal structure, with an unusual qualification, which divides the content of one of the sites into two, based on valency. The general structural formula can be written:

$$^{M(2)}A_6{}^{M(1)}(B_4C_2)^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z,$$

where the superscript prefixes, M(1), M(2), X(3), S(1) and S(2), represent particular sites in the crystal structure and the 'placeholders', *A*, *B*, *C*, *D*, *Y* and *Z*, may contain the following elements:

A = Cu^+, Ag^+, a vacancy □, and $(Ag_6)^{4+}$ clusters;
B = Cu^+ and Ag^+;
C = Zn^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Cu^+ and Fe^{3+};
D = Sb^{3+}, As^{3+}, Bi^{3+} and Te^{4+};
Y = S^{2-} and Se^{2-};
Z = S^{2-}, Se^{2-} and □.

The presence of both univalent and divalent cations at the M(1)-site is an example of a multivalent site-occupancy imposed by charge-balance. Unusually in mineral nomenclature, different combinations of constituents (*B* and *C*) at the same crystallographic site are used to define different mineral species[2]. The dominant *C*

[2] The mica group of minerals provides another familiar example.

constituent (also described as the charge compensating constituent) is added as a modifier to a 'root name', which is decided on the basis of the dominant constituents at the other sites. Eleven valid species: argentotennantite-(Zn), argentotetrahedrite-(Fe), kenoargentotetrahedrite-(Fe), giraudite-(Zn), goldfieldite, hakite-(Hg), rozhdestvenskayaite-(Zn), tennantite-(Fe), tennantite-(Zn), tetrahedrite-(Fe) and tetrahedrite-(Zn) are listed by Biagioni *et al*. (2020) and a survey of published analyses suggests that a number of others await formal approval.

Complications in the nomenclature arise because of complexities in the silver-dominant members of the group (notably in the mineral formerly known as freibergite). Silver may be present as discrete four-valent $(Ag_6)^{4+}$ clusters as well as the more typical Ag^{+} cations at the M(2)-site. This issue is of no concern in this account as even the most silver-rich compositions have fewer than six atoms per formula unit. All of the analyses fall well within the tennantite-(Fe) and tennantite-(Zn) composition fields. Interested readers are urged to consult Biagioni *et al*. (2020) for a detailed account of tetrahedrite-group classification and nomenclature.

ANALYSIS

Tennantite in the collections of two of the authors (NH and DG) was analysed by wavelength-dispersive X-ray spectrometry (WDS) on a Cameca SX100 microprobe at the Open University. Selected grains were embedded in resin and ground and polished to produce a suitable flat surface (Fig. 2). Analytical conditions were 20 kV, 20 nA with a 10 µm diameter beam. The major elements present in typical tetrahedrite-group minerals: arsenic, antimony, copper, iron, silver and zinc, were determined. Lead was also sought but only identified in more than trace amounts in one instance.

Nine specimens from five locations were sampled. The results of seven sets of analyses from four locations are listed as weight percent elements in Table 1. One set of analyses (grain 394) has been discarded because the analytical totals do not sum to 100 wt%; another set (grain 396) proved to be of enargite rather than tennantite and are of no relevance to this study

The empirical formulae of tetrahedrite-group minerals can be calculated on the basis of 26 negative charges (effectively 13 sulphur atoms) or 29 atoms per formula unit. The formulae here are calculated on the basis of 29 atoms per formula unit to allow easy comparison with the data presented in George *et al*. (2017). The results are not listed for all analyses in the interests of brevity. Average and extreme compositions are noted in the discussion, and ranges are shown graphically.

The grain mount (Fig. 2) was examined by reflected light microscopy before it was carbon coated to check if other minerals were intergrown with the tennantite. Chalcopyrite and galena were identified on several specimens and an unidentified phase overgrowing tennantite was found on grain 392 (Fig. 3). Five analyses of this mineral are included in Table 2.

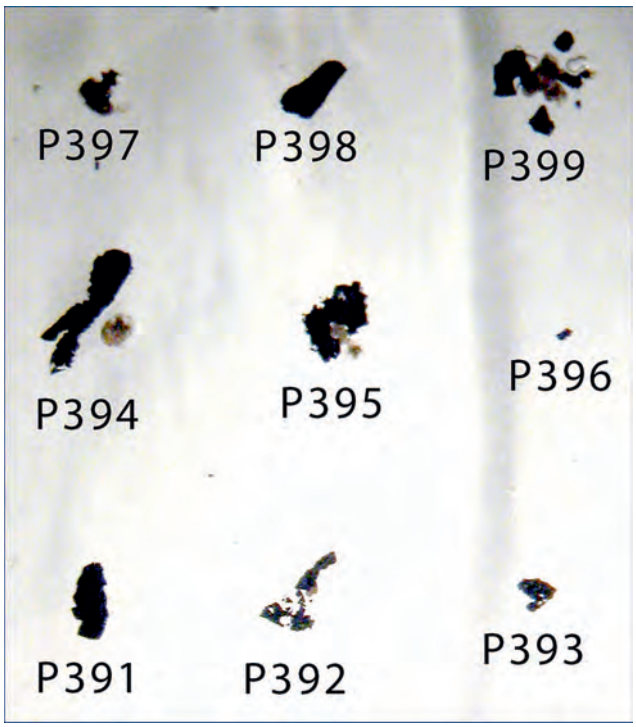

Figure 2. Grains from specimens collected by DG and NH, mounted in epoxy resin and ground and polished for analysis by wavelength-dispersive spectrometry. The field of view is 12 mm across; typical grains are between 1 and 2 mm. Analytical data for grains 391, 392, 393, 395, 397 and 398 are summarised in Table 1. The analytical totals for grain 394 are systematically low and these data are not included in this study. Grain 396 from location 6 is enargite rather than tennantite. Minute crystals of plagionite overgrow galena on grain 399, but no tennantite is present. Grain 401 is not shown.

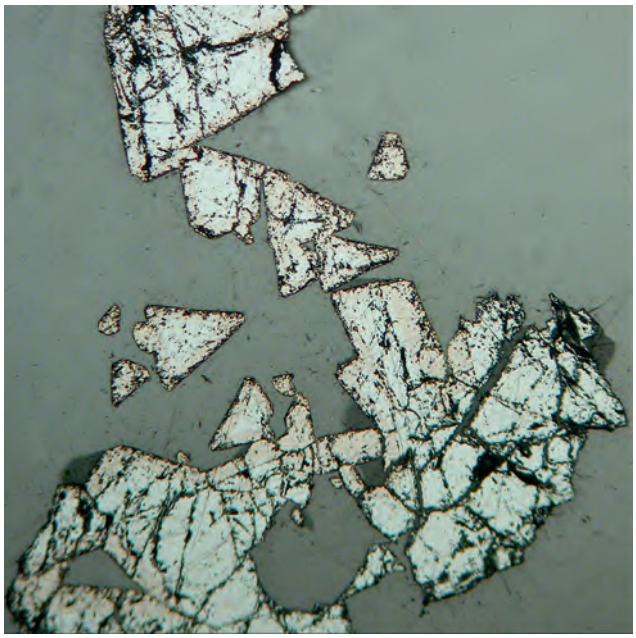

Figure 3. Part of grain 392, imaged in reflected light (10 × objective; Leica DMRB microscope), showing grey tennantite mantled by an unidentified faintly pink phase. The field is 1 mm across. Photo David Green.

	Fe	S	Cu	Zn	As	Ag	Sb	Total
Main Vein (395) and nearby calcite-filled fractures (397) (both location 1)								
395 DC	1.63	27.71	41.96	6.60	17.70	0.03	4.71	100.34
395 DD	3.00	28.49	42.09	5.07	19.75	0.06	0.18	99.06[1]
395 DG	1.63	27.76	42.14	6.60	17.58	0.03	4.16	99.90
395 DH	4.04	27.13	40.55	3.36	18.48	0.03	0.44	100.69[2]
395 DI	1.13	27.99	42.10	6.90	16.80	0.04	4.55	99.50
395 DJ	3.42	28.20	42.56	4.45	19.58	0.04	0.67	98.90
395 DQ	1.12	27.48	41.37	7.06	15.00	0.09	7.05	99.16
395 DR	2.15	28.00	41.70	5.82	17.31	0.04	4.37	99.39
395 DT	1.88	28.02	42.36	6.33	18.55	0.02	2.88	97.81
397 NA	2.66	28.13	42.37	5.60	20.03	0.04	0.18	100.04
397 NB	2.72	28.51	42.86	5.39	19.71	0.00	0.35	99.00
397 NC	1.52	27.27	41.95	6.52	14.51	0.03	7.86	99.53
397 ND	1.02	26.96	41.15	7.19	13.86	0.02	9.97	99.65
397 NE	2.91	28.37	42.92	5.27	19.17	0.05	0.44	100.17
397 NF	1.56	27.02	41.06	6.55	13.72	0.05	9.32	99.11
397 NG	1.88	28.02	42.36	6.33	18.55	0.02	2.88	99.30
Silver Vein (location 15)								
401 LA	5.42	26.32	33.69	0.01	18.23	14.52	0.00	98.19
401 LB	5.25	26.44	34.63	0.00	17.99	13.65	0.00	97.97
401 LD	5.73	26.84	33.71	0.00	19.58	14.26	0.00	100.13
401 LH	5.60	26.18	33.19	0.00	18.20	15.00	0.00	98.18
401 LC	5.26	26.03	32.27	0.01	18.89	14.58	0.00	97.04
391 BC	7.30	28.64	43.40	0.00	19.84	0.10	0.00	99.28
391 BD	7.20	28.41	43.40	0.00	20.25	0.06	0.00	99.31
391 BE	7.43	28.33	43.58	0.00	19.66	0.00	0.00	99.00
391 BF	7.48	28.46	43.01	0.00	20.10	0.09	0.02	99.15
391 BG	7.31	28.36	43.74	0.00	19.50	0.01	0.00	98.92
392 AA	7.21	28.27	43.68	0.00	19.72	0.03	0.22	99.13
392 AC	7.50	28.52	43.12	0.00	20.36	0.00	0.18	99.67
392 AD	7.53	28.66	43.23	0.01	20.29	0.01	0.17	99.91
392 AE	7.04	28.77	43.36	0.03	20.40	0.05	0.00	99.62
392 AF	7.16	28.81	43.23	0.00	21.03	0.02	0.20	100.45
392 AG	5.91	28.17	43.31	0.00	21.20	0.30	0.01	98.90
392 AK	6.87	28.62	43.61	0.00	20.63	0.13	0.00	99.85
392 AL	6.94	28.43	43.36	0.01	20.31	0.06	0.00	99.11
Carbonate Vein (location 19)								
393 QA	2.80	27.56	40.92	4.90	19.99	3.10	0.04	99.86[3]
393 QB	2.63	27.63	41.24	5.09	19.90	2.56	0.53	99.59
393 QC	1.88	27.63	41.31	6.10	19.56	2.62	1.02	100.26[4]
393 QD	2.86	27.99	41.09	5.19	19.87	2.43	0.11	99.53
393 QE	2.46	27.83	41.01	5.44	18.97	2.74	0.28	98.89[5]
393 QF	2.45	27.92	41.44	5.44	19.88	2.41	0.18	99.86[6]
393 QG	2.41	27.89	41.58	5.66	19.94	2.11	0.00	99.59
393 QH	2.21	28.21	41.64	5.91	19.90	2.28	1.06	101.22
393 QI	2.84	28.04	41.10	5.30	19.49	2.57	0.35	99.70
393 QJ	2.94	27.44	40.76	4.93	19.92	2.73	0.83	99.54
Tennantite Pod in Dolyhir Limestone (location 25)								
398 GA	1.46	27.98	43.01	6.63	19.20	0.05	1.85	100.18
398 GB	1.62	28.00	43.00	6.58	19.68	0.02	0.17	99.08
398 GE	2.21	28.11	42.91	5.85	20.48	0.05	0.08	99.69
398 GH	1.47	28.02	43.08	6.80	20.04	0.07	0.13	99.60
398 GI	2.29	28.33	42.97	5.88	20.20	0.02	0.00	99.69
398 GJ	1.50	27.57	42.22	6.51	17.91	0.08	4.01	99.81

[1] also includes 0.43 wt% Pb; [2] includes 6.67 wt% Pb; [3] includes 0.55 wt% Pb; [4] includes 0.14 wt% Pb; [5] includes 0.17 wt% Pb; [6] includes 0.13 wt% Pb.
Table 1. Selected microprobe analyses as wt% elements for tetrahedrite-group minerals from Dolyhir Quarry. The locations are listed in and described in Figure 1.

DISCUSSION

The analyses listed in Table 1 all lie within the composition field of tennantite-(Fe) or tennantite-(Zn), common and widespread tetrahedrite-group minerals with ideal formulae $Cu_6(Cu_4Fe_2)As_4S_{13}$ and $Cu_6(Cu_4Zn_2)As_4S_{13}$ (Biagioni *et al*., 2020). Copper is included in two places in these formulae [as Cu_6, and (Cu_4Fe_2)], rather than as Cu_{10}, to emphasise its presence at two distinct sites in the crystal structure. It occurs at both *A* and *B* in the general formula as Cu^+, and may also be present as either Cu^+ or charge compensating Cu^{2+} at *C*.

Comparing the general structural formula with the data listed in Table 1 shows that there is considerable substitution of silver for copper at *A*, zinc for iron at *C*, and antimony for arsenic at *D*, in tennantite-series

Analysis	Fe	S	Cu	Zn	As	Ag	Sb	Total
392 AB	13.96	31.61	35.97	0.01	15.60	0.00	1.58	98.74
392 AH	13.81	31.57	35.95	0.02	16.04	0.04	1.67	99.09
392 AI	13.81	31.65	35.46	0.02	15.48	0.12	1.90	98.44
392 AJ	14.42	31.76	35.31	0.04	15.49	0.08	1.42	98.51
392 AM	12.99	31.18	35.52	0.04	16.23	0.14	1.97	98.06

Table 2. Microprobe analyses, as wt% elements, of an unidentified sulphosalt found with tennantite-(Fe) on specimen 392 from location 15 (the 'silver vein') at Dolyhir Quarry.

minerals from Dolyhir Quarry. These substitutions can be explored using average and extreme compositions and appropriate plots (cf. George *et al*., 2017).

The trivalent cations arsenic and antimony are the principal constituents at the X(3)-site in almost all tetrahedrite-group minerals. The mean *D*-cation content for the fifty formulae calculated in this study[3] is 3.985±0.025. This is identical to the ideal value of 4.00 within statistical uncertainties. It shows that no other elements are present at the X(3)-site and gives confidence in the analyses.

The relationship between the As and Sb content (in those analyses which contain significant Sb) is shown in Figure 4. Linear regression of the full dataset produces a slope of −0.99±0.04 which indicates that arsenic substitutes for antimony on a one-for-one basis: As ↔ Sb. This is in accord with a large dataset presented by George *et al*. (2017: p. 11) which has a similar trend-line with little departure from one-for-one substitution of As for Sb at a fully populated X(3)-site[4].

The divalent charge balancing *C* constituents, primarily Fe^{2+} and Zn^{2+}, at the M(1)-site in tennantite-series minerals are limited to 2 atoms per formula unit according to Biagioni *et al*. (2020). Figure 5 suggests that there is a simple one-for-one substitution of these elements in the grains from locations 1, 19 and 26. The mean Zn+Fe content[5] is 1.927±0.016 atoms per formula unit, which is slightly less than the limiting value of 2.0. A small amount of another charge-balancing divalent ion, probably copper, may also be present. Linear regression produces a slope of −0.97±0.04, which indicates that zinc substitutes for iron on a one-for-one basis: $Zn^{2+} \leftrightarrow Fe^{2+}$.

Substitutions at *C* in tetrahedrite-group minerals from worldwide localities are complex and varied. There are other possible substituents in addition to zinc and

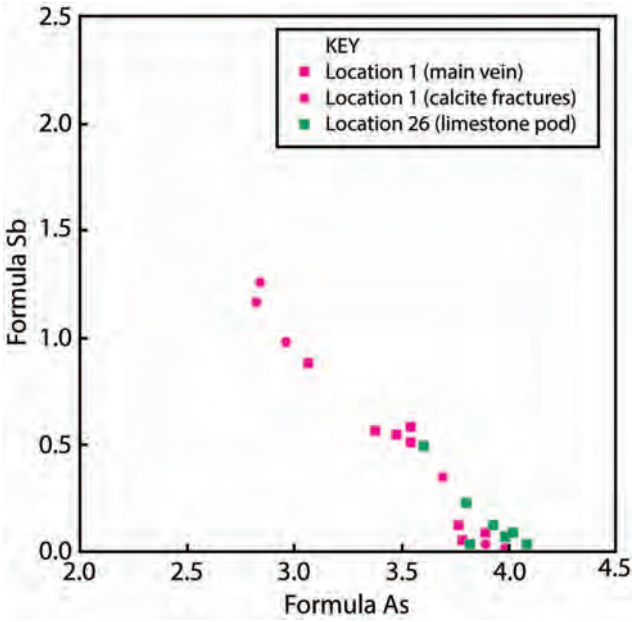

Figure 4. Plot of formula Sb versus formula As for those analyses (all from localities in the Dolyhir Limestone listed in Figure 1) with more than about 0.05 atoms of antimony per formula unit. The remaining data points lie in a small region on the *x*-axis at As = 4 and overlap to such an extent that they cannot be shown at this scale.

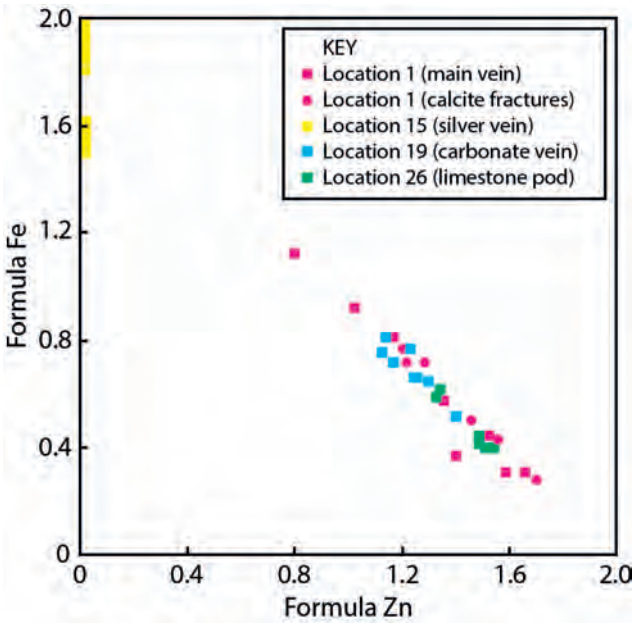

Figure 5. Plot of formula Fe versus formula Zn for all of the tetrahedrite-group analyses. Data for locations 1, 19 and 26 shows a simple reciprocal relationship. No zinc is present in the analyses from location 15 (yellow squares), which all lie along the *y*-axis. The localities are described in more detail in Figure 1.

[3] Mean Sb+As is 3.985±0.025 (n=50), with errors quoted at 2σ; the standard deviation of the distribution is 0.086.

[4] Two anomalous points at the Sb-dominated end of the solid solution may be due to substitution by other cations (George *et al*., 2017: p. 11).

[5] Mean Fe+Zn is 1.927±0.016 (n=35), with errors quoted at 2σ; the standard deviation of the distribution is 0.044.

Analysis	Formula Cu	Formula Fe	Formula As	Formula Sb	Formula S	Cu^{+}	Cu^{2+}	*C* cations
401 LA	8.42	2.14	1.54	3.86	13.04	7.57	0.84	2.38
401 LB	8.63	2.00	1.49	3.80	13.07	7.53	1.10	2.59
401 LD	8.25	2.06	1.60	4.07	13.03	7.90	0.35	1.95
401 LH	8.32	2.21	1.60	3.87	13.00	7.64	0.68	2.27
401 LC	8.17	2.18	1.52	4.06	13.07	7.59	0.58	2.10

Table 3. Calculated formulae for silver-rich tennantite-(Fe) from location 15 at Dolyhir Quarry (grain 401). Columns 2 to 6 give the empirical formulae on the basis of 29 atoms per formula unit. Copper is apportioned as Cu^{+} and Cu^{2+} to maintain charge balance in columns 7 and 8. Total charge balancing divalent *C* cations (Fe^{2+}+Cu^{2+}) are listed in column 9.

iron, and therefore the sum of Zn+Fe is often less than 2.0. Nonetheless, tetrahedrite-group minerals with simple one-for-one Zn for Fe substitution and a cation sum close to 2.0 are common (George *et al*., 2017).

Zinc is either absent or present in trace quantities in all of the analyses from location 15 (Fig. 5). The most iron-rich of these analyses (392 AC) has a composition very close to ideal end-member tennantite-(Fe), with an empirical formula $Cu_{9.96}Fe_{1.97}As_{3.99}Sb_{0.02}S_{13.06}$; however, 392 AG, with an empirical formula $Cu_{10.13}Ag_{0.04}Fe_{1.57}As_{4.20}S_{13.06}$ is very low in charge balancing iron, has unusually elevated As, and requires some charge balancing Cu^{2+} at the M(1)-site. Apportioning copper to maintain charge balance produces an empirical formula $Cu^{+}_{9.92}Ag^{+}_{0.04}Cu^{2+}_{0.21}Fe^{2+}_{1.57}As^{3+}_{4.20}S_{13.06}$.

The elevated arsenic level in this analysis allows the possibility that there might be intergrowth with the structurally related mineral watanabeite, ideally $Cu_4(As,Sb)_2S_5$ (Shimizu *et al*., 1993); this would be difficult to see at a micrometre scale, but the slight anisotropy which is characteristic of the species would be worth searching for in polished sections of tennantite-series minerals from Dolyhir.

The silver-rich tennantite-(Fe) from location 15 has even less charge balancing iron and much less arsenic and therefore cannot be an intergrowth with watanabeite. Analysis 401 LB corresponds to $Cu_{8.63}Ag_{2.00}Fe_{1.49}As_{3.80}S_{13.07}$ and requires considerable Cu^{2+} to maintain charge balance. Iron-deficient tennantite-series compositions with no zinc and charge balancing copper are unusual in nature. There are no points in this region of the composition space illustrated by George *et al*. (2017) [compare Fig. 5 herein with their Fig. 6b on p. 11]. Apportioning copper to maintain charge balance in analysis 401 LB produces an empirical formula $Cu^{+}_{7.53}Ag^{+}_{2.00}Cu^{2+}_{1.10}Fe^{2+}_{1.49}As^{3+}_{3.80}S_{13.07}$. This has much more than the two divalent cations per formula unit allowed in the general formula (Fe^{2+}+Cu^{2+}=2.59)[6]. Analysis 401 LB is an extreme case, but two of the other formulae calculated for grain 401 require significantly more than two divalent cations to maintain charge balance (Table 3). Analysis 392 AG, on the other hand, requires rather less, with Fe^{2+}+Cu^{2+}=1.87.

If these data are reliable, and this simple interpretation is correct, in some situations (e.g. the iron- and arsenic-poor compositions at Dolyhir Quarry) the charge balancing *C* constituents in tetrahedrite-group minerals may rise significantly above the limiting value of 2.0 and the corresponding *B* constituents compensate. Such variations may reflect the presence of vacancies at sites in the structure or clusters of atoms with non-integer formal charge. In a small dataset it is also possible they arise from random errors. More extensive studies including structural analysis might be of interest.

Fanlo *et al*. (2010) use small differences in mean composition to characterise tetrahedrite-group minerals with different genetic origins at the Pardos deposit in Spain. Similar analysis might be valuable at Dolyhir, but the current dataset, with only fifty analyses of seven separate grains, is not large enough.

The ratios of Zn:Fe (the dominant elements at *C*) and As:Sb (the dominant elements at *D*) are plotted with Fe increasing to the right on the *x*-axis and Sb increasing upward on the *y*-axis in Figure 6. This provides a simple way to visualise the range of compositions. It shows that the iron-dominated compositions contain very little antimony and that the antimony-rich compositions tend to be found at localities in the Dolyhir Limestone, but reveals no obvious trends in composition.

Concentrations of antimony in some of the tennantite-(Zn) from the calcite-filled fractures surrounding the main lead-copper vein (location 1) are high. Analysis 397 NE has an empirical formula $Cu_{9.97}Zn_{1.69}Fe_{0.28}As_{2.85}Sb_{1.26}S_{12.95}$, with the largest proportions of antimony and zinc in the dataset. The antimony distribution in grains from this locality is sporadic and little or none is present in other analyses. The presence of antimony is of interest in view of the recent report of the rare antimony-bearing supergene mineral richelsdorfite, associated with partly oxidised tennantite, in calcite-filled fractures surrounding the main lead-copper vein (Hubbard and Green, 2020). It seems likely that oxidation of antimony-bearing tennantite-(Zn) supplied the antimony required for the richelsdorfite to form.

[6] The total number of *A*+*B*+*C* cations, at 12.12, is close to the ideal value of 12.00. They might be apportioned $C = Cu^{2+}_{1.10}Fe^{2+}_{1.49}$; $B = Cu^{+}_{3.41}$ and $A = Ag^{+}_{2.00}Cu^{+}_{4.12}$. At 13.07, sulphur is very close to the ideal value of 13.00, but *D* is only 3.8, which is less than the ideal value of 4.00. This appears to be a credible example in which *C*>2 and *B*<4.

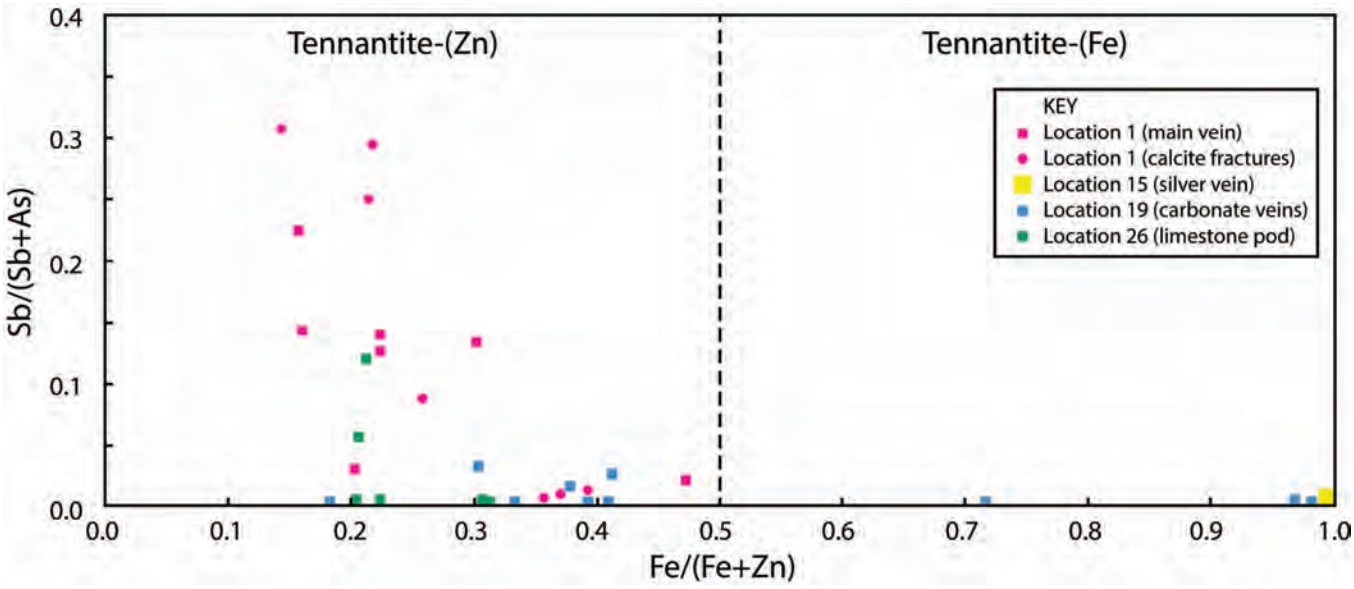

Figure 6. The composition of tennantite-series minerals from the localities at Dolyhir Quarry listed in Figure 1. All of the 18 analyses from location 15 lie within the large yellow square at the lower right-hand corner. Other analyses are single data points. Analyses from location 1 are shown as magenta squares (main vein) and circles (surrounding calcite-filled fractures). The dashed line separates the composition field of tennantite-(Zn) from that of tennantite-(Fe).

Lead is not listed as a potential substituent in tetrahedrite-group minerals by Biagioni *et al*. (2020) but is described as common by George *et al*. (2017). It may be that some of these lead values represent very fine scale intergrowths with galena (Chris Stanley, *personal communication*, 2020). Lead is present in six of the analyses listed in Table 1. It is highly elevated in only one of these: analysis 395 DH has a remarkably high 6.67 wt% lead. The corresponding empirical formula, $Cu_{9.79}Pb_{0.49}Zn_{0.79}Fe_{1.11}As_{3.78}Sb_{0.06}S_{12.98}$, is unlikely to be correct as the sum of the M(1)- and M(2)-site cations exceeds 12.0 by a significant margin. It may be that the volume that was excited by the electron beam included a small amount of a discrete lead-bearing phase. Intergrown galena, which is common at Dolyhir, is unlikely as it would reduce S from a near ideal value of 12.98, but a mineral such as cerussite, with no other heavy elements, is a possibility. The other lead values are much lower and lie well within levels recorded for tetrahedrite-group minerals at worldwide localities (George *et al*., 2017: p. 16)

Silver commonly partitions into tetrahedrite-group minerals in base-metal deposits (George *et al*., 2017). It is below detection limits in some of the Dolyhir analyses, but is significantly elevated at location 15, where rare silver sulphosalts were also found, and location 19, where tennantite occurs with barium-calcium and rare earth carbonates. None of the silver values are high enough to place the compositions in the freibergite series or to present the analytical and classification problems associated with the presence of $(Ag_6)^{4+}$ clusters. The most argentiferous analyses (grain 401; Table 3) are all relatively similar, with a mean empirical formula $Cu_{8.36}Ag_{2.12}Fe_{1.55}As_{3.93}S_{13.04}$. Back-scattered electron images of this grain do not reveal any obvious compositional zoning (Fig. 7).

The silver content of tennantite-series minerals at Dolyhir is highly variable, even in material from the same vein (compare analyses 391, 392 and 401 from specimens from the 'silver vein' at location 15). Several pathways by which silver is incorporated into tetrahedrite-group minerals have been described. These include fractional crystallisation (Hackbarth and

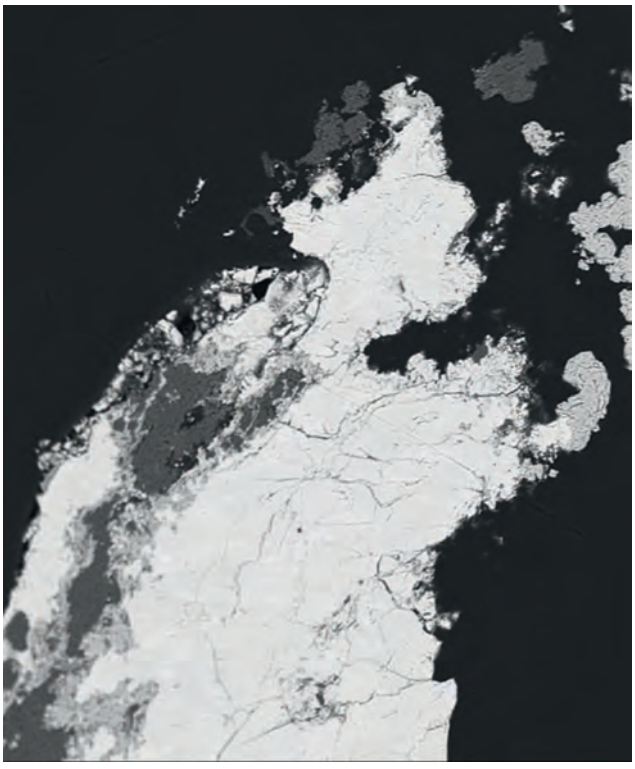

Figure 7. Back-scattered electron image of silver-rich tennantite (light grey) with a somewhat colloform appearance (grain 401) from location 15. There is no obvious compositional zoning (which would show up in the image as atomic number contrast), a conclusion which is supported by the similarity in composition from core to rim (Table 3). The grain is 0.4 mm across. Photo Andy Tindle.

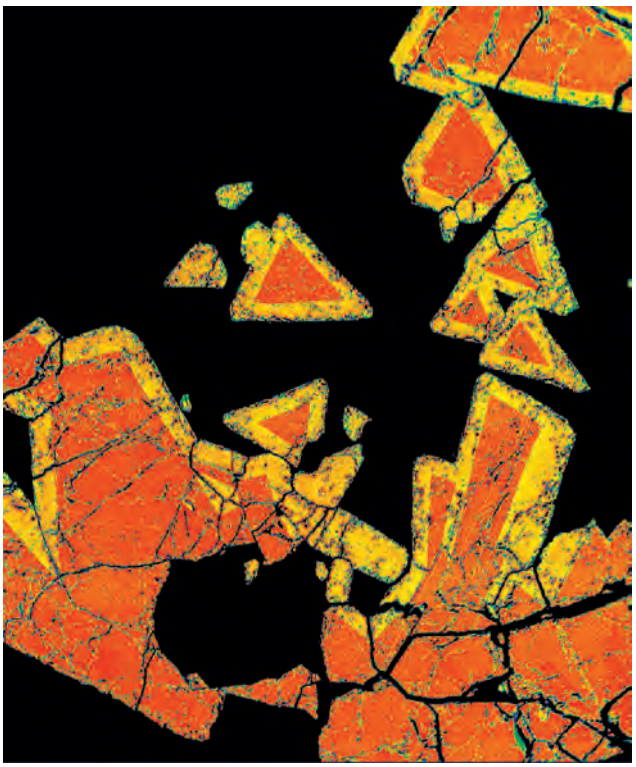

Figure 8. Back-scattered electron image with false colour added to emphasise the boundary between tennantite (orange) and the uncharacterised sulphosalt overgrowth (yellow). The image is 0.7 mm across and the overgrowth typically about 20 μm thick. Photo Andy Tindle.

Petersen, 1984), retrograde enrichment (Sack and Goodell, 2002; Sack *et al*., 2002, 2003) and supergene enrichment (Fanlo *et al*., 2010). There is no compelling evidence for any of these at Dolyhir Quarry. The silver-bearing grains are not obviously zoned (Table 3; Fig. 7) as might be expected if silver had been enriched by fractional crystallisation and the assemblage does not contain minerals such as bournonite, which Sack and coworkers suggest should be present if the silver-rich tennantite had formed as a result of retrograde enrichment. Supergene enrichment is perhaps the most likely mechanism. Numerous copper minerals which are characteristic of the zone of supergene sulphide enrichment occur at Dolyhir Quarry (Cotterell *et al*., 2011); however, calcite at the 'silver vein' (location 15) is not obviously altered. The vein was not extensive and very few specimens were recovered. It remains an isolated and enigmatic occurrence that is difficult to place in context.

The composition of the phase which overgrows tennantite-(Fe) on grain 392 does not correspond with any known mineral. The faint pinkish colour in reflected light (Fig. 3) and association are consistent with luzonite, ideally Cu_3AsS_4, which is well known at Dolyhir Quarry (Cotterell *et al*., 2011), but the analyses (Table 2) include a large amount of iron. The boundary with tennantite-(Fe) is sharp and planar (Fig. 8) and this suggests the unidentified phase crystallised on the tennantite-(Fe) and is unlikely to be a product of retrograde alteration. It occurs as an overgrowth, typically about 20 μm thick but exceptionally reaching 50 μm, on the outer surfaces of euhedral crystals of tennantite-(Fe).

Chemical formulae calculated on the basis of four sulphur atoms are listed in Table 4. The mean empirical formula is $Cu_{2.28}Fe_{1.00}\ As_{0.86}Sb_{0.06}S_4$, with very little variation in any of the indices. This is unlikely to represent a luzonite–famatinite intermediate with a large amount of Fe^{2+} substituting for Cu^{2+}. Minor iron is reported in luzonite by Gaines (1957), but careful study indicated that (unlike tetrahedrite-group minerals) substitutions other than As ↔ Sb in luzonite–famatinite are very limited.

Luzonite is a member of the stannite group of minerals, sulphides structurally related to sphalerite with a general formula A_2DEX_4, where A = Ag, Cu; D = Cu, Cd, Fe, Hg, Zn, Ag; E = As, Ge, In, Sb, Sn; X = S, Se. It is possible that the unknown mineral might also be a member of this group, perhaps with an ideal formula Cu_2FeAsS_4. As yet no such mineral has been described. Luzonite has a structure that is more complex than its simple ideal formula suggests (Pósfai and Buseck, 1998), and some type of polytypic intergrowth, perhaps with the related mineral idaite, is also a possibility. Chemical data are included here in case similar phases are encountered in other studies.

CONCLUSION

Dolyhir Quarry is one of the most diverse mineral localities in the British Isles. This study confirms the occurrence of two newly described members of the tetrahedrite-group, tennantite-(Fe) and tennantite-(Zn), and a companion study adds the first British occurrence of richelsdorfite (Hubbard and Green, 2020).

Analysis	Formula Cu	Formula Fe	Formula As	Formula Sb	Formula S
392 AB	2.30	1.01	0.84	0.05	4.00
392 AH	2.30	1.00	0.87	0.06	4.00
392 AI	2.26	1.00	0.84	0.06	4.00
392 AJ	2.24	1.04	0.83	0.05	4.00
392 AM	2.30	0.96	0.89	0.07	4.00
Mean	**2.28**	**1.00**	**0.86**	**0.06**	**4.00**

Table 4. Formulae of an unidentified sulphosalt associated with tennantite on specimen 392 from location 15 (the 'silver vein') at Dolyhir Quarry. Calculations are based on four atoms of sulphur per formula unit for comparison with luzonite.

The microprobe analyses reveal anomalous tennantite-(Fe) compositions with more than the expected number of charge balancing divalent cations and an as yet uncharacterised phase with possible stannite group affinities. The mineralisation is far from fully described and fieldwork and subsequent analytical investigation continue to produce interesting results.

ACKNOWLEDGEMENTS

The authors would like to thank Nash Rocks and Tarmac, the former and current owners of Dolyhir Quarry, for access to the locality. Without their cooperation, none of the minerals recorded in this study would have been saved. Cristiano Biagioni is thanked for providing a copy of the recently updated classification of the tetrahedrite group. Thanks go to John Mason, Malcolm Southwood and Chris Stanley for interesting discussions which materially improved the content.

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ORE MINERALOGY OF THE CLARGILLHEAD VEIN, TYNEHEAD, CUMBRIA: THE FIRST REPORT OF NATIVE SILVER FROM THE NORTHERN PENNINE OREFIELD

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Veinstone samples collected from old workings at Clargillhead, Tynehead, Cumbria, contain assemblages of sulphide, sulphosalt and sulpharsenide minerals which add to the diversity of ore minerals found within the deeper levels of the zoned Northern Pennine Orefield. The veins from which these samples were collected coincide with the area from which lead ores with the orefield's highest concentrations of silver have been recorded, above the Tynehead Cupola of the Caledonian Northern Pennine granitic batholith. Very small grains of native silver, of supergene origin, within these samples represent the first record of this mineral from the Northern Pennine Orefield.

INTRODUCTION

The numerous veins and associated deposits of the Northern Pennine Orefield comprise mineralised fillings and wall-rock replacements within a conjugate set of mainly normal faults hosted within cyclothemic beds of the Great Scar Limestone, Yoredale and Pennine Coal Measures groups of Carboniferous age which lie unconformably above the concealed granitic Caledonian Northern Pennine Batholith (Dunham *et al*., 1965; Dunham, 1990). More recent studies of the batholith reveal this to be a composite intrusion with the greatest concentrations of mineralisation centred above its Weardale and Tynehead cupolas (Kimbell *et al*., 2010; Stone *et al*., 2010).

Within these deposits, the classic zonal distribution of constituent minerals, most notably fluorite and barium minerals, described by Dunham (1934, 1948, 1990) reflect depositional temperatures above the concealed cupolas of the batholith. The major sulphide minerals are galena and sphalerite with local concentrations of chalcopyrite, pyrite, marcasite and pyrrhotite (Dunham, 1990; Ixer and Vaughan, 1993). Over centuries of working the orefield's deposits have yielded reliably recorded commercial outputs of over 4 million tonnes of lead, 0.3 million tonnes of zinc and around 1500 tonnes of copper ores with very small but unrecorded tonnages of iron sulphides (Dunham, 1944, 1990; Fairbairn, 1993).

In addition, a variety of other sulphides, sulphosalts and sulpharsenides including argentopentlandite, arsenopyrite, bismuthinite, bournonite, cobaltite, cubanite, gersdorffite, mackinawite, niccolite, skutterudite, tetrahedrite and ullmannite have been recorded, together with synchysite and rarely cassiterite and adularia, mostly as microscopic inclusions within the most common sulphide ores (Ixer *et al*., 1979; Vaughan and Ixer, 1980; Young *et al*., 1985; Ixer, 1986; Dunham, 1990; Ixer and Vaughan, 1993; Ixer *et al*., 1996). Many of these have been found in deposits above the Tynehead cupola of the Northern Pennine Batholith. Although providing important insights into the origins of these deposits, none of these minerals approach anything like economic concentrations.

Northern Pennine lead ores have long been known to be silver-bearing and were routinely processed to recover their silver content during smelting. However, despite claims made in several historical publications, the overwhelming majority of lead ores from this field are distinguished by their comparatively low silver content, typically between 111–251 ppm, compared to many other British lead ores (Dunham, 1990; Dunham *et al*., 2001). Notwithstanding this, very much more silver-rich lead ores with up to 2511 ppm silver have been recorded from several Northern Pennine locations, most notably in the Tynehead area in veins associated with the Sir John's Vein, one of the major veins of this part of the orefield, together with the small parallel Stow Crag Vein which may be regarded as a branch of that vein (Dunham *et al*., 2001).

Specimens in the Kingsbury Collection held by the Natural History Museum, from which Ixer and Stanley (1987) described a suite of silver minerals, have subsequently been shown to be one of a number of false locality attributions made by Kingsbury, a deception that was unknown to the authors at the time of their investigation (Ryback *et al*. 1998; 2001). The true source of these specimens may lie within Eastern Europe: they certainly did not originate in the Northern

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Pennines and thus no longer have relevance to Northern Pennine mineralisation.

THE TYNEHEAD VEINS

The pattern of vein outcrops in the vicinity of Tynehead are shown in Figure 1. At surface, the veins in this area cut Yoredale Group beds between the Tynebottom and Little limestones together with the Whin Sill which here lies beneath the Tynebottom Limestone, on the southern flank of the Great Sulphur Vein (British Geological Survey, 1973). All of these veins have been worked or explored as sources of lead and locally copper ores.

Approximately 0.5 km southeast of Tynehead, the River South Tyne and Clargill Burn cross the outcrop of the eastern extremity of the east–west to WNW–ESE trending Great Sulphur Vein. This, one of the longest and widest mineralised structures within the orefield, comprises a north facing monoclinal structure associated with a prominent shear belt on its northern side (Thompson, 1933; Dunham, 1990). From its orientation and mineral content it may be regarded as being an expression of the mineralisation characteristic of the deeper levels of the orefield's other roughly east–west trending mineralised fractures, known as the 'Quarter Point' veins.

Between the South Tyne and Clargill Burn the Great Sulphur Vein is crossed by the northwest–southeast trending Sir John's Vein, one of the major mineralised fractures of the upper part of the South Tyne Valley (Dunham 1990: p. 130; Bevins *et al.*, 2010). Although the existing surface mapping suggests that this vein is shifted a few metres S side E by the Great Sulphur Vein, Dunham (1990) comments that underground exposures appear to show that the Great Sulphur Vein is shifted a few metres E side S by Sir John's Vein. The detailed structural relationship of these two veins thus appears to be ambiguous.

The upper reaches of the Clargill Burn follow closely, and are almost certainly determined by, a NNE–SSW trending branch from the northeast side of Sir John's Vein known as the Clargillhead Vein. Two other minor veins, known as the Baxter's and Steel Ore veins, which crop out on the southwest side of Sir John's Vein a few metres south of its junction with the Clargillhead Vein, may be branches from this. These veins were worked in the Scar Limestone both from surface excavations and from short levels at Clargillhead and Hiddenholes mines, though Dunham (1990: p. 130) notes that the oreshoots were probably no more than small pockets.

Approximately 300 m north of the junction of Clargill Burn with the South Tyne, the small roughly north–south trending Stow Crag Vein appears to be a further fracture branching from the eastern side of Sir John's Vein.

The Tynehead deposits, particularly those of the Sir John's and Stow Crag veins, are notable for silver contents significantly higher than normal for the vast majority of Northern Pennine deposits with assay values of >2000 ppm Ag reported from one location (Dunham, 1990; Ixer and Vaughan, 1993; Dunham *et al.*, 2001).

MINERALOGY

Small dumps at Hiddenholes Mine, on the west bank of Clargill Burn [NY 7706 3700] contain accumulations of partially dressed vein material derived from workings on Clargillhead Vein. Fluorite- and quartz-rich veinstone, in some of which are silicified shale clasts, are abundant. Galena and chalcopyrite are conspicuous in hand specimen in many of these. Reported here are descriptions of the ore minerals found in two polished sections prepared from representative samples of this veinstone. Both were investigated in reflected light using $\times 8$ air, $\times 16$ oil immersion and $\times 40$ oil immersion objectives. All identifications of the opaque phases are by reflected light microscopy.

Descriptions of the sulphide, sulphosalt and sulpharsenide minerals, in approximate order of abundance, are followed by brief comments on other species present in the samples.

Sulphide Minerals

Galena (PbS) is the dominant opaque phase and mainly forms euhedral and subhedral crystals up to a few millimetres in diameter. Locally it shows growth zoning as seen by differential polishing and incipient alteration, with 20–70 μm wide zones themselves composed of thinner, up to 2 μm wide, subzones comprising abundant 1–2 μm diameter pits. Whereas some of the galena is inclusion-free, some carries inclusions of other sulphide and sulphosalt minerals. The most abundant of these is bournonite ($PbCuSbS_3$) which locally makes up to 5% of the surface of the galena and typically occurs as disc-like inclusions up to 10×2 μm across and locally as strings defining the boundaries of polygonal galena grains. Inclusions of chalcopyrite ($CuFeS_2$) between 20 and 60 μm across, pyrite (FeS_2) in aggregates up to 80 μm across, ullmannite (NiSbS) up to 10 μm across, and sphalerite (ZnS) up to 5 μm across are common inclusions in the galena with much rarer grains of gersdorffite (NiAsS), up to 10 μm across, and boulangerite ($Pb_5Sb_4S_{11}$) up to 5 μm across. Galena is locally intergrown with chalcopyrite. A rare, poorly polished, subhedral lavender coloured phase in grains up to 10 μm across may be the nickel-rich variety of pyrite, bravoite.

Chalcopyrite ($CuFeS_2$) is second to galena as the most common sulphide seen in these specimens. In addition to its presence as inclusions in galena it infills void spaces within radiating quartz and appears to be free of inclusions though rare masses of pyrite and gersdorffite up to 5 μm across were found locally within it. As already noted, chalcopyrite is locally intergrown with galena. It is locally altered to thin, 1–4 μm wide white CuS rims, or to the copper sulphides 'chalcocite' (Cu_2S) and covelline (CuS), or to banded limonite, or to banded

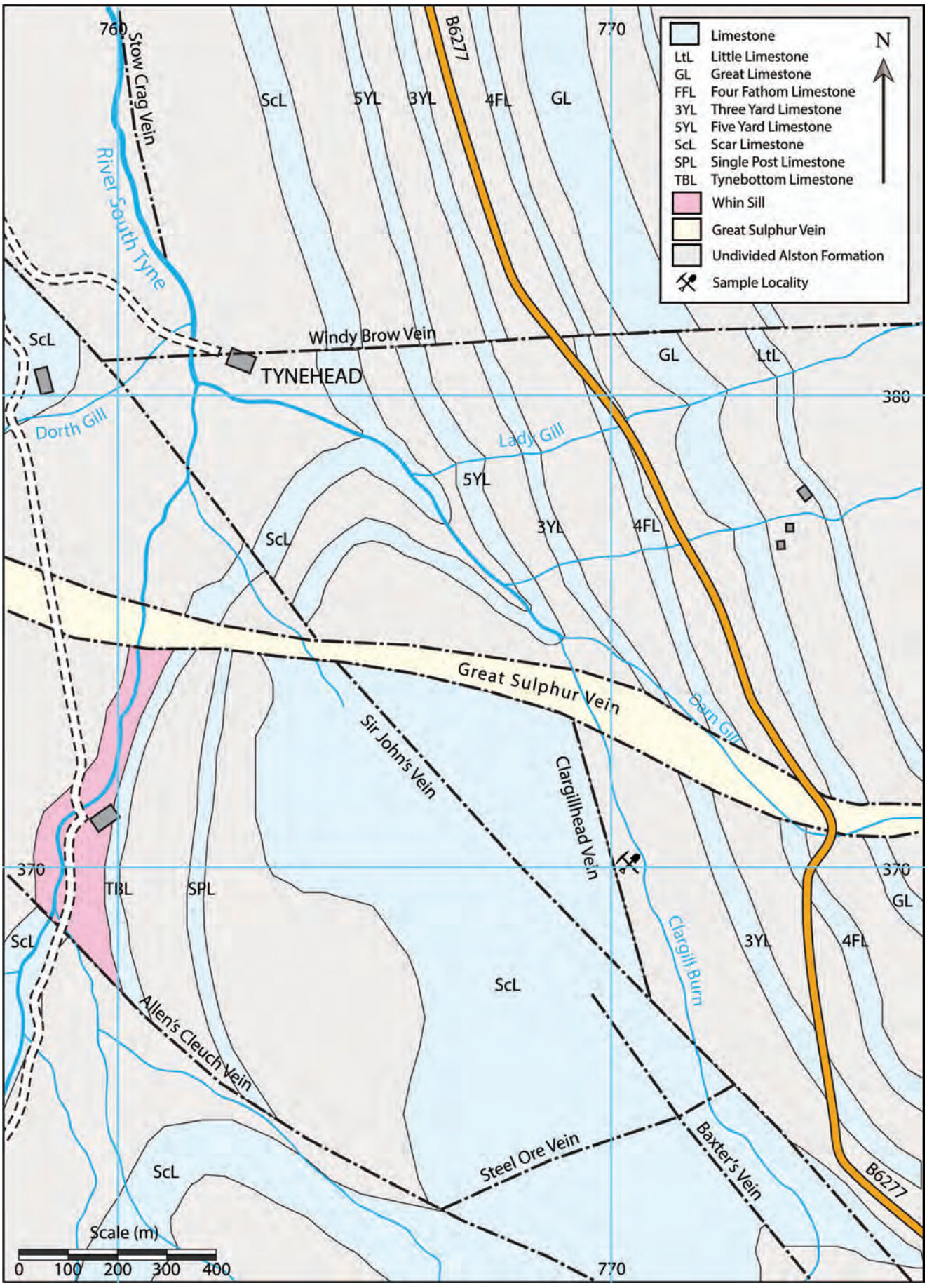

Figure 1. Geological sketch map of the Tynehead area showing the location on Clargillhead Vein where the specimens were collected. Reproduced with permission: CP20/021 British Geological Survey © URKI 2020. All rights reserved. https://www.bgs.ac.uk/data/maps/maps.cfc?method=viewRecord&mapId=10259.

limonitic intergrowths with thin, 1–2 μm diameter native silver (Ag) droplets.

Pyrite (FeS_2) is present in minor amounts within a number of textural generations both in the fluorite and quartz gangue and in shale clasts. Early framboidal pyrite, up to 10 μm in diameter, occurs in galena and in the gangue. The main generation of pyrite forms 2–80 μm diameter, euhedral to subhedral pentagonal dodecahedral crystals in both galena and the quartz and fluorite gangue. Some pyrite is zoned with yellow-pink cores within paler rims or 20 μm diameter, pale-coloured pyritic cores within 5 μm wide, lavender-coloured, bravoitic rims. Post-galena pyrite forms 2–10 μm wide veinlets up to several hundreds of micrometres in length along open cleavage planes in galena. Locally pyrite is oxidised to 'limonite'. Marcasite (FeS_2) grains up to 5 μm, though very rare, are enclosed within pyrite grains and are also present in the gangue.

Bournonite ($PbCuSbS_3$) is also present as discrete 10–100 μm diameter masses, in which its characteristic 'parquet' twinning is conspicuous, filling voids within the radiating quartz gangue. Here it is locally intergrown with galena in which bournonite inclusions are present, and locally accompanies 10–20 μm chalcopyrite masses at the margins of some galena crystals. Bournonite is locally altered to yarrowite with very rare masses, up to 2 μm across of probable enargite (Cu_3AsS_4).

Yarrowite (Cu_9S_8) occurs locally as swags comprising <1 μm diameter crystals, accompanied by similar sized zones of heavily tarnished unidentified blue copper sulphides, interbanded with cerussite, some of which is associated with a <1 μm unidentified argentiferous photosensitive phase. Spionkopite ($Cu_{39}S_{28}$) occurs as rare grains up to 30 μm in cerussite and also in association with tarnished copper sulphide swags.

Other Minerals

Cerussite ($PbCO_3$) is the most abundant supergene phase, commonly directly replacing galena but also as neomorphic crystals infilling void spaces. The earliest cerussite occurs as mosaics of 10–80 μm crystals which form replacive rims to galena up to 100 μm thick. Close to the galena this cerussite is dark-coloured with minute inclusions of either relict galena or yarrowite. It is commonly overgrown by 5–40 μm diameter, pale-coloured, inclusion-free cerussite. Pale coloured, inclusion-free cerussite also forms euhedral, acicular to tabular crystals up to 40 μm in size, infilling void spaces. Locally, 60–200 μm diameter cerussite crystals carrying fine-grained copper sulphides are present as coarse-grained mosaics in galena.

'Limonite' replaces 10–40 μm diameter pentagonal dodecahedral pyrite crystals, locally forming aggregates up to 200 μm across. Banded 'limonite' also replaces chalcopyrite and pale-coloured secondary copper sulphides.

Pyrolusite ($Mn^{4+}O_2$) occurs as rare fibrous aggregates up to 60 μm in diameter in the quartz-fluorite gangue.

Native silver (Ag) occurs both as 1–2 μm diameter 'droplets' within banded 'limonite' which locally forms alteration crusts on chalcopyrite and rarely as discrete grains up 8 μm within the quartz-fluorite gangue

The shale clasts, seen in many veinstone fragments, carry 2–10 μm grains of carbonaceous matter together with pale coloured grains of unidentified titanium oxide minerals up to 60 μm across. A few lath-like grains which may either be a mica or a mineral of the synchysite series ($Ca(Ce,La)(CO_3)_2F$) were also noted.

Very minor amounts of an unidentified green supergene copper mineral that does not exhibit the optical properties of malachite were also noted.

DISCUSSION

The veins from which these mineral assemblages were derived lie within the innermost zones of the Northern Pennine Orefield (Dunham, 1990) and above the highest point of the Tynehead Cupola of the North Pennine Batholith (Kimbell *et al*., 2010). The most prominent mineralised structure here is the Great Sulphur Vein which, from its orientation and mineral content, has been interpreted as characteristic of the root zones of the orefield's major mineral veins (Young *in* Bevins *et al*., 2010).

Ixer *et al*. (1996) demonstrated that distinctive fine-grained quartz-chalcopyrite-rich veinstone with conspicuous concentrations of bismuthinite found in the Great Sulphur Vein at Tynehead, occurs widely across the innermost zones of the orefield above the Weardale and Tynehead cupolas of the concealed North Pennine Batholith. This mineralisation reflects significantly higher emplacement temperatures than those established for the main lead-zinc-fluorite mineralisation, which it clearly pre-dates. The mineral assemblages described here are consistent with being an expression of this early mineralisation and add to the diversity of ore minerals found at this level within the orefield.

These veins also lie within the small area from which the orefield's highest concentrations of silver have been recorded (Dunham, 1990). As already noted, North Pennine lead ores were typically characterised by a relatively low silver content (typically between 111 and 251 ppm silver) compared with many other British lead ores. However, much higher silver assay values of up to 1119 ppm were recorded from galena from the Sir John's and Stow Crag veins, with assay values as high as 2106.4 ppm reported from loose galena fragments collected in a field known as 'Chesters' at Tynehead (Dunham *et al*.,

2001). Whereas it was not possible to determine the silver content of the galena examined in this study, Dunham (1990: p. 130) recorded that 18 tons of lead concentrates raised from the Clargillhead and Hiddenhole mines between 1856 and 1867 yielded 43 ounces of silver per ton of lead (approximately 1200 ppm). Whereas there is evidence for enhanced silver values associated with the outline of the concealed North Pennine Batholith (British Geological Survey, 1992), the reasons for significantly higher silver values in the Tynehead area remain unexplained. The discovery of native silver, both as discrete grains and within the secondary alteration of chalcopyrite at Clargillhead suggests a mainly supergene origin associated with copper mineralisation. However, it should be noted that unidentified photosensitive minerals, also presumed to be silver-bearing, are associated with the alteration of galena.

This work thus appears to fulfil the speculative prediction of Dunham *et al*. (2001) that the discovery of supergene native silver within the Northern Pennines may be "only a matter of time".

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THE DOLGELLAU GOLD-BELT, THE SNOWDON CALDERA AND THE DISTRICT IN BETWEEN: A SINGLE LATE ORDOVICIAN METALLOGENIC PROVINCE?

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The pre-Acadian polymetallic lodes of two well known orefields in North Wales, the Dolgellau Gold-belt and the copper-mining district of the Snowdon Caldera, have remarkably strong similarities in their paragenetic structure. These similarities are shared by the numerous pre-Acadian lodes of the country in between the two orefields, forming a curved belt extending for 60 km, from the vicinity of Bethesda in the northwest, to Porthmadog in the south and to beyond Blaenau Ffestiniog in the east. The paragenetic structure of this third district is systematically described for the first time. It is proposed that the lodes of the Dolgellau Gold-belt and the Snowdon Caldera, plus the district in between them and the Castell Carn Dochan Mine near Bala Lake, are contemporaneous reflections of the same regional-scale hydrothermal system that deposited a variety of metals at a range of structural levels in the upper few kilometres of the crust. Several lines of evidence favour a late Ordovician origin.

INTRODUCTION

Lodes that pre-date the Middle Devonian Acadian compressive deformation and which carry polymetallic mineralisation, are known from the Lower Palaeozoic strata of four adjacent parts of North Wales, namely: the Dolgellau Gold-belt; the apparently isolated Castell Carn Dochan Mine near Bala Lake; the Snowdon Caldera; and the arc of older (pre-Longvillian) strata surrounding the Caldera, henceforth referred to as the circum-caldera lodes (Fig. 1). The southern sector of the latter tract of country divides the Gold-belt, in the south, from the Snowdon Caldera, in the north.

There are numerous mines and trial workings throughout these four districts, although significant producers of gold, copper and other metals are more localised. Production figures, along with historical accounts, are provided by Hall (1990) with respect to the Gold-belt and by Bick (1985) for the Snowdonia copper mines. Only three mines in the Gold-belt, namely Clogau, Gwynfynydd and Cefn Coch, produced >1,000 ounces of gold. Clogau was the most productive, with official figures recording 81,049.75 ounces (2521 kg) from 1860 to 1911. Prior to the discovery of gold in 1854, Clogau and the adjacent Old Clogau and Vigra mines were primarily worked as one sett, for copper, and were almost certainly the most important copper producers in the Gold-belt. However, production records are elusive: 776 tons of chalcopyrite concentrates were sold in 1845–46 (Anon, 1978); another 421 tons in 1858–62 (Hall, 1990) and Hall also reports that in 1900, 15 to 40 tons were being produced every month. The total copper concentrate production, given that Clogau was working and producing gold intermittently over at least 27 years, is therefore likely to have been substantial. It should be noted that the important copper producer in the same district, Glasdir Mine, is considered to have worked an earlier phase of porphyry copper-related mineralisation, unrelated to the lodes described here (Bevins *et al*., 2010).

Within the Snowdon Caldera, only three mines, Snowdon, Lliwedd and Sygun, sold >1,000 tons of chalcopyrite concentrates. Snowdon, also known as Britannia Mine, was apparently the most productive, with sales of 3,160 tons recorded between 1804 and 1913. In the district surrounding the Snowdon Caldera, again only three mines, Drws-y-Coed, Simdde Dyllaun and Llanberis, produced >1,000 tons of chalcopyrite concentrates. Drws-y-Coed was the most productive with sales of 12,939 tons between 1804 and 1913. Galena and sphalerite concentrates were intermittently sold at several mines working the pre-Acadian lodes (e.g. Hall, 1990; Dewey and Smith, 1922), but yields were insignificant, compared to neighbouring post-Acadian orefields such as Llanwrst, Llangynog and Central Wales (Dewey and Smith, 1922; Jones, 1922). Cited production figures, however, represent unknown percentages of the totals in many cases: at Drws-y-Coed, for example, mining had gone on for decades prior to the advent of the official recording and collation of mineral statistics in the nineteenth century.

Gold at Clogau was predominantly coarse and recovery from its sulphide-poor quartz host was reasonably efficient; in contrast, the intergrown chalcopyrite-pyrrhotite mixture, typical of the copper ore from mines throughout this district, must have made clean chalcopyrite concentrates extremely difficult to prepare. At Drws-y-Coed, chalcopyrite concentrate grades were recorded between 1855 and 1909 and they varied between 9% and 14% Cu (Dewey *et al*., 1925), pure chalcopyrite being 34.63% Cu. Such grades are not atypical for the time: in the Cornubian Orefield, the

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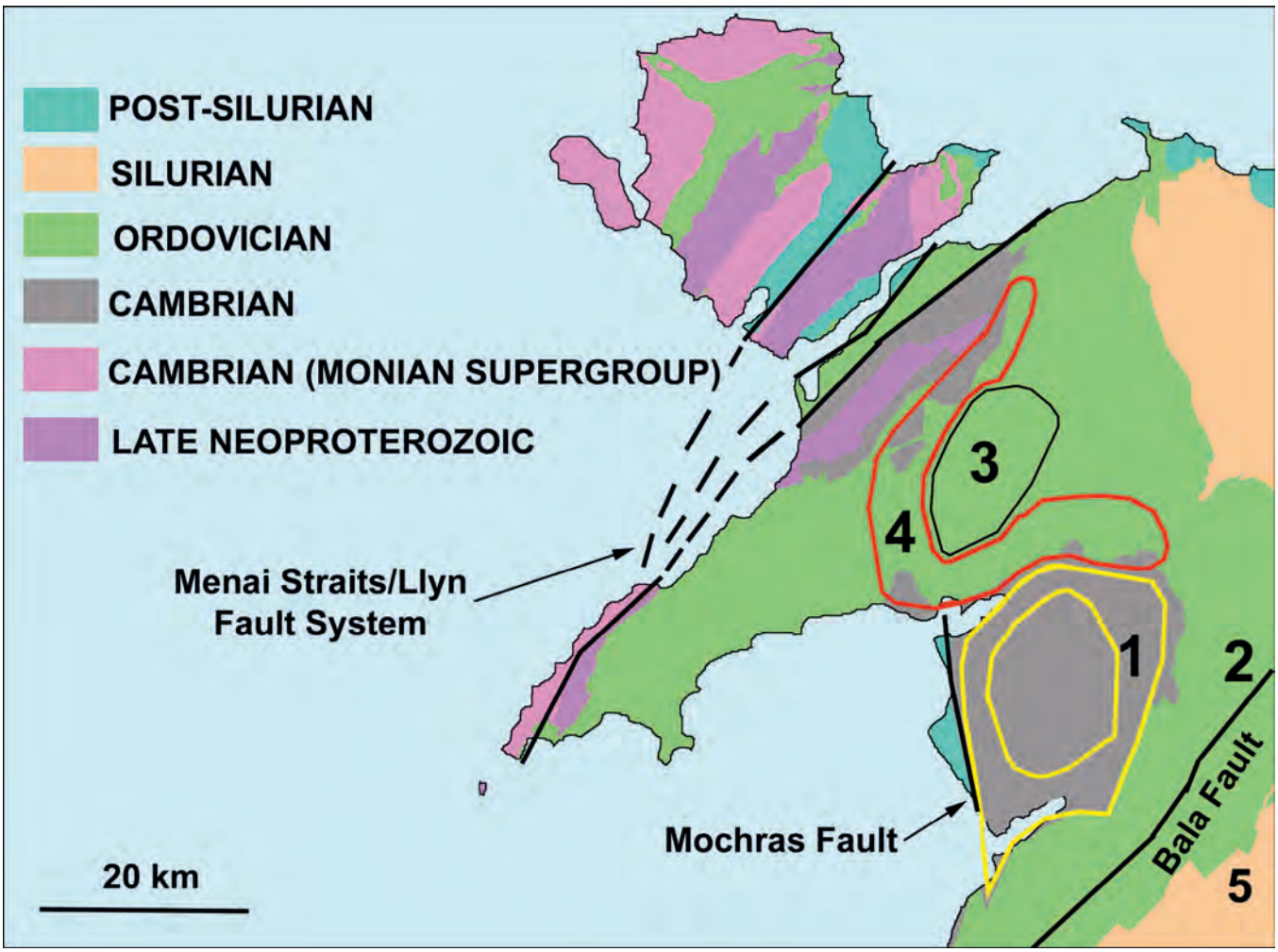

Figure 1. Simplified geological sketch map of North Wales showing the positions of the mineralised districts: 1 = Dolgellau Gold-belt; 2 = Castell Carn Dochan; 3 = Snowdon Caldera; 4 = circum-caldera lodes; 5 = northwestern margin of the post-Silurian orefields of Llangynog and Central Wales.

celebrated Devon Great Consols produced almost three-quarters of a million tons of chalcopyrite concentrates between 1845 and 1903, but the grade was only 6.5% Cu (Dines and Phemister, 1956). At Clogau, concentrate grades were poor in 1900, at 3–4% Cu (Hall, 1990): however, given that the quartz of the lodes had already been finely pulverised for the recovery of its gold content, separating sulphides from the resultant sand would have been relatively inexpensive.

Two of these orefields, the Dolgellau Gold-belt and the Snowdon Caldera, have been studied and described in the literature in considerable depth. Brief descriptions of their respective lodes, taken from these studies, are provided below. The important circum-caldera lodes have received no systematic description to date, the rectification of which is the purpose of this paper.

GEOLOGICAL SETTING

During the late Neoproterozoic and much of the Cambrian, the lithospheric components now making up Wales lay scattered along the northern margin of the continent of Gondwana, with the Iapetus Ocean situated to their north. By the early Ordovician, the composite sliver of Ganderian lithosphere comprising the multiple, fault-bounded Neoproterozoic and Cambrian terranes of Anglesey and the northwestern Llŷn Peninsula, became juxtaposed with the rest of Wales (Pothier *et al.*, 2015). During this process, a strong transpressive deformation, the Monian Orogeny, related to the Penobscottian Orogeny in the northern Appalachians, affected Anglesey but was less intense in mainland Wales (Schofield *et al.*, 2020). The boundary between the Ganderian terranes and the rest of Wales is represented by the major, trans-crustal fracture-system known as the Menai Straits Fault Zone (MSFZ), components of which are still seismically active today.

Another fault-bounded sliver of Neoproterozoic to Cambrian lithosphere, represented by the Arfon terrane, occupies a narrow strip within the MSFZ, between Anglesey and the rest of mainland Wales. The terrane probably also includes the Neoproterozoic intrusive rocks of the Sarn Complex, cropping out on the western Llŷn Peninsula and separated from the Ganderian composite terrane to the northwest by the Llŷn shear zone, this being the southwestern continuation of the MSFZ. The terrane boundary between Arfon and the rest of mainland Wales, likely to be another major fracture within the MSFZ, lies concealed beneath Ordovician strata, somewhere under the Snowdon district.

The rest of mainland Wales consists of two currently recognised component terranes, Megumia to the west and Avalon to the east, the two separated by the Welsh Borderland Fault System (Waldron *et al*., 2011). From the early Cambrian onwards, Megumia was the host to the ensialic, fault-controlled marine Welsh Basin, with the Arfon Terrane accommodating a second, smaller basin until the two became tectonically juxtaposed in the latest Cambrian to earliest Ordovician (Fig. 2). In terms of structures controlling subsidence and sedimentation, North Wales is dissected by a conjugate system of transcrustal-scale fractures. One set of fractures trends northeast–southwest and includes the major MSFZ and Bala Fault Systems, while other set trends broadly north–south and includes the Mochras-Cwm Pennant, the Trawsfynydd and the Conwy Valley faults. Movements involving these major structures and numerous subordinate fractures essentially drove local variations in the sedimentary and igneous histories of the district throughout the Lower Palaeozoic.

In Megumia, transtensional basin subsidence, along a southwest–northeast fault-bounded rift, dominated the picture during much of the Cambrian, with the deposition of increasingly deep-water sediments, some notably enriched in manganese (Allen and Jackson, 1985; Howells *et al*., 1985, 1997). In the Middle Cambrian, there was a lengthy and widespread episode of marine hypoxia and/or anoxia and black hemipelagite deposition in the main Welsh Basin, the product of which was the Clogau Formation. Such facies are absent from the Arfon terrane, where often coarse-grained clastic sediment deposition prevailed. Later in the Cambrian, a shallowing trend set in across both basins with deposition of shallow water sediments, before a further episode of subsidence in the latest Cambrian and a resumption of grey mudstone sedimentation through much of the Tremadoc.

Late in the Tremadoc, these amalgamated terranes, together making up the microcontinent of Avalonia, rifted away from Gondwana. The microcontinent began drifting northwards, movement that resulted in the initiation of oblique subduction of Iapetean oceanic lithosphere beneath Avalonia. The subduction zone lay to the northwest of Avalonia (in terms of today's geography) and its evolution through the Ordovician had major consequences in terms of volcanism and tectonics across much of Wales. Volcanism was preceded by a phase of uplift, folding and emergence, focussed in its intensity along the eastern flanks of what is now the Harlech Dome. The eruption of the calc-alkaline, island arc related Rhobell Volcanic Group and the emplacement of widespread subsurface intrusions followed, particularly along a north–south linear zone of significant crustal extension (Kokelaar, 1979, 1986; Kokelaar *et al*., 1984). Smaller intrusions, mostly in the form of sills and associated with the same episode of volcanism, occur widely throughout the Cambrian strata of the Harlech Dome and are especially concentrated in the younger formations belonging to that system.

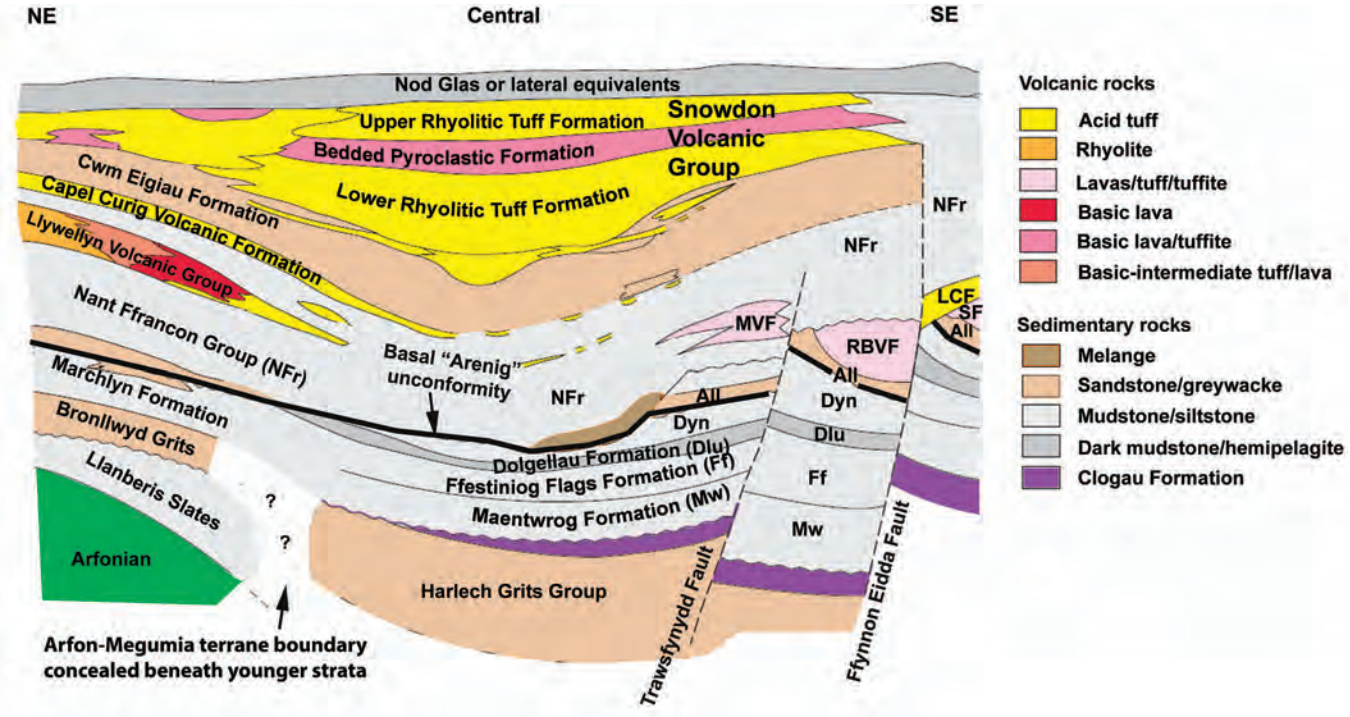

Figure 2. Schematic section of the Neoproterozoic, Cambrian and Ordovician sedimentary and volcanic sequences of northern Snowdonia, from the Bangor district SSW to the vicinity of Snowdon then southeast past Blaenau Ffestiniog into the Migneint. Abbreviations are: MVF = Moelwyn Volcanic Formation; RBVF = Rhiw Bach Volcanic Formation; LCF = Llyn Conwy Formation (lateral equivalent to Aran Fawddwy Formation); SF = Serw Formation (both equate to the Aran Volcanic Group); All = Allt Lwyd Formation with Garth Grit Member at base; Dyn = Dol-cyn-afon Formation; Dlu = Dolgellau Formation; Ff = Ffestiniog Flags Formation and MW = Maentwrog Formation. Intrusions are not shown. Maximum thickness is approximately six kilometres. Adapted from the work of Rushton and Howells (1999) with kind permission. Permit Number CP20/050 British Geological Survey` UKRI 2020. All rights reserved.

Post-Rhobell history involved further relatively weak folding, followed by a resumption of subsidence in the Floian (Arenig), gradual at first and marked by a regional diachronous unconformity across mainland Wales and Anglesey alike (Allen and Jackson, 1985; Pratt *et al.*, 1995, Howells *et al.*, 1997). By Sandbian (Caradoc) times, subsidence along a southwest–northeast rift, situated in central Snowdonia, was occurring in earnest (Campbell *et al.*, 1998). Volcanism had recommenced in the Floian, widely but of low intensity at first, then intensifying and peaking during the Longvillian Stage of the Sandbian. During this roughly twenty million year period, the focus of volcanic activity transferred progressively northwest, culminating in the eruption of the Snowdon Volcanic Group (SVG) (Leat and Thorpe, 1989; Thorpe *et al.*, 1993).

The SVG volcanism was bimodal in nature, in a back-arc basinal setting, indicating that the Iapetus subduction zone and accompanying island arc had re-established itself further to the northwest of North Wales. Towards the end of the volcanism, there was a change in its nature, with basalts of ocean island chemistry being erupted (Leat and Thorpe, 1989). That compositional shift is thought to have followed ridge-trench collision, causing the cessation of subduction, followed by slab break off and magma generation directly from asthenospheric mantle. The originally destructive plate boundary between Avalonia and Iapetus thereafter became one characterised by sinistral, transtensional strike-slip tectonics.

Cessation of volcanic activity in North Wales, in the late Longvillian, was followed by rapid subsidence and widespread marine anoxia, leading to blanketing of the basin floor with black, hemipelagic sulphidic muds, now preserved as the Nod Glas Formation. The remainder of the Ordovician saw the development of thick turbidite sequences (e.g. Pratt *et al.*, 1995), with conditions fluctuating dramatically during its final two million years, the Hirnantian Stage. This fluctuation was due to substantial eustatic sea-level changes associated with periods of glaciation/deglaciation on Gondwana. Sedimentary rocks dating back to this time are exposed mainly in the far south of the district under consideration.

In the Silurian and early Devonian, clastic sedimentation continued but with a transition in the late Silurian to a terrestrial setting. Approximately 3.5 km of Lower Old Red Sandstone fluvial sediments accumulated in parts of North Wales, prior to the mid-Devonian crustal shortening and inversion of the Welsh Basin during the Acadian Orogeny (Soper and Woodcock, 2003). During this phase of orogenesis, involving hard collision to the south of Avalonia (Woodcock *et al.*, 2007), the basin-fill was folded, faulted and cleavage was imposed. The regional metamorphic grade in North Wales, a product of both deep burial and orogenesis, reached lower greenschist (epizone) facies across a wide area (Robinson and Bevins, 1986).

THE GOLD BELT, SNOWDON CALDERA AND CASTELL CARN DOCHAN

The Lodes of the Dolgellau Gold-belt

At outcrop the geology of the Dolgellau Gold-belt is dominated by sedimentary rocks of Cambrian age, accompanied by numerous, often heavily altered mafic to intermediate sills (locally termed "greenstones"). The total pre-Acadian stratigraphic thickness, from the Hafotty Formation (the lowest horizon in which lodes have been examined) to the top of the Mawddach Group, is approximately 3 km, and sills add to that figure by a variable but considerable amount. The intrusive rocks, while not directly dated, are predominantly considered from their geochemistry to have been emplaced in the late Tremadoc, as part of the magmatic arc-type system that generated the Rhobell Volcanic Group, during the fractionation of a large, sub-crustal magma chamber (Kokelaar, 1979, 1986; Allen and Jackson, 1985). Porphyry-type copper-dominated mineralisation is associated with some of the larger intrusive bodies (Rice and Sharp, 1976; Allen and Jackson, 1985; Bevins *et al.*, 2010). To the east and south of the Cambrian outcrop, strata above the Arenig unconformity consist of marine clastic sedimentary rocks plus the extrusive, bimodal Aran Volcanic Group, making up a thickness of over 1 km, again variably supplemented by intrusive rocks.

The gold-bearing lodes are hosted by both sedimentary and Rhobell-related intrusive rocks, implying that the mineralisation is post-Tremadoc in age. More locally, intrusive rocks having a geochemistry more akin to the Aran Volcanic Group are cut by the lodes, implying a mid-Ordovician or later age to the mineralisation. The geochemical hallmark of these distinctive intrusions is co-existing relatively high Ti, Nb and Zr levels, meaning they plot well away from the Rhobell-related rocks on geochemical discrimination diagrams (data from Allen and Jackson, 1985; Bottrell, 1986; Kokelaar, 1986 and the author). Lodes consist of anastomosing, frequently branched and composite zones of quartz-dominated vein mineralisation occupying normal faults, mostly with an northwest–southeast to southwest–northeast strike and, mostly, with displacements of <10 m (Bottrell *et al.*, 1990). Individual lodes may be continuous on a kilometre-plus scale. The lodes are discordant to bedding, with a stair-case geometry, steepening as they pass through competent units such as sandstones and intrusive rocks and flattening out in more ductile lithologies such as hemipelagites. Both sulphide-rich and sulphide-poor component veins occur within the lodes, with laminated book-and-ribbon textures a frequent feature and indicative of multiple successive phases of fracture opening and mineral deposition. Component veins can be millimetres up to several metres in thickness. Other non-metallic minerals in the lodes are subordinate to quartz and include carbonates, white mica and chlorite (Mason *et al.*, 2002 and references therein).

Wall-rock alteration adjacent to the Gold-belt lodes involved the introduction of carbonates, sericite, chlorite, pyrite and arsenopyrite, although the "greenstones" had already been pervasively altered by alkali-metasomatism during earlier hydrothermal events, prior to lode emplacement. An important aspect of the lode-related alteration involved the addition of significant amounts of Cr and Ni to the wall-rocks, interpreted to indicate that the hydrothermal fluids had interacted, at an unknown depth, with mafic or ultramafic rocks (Bottrell, 1986).

Metalliferous minerals within the Gold-belt lodes comprise sometimes abundant early arsenopyrite and pyrite, with minor cobaltite. A later stage involved the deposition of abundant pyrrhotite, locally with mackinawite and pentlandite inclusions and commonly associated with chalcopyrite. The chalcopyrite contains exsolved sphalerite stars and, more rarely, lamellae of cubanite. Locally abundant galena and sphalerite are still later in the paragenesis, the galena in places containing inclusions and intergrowths of tetrahedrite, boulangerite and pyrargyrite (Gilbey, 1968; Mason *et al.*, 2002). Some lodes only feature one or other of these stages: others may feature them all. Some minerals recorded from Clogau (Naden, 1988), namely bournonite, tetrahedrite, boulangerite, stibioluzonite and hedleyite, were only identified in polished sections prepared from two samples (K2 and K3) from the Arthur Kingsbury collection at the British Museum (Natural History). Since Kingsbury faked so many of his specimen localities (e.g. Ryback *et al.*, 1998; 2001) and none of these minerals have been found in any other Clogau samples, these occurrences should be regarded as suspect.

Native gold occurs visibly within these lodes as localised but extremely rich (tens to thousands of grams per ton) bonanza-type shoots, locally and variably accompanied by galena, bismuthinite, native bismuth, altaite, hessite, tellurobismuthite, tetradymite and other sulphotellurides of bismuth and lead (Bevins and Stanley, 1990; Cook *et al.*, 2007). Outside of such localised enrichments, which have both lithogeochemical and structural controls, gold grades are much lower, often falling below 0.5 grams per ton (Dominy *et al.*, 2001). The paragenetic position of this localised Au-Ag ± Bi-Pb-Te mineralisation is clearly later than the arsenopyrite but apparently earlier than pyrrhotite plus chalcopyrite and the main generation of galena and sphalerite. The relative abundance of gold and its associated minerals is unrelated to the abundances of the other base-metal sulphides.

The pre-Acadian age of the Gold-belt lodes is evidenced, in thin and polished sections, by widespread sulphide deformation and recrystallisation and by recrystallisation of quartz into mosaics with heavily sutured grain-boundaries. In the field, folding and boudinage are observed in suitably orientated lodes (Mason *et al.*, 1999; Platten and Dominy, 1999). The fact that latest Ordovician and Silurian strata do not appear to host lodes of this type favours an earlier (Caradoc) age of emplacement.

The Lodes of the Snowdon Caldera

The lodes worked within the Snowdon Caldera are chiefly hosted by the late Ordovician Lower Rhyolitic Tuff Formation and the lower parts of the succeeding Bedded Pyroclastic Formation. Mineralisation also occurs in sandstones of the older, pre-Caldera, Cwm Eigiau Formation, so that the total pre-Acadian stratigraphic thickness involved is some 1.5 km. Lodes occupy a conjugate fracture system, with northeast–southwest and northwest–southeast striking components, although ENE–WSW lodes are also developed. These fractures were originally developed along the apical graben of the Snowdon Caldera and are thought to have been cogenetic with caldera subsidence (Reedman *et al.*, 1985).

Wall-rocks are commonly sericitised and chloritised and styles of mineralisation include clast-free ribs, breccia cements and stockwork-like zones of veining. Mineralisation consists of quartz, with chlorite plus rare carbonates, all of which are accompanied by locally abundant finely intergrown sulphides. Pyrite, chalcopyrite, galena and sphalerite are the chief metalliferous species; pyrrhotite is localised, as is arsenopyrite, which is mostly microscopic, although the mineral (and its alteration product, scorodite) is identifiable in the field at Cwm Bychan Mine and a further coarse-grained occurrence is at Moel Hebog Mine, near the Caldera's western margin (Bevins and Mason, 1998). Generally, though, arsenopyrite seems to be much more important in lodes emplaced at structural levels beneath the Caldera-fill.

The paragenetic sequence of the sulphides shows a degree of overlap, but pyrrhotite and chalcopyrite deposition commenced before and ended before that of galena and sphalerite (Lusty *et al.*, 2017). These authors also mention the presence of traces of cobaltite. Bismuth minerals (cosalite, bismuthinite, native bismuth and an un-named bismuth selenide) occur, sometimes macroscopically, at a number of sites (Reedman *et al.*, 1985; Bevins and Mason, 1998; Lusty *et al.*, 2017). Native gold occurs widely as micrometre-scale inclusions in other sulphides and along chalcopyrite-pyrite grain boundaries (Lusty *et al.*, 2017), but assay values of more than 0.5 ppm Au are uncommon, exceptionally reaching 1.8 ppm in a sample from Hafod-y-Porth Mine (Tim Colman, *personal communication*).

A second and distinctly different style of mineralisation, apparently confined to the lowest part of the Lower Rhyolitic Tuff Formation, is highly localised and consists of breccia cemented by magnetite with hematite and pyrite plus minor chalcopyrite. Cassiterite and scheelite occur as minor, microscopic components of this assemblage, along with minor late baryte (Colman and Appleby, 1991; Bevins *et al.*, 2010; Lusty *et al.*, 2017).

The lodes are clearly pre-Acadian. Deformation is evidenced by sulphide recrystallisation, pressure-shadows around suitably orientated refractory mineral grains and cataclasis. Folding and boudinage of veins are occasionally observed (Fitches, 1987). That the mineralisation may be temporally cogenetic with the volcanic rocks is suggested by the presence of epiclasts of chalcopyrite-bearing vein-quartz within the Bedded Pyroclastic Formation, indicative of near-surface emplacement of veins and their subsequent erosion (Lusty *et al.*, 2017).

The Castell Carn Dochan Lode

Castell Carn Dochan Mine, near Bala [SH 8489 3070], is a well known site, but although details of its history have been published (Hall, 1990; Hughes, 1994), there is very little in the geological literature regarding the deposit. A brief description may be given here, based upon site visits and examination of the mineralisation by the author and others. The deposit, with a recorded nineteenth century gold production of 1913 ounces, consists of a northeast–southwest trending, steeply southeast dipping lode up to 2 m in width, dominated by compact, milky quartz and hosted by highly competent ash-flow tuffs of the Aran Fawddwy Formation, of Caradoc age but a little older (Costonian) than the Snowdon Volcanic Group.

The lode contains rather sparse bands of scattered small (millimetre to centimetre scale) sulphide grains: minor euhedral arsenopyrite and pyrite are early and are followed by rare pyrrhotite and chalcopyrite then minor galena and sphalerite, the gold mostly being spatially associated with the galena. Gold occurs as scattered, often inclusion-forming microscopic to visible, millimetre-sized particles. Some gold-bearing samples collected by the author include grains that have a pale pinkish tint, suggesting that auricupride (Cu_3Au) or a related mineral may also be present. The richest samples, in terms of gold visibility, are those in which weathering has removed the enclosing sulphides, leaving areas of boxwork quartz with a scattering of gold grains. Bismuthinite has also been recorded, forming millimetre-scale nests of silver-grey acicular crystals in quartz (Steve Rust, *personal communication*). Post-Acadian, vuggy calcite-marcasite veining cross-cuts the quartz-sulphide lode filling in places.

Although this paragenetic structure is similar to that of the pre-Acadian Dolgellau Gold-belt, sulphide deformation at Castell Carn Dochan appears in many samples to be relatively minimal. However that observation is perhaps due to the fact that sulphide grains are often just a few millimetres across and sealed in massive quartz, itself hosted by highly competent, massive felsic ash-flow tuff. These factors would have served to provide the sulphides with a degree of protection.

To the southwest of Castell Carn Dochan, arsenopyrite-bearing vein mineralisation has been recorded with few details at two localities near Benglog (Cooper *et al.*, 1983): both occurrences are within the Melau Formation, at a median level within the Aran Volcanic Group.

THE CIRCUM-CALDERA LODES: MINERALOGY, TEXTURES AND DEFORMATION

Some of the mineralisation of the pre-Acadian circum-caldera lodes has received previous attention (Colman, 1990), but no systematic description has hitherto been attempted. The pre-Acadian circum-caldera lodes occur in an arc of ground, approximately 60 km in length and generally less than 10 km in width, concentrated around the Snowdon Caldera's northwestern, southwestern and southeastern flanks. There are numerous mines and mineralised outcrops within this arc, from the Bethesda district southwards through Llanberis, Nantlle and Cwm Pennant to Porthmadog and eastwards along the northern side of the Vale of Ffestiniog and in the country to the east and north of Blaenau Ffestiniog. The oldest host-rocks to the circum-caldera lodes are the Middle Cambrian Bronllwyd Grits Formation. The youngest are dolerite intrusions, emplaced into mudstones of the upper part of the pre-Longvillian Nant Ffrancon Group and the lodes also cut the Tanygrisiau Microgranite. This represents a variable, sub-caldera and pre-Acadian stratigraphic thickness of host-rocks of up to 3.75 km. That figure may be greater if the nature of the vein mineralisation can be established at the Coed y Dinas trials (see text), northwest of Bethesda and in the Fachwen Formation, which is late Neoproterozoic to Cambrian in age.

Lodes within this arc consist of fractures filled with variable amounts of milky quartz, chlorite, mostly minor carbonates and sparse to highly abundant metalliferous minerals. Massive, complexly intergrown sulphides are characteristic of many, but not all, lodes. The lodes range in width from a few centimetres up to several metres and they have trends from southwest–northeast around clockwise to northwest–southeast with dips ranging from vertical to northerly: in the southern part of the district, northerly dips as low as 20–30° are locally encountered. Lode continuity along-strike is often difficult to establish but tens to locally hundreds of metres appear to be typical values.

Studies of these lodes were facilitated firstly by site examinations during the Gwynedd phase of the Minescan project in 1997 (Bevins and Mason, 1998), secondly by more detailed re-examination of the most scientifically valuable sites in the mid-2000s, this time in association with Gwynedd Môn RIGS (Regionally Important Geological Sites), and thirdly in follow-up field and laboratory work by the author, in more recent years. Much of this work was done alone, so for safety reasons had to be confined to surface workings. Through these programmes, more than 180 hand specimens of mineralisation were obtained, both from mine spoil and

outcrops. Thirty-five polished sections were prepared from selected samples for petrological examination, which is essential due to the finely intergrown nature of the mineralisation. A smaller number of large (~30 cm) blocks of mineralised material were also cut and polished for textural interpretation on a macro-scale, a technique that usefully compliments ore microscopy. Representative material is preserved at Amgueddfa Cymru – National Museum Wales, together with extensive sample suites from both the Snowdon Caldera and the Dolgellau Gold-belt.

The most significant locations, both mines and outcrops, are hereby described in an anticlockwise circuit around the Snowdon Caldera, from the northwest to the southeast. Sites that are omitted have proved poor sources of study material, either through scarcity [e.g. Hafod-Boeth Mine, SH 6366 4134], or due to excessive contamination by post-Acadian veining [e.g. Bwlch-y-Plwm Mine, SH 6290 4145]. Veins that are post-tectonic, with respect to the Acadian deformation, are common in the district (and indeed within the Snowdon Caldera and the Dolgellau Gold-belt). Post-tectonic veins are typically open and vuggy, often with delicately crystallised crustiform arrangements of sulphides, quartz and calcite (Mason, 2018). Where both types of veins occur, along structures of pre-Acadian origin but which have undergone post-Acadian reactivation, the strong textural contrast between the two styles of mineralisation is immediately apparent.

Tan-y-Garth Mine [SH 6394 6678] is situated about a kilometre ENE of Bethesda and the mineralisation is hosted by the late Cambrian Marchlyn Formation. An opencast working shows little more than pyrite veinlets, but suggests the extraction of a WNW-trending lode. According to Bick (1985) the mine yielded 232 tons of arsenopyrite, although dates of working are not cited. Post-mining oxidation has been intense at this site, with the tips cemented together in places by secondary products including earthy probable scorodite. Part-oxidised arsenopyrite, pyrite, chalcopyrite, galena and sphalerite have all, however, been identified. Polished sections are difficult to make due to the crumbly nature of the material; one section revealed arsenopyrite traversed by part-oxidised chalcopyrite veinlets.

Some of the mines and trials known to exist historically in the Bethesda district have long since vanished, as noted by Bick (1985), covered over by the extensive tips from the huge Penrhyn Slate Quarry. Coed y Dinas Mine [SH 6116 6806] is a small group of workings on the east and west banks of the Ogwen northwest of Bethesda; photos taken underground and examined by the author show limited narrow stoping and steeply dipping quartz veins that appear to be boudinaged, so this was clearly not a slate working. An account in *Observations of the Snowdon Mountains*, by William Williams (1802), noted the presence of strings and veins of copper ore, with some lead, at the site. The interesting feature of this working is that it is within the Fachwen Formation of the Arfon Terrane and it is a pity that the surface of the site does not yield sample material: the waste probably ended up in the river, a common practice in historical times.

Ceunant Mine yields little material at surface but is of interest to the industrial archaeologist, for the remains of a system of arsenic condensation-flues and a calcination furnace for the arsenopyrite, these being situated in open woodlands [SH 6324 6456] and constituting the only known arsenic production plant in North Wales.

Cwm Ceunant Mine [SH 6258 6375] is situated in a lofty position on the hillside above Ceunant. Here, three levels have been driven on a WSW-striking lode in the Marchlyn Formation, including the Carnedd y Filiast Grit facies. The underground workings are extensive and photographs of stopes suggest the lode was over a metre wide, although little is known of the mine's history or how much ore it produced. Samples occur in abundance on the tips and this is the best study site in the Nant Ffrancon valley, since much fresh lode material may be examined, compared to other sites. Parts of the lode contain brecciated dark grey sandstone: other parts are clast-free. Mineralisation consists of variable amounts of milky quartz with sulphides: samples range from quartz and chlorite with chalcopyrite spots through to massive intergrown pyrrhotite and chalcopyrite with less than 5% quartz. Arsenopyrite is common and forms small, millimetre to sub-millimetre scale subhedral to euhedral crystals. Among the massive sulphides on the tips, pyrrhotite is the dominant species and typically shows a finely granular, recrystallised texture (Fig. 3). In polished section, this texture is seen to be granoblastic: in plane polarised light, pyrrhotite grain boundaries are picked out by thin rims of oxidation products, but under crossed polars the differing orientations of pyrrhotite grains may be clearly seen through their anisotropy. Grain triple-junctions are often close to 120^{o} and individual grains are typically 0.5–1.0 mm in diameter.

The paragenetic relationship between pyrrhotite and chalcopyrite must have been obscured by recrystallisation to an extent. However, the facts that chalcopyrite forms cross-cutting veins in some cases, that more

Figure 3. Hand specimen of typical massive granoblastic pyrrhotite from Cwm Ceunant Mine.

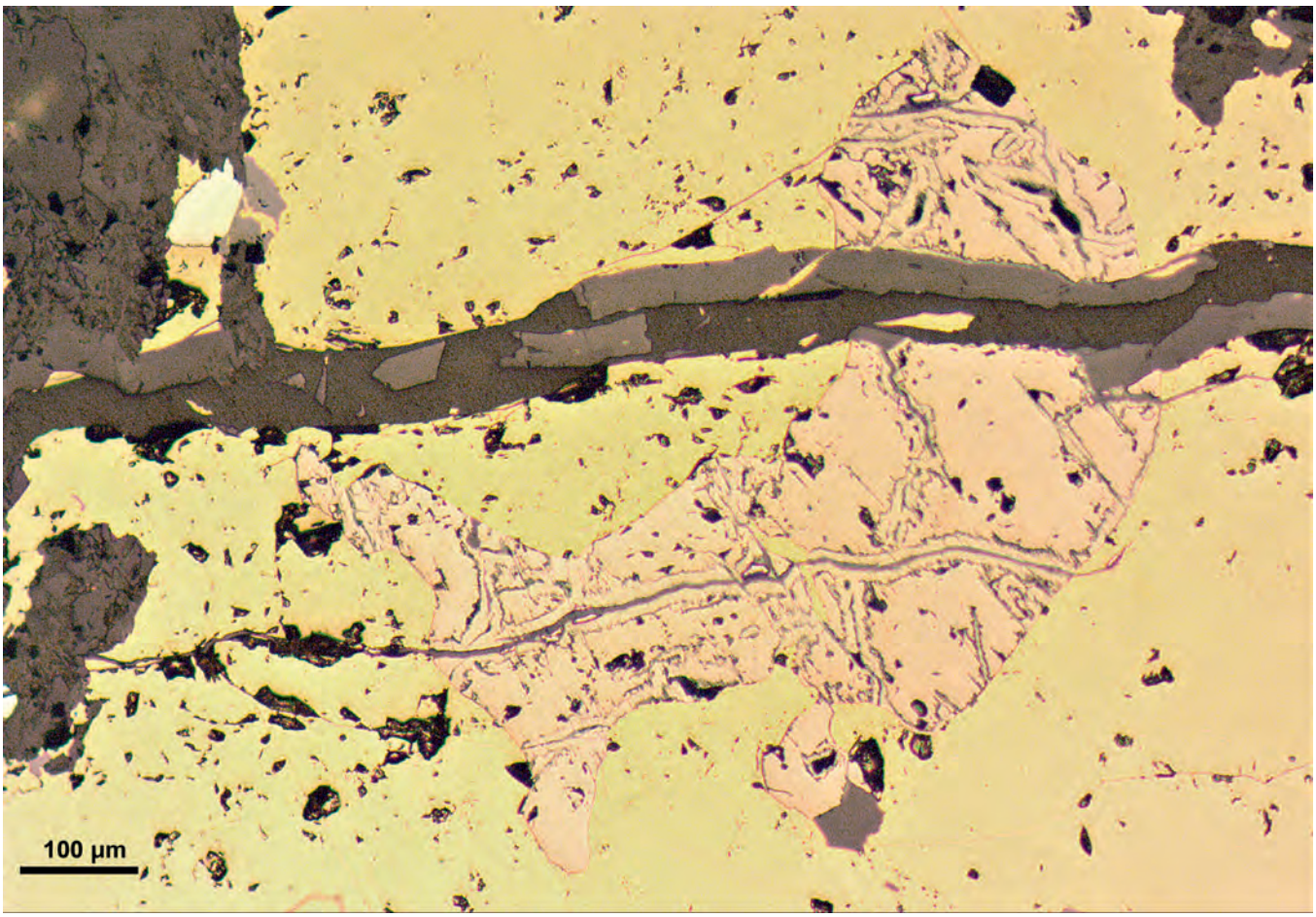

Figure 4. A large inclusion of pyrrhotite (pinkish) in chalcopyrite (yellow). Both have been cut by a quartz-carbonate-chalcopyrite veinlet. The bright crystal (upper left) is arsenopyrite. Polished section, plane polarised light. Cwm Ceunant Mine.

extensive chalcopyrite domains often carry pyrrhotite inclusions, and finally that intergrown chalcopyrite and pyrrhotite may be cut by quartz-chlorite-chalcopyrite veins (Fig. 4), indicate most of the chalcopyrite mineralisation to have been later in the original sequence of deposition. Arsenopyrite is clearly early: it forms euhedral inclusions in, and is veined by, both pyrrhotite and chalcopyrite (Fig. 5). Pyrite occasionally accompanies the arsenopyrite, forming subhedral to anhedral grains of a similar size. Sphalerite occurs as infrequent anhedral inclusions to around 0.5 mm in chalcopyrite: due to recrystallisation, its paragenetic position is difficult to interpret. The sphalerite is free from classic ''chalcopyrite disease'', but does contain scattered minute teardrop-shaped chalcopyrite inclusions.

Later cross-cutting veinlets (1−3 mm in thickness) are common and consist of poorly polishing pyrite with a distinctively spongy appearance, accompanied by a little quartz in some cases. The age of these veinlets is uncertain except that they appear to post-date the recrystallisation event, so a post-Acadian origin seems likely. The spongy pyrite oxidises readily, leading to destructive sample decay outside of controlled environments.

Part-oxidised samples from Cwm Ceunant show excellent and highly photogenic examples of pyrrhotite decay, initially via the distinctively streaky, strongly orientated ''intermediate product'' of Ramdohr (1969), also known as ''zwischen-produkt'', then to ''marcasite'' and eventually to iron oxides (Fig. 6). Characteristic 'birds-eye' textures also occur in more altered samples (Fig. 7). Textures frequently show that the decay had set in along pyrrhotite grain boundaries. However, even in heavily altered samples, despite a large proportion of pyrrhotite having been converted to the intermediate

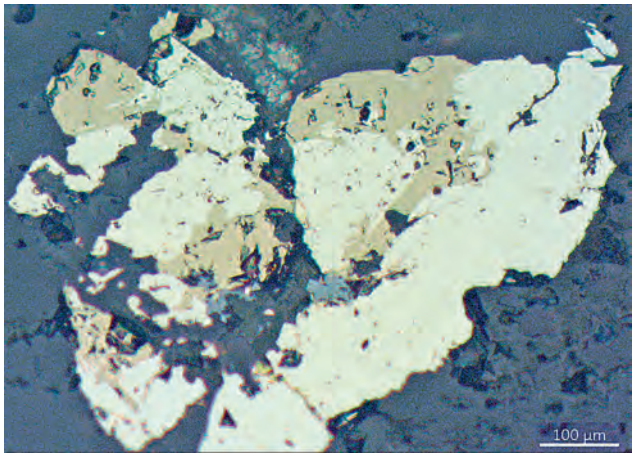

Figure 5. Pyrrhotite (pinkish brown) and chalcopyrite (yellow) veining arsenopyrite (white) in a quartz-chlorite matrix. Minor sphalerite (grey) is also present in the cracked arsenopyrite. Polished section, plane polarised light. Cwm Ceunant Mine.

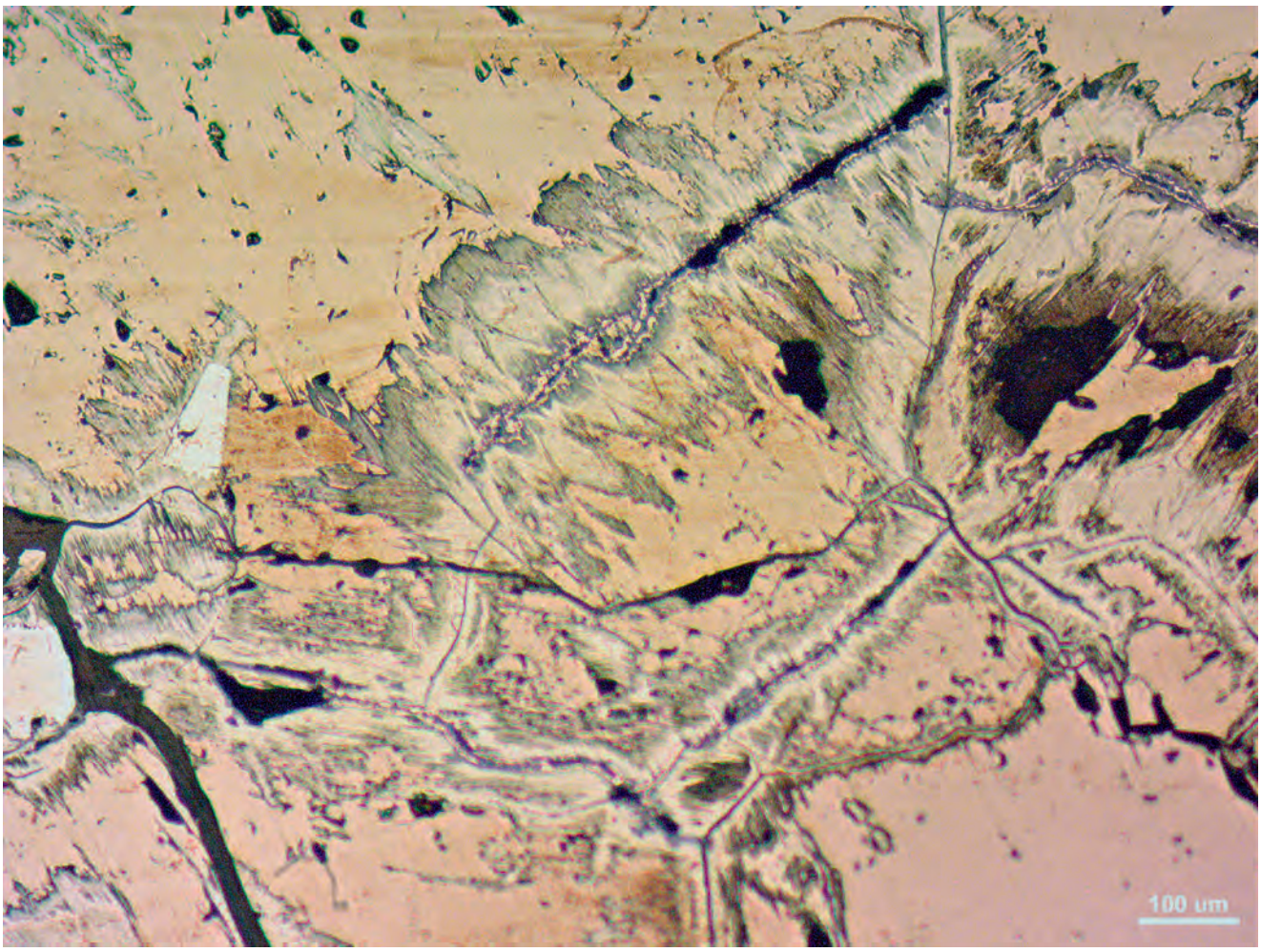

Figure 6. Pyrrhotite altering to oxides and marcasite via a streaky, strongly orientated "intermediate product". A rhomb of arsenopyrite (white) is included in the pyrrhotite (centre-left). Polished section, plane polarised light. Cwm Ceunant Mine.

product and marcasite, the arsenopyrite euhedra and chalcopyrite domains have remained largely intact. The intermediate product veinlets are confined to the pyrrhotite and stop abruptly at pyrrhotite-chalcopyrite grain boundaries.

If the material on the dumps is representative of the lode-filling, high-grade chalcopyrite concentrates would have been difficult to prepare at Cwm Ceunant, owing to the rather similar densities of that mineral and pyrrhotite. However, the presence of hand-cobbing floors suggests some of the richer chalcopyrite mineralisation could have been selectively dressed.

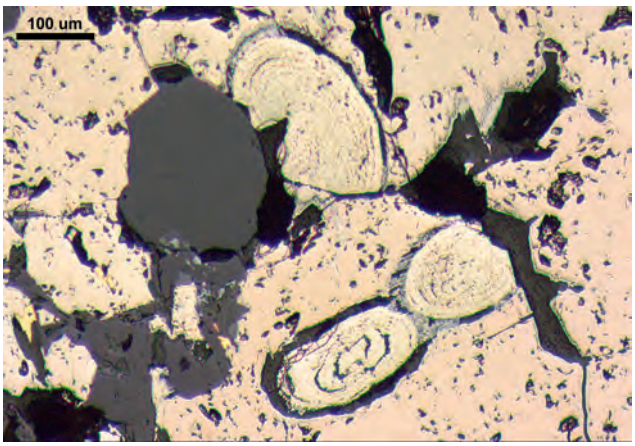

Figure 7. Pyrrhotite alteration to marcasite and iron oxides with classic 'bird's eye' texture. Polished section, plane polarised light. Cwm Ceunant Mine.

At the foot of the Llanberis Pass and less than 2 km from the northwestern margin of the Snowdon Caldera are the extensive remains of the productive Llanberis Mine [SH 5968 5878], one of three GCR sites selected to represent this mineralised district (Bevins *et al.*, 2010). The lodes are hosted at this mine by both the Bronllwyd Grit Formation and the Marchlyn Formation, with interbedded coarse grits, sandstones and mudstones. Lodes trend WNW–ESE and northwest–southeast: they have been worked both by opencasting and underground development. Production was, by the standard of the Snowdonia copper mines, substantial: Bick (1985) cites a yield of 7,499 tons of copper ore concentrates between 1804 and 1913 and the mine was reportedly at work long before the start of the nineteenth century.

The lodes worked at Llanberis consist of quartz and chlorite together with massive sulphides, samples of which are numerous. Abundant early euhedral to subhedral arsenopyrite, with individual crystals to >10 mm, is associated with minor pyrite, both in

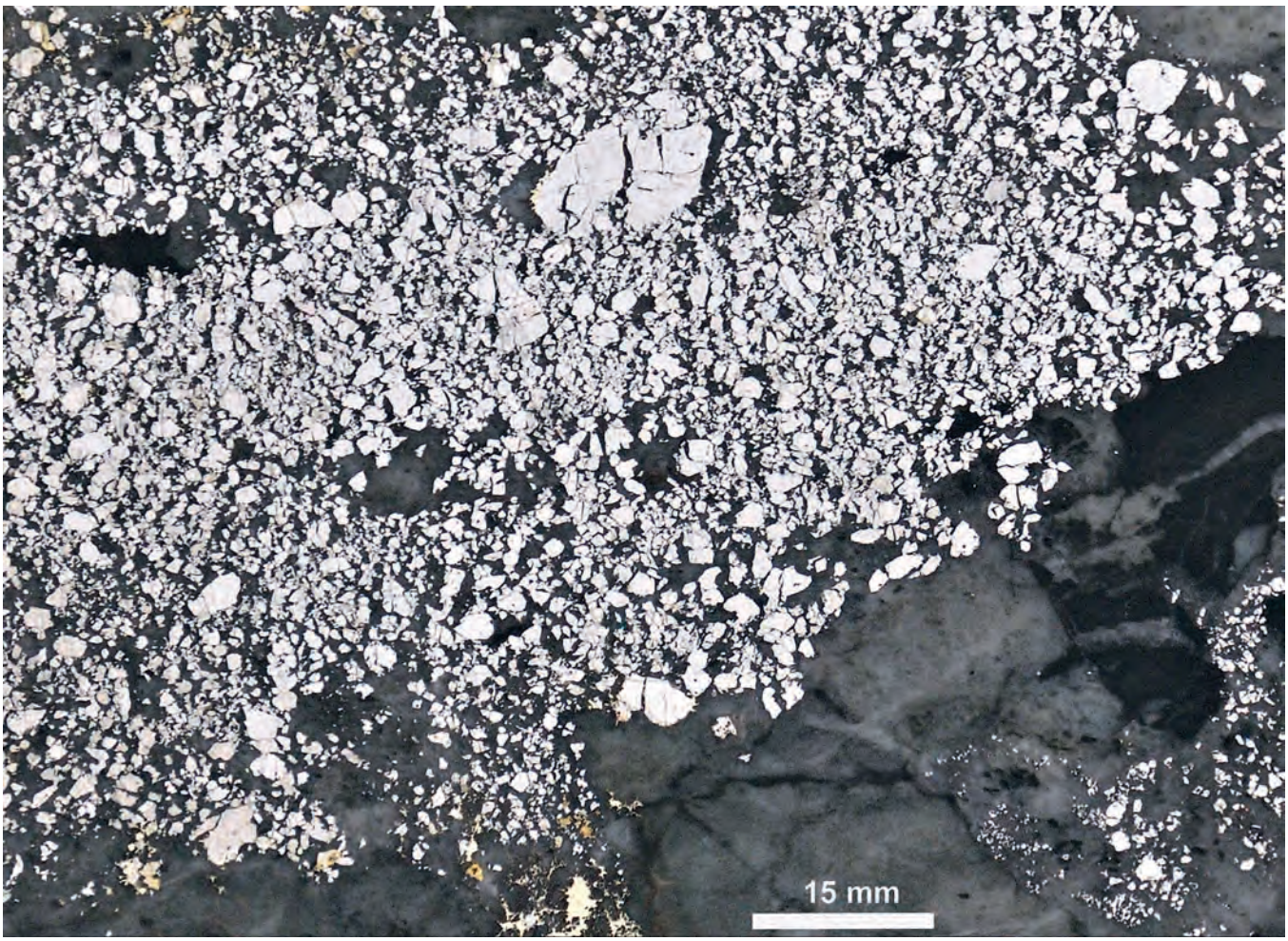

Figure 8. Polished slab of arsenopyrite-rich veinstone, Llanberis Mine. Originally euhedral arsenopyrite has undergone a degree of cataclasis in response to Acadian compressive deformation. However, the larger crystal (centre-top) has well developed pressure-fringes of quartz on both its left- and right-hand sides. Minor chalcopyrite is present toward the bottom of the image.

quartz, where brecciated wallrock may occur, and as porphyroblast-like crystals within chloritised wall-rocks (Fig. 8). Chalcopyrite forms peripheral rims around arsenopyrite grains and also commonly occurs as cross-cutting veinlets. A pyrrhotite-chalcopyrite association, identical in its paragenesis to that at Cwm Ceunant, is abundant in the workings in the southeastern part of the site: chalcopyrite, with minor included sphalerite, forms cross-cutting veinlets and intergrain masses in the pyrrhotite (Fig. 9), and arsenopyrite euhedra occur as inclusions in both minerals. Chalcopyrite also occurs throughout the site as massive aggregates in a quartz-chlorite matrix. Post-depositional deformation has caused cataclasis of some arsenopyrite crystals, and others have developed pressure-shadows composed of fibrous quartz. Pyrrhotite typically displays the same finely granoblastic recrystallised texture as seen at Cwm Ceunant, which is particularly evident when viewed in polished section under crossed polars (Figs 10 and 11). Oxidation of pyrrhotite is commonly observed, although in the illustrated sample the effect is relatively minimal.

An apparent gap in this style of mineralisation, of about 5 km, separates Llanberis from the next mine to the southwest. This site, Llyn Cwellyn, is little more than a trial, situated a couple of hundred metres from the northwest end of the lake of the same name [SH 5484 5571]. Old Series BGS maps dating back to the 1850s show a northwest–southeast trending lode close to here and aerial photographs reveal two prominent fractures of that orientation extending for nearly 300 m to the southeast of the workings. However, the lode is shown as entirely within the Mynydd Mawr Microgranite,

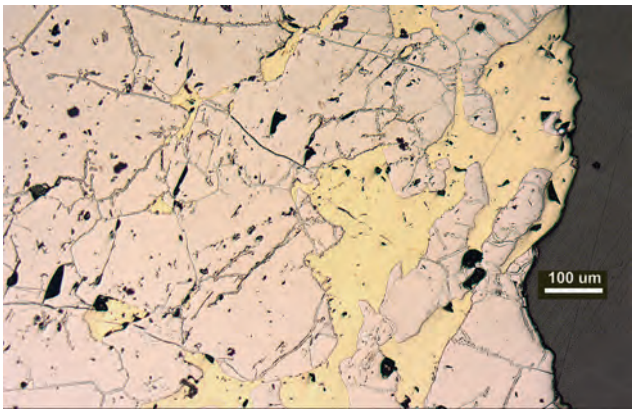

Figure 9. Chalcopyrite (yellow) forming veinlets and intergrain domains in pyrrhotite (pinkish). Polished section, plane polarised light. Llanberis Mine.

Figure 10. Hand specimen of granoblastic pyrrhotite, Llanberis Mine.

whereas the trial explored mineralisation within the rocks marginal to the intrusion, these belonging to the Marchlyn Formation. The underground workings are not accessible. Small tips provide samples of the mineralisation in blocks that indicate a narrow lode, less than a metre in width.

The mineralisation at Llyn Cwellyn was originally described by Colman (1990) and additional information was provided by Bevins *et al*. (2010), as it is a GCR site. Uniquely for the district, the lode-filling is dominated by fluorite. Early magnetite-pyrite-chlorite aggregates occur as impregnations of rock clasts in a cement of massive fluorite, predominantly white but also in shades of purple and green. The fluorite is brecciated and veined, with a quartz ferroan dolomite cement. Sulphides accompany the quartz and ferroan dolomite but are typically present as scattered grains less than 2 mm in size, a paucity that probably explains the small size of the trial. Chalcopyrite and lesser pyrite dominate in hand specimens. In polished section, pyrrhotite encloses pyrite. Minor sphalerite, galena and unidentified but qualitatively confirmed tellurides of bismuth and lead are also present, the latter forming complex

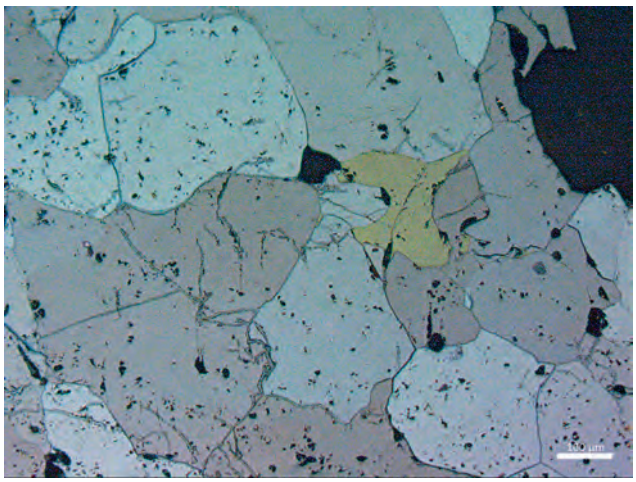

Figure 11. Pyrrhotite showing granoblastic texture with minor chalcopyrite. Polished section, moderately crossed polars. Llanberis Mine.

myrmekite-like intergrown bodies a few tens of micrometres across.

Colman (1990) and Colman and Appleby (1991) noted that the rare earth element profile of the fluorite strongly resembled that of the Mynydd Mawr Microgranite, suggesting a genetic relationship between the intrusion and the fluorite mineralisation, a hypothesis with which the author would concur. The microgranite suite of Snowdonia does locally carry minor cogenetic mineralisation that includes molybdenite from the Blaen-y-nant intrusion near Ogwen (Amgueddfa Cymru – National Museum Wales specimen NMW 27.111.GR.288) and in the roof-zone of the Tanygrisiau intrusion, pipe-like pegmatitic bodies and drusy cavities contain molybdenite, allanite, pyrophyllite, calcite and quartz (Bevins *et al*., 2010). However, the quartz, ferroan dolomite, sulphides and tellurides at Llyn Cwellyn clearly belong to a later, post-fluorite mineralising event.

Southwest of Llyn Cwellyn lies the historic and important mine of Drws-y-Coed [SH 5440 5338], whose extensive remains lie mainly on the hillside to the south of the B4418 road. Production of 12,939 tons of chalcopyrite concentrates was cited by Bick (1985) between 1804 and 1913: however, the site was worked well before that. The lode was reportedly up to seven metres wide in places (Bick, 1985). Mineralisation here is hosted by grits belonging to the Marchlyn Formation: impoverishment reportedly occurred outside of this lithology. Sulphide-rich mineralisation is poorly exposed at the foot of the crag-line at the top of the site, where a network of open workings testifies to the somewhat irregular nature of the lodes, although according to Dewey *et al*. (1925) the main trend of the lodes was east–west with a northerly dip of around 60°. Massive milky quartz veins are abundant in the outcrops above the mine, but many of these veins may belong to the class known as the "regional veins" of Fitches (1987): they are apparently devoid of sulphides.

The sulphide mineralisation at Drws-y-Coed is texturally complex, typical samples showing mixed sulphides forming massive intergrowths with quartz, chlorite and minor carbonates: in places the sulphides also impregnate the host-rock. Polished sections are required to appreciate the paragenesis in detail. Arsenopyrite, associated with pyrite (which it encloses), is again abundant and early in the depositional sequence, forming idiomorphic crystals in quartz and impregnating chloritic rock. Some specimens of arsenopyrite consist of densely packed, bent and cracked columnar to needle-like crystals to over 2 cm in length (Fig. 12). Minor pink encrustations of the secondary cobalt arsenate, erythrite, indicate either that the arsenopyrite is cobaltian or that there is associated minor cobaltite.

Chalcopyrite forms crack-filling veins in shattered arsenopyrite and massive intergrowths with pyrrhotite. Later in the sequence are massive, granular sphalerite, which often reveals intense "chalcopyrite-disease"

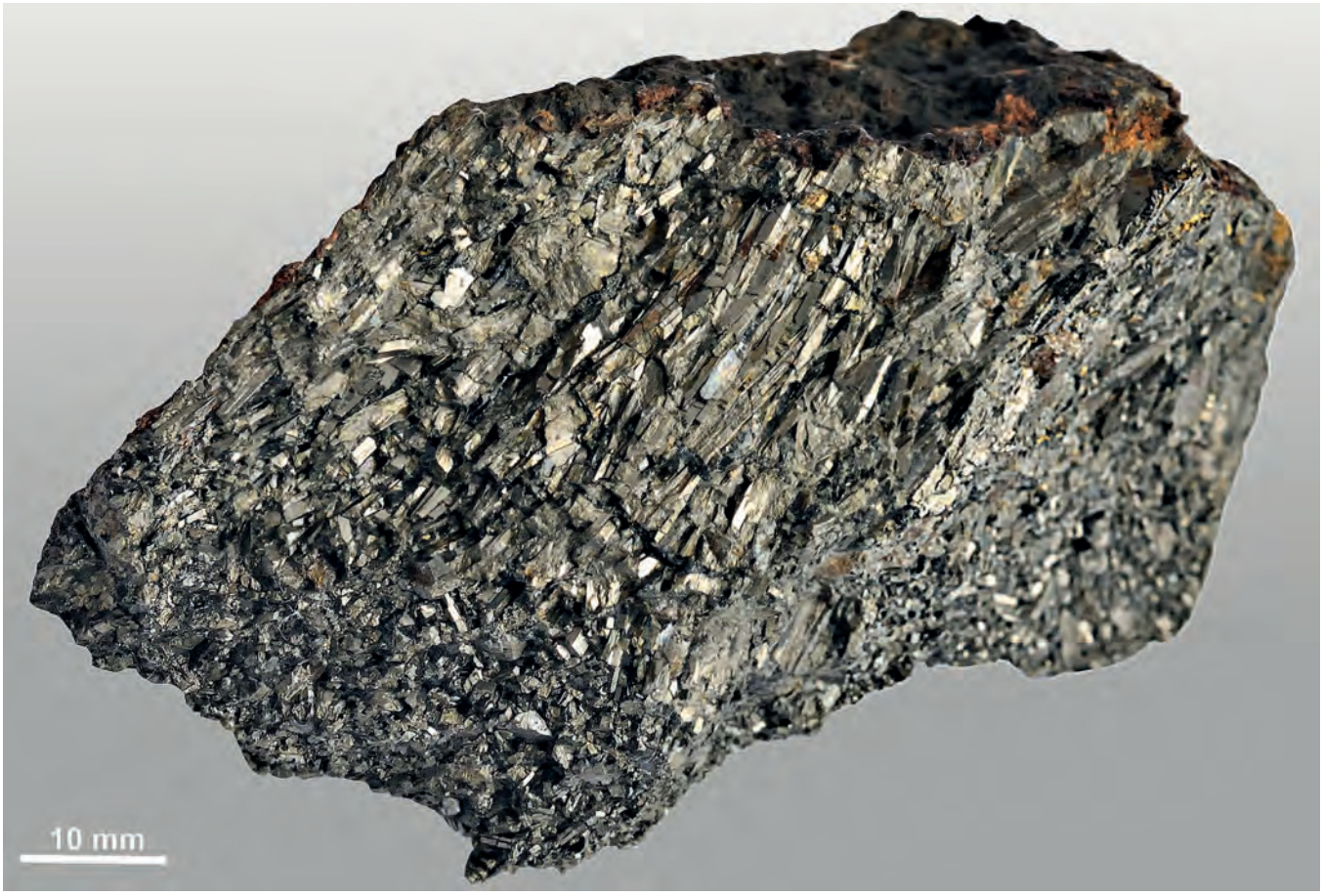

Figure 12. Hand specimen of arsenopyrite showing columnar crystals, slightly bent and broken due to Acadian compressive deformation. Drws-y-Coed Mine.

texture in polished section, and also contains blebs of pyrrhotite, plus relatively minor galena. According to Bick (1985), gold was recorded at the site during mining operations, although amounts were trivial. The nickel sulphide millerite occurs on a sample NMW 82.22G.M.1, donated to Amgueddfa Cymru – National Museum Wales by Neil Hubbard in 1982. The sample features small, brassy metallic needles, some of which pass through tiny siderite rhombs (Tom Cotterell, *personal communication*). The not infrequent occurrence of leaf-like growths of native copper up to around 5 mm across, mainly in the wall-rocks, was noted by the Welsh naturalist, Thomas Pennant, as long ago as 1781 (Bick, 1985). The copper, conspicuous in freshly broken samples, rapidly develops a black tarnish.

Identical mineralisation was worked at the Simdde Dyllaun Mine [SH 5374 5330] further down the valley, although less study material is present at this site. According to Bick (1985), 7,719 tons of chalcopyrite concentrates were sold from this mine, which is the deepest in Snowdonia, the bottom being 116 fathoms (212 metres) below surface. On the opposite side of the valley is the smaller Benallt Mine [deep adit at SH 5353 5343], where arsenopyrite is apparently absent: intergrown galena, sphalerite, chalcopyrite and pyrite occur in a quartz-chlorite matrix, the pyrite forming porphyroblast-like crystals embedded in the other sulphides which form a fine-grained, emulsoid-like intergrowth that must have been impossible to process. Colman (1990) presented a survey of the accessible underground workings at both sites.

To the south of Drws-y-Coed are several small trial workings on the north-facing slopes of Mynydd Tal-y-mignedd, covered in detail by Colman (1990). Of note is the occurrence of "secondary pink cobalt bloom", associated with pyrite, chalcopyrite and pyrrhotite at SH 5443 5284. At SH 5314 5196, a cross-cut has been made to a lode striking approximately east–west and at the contact between microgranite and Nant Ffrancon Group mudstone. The lode contains pyrrhotite, chalcopyrite, sphalerite and galena, occurring in equigranular, emulsoid intergrowths with quartz: the average grain size of the sulphides is <0.25 mm.

On the southern side of the Nantlle Ridge lies Cwm Pennant, home to a number of workings. Blaen-y-Pennant Mine [SH 5410 5061] (also worked as Cwmdwyfor) lies at the head of the valley and is extensive. The mine has a colourful history, covered by Bick (1985): the lode was dominated by massive and worthless pyrrhotite, large (30 cm plus) blocks of which still littered the ground in 1997 (Bevins and Mason, 1998). Some galena concentrates were reportedly sold but the lead mineralisation comes from coarsely crystalline, vuggy post-Acadian veins that exploited the same fracture system, hosted by the Marchlyn and Dol-cyn-

afon formations. The massive pyrrhotite is also cut by late pyrite veins, similar to the ''spongy pyrite'' described at Cwm Ceunant and equally unstable. Veinlets of chalcopyrite occur within the pyrrhotite but in quantitative terms the mineralisation can hardly be referred to as a copper deposit. Arsenopyrite is here limited in its occurrence to sub-millimetre, parallel-orientated euhedral inclusions in the pyrrhotite. Another association seen at this site is milky quartz with minor dolomite and chalcopyrite; whether this represents a separate lode is unknown.

Paragenetically early arsenopyrite also occurs at Cwm Ciprwth Mine [SH 5257 4778], a site more rewarding for its industrial archaeology than for its mineralogy. Limited material at the site reveals sheared, locally pyritic mudstone of the Marchlyn Formation, carrying sphalerite, pyrite, arsenopyrite and galena in quartz veinlets. Colman (1990) additionally reported the presence of cream-coloured baryte, although its paragenetic position is uncertain.

To the south and southeast of the Snowdon Caldera margin, scattered mines that exploited pre-Acadian mineralisation continue around in an arc to the north of the Vale of Ffestiniog and in the direction of Moel Siabod. However, in this district there is heavy overprinting at some mines by post-Acadian mineralisation and unaffected study sites are limited in number. At Pant-y-wrach Mine [SH 6169 4019], a northwest-trending lode has been extensively tried for copper, although only 45 tons of concentrates were sold between 1804 and 1913 (Bick, 1985). The mineralisation is hosted by mudstones and fine sandstones of the Dol-cyn-afon Formation (of early Tremadoc age) and consists of milky quartz veins with ferroan carbonate in cavities; both quartz and carbonate carry pyrite, chalcopyrite and pyrrhotite. Arsenopyrite is a minor phase, occurring early in the paragenesis, but good study material is in limited supply at this site.

Catherine and Jane Consols [SH 6324 4110] exploited an WNW–ESE trending lode cutting highly disturbed Ordovician Nant Ffrancon Group mudstones, these being within the Rhyd Melange (Howells *et al.*, 1997). Although a strong post-Acadian Pb-Zn-calcite mineralisation overprint is present at this mine, the pre-Acadian mineralisation is reasonably well represented. Hard, milky quartz carries disseminations of fine-grained arsenopyrite, pyrite and chalcopyrite. Only 159 tons of copper ore concentrates were sold from this mine, between 1804 and 1913 (Bick, 1985).

Just over 2.5 km to the northeast of Catherine and Jane Consols is Coed Llyn-y-Garnedd, an extensive afforested area in the foothills of the Moelwyns, where a system of forestry tracks was cut in the mid-1990s. The fresh exposures provided by the numerous rock-cuttings revealed useful data, at the time, on this pre-Acadian mineralisation. Twenty years plus of weather and moss and lichen growth have now obscured a lot of the features. Exposures originally provided clean sections through the Dol-cyn-afon and Allt Lwyd Formations (including the Garth Grit) and Nant Ffrancon Group mudstones, with lava-breccias of the Moelwyn Volcanic Formation appearing in the uppermost part of the forest. One of the tracks also cuts through the dyke-like southwest extension of the Tanygrisiau Microgranite. Vein exposures were plentiful around SH 6542 4265 and in track-side exposures for several hundred metres westwards. The veining is narrow, with individual veins no more than a few centimetres in thickness and consisting of milky quartz with pyrite, chalcopyrite and granular sphalerite. One set of veins is low-angle, dipping NNW at 25–30° and virtually concordant with local bedding; another set is steep and has an ENE to northeast strike: the sets are linked together. Importantly for age-constraining purposes, identical veins also cut the microgranite, in the vicinity of SH 6488 4207, the sharply-defined vein margins indicating that by the time of vein emplacement, the microgranite was cold and behaved in a brittle manner.

Another 2.3 km to the northeast again, above the southwest end of Tanygrisiau Reservoir, lie the extensive remains of the Moelwyn Mine [SH 6738 4360 and on the hillside above]. Here, several east–west trending, northerly dipping (50–60°) pre-Acadian lodes, generally less than a metre in width, have either been tried or worked, unusually in this district, for zinc. The dumps contain much granular sphalerite forming veins coursing through brecciated sandstone and mudstone of the Dol-cyn-afon Formation, within the contact aureole of the Tanygrisiau Microgranite. Although Dewey and Smith (1922) reported that considerable amounts of sphalerite were both in stock and available underground, the grade was typically low and the mine had apparently closed by the time of the publication of that memoir. The sphalerite is late in the paragenesis, following earlier quartz with pyrrhotite and minor chalcopyrite.

Within the historical Moelwyn sett there is also the best site for studying the effects of Acadian deformation on the circum-caldera lodes *in situ*. The Afon Stwlan GCR site, as it is called (Bevins *et al.*, 2010), consists of a man-made exposure [SH 6707 4458] on a hairpin bend on the private service-road up to the Llyn Stwlan hydro-electric dam. The outcrop is protected, but sulphide-rich debris is present below the road and study samples prepared from this debris, including polished sections and a large polished slab, are preserved at Amgueddfa Cymru – National Museum Wales.

The northeast–southwest trending lode at Afon Stwlan is hosted by dark grey mudstones of the Nant Ffrancon Group. Brecciated clasts within the lode show thermal spotting from the nearby Tanygrisiau Microgranite intrusion. The lode consists up to 0.3 m of intergrown sphalerite and galena in quartz, with a number of parallel quartz-sulphide stringers and clay-gouge planes. In polished section, sphalerite-rich domains show a near-equigranular mosaic of small (0.5–0.75 mm) sphalerite grains that carry chalcopyrite-disease within their inner zones. Chalcopyrite,

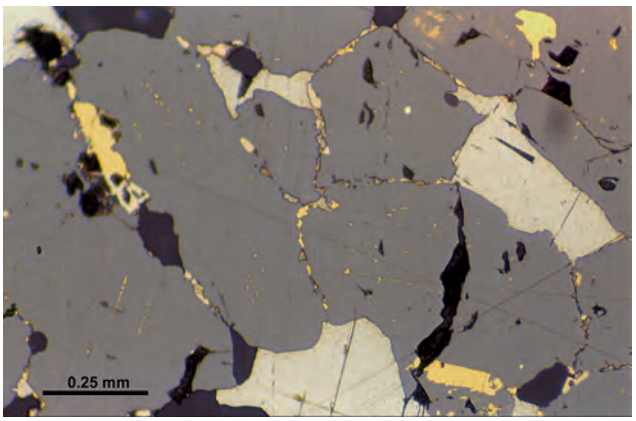

Figure 13. Sphalerite (darkish grey) grain-boundaries are picked out by aggregates of chalcopyrite (yellow) and pyrrhotite (pinkish-brown). Inner areas of sphalerite grains have chalcopyrite-disease. A single inclusion of arsenopyrite (bright white) is upper right of centre. Galena lines larger interstices between some sphalerite grains. Polished section, plane polarised light. Afon Stwlan GCR site.

pyrrhotite and galena are all concentrated along the boundaries between sphalerite grains, as scattered blebs a few tens of micrometres in diameter (Fig. 13). Larger galena grains to 0.5 mm have caries-texture at contacts with sphalerite, the sphalerite being the replacing phase. Galena-rich domains have an emulsoid appearance, being cluttered with sub-rounded bodies of quartz and

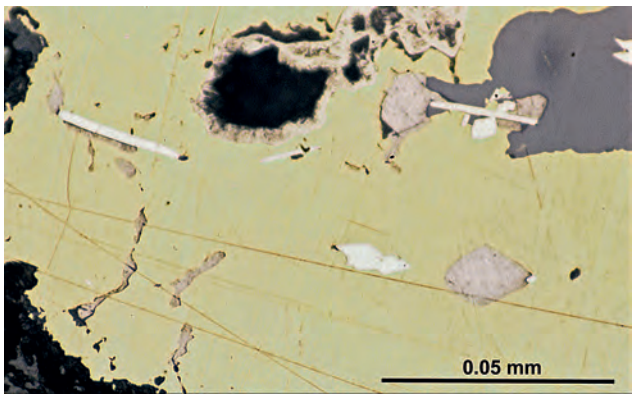

Figure 15. Chalcopyrite (yellow) dominates the field of view and features anhedral inclusions of pyrrhotite (pinkish-brown) and euhedral rod-like and rhomb-shaped arsenopyrite crystals, hosted by both chalcopyrite and pyrrhotite. Polished section, plane polarised light. Afon Stwlan GCR site.

sphalerite to 0.5 mm, around which are concentrated smaller, sub-rounded to ragged aggregates of pyrrhotite and chalcopyrite, the chalcopyrite locally enclosing the pyrrhotite (Fig. 14). Lath-like crystals and broken crystal fragments of arsenopyrite occur in sphalerite, galena, pyrrhotite and chalcopyrite alike (Fig. 15).

Granoblastic sulphide textures are indicative of recrystallisation under strain and further signs of

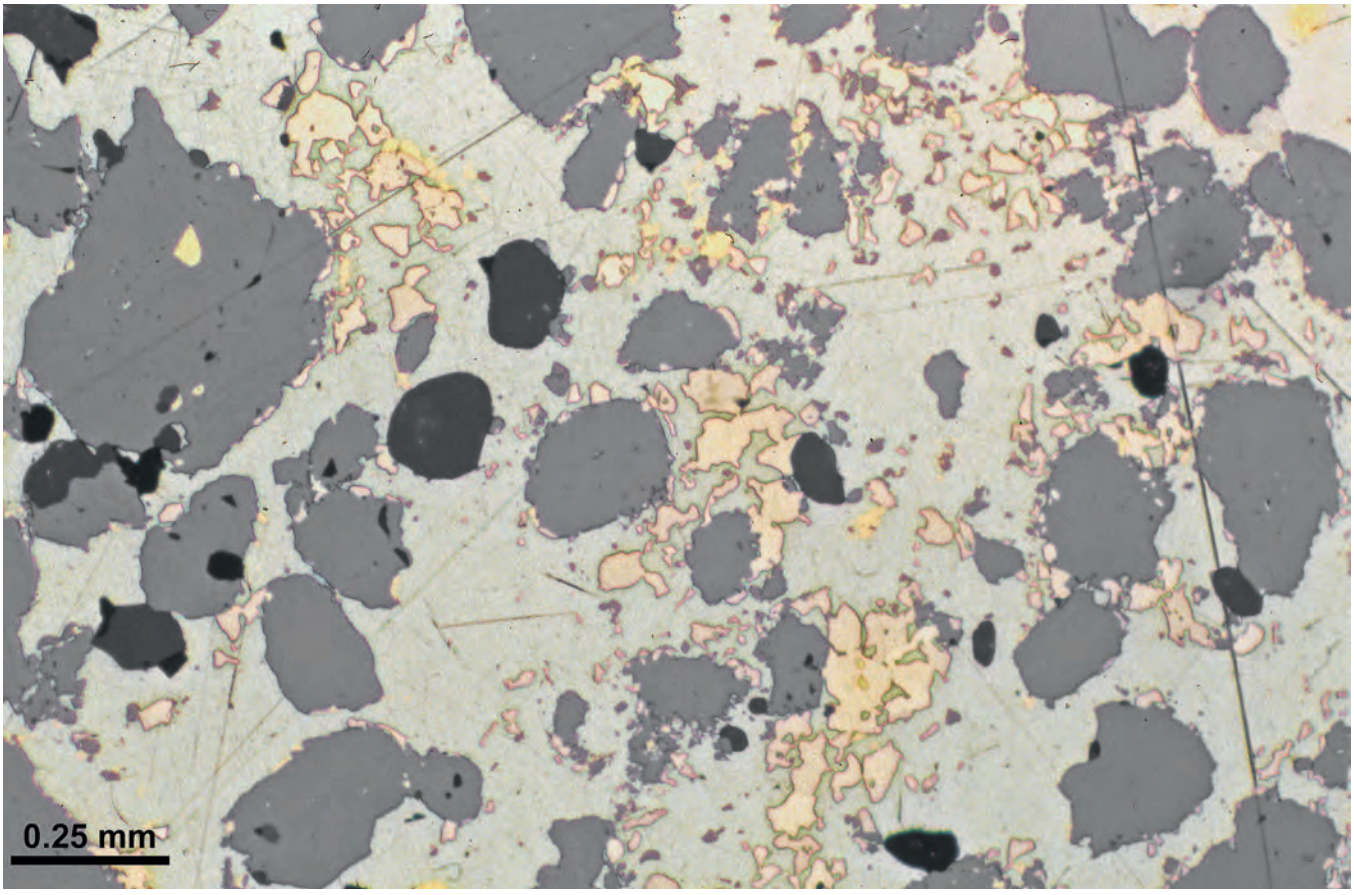

Figure 14. Galena (pale grey-white) carries rounded to sub-rounded domains of sphalerite (mid-grey) and quartz (dark grey), plus arsenopyrite (bright white, high relief, especially upper centre). Ragged aggregates of pyrrhotite (pinkish brown) and chalcopyrite (yellow) are common. Typical recrystallisation texture. Polished section, plane polarised light. Afon Stwlan GCR site.

Figure 16. Afon Stwlan GCR site. The vein outcrop. To the right of the hammer is the sulphide vein: right again is sheared clay-gouge carrying a quartz vein showing strong boudinage due to Acadian compressive deformation.

deformation can be seen in the outcrop: its northern (hanging-wall) side carries a 2–4 cm wide quartz-dominated vein that displays well developed boudinage (Fig. 16). A large polished slab made from a loose block of sulphide, found below the track, again reveals rounded boudins of quartz around which ductile flowage of galena has taken place.

The occurrence of thermally spotted rock clasts within the lode indicates that the rocks had already been thermally metamorphosed, prior to the time of their brecciation during emplacement of the mineralisation. This is consistent with the lode-microgranite relationships exposed in Coed Llyn-y-Garnedd and again in shallow rock-cuttings along the A496 road near Tanygrisiau [SH 6925 4409], where veins occupying brittle fractures and consisting of milky quartz, chlorite and granular sphalerite with pyrite, cut the Tanygrisiau Microgranite.

Newborough Mine [SH 7304 4659], also known as Offeren, is a small working situated among the vast spoil heaps of slate quarries, 2.5 km ENE of Blaenau Ffestiniog. This mine appears, both from site visits and from Bick (1985), to have been an unsuccessful venture, although there are extensive and conspicuous spoil heaps dominated by white quartz. The north-west–southeast striking lode is developed in intrusive rhyolite, hosted by Nant Ffrancon Group mudstones. Within the milky quartz gangue there occur abundant stringers, a few millimetres to several centimetres wide, of intergrown galena and sphalerite, the latter dominant and apparently later than the galena, which it can be seen to have replaced in polished section. Chalcopyrite is subordinate and frequently occurs as inclusions in both other sulphides (Fig. 17). Pyrite is present as a minor early mineral. Both galena and sphalerite have a finely granular texture on broken surfaces, indicative of recrystallisation under strain.

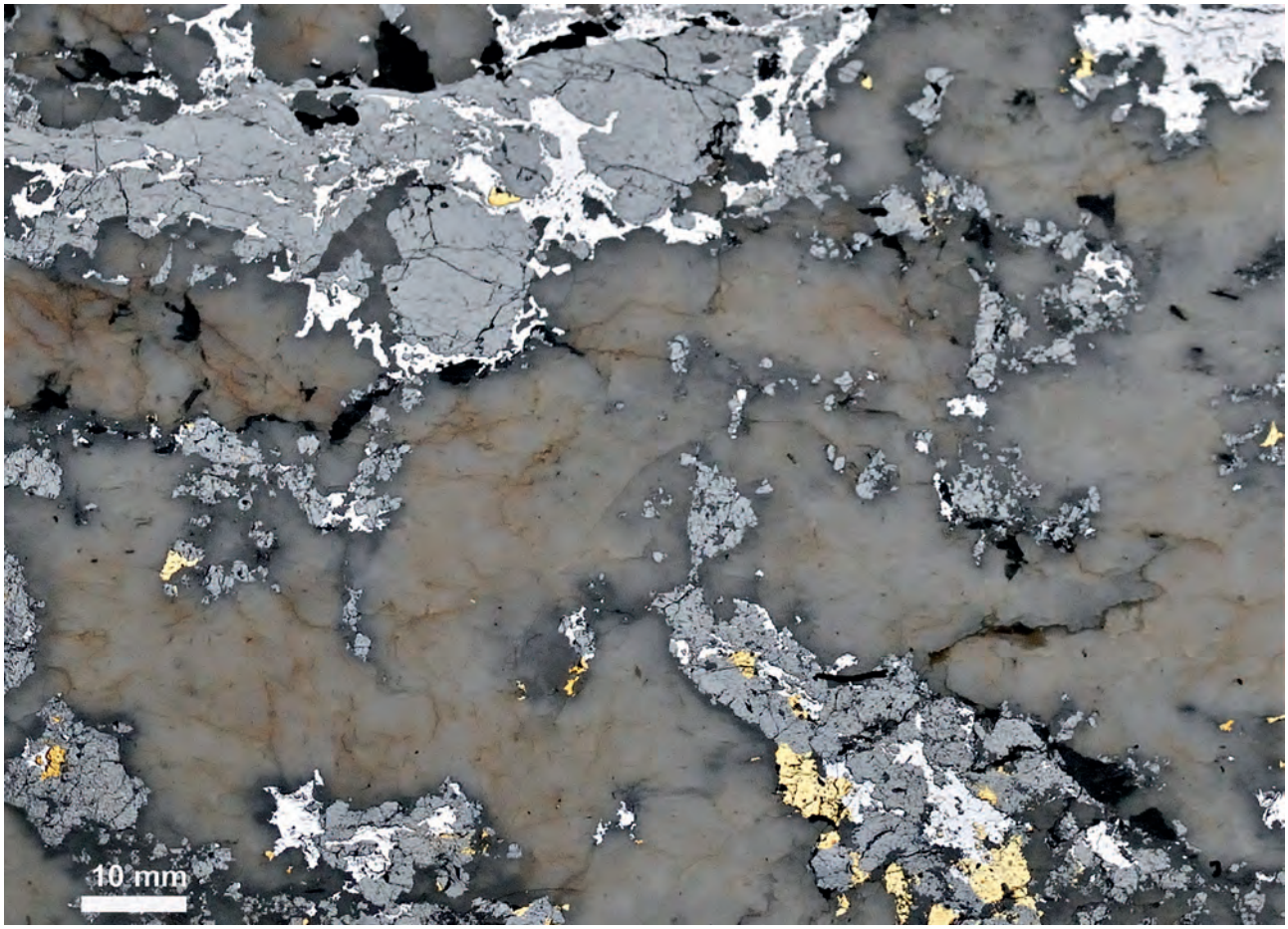

Figure 17. Polished slab of vein-quartz from Newborough Mine. Sphalerite dominates the sulphides and contains numerous galena inclusions. Chalcopyrite form inclusions in both sphalerite and galena.

On the far side of the Crimea Pass, in a remote situation some 3 km to the northwest of Blaenau Ffestiniog, lies the final mine to be described here, Moel Fleiddiau [SH 6755 4930]. An east–west lode was tried by an open-cut and adit, although nothing is known about its history or production. The mineralisation visible at outcrop consists of brecciated and quartz-veined, altered greenish grey dolerite, forming an intrusion hosted by mudstones high in the Nant Ffrancon Group. Samples from the dumps show that an early assemblage consists of pyrite and abundant, subhedral to euhedral arsenopyrite impregnating the host rock; where in contact, arsenopyrite overgrows pyrite. Brecciation of this early assemblage was followed by the deposition of abundant dark brown granular sphalerite which contains numerous microscopic inclusions of chalcopyrite, pyrrhotite and galena (Fig. 18).

DISCUSSION

One Hydrothermal Province?

The northernmost historically gold-producing locality of the Dolgellau Gold-belt is Prince Edward Mine, near Trawsfynydd [SH 7424 3854], where the mineralisation, hosted by the upper Cambrian Maentwrog Formation and associated altered sills, has a characteristic Gold-belt paragenesis, including the limited presence of high-grade gold ore, as evidenced by production figures that include 5.5 ounces of gold from a quarter of a ton of quartz in 1890 (Hall, 1990). Prince Edward Mine is less than 10 km to the south of several of the circum-caldera locations described in the foregoing text. Furthermore, along the northern flank of the Harlech Dome, to the west of Prince Edward Mine, are various small trials, on lodes occurring in Cambrian strata and sills, whose historical documentation is poor to apparently non-existent, although some are marked on older six-inch OS maps. In the vicinity of Llandecwyn, for example, the Caerwych Mine lies upstream of a BGS drainage sampling site [SH 6430 3678], where gold was identified in panned concentrates along with arsenopyrite, galena, sphalerite and pyrite (Cooper *et al.*, 1985). These localities lie only 3–4 km south of some of the sites described above.

Such proximity between these various mineralised occurrences, separated on the ground only by the drift-filled Vale of Ffestiniog, raises the following question: just where does the Dolgellau Gold-belt end and the circum-caldera mineralisation begin, if they are supposedly separate provinces? Exactly the same question can be raised regarding the circum-caldera and caldera

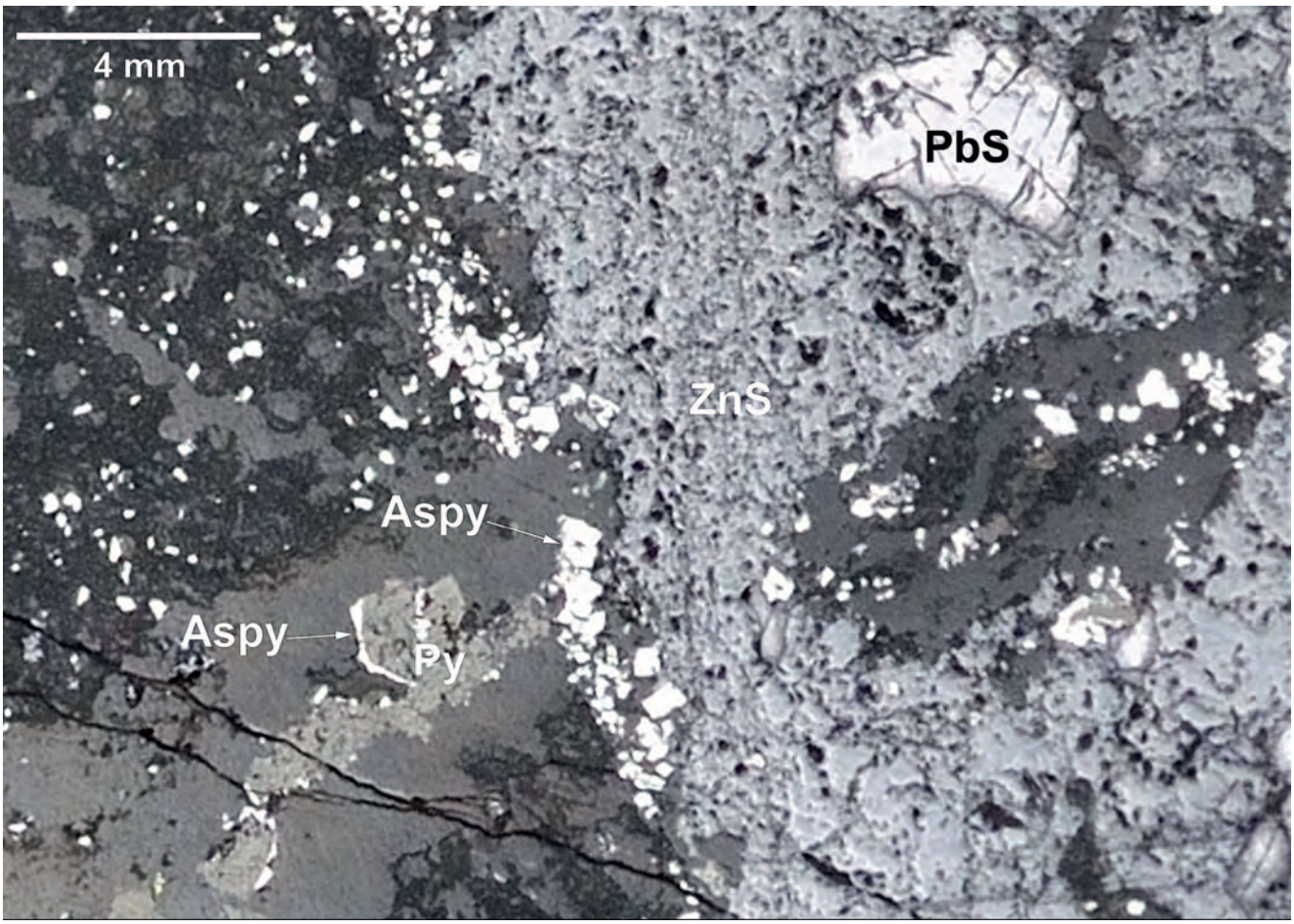

Figure 18. Polished slab of mineralisation from Moel Fleiddiau Mine. Pyrite (Py) is overgrown by arsenopyrite (Aspy) forming euhedral to subhedral crystals in quartz. This association has subsequently been cracked and brecciated with a later sphalerite cement (ZnS). The sphalerite contains inclusions of galena (PbS) plus chalcopyrite and pyrrhotite (not seen here).

lodes: the Llanberis and Snowdon mines are only about 4 km apart. But perhaps a better question, based on this study, is as follows: are the Dolgellau Gold-belt (plus Castell Carn Dochan), the Snowdon Caldera, and the circum-caldera lodes all different expressions, exposed at different structural levels, of the same regional-scale, pre-Acadian hydrothermal system? If the answer to the question is yes, then one would be contemplating a metallogenic province with an exposed surface extent of about 60×35 kilometres and mineralisation being developed through a total pre-folding stratigraphic thickness of about 5 km with lodes hosted by rocks of Lower Cambrian to late Ordovician age. If the answer is no, then explaining the distribution and apparently close timing of all of this remarkably similar lode-type mineralisation becomes more difficult.

The pre-Acadian lodes of North Wales are all problematic study subjects. Due to Acadian folding, the lodes are now situated at different structural levels than was the case when they were originally emplaced. The degree of mineral rearrangement within the lodes, due to recrystallisation, means that one cannot be absolutely certain whether some features are original or were produced as a consequence of Acadian compressive deformation. A similar problem exists with regard to fluid inclusions and the interpretation of the data obtained from them.

What one can say with more confidence is that there are several major components in the paragenetic structure whose consistent relationships with one another show that the mineralisation occurred in several successive stages. As Table 1 shows, the lodes have a remarkable commonality in terms of mineralogy and paragenesis. Early pyrite (Py) + arsenopyrite (Asp) ± cobaltite (Co), intermediate pyrrhotite (Pyrr) + chalcopyrite (Cpy) ± cubanite (Cb), pentlandite, mackinawite and millerite (Ni) and final galena (Gn) + sphalerite (Sph) ± tetrahedrite, pyrargyrite (Ag) and boulangerite (Sb) plus in all areas the presence of gold (Au), bismuth minerals (Bi) tellurides (Te) and in the Snowdon Caldera, a selenide (Se), is a strong consistency in paragenetic terms.

Pentlandite (in pyrrhotite), cubanite and mackinawite (in chalcopyrite) and tetrahedrite plus pyrargyrite and boulangerite (in/adjacent to galena) have only been recorded from the Dolgellau Gold-belt lodes. However, the identification of these species, from the Dolgellau Gold-belt alone, could plausibly be an artefact of the relatively large number (hundreds) of polished sections prepared from the lodes of the district and studied by multiple research workers since the 1960s. The author curated the J. W. G. Gilbey PhD collection, from the Dolgellau Gold-belt, in 2001 and 2002 at Amgueddfa Cymru – National Museum Wales: out of 248 repolished sections, representing 41 different localities,

District	Snowdon Caldera	Circum-Caldera belt	Dolgellau Gold-belt and areas to its east
Predominant Strike of lodes	NE–SW; NW–SE	NE–SW; NW–SE	NE–SW; NW–SE less common
Host	Cwm Eigiau Formation up to Bedded Pyroclastic Formation and associated intrusions.	Bronllwyd Grits up to upper part of Nant Ffrancon Group and associated intrusions, including Tanygrisiau Microgranite	Rhinog Formation up to Ffestiniog Flags Formation and Rhobell- and Aran Volcanic Group-related intrusions. To the east, the Aran Volcanic Group.
Paragenesis	**Py**-Asp-Co-Ag-Au-Pyrr-**Cpy**-Bi-Se-**Gn-Sph**	**Py-Asp**–Co-Ag-Au-Bi-Te-**Pyrr**-Ni-**Cpy-Gn-Sph**	**Py-Asp**-Co-**Au-Bi-Te***-**Pyrr**-Ni-**Cpy**-Cb-Ag-Sb**-Gn-Sph**
Alteration	Chlorite, sericite, sulphides, + K, Ba, F	Chlorite, sulphides	Chlorite, sericite, sulphides, + Cr and Ni
Non-metallics	Quartz, chlorite, rare carbonates	Quartz, chlorite, carbonates	Quartz, carbonates, sericite, chlorite
δ^{34}S lode sulphides	+3.7 to +22.3 0‰ CDT (average +13.0 ± 3.4‰) (Lusty *et al.*, 2017)	No data	−2.5 to +11.0‰ (Shepherd and Bottrell, 1993).
δ^{18}O lode quartz	No data	No data	+9.6 to +11‰ SMOW
Fluid inclusions	Too damaged by deformation (Lusty *et al.*, 2017).	No data	Type 1: 0–19% NaCl; <3 mol% CH_4; <1 mol% N_2; type 2: 0% NaCl; <35 mol% CH_4; <20 mol% N_2; 5 mol% CO_2; positive correlation between CH_4, N_2 and gold grade (Shepherd and Bottrell, 1993).
Age-constraints	At least partly syn-Bedded Pyroclastic Formation (Lusty *et al.*, 2017).	Post-Tanygrisiau Granite, pre-Acadian	Post-dates intrusions with Aran Volcanic Group-like geochemistry, pre-Acadian. In east: post-dates the Aran Volcanic Group.
P-T	Shallow sub-seafloor with contemporary volcanism	No data	Estimated at 320°C, pressure ca. 1.8 kbar
Previously-published model	VMS-type system involving Ordovician seawater but with little surface expression (Lusty *et al.*, 2017)	None	External metamorphic fluid interacting with mafic-ultramafic rocks at depth (Shepherd and Bottrell, 1993); gold precipitation through reaction between fluid and wall-rock graphite.

* variable Au ± Bi, Te very localised in high-grade occurrences

Table 1. Comparison of the essential features (where data are available) between the three key areas of North Wales.

pentlandite was only identified in two and tetrahedrite in nine. Smaller sample populations clearly increase the chance of missing such minerals completely.

Age-constraining of these lodes, in terms of a maximum age, gives a spread of results due to the varied ages of the host-strata. The latest date for emplacement comes from the Snowdon Caldera, where epiclasts of sulphide-bearing vein-quartz occur in tuff deposits within the Bedded Pyroclastic Formation (Lusty *et al.*, 2017), indicating contemporary vein mineralisation ongoing at high structural levels and its destruction by erosion, during Longvillian times. The Bedded Pyroclastic Formation therefore represents both the highest structural and stratigraphic level affected by the proposed regional hydrothermal system.

In the Dolgellau Gold-belt, the host rocks are mostly much older, (Lower Cambrian to late Tremadocian), but the cutting by some lodes of intrusions with non-Rhobell geochemistry, likely to be related to the Aran Volcanic Group, again implies a later Ordovician age. At Castell Carn Dochan, the lode clearly post-dates the Aran Fawddwy Formation, at the top of the Aran Volcanic Group but at a stratigraphically lower position than the Bedded Pyroclastic Formation of the Snowdon Volcanic Group.

The youngest rocks cut by the circum-caldera lodes are the dolerite at Moel Fleddiau, intruded at a high level in the Nant Ffrancon Formation, and the Tanygrisiau Microgranite. Although a precise age for the latter intrusion is not available, it was evidently cool and brittle at the time of vein emplacement. Data from other similar North Wales intrusions and their metamorphic aureoles indicate a late Ordovician (Caradoc) origin for the thermal metamorphism. Later (Devonian) regional metamorphism has variably reset the Rb-Sr isotopic systems in the microgranites themselves (Evans, 1990).

All of these data therefore raise the possibility that this whole district of North Wales comprises a single, pre-Acadian metallogenic province and that the lode mineralisation was emplaced close to, during or shortly after Caradoc (Longvillian) times, so that younger Ordovician sedimentary rocks were not affected by the mineralising event. The switch during late Ordovician times from a destructive Avalonia-Iapetus plate boundary to a regime of sinistral transtension, during which widespread incremental extensional fracturing would be expected, is consistent with this hypothesis.

The Gold Problem

The outstanding difference between the Dolgellau Gold-belt and the lodes both within and around the Snowdon Caldera is the very localised occurrence, apparently in the Gold-belt alone, of bonanza-shoots of extremely high-grade ore in which visible gold is abundant and which accounted for all significant production. Castell Carn Dochan was a relatively minor deposit with worthwhile gold grades encountered at times (production figures in Hall, 1990), but it does not feature bonanza-type mineralisation *sensu stricto*. The visible gold-bearing quartz, in contrast, can be extraordinarily rich: the author has seen ore, raised at Clogau in the early 1980s, in which gold was present at percentage levels. Historically, the most profitable mining companies were those who carefully followed such visible gold-shoots and hand-picked the ore. Hall (1990) cited one such example, again at Clogau Mine:

> "During the six months to March 14th 1892 a total of 78 fathoms of ground were worked away and 289 tons of rock brought out of the mine, of which 25 tons 18 cwt crushed yielded 1,636 ozs [of gold] worth £5,776. Costs for the period were but £1,075."

That amount of gold, obtained in just a few months, is not far short of the entire recorded production of Castell Carn Dochan Mine, over the eight years in which gold sales were declared there. In addition, it significantly exceeds the entire produce of many of the other Gold-belt mines, some of which were worked over many years. Furthermore, there are numerous unsuccessful trials in the Gold-belt and there were a considerable number of historical ventures that, despite high levels of investment and work done, were abject failures. There was, at the time, a stubbornly held belief that bulk lode-stuff could be made to pay, regardless of its geological setting (Hall, 1990). Geochemical data clearly refute that belief, although they confirm the widespread, regional nature of anomalously high gold levels.

In the Snowdon Caldera lodes, gold is likewise frequently present in anomalous quantities but the grade is mostly <1 gram per ton, with the gold occurring as scattered microscopic inclusions within sulphides (Lusty *et al.*, 2017; Tim Colman, *personal communication*). A series of 24 assays of grab-samples from mine tips in both the Gold-belt and the circum-caldera district, collected by Carnon Holdings in the 1980s, likewise reveals that gold grades are mostly below 1 gram per ton, although arsenic and base-metals range up into percentage levels (data provided by BGS). More tellingly, figures provided by Dominy *et al.* (2001) from Gwynfynydd Mine, show that, even in the close vicinity of high-grade visible gold-shoots, large parts of these lodes, heavily mineralised with base-metal sulphides as they are at that locality, may contain only 0.5 gram per ton of gold or less. Therefore, throughout North Wales, but away from the geologically constrained high-grade shoots, gold is always present in these pre-Acadian lodes, but at much lower concentrations, throughout the bulk of the mineralisation.

In the Gold-belt, the very localised high-grade gold-shoots are both spatially and genetically associated with black, organic and sulphide-rich hemipelagic mudstones and associated intrusions within the Middle to Upper Cambrian Clogau and Maentwrog formations, especially the former. The Clogau Formation represents the oldest known occurrence of black hemipelagite in the local stratigraphic column and therefore was the first to be encountered by rising auriferous hydrothermal fluids: essentially, it has acted as a gold-trap (Bottrell *et al.*,

1988; Shepherd and Bottrell, 1993). No such hemipelagites are known from the equivalent part of the Cambrian sequence of the Arfon Terrane where, due to a different sedimentary history at the time (Howells *et al.*, 1985), coarse siliciclastic sediments instead prevail. Likewise, black, Clogau-type hemipelagites are absent from the much younger Snowdon Caldera stratigraphic sequence. To the immediate south and southwest of the caldera, beyond the Arfon-Megumia terrane boundary, the Clogau Formation should be present, but will be mostly at a substantial depth beneath present day erosion levels. If the hypothesis of Bottrell *et al.* (1988) is correct, and it would be extremely difficult to account for the spatial distribution of high-grade gold-shoots within the lodes if it were not, then that absence (or inaccessibility in mining terms) of these black, organic and sulphide-rich mudstones in the other parts of this proposed single mineralised province becomes a critically limiting factor.

The richest gold deposits, with yields exceeding 1,000 ounces (Clogau, Cefn Coch, Gwynfynydd, Castell Carn Dochan), all lie within a northeast–southwest trending zone parallel to and within 10 km of the trans-crustal Bala Fault. The relevance of this apparent confinement is uncertain. Much of the Gold-belt is poorly-explored in modern terms so one possibility is that further significant gold deposits remain undiscovered outside of this zone. However, the occurrence of major lode-gold deposits along second- and third-order faults spatially adjacent to first-order, trans-crustal fractures is a well known global phenomenon (e.g. Groves *et al.*, 1998).

Fluid Origins

With the exception of the relatively high structural level Snowdon Caldera, where convectively circulating late Ordovician seawater may well have had a role, the source for the colossal volumes of hydrothermal fluids required to create a hypothesised late Ordovician metallogenic province of this size is an interesting problem. It can be assumed that the deformed late Neoproterozoic basement lying beneath the unconformable base of the host strata was either water-poor in the first place (igneous rocks) or significantly dewatered (sedimentary rocks) by the time of lode emplacement. Likewise, the Cambrian sedimentary sequence, at least in the Dolgellau Gold-belt, had been folded, widely faulted and multiply intruded around the time of the Rhobell volcanism. Neither are therefore especially promising as potentially copious fluid sources at the relatively low metamorphic grade that would have prevailed at the inferred time of mineralisation; peak metamorphism in North Wales was probably close to the time of Acadian cleavage-imposition and the widely reported resetting of the Rb-Sr isotopic system (Howells *et al*., 1997). The same point applies to the Ordovician sedimentary rocks of the district: if the inferred late Ordovician age for the mineralisation is correct, then dewatering would have peaked with metamorphism some tens of millions of years later. Therefore, alternative fluid sources need to be considered.

A subduction-related fluid source, involving the dehydration and release of metals in the subducting Iapetus oceanic crust and its sediment cover and/or the dehydration of the overlying metasomatised mantle wedge, cannot be ruled out as at least a contributor to the mineralisation. Such processes, widely cited in the case of orogenic gold deposits for more than twenty years (e.g. Groves *et al.*, 1998; Groves, 2019) would certainly provide sufficient fluids to mineralise an entire region in one event, as has apparently happened in this case. Orogenic gold deposits characteristically post-date the mountain-building, main kinematic phase of orogenesis, by up to 100 million years in some cases (e.g. Gaboury, 2019). The suggested maximum age of the mineralisation described herein is some 32 million years after the beginning of the Tremadoc and the accompanying Monian deformation, and 24 million years after the deformation and arc-volcanism of the Rhobell episode. Therefore, the mineralisation would be late orogenic with respect to that sequence of disturbances.

There are, however, important differences between many of the lodes described here and the many described low-sulphidation orogenic gold ("gold-only") occurrences, in which Cu, Pb and Zn sulphides are generally unimportant. The bonanza-shoots of gold plus tellurides at Clogau Mine, however, are clearly low-sulphidation deposits, as is the gold mineralisation at Castell Carn Dochan, with galena, chalcopyrite and sphalerite being minor phases there. One possibility, deserving of further investigation, is that there is an orogenic gold element to these veins but with heavy base-metal mineralisation being present at some localities as a paragenetically later overprint due to repeated fracture reactivation, in a broadly analogous fashion to that described by Molnár *et al*. (2017), from the Central Lapland Greenstone Belt, Finland, where both "gold-only" and gold-copper deposits are present.

Significant, in some cases tenfold addition of Cr and Ni to lode-proximal sills at Clogau (Bottrell, 1986) and that author's interpretation that the hydrothermal fluids must have interacted at an unknown depth with mafic or ultramafic rocks, implying a deep-seated fluid source, seems relevant to this discussion. No Cr + Ni-rich rocks are exposed within the Gold-belt: where distal to Gold-belt lodes, the Rhobell intrusive suite consistently contains relatively low levels of both, whether affected by earlier alteration events or not (Kokelaar, 1986; author's unpublished data). Again, this brings up the possibility of the fluids having originated at a sub-crustal level, since it is the one of few deep-seated settings where large volumes of fluids can be generated, during the subduction process.

Clearly, further work is required in order to address the points raised above. However, any planned investigation would need to first take into account that these lodes have all undergone Acadian strain-related recrystallisation, placing limitations on the techniques that may be applied.

Comparison with Neighbouring Mining Districts

The Bala Fault separates the districts described above from two other historically important orefields whose earliest mineralisation dates back to a time close to the Acadian Orogeny: Central Wales and Llangynog. The Llangynog Orefield is poorly understood and deserving of a detailed study, but it at least appears to have a similar paragenetic structure to Central Wales, with early polymetallic mineralisation in quartz-cemented breccias followed by later, less diverse crustiform deposits. Central Wales, where multiphase lode mineralisation is hosted by late Ordovician to early Silurian turbidite sequences, is better understood, in terms of the mechanism of deposit formation (Phillips, 1972; James, 2011), paragenesis (Mason, 1997) and timing (Fletcher *et al.*, 1993). In broad terms, an early polymetallic phase of mineralisation of mid-Devonian age and close to or closely following peak Acadian deformation, was followed by intermittent episodes of often crustiform veining, with productive but non-diverse mineral assemblages, from early Carboniferous through to Permo-Triassic (and possibly later) times.

In Central Wales, lead isotope evidence (Fletcher *et al.*, 1993) indicates fluids tapped the same lead-source multiple times, that source being the well mixed, multicycled sediments of the Welsh Basin, strata that have a thickness of around four kilometres, above the top of the Ordovician volcanics. The older basin-fill beneath that depth would have also been a likely contributor, the fluids that deposited the early polymetallic mineralisation being generated by metamorphic dewatering of the post-Tremadoc basin contents. Later periods of mineralisation, with their non-diverse mineralogy and vuggy, crustiform textures, suggest development in an intermittent extensional tectonic regime both prior to and following the Variscan Orogeny, and may be connected to both the Irish early Carboniferous Pb-Zn and the late Palaeozoic to early Mesozoic, widely developed Mississippi Valley type mineralising events.

The early polymetallic Central Wales mineralisation most closely resembles the pre-Acadian lodes of North Wales but it is far less deformed: any recrystallisation is localised and can be readily attributed to local compression and shear during movements along often sinuous faults. In addition, there are important geochemical differences. Although the early mineralisation of Central Wales is auriferous (<0.5 ppm Au), it also contains locally common Co and Ni minerals that may be visually conspicuous. Analyses of grab-samples of mineralisation from mine-tips have shown that combined Ni-Co grades frequently exceed 500 ppm, exceptionally reaching 2% or more (Mason, 1997). The latter levels are far higher than any seen in the North Wales lodes with maxima of 738 ppm Co and 134.8 ppm Ni reported from analyses of 82 Snowdon Caldera ore-samples (Lusty *et al.*, 2017). A series of 17 analyses of sulphide-rich lodestuff, collected during exploration at Prince Edward Mine in the Dolgellau Gold-belt in 1998 (Cambrian Goldfields Ltd, unpublished data) showed Ni-Co combined levels did not exceed 250 ppm and were mostly much lower. Thus, despite the addition of Ni to the wall-rocks at Clogau, and the general presence of minor cobaltite in the pre-Acadian lodes of North Wales, the Central Wales Orefield is a much richer repository of these two metals.

Similarly, silver is much more important in the early mineralisation of Central Wales than in the majority of the North Wales lodes, with historic grades in lead concentrates approaching 1000 ppm at some mines; tetrahedrite is widespread and a major silver carrier. Conversely, data from the Snowdon Caldera ore samples show silver enrichment to be modest with a maximum value of 200 ppm (Lusty *et al.*, 2017). In the circum-caldera lodes and Dolgellau Gold-belt, the Carnon Holdings assays had a maximum silver grade of 128 ppm, although base-metals in the same sample run into percentage levels (data provided by BGS). Tetrahedrite is uncommon in the Dolgellau Gold-belt, with one unusual and to date unexplained exception, Tyddyn Gwladys Mine in the Mawddach Valley (Mason *et al.*, 2002). The mineral has not to date been recorded from either the Snowdon Caldera or circum-caldera lodes.

In the early Central Wales ores, antimony concentrations exceed those of arsenic, typically by an order of magnitude, whereas in the Snowdon and Prince Edward Mine datasets the exact reverse is the case. Bismuth is close to detection limits in the Central Wales ores (author's unpublished data) whereas in the Snowdon Caldera analyses, Bi averaged 242 ppm with a maximum of 3885 ppm (Lusty *et al.*, 2017). The Prince Edward Mine dataset shows Bi values not exceeding 178 ppm, but at some Gold-belt mines, especially Clogau, bismuth tellurides occur visibly in hand specimen associated with native gold. Finally, pyrrhotite, near-ubiquitous in the pre-Acadian lodes of North Wales, is extremely rare in Central Wales. These observations serve to emphasise the differences between the two metallogenic provinces and are likely to be indicative of different sources for both fluids and metals.

CONCLUSIONS

Differing strongly in their chemistry and probable emplacement age from nearby mining districts such as Central Wales, the pre-Acadian lodes of the Dolgellau Gold-belt, Castell Carn Dochan, the Snowdon Caldera and the circum-caldera districts have a near-identical overall paragenetic structure. Such commonality would be difficult to explain in these closely adjacent areas without a single, regional hydrothermal system being responsible for the mineralisation. Lode development evidently occurred in all four districts either during or shortly after the cessation of late Ordovician (Longvillian) volcanism: younger Ordovician sedimentary rocks are apparently unmineralised. High-grade gold mineralisation, locally well-developed in the Dolgellau Gold-belt, is tightly constrained by

lithogeochemical factors only present and accessible in that district and also, more speculatively, by proximity to the Bala Fault. Further detailed research is required, firstly to test the presented hypothesis and secondly, given the present understanding of orogenic gold deposits, to determine what, if any, role was played by the Iapetus subduction zone and the changes that took place therein, at approximately the same time as the emplacement of the mineralisation.

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LEAD MINERALISATION WITHIN THE STUBLICK FAULT SYSTEM AT CHURCH BURN AND WOLF HILLS, HALTWHISTLE, NORTHUMBERLAND

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Two hitherto unreported small clusters of lead-bearing veins and associated workings at Church Burn and Wolf Hills, south of Haltwhistle, described here, add to the group of mineral deposits within the main Tyne Valley, sometimes collectively referred to as the Haydon Bridge Orefield. Long regarded as an outlying portion of the Northern Pennine Orefield, with which they share close structural and mineralogical similarities, these deposits are separated by approximately 15 km of barren ground from the nearest mineralisation in the orefield and lie adjacent to the Stublick Fault, part of the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System. This major fault belt acted as a syn-sedimentary 'hinge zone' during Carboniferous times resulting in the accumulation of substantially greater thicknesses of Carboniferous sediments in the Northumberland–Solway Basin than on the Alston and Lake District blocks to the south. Similar base metal and barium mineralisation is common within a narrow belt along this structural line from coast to coast. It is suggested that the Church Burn and Wolf Hills mineralisation adds further weight to the hypothesis that this belt of mineralisation is both structurally and genetically related to the development of this major Carboniferous fault line. Also reported here is the first reliable record of plumbojarosite from a Pennine location.

INTRODUCTION

Substantial tonnages of galena, witherite and subordinate amounts of sphalerite and baryte have been worked from veins in Carboniferous and Whin Sill wall-rocks at several mines in the Tyne Valley between Haltwhistle and Hexham. The most prominent of these were at Langley Barony, Stonecroft, Greyside, Settlingstones, and Fallowfield, the latter two being most celebrated as major world sources of witherite. Very much smaller quantities of these minerals were also raised from a handful of smaller mines and trial workings. The geology and mineralisation of all of these deposits have been well documented by Wilson *et al*. (1922), Smith (1923) and Dunham (1990).

The workings and explorations for lead ore at Church Burn and Wolf Hills south of Haltwhistle, described here, are remarkable for having hitherto escaped published description despite, in the case of Church Burn, being comparatively conspicuous within the local landscape. The sole reference to lead mineralisation at Church Burn is the depiction of a single NNE–SSW trending lead-bearing vein on the 1:50,000 scale BGS sheet 19 (Hexham) (British Geological Survey, 1975). No evidence of mineralisation at Wolf Hills is depicted on this map.

The mineralised veins of the Tyne Valley downstream from Haltwhistle have traditionally been regarded as an outlying expression of Northern Pennine mineralisation, referred to by Dunham (1990) as the Haydon Bridge portion of this orefield. However, this cluster of deposits is separated from the main concentrations of Northern Pennine mineralisation by at least 15 km of ground in which mineralisation is conspicuously absent, and it is notable that the veins lie close to, and mostly within, the hanging wall zone of the Stublick–Ninety Fathom Fault System of fractures which, together with its westerly extension in Cumbria, the Maryport–Gilcrux Fault, defines the boundary between the structural units of the Lake District and Alston blocks and the Northumberland–Solway Basin. The Church Burn and Wolf Hills deposits lie within the footwall of this fault zone.

Drawing upon the few surviving historical documentary sources and the results of recent field surveys and mineralogical investigations, the geology and mineralisation of the Church Burn and Wolf Hills veins are described and their relationship with the deposits of the main body of the Northern Pennine Orefield are discussed. As these deposits add to the numerous known mineralised sites along the length of the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System, the hypothesis that this belt of mineralisation may be structurally and genetically related to this major Carboniferous fault line is also explored.

Within the following text, reference will be made to the individual sections of the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System relevant to the area being discussed: use of the structure's full name will be reserved for discussion of the full regional context.

GEOLOGICAL SETTING

Church Burn and Wolf Hills lie on the northern flanks of the Alston Block, a major structural unit composed of Lower Palaeozoic rocks, including the granite of the Caledonian North Pennine Batholith, which is overlain unconformably by a comparatively thin cyclothemic succession of Carboniferous sediments. The block is separated from the Northumberland–Solway Basin on its northern side by the east–west trending Stublick–Ninety Fathom Fault System, a complex fault zone which was active during Carboniferous times, allowing the accumulation of very much greater thicknesses of similar Carboniferous cyclothemic sediments in the basin than on the adjoining block (Fig. 1).

The sites described here lie on the outcrop of the succession of Carboniferous rocks formerly known and

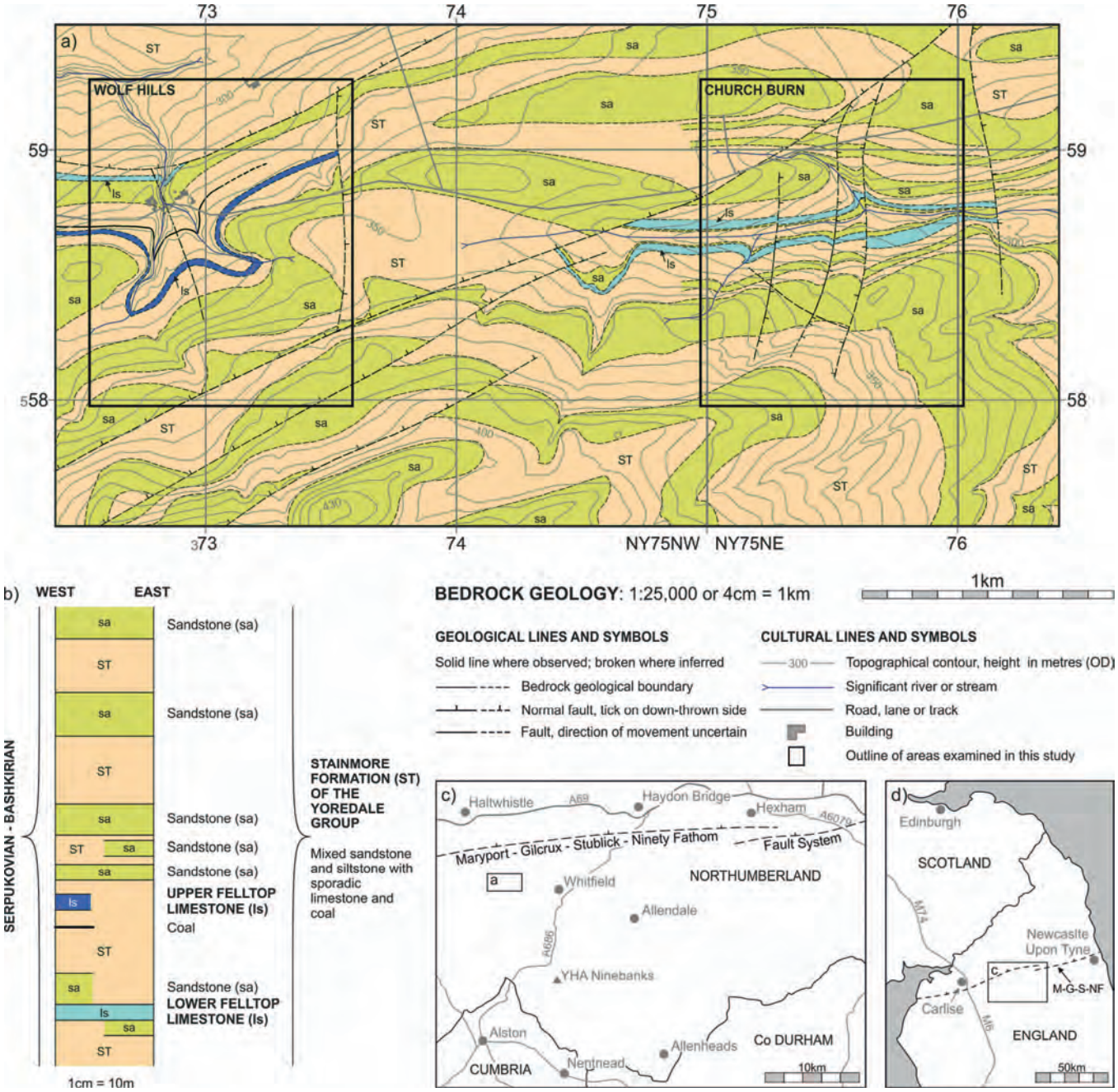

Figure 1. Geological map, section and location maps. a). Bedrock geological map showing key faults and veins, with the locations of the two studied areas, Church Burn (Fig. 2) and Wolf Hills (Fig. 10), indicated. b). Generalised vertical section for the map showing the relative positions of the Lower and Upper Felltop limestones. c). Index map showing principal settlements, with the position of the geological map (a) indicated with respect to the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System. d). The position of the index map (c) in the UK. The contraction M–G–S–NF refers to the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System.
Bedrock geology based on mapping by S. M. Clarke and C. Vye-Brown (2004) with modifications by the present authors. Some veins and workings derived from mine plans. CP20/021 British Geological Survey © URKI 2020. All Rights Reserved.

depicted on the current 1:50,000 Hexham Sheet 19 as the Upper Limestone Group (British Geological Survey, 1975) but today classified as the Stainmore Formation of the Upper Carboniferous Yoredale Group (Stone *et al*., 2010). Here, as in much of the Northern Pennines, these comprise a cyclothemic succession of mudstone, siltstone and numerous sandstones with a few thin and generally impure limestones and locally some thin coals. South of Haltwhistle, these rocks dip gently towards the south and east within the footwall zone of the Stublick Fault.

Within the Stublick Fault System and approximately 4 km northwest and 2 km north of Church Burn and Wolf Hills, respectively, small east–west elongated fault-bounded outliers of Upper Carboniferous Coal Measures rocks, which comprise the Midgeholme and Plenmeller coalfields, reflect post-Carboniferous movement of this fracture system.

An extensive mantle of superficial deposits, mainly of Quaternary age, conceals substantial parts of the bedrock geology though low scarp features, which locally mark the outcrops of sandstones within the Stainmore Formation, constrain the main geological features.

CHURCH BURN MINE

Church Burn Mine comprises a series of long-abandoned workings on a set of mineralised faults within Stainmore Formation rocks on Agarshill Fell, on the south side of the Tyne Valley, approximately 6 km southeast of Haltwhistle, centred around old dressing floors at NY 7532 5869.

Mapping within the headwaters of the Church Burn reveals a limestone, tentatively correlated with the Lower Felltop Limestone, on both sides of the burn, overlain and underlain by a series of sandstones that form prominent ridges, interbedded with siltstones. These rocks are cut by three roughly north–south to NNE–SSW trending faults (Fig. 2). The two western fractures exhibit small throws of only a few metres to the east. The easternmost fault throws down a few metres to the west. In addition to the comparatively conspicuous displacement of surface features, the course of the two western faults is traceable on the ground from the

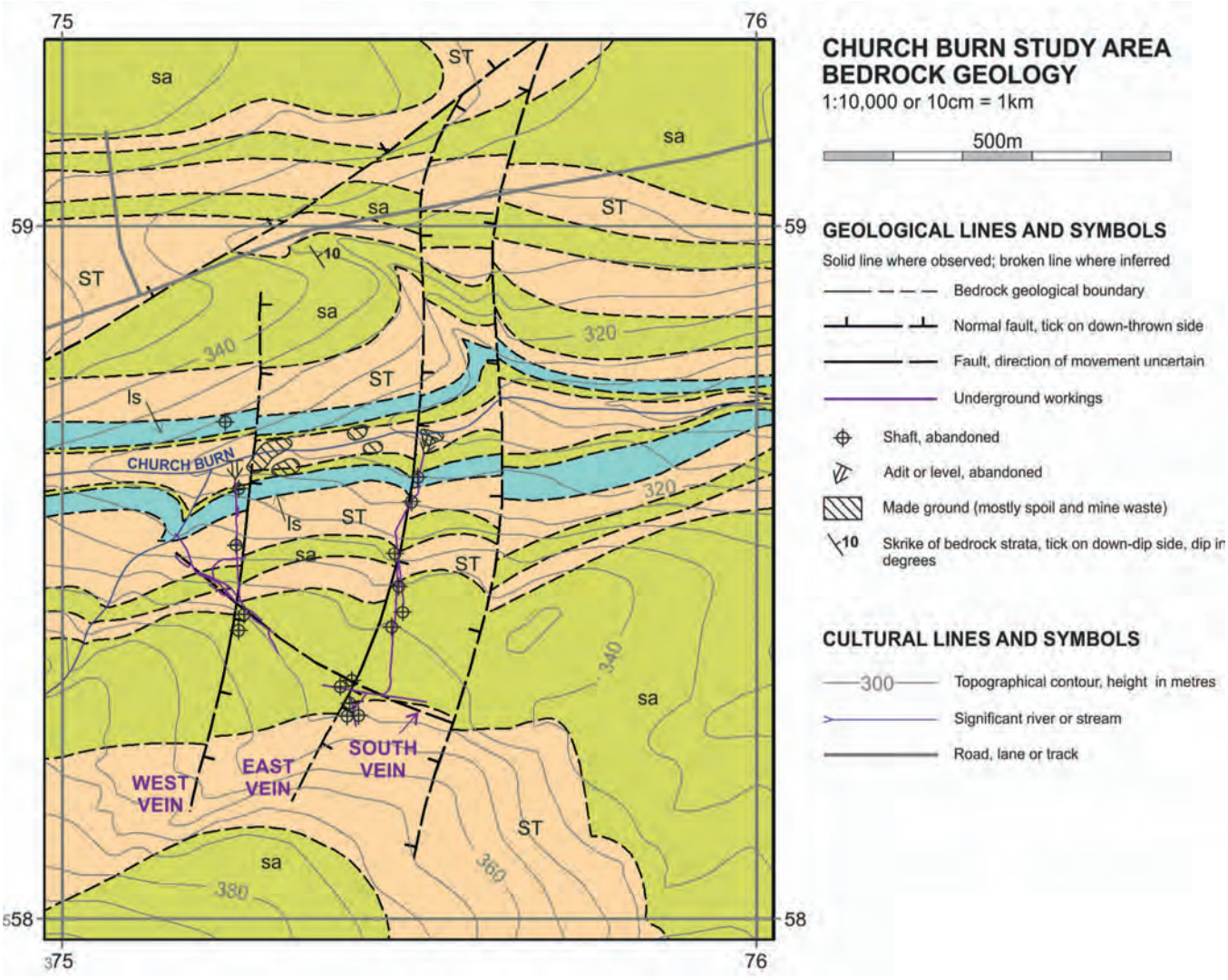

Figure 2. Surface geology of Church Burn study area based on mapping by S. M. Clarke (2004) with underground workings derived from mine plans. For key to the bedrock geological colours see Figure 1. CP20/021 British Geological Survey © URKI 2020. All Rights Reserved.

position of collapsed adit levels and several small spoil heaps from surface shafts sunk on, or close to, their outcrops. It is clear from material remaining on the small adjacent dumps that the two western faults carry lead mineralisation. For convenience of description the mineralised faults are identified here as the Church Burn West and Church Burn East veins. No signs of working are associated with the easternmost fault and there is no evidence of any mineralisation associated with it.

Three mine plans dating from 1854 and 1884, held by the North of England Institute of Mining and Mechanical Engineers, record levels driven on both the West and East veins in beds beneath the sandstone that immediately underlies the Lower Felltop Limestone. On the plan of the workings in the East Vein, this sandstone unit is identified as the 'High Slate Sill'. In addition, both plans depict a roughly WNW–ESE trending vein, identified on the 1854 plan as the 'Principal Vein', which for convenience of description in this account we refer to as the South Vein. This vein has no obvious surface expression.

The following descriptions of the Church Burn veins are derived from these plans together with recent field observations of surface features. As none of the veins is exposed at the surface and all of the underground workings are inaccessible, the descriptions of the content of the veins are necessarily based upon material present on the numerous small, though much overgrown, spoil heaps.

Church Burn West Vein

A plan entitled 'Plan of Church Burn Lead Mines in the Parish of Whitfield belonging to William Ord Esq., surveyed by John Nevin in September 1854', shows a level driven south towards this vein from the southern bank of the burn [NY 7525 5863]. However, as substantial parts of the plan covering this part of the workings are missing, it is unclear how extensive these workings may have been at that time. A later plan entitled 'Church Burn Lead Mine. Whitfield, County of Northumberland', attributed to the Church Burn Mining Co. Ltd, and dated July 1884, is complete and shows this level driven 267 m south to its intersection with the South Vein. Neither plan contains any indication of the throw of the vein or of its width, wall-rock or contents. However, a small rise of unknown height at 60 m from the portal, depicted on the 1884 plan, may indicate some exploration of the vein above the level at this point. A small area of stoping of unrecorded, but almost certainly very small extent, is also recorded between 84 and 108 m inbye from the portal. The plan also notes a small roughly east–west 'string', though without further description, at 144 m inbye.

Dumps from the level lie on both sides of the burn and are likely to include material derived from both the West and South veins (Fig. 3). They are composed mainly of grey fissile siltstone and sandstone accompanied by

Figure 3. The collapsed entrance to the level on the West Vein lies immediately to the right of the large boulder (centre left). Unvegetated dumps from the level lie on both sides of the burn. The figure stands on the site of the dressing floors. Photo Brian Young.

fragments of coarse-grained crystalline galena up to several centimetres across, associated with some of which are rare anhedral grains of chalcopyrite up to a few millimetres across. One block of the distinctive 'steel ore' variety of galena, indicative of post-mineralisation shearing, was found.

Supergene minerals are present in small amounts. The most abundant of these is cerussite, $PbCO_3$, which typically occurs as greyish white compact crystalline or earthy crusts on galena fragments and may, at least in part, be of post-mining origin (Fig. 4). A few specimens of such deeply altered galena, in which tiny chalcopyrite grains are also present, exhibit thin crusts of microcrystalline vivid deep blue linarite, $PbCu^{2+}(SO_4)(OH)_2$,

Figure 4. Galena with superficial crusts of cerussite. Specimen is 7 cm across. Brian Young specimen, No. BY8055/A. Photo Andy Hopkirk.

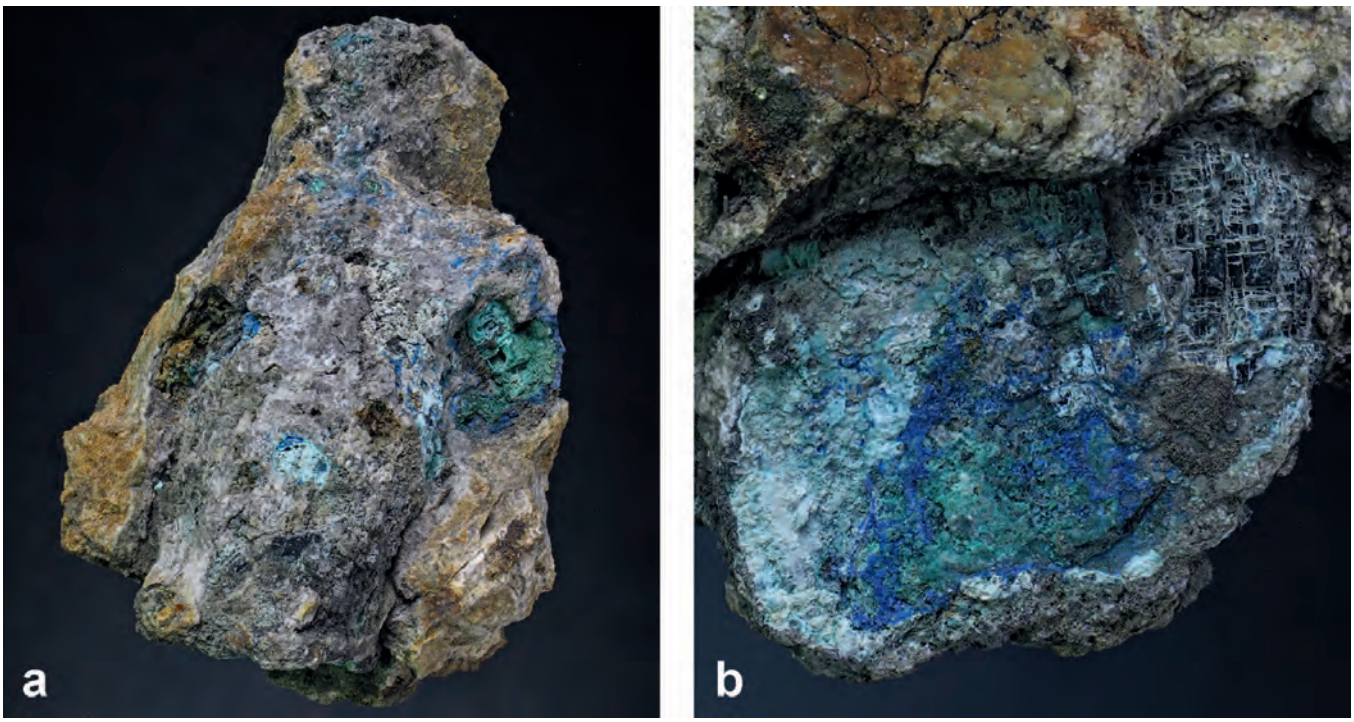

Figure 5. a). Crusts of microcrystalline blue linarite and green malachite on grey cerussite coating galena. Specimen is 7 cm across. b). Detail of the specimen shown in (a) showing microcrystalline linarite with minor malachite coating cerussite on altered galena. A rectilinear network of pale grey cerussite, developed along cubic cleavage planes of galena, is conspicuous at the top right. Field of view 1 cm. Brian Young specimen, No. BY8055/A. Photos Andy Hopkirk.

and bright green malachite, $Cu_2^{2+}(CO_3)(OH)_2$, up to a few millimetres across (Fig. 5).

Yellowish buff earthy coatings, up to several centimetres across, on galena from this dump were identified by a combination of powder X-ray diffraction and energy dispersive X-ray analysis as the rare lead-iron sulphate hydroxide mineral plumbojarosite, $PbFe_6^{3+}(SO_4)_4(OH)_{12}$, (David Green, *personal communication*, 2006) (Fig. 6). The sole previous record of this mineral from a Pennine location is that from Grassington Moor, Yorkshire (Kingsbury, 1965; Dunham and Wilson, 1985). However, in view of serious doubts over the true provenance of many of Kingsbury's records, including those from Grassington (Ryback *et al*., 1998, 2001; Green and Briscoe, 2002) the presence of this mineral at Grassington cannot be reliably confirmed. The identification of plumbojarosite at Church Burn Mine may therefore be regarded as the first reliable record of this mineral from a Pennine location.

Apart from a few coatings of compact crystalline baryte up to about 3 mm thick on sandstone, and rarely some similarly thin coatings of quartz, no gangue minerals were noted in this spoil. None of the baryte or quartz was found in association with sulphides. Gangue minerals thus appear to be extremely rare in these veins.

Recent mapping identified the presence of several old shafts along the length of this vein (Fig. 2), but their associated small dumps are overgrown and most reveal no evidence of any of the rocks or minerals penetrated. A single shaft near the access track north of the burn [NY 7523 5873] almost certainly marks an unsuccessful trial of this vein.

Church Burn East Vein

The 1854 plan depicts a level [NY 7552 5869] driven south on Church Burn East Vein from the southern bank of the burn for 362 m to its intersection with the South Vein. Apart from a single note stating that the level is driven beneath the High Slate Sill, the plan provides no information on the nature of the vein or its wall-rocks. From its intersection with the South Vein the level turns to follow that vein for around 20 m, whence it returns to its roughly NNE–SSW bearing, presumably following the continuation of the East Vein, suggesting that this vein may be displaced westwards by around 20 m by the South Vein. The drive appears to terminate after a further 100 m after passing through a cross vein of unrecorded

Figure 6. Pale buff crusts of plumbojarosite on galena. Specimens are each 6 cm across. Brian Young specimen, No. BY8056/A & B. Photo Andy Hopkirk.

throw and two closely spaced veins recorded as the Sun No. 1 and 2 veins, though the plan records no other information on these. No stopes are shown on any of these drives.

The small overgrown dump on the southern side of the burn, derived from the level, contains much sandstone and fissile siltstone together with small fragments of compact crystalline pale grey cerussite, some of which have residual cores of unaltered galena. A few fragments of brecciated sandstone on this heap contain coatings of scaly white kaolinite though, as none of this is associated with ore or other gangue minerals, it is not clear whether this is a minor gangue or an authigenic mineral within the sandstone and thus unrelated to the metalliferous mineralisation. No other gangue minerals have been seen here.

There is no evidence of any trials on this vein north of the burn.

The small dumps from several shafts along this vein, south from the level dump are completely overgrown (Fig. 7) and, except for the dump at NY 7547 5843 where fragments of galena much altered to cerussite are common together with traces of malachite and linarite, no wall-rock or vein minerals can be seen.

A small cluster of old shafts centred on NY 7542 5832 appears to coincide with the intersection of the East and South veins and may indicate that some ore was obtained hereabouts from unrecorded workings above the level. Spoil on what appears to be an old sorting area contains abundant small fragments of galena, much of it considerably altered to cerussite. A few fragments of brecciated sandstone exhibit small patches of scaly white kaolinite but, as in the previously mentioned level dump, it is unclear whether this was part of a meagre gangue assemblage or an authigenic mineral. A few blocks of sandstone breccia cemented by brown-weathering calcite here contain rare scattered anhedral grains of chalcopyrite up to around 2 mm across (Fig. 8). Apart from this, no other gangue minerals have been observed here suggesting that, as with the West Vein, gangue minerals are extremely rare. A few blocks of pale buff limestone, which weathers to dark brown and contains conspicuous crinoid and shell fragments, are incorporated into a wall surrounding the shaft, suggesting that the shaft may have reached or penetrated the Lower Fell Top Limestone. These blocks offer the only convincing evidence that this limestone was reached in any part of the Church Burn workings.

Figure 7. Looking north along the outcrop of the East Vein showing overgrown shaft dumps. Photo Brian Young.

Church Burn South Vein

Church Burn South Vein is known only from the mine plans and has no obvious surface expression. Its position and extent on the geological maps (Figs 1 and 2) are based on subsurface data and it must be considered in this light.

Whereas the vein was encountered in the level driven on the East Vein, as noted above, there is no evidence of any development or significant exploration of it from that point.

The 1884 plan shows drivages of up to 168 m northwest and 108 m southeast along the vein from the head of the level on the West Vein, though no indication of its throw, width, wall-rock or mineral content are recorded. The westerly bend in the level that follows the East Vein, and the displacement of the East Vein that this implies, suggests a southerly throw for the South Vein, though in the absence of conclusive evidence in this regard, no direction of movement for the south Vein is indicated on the geological maps (Figs 1 and 2). The plan also depicts the positions of internal shafts and sumps and shows a sub-level approximately 4 m below the main level, reached by a 6 m deep sump sunk in the South Vein. A section on this plan shows small stopes up to 111 m long and up to 3 m high in this vein northwest of its intersection with the West Vein above both the main

Figure 8. Calcite-cemented sandstone breccia. The cementing calcite contains a few tiny grains of chalcopyrite, though none is visible in this photograph. Photo Brian Young.

level and sub-level (Fig. 9). Although the section includes no guide to the notation used, the blue colouring used for the lowest levels may follow the convention of some northern Pennine plans and indicate that it was driven in limestone, which in this instance would be the Lower Felltop Limestone, though insufficient information is contained in the plans to be confident of this. It is likely that most of the mine's modest recorded output of lead ore was obtained from these stopes. A small area of subsidence above these stopes, indicated on the plan, is not obvious at the surface today.

Mining History and Output

Apart from the mine plans discussed above and a single record of output for the years 1854 and 1884, we have been unable to trace any other references to working at Church Burn.

The 1854 plan shows a 'shop' adjacent to the level entrances on both the East and West veins, though without any indication of sorting or dressing facilities. The 1884 plan depicts only the first 140 m of the East Vein level, suggesting that by then it was impassable beyond that point and was not considered worthy of reopening or of further exploration. It seems probable that the mine lay unworked between 1854 and 1884, though the extent or date of any exploration between those years is unknown. However, the surface arrangements for ore dressing depicted on the 1884 plan, including a 12 bay set of bouse teams, adjoining sorting area with knock stone, bingstead, dressing house with waterwheel and settling pits and buddles, appear to indicate an optimistic view of the enterprise that was plainly not realised.

Although the plans record horizontal drivages on all three veins the few modest attempts to explore the veins in beds both above and below the levels suggest that they offered little incentive for further exploration at other horizons.

The only records of production from Church Burn Mine in the documents seen are a return of 16.25 tonnes of lead ore for 1854 and one of 35.56 tonnes for 1884. With such a meagre output the mine must be seen as a short-lived and unsuccessful venture.

WOLF HILLS WORKINGS

Whereas the occurrence of lead mineralisation in a single vein at Church Burn was recorded by the Geological Survey on 1:50,000 scale geological sheet 19 (Hexham), albeit without further description, no indication of any mineralisation is recorded on that map at Wolf Hills [NY 7286 5876] which lies approximately 2.5 km west of Church Burn Mine (Fig. 1). In common with Church Burn, neither Smith (1923) nor Dunham (1990) make any reference to mineralisation at Wolf Hills, but documents held by the Northumberland Archive (NRO) refer to exploration for, and perhaps some small scale working of, lead ores at Wolf Hills during the eighteenth century.

These records indicate that lead minerals were known here from at least the early eighteenth century for, in 1733, a tacknote was granted for lead mines at Wolf Hills for one seventh duty (NRO 324/W.2/4). Twenty years later, in 1753, the London Lead Company, one of the major mining enterprises responsible for developing the Northern Pennines as a major lead producer, was granted a 31 year lease for lead and copper ores, but not coal, for the whole manor of Coanwood, in which Wolf Hills lies (NRO 324/W.2/8). The reference here to copper is interesting as it was not standard practice in the Northern Pennine leases to mention copper in such agreements, perhaps indicating some hope or expectation of copper ores at this location, though the grounds for this are not known. The traces of chalcopyrite and copper-bearing supergene minerals at Church Burn are much too small to have given grounds for suspecting the presence of workable copper ores in this area.

It is clear from these documents that the London Lead Company's main focus of interest was Wolf Hills where reference is made to up to four named veins, though the only known document illustrating the position of these is an extremely crude sketch plan (NRO324/W.2/6) dated 1754 which related to a contemporary dispute over the ownership of mineral rights. The plan lacks any

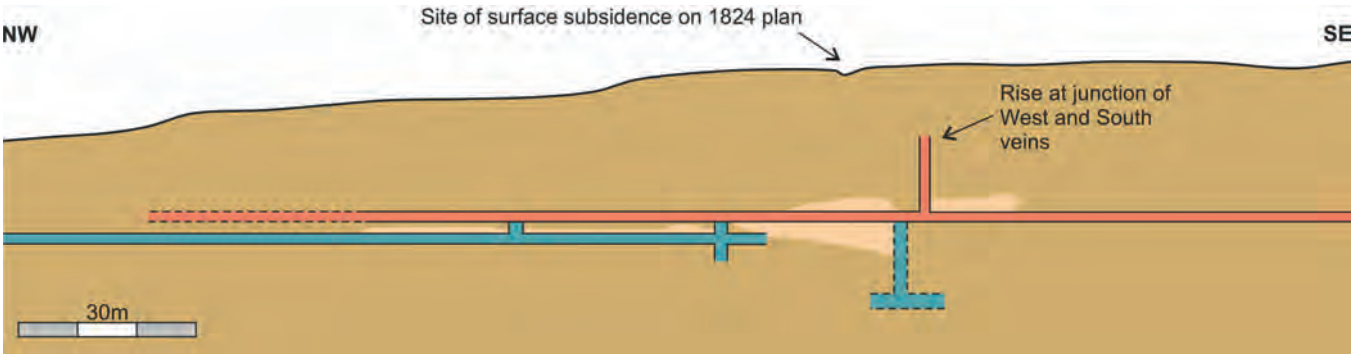

Figure 9. Section of stopes on Church Burn South Vein. The colours are those shown on the surviving plans: the West Vein Level is depicted in deep pink and the sub-level and sumps beneath it in blue. Although the mine plan from which this figure is derived gives no position for the end points on the section, it gives an indication of the modest area of stoping (pale pink) on the South Vein in the vicinity of its junction with the West Vein.

indication of scale or orientation and, apart from the approximate position of 'Wolf Hills House', contains no topographical reference points identifiable on the ground today. Moreover, very considerable caution must be applied to its reliability as it is reported to have been drafted by agents of the aggrieved party who had no access to the London Lead Company's records or workings and who relied heavily upon anecdotal information from miners employed by the company, combined with some meagre surface observations. Nevertheless, the plan depicts two roughly parallel west–east or northwest–southeast trending veins a short distance north of Wolf Hills Farm named as the North and Level veins which appear to be crossed by north–south to NNW–SSE trending veins identified as the Son (presumably Sun or South) and Snab veins.

It is impossible to reconcile, with confidence, the position of any of these veins with Geological Survey mapping, the most recent versions of which are incorporated into Figure 10. Like Church Burn, Wolf Hills lies on the outcrop of Stainmore Formation rocks but is separated from the former by a series of northeast–southwest trending sub-parallel faults that throw down towards the northwest. Stream sections around Wolf Hills expose the Lower and Upper Felltop limestones, along with an intervening thin coal, and overlying and underlying sandstones. In this area, the Upper Felltop Limestone is sufficiently well developed to form conspicuous landscape features and is mapped as a separate unit. A prominent west–east to SSW–ENE trending fault, which comprises part of the Stublick Fault System crops out roughly 150 m north of Wolf Hills Farm and displaces the strata to the north. Two closely spaced shafts [NY 7278 5893] on the west side of Wolf Hills Burn, roughly 150 m north of Wolf Hills Farm, lie on the outcrop of this fault close to the outcrop of the Lower Felltop Limestone. This fault may coincide with the North Vein depicted on the sketch plan and referred to in the London Lead Company documents (NRO324/W.2/6) as being worked on the west side of the burn. These documents also report that pieces of galena could be found in the burn at the point where it crosses the vein outcrop and add that the vein continued east of the burn where it was described as "very promising ...". An overgrown spoil heap from a shaft immediately east of the burn, and also on the outcrop of this fault, [NY 7284 5893] may relate to these workings (Fig. 11). During the present investigation no exposure of a fault or vein was seen in the burn and no traces of galena or of any other mineralised material was found either here or in

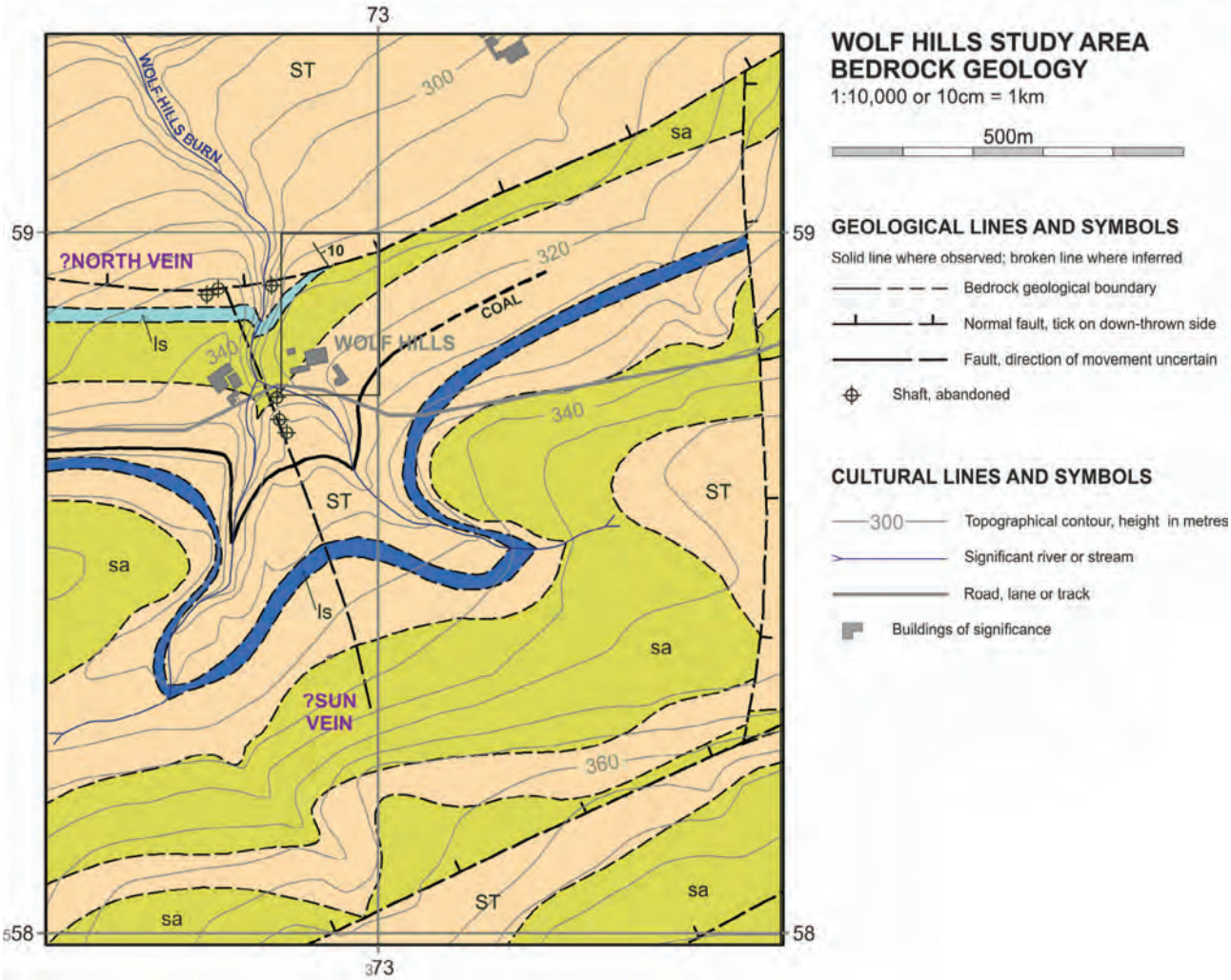

Figure 10. Surface geology of Wolf Hills study area based on mapping by C. L. Vye-Brown (2004) with modifications by the present authors. Vein names and positions are derived, in part, from mine plans. For key to the bedrock geological colours see Figure 1. CP20/021 British Geological Survey © URKI. All Rights Reserved.

Figure 11. Overgrown spoil heap, probably on North Vein, on the east side of Wolf Hills Burn. Photo Brian Young.

the modest and almost wholly overgrown spoil heaps adjacent to these shafts: only a few fragments of grey fissile siltstone and sandstone were seen.

A line of three closely spaced shafts with adjacent spoil heaps [NY 7286 5877] lies on the east side of the burn immediately south of the road at Wolf Hills Farm (Figs 10 and 12). Although a coal seam is mapped hereabouts beneath the Upper Felltop Limestone, the shafts lie north of its outcrop and in an obvious NNW–SSE linear alignment, and are thus extremely unlikely to relate to workings in that seam. However, their alignment, together with evidence of surface features consistent with the presence of a minor roughly north–south trending fault in nearby sandstone outcrops on the east side of the burn approximately 450 m south of Wolf Hills (C. Vye-Brown, *personal communication*), may mark the position of the vein identified on the sketch plan as the Son (or, more likely, Sun) Vein. For the purposes of this description, the position of this vein has been tentatively included on Figure 10, though in the absence of adequate information no attempt has been made to suggest the direction or amount of throw. Like the previously mentioned shafts, the accompanying spoil heaps here are small and overgrown and reveal only fragments of fissile siltstone and sandstone without any trace of mineralisation.

The Northumberland Archive documents refer to a shaft lying in the enclosed ground at East Wolf Hills, which was being sunk in 'hard sill' (sandstone) between depths of 11.9 and 17.7 m with a comment that the miners were expecting to "... be through it and into plate (fissile siltstone) within two or three days ...". Insufficient information is contained in these records either to identify the position of this shaft or the stratigraphical horizons of the beds penetrated by it. None of these records for Wolf Hills includes any descriptions of the veins or their contents and it is uncertain in which vein or veins any workable ore may have been encountered.

No evidence has been found on the ground to give any clue to the presence or position of the other veins depicted on this plan.

Figure 12. Overgrown shaft dumps, probably on Sun Vein, south of Wolf Hills Farm. Photo Brian Young.

The only record of any commercial output of ore from Wolf hills is contained in a letter dated December 1757 (NRO324/W.2.6) which states that " the men have got 15 bings (6 tonnes) of ore out of that vein and expected to have 20 by Christmas ...". From these records it is likely that the Sun Vein was the source of this ore. No further reports of any production are known from here and it must be concluded that the workings amounted to little more than unsuccessful trials.

DISCUSSION

In addition to the veins at Church Burn and Wolf Hills, similar mineralisation was encountered in the nearby Plenmeller Opencast Coal Site [NY 735 605]. Here, lenses of massive baryte up to 0.3 m wide in the fissile siltstone gouge of splinter faults off the main Stublick Fault were exposed, in 1997, in the 'Area A East' workings, approximately 2 km north of Church Burn. Turner (1997) also noted the occurrence of unspecified sulphides coating fault planes and minor fractures and in 1996 one of the present authors (BY) found well crystallised pyrite, locally accompanied by white kaolinite, coating joint surfaces in sandstone here. As the veins at Church Burn, Wolf Hills and Plenmeller share close structural and mineralogical similarities with those of the main Northern Pennine Orefield they may reasonably be seen as being additional members of the Haydon Bridge group of deposits regarded by Dunham (1990) as part of that field.

However, although substantial parts of the area south of the Tyne Valley are mantled by superficial deposits, mainly of Quaternary origin, exposure of bedrock geology is sufficient to conclude that this group of deposits is separated from the main body of the orefield by around 15 km of unmineralised ground. It is also important to note that they lie within an east–west elongated belt close to and parallel with the Stublick Fault, adjacent to which similar mineralisation is common along most of its length throughout Northumberland and Cumbria. It is therefore appropriate to consider the possible relationships of these deposits to that structure.

East of Haydon Bridge, Smith (1923) referred to a trial working for lead in a vein in the Thornbrough Limestone and adjacent beds at Thornbrough, near Corbridge [NZ 0094 6490] as well as to an eighteenth century report of an attempt to work a lead vein at Dilston Park, also near Corbridge. However, he offered no descriptions of the mineralisation at either location. No remnants of mineralisation are visible at Thornbrough today and the exact location of the Dilston trial is not known. Land *et al*. (1974) described lead-zinc-barium mineralisation within the Ninety Fathom Fault System in both Coal Measures and Permian rocks on the North Sea coast at Cullercoats [NZ 3668 7107].

Approximately 18 km west of Church Burn and Wolf Hills, Young *et al*. (1989) reported lead-zinc-copper-barium-mercury mineralisation in the Four Fathom Limestone within the Stublick Fault Zone at Silvertop Quarry, near Brampton [NY 586 606].

The fault zone is concealed for approximately 15 km west of Brampton beneath an almost complete mantle of thick superficial deposits overlying Permo-Triassic rocks. Where it re-emerges as the Maryport–Gilcrux Fault System in Carboniferous rocks in the country between Caldbeck and Cockermouth, it is closely associated with numerous local concentrations of mineralisation. These are dominated by barium accompanied by some copper and lead, within a belt up to 5 km wide (Cooper *et al*., 1991; 1992). At least two small workings for baryte are known from such concentrations at Gilcrux, near Maryport [NY 090 374] (Eastwood, 1930) and at Ruthwaite, near Ireby [NY 238 369] (Eastwood, 1959) together with a trial working in chalcopyrite-galena-baryte mineralisation within the Gilcrux Fault at Threapland, near Plumbland [NY 1619 3942] (Eastwood *et al*., 1968).

Crowley *et al*. (1997) identified close similarities between sulphur isotope ratios obtained from baryte samples collected from locations along the Maryport–Gilcrux–Stublick–Ninety Fathom Fault Zone in Cumbria and Northumberland and Lower Carboniferous anhydrites penetrated in deep boreholes within the Northumberland-Solway Basin to the north. From this they concluded that these were the likely source of sulphur in the baryte deposits of both the Northern Pennines and northern Lake District which have since been considered as possible expressions of the same mineralising episode (Stone *et al*., 2010).

A study by Young *et al*. (1992) reviewed the nature, distribution and possible origins of mineralisation along the full length of the Maryport–Gilcrux–Stublick–Ninety Fathom Fault System and highlighted structural similarities between the geological setting of these deposits and those of Ireland, such as Tynagh.

Whilst not ruling out a genetic connection between the Haydon Bridge mineralisation and the main body of North Pennine mineralisation, Young *et al*. (1992) speculated on the possible role of the Stublick–Ninety Fathom Fault system in the emplacement of these deposits. They considered the possibility that the fault system may have acted as a major conduit for mineralising fluids that may have, at least in part, have remobilised certain components from syngenetic mineralisation within the Carboniferous rocks at depth, a situation comparable with the southern Irish deposits.

There is insufficient evidence to propose a definitive model for the nature and origins of this mineralisation. However, we suggest that there are valid grounds for speculating both on the possible presence of syngenetic mineral deposits at depth and the role that this fault zone may have played in the emplacement of both those deposits so closely associated with it and perhaps those of the Northern Pennines and northern Lake District.

A similar situation may exist along the Lunedale–Butterknowle Fault System, the hinge fault that bounds the southern edge of the Alston Block. Here substantial baryte deposits are emplaced within the fault itself at Closehouse Mine in Lunedale [NY 850 228] (Dunham, 1990). Further east, extensive low-grade baryte-fluorite-galena and localised copper mineralisation in the Ferryhill area was interpreted by Hirst and Smith (1977) as evidence of the fault having acted as a conduit for upwelling mineralising brines. This is consistent with the conclusions of Bott *et al*. (1972) who interpreted the high heat flows reported from the Woodland Borehole [NZ 0910 2770], drilled approximately 2 km north of the surface outcrop of the Lunedale–Butterknowle Fault, as due to the upward convection of geothermal brines in the fault system and its associated fracture zones.

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Figures 1, 2 and 10: Maps created using BGS?SIGMA 2015 digital geological mapping software (https://www.bgs.ac.uk/research/sigma/home.html) with cultural data derived from OS Open Map – local [SHAPE geospatial data], Scale 1:10,000, Tiles: NY, Updated: 11 October 2019, Ordnance Survey (GB), Using: EDINA Digimap Ordnance Survey Service, https://digimap.edina.ac.uk, Downloaded: 2020-04-10 12:12:42.774; and OS Terrain 5 [SHAPE geospatial data], Scale 1:10,000, Tiles: NY75NE/NW, Updated: 3 December 2019, Ordnance Survey (GB), Using: EDINA Digimap Ordnance Survey Service, https://digimap.edina.ac.uk, Downloaded: 2020-04-10 10:40:10.904

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MORDENITE FROM GLEN BRITTLE, ISLE OF SKYE

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The occurrence of the comparatively uncommon zeolite mordenite is described from vesicles in a basaltic lava within the Skye Lava Group at Glen Brittle, Isle of Skye. The form of the mineral here differs from that at its sole previously recorded location on the island at Sgùrr nam Boc. At Glen Brittle mordenite is locally intergrown with quartz. Laumontite, prehnite, chabazite, calcite and saponite are also present in very small amounts.

INTRODUCTION

The basic lavas of the Palaeogene Hebridean Igneous Province have long been famous for the variety of zeolites and related minerals found within vesicles, most notably those within alkali olivine basalts (Heddle, 1901; Walker, 1971; Emeleus and Bell, 2005). The basalts of the Skye Lava Group are particularly noted for magnificent examples of many species from numerous locations including The Storr, Quiraing, Moonen Bay, Oisgill Bay and Sgùrr nam Boc (e.g. Heddle, 1901; Anderson and Dunham, 1966; Green and Wood, 1996; Green and Todd, 1996; 2001; Tindle, 2008).

The relatively uncommon zeolite mordenite, $(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}{\cdot}28H_2O$, has hitherto been recorded from a single location on the Isle of Skye, at the celebrated coastal zeolite locality of Sgùrr nam Boc [NG 3590 2090], between Loch Brittle and Loch Eynort on the island's west coast (Green and Wood, 1996; Green and Todd, 2001). Here it occurs as fibrous masses of delicate white capillary crystals up to 2 cm in length. A fine example, associated with stilbite, from this location is figured by Tindle (2008: p. 358).

Elsewhere in Scotland mordenite has been reported from cavities in a trachyte lava at Dumbarton, Strathclyde (Bøggild, 1922), from Aros on the Isle of Mull (Waymouth *et al*., 1938) and from an olivine basalt at Todhead Point, near Stonehaven (Dyer *et al*., 1993). Reported here are fine specimens of mordenite from a hitherto unrecorded occurrence in Glen Brittle Forest on the Isle of Skye.

GEOLOGICAL SETTING

Basaltic lavas within the Cruachan Formation of the Skye Lava Group (Williamson and Bell, 1994) form much of the ground between Glen Brittle and Glen Eynort. Modern geological mapping (British Geological Survey, 2000) indicates that these lavas lie approximately 4 kilometres west of the outermost limit of thermal metamorphism resulting from the intrusion of the gabbros of the Cuillin Hills within the Skye Central Complex. Whereas extensive forestry plantations in Glen Brittle severely obscure exposure except on the higher slopes of Beinn Staic and Beinn a' Bràghad, insights into the nature of the local lava sequence can be gained from the material in forest tracks derived from borrow pits adjacent to these tracks. It is in such material within the forest track between NG 4110 2720 and NG 4135 2715 that conspicuous examples of mordenite were discovered in 2014. At that time all of the borrow pits along the tracksides were heavily overgrown and provided no exposures of solid rock. However, recent reworking of the most substantial of these borrow pits at NG 4131 2719 has revealed clear sections through a vesicular basaltic lava in which good specimens of mordenite, identical in appearance to those originally found in the track, are plentiful. Minor amounts of other minerals typical of the vesicle fillings of the Skye Lava Group are also present.

Beneath a superficial cover of up to 1 m of peat, the pit exposes an aggregate thickness of around 5 m of dark grey olivine basalt apparently within a single lava flow (Fig. 1). Vesicles are abundant, particularly within the topmost 2 m of the exposed faces, perhaps suggesting the proximity of the top of the flow, though neither the top nor base of the flow are exposed. Whereas most vesicles are roughly rounded and approximately 50 mm across or less, a substantial number of larger, much more irregular vesicles, up to around 100 mm across, typically with a horizontally elongated profile, are conspicuous (Fig. 2). Mordenite fills the overwhelming majority of vesicles seen in this pit with other minerals characteristic of the vesicular lavas of Skye present only in very subordinate amounts.

Figure 1. A general view looking east across the borrow pit, showing basaltic lava up to 2 m thick overlain by peat. Mordenite-filled vesicles are common in the north face to the left of the figure and in the large loose blocks in the foreground. Photo Jane Young.

VESICLE FILLINGS

The minerals found within vesicles at this site are described here in approximate order of abundance.

MORDENITE, $(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}\cdot 28H_2O$

Mordenite occurs as masses composed of compact sprays of pure white radiating crystals up to 30 mm long, with a distinctive silky lustre, which typically completely fill the vesicles (Fig. 3). A handful of specimens display terminated free-standing colourless acicular crystals up to around 6 mm long, projecting from the radiating masses into cavities up to around 10 mm across (Fig. 4). An investigation of the mineral using powder X-ray diffraction (PXRD) at the National Museum of Wales provided excellent and definitive identification data (NMW 2020.11G.M.1a; PXRD No. NMW X-3787) (Fig. 5).

Identical masses of pure mordenite up to 100 mm across are locally conspicuous in the track surface extending for about 350 m west of the pit (NMW 2020.11G.M.2; PXRD No. NMW X-3788).

A handful of vesicles up to 100 mm across, found in loose blocks within the pit, are partially filled with white

Figure 2. Irregular horizontally elongated mordenite-filled vesicles in weathered basalt exposed in the north face of the borrow pit. The hammer shaft is 30 cm long. Photo Jane Young.

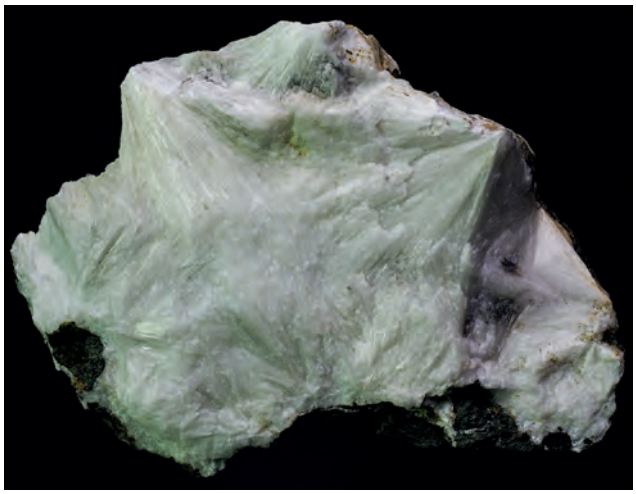

Figure 3. Compact sprays of white mordenite crystals. The patchy green colouration is due to algae. Specimen is 10 cm across. Brian Young specimen, No. BY9140/B. Photo Andy Hopkirk.

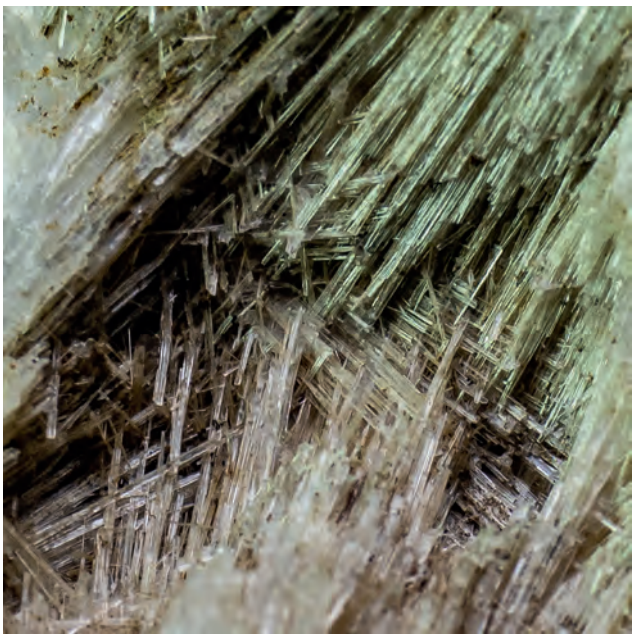

Figure 4. Colourless acicular mordenite crystals in the centre of a vesicle. The slight green tinge is due to a patchy surface coating of algae. Field of view is 1 cm across. Brian Young specimen, No. BY9657. Photo Andy Hopkirk.

intergrowths of fibrous radiating quartz and mordenite (NMW 2020.11G.M6; PXRD No. NMW X-3785) (Fig. 6).

QUARTZ, SiO_2

The vesicles filled with intergrowths of quartz and mordenite, noted above, locally exhibit open central cavities lined with distinctive radiating clusters of doubly terminated white quartz crystals up to 2 mm across (Fig. 7).

Figure 6. Portion of a vesicle partially filled with a white intergrowth of mordenite and quartz. Small terminated quartz crystals in the central void are locally overgrown by white laumontite crystals. Specimen is 5 cm across. Brian Young specimen, No. BY9674/A. Photo Andy Hopkirk.

In some specimens the radiating fibrous crystalline form of the mordenite-quartz intergrowth, which is conspicuous in the outermost few millimetres of the filling, gives way internally to a much more compact and locally granular texture, perhaps suggesting some progressive replacement of mordenite by quartz.

Colourless to white quartz with a coarsely granular texture is the dominant filling of the prehnite-bearing vesicles described below.

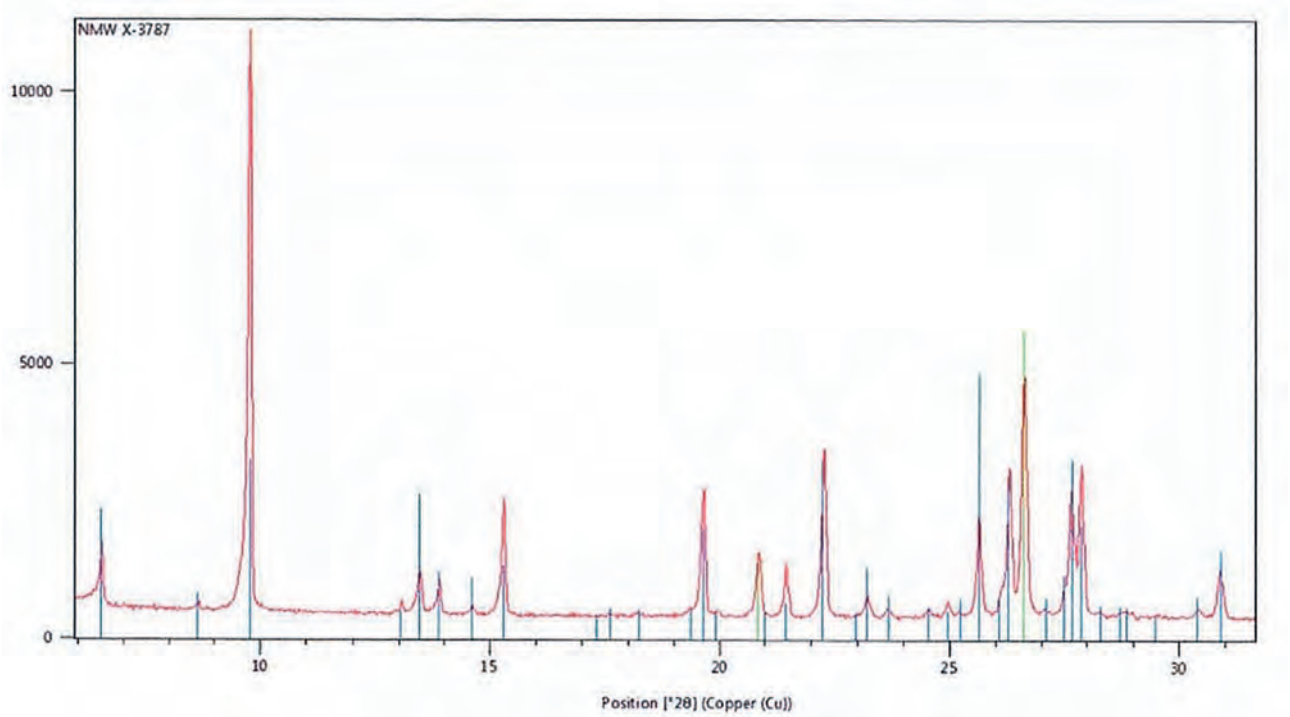

Figure 5. Powder X-ray diffraction pattern (NMW X-3787) (red line) from specimen NMW 2020.11G.M.1a. The *d*-spacings in the powder diffraction file for mordenite are shown by the blue lines and for quartz by the green lines.

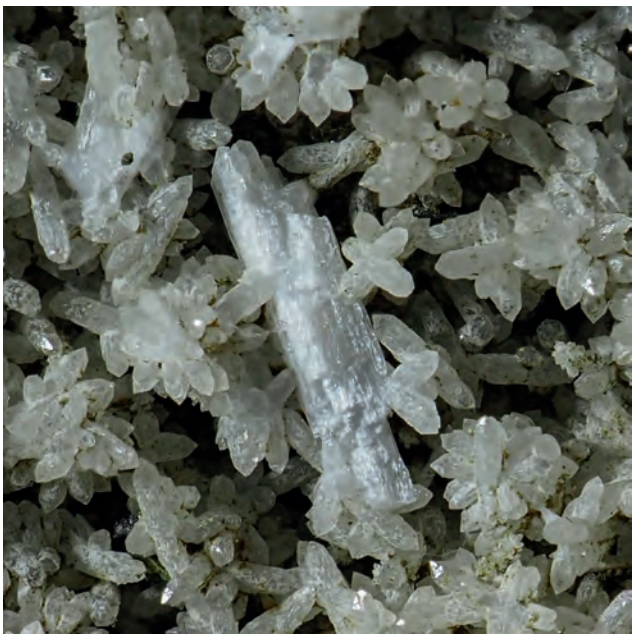

Figure 7. Clusters of colourless radiating quartz crystals lining the central cavity in the vesicle, overgrown in the centre of view by an elongated 4 mm long white laumontite crystal. Brian Young specimen, No. BY9674/B. Photo Andy Hopkirk.

LAUMONTITE, $CaAl_2Si_4O_{12}{\cdot}4H_2O$

In a few of the open cavities in the vesicles filled with mordenite-quartz intergrowths, the central terminated quartz crystals are overgrown by scattered small white to colourless bladed crystals up to 5 mm long with a characteristic pearly lustre. These have been identified as laumontite (NMW 2020.11G.M.6; PXRD No. NMW X-3783) (Figs 7 and 8).

Figure 8. White laumontite crystals coating quartz in the central void in a vesicle. Field of view is 12 mm across. Brian Young specimen, No. BY9674/A. Photo Andy Hopkirk.

PREHNITE, $Ca_2Al_2Si_3O_{10}(OH)_2$

A few vesicles, up to 90 mm across, collected from loose blocks within the pit exhibit fillings dominated by coarse-grained quartz and calcite, without mordenite. In these, the outermost few millimetres of the filling comprises a greyish white radiating mineral, commonly in the form of spherules up to 3 mm across, identified as prehnite (NMW 2020.11G.M.5; PXRD No. NMW X-3786) (Fig. 9).

CALCITE, $CaCO_3$

A central filling of white calcite, seen as rhombic cleavage surfaces up to 150 mm across, is present in a small number of the mordenite-filled vesicles (Fig. 10). Similar coarsely crystalline calcite is conspicuous constituent of the filling of the prehnite-bearing vesicles.

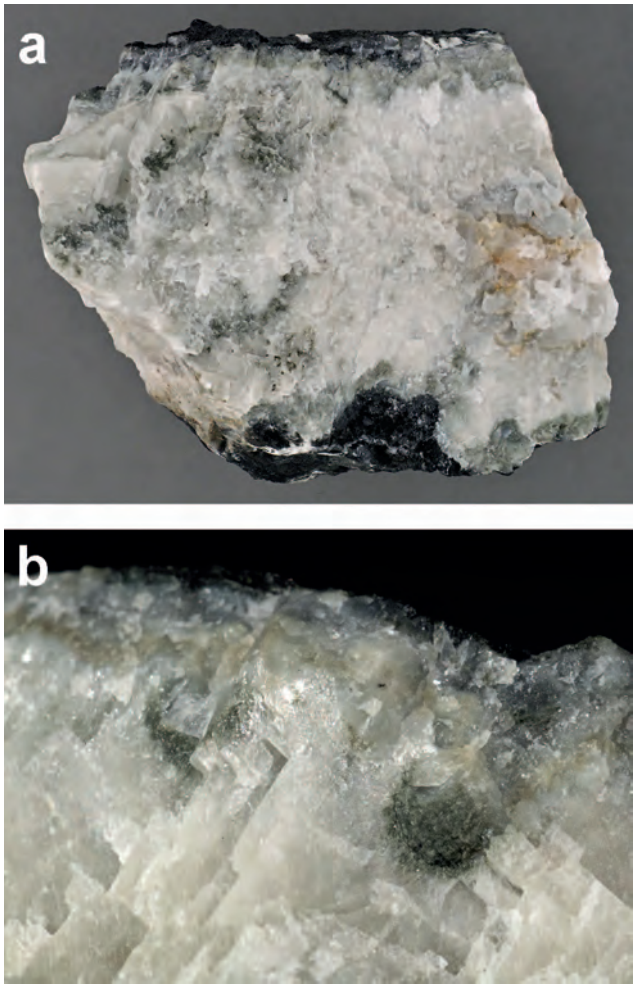

Figure 9. Vesicles containing quartz, calcite, prehnite and saponite: (a) a vesicle filled predominantly with a coarse-grained aggregate of white quartz and calcite. Pale greenish-grey prehnite forming spherules up to 3 mm across are present in the outermost parts of the vesicle (top and bottom of specimen). The grey-green tinge appears to be due to minute inclusions of saponite which form the outermost lining of the vesicle. Specimen is 7 cm across. Brian Young specimen, No. BY9675/A; (b) dull green 3 mm prehnite spherules embedded in calcite. Brian Young specimen, No. BY9675/D. Photos Andy Hopkirk

Figure 10. White cleavage surfaces of calcite up to 15 mm across in the centre of a mordenite-lined vesicle. Specimens are 3.5 cm across. Brian Young specimens, Nos. BY9659/A and BY9675/B. Photo Andy Hopkirk.

SAPONITE,

$$Ca_{0.25}(Mg,Fe^{2+})_3(Si,Al)_4O_{10}(OH)_2{\cdot}nH_2O$$

In common with many of the zeolite-bearing vesicles of the Skye lavas, many of the mordenite-bearing vesicles at this locality exhibit a thin (>0.5 mm) lining of a soft mid- to dark-green clay-like mineral, presumed to be saponite. Locally this infiltrates up to a few millimetres into the immediately adjacent mordenite and prehnite where it imparts a patchy grey-green tint to these minerals. Some specimens display thin films (>0.5 mm) of waxy-looking olive-green saponite up to 10 mm across coating fracture surfaces in the adjacent basalt.

CHABAZITE, $CaAl_2Si_4O_{12}{\cdot}6H_2O$

A single specimen of a mineral of the chabazite series, composed of characteristic lustrous white rhombic crystals up to 6 mm across, and unaccompanied by any other mineral, was found in loose quarried material. No other examples of this mineral were located either in loose rock or *in situ*.

DISCUSSION

The mordenite from Glen Brittle differs in appearance from that seen at its only other reported Skye occurrence at Sgùrr nam Boc, where it typically forms delicate capillary crystals, commonly associated with stilbite (Tindle, 2008: p. 358). As many of the fine zeolite specimens from Sgùrr nam Boc were recovered from fallen boulders at the foot of high sea cliffs, the stratigraphical horizon from which they were derived is unclear. Lavas of the Bualintur Formation of the Skye Lava Group form the sea cliffs here, though it possible that fallen blocks from the overlying Cruachan Formation may also be present at the foot of Sgùrr nam Boc. If so, the two Skye occurrences of this unusual zeolite may lie at, or close to, the same stratigraphical horizon within the lava sequence

Radiating crystalline zeolites are common vesicle fillings at many locations within the basalts of Skye but they are often overlooked and not specifically identified by collectors searching for larger and more spectacular species. It is therefore possible that more determinative work on these unidentified vesicle fills may reveal more occurrences of this zeolite.

ACKNOWLEDGEMENTS

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LINARITE FROM CONONLEY MINE, SKIPTON, NORTH YORKSHIRE

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Cononley Mine, 6 km south of Skipton in North Yorkshire, worked lead veins in a folded sedimentary sequence of Lower Carboniferous age at the northern edge of the Craven Basin. Calcite, copper sulphides, fluorite, galena, iron sulphides, sphalerite, witherite and various 'clay infills' occur in coarse baryte. Linarite has been identified in a small cavity on an old specimen with cerussite and partly oxidised galena. It appears to have formed by natural supergene oxidation in circumneutral to slightly alkaline conditions. Carbonates dominate the lead- and copper-bearing supergene mineralisation at most Pennine localities. It is suggested that the absence of carbonates in the wall-rocks at Cononley Mine, and the abundance of relatively inert baryte in the veins, allowed linarite to form.

INTRODUCTION

Linarite, ideally $PbCu(SO_4)(OH)_2$, is widespread in the British Isles. It is typically found in the supergene zones of orebodies containing mixed lead and copper sulphides. The azure-blue colour makes linarite conspicuous even if it is present in small quantities. It is readily distinguished from azurite, the only common supergene mineral with a similar colour, by its reaction in dilute mineral acids. Linarite decomposes without effervescence, changing from blue to white as it does so, and the resulting solution gives a strong positive test for lead. Azurite dissolves rapidly with effervescence and the resulting solution is lead free.

Two mining districts in the British Isles have produced linarite specimens which rank among the best in the world: the Caldbeck Fells in Cumbria and Leadhills–Wanlockhead in southern Scotland. In the mid nineteenth century remarkable prismatic linarite crystals to more than 25 mm in length were found at Red Gill Mine (Bridges *et al*., 2008; Young, 2010). The mineral is common at nearby localities in the Caldbeck Fells (Cooper and Stanley, 1990) and is widespread in the oxidised zones of lead-copper veins in the Lake District (Young, 1987).

Centimetre-size flattened prismatic linarite crystals were found in the supergene zones of lead-copper veins at Leadhills and Wanlockhead when the mines were being worked (Livingstone, 2002). Heddle (1901: p. 178) describes linarite from the area as follows:

> "In the Susanna Mine, its associates being Anglesite, Caledonite, and all except Susannite. In the Leadhills Dod it occurs with pointed Leadhillite, associated with Cerussite, Caledonite, Chrysocolla, and Malachite. In the Wanlockhead Dod, in the Belton Grain Vein, and in the High Pirn Mine, with Caledonite, Chrysocolla, and Tile Ore. Also in the Bay Vein, with flat, nailhead Calcite, Cerussite, Wad, and Leadhillite. Lately, in small crystals, with new faces, at the Glengonner Shaft".

This short paragraph shows that linarite is rather more catholic in its associations than most of the other members of the Leadhills-suite[1] of supergene lead and copper minerals.

In recent decades, dump-formed micro-crystalline linarite has been reported at numerous mines in the Central Wales Orefield (Bevins, 1994). A few localities in Cornwall, notably Penberthy Croft Mine (Betterton *et al*., 2000), have produce similar material.

Low-temperature veins containing abundant lead and minor copper mineralisation were worked at numerous localities in the Pennine orefields, but records of linarite are few. Scattered localities in the northern portion of the orefield (effectively the Alston Block) are summarised in Bridges and Young (1998). Subsequent reports include dump-formed crystals up to about 0.5 mm in length, found during track repairs at Westernhope Old Mine near Stanhope (Bridges, 2010), and dark blue crusts with cerussite and malachite, recently described from Church Burn Mine south of Haltwhistle (Young *et al*., 2020). Fan-like crystal groups up to 2 mm across and dark blue bladed crystals up to 6 mm long span cavities in quartz-rich matrix from highly oxidised replacement flats below the Whin Sill at Murton Mine in Scordale, and bladed crystals up to about 1.5 mm long occur in cavities in fluorite in flats at the same horizon at nearby Hilton Mine (authors' unpublished data).

Linarite occurrences in the South Pennine Orefield are summarised in Ford *et al*. (1993) and Tindle (2008). The most notable locality is Waterbank Mine near Ecton in Staffordshire, where divergent azure-blue crystal sprays up to about 1.5 mm have been reported (Rust, 1995). Much of the linarite at Waterbank Mine appears to have formed by post-mining oxidation in the dumps.

[1] The 'Leadhills-suite' is a subset of what Heddle (1901: p. 178) described as the "special Leadhills minerals". It includes caledonite, linarite, leadhillite, lanarkite and susannite, and the more recently discovered chenite, macphersonite, mattheddleite and scotlandite, all of which are found in close association at Leadhills–Wanlockhead.

Records of linarite in the Yorkshire Pennines are few. Minute crystals have been visually identified at Wet Grooves Mine near Carperby in Wensleydale (Rust, 1987) and at Grovebeck Mine near Grinton in Swaledale (Young *et al*., 2012). Dark blue patches on a specimen in the DG collection from Grassington Moor [SE 029 669], found in the early 1980s when the dumps were being reworked for fluorspar, appear to be the only Yorkshire specimen that has been identified by X-ray diffraction. Pale blue lath-like crystals, up to about 0.5 mm long, in massive baryte from the nearby Hebden Moor mines have been visually identified as linarite (David McCallum, *personal communication*, 2018).

LOCATION

Cononley Mine is situated in undulating upland country to the southwest of Cononley village about 6 km south of the market town of Skipton in North Yorkshire. The principal remains are around the Engine Shaft [SD 979 461] 750 m west of the summit of Gib Hill. The buildings in this area are grade II listed. They form one of the most complete nineteenth century lead mining sites anywhere in Yorkshire (Fig. 1).

For many years, the engine house and surrounding structures were conserved by the Earby Mines Research Group, who restored and maintained the buildings. Sadly, this is no longer the case. The site is still accessible via the Cononley lead mine trail (Mason, 2018), a steep climb from Cononley village, but it is now rather neglected. There is no public access along the unmetalled road from Stockshott Lane and almost all of the other mining features along the 1.6 km strike length of the vein system are on private land (Gill, 1987). These include the remains of the smelting works and deep drainage level in Nether Gill Beck and the smelter flue and chimney on Gib Hill. The twentieth century baryte workings around Garforth Shaft, south of Manor House Farm, are cut by a public footpath, but have been almost completely obliterated.

A detailed account of the workings, with biographies of the Eddy family who managed the mine on behalf of the Duke of Devonshire in the nineteenth century, is provided by Gill (1987). The social history of Cononley village, with a particular focus on lead mining, is described in a later work by the same author (Gill, 1999).

GEOLOGY

At the beginning of the Carboniferous period, a 'basin and block' topography developed in the epicontinental sea that covered much of northern England. Rates of subsidence were relatively low in the Askrigg Block, which lay on the buoyant and competent Wensleydale Granite, but were episodically much higher in the Craven Basin to the south (cf. Dunham and Wilson, 1985; Arthurton *et al*., 1988). Cononley Mine lies at the northern edge of the Craven Basin, a few kilometres to the south of the Craven Fault System (Stephens *et al*., 1953).

A thick sedimentary sequence, dominated by fine-grained clastic rocks and also including coarse sandstone, limestone and minor coal accumulated in the Craven Basin in early Carboniferous times. Lateral displacements, which did not affect the rocks of the

Figure 1. Cononley Mine from Babyhouse Lane to the northeast. An unroofed but remarkably complete engine house, with 15 m chimney, dating from about 1842, are conspicuous at the centre of the photo. The steam engine was used for pumping, winding and crushing. The original crushing mill appears to have been in front of the engine house, where the remains of baryte processing tables, which were installed in the 1950s, are currently visible. The building next to the unmetalled track on the right-hand side of the photo is the old smithy (originally a two-storey building). On the far right, the mine reservoir, which supplied water for ore dressing and regulated the flow of Nether Gill Beck, is just visible. The stone-arched entrance behind the engine house provides access to a roofed 'lobby' built to house an angle bob which translated the horizontal motion of rods driven by the engine to vertical motion of pump rods in the shaft. The engine shaft, now covered by a sturdy metal grill, is just behind; it was begun in about 1840 and eventually reached a depth of 146 m. The roofed thick-walled building at the top left is presumed to be the powder store. Photo John Chapman.

Askrigg Block, folded these rocks into an *en échelon* set of southwest trending anticlines and synclines known as the Ribblesdale Fold Belt.

Cononley Mine worked four major NW–SE to WNW–ESE trending veins in fine- to coarse-grained clastic sedimentary rocks of the Craven and Millstone Grit groups (Stephens *et al*., 1953; Gill, 1987). James Ray Eddy[2], who was mineral agent for the Duke of Devonshire in the latter part of the nineteenth century, produced the only contemporary record of the workings with useful mineralogical detail in his account of the lead veins in the neighbourhood of Skipton, published in 1882.

The Main Vein occupies a fault with a large downthrow to the southwest and is mineralised along a strike length of at least 1.6 km. Baryte is the most abundant primary vein-filling, with minor witherite, fluorite, calcite and significant quantities of 'ochreous marl' and 'black clay' (Eddy, 1882). Galena was the principal lead ore, but workable quantities of cerussite were found in the upper oxidised zones. Sphalerite and smithsonite are added to this list in a short summary by Stephens *et al*. (1953).

There are no modern descriptions of the mineralisation, but material on the dumps and in poor surface exposures at the southeast end of the vein system suggest that it consists of metre-scale symmetrical fissure veins, dominated by coarse baryte, with discontinuous masses of galena in bands roughly parallel to the vein walls. Baryte was (and remains) abundant on the dumps around the engine shaft. It rarely contains cavities lined with iron-stained tabular to cockscomb crystals and occasionally encloses fragments of coal, presumably derived from the wall-rock, as one of the veins is named "Coal Vein" (Gill, 1987).

Galena occurs commonly as centimetre-size masses in baryte veinstone and less commonly as crude cubic to cuboctahedral crystals in cavities. It is usually surrounded by a thin (<1 mm) rim of an uncharacterised metallic blue copper sulphide[3]. Iron sulphides, chalcopyrite and sphalerite occur as small euhedral crystals in cavities, but are rare in the baryte veinstone. Limited evidence suggests that fluorite and witherite are late-stage local infills.

[2] James Ray Eddy (1833–1918) was the son of Stephen Eddy, who managed the Duke of Devonshire's mining interests at Grassington and Cononley in the mid nineteenth century. He was involved in mining throughout his life, working at Grassington, Cononley and Alport in Derbyshire, and taking over at Snailbeach in Shropshire when his father died in 1861. The family lived at Carleton Grange, a grand house near Skipton, which the Duke built for them in 1857. James, who was a Fellow of the Geological Society, included a large coloured plan and section of Cononley Mine in his account of 1882. Further biographical details are recorded by Moorhouse (1961) and Gill (1987).

[3] Metallic blue alteration rinds around galena are often described as 'covellite' but research has shown they commonly contain non-stoichiometric copper sulphides such as spionkopite and yarrowite.

SPECIMEN DESCRIPTION

The specimens described here were collected by one of the authors (JC) in 1966 on an A-level geology field trip. At the time, students were encouraged to collect representative rock, mineral and fossil specimens for personal study. At Cononley Mine, the principal species of interest were baryte and galena. Among the material collected on that day, a small (ca 50 × 60 mm) specimen of massive baryte (catalogue number Pb4) contained a cavity with a few azure blue crystals which were visually identified as linarite. The specimen was placed in a display cabinet (with other specimens collected at the same time) and remained in essentially the same place, regardless of house moves, for the next fifty years.

A renewed interest in the minerals of the local area, fostered by voluntary work for Bradford Museums and Galleries at Cliffe Castle Museum, led to a re-examination of the specimen in 2019. The linarite was photographed to provide a record, trimmed in the hope that fresh material would be found in sealed cavities, and cleaned in an ultrasonic bath. The fragments were mounted in plastic boxes and assigned catalogue numbers Pb4a–d.

Specimen Pb4a, the only piece of the original specimen with obvious blue crystals, is a roughly cuboidal fragment of massive baryte (14 × 15 × 18 mm) with some iron staining. Linarite overgrows partly oxidised galena and cerussite in an approximately spheroidal cavity, about 4 mm in diameter, on the original outer surface of the block (Fig. 2). The visual identification was confirmed by wet chemistry. A tiny crystal fragment was detached and placed in a drop of dilute nitric acid. It decomposed without effervescence, changing from blue to white, and the resulting solution gave a strong positive test for lead and copper.

Small irregular cavities containing cerussite, traces of an unidentified green powdery phase and thin pale-blue coatings of linarite are present on specimens Pb4b and Pb4d, but no further crystals were found. Rims of a dark blue metallic copper sulphide surround kernels of galena on all of the specimens and an otherwise empty cavity in baryte on specimen Pb4d has a discontinuous lining of this material. An irregular, centimetre-size, partly oxidised mass of galena on specimen Pb4c is surrounded by an oxidation rind containing colourless, transparent, blocky euhedral anglesite crystals up to about 0.2 mm across. Squat prismatic cerussite, a pale brown botryoidal phase tentatively identified as smithsonite, and bright white crustose hydrozincite are also present on this specimen.

DISCUSSION

Linarite is commonly found where oxidising solutions percolate through mixed lead and copper sulphides. It is present at almost every suitable locality in the Lake District (Young, 1987; Cooper and Stanley, 1990) and is abundant in dump-formed supergene assemblages

Figure 2. Curved tabular aggregates of azure blue linarite up to 0.8 mm in length with resinous to powdery cerussite and a thin crust of a poorly formed unidentified pale blue phase (bottom centre). When the specimen was found, the cavity had been exposed to the weather for some time and this almost certainly accounts for the less-than-pristine appearance of the crystals. The supergene minerals are in a cavity in massive baryte which contains a kernel of partly oxidised galena. Specimen Pb4a in the John Chapman collection. Photo John Chapman.

produced by the oxidation of mixed lead-copper ores at the lead mines in Central Wales (Bevins, 1994). A recent description of the post-mining sulphates at one such locality includes numerous photos of euhedral crystals (Rust, 2019: pp. 96–103).

The relative rarity of linarite in the Pennine orefields, and in the Yorkshire Pennines in particular, makes its occurrence at Cononley Mine noteworthy. Cerussite is the most abundant supergene lead mineral at most Pennine localities and it occurs almost everywhere galena has been subject to oxidation; supergene copper assemblages in the area are also dominated by carbonate minerals (Dunham and Wilson, 1985; Dunham, 1990; Bridges and Young, 1998). Malachite, rosasite and aurichalcite are widespread; azurite is conspicuous at a few localities around the periphery of the Askrigg Block, but is only present in any quantity near Malham and at the old copper mines around Middleton Tyas (Dunham and Wilson, 1985; Arthurton *et al*., 1988). The complex sulphate-dominated lead-copper supergene assemblages that are characteristic of the Caldbeck Fells, Leadhills–Wanlockhead and the Central Wales Orefield are generally absent. Geochemical reasons for the differences between the supergene assemblages are explored by Bridges (2015). The abundance of carbonate host rocks in the Pennine orefields has a considerable influence on the assemblages that develop. It seems likely that the absence of carbonates in the wall-rocks at Cononley Mine and the abundance of relatively inert baryte in the veins allowed linarite to form. More supergene sulphates may come to light if further specimens can be located.

Two pathways which lead to the crystallisation of linarite are described by Bridges (2015). In one scenario, concentrations of $Pb^{2+}_{(aq)}$ build up in an environment dominated by copper minerals; in the other concentrations of $Cu^{2+}_{(aq)}$ build up in an environment dominated by lead minerals. The second model applies at Cononley where linarite overgrows cerussite in a cavity containing partly oxidised galena. Theoretical predictions of the minerals which should crystallise in this process are at variance with the parageneses observed in nature and Bridges (2015: p. 15) suggests that there may be a small error in the thermodynamic data for caledonite, which is less common than geochemical models suggest it ought to be.

Regardless of the detailed thermodynamic data, stability field diagrams show that the change from the paragenetic sequence cerussite–caledonite–linarite to cerussite–linarite is pH dependent and that the direct overgrowth of cerussite by linarite is favoured by slightly alkaline conditions. In this context it is interesting to speculate whether the minute pale blue patches on cerussite on specimen Pb4a might be caledonite. The crystals are too small to identify with the equipment available to this study, but further analysis would be of interest as caledonite is extremely rare in the Yorkshire Pennines.

There is no evidence that the linarite on specimen Pb4a is post-mining in origin as it does not encrust broken surfaces. It is almost certainly part of the mineral assemblage produced by natural oxidation in the relatively extensive supergene zone. Eddy (1882: p. 69) records that workable quantities of cerussite were found near the top of the vein, and this is corroborated by a rich specimen collected by Harry Edmond[4] who was involved in a short-lived mid twentieth century attempt to rework the veins for baryte[5].

Cononley Mine was the most productive lead working in the Craven Basin. Its position near the Craven Fault System, a few kilometres to the south of the Askrigg

[4] Harry Edmond (1898–1994) was a mining engineer and mineral collector who assembled a remarkable collection of more than 5,000 specimens from localities across the world. Born in Wanlockhead, where he began work as a miner, he spent the majority of his working life in Africa. He contributed outstanding specimens to the collections of the National Museum of Scotland (Livingstone, 2002: p. 74).

[5] In 1957, McKecknie Brothers of Wigan reopened the incline and produced baryte from workings above the old Upper Adit. A disagreement with the owner of the mineral rights brought the operation to a premature end in the next year (Gill, 1987: pp. 20–21).

Block, may be of significance in genetic studies of mineralisation in the Pennine orefields. Yet it is little known to earth scientists, there is no modern description of the mineralisation and few specimens are preserved in public collections.

Sir Arthur Russell surveyed the site in 1918 and witherite and baryte are preserved in his collection at the Natural History Museum (Roy Starkey, *personal communication*, 2020). Fluorite and baryte are preserved in the collections of Bradford Museums and Galleries at Cliffe Castle in Keighley. A collection formerly in the possession of the Earby Mines Research Group has been assimilated by the Dales Countryside Museum in Hawes, but it is not known whether it contains any geological specimens (Mike Samworth, *personal communication*, 2019). There is anecdotal evidence that James Ray Eddy donated material to the University of Leeds, but once again whether this contained any geological specimens is unknown. Requests for information from Russell Society members have (as yet) revealed very few specimens in private hands. The authors are currently collecting information about the distribution of minerals in Yorkshire and would be pleased to hear from any reader who has further information about minerals from Cononley Mine.

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AN UNUSUAL MAGNESIUM-BEARING VIVIANITE WITHIN A SANDSTONE HONE FROM CANTERBURY, KENT

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The petrography of Roman to post-medieval hones/whetstones from Canterbury, Kent shows that a range of lithologies was used, including Scandinavian mica schists (Norwegian Rag), regionally sourced sandstones and locally/regionally sourced glauconitic calcareous siltstones (often called Kentish Rag). One feldspathic sandstone hone, excavated from an AD 1600–1700 context from Rose Lane in Canterbury, contains fine-grained, radiating, optically zoned, magnesium-bearing (up to 7.78 wt% MgO) vivianite crystals with an empirical formula $(Fe^{2+}_{2.05}Mg_{0.74}Ca_{0.10}Mn_{0.04})_{2.93}(PO_4)_{2.01}\cdot 8H_2O$. These form dark spots, and when oxidised, very dark spots, and occur as a very local late-stage cement to clastic quartz and feldspar grains. Vivianite cements in siliciclastic rocks are rare. This is the first record of this type of vivianite occurrence in an archaeological context.

INTRODUCTION

Petrography of Hones/Whetstones

Hones/whetstones, used for the sharpening of metal objects (such as blades and pins) first appear in later prehistoric contexts and are common artefacts at Roman and post-Roman sites in Britain. In order to be effective, they comprise grains of a hard, angular mineral, usually quartz, set within a soft matrix, the two most common soft minerals being calcite and muscovite (Ellis and Moore, 1990); characteristically they are of a fine to medium sand grain size.

Hones are defined as primary if their original intention is sharpening and secondary if they are reused lithologies. Primary hones are important as a source of information on trade: Norwegian Rag from central southern Norway is a primary hone in the sense of Moore (1978).

Although the petrographical identification of prehistoric axe heads is well established, far less work has been undertaken on hones/whetstones. Indeed, in *The Archaeology of Stone*, Peacock *et al*. (1998) note that, whilst medieval whetstones have been better researched than Roman ones, much more work is needed; this is echoed more recently by Allen (in press).

The large collection of hones, whetstones and rubbing stones from the Whitefriars and Rose Lane excavations in Canterbury afforded the opportunity to contribute to the detailed description of the major rock types used for whetstones, most notably Norwegian Rag (quartz mica-schist) (Ixer, 2018) and 'Kentish Rag' (glauconitic calcareous siltstone). This is the first collection of hones/whetstones to be described microscopically using total petrography as defined by Ixer *et al*. (2004). The reflected light descriptions complement earlier descriptions of these two classes of hone and complete their petrographical characterisation.

One post-medieval feldspathic hone was unusual in having blue spots in thin section despite an absence of any blue colouration on its surfaces; on analysis these were shown to be vivianite (oxidised vivianite).

Vivianite

Vivianite, ideally $Fe_3(PO_4)_2\cdot 8H_2O$, was named after John Henry Vivian FRS (1785–1855), an industrialist and member of Parliament for Truro, by the influential German geologist Abraham Gotlobb Werner[2] (Embrey, 1994; Tindle, 2008). It belongs to the eponymous group of phosphate and arsenate minerals, which have a general formula $M_3^{2+}(XO_4)_2\cdot 8H_2O$, where M can be Fe, Mg, Mn, Ni, Zn or Co and X can be P or As. It is notable for its tendency to change colour from white or greyish to blue on exposure to light and air.

Unoxidised vivianite is colourless and translucent. On exposure, Fe^{2+} is gradually oxidised to Fe^{3+}, and the mineral changes from colourless to vivid blue/green to light brown and eventually to dark brown. The oxidation process has been studied in detail (McCammon and Burns, 1980; Manning *et al*., 1991; Rouzies and Millet, 1993; Frost *et al*., 2004) but there is still discussion with regard to the rate of oxidation (this may vary with temperature, differing compositions/minor substitutions for iron) and the physical and chemical changes during the process. Chua *et al*. (2016) succinctly describe the alteration sequence and Rothe *et al*. (2016) provide a review of the oxidation process and its products.

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[2] Abraham Gottlob Werner (1749–1817) was Inspector and Teacher of Mining and Mineralogy at the Freiberg Mining Academy. An influential teacher, he propounded a theory of the Earth which came to be known as Neptunism.

The composition of vivianite is influenced by the chemistry of the solutions in which it forms. Significant amounts of magnesium and/or manganese commonly replace iron in material from the near subsurface (Rothe *et al*., 2016). Substitutions at the M^{2+}-site are more diverse and complex in specimens from polymetallic ore deposits.

Vivianite is well known to mineralogists as large fine crystals which occur in the late-stage primary assemblage in polymetallic deposits[3]. In the near subsurface, vivianite forms at low to intermediate Eh where there are low concentrations of reduced sulphur (which would otherwise precipitate iron sulphides) and high concentrations of dissolved phosphate (Virtanen, 1994). It is found in bog iron ores, organic-rich lake sediments and encrusting fossil bones/teeth (Nriagu and Dell, 1974; Emerson, 1976). Rothe *et al*. (2016) provide a comprehensive list of such occurrences. Vivianite is found in decaying plant and animal tissue including human corpses (Tessadri, 2000), coprolites, bones, shells and in organic-rich anthropogenic sediments, particularly those contaminated by sewage (Dodd *et al*., 2000; Taylor and Boult, 2007).

Vivianite has been recorded in a variety of archaeological settings, particularly those associated with human remains or ancient industries closely associated with organic materials, notably leather and bone (Jakobsen, 1988; McGowan and Prangnell, 2006; Nutt and Swihart, 2012). Here its presence is attributed to the release of Fe^{2+} ions from metal artefacts and phosphate from bone/organic matter. Vivianite formation has been reported in human remains including American soldiers in Vietnam (Mann *et al*., 1998) and skeletons from cemeteries in Queensland, Australia (McGowan and Prangnell, 2006), but perhaps its most noteworthy archaeological occurrence is with Ötzi, the Bolzano iceman from Tyrol (Tessandri, 2000; Pabst *et al*., 2009).

Archaeological vivianite was identified by its characteristic colour for most of the twentieth century. More recently the mineral has been investigated by a range of more sophisticated techniques, including optical petrography, X-ray diffraction, SEM EDAX and Raman and Mössbauer spectroscopy. Analytical methods are discussed in some detail by Rothe *et al*. (2016). However, there are few detailed reports of the chemistry of archaeological occurrences.

[3] It is commonly stated that vivianite forms in the oxidised zones of polymetallic orebodies (e.g. Bideaux *et al*., 2000). This is a misconception: vivianite from famous localities such as Huanuni and Llallagua in Bolivia and Trepča in Kosovo is part of a late-stage primary assemblage found in cavities below the supergene zone. The same is true at the type locality at Wheal Kine, St Agnes, Cornwall, where vivianite crystals encrust pyrrhotite, and are associated with siderite, and the more famous occurrence at Wheal Jane, where vivianite is found with cronstedtite and ludlamite.

ANALYSIS

Petrography of the Rose Lane Vivianite-bearing Sandstone

The Rose Lane vivianite-bearing sandstone is a fine-grained well-sorted quartz arenite (Fig. 1). There is little sign of bedding and the rock is clast-supported with little or no detrital interstitial material. Void spaces comprise approximately 10–20% of the rock by volume. Euhedral, authigenic, syntaxial, quartz and feldspar overgrowths locally grow into the voids and they are partially infilled with minor kaolinite or with fibrous, highly pleochroic vivianite. Quartz (>80%) is accompanied by untwinned and plagioclase feldspars (combined <10%) and by minor to trace amounts of muscovite, chlorite, zircon, tourmaline, rutile and garnet. Untwinned feldspar is more abundant than plagioclase.

Monocrystalline quartz with uniform or patchy extinction is cemented by authigenic quartz that can show euhedral terminations into voids. All feldspars are unaltered and include plagioclase, microcline and perthite; some grains are enclosed within euhedral feldspar overgrowths. Muscovite flakes show kinking and splayed ends indicating that the long flakes have suffered compaction. The flakes are subparallel to each other and also to rare, pale-coloured chlorite flakes, which both define a very poor, planar fabric. Trace amounts of 40–120 μm long, subhedral to euhedral, zoned or unzoned zircon; 40–100 μm diameter, unaltered, brown chromite; 50–150 μm diameter, deep green or brown tourmaline; 40–200 μm long, rounded, twinned, orange to red-orange rutile; 60–120 μm diameter pale-coloured TiO_2 minerals pseudomorphing original iron-titanium oxides; 50–200 μm diameter, fine-grained white or yellow TiO_2 minerals and a single zoned garnet are present. Single, 5–20 μm diameter crystals of chalcopyrite, ilmenite and hemoilmenite are present in detrital quartz grains. Trace amounts of 2–10 μm long TiO_2 grains may be authigenic.

Figure 1. Random small dark vivianite spots cement silicate grains within the hone. Similar sized brown to dark brown spots of highly oxidised vivianite occur towards the surfaces of the artefact. Photographed soon after manufacture of the thin section and before extensive oxidation.

Hematite and iron sulphides either as detrital grains or authigenic phases are absent.

Rock fragments are minor and are almost all quartz-rich. Polycrystalline quartz and rounded, fine-grained 'chert' are more common than fine-grained phyllite.

Radiating kaolinite books infill void spaces and elsewhere pale-coloured phyllosilicate also may be a local cement.

Macroscopically visible black patches are seen in thin section to comprise up to 300 μm diameter rosettes of radiating, zoned vivianite crystals with indigo blue/blue-emerald green cores and thin pale brown rims (Fig. 2). The spots are locally concentrated, although do not occur on the surface of the artefact and enclose quartz and feldspar, both minerals showing euhedral terminations.

After some months, as the mineral oxidises, the core-colour changes to emerald green, losing much of its blue tint, and the outer brown zones increase in size and darken. Then vivianite becomes far more difficult to recognise and indeed fully 'oxidised vivianite' would be difficult to distinguish from limonite-stained phyllosilicates and easy to overlook.

Electron microprobe analyses were made at the Open University using a Cameca SX100 electron microprobe fitted with five wavelength-dispersive spectrometers, operating at 20 kV, 20 nA beam current and a 10 μm spot size; standards included a suite of natural and synthetic materials. Data were processed using the PAP method of Pouchou and Pichoir (1985) for improved quantitative microanalysis.

Typical elemental analyses of these vivianite crystals are shown in Table 1 and include cores and margins of single crystals. These electron microprobe analyses show that vivianite carries significant magnesium (up to 7.78 wt% MgO) along with minor amounts of calcium (up to 2.52 wt% CaO) and manganese (up to 0.65 wt% MnO). Soda and potash are up to 0.25 and 0.60 wt% respectively and silica and alumina are both less than 0.14 wt%. Analyses of the core (AN) and rim (AO) of a single vivianite crystal show little chemical difference.

DISCUSSION

The analyses of the cores and margins of the Rose Lane vivianite crystals, listed in Table 1, show them to be magnesium- and calcium-rich and that despite a colour change from blue/blue-green cores to pale brown rims there is no alteration in their overall chemistry. This is in accord with earlier studies which suggest that the colour change is associated with the changes in the oxidation state of iron rather than any chemical change (Burns, 1993: pp. 121–124; Nassau, 2000: p. 147).

After some months exposure to light the vivianite core had changed colour from blue to emerald green suggesting its alteration to yellow-green metavivianite, $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2{\cdot}6H_2O$ and the brown rim thickened and darkened possibly due to the formation of amorphous yellow-brown santabarbaraite, $Fe^{3+}_3(PO_4)_2(OH)_3{\cdot}5H_2O$. This is the standard low-temperature vivianite alteration sequence as determined by

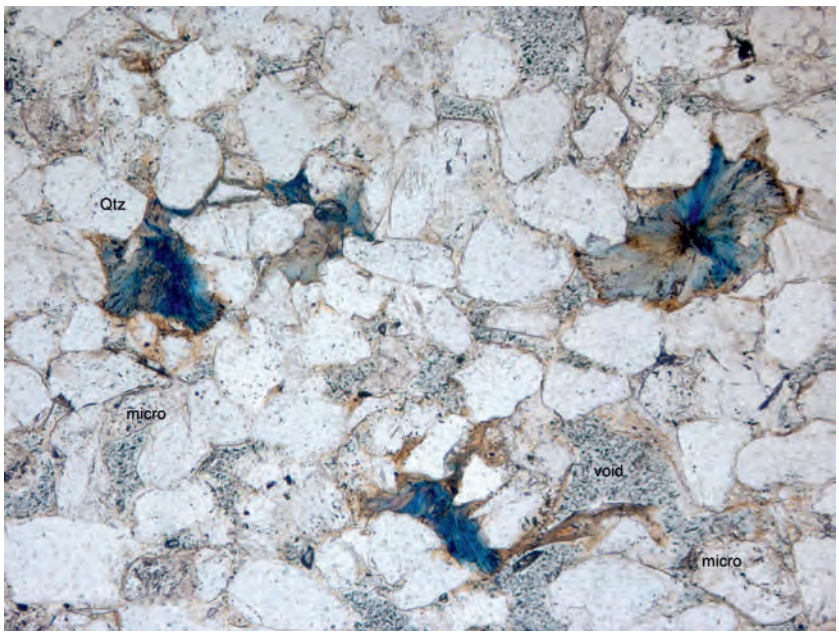

Figure 2. Radiating crystals of vivianite show pale to dark blue pleochroism and brown coloured outer rims. Vivianite infills void spaces between angular quartz and minor amounts of feldspar. Quartz (Qtz) shows euhedral authigenic overgrowths. Minor microcline (micro) and void spaces (void) accompany the quartz. The largest vivianite mass is approximately 300 μm across. Brown, non-pleochroic wisps around the void margins are highly oxidised vivianite or possibly santabarbaraite. Image in transmitted plane-polarised light.

	FeO	MgO	CaO	MnO	Na_2O	K_2O	SiO_2	P_2O_5	Total*	Empirical Formula
AB	33.44	7.54	0.71	0.60	0.04	0.03	0.08	32.17	100.11	$(Fe_{2.06}Mg_{0.83}Ca_{0.06}Mn_{0.04})_{2.99}(PO_4)_{2.00}.8H_2O$
AF	32.63	7.78	0.72	0.63	0.06	0.04	0.06	32.26	99.68	$(Fe_{2.01}Mg_{0.74}Ca_{0.11}Mn_{0.03})_{2.89}(PO_4)_{2.01}.8H_2O$
AG	34.18	5.96	0.90	0.53	0.20	0.10	0.11	31.34	98.82	$(Fe_{2.16}Mg_{0.67}Ca_{0.07}Mn_{0.03})_{2.93}(PO_4)_{2.01}.8H_2O$
AL	35.18	4.57	2.52	0.65	0.23	0.37	0.14	32.54	101.70	$(Fe_{2.16}Mg_{0.50}Ca_{0.20}Mn_{0.04})_{2.90}(PO_4)_{2.02}.8H_2O$
AM	36.10	4.44	1.17	0.58	0.26	0.60	0.07	31.59	100.31	$(Fe_{2.28}Mg_{0.50}Ca_{0.10}Mn_{0.04})_{2.92}(PO_4)_{2.01}.8H_2O$
AN core	34.86	6.63	1.11	0.62	0.13	0.12	0.10	32.50	101.57	$(Fe_{2.12}Mg_{0.72}Ca_{0.09}Mn_{0.04})_{2.97}(PO_4)_{2.00}.8H_2O$
AO rim	34.16	6.64	0.79	0.59	0.11	0.08	0.04	31.95	99.86	$(Fe_{2.12}Mg_{0.74}Ca_{0.06}Mn_{0.04})_{2.96}(PO_4)_{2.02}.8H_2O$
Vechten	51.33	4.09	0.75	2.61	n.d.	n.d.	n.d.	41.25	100.00	$(Fe_{2.46}Mg_{0.35}Ca_{0.05}Mn_{0.13})_{2.99}(PO_4)_{2.00}.8H_2O$

* Includes H_2O estimated to be 25.50 wt% for Canterbury hones. Alumina <0.14 wt%. The abbreviation n.d. = not done.

Table 1. Chemical analyses of vivianite from the Rose Lane Hone with data for Fort Vetchen in The Netherlands (Kloprogge *et al*., 2003) included as the bottom row.

Chukanov *et al*. (2012). However, it should be noted that in calcareous media other dark brown final oxidation products have been suggested, including lepidocrocite, γ-$Fe^{3+}O(OH)$ (Roldán *et al*., 2002).

The slow rate of oxidation is in marked contrast with the results of Wilfert *et al*. (2018) who found that, unlike pure synthetic vivianite which remained unoxidised, synthetic magnesium- and calcium-bearing vivianite oxidised within two days. They suggested that the impure nature of this vivianite was the cause.

There are too few quantitative chemical analyses of archaeological vivianite for a detailed discussion. However, magnesium, calcium and manganese, in addition to iron, are incorporated into the structure of the Rose Lane vivianite (Table 1), hence it shows some similarities with the calcium-bearing magnesian vivianite with an empirical formula $Fe^{2+}_{2.5}(Mg,Mn,Ca)_{0.5}(PO_4)_2{\cdot}8H_2O$ identified from soil samples from a Roman camp near Fort Vechten in The Netherlands (Kloprogge *et al*., 2003).

The present occurrence of oxidised vivianite as a very late diagenetic phase within the pore space of a very open feldspathic sandstone hone is doubly unusual. Firstly, most vivianite in archaeological contexts occurs as a coating rather than within an artefact. Secondly, most commonly, vivianite is recorded from fine-grained, often organic-rich, argillaceous (natural and anthropogenic) rather than arenaceous sediments. However, previously it has been recorded as 'radiating acicular spheroids' within soft Quaternary sandstones from New Zealand (Rogers, 1977); this appears to be the closest analogue to its occurrence here.

It has been suggested that the sources of iron and phosphorus for vivianite precipitation in siliciclastic rocks are local or very local (Nutt and Swihart, 2012) and this is probably true for the Rose Lane occurrence. In archaeological contexts the sources of phosphorus and calcium are often bone and so it may be of significance that at Rose Lane abundant fish bones were found 'packed in a large pit' probably associated with a sixteenth century building on the south of the site and that there are also records of small-scale iron working possibly providing a source for the iron (Barrett and Westmacott, 2006).

CONCLUSIONS

The occurrence, within an archaeological context, of magnesium-rich and calcium-bearing vivianite as a late-stage cement within a sandstone artefact has hitherto not been recorded and is surprising.

The surprise is largely due to the absence of any vivianite on the surface of the hone (in most archaeological contexts vivianite is a surface feature/coating). As the thin section clearly shows there is no blue vivianite close to the surface of the artefact, instead there are brown oxidised pseudomorphs. The final oxidation product(s) are brown and amorphous and without detailed inspection or analysis would probably be dismissed as 'iron staining' or as natural limonite.

Although searching for it within curated thin sections is probably fruitless, vivianite (an iron, phosphate and organic matter indicator) and calcium-bearing vivianite (a potential bone indicator) may have a more extensive archaeological occurrence than has been assumed, potentially occurring within a wide range of lithic materials.

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SUPERGENE MANGANESE MINERALISATION IN THE NORTHERN PENNINE OREFIELDS

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The occurrence and distribution of previously reported manganese oxide minerals within the Northern Pennine orefields of the Alston and Askrigg blocks is reviewed and several hitherto unreported occurrences described. A supergene origin, resulting from the alteration of primary manganese-bearing iron carbonate minerals is proposed, with significant chemical input from associated lead, zinc and barium minerals. The abundance and distribution of manganese oxides is consistent with the widespread abundance of primary iron carbonates in the Alston orefield and their much more restricted occurrence in the Askrigg orefield. In the main, the manganese oxides are lead- or barium-containing species, demonstrating the importance of primary galena, baryte and witherite in the oxidation process. In the Middle Fell area of Alston Moor, zinc-bearing manganese oxides occur, reflecting the extensive development of supergene zinc mineralisation in that area. Thin, poorly crystalline coatings of zinc-bearing manganese oxides reported on the walls of Hudgill Burn Mine caverns at Middle Fell, although uncharacterised, probably represent a similar but weakly developed extension of this mineralisation in the host limestone.

INTRODUCTION

The area covered by this review encompasses the Northern Pennine orefields of both the Alston and Askrigg blocks as described by Dunham (1948, 1990) and Dunham and Wilson (1985). Although the past few decades have seen numerous reports of hitherto unrecorded supergene species from these areas, manganese oxide minerals have attracted comparatively little attention. This may almost certainly be attributed both to the generally inconspicuous nature of these minerals and the difficulty of obtaining precise identifications.

GEOLOGICAL OUTLINE

The regional geology, structural setting, nature and origin of the orefields' mineral deposits have been the subject of detailed studies by many authors, the most comprehensive and detailed of which are those of Dunham (1934, 1948, 1974, 1990), Dunham and Wilson (1985), British Geological Survey (1992, 1996), Stone *et al*. (2010) and Bevins *et al*. (2010).

Whereas detailed descriptions of the geology of these orefields are not appropriate here, the following brief summary draws upon these texts to offer a background to understanding the context of the minerals described in this paper.

The Northern Pennine orefields coincide with the major fault-bounded structural units known as the Alston and Askrigg blocks. These comprise areas of comparatively thin successions of Carboniferous sedimentary rocks which rest unconformably upon Lower Palaeozoic sedimentary and volcanic rocks in which lie the Caledonian granitic batholiths of Weardale and Wensleydale, respectively. Substantial parts of the Lower Carboniferous successions, especially in the Askrigg Block, consist of marine limestones, which in both areas pass upwards into cyclical 'Yoredale-type' sequences composed of regularly repeated cyclothems of limestone, mudstone, sandstone and locally thin coals. In the Alston Block, the extensive quartz-dolerite intrusion of the Whin Sill was emplaced within the Carboniferous sedimentary succession during Permo-Carboniferous times. No such comparable intrusion is present in the Askrigg Block.

The gentle easterly regional dip of the Carboniferous rocks, and in the Alston Block the Whin Sill, is disrupted by local flexing and a widespread conjugate network of normal faults with displacements typically of only a few metres. During Hercynian times, convective flow of warm saline brines, driven mainly by the comparatively high heat-flow of the concealed granites, emplaced the orefields' extensive suite of mineralised veins within these fractures and created a suite of associated replacement deposits within some limestone wall-rocks.

The orefields, which are regarded as examples of the worldwide Mississippi Valley-type (MVT), are characterised by marked zonal distributions of constituent

minerals. This is especially prominent in the gangue mineral assemblages of the Alston Block. Here, deposits within an inner zone are characterised by the almost universal presence of abundant fluorite: the surrounding outer zones are characterised by the abundance of barium minerals, predominantly baryte and witherite, though with local concentrations of barytocalcite and rare alstonite. The demarcation of these zones is typically sharp with the mineral content being almost mutually exclusive. A similar, though very much less obvious, zonation can be discerned in the deposits of the Askrigg Block. It was this zonation and suggestions of its possible relationship to concealed granitic bodies that led to speculation on the possible presence of concealed granites beneath both the Alston and Askrigg blocks and their subsequent proving in deep boreholes at Rookhope and Raydale (Dunham *et al*., 1965; Dunham, 1974).

Throughout both orefields the main ore minerals, galena and sphalerite, together with small local concentrations of copper sulphides, are accompanied by an abundance of fluorite, baryte, witherite, and locally calcite as the main gangue species. In addition, in the Alston Block, quartz and iron carbonate minerals are extremely widespread and abundant, a feature which distinguishes this area from that of the Askrigg Block. Dunham (1990) attributed this to the derivation of the requisite iron and silica from the Whin Sill by the mineralising fluids.

The orefields, especially that of the Alston Block, have long enjoyed a worldwide reputation as a source of magnificent specimens of many of these species, most notably fluorite, witherite, barytocalcite and alstonite, though a large variety of other minerals are recorded, including a wide variety of supergene species. Amongst the latter is the range of manganese minerals reviewed here.

MANGANESE MINERALS

The species confirmed beyond reasonable doubt are listed below in capitals whilst those that have been mentioned but are unconfirmed, or discredited, are listed in italics; obsolete species names are listed in italics in inverted commas.

Birnessite, $(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$

Birnessite is an uncommon hydrated manganese oxide with a complex layer structure (Post and Veblen, 1990; Holland and Walker, 1996; Post and Heaney, 2014). The type locality is a road cutting at Birness north of Aberdeen (Jones and Milne, 1956). British localities, most of which are in Scotland, are summarised in Tindle (2008).

Dale *et al*. (2015) described in detail the Hudgill Burn Mine caverns, near Alston, including a large section devoted to the geochemistry of the cave deposits. They included a particularly detailed description of the manganese oxides. One of the minerals is described as:

> "very heavily zinc-sorbed birnessite-type phyllomanganate with a 7 Å layer spacing, having a structure and zinc content that approach those of chalcophanite".

Unfortunately, despite presenting large quantities of geochemical and structural data, their interpretation of this is rather confused.

Firstly, it is unclear if their data are derived from material obtained from one discrete locality within the cave system, or from several localities and combined. If the latter, there are major issues in how they have interpreted the geochemical and structural data. More critically, however, scrutiny of their interpretation of the analytical data shows an apparent lack of understanding of what each analytical technique reveals. This is amply demonstrated by their statement reproduced above.

The manganese minerals birnessite and chalcophanite have structural similarities (Drits *et al*., 1997; Post and Heaney, 2014). They are tetravalent manganese oxides with a layer structure (phyllomanganates) but there is little evidence of Zn cations being replaced by other elements in naturally occurring chalcophanite (Post and Heaney, 2014: p. 1957). An inspection of the published data (Dale *et al*., 2015) allows some of the errors to be explained, but a full characterisation of the minerals needs a detailed consultation of the full dataset, which is beyond the scope of the present paper. Many manganese oxide species are poorly crystallised in nature and birnessite can be difficult to identify even when detailed structural and chemical analyses have been undertaken (Post and Heaney, 2014). Chalcophanite, on the other hand, is often remarkably well crystallised. Post and Heaney (2014) speculated that the Zn cation is particularly well suited for growing a well crystallised birnessite-like phase.

Dale *et al*. (2015) used X-ray diffraction (XRD) data as their main argument for suggesting the presence of a birnessite-type mineral. However, their statement, "unequivocal evidence that Hudgill's deposits are largely or wholly birnessite-type structures" is not in our opinion proven by their data. Using XRD, pure birnessite is characterised by a very intense peak (100% intensity) at around 7.144 Å, with many other less intense peaks, the most significant at 3.572 Å (27%), 2.519 Å (14%) and 2.429 Å (13%) (ICDD Powder diffraction File No. 00-043-1456). The XRD data presented by Dale *et al*. (2015) in their Table 3 and Figure 22a reveals that despite recording a peak at 7.20729 Å, it has an intensity of only 56.3% compared with the most intense (100%) peak at 2.45017 Å. Preferred orientation of crystallites caused during sample preparation can result in dramatic differences in the expected intensities, but this has no effect on peak position. The data presented by Dale *et al*. (2015) shows a small, but noticeable shift (typically at least 0.06 Å) in the overall peak positions (*d*-spacings) compared with those expected for birnessite. Peak position can be influenced by chemistry, particularly where solid-solution series exist. Dale *et al*. (2015) suggested that

their analyses which recorded 17.3 % Zn showed "a very heavily zinc-sorbed birnessite-type phyllomanganate with a 7 Å layer spacing, having a structure and zinc content that approaches that of chalcophanite", but there is no proven solid-solution series between the two minerals. Furthermore, if there was a series, one would expect that with increasing Zn content the position of the main birnessite peak at 7.144 Å would shift towards that of the main chalcophanite peak at 6.96 Å. The data presented by Dale *et al*. (2015) shows the opposite.

There is a possibility that the data presented by Dale *et al*. (2015) could represent an entirely new mineral with structural similarities to a birnessite-group phase, but zinc-dominant. However, uncertainties over whether their analytical data was obtained from a single sample, or a multitude from different localities within the cave system at Hudgill Burn Mine caverns would have to be resolved. Other members of the birnessite group, ranciéite and takanellite, as expected, show structural similarities, but both exhibit a much greater shift in peak positions (0.17 Å in the case of the strongest ranciéite peak) in relation to the material analysed by Dale *et al*. (2015).

A Raman spectrum presented by Dale *et al*. (2015) (their Figure 23) from a "sooty" deposit bears no resemblance to birnessite and despite their assertion that the spectra may represent a chalcophanite-type structure obvious differences exist. We conclude that based on the available data birnessite should not be listed as occurring in the Northern Pennine orefields.

CHALCOPHANITE, $(Zn,Fe^{2+})Mn^{4+}{}_3O_7 \cdot 3H_2O$

Previous British records of chalcophanite are restricted to the manganese deposits of the Lecht mines, Tomintoul, Grampian Region (Nicholson, 1987, 1989a, 1989b, 1992; Nicholson and Anderton, 1989) and a small number of localities in the Central Wales Orefield (Cotterell and Mason, 2003; Cotterell, 2009).

Chalcophanite, accompanied by hetaerolite, has been identified from a dump at the Bayle Hill mines on Middle Fell, Alston [NY 7285 4565]. The Bayle Hill mines worked small vein and replacement deposits of supergene smithsonite associated with the Bayle Hill and Middle Fell Cross veins within the Great Limestone. In his description of these deposits, Dunham (1990: p. 123) noted that the only accompanying minerals were calcite and aragonite, though the presence of 'limonite', found during the present study, suggests that iron carbonate, either as siderite or ankerite, may also have been present within the primary mineralisation. In a recent description of smithsonite replacements of rugose corals from this site, Young and Hopkirk (2019) commented on the unusual extent of intense supergene mineralisation in the Middle Fell area, including that at Hudgill Burn, and suggested that this may be due to the deposits being protected from Quaternary glacial stripping by a local area of cold-based static ice.

Chalcophanite and hetaerolite occur at the Bayle Hill mines as finely crystallised crusts and masses composed of sparkling dark blue-grey to black micro-crystals (Fig. 1) overgrowing stalactitic or colloform limonite. So far it has proved impossible, using a stereomicroscope, to distinguish one Mn oxide phase from the other, but powder X-ray diffraction (PXRD No. NMW X-3764; NMW 2020.12G.M.1) performed at AC–NMW clearly confirms the presence of both minerals (Fig. 2). No direct chemical data has been acquired, but the detection of two zinc-bearing phases within the PXRD data and the associated abundance of supergene zinc mineralisation across the Middle Fell area is compelling evidence for its presence.

A Raman microscopic analysis of a "sooty" deposit from the Hudgill Burn Mine caverns, approximately 2 km east of the Bayle Hill deposit, near Alston, Cumbria [NY 7505 4546] presented by Dale *et al*. (2015) as evidence of a chalcophanite-type structure is not sufficiently convincing to draw such a conclusion. Furthermore, XRD data obtained from "sooty" deposits from "the north of the cave system" reveal no structural peaks that one would expect for chalcophanite. Some similarities with a birnessite-type structure exist, but not enough for a reliable identification. However, combined with a single semi-quantitative XRF analysis on material from the Urals sector of the maze cave indicating the presence of 54.5% Mn, 17.3% Zn, 1.7% Ca, and many other elements, Dale *et al*. (2015) concluded that it represented some sort of hybrid between birnessite and chalcophanite. Based on the data presented by Dale *et al*. (2015) such a conclusion is unsafe. Indeed, their data fail to identify what the substance is. Perhaps a more detailed set of analyses may reveal a hitherto undescribed manganese oxide mineral structurally and chemically distinct from birnessite and chalcophanite, but at present this mineral remains unclassified.

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

Coronadite is the lead-dominant member of the cryptomelane group. It is uncommon but widespread in the British Isles (Tindle, 2008).

Coronadite was first reported from the Northern Pennines by Young *et al*. (1996) who described its occurrence on spoil heaps from shallow workings on Sedling Vein at High Sedling Mine, Cowshill, Weardale, Co. Durham [NY 8698 4076] on the basis of PXRD data alone. This technique is not wholly reliable in characterising coronadite-group minerals to species level. The mineral here occurs in some abundance, as blocks up to 20 cm across composed of compact steel-grey masses of mammillated crusts, many of which enclose angular clasts of fluorite and vein quartz (Figs 3 and 4). Dark brown cellular goethite locally accompanies the coronadite. A subsequent study using X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses reported by Moreton and Lawson (2013) confirmed the identity of coronadite from this location. Their XRF data showed that samples collected from a tip

Figure 1. Dark blue-grey to black finely crystallised intergrown chalcophanite and hetaerolite enclosing yellow-orange limonite stalactites from the Bayle Hill mines, Middle Fell, Alston. The specimen is 9 cm across. Brian Young specimen, No. BY9672/B. Photo Andy Hopkirk.

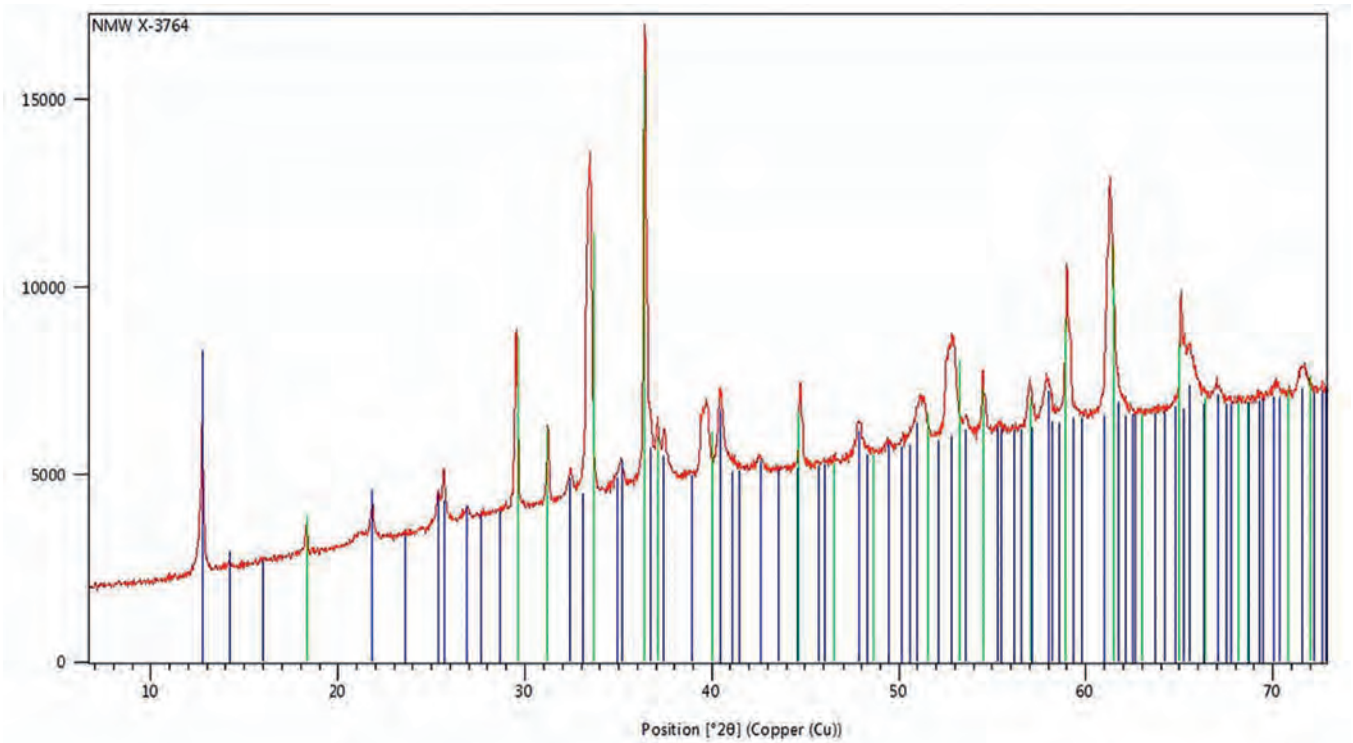

Figure 2. PXRD pattern NMW X-3764 (red line) of specimen NMW 2020.12G.M.1 from the Bayle Hill mines, Middle Fell, Alston. The blue lines represent the structural peaks for chalcophanite and the green lines 'hydrohetaerolite'.

Figure 3. A cellular mass of coronadite with smooth mammillated crusts on quartz. High Sedling Mine, Cowshill, Weardale. The field of view is 4 cm across. Brian Young specimen, No. BY6931. Photo Andy Hopkirk.

at Sedling Vein and a track nearby are near end-member coronadite in composition. Powder X-ray diffraction data (NMW X-2641) acquired as part of this study from a specimen collected by BY in 1995 (NMW 2020.12G.M.3; part of Brian Young specimen, No. 6929) indicate the hard black material to be a member of the coronadite group. Energy-dispersive spectroscopy (SEM-EDS) analysis of a carbon-coated, but unpolished, flat fracture surface on a small fragment derived from specimen NMW 2020.12G.M.3 revealed that marginally more potassium than lead was present (suggesting the presence of cryptomelane); a second analysis of a finely mammillated crust revealed almost pure coronadite. Chemical zonation is extremely common in coronadite-group minerals and therefore it is highly probable that individual specimens contain both coronadite and cryptomelane, although it would appear from the limited chemical analyses that material from Sedling Vein is more likely to be lead-dominant.

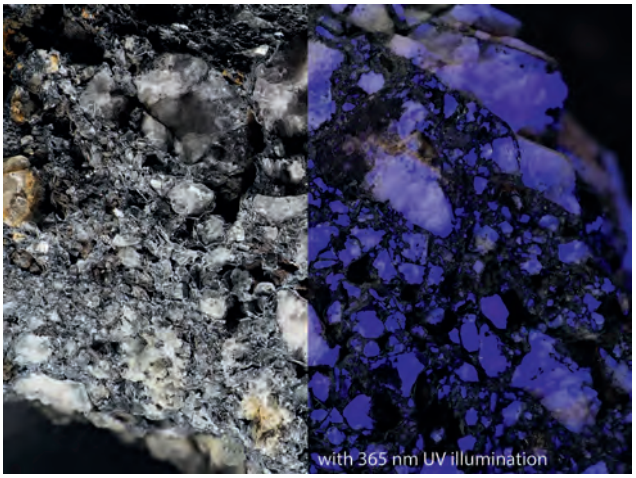

Figure 4. Steel-grey cellular crusts of coronadite enclosing angular fluorite clasts. The latter are particularly conspicuous in the right hand portion of the view, which is illuminated by 365 nm ultra-violet light. High Sedling Mine, Cowshill, Weardale. The field of view is 8 cm across. Brian Young specimen, No. BY6932. Photo Andy Hopkirk.

The Grasshill mines, in upper Teesdale, Co. Durham [NY 819 355] have long been known for the local abundance of deep green crystalline pyromorphite (Jameson, 1816; Winch, 1817; Greg and Lettsom, 1858; Young, 1985) which here typically occurs as roughly concentric banded cellular masses intergrown and inter-layered with dark grey to black manganese oxides described by Young (1985) as "brownish-black earthy 'limonite'". Symes and Young (2008: p. 166) figured a fine example from the Russell Collection at the Natural History Museum [BM 1964, R 7998] showing the contrast between pyromorphite and manganese oxides. Cotterell *et al*. (2012) identified the manganese oxides as coronadite on the basis of XRD in combination with its intimate association with abundant supergene lead-bearing mineralisation including plumbogummite.

The grid reference for the pyromorphite-rich dump was erroneously given by Cotterell *et al*. (2012) as NY 8165 3560 which lies just inside an enclosed field devoid of any obvious spoil. During fieldwork by TFC in July 2018, traces of pyromorphite were observed nearby in one of the westernmost hushes at NY 8165 3551, but no manganese oxides were noted and pyromorphite was very sparse. This additional fieldwork suggests that there might be several discrete pyromorphite-rich dumps within the extensive tract of exposed spoil known as Highfield Hushes rising up the hillside northeast of the derelict Grasshill Farm. Cotterell *et al*. (2012) cited a specimen in the R. J. King collection at AC–NMW (NMW 83.41G.M.9525) recorded as collected from dumps on Black Streak Vein at NY 821 357 by J. A. Jones in 1983 as being particularly rich in pyromorphite-plumbogummite and what appears to be coronadite. This dump has not been relocated, but several others extremely rich in pyromorphite, plumbogummite and probable coronadite were identified during the same fieldwork (at NY 8192 3560, NY 8193 3559 and NY 8189 3558).

Whereas the vein, or veins, from which this material was derived is not exposed, Cotterell *et al*. (2012) also identified coronadite, also on the basis of XRD, as irregular massive concentrations, up to 10 cm across, in the earthy brown 'limonitic' walls of a galena and baryte bearing vein exposed *in situ* in a nearby temporary excavation [NY 8180 3551]. Moreton and Lawson (2013) highlighted the absence of detailed chemical data in the identification of coronadite, which was subsidiary to the focus of the paper by Cotterell *et al*. (2012). It remains true that no chemical data has been obtained for these manganese oxides, the sheer abundance of pyromorphite and plumbogummite in direct contact with the manganese oxides and the absence of any other associated minerals on the weathered spoil makes a compelling case for this being the lead-dominant member of the coronadite group. With regard to the *in situ* occurrence the case is less clear: although primary lead mineralisation is evident, the presence of baryte might have a bearing on the chemistry of the supergene manganese oxide phase.

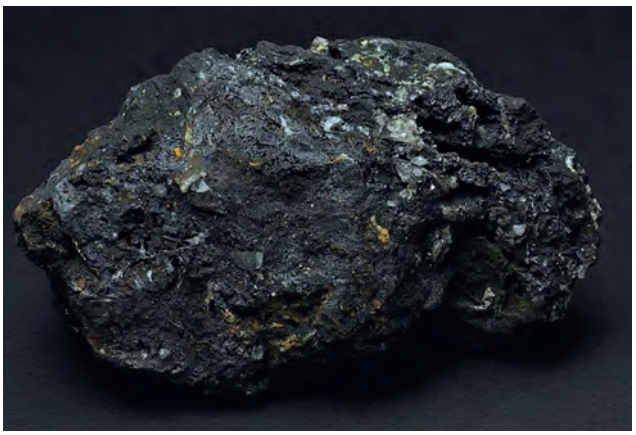

Figure 5. Dense mass of a dark grey coronadite-group mineral with a few scattered angular quartz clasts, from the Cashwell mines, Alston Moor. The specimen is 8 cm across. Brian Young specimen, No. BY9492/A. Photo Andy Hopkirk.

Elsewhere in Teesdale, steel-grey to black, friable, locally mammillated, crusts on fluorite from two underground locations in the long abandoned Firestone Level of Skears Mine, near Middleton-in-Teesdale, Co. Durham [NY 9424 2786] were identified by Moreton and Lawson (2013), using a combination of XRD and XRF, as containing coronadite. One of the samples also contained romanèchite mixed with coronadite. Semi-quantitative energy-dispersive X-ray analyses of a compact black manganese oxide from the dumps on Knapside Vein at Hard Rigg Edge [NY 6549 3869] (Young, 1985) reveal a composition which is consistent with coronadite (Stephen Moreton, *personal communication*, 2020).

Young and Pacey (2016) described the occurrence of segnitite within pockets and botryoidal crusts of unidentified black manganese oxides up to 5 cm wide within the weathered surface exposures of Slitt Vein at Heights Pasture Mine in Weardale, Co. Durham [NY 9220 3882]. Subsequent PXRD analysis (NMW X-3560; NMW 2020.12G.M.7) has identified grey botryoidal crusts on quartz as a coronadite-group mineral. Its association with small white crystals of cerussite strongly suggests that it is the lead-dominant member of the group, a conclusion which is supported by recent semi-quantitative energy-dispersive analyses on a scanning electron microscope (Stephen Moreton, *personal communication*, 2020).

Fieldwork during 2016 revealed the abundance of a dark grey to black manganese-oxide-rich mineral in the spoil from old opencast trenches along the outcrop of the West Cross-Doukburn Vein at the Cashwell mines, which are remotely situated close to the Pennine Way on Alston Moor, Cumbria [NY 7100 3574]. This mineral is present as irregular blocks up to about 6 cm across in which angular clasts of white vein quartz are locally common (Figs 5 and 6). Within many small cavities the mineral exhibits crude mammillated surfaces. This material closely resembles the manganese-rich vein-stone described by Young *et al*. (2012) from High Sedling Mine, Weardale (see above). A PXRD analysis (NMW X-3558; NMW 2020.12G.M.6) of black porous and hard grey manganese oxides indicates that it is a member of the coronadite group, but the exact species has not been confirmed by chemical analysis.

The dumps from old workings along the outcrop of Old Rake Vein on Friarfold Moor, Swaledale, North Yorkshire [NY 957 014] locally contain blocks, up to about 30 cm across composed of cellular masses of fine-grained white baryte in which irregular pockets of a hard dark steel grey massive manganese oxide mineral, locally with mammillated surfaces up to 3 cm across in cavities, are conspicuous (Fig. 7). An XRD analysis of this material (part of Brian Young specimen No. 7115) at the laboratories of the British Geological Survey in Edinburgh (BGS X-ray No. XE912) indicated the presence of romanèchite, but subsequent PXRD analysis at AC–NMW (NMW X-2643; NMW 2020.12G.M.5) suggested the presence of a coronadite-group mineral mixed with pyromorphite. The association with a

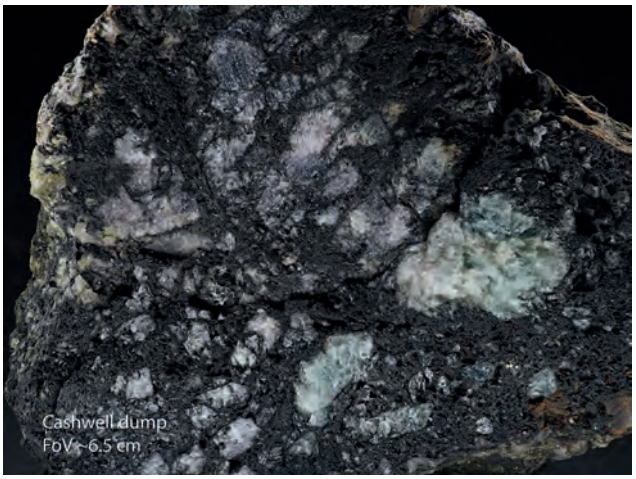

Figure 6. Dark grey dense cellular mass of a coronadite-group mineral enclosing abundant angular quartz clasts from the Cashwell mines, Alston Moor. The field of view is 6.5 cm across. Brian Young specimen, No. 9492/A. Photo Andy Hopkirk.

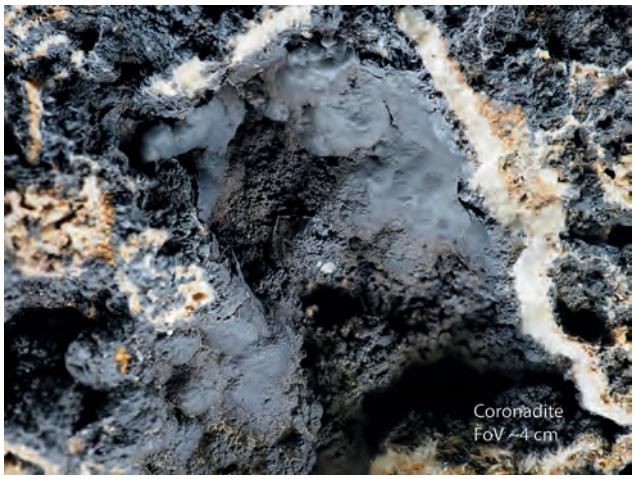

Figure 7. Dark grey mammillated crusts of coronadite coating baryte. Old Rake, Friarfold Moor, Swaledale. The field of view is 4 cm across. Brian Young specimen, No. BY7114. Photo Andy Hopkirk.

supergene lead-bearing phase suggested that coronadite was the most likely candidate and this was confirmed by semi-quantitative SEM-EDS at AC–NMW on a small powdered sample: Mn>Pb>Ba.

Subsequent to this, in 2017, a series of very rich manganese oxide coated specimens from Old Rake were submitted to AC–NMW by JACL for identification. On these both romanèchite and a coronadite-group mineral have been identified. The coronadite-group mineral has only been formally identified in one specimen (NMW 2019.6G.M.4) where it occurs as porous black cellular 'boxwork' crusts in intimate association with pyromorphite and baryte (PXRD No. NMW X-3556) and as a mixture with romanèchite and minor pyromorphite in a hard grey massive manganese oxide which displays a prominent black surface coating (PXRD No. NMW X-3557).

A similar assemblage of minerals from the Hungry Hushes area in Arkengarthdale in the JACL collection has not been analysed. However, mammillated black coatings on cockscomb baryte with minor galena from a thin (<10 cm thick) vein cutting chert in the upper parts of Hungry Hushes has been identified by XRD and quantitative XRF on a composite sample as coronadite (Stephen Moreton, *personal communication*, 2020).

CRYPTOMELANE, $K(Mn_7^{4+}Mn^{3+})O_{16}$

The sole record of cryptomelane from the Pennine orefields is that of Cotterell *et al*. (2012) who identified it using XRD (NMW X-2230) and SEM-EDS on specimen NMW 2008.26G.M.14 as black to dark grey masses within abundant blocks of rusty orange, massive, cellular and mammillated goethite found at NY 8178 3549 in the extensive spreads of mine waste from ancient workings in the Grasshill North, Middle and Black Leader veins in the Great Limestone and overlying sandstones at Highfield Hushes, Grasshill mines, Teesdale, Co. Durham (Fig. 8). Cryptomelane is a minor constituent within what is dominantly goethite and occurs as a later coating. This occurrence is separate to the pyromorphite-rich dumps at that site.

Figure 8. Smooth mammillated crusts of dark grey cryptomelane. Grasshill mines, Teesdale. The field of view is 3 cm across. Brian Young specimen, No. BY8570. Photo Andy Hopkirk.

HETAEROLITE, $ZnMn_2O_4$

Ryback and Tandy (1992) reported hydrohetaerolite on calcite within oxidised vein material at Copperthwaite Vein in Swaledale, North Yorkshire. No details of its identification are recorded. Hydrohetaerolite is currently regarded as a hydroxyl-bearing variety of hetaerolite (Bosi *et al*., 2019).

Recent investigations have identified well crystallised chalcophanite and hetaerolite in porous lustrous black aggregates associated with stalactitic or colloform limonite at the Bayle Hill mines [NY 7280 4564] near Alston, Cumbria. Identification was by PXRD at AC–NMW (NMW X-3764; NMW 2020.12G.M.1) which produced an excellent structural match with 'hydrohetaerolite' (Fig. 2). Given the conditions under which manganese oxides form it is unlikely that this occurrence is dump formed. It is most likely that *in situ* supergene oxidation of a sphalerite vein is responsible. Such oxidation of primary sphalerite is well documented in this part of Alston Moor, but the secondary product is usually the zinc carbonate smithsonite (Bridges and Young, 1998). Its association with chalcophanite is interesting as the name hetaerolite is derived from the Greek ἑταίρος, "companion", in allusion to the original association with chalcophanite at the type locality (Moore, 1877).

'*Psilomelane*'

Davidson and Thomson (1951) and Seager and Davidson (1952) refer to the occurrence of 'psilomelane' at Silverband Mine, Great Dun Fell, Cumbria [NY 705 319]. 'Psilomelane' is an obsolete name which has been variously used for hard black massive manganese oxides including romanèchite and hollandite (Clark, 1993). As it has not been possible to examine the specimens referred to by these authors, it is impossible to suggest the precise identity of the mineral or minerals present. The 'psilomelane' noted by Dunham (1990) from old workings on Remmington's Vein on Great Dun Fell has been identified as romanèchite (see below).

Pyrolusite, MnO_2

Orchard (1921) referred to a bed of pyrolusite up to 20 cm thick and "... resembling soft coke ..." at Silverband Mine, on Great Dun Fell, Cumbria [NY 705 319], though without any other details of its occurrence or composition. As the whereabouts of Orchard's specimens are unknown and as we have been unable to trace examples of this mineral from this location, it is not possible to verify this record. At the nearby Remmington's Vein on the east side of Great Dun Fell [NY 7180 3240], Young (*personal communication* in Dunham 1990) suggested that soft black crystalline coatings on romanèchite may be pyrolusite, though the identity has not been confirmed.

RANCIÉITE, $(Ca,Mn^{2+})_{0.2}(Mn^{4+},Mn^{3+})O_{2.0}\cdot 0.6H_2O$

Ryback and Tandy (1992) reported pink-brown powdery ranciéite from Newbiggin, Teesdale based on XRD analysis performed at the Natural History Museum, London, in 1985. No further details of this rather vague record have come to light (Tindle, 2008).

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

Romanèchite is typically found as black botryoidal masses (Post, 1999). It is widespread in the British Isles (Tindle, 2008). Dunham (1990) noted the presence of 'psilomelane' in the dumps from old workings on Remmington's Vein on Great Dun Fell. Young *et al*. (1996) identified that material using XRD as romanèchite (BGS X-ray No. XE879).

Unlike coronadite-group minerals, the XRD pattern for romanèchite is distinctive enough as to not require additional chemical data for a reliable identification. However, comprehensive identification of this material collected from Remmington's Vein, by BY in 1983 (part of Brian Young specimen, No. 2715) has been performed using a combination of PXRD (NMW X-2642) and semi-quantitative SEM-EDS as part of this present study. The small specimens, up to 3 cm across, consist of hard, dense, dark steel-grey romanèchite with irregular mammillated surfaces and feathery inclusions (Fig. 9). Three SEM-EDS analyses (data preserved at AC–NMW in the accession file for NMW 2020.12G.M.4) all show major Ba, but with a small (0.72 to 2.1 atom%) proportion of zinc. Traces of lead were identified in one analysis.

In Teesdale, Moreton and Lawson (2013) identified romanèchite as a constituent (with a coronadite-group phase) of black friable material, often showing a mammillated appearance, on crumbly fluorite from Skears Firestone Level on the west side of Hudeshope Beck near Middleton-in-Teesdale.

Figure 9. Irregular mammillated mass of dark grey romanèchite. Remmington's Vein, Great Dun Fell. The field of view is 15 mm across. Brian Young specimen, No. BY2922/C. Photo Andy Hopkirk.

As noted under coronadite, further south in the Askrigg Block, romanèchite has been identified as hard dark grey to black, mammillated crusts on baryte veinstone from Old Rake, Friarfold Moor, Swaledale [NY 957 014]. The presence of romanèchite from this location was indicated during XRD analysis of material (part of BY specimen No. 7115) at the laboratories of the British Geological Survey in Edinburgh during the 1980s, but subsequent PXRD analysis of material from the same batch, at AC–NMW (NMW X-2643; NMW 2020.12G.M.5), in 2012, identified a coronadite-group phase mixed with pyromorphite.

Romanèchite has been confirmed, on baryte, as botryoidal crusts with a compact, massive, internal form (NMW X-3453; NMW 2019.6G.M.1), and as feathery black manganese oxides (NMW X-3552; NMW 2019.6G.M.3) overgrown by the botryoidal form in a series of rich specimens from Old Rake submitted to AC–NMW for identification by JACL in 2017. Small, green euhedral prismatic pyromorphite crystals are sparsely scattered on the surface of the manganese oxides. A coronadite-group mineral is also present in this suite of samples (NMW X-3556 and X-3557; NMW 2019.6G.M.4). Romanèchite has been identified as pure coatings on baryte and as a mixture with a coronadite-group mineral where minute pyromorphite crystals occur in association (for example NMW X-3557). One specimen displays black manganese oxide epimorphs after 8 mm long pyramidal witherite crystals, indicating the source of barium required for romanèchite to form.

Manganese oxides similar in appearance to those from Old Rake have been collected by JACL in the Hungry Hushes area in Arkengarthdale, but no formal identifications have been made.

Todorokite, $(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12}\cdot 3-4H_2O$

Although known from localities in Cumbria (e.g. Milodowski *et al*., 1998), Wales and Scotland (Tindle, 2008), todorokite has not hitherto been reported from the Northern Pennines.

Todorokite was identified by XRD (MANCH: XRD847) on a specimen from Broadwood Quarry near Frosterley, Co. Durham [NZ 032 364], which was submitted for identification to Manchester Museum in 2003 (Peter Briscoe, *personal communication*, 2020). It occurs as silvery brown masses with a pearly to resinous lustre associated with siderite, ankerite or ferroan dolomite, quartz and aragonite.

A mineral similar to todorokite is recorded here from the dumps derived from old shafts, almost certainly sunk to the Great Limestone, at the junction of Grassfield North Vein with Ashgill Head Vein, north of Currick High Field, near the head of the Ireshope Burn, Weardale, Co. Durham (Dunham, 1990). A PXRD

analysis (NMW X-3765; NMW 2020.12G.M.2) of material from an old shaft dump [NY 8265 3630] reveals a substance with a structure similar to todorokite (Fig. 10). No chemical data has been obtained and therefore its full identity has not yet been ascertained. Visually, it consists of dark grey radiating to colloform masses overgrowing limonitic goethite. It is porous and soft enough to be cut with a knife. Its intimate association with 'limonite' suggests that iron carbonates were a major component of the primary assemblage within the deposits worked, or explored, here.

Dale *et al*. (2015) compared XRD data from "sooty" deposits from a high cave wall in a rift in the Urals sector of the maze north of the Hudgill Burn Mine caverns, Alston, to XRD 'standards' for birnessite and todorokite. Although they did not specifically claim to have identified todorokite the presentation of todorokite structural peaks overlain upon XRD data obtained from the "sooty" deposits gives a confused message. Furthermore, as clearly shown in their Figures 22a and b, the main peak for todorokite at 9.65399 Å (note that in their table 3 they erroneously switch this *d*-spacing with that of the air-dried sample) is very small. If present at all, todorokite would be in such low proportions as to make its other structural peaks so small as to be indistinguishable from background in their mixture. The position of the main peak is 0.05 Å away from that expected based on ICDD data. Based on the evidence presented by Dale *et al*. (2015) the presence of todorokite in their material is unlikely.

DISCUSSION

The majority of manganese minerals discussed here occur as part of the assemblage of supergene species found within the oxidised near-surface outcrops of the host deposits. In most cases, they are associated with abundant supergene iron oxide minerals in deposits in which iron carbonate minerals comprise a significant proportion of the primary mineral suite. In many cases lead, zinc or barium are essential constituents for the formation of the manganese oxides recorded, indicating an influence from a range of primary vein minerals, notably galena, sphalerite, baryte and locally witherite.

No primary manganese minerals are known from the Northern Pennine orefields. However, the iron-bearing carbonate minerals, siderite and ankerite are extremely widespread and locally abundant within the Alston Block orefield. Note that the term ankerite is here used *sensu lato*, and includes what would be described in modern nomenclature as iron- and manganese-bearing dolomite (Bridges *et al*., 2014). Where they have been subjected to supergene alteration to form 'Bilbao-type' bodies of iron oxides, they have historically been major sources of iron ore (Cantrill *et al*., 1919; Dunham 1990). In contrast, iron carbonates are comparatively rare within the otherwise similar deposits of the Askrigg orefield. As noted above, Dunham (1990) has ascribed this difference to the derivation of abundant iron from the Whin Sill of the Alston orefield, whereas the virtual absence of such iron mineralisation in the Askrigg orefield may be attributed to the absence of a suitable source rock for iron in that area.

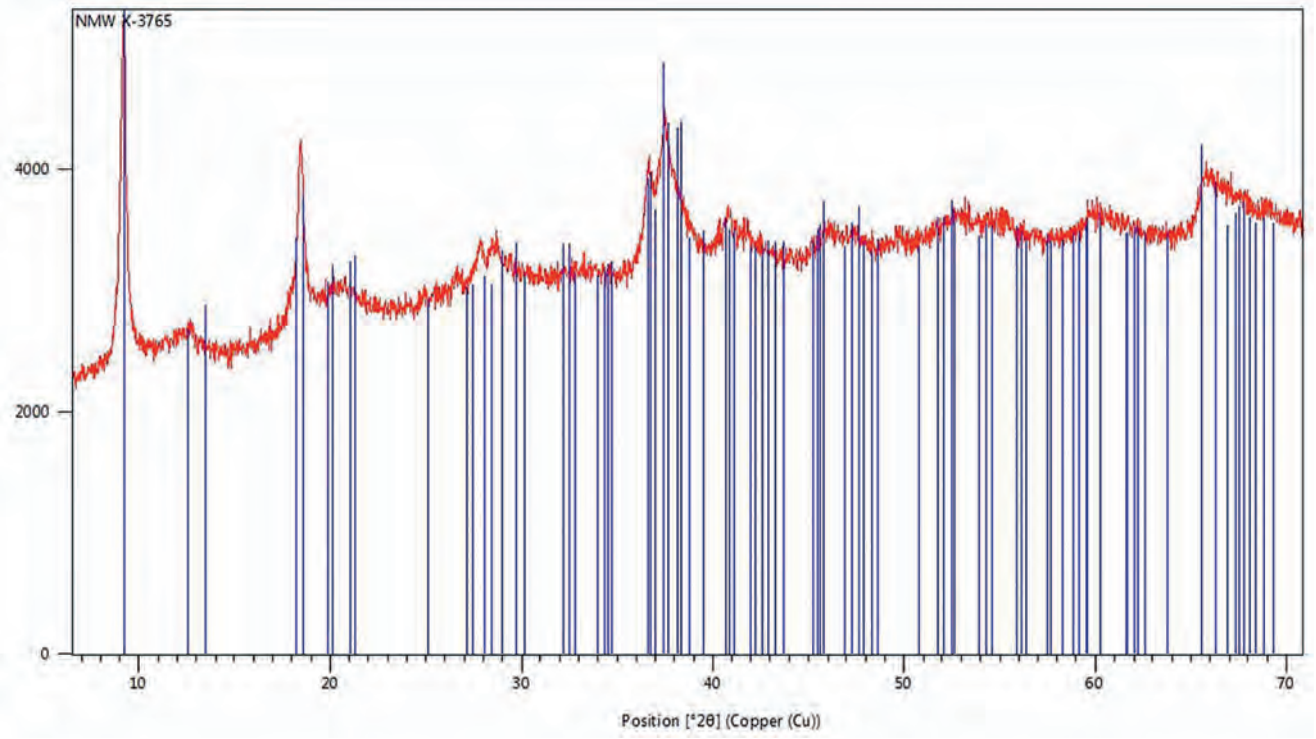

Figure 10. PXRD pattern No. NMW X-3765 (red line): a soft grey manganese oxide from north of Currick High Field, near the head of Ireshope Burn, Weardale, Co. Durham, on NMW 2020.12G.M.2. Blue lines represent the structural peaks for todorokite. It should be noted that the hydrated zinc manganese oxide woodruffite has a similar structural pattern.

Published analyses of epigenetic iron ores from the Alston Block orefield (e.g. Cantrill *et al*., 1919; Dunham, 1990) reveal manganese contents of up to a little over 3% in siderite ores, around 6% in 'limonitic' ores and an equivalent of around 4% $MnCO_3$ in ankerite. As ankerite and siderite are almost ubiquitous in the deposits of this area it seems most probable that the manganese oxide minerals from most of the localities reviewed here formed by localised concentration of manganese during supergene alteration of primary iron carbonate minerals, with a geochemical influence from the associated ore and gangue minerals.

An apparent exception to this is the occurrence of widespread, but poorly developed manganese oxides as coatings on limestone cave walls at Hudgill Burn Mine caverns, Alston Moor as reported by Dale *et al*. (2015). Reinterpretation of their data indicate that full characterisation of the manganese oxides is not possible. However, the presence of significant zinc suggests that alteration of primary sulphide mineralisation must have had a role in the supergene environment even within the cave environment. The wider Middle Fell area is host to the renowned smithsonite deposits at Farnberry and Holyfield mines (Dunham, 1990; Symes and Young, 2008), the lesser known Bayle Hill mines (Young and Hopkirk, 2019) and Hudgill Burn Mine where Dunham (1990) reported the presence of smithsonite and hydrozincite. Extensive supergene oxidation of primary sphalerite-bearing orebodies is obvious and, in combination with small-scale alteration of iron-bearing carbonates, could easily have resulted in the localised development of zinc-bearing manganese oxides, as observed. At the Bayle Hill mines, the supergene geochemical environment allowed the formation of crystallised zinc-bearing manganese oxides. In the Hudgill Burn Mine caverns, conditions are less favourable on cave walls away from the primary mineral veins, but demonstrate the migration of supergene manganese-bearing solutions.

Although scarce within the deposits of the Askrigg orefield, siderite and ankerite are present locally in small amounts. Although little is known of the manganese content of these minerals in this area, Dunham and Wilson (1985) reported the presence of up to 1.22% $MnCO_3$ in an ankerite from Lownathwaite Hush in Swaledale. As this former working lies on the same major belt of mineralisation as that from which the coronadite and romanèchite described from Old Rake was obtained, it is reasonable to suppose that small concentrations of manganese-bearing ankerite may here have contributed to the formation of this mineral in the supergene assemblage. At Hungry Hushes, limonite pseudomorphs after siderite or ankerite occur in association with manganese oxides, pyromorphite and supergene baryte.

In the light of the identification of the manganese oxide minerals reviewed here from a wide scatter of locations across the Alston orefield in which supergene alteration is comparatively well developed, and in view of their likely origin during supergene alteration of primary iron carbonates, it is likely that they may prove to be extremely widespread, though easily overlooked, across the orefield. In the Askrigg Block, the apparent restriction of such manganese oxide minerals to the two known occurrences in Swaledale, may attest to the scarcity of iron carbonate minerals within this part of the Pennine orefield.

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POWELLITE IN THE BRITISH ISLES: ASSESSING A KINGSBURY FIRST OCCURRENCE

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Powellite has been identified as crusts, typically a few micrometres thick, surrounding molybdenite at a number of new locations in the British Isles. Specimens in the collection of the Natural History Museum were selected for analytical study on the basis of their pale yellow fluorescence in shortwave ultraviolet light. Identifications were then confirmed by energy-dispersive X-ray spectrometry. New discoveries include the first three Irish localities at North Cannaver Island and Murvey Opencut, Co. Galway and Ballycummisk Mine, Co. Cork. The survey suggests that powellite is a common but inconspicuous alteration product of molybdenite in the absence of geochemically significant amounts of lead, bismuth and iron. Five previous descriptions of powellite from the British Isles are reviewed and select further specimens described. The published occurrences at Traprain Law, East Lothian and Benallt Mine, Gwynedd are isolated crystals in gas cavities within basic igneous intrusions. Those at Coire Buidhe, Argyll and Carrock Mine, Cumbria are thin crusts around molybdenite similar to the new occurrences described herein. At Castle Hill Quarry, Leicestershire, powellite is claimed as small anhedral masses in molybdenite-bearing veins. The record of powellite at Carrock Mine is based on work carried out by Arthur Kingsbury and Jack Hartley in the 1950s. Kingsbury's claims have come under scrutiny in recent years, but his Carrock powellite occurrence is valid. The first British occurrence of a betpakdalite-group mineral, also from Carrock Mine, is briefly mentioned.

INTRODUCTION

Powellite, ideally $CaMoO_4$, was characterised as a new mineral on specimens from the Peacock Mine, Idaho, USA (Melville, 1891). The name honours John Wesley Powell (1834–1902), the second director of the United States Geological Survey. Powellite is the less common molybdate analogue of scheelite, $CaWO_4$. The two minerals are commonly regarded as forming a complete solid solution series although recent work indicates that the situation may be more complex (Smedley and Kinniburgh, 2017).

In shortwave (254 nm) ultraviolet light, powellite has a strong pale yellow fluorescence. End-member scheelite fluoresces pale blue. This has the potential to provide a quick and easy means of analysis, and in the 1940s equipment based on this distinction was patented to characterise the molybdenum content of scheelite ore (Cannon and Murata, 1944). Unfortunately, the relationship is not linear. As little as 0.2% molybdate replacing tungstate produces a noticeable change in the blue fluorescence colour of scheelite and if 10% of the tungstate is replaced by molybdate the fluorescence is indistinguishable from end-member powellite (Tyson *et al*., 1988).

Although powellite occurrences in ore deposits and skarns dominate the geological literature, the remarkable crystals found with zeolites in amygdaloidal basalts are probably best known to mineral collectors (Xu *et al*., 2019; Ottens *et al*., 2019). Recent reports of authigenic powellite suggest that the mineral may be more widespread than previously supposed (Pichler *et al*., 2016; Smedley and Kinniburgh, 2017). Inconspicuous crusts are a possibility wherever primary molybdenum minerals are exposed to weathering.

LOCALITIES

To date, powellite has been reported at five localities in the British Isles. Specimens from Carrock Mine in the Caldbeck Fells, Cumbria were identified in the early 1950s by Arthur Kingsbury and Jack Hartley, but their data was not published until thirty years later (Hartley, 1984). The first published record from the British Isles is from Traprain Law, East Lothian (Battey and Moss, 1962). Powellite has subsequently been reported from Coire Buidhe, Glen Creran, Argyll (Ingram, 1996); and Benallt Mine, Llŷn Peninsula, Gwynedd (Dossett *et al*., 2007). A fifth occurrence, at Castle Hill Quarry, Leicestershire, was never published formally, but it is described in considerable detail in the PhD thesis of Dr Bob King (1973).

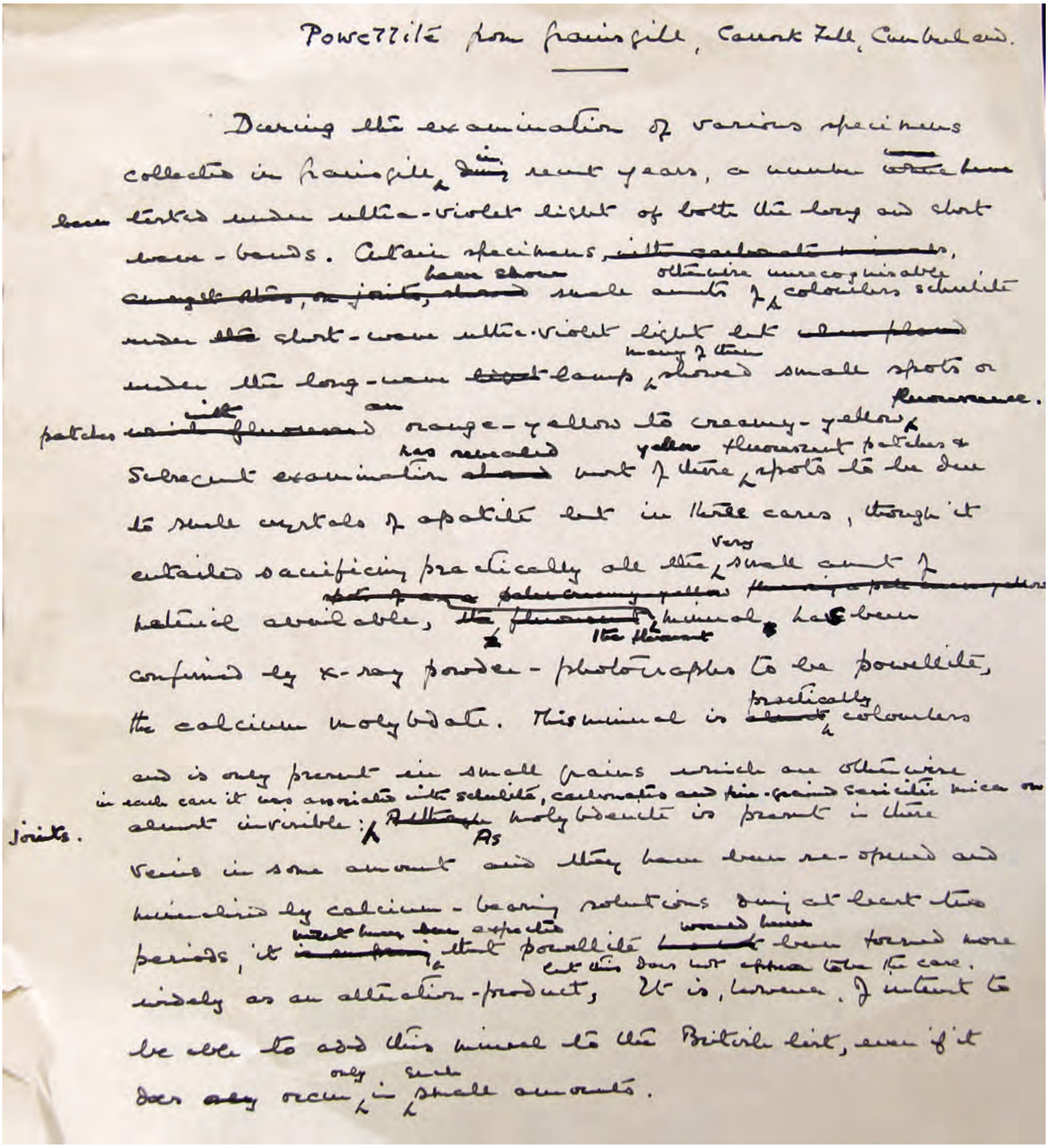
A limited survey of specimens in the collections at the NHM, using fluorescence in shortwave ultraviolet light as a guide to select appropriate material for analysis by energy-dispersive X-ray spectrometry (EDS), has revealed a number of new localities. Powder X-ray diffraction, the normal 'gold-standard' in mineral identification, was not used in the survey as it is unsuited to characterisations of micrometre-thick crusts. As powellite is the only calcium- and molybdenum-bearing mineral with strong pale yellow fluorescence in shortwave ultraviolet light, EDS is considered sufficient for its identification.

Reviews of all published occurrences of British powellite and descriptions of the new localities identified in the course this research, including the first three Irish occurrences, are provided in the following text.

Carrock Mine

An unpublished manuscript in archives associated with the Kingsbury collection at the NHM entitled "Powellite from Grainsgill, Carrock Fell, Cumberland", which describes powellite from Carrock Mine (Kingsbury, 1954), provided the impetus for this study (Fig. 1). Powellite, identified by its characteristic fluorescence, is reported as fine, almost invisible, grains in fractures and joints associated with apatite, carbonates, scheelite and flaky sericite mica. Further details in a contemporary notebook reveal that the specimens were collected in 1951 (Kingsbury, n.d.). The two richest specimens (registered as K53/189 and K53/190) were sacrificed by Kingsbury to obtain sufficient material for confirmatory analysis by X-ray powder diffraction. It is clear that Kingsbury intended to add powellite to the 'British list' even though it occurred in such small amounts, but this manuscript was never published.

In 1984, Jack Hartley published a list of the Caldbeck Fells species identified in the research he did with Arthur Kingsbury during the 1950s. Powellite receives a single-word mention in a tabulation of forty minerals from the



Powellite from Grainsgill, Carrock Fell, Cumberland.

During the examination of various specimens collected in Grainsgill in recent years, a number have been tested under ultra-violet light of both the long and short wave-bands. Certain specimens have shown small amounts of otherwise unrecognisable colourless scheelite under the short-wave ultra-violet light but many of them under the long-wave lamp showed small spots or patches with an orange-yellow to creamy-yellow fluorescence. Subsequent examination has revealed most of these yellow fluorescent patches & spots to be due to small crystals of apatite but in three cases, though it entailed sacrificing practically all the very small amount of material available, the fluorescent mineral has been confirmed by X-ray powder-photographs to be powellite, the calcium molybdate. This mineral is practically colourless and is only present in small grains which are otherwise almost invisible; in each case it was associated with scheelite, carbonates and fine-grained sericitic mica on joints. As molybdenite is present in these veins in some amount and they have been re-opened and mineralised by calcium-bearing solutions during at least two periods, it would have been expected that powellite would have formed more widely as an alteration-product, but this does not appear to be the case. It is, however, of interest to be able to add this mineral to the British list, even if it does only occur in such small amounts.

Figure 1. The draft version of Kingsbury's powellite manuscript, with notes and improvements, ready for publication at some future date.

main dumps at Carrock Mine. This is quoted in later works including Young (1987) and Cooper and Stanley (1990) where the occurrence is claimed as the first in the British Isles.

In recent years, much of Kingsbury's topographic work, and by association the list of minerals from the Caldbeck Fells produced by Hartley, has come under scrutiny (Ryback *et al*., 1998, 2001; Bridges, 2009; Rumsey, 2016). Some of Kingsbury's claims, especially of new or rare British minerals, are misleading. This does not mean that his powellite specimens are necessarily fraudulent, but it increases the amount of evidence required to establish their occurrence beyond reasonable doubt.

Many unregistered Kingsbury specimens from Carrock Mine were examined in this study. Some showed a distinctive pale yellow fluorescence in shortwave ultraviolet light. In corroboration of Kingsbury's manuscript notes, most of the fluorescent material occurs as a thin coating in mica-rich joints and fractures around molybdenite and it is occasionally also present on the surface of molybdenite grains. The Kingsbury specimens look authentic, but in light of other publications (Ryback *et al*., 1998, 2001; Bridges, 2009; Rumsey, 2016) this does not provide a cast-iron guarantee that they are from Carrock Mine. To be absolutely sure of the validity of the occurrence material known to have been collected independently has also been examined.

Samples from the Russell collection and the main NHM collections were therefore investigated: specimen BM 1964R,3711, collected by Arthur Russell in 1933 from 'Carrock Fell Mine, Caldbeck'; and specimen BM 57943 (Fig. 2) registered in the NHM collection in 1883 from 'Brandy Gill, Carrock Fell, Caldbeck'[1] showed promising pale yellow fluorescence. Powellite was confirmed by EDS in both instances. Specimen BM 1964R,3711 contains material that is identical to Kingsbury's descriptions. On specimen BM 57943 powellite occurs as a white to cream pearly crust in a cavity created by the apparent removal of a molybdenite crystal. It seems likely that powellite formed at the interface between a molybdenite crystal and the quartz matrix, and that the crystal subsequently fell out leaving a cavity.

Traprain Law

A single subhedral powellite crystal, about 1 cm across, was reported with analcime, apophyllite and calcite in a cavity in Carboniferous phonolite at Traprain Law, East Lothian by Battey and Moss (1962). Fragments are described as light blue-green in transmitted light and dark green with a somewhat submetallic lustre in hand specimen. The powellite appears to have formed in a late-stage hydrothermal fluid containing high concentrations of molybdenum which accumulated in gas cavities in the phonolite as the intrusion cooled. This mode of occurrence is similar to the famous specimens from the Deccan traps of India, to which a late-stage hydrothermal origin is also tentatively ascribed (Ottens *et al*., 2019).

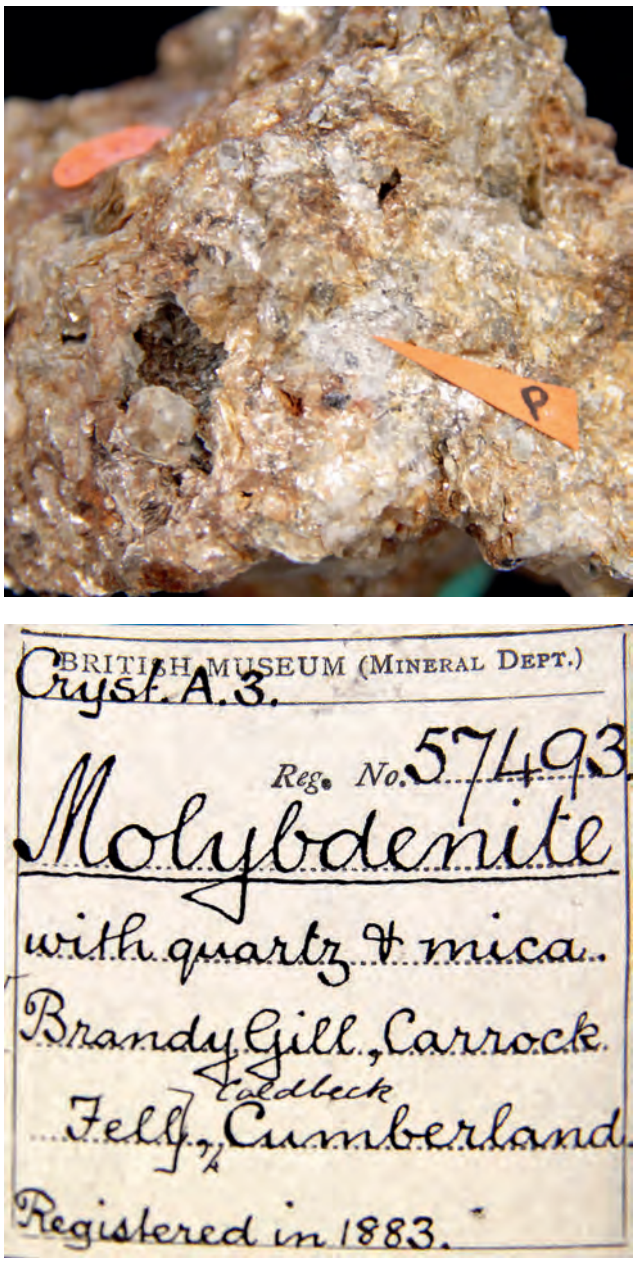


Figure 2. Specimen BM 57493: traces of molybdenite in fractured quartz and mica rich matrix from the vein near the confluence of Grainsgill and Brandy Gill before the modern workings at Carrock Mine were developed. Characteristic pale yellow powellite fluorescence (labelled P) can be seen in a darkened room if the specimen is illuminated by shortwave ultraviolet light.

Samples from what is probably the original study are preserved in the collections of the National Museum of Scotland, donated by Hugh Battey in 1984, a few further

[1] For nineteenth-century specimens the terms Brandy Gill and Grainsgill are essentially synonymous with the deposits worked (almost entirely in the twentieth century) at Carrock or Carrock Fell Mine, they are historic names for exposures in the same area, generally upon the same set of veins. Brandy Gill Mine now describes a different location to Carrock Mine (Cooper and Stanley, 1990). There is little doubt that the 'Brandy Gill' BM 57943 specimen is from what would currently be considered to be Carrock Mine. As documented by Bridges *et al*. (2008), attributions of nineteenth-century specimens to specific Caldbeck Fells localities can be misleading.

examples exist in the Hunterian Museum in Glasgow. A search of more than sixty specimens from Traprain Law in the rock collections at the Natural History Museum (NHM) revealed no further crystals and to the author's knowledge searches of the locality, which is now a Site of Special Scientific Interest, have produced very little material.

The green colour of the crystal mentioned in the original publication from Traprain Law is unusual (note: the samples from Battey at the NMS are described as blue-grey); most powellite is pale yellow-brown. An apple-green copper-bearing variety has been reported in the oxidation zone of a copper deposit in Mexico (Francis *et al*., 1997), and dark green crystals, coloured by celadonite inclusions have been found at several localities in the Deccan traps (Mindat, 2020a).

Coire Buidhe

Powellite occurs at Coire Buidhe, Glen Creran in Argyll in a small skarn-type occurrence. It was first reported as squat bipyramids in cavities (Ingram *et al*., 1993). Subsequent analysis showed that these crystals were scheelite (Starkey, 1995), but powellite was later identified as yellowish buff poorly crystalline crusts (Ingram, 1996).

Samples from Coire Buidhe were examined in this study. A very thin pale yellow coating on molybdenite was confirmed as powellite by EDS and is assumed to be equivalent to the material reported by Ingram (1996). The powellite appears to be an alteration product of molybdenite. In contrast, very pale blue-green polycrystalline scheelite is a primary 'rock-forming' component of the skarn (Fig. 3). The scheelite aggregates contain numerous flaky molybdenite inclusions. Intergrowths of scheelite and molybdenite are not uncommon in skarn deposits. Hsu (1977) suggests that they reflect the relative values of $f(O_2)$ and $f(S_2)$ during skarn formation: powellite requires higher $f(O_2)$ than scheelite to form; if $f(S_2)$ is high and $f(O_2)$ low, scheelite and molybdenite co-crystallise rather than a powellite-scheelite intermediate.

It is not clear whether the 'rock-forming' scheelite noted in this study is equivalent to the bipyramidal crystals reported by Ingram *et al*. (1993). Unfortunately no powellite or scheelite specimens from Coire Buidhe are preserved in the Ingram collection at Tullie House Museum in Carlisle.

Benallt Mine

In 2006, pale yellow bipyramidal crystals of powellite up to about 0.4 mm across were identified in a small cavity in a medium-grained basic igneous rock at Benallt Mine on the Llŷn Peninsula, Gwynedd (Dossett *et al*., 2007). The occurrence is the first in Wales, and like the locality at Traprain Law appears to be related to late-stage and localised molybdenum-rich hydrothermal fluids accumulating in vesicles in igneous rock.

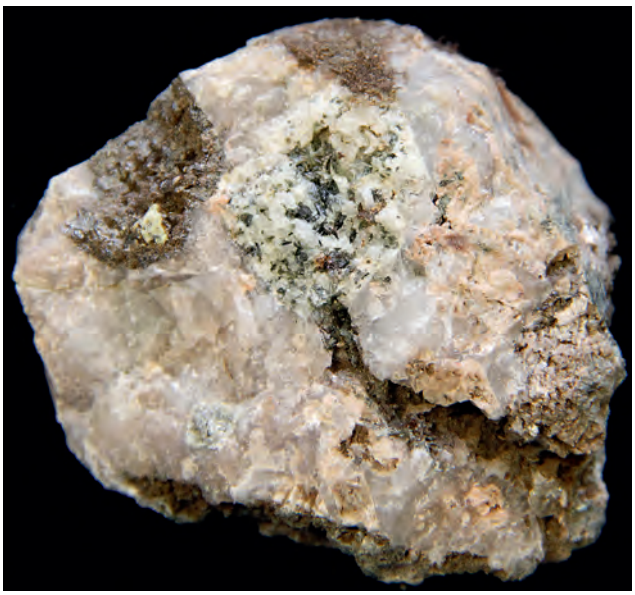


Figure 3. Pale bluish green 'rock-forming' scheelite from the skarn-like occurrence at Coire Buidhe, Glen Creran, Argyll. The sample is about 5 cm across, the black flecks within the scheelite are molybdenite and the pale yellow material is titanite.

Castle Hill Quarry

Powellite is noted in the Mountsorrel Granodiorite at Castle Hill Quarry[2], Mountsorrel, Leicestershire by King (1973: pp. 490–491):

> "During a routine examination of specimens from the hypothermal paragenesis of Mountsorrel, small masses (maximum diameter; 2.8 mm) were observed to fluoresce a strong light-orange colour ... under short wave ultraviolet light, but to give no reaction under long wave light. After marking, and examining the masses under ordinary light, they were found to be uncleaved, granular, highly vitreous and crystalline, completely anhedral in form and of a greyish-yellow colour".
>
> "A portion of a specimen, rich in fluorescent masses of the unknown, was crushed and run through bromoform. The heavy residue was then hand picked under short wave ultraviolet light, and a concentrate of sufficient size produced for qualitative analytical purposes. A strong reaction for molybdenum was produced, but tungsten was undetected. The mineral was powellite. Additional confirmation was forthcoming in the finding of a patch of powellite in incomplete pseudomorphism of a small mass of molybdenite. Relics of the latter remained in the powellite as fibrous masses".

The specimen (originally K950-47), which is preserved in the King collection at Amgueddfa Cymru – National Museum Wales, has not been re-examined during this study. The analysis appears sufficient to be reasonably sure of powellite, although the 'orange' fluorescence is intriguing and the pseudomorphism

[2] The quarry is also described as "Main Quarry, Mountsorrel" and "Mountsorrel Quarry". In 1947, when K950-47 was accessioned, Buddon Wood Quarry, which confusingly is now known as 'Mountsorrel Quarry' had not started (Frank Ince, *personal communication*, 2020).

suggests a significant change in the chemical environment during crystallisation (Hsu, 1977). As some chemical tests for tungstate are masked by the presence of molybdate a confirmatory EDS analysis is desirable.

North Cannaver Island

The first new locality for powellite found during this study was at North Cannaver Island in Co. Galway on a specimen from the Russell collection (Fig. 4). In a description of specimen BM 1964R,3717, Russell records in his catalogue:

> "Molybdenite, Two halves of a specimen consisting of a cinnamon coloured garnet with dark greyish green fibrous amphibole, and quartz, and a small eye of bright foliated molybdenite surrounded by a film ring of brownish yellow molybdite[3], while both in contact with the molybdenite and as an outer ring there is a pearly-white undetermined mineral. North Cannaver Island (South shore), Lough Corrib, Co. Galway. Collected by Arthur and Christopher Russell 1946."

His 'undetermined mineral' has a pale yellow fluorescence in shortwave ultraviolet light, and a small fragment was confirmed as powellite by EDS. It appears to have formed as a result of weathering of a molybdenite crystal, which is still largely intact.

Ballycummisk Mine

Fine-grained molybdenite from Ballycummisk Mine, Ballydehob, Co. Cork is commonly coated by a thin dirty yellow crust. The crust was thought to be ferrimolybdite, but it has pale yellow fluorescence in shortwave ultraviolet light. A small sample removed from specimen BM 1917,446 and analysed by EDS shows that it contains powellite, clay minerals and possible ferrimolybdite.

Murvey Opencut

Massive poorly crystalline molybdenite from Murvey Opencut, Roundstone, Co. Galway on Russell collection specimen BM 1964R,3720 has a broad pale yellow fluorescent rim extending up to 1 cm into the surrounding rock. Despite its relatively large extent, the fluorescent mineral is invisible to the naked eye. Scraping a powder sample from the reactive surface and analysing it by EDS revealed the presence of calcium and molybdenum. The only reasonable interpretation is that the rim consists of extremely thin films of powellite, which are optically invisible. It is important to note, particularly in this case, that great care was taken to avoid cross contamination with other samples.

Barlocco Mine

In 1917, Sir Arthur Russell noted an occurrence of molybdenite in loose granite blocks from surface workings at Barlocco Mine, Auchencairn, Dumfries and Galloway. The crystal surfaces and surrounding rims fluoresce a characteristic pale yellow colour in shortwave ultraviolet light. An EDS analysis of specimen BM 1964R,227 confirms the presence of powellite.

Figure 4. Sir Arthur Russell specimen BM 1964R,3717, from North Cannaver Island, with the original label. Recently the author was lucky to meet Christopher Russell who remembered the day that he and his father collected this specimen by rowing out in a small boat, which nearly gave up on them (Christopher Russell, *personal communication*, 2019).

Upper Middleton Farm Quarry

A small specimen from what is probably the old locality at Middleton of Balquhain, Inverurie, Aberdeenshire (Heddle, 1901: p. 16) was donated to the NHM in 2006 by Roy Starkey. Molybdenite occurs in cavities with grey-brown scheelite and bright yellow sheaves of ferrimolybdite in a quartz-rich gneiss. Examination in shortwave ultraviolet light revealed minute sub-millimetre regions with the characteristic pale yellow fluorescence of powellite. The identification was confirmed by EDS. The occurrence is unusual in that powellite occurs in small cavities in the quartz groundmass near to the molybdenite, rather than as rims, crusts or films surrounding the crystals.

Gleann a'Chaolais

Molybdenite is found sparingly throughout the Ballachulish Igneous Intrusion in Gleann a'Chaolais, Argyll (Evans *et al.*, 1980). A 15 mm quartz vein, exposed along a stream in the remote Coire Dearg, contains small flakes of molybdenite with pyrite and chalcopyrite altering to malachite and 'limonite'.

[3] Molybdite (MoO_3) was not found on the specimen and is almost certainly an incorrect identification.

Occasionally, the molybdenite is entirely or partially removed from the vein leaving distinctive cavities. These are rarely coated in a fine dusting of powellite. The powellite crusts are almost invisible to the naked eye but are clearly revealed by their pale yellow fluorescence under shortwave ultraviolet light. The identification was confirmed by EDS.

DISCUSSION

Arthur Kingsbury's claims of powellite associated with molybdenite from Carrock Mine in the Caldbeck Fells, Cumbria provided the impetus for this study. A careful examination of specimens in his collection and comparison with other material at the NHM validates his observations and ideas. They provide a reminder that although he may have muddied the waters, Kingsbury was an excellent collector and mineralogist with a genuinely keen eye. He is one of the forefathers of topographic mineralogy and a pioneer of concepts of geodiversity. It is unfortunate that much of his work has had to be reassessed due to the misleading claims he made toward the end of his career. His collection and manuscript notes, which are preserved at the Natural History Museum, are of considerable scientific value.

Molybdenite, MoS_2, is the only important ore of molybdenum. It is unstable in the oxidising conditions at the Earth's surface, but is relatively resistant to alteration and commonly persists in the near subsurface. At every locality listed in the text except Traprain Law, Benallt Mine and possibly Castle Hill Quarry, powellite occurs as crusts, films or powdery masses as a coating on or in fractures around a 'parent' molybdenite mass or crystal (or in a cavity left by such a crystal). These occurrences are independent of the wider geological setting, providing strong evidence that powellite is an inconspicuous but widespread alteration product of molybdenite.

The enigmatic powellite crystals found with zeolites in vesicles in the Deccan basalts (Ottens *et al*., 2019) mean that mineralogically similar occurrences are of significant scientific interest. The geochemical processes which concentrate molybdenum in late-stage hydrothermal fluids in sufficient quantities to form large isolated powellite crystals remain mysterious. The isolated specimens from gas cavities at Traprain Law and Benallt Mine show that the process is not specific to a particular magmatic province and requires a more general explanation.

Depending on pH, the relatively unreactive molybdate ion $(MoO_4)^{2-}{}_{(aq)}$, or acid molybdate ion, $(HMoO_4)^{-}{}_{(aq)}$, may dominate the aqueous geochemistry of molybdenum (Smedley and Kinniburgh, 2017; Chu, 2019). Complexity arises in acid solutions if the molybdenum concentration increases sufficiently for heteropoly anions to develop. Heteropolymolybdate minerals of the betpakdalite group are increasingly identified in 'molybdenum ochres' at sites where molybdenite has been exposed to particularly acidic oxidising conditions (Kampf *et al*., 2012; Mindat, 2020b; Sutton, 2020). A betpakdalite-group mineral has been identified at the NHM by XRD (X-ray reference 10903F) on sample BM 1993,327 from Carrock Mine. A description to species level will be the subject of a short future article. The rarity of betpakdalite-group minerals indicates that molybdate and acid molybdate ions dominate supergene molybdenum mineralogy in the British Isles.

Alongside calcium; lead, iron and bismuth activities commonly exert controls on the minerals that form during the weathering and oxidation of molybdenite (Williams, 1990). Wulfenite is the best known supergene molybdate and is widespread in small amounts in the British Isles (Rothwell and Mason, 1992; Tindle, 2008; McMullen, 2019). Most British reports are from the supergene zones of base-metal deposits. The source of the molybdenum at these localities is usually obscure. Wulfenite is extremely insoluble[4] and its widespread but patchy distribution is probably a reflection of variations in the background molybdate concentrations in local groundwaters.

Primary lead and molybdenum minerals are rarely found in close association in the British Isles. Wolframite is associated with molybdenite at most such localities and stolzite tends to form in supergene zones in preference to wulfenite. Stolzite is far more common than wulfenite at Carrock Mine and Brandy Gill in the Caldbeck Fells (Cooper and Stanley, 1990) and it occurs with partly oxidised galena at Cligga Head in Cornwall (Green and Tindle, 2013). However, wulfenite crystals have been reported as an overgrowth on oxidising molybdenite at Shap Quarry, Cumbria (Green and Wirth, 2002: p. 50), a direct association worthy of more attention.

The low solubility product of wulfenite means that lead controls molybdate activity at a level which is too low for powellite to form if lead is present in more than trace quantities; Williams (1990: p. 228) notes that the equilibrium constant for the reaction:

$$PbMoO_{4(s)} + Ca^{2+}{}_{(aq)} \rightleftharpoons CaMoO_{4(s)} + Pb^{2+}{}_{(aq)},$$

is 4.4×10^{-8}. Consequently, the lead ion activity must be very low before powellite can crystallise in a molybdenum-bearing geochemical system.

Iron also has a significant influence on the aqueous geochemistry of molybdenum. Precipitation of discrete iron-bearing phases and sorption of molybdenum onto iron oxyhydroxide surfaces have long been recognised as important controls on the activity of molybdate ions. The literature relating to sorption onto different substrates in a wide variety of environmental conditions is extensive (Smedley and Kinniburgh, 2017). The acid

[4] K_{sp} for wulfenite is listed as 2.3×10^{-16} mol^2dm^{-6} in Williams (1990: p. 227).

molybdate ion, $(HMoO_4)^-_{(aq)}$, reacts with $Fe_{(aq)}$ in acid oxidising conditions to form the mineral ferrimolybdite, $Fe^{3+}_2(MoO_4)_3{\cdot}7H_2O$ (Hansuld, 1966). Ferrimolybdite is an important constituent of many 'molybdic ochres' (Kerr *et al*., 1963). Iron, therefore, acts as a control on molybdenum in solution, and by extension on powellite formation, in two different ways.

Calcium is commonly present in surface waters. The $(MoO_4)^{2-}_{(aq)}$ and $Ca^{2+}_{(aq)}$ ion activity product must exceed the solubility product of powellite[5] for the mineral to crystallise (Conlan *et al*., 2012). A sufficient increase in the activity of either $Ca^{2+}_{(aq)}$ or $(MoO_4)^{2-}_{(aq)}$ can lead to precipitation, however the ubiquitous presence of $Ca^{2+}_{(aq)}$ in groundwater makes it most likely that powellite formation is generally a reflection of increased molybdate activity. A good example of this is the precipitation and dissolution of authigenic powellite in a limestone aquifer in Florida (Pichler *et al*., 2016). In this environment, which is clearly very rich in $Ca^{2+}_{(aq)}$ because of its carbonate-dominated geology, variations in $(MoO_4)^{2-}_{(aq)}$ are the logical control. In the weathering environment, the activity of molybdate in solution will be increased around a molybdenite crystal.

The geochemical arguments outlined above suggest that powellite can be expected as a weathering-product of molybdenite where relatively little iron or lead are present in solution. In such situations, if there is sufficient time for the molybdate activity to increase around a mass of molybdenite, powellite may form. If water flows through the system at a rate which is rapid compared to the oxidative degradation of molybdenite, the $(MoO_4)^{2-}_{(aq)}$ activity may never increase sufficiently for powellite to form. In such a situation, previously formed powellite may dissolve.

The fact that powellite forms very thin crusts on the specimens observed in this study is worthy of note. It is plausible that precipitation of powellite limits molybdenite dissolution by forming a barrier around the sulphide, passivating its surface and limiting the build up of molybdenum-bearing ions in solution.

The specimen from Cannaver Island exemplifies the influence of iron oxyhydroxides on powellite formation. The central molybdenite crystal is surrounded by a ring of molybdenum-bearing 'limonite' and then by a powellite halo (Fig. 5). As no ferrimolybdite is present, it seems reasonable to assume that the $(MoO_4)^{2-}$ ion dominated the aqueous chemistry and that the pH was >5. The silicates in the rock matrix are unlikely to have contributed to any of the reactions and probably acted simply as substrates. The separation of the rims suggests that sorption onto iron oxyhydroxides reduced the molybdate activity to a level at which powellite could not form. Once the limonite surfaces were 'saturated' the activity of molybdate diffusing into unreactive silicates increased sufficiently for thin films of powellite to develop.

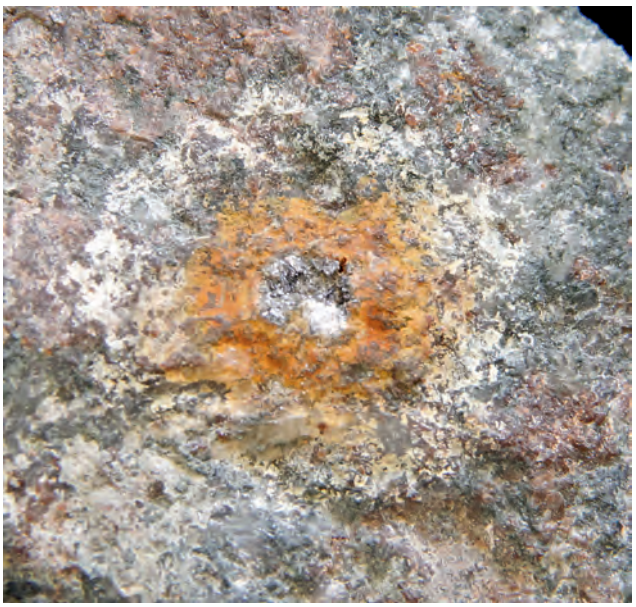


Figure 5. Close up of the goethite rim surrounding the molybdenite crystal illustrated in Figure 4 (BM 1964R,3717) both of which are surrounded by a pale yellow powellite halo, which is noted in Russell's manuscript catalogue as 'undetermined'. The feature is about 15 mm in diameter.

The claimed occurrence of the copper molybdate lindgrenite, $Cu_3(MoO_4)_2(OH)_2$, in the Caldbeck Fells is worthy of comment in the context of this discussion. No further discoveries have been made since it was reported at Brandy Gill Mine by Kingsbury and Hartley (1955). The supergene assemblage at Brandy Gill is dominated by lead minerals: bayldonite and mimetite are abundant, stolzite is widespread and wulfenite is rare (Cooper and Stanley, 1990). This is an example where 'big data' may provide a useful adjunct to geochemistry. Lindgrenite is not closely associated with supergene lead minerals at any of the worldwide localities where it is listed and photographed on Mindat (2020c). As lead minerals are ubiquitous at Brandy Gill, considered alongside the geochemical arguments presented above, the presence of lindgrenite is highly unlikely.

This review is based on a survey of molybdenum minerals in the collections of the NHM. Although it is inappropriate to record every negative or incidental result, observations which may be of value to future studies or to collectors cataloguing specimens are worthy of inclusion.

Yellow crusts of ferrimolybdite, which are closely associated with molybdenite and scheelite at Upper Middleton Farm Quarry, may be confused with powellite if they are sufficiently thin. They can be distinguished by the absence of fluorescence in shortwave ultraviolet light. A bright greenish yellow material found between molybdenite laminae at Coire Buidhe is similarly non-fluorescent. Analysis shows that it is fine-grained epidote.

[5] K_{sp} for powellite is listed as 5.2×10^{-9} mol^2dm^{-6} in Williams (1990: p. 227).

Molybdenite or 'molybdic ochres' with a faint pale yellow fluorescence were found at a number of localities where powellite was not confirmed by EDS. These include Doon Cottage, Co. Clare; Water Crag, Eskdale, Cumbria; and Newlyn, Kit Hill and Drakewalls Mine, in Cornwall. In these cases it seems likely that the mineralisation was so sparse that powellite was not easily detected or accurately sampled. They are listed here in the hope that richer specimens will be identified in future.

Pale yellow fluorescence in shortwave ultraviolet light is not an infallible guide to the presence of powellite. A pale yellowish fluorescence was observed on molybdenite-rich material from the famous old locality at Stenna Gwynn, St Austell, Cornwall, but the opaque, dirty white grains were identified by EDS as apatite.

Euhedral straw-yellow glassy crystals up to 6 mm across in a molybdenite-bearing quartz vein in the pink granite of 'Wasdale Crag', at the Shap Granite Quarry, Shap, Cumbria, show pale yellow fluorescence in shortwave ultraviolet light. Analysis by EDS shows that the crystals are scheelite containing a small amount of molybdenum. This corroborates a previous report by Green and Wirth (2002). As noted in the introduction, fluorescence colour does not provide an infallible guide to the composition of powellite-scheelite intermediates.

Pale yellow powdery coatings associated with molybdenite at Shap Quarry were examined, but they do not fluoresce in shortwave ultraviolet light. Analyses by EDS suggest that they may contain the uncommon calcium bismuth carbonate beyerite, which Green and Wirth (2002) noted as a possible constituent of yellow powdery crusts on bismuthinite. Bismutite, $(BiO)_2CO_3$; beyerite, $Ca(BiO)_2(CO_3)_2$; and kettnerite, $CaBiCO_3OF$, are difficult to distinguish and a positive identification requires XRD.

Pale yellow micro-botryoidal material is occasionally found in small cavities in molybdenite-bearing quartz at Carrock Mine. It is similar in colour to powellite, but does not fluoresce in shortwave ultraviolet light. Analyses by EDS show that the crusts are made up of a poorly crystalline, impure russellite-like bismuth tungstate (Rumsey *et al*., 2007). Darker yellow, non-fluorescent crusts from the same locality are ferrimolybdite.

CONCLUSIONS

Powellite is one of several minerals which occur as pale yellow crusts in weathered molybdenum-bearing assemblages. Examination in shortwave ultraviolet light combined with EDS is sufficient to differentiate it from similar looking minerals.

Arthur Kingsbury discovered the first British powellite at Carrock Mine in the Caldbeck Fells in the early 1950s but the occurrence was not published until 1984, long after his death. Although some of Kingsbury's claims have been shown to be misleading, his observations on powellite are accurate and astute. It serves as a reminder that he was an excellent mineralogist with a genuinely keen eye. It is unfortunate that much of his work requires reassessment.

Careful examination of specimens in the collection of the Natural History Museum shows that powellite occurs as inconspicuous crusts and films surrounding molybdenite at a number of localities in the British Isles, just as Kingsbury predicted. These include the first three Irish occurrences at North Cannaver Island and Murvey Opencut, Co. Galway, and Ballycummisk Mine, Co. Cork, as well as new localities at Barlocco Mine, Dumfries and Galloway, Upper Middleton Farm Quarry, Aberdeenshire and Gleann a'Chaolais, Argyll.

Geochemical arguments suggest that powellite should be sought at near-surface localities where molybdenite has been subjected to weathering and oxidation. The associated mineral assemblage is probably important. If groundwaters are too acidic, or too rich in iron, molybdenite alters to ferrimolybdite or aqueous molybdate is removed by sorption onto iron oxyhydroxides. The co-occurrence of molybdenite with lead minerals may also limit powellite formation. Rapid dissolution in acid conditions probably favours the formation of betpakdalite-group minerals. These conditions are most commonly encountered in arid environments and it follows that betpakdalite-group minerals are likely to be of relatively limited occurrence in the British Isles.

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GOLD OCCURRENCES IN THE UK

A Gold Prospector's Guide

by Lee Gary Palmer

First edition, published in November 2019 by Gold Productions:
40 Archers Avenue, Irvine, Ayrshire, KA11 2GB, Scotland

with 136 pages, colour throughout, 297 × 213 mm, softback, ISBN 978-1-9162803-0-4,
Available from https://goldpublications.co.uk/; price £28.

Self-published by Lee Palmer in November 2019, 'Gold occurrences in the UK' is a glossy A4-sized paperback containing a wealth of information on localities across the four nations at which gold has been found or reported. The 136-page book is clearly a 'labour of love' by this gold-panning enthusiast and his family: included are photographs of his two children equipped with shovels and pans. An impressive 648 localities with grid references are described with entries ranging from one line to a full page or more. A numbering system allows the approximate location of almost every locality to be found on road map extracts, of which there are 34. Preceding the catalogue of localities which forms the bulk of the book, are sections on 'notable nuggets of the UK' including colour photographs, a preface on the author's chronology of interest (obsession?) in gold prospecting, and two pages introducing elemental gold and its origin. The final sections of the book describe evidence for prehistoric extraction and use of gold ('the ancient link') and the Prehistoric Gold Network programme (ongoing in 2019 but since completed). A paragraph on gold panning techniques is followed by sound advice on seeking permission for recreational gold-panning activities including ecological considerations and UK regulations on gold ownership. The book finishes with photograph credits and a numbered reference list of 409 attributed sources.

The remit of the book extends beyond a compilation of alluvial gold sites: in addition Palmer includes extracts of published geological descriptions of auriferous bedrock mineralisation and historical accounts of gold mining ventures. To his credit, Palmer has included most of his sources in the reference list and in many cases provided a citation number within or before the relevant text. However, large amounts of text have been copied verbatim from publications available online, such as abstracts of British Geological Survey Mineral Reconnaissance Programme reports. It would have been better to have provided jargon-free simplified versions appropriate for the non-specialist reader. Extracts of various other publications have been incorporated, and even the definition of citations (page 10) is copied from an online source, in this case Wikipedia. In the reviewer's opinion, the inclusion in this book of swathes of text composed by other authors, seldom acknowledged as specifically as would be desirable, is a flaw in an otherwise commendable publication.

Overall, Palmer's book is not a scholarly work and so by academic standards falls short, but it meets fairly well the interests of his target audience, the amateur prospecting community. To his credit he has not hyped up localities where many panners know there to be substantial amounts of gold, and thus has acted in an ethically responsible manner. Buy this book if you are interested in where gold may be found in the 'four nations' and a handy geographical compilation of previously published scientific and historical accounts of gold occurrences in the UK.

Norman R. Moles

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.

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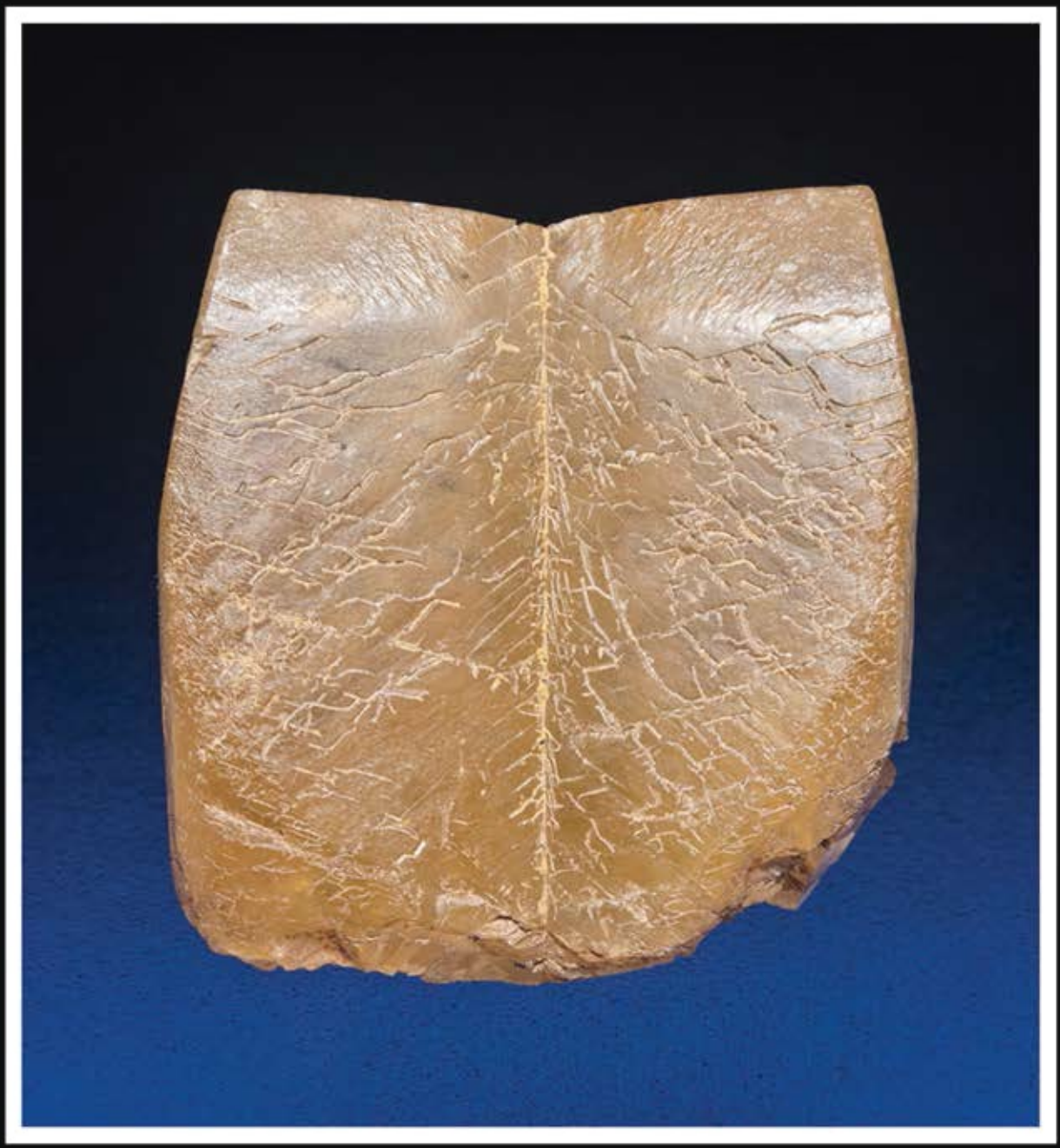
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