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A Journal of the Topographic Mineralogy of Britain and Ireland

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Aims and Scope: the Journal publishes articles by amateur and professional mineralogists dealing with all aspects of the mineralogy of the British Isles. Contributions are welcome from members and non-members of the Society. Notes for contributors can be found at the back of this issue. The views and opinions expressed in this journal are not necessarily those of the Journal Editor, the Society or the Editorial Board.

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FRONT COVER: Twinned pseudohexagonal witherite crystals to 35 mm on alstonite from Fallowfield Mine, Hexham, Northumberland. Formerly in the collections of August P. Pohndorf (1886-1939), Emory Mitchell Gunnell (1903–1986) and Lindsay Greenbank (1941–2017). John Hall Collection. Photo © John Hall.

BACK COVER: Gold on iron-stained vein quartz collected in 1958 from the hills east of Bridge of Orchy, Argyll. Calum Anton Collection. The field of view is 6.2 mm across. Photo John Chapman.

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ERRATA

In Briscoe *et al*. (2021: p. 87):

> "Lanarkite is the quintessential Leadhills-suite supergene mineral. It requires a very low carbonate ion activity ($p\mathrm{CO}_2$ −7.2) and relatively alkaline conditions to form (Bridges, 2015: pp. 10−11)",

the sign and power of ten have been omitted and the sentence should read:

> Lanarkite is the quintessential Leadhills-suite supergene mineral. It requires a very low carbonate ion activity ($p\mathrm{CO}_2$ $<10^{-7.2}$) and relatively alkaline conditions to form (Bridges, 2015: pp. 10−11).

In Bateman *et al*. (2018: pp. 54 and 55), Mike Walter (*personal communication*, 2022) notes:

> "Backford Lane Borehole" should be Rackford Lane Borehole.

In Bridges (2015: p. 8):

> "As an example, with the atmospheric concentration of CO_2 of 300 ppm, $p\mathrm{CO}_2$ is 0.0003 which gives a log($p\mathrm{CO}_2$) of $10^{-3.52}$",

there is a mistake in the definition of a logarithm and the paragraph should read:

> As an example, with the atmospheric concentration of CO_2 of 300 ppm, $p\mathrm{CO}_2$ is 0.0003 which gives a $\log_{10}$($p\mathrm{CO}_2$) of −3.52.

In Bridges (2015: p. 11) the formula in the title for hydrocerussite is given incorrectly:

> "Hydrocerussite, $\mathrm{Pb_3CO_3(OH)_2}$" should be Hydrocerussite, $\mathrm{Pb_3(CO_3)_2(OH)_2}$

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EDITORIAL

Mineralogical Jubilees

Welcome to JRS 25 which, by a mathematical coincidence, celebrates the Journal's Silver Jubilee in the Society's Golden Jubilee year. Previous editions of the Journal show how connected mineralogy is to other subject areas. There are historical distractions in many articles, and occasional diversions into archaeology (hone-stones in JRS 23) and even botany (lichens in JRS 5). Recent research has highlighted the connections between mineral assemblages and the biosphere (Hazen and Morrison, 2022). Oxygen is a highly reactive element and our planet's atmosphere is almost absurdly improbable. It is responsible for the formation of the unusual supergene minerals beloved of collectors (Fig. 1) and sustains life into the bargain.

As promised in the preceding Editorial, this journal features a number of articles on the history of British mineralogy. In this jubilee year, authors have surpassed themselves. There are descriptions of little known localities, rare species (including several first occurrences in the British Isles), topographic studies, and technical notes. We begin with witherite, a mineral with a strong British following and the subject of two articles which draw these themes together.

Popular culture has a fascination with lists. A newspaper article which listed the 'ten strangest things found whilst metal detecting' led to a deliberation on the top ten British mineral species. A nonsensical question with many possible resolutions. Beauty, after all, is in the eye of the beholder. Roy Starkey's recent biography of Sir Arthur Russell (see book review in this journal), provides one possible solution. The top ten British species in the Russell Collection, in descending order, are: fluorite, calcite, baryte, cassiterite, quartz, galena, sphalerite, witherite, pyromorphite and apatite (Starkey, 2022: p. 242). Collectors might disagree with some of these choices, but many would include witherite in their personal 'top ten'.

The north of England has a remarkable concentration of world-class witherite localities. Most collectors will be familiar with the outstanding specimens from Fallowfield Mine in Northumberland and Nentsberry Haggs Mine on the border between that county and Cumbria. To these can be added Settlingstones Mine in Northumberland, which produced huge globular masses; veins in the Durham Coalfield, which produced superb pseudohexagonal crystals; sites in Arkengarthdale, North Yorkshire, from which James Sowerby figured exceptional specimens; and mines around the village of Nenthead in Cumbria. The locality from which the mineral was described by William Withering in the 1780s has become lost in this embarrassment of riches. Modern texts commonly suggest that the first specimens were from Alston Moor, but this appears to be the result of deliberate misdirection. A careful examination of early references and specimens in contemporary collections, reported by Tom Cotterell in this issue, together with an examination of well provenanced modern specimens in the collections of two former Society members, shows that Lead Mines Clough in the parish of Anglezarke near Chorley, Lancashire, is the type locality.

Pyromorphite (see Fig. 1) sits next to witherite in Sir Arthur Russell's list and would probably also feature in the 'top ten' of many British collectors. The 'lead-apatites', principally pyromorphite, mimetite and vanadinite, together with the less common hedyphane and phosphohedyphane, occur at numerous British localities, a few of which are of international importance. These include Wheal Alfred, Cornwall; Bwlch Glas Mine, Ceredigion; several sites in the Caldbeck Fells, Cumbria; and the Leadhills–Wanlockhead district in southern Scotland. The composition of specimens from the Leadhills–Wanlockhead district is discussed by David Green and Andy Tindle in this issue. The results of these analyses are used to explore the nature of the now discredited mineral 'collieite'. Collieite is a mixture of mottramite, pyromorphite–phosphohedyphane and vanadinite. Many specimens labelled pyromorphite from Leadhills–Wanlockhead are the closely related species phosphohedyphane. This common misidentification is explored by Tom Cotterell and Piotr Skotnicki.

Figure 1. A natural micromount and homage to the work of Hazen and Morrison (2022). Bright green pyromorphite on a crinoid columnal from an exposure of the Carboniferous Crow Limestone in Arkengarthdale, North Yorkshire. Connections between the minerals illustrated in this image and the biosphere are writ large. The crinoid columnals would originally have been preserved as calcite, but at some point the fabric of the rock has been almost completely replaced by silica (of possible biogenic origin). Local deposits of galena have subsequently destabilised in oxygenated solutions (generated by photosynthesis). In the absence of overwhelming carbonate, pyromorphite rather than cerussite has formed. David McCallum Collection. The field of view is 8.6 mm from top to bottom. Photo John Chapman.

Three articles in JRS 25 rehabilitate overlooked collectors and collections. Hamish Johnston and Michael McMullen combine to give an account of Alexander Thoms, whose collection is preserved at The Hunterian, Glasgow. Thoms will be familiar to many collectors for his role in bringing *The Mineralogy of Scotland* to publication following the death of Matthew Forster Heddle. His life, personal collections and other contributions to mineralogy have gone unrecorded until now.

Peter Briscoe and colleagues shine some light into the obscure world of nineteenth-century Yorkshire collectors and the contributions of Jamaican-born Peter Murray. Murray, a physician and philanthropist, discovered the first celestine and strontianite in the county and made considerable contributions to many institutional collections. Sadly, almost nothing can be identified of his generous donations to the many provincial museums with which he was involved. The only minerals which have survived with definite attributions are at the Natural History Museum, London.

Thoms and Murray both have strong associations with the universities of St Andrews and Edinburgh, and although no direct links between the two have been established, nineteenth-century mineralogy was a ‘small world’ in the mathematical sense and their social networks certainly overlapped (a link between Thoms and Murray in two steps or less is left as an exercise for any interested reader who is interested in a mineralogical equivalent of the ‘Kevin Bacon game’).

In addition to his biographical sketch of Thoms, Hamish Johnston has contributed an account of *The Geognosy and Mineralogy of Scotland*, a fascinating work by Thoms’ mentor Matthew Forster Heddle. Anyone lucky enough to own a copy of this rare book is almost certain to have something that is genuinely unique: no two copies (as far as the author is currently aware) are the same. A detailed catalogue of the contents of different copies is currently being prepared and Hamish would be pleased to hear from any reader who has a copy.

Maintaining a Scottish theme, Mike Rumsey and Steve Rust have contributed a description of the rare lead carbonate-silicate ferrisurite from Whyte’s Cleuch, Wanlockhead (the first British occurrence). The Leadhills–Wanlockhead district is something of a hotspot for unusual lead silicates and readers are urged to search their collections for further species.

A first Scottish occurrence of the vivianite-group mineral köttigite is recorded on specimens collected by David McCallum at Strontian, Argyll. Köttigite was identified by chance in the search for millerite in veined metabasite. Things are not always as they seem in the minerals of the vivianite-group. Colour is a poor guide to composition and köttigite may prove to be more common than the few British records suggest.

Localities in the Caldbeck Fells, Cumbria have occupied more column-inches in this journal than any comparable area of the British Isles. Mike Rumsey describes the first British occurrence of a betpakdalite-supergroup mineral at Carrock Mine. The minerals of this supergroup are difficult to characterise to species level and easily confused with other powdery yellow phases produced by the oxidation of molybdenite.

Remaining with colourful rarities, Steve Rust describes the lead copper chloride diaboleite from Penberthy Croft Mine, St Hilary, Cornwall. Although Cornwall is the jewel in the crown of British mineralogy, its minerals have not featured in recent editions of JRS. The former vibrancy of collecting in the county is captured by David Lloyd in his recently published diaries *Portals Picks and Pasties* (Lloyd, 2022). Judging by David’s entries, many unusual and interesting localities remain to be described.

The Royal Cornwall Museum in Truro will be familiar to many readers (Penhallurick, 1995). Sir Arthur Russell, held the collection in very high regard and was of the opinion (Russell, 1952) that:

> “[The Rashleigh collection] was for many years without parallel, both in the County of Cornwall and in fact in Great Britain, and as far as many Cornish minerals are concerned will always remain unrivalled”.

The only publication that makes a direct comparison of Europe’s major mineral museums (Burchard and Bode, 1986) concludes that:

> “The little known County Museum in Truro surely has the largest and finest collection of minerals from classic Cornish localities”,

and the authors go on to list more minerals in their ‘excellent’ category (reserved for the very finest specimens) than at any other British museum except the Natural History Museum. Figures 2 and 3 fit with the theme of this editorial.

The current parlous state of the organisation’s finances leaves the collections in danger. Museums have suffered serial cutbacks in recent years and, although organisational standards have improved, the lack of interest and understanding of collections in many management structures is shocking. It would be a tragedy if Britain’s last great provincial mineral collection were to fall by the wayside.

Topographic studies are a mainstay of JRS and in this volume Brian Young and colleagues have produced an outstanding account of antimony mineralisation in the Palaeozoic rocks of the Lake District. This article, which includes several descriptions of sites where further research is desirable, will become the go-to reference for future studies of this style of mineralisation in the area.

A thread which runs through several articles in JRS 25 (collieite and witherite for example) is ‘unreliable evidence’. Such mistakes eventually become entrenched in the literature. The internet (which did not exist when the first volume of this journal appeared) is not immune to error and researchers should be appropriately sceptical. The claim that Brownley Hill Mine in Cumbria is the type

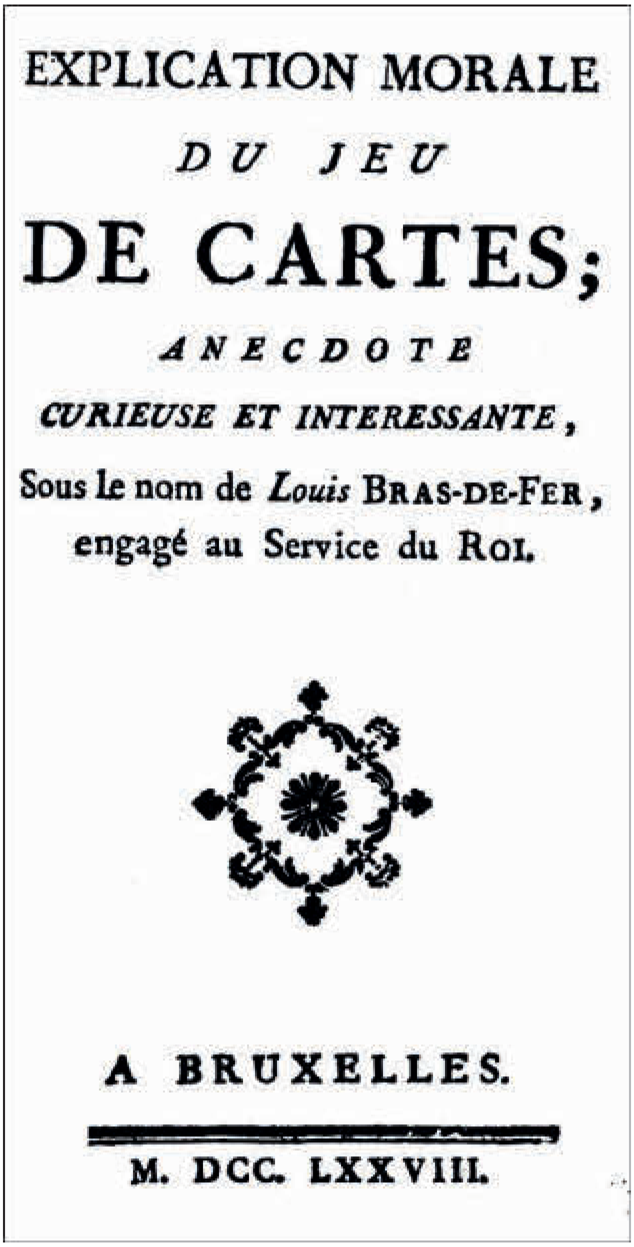
Figure 2. Wire silver, 60 mm from top to bottom, from Wheal Herland, Gwinear, Cornwall. Part of the Carlyon Collection which was presented in 1963. Specimen RCM: 801.1595 in the collection of the Royal Cornwall Museum, Truro. Photo David Green.

Figure 3. A gold nugget, 30 mm from top to bottom, from the Goldmines River, Co. Wicklow, obtained by Philip Rashleigh sometime before 1795. This is one of the very few large nuggets to have survived from the area. Specimen RCM: 1903.1.83, in the collection of the Royal Cornwall Museum, Truro. Photo David Green.

locality for witherite is comprehensively demolished by Tom Cotterell in this journal.

The Editor has come across similarly odd claims while researching the early history of strontium minerals (see the article about Peter Murray in this issue). The normally reliable RRuff® website suggests that the first use of the name celestine is in Bras-de-Fer (1778: p. 99) (Fig. 4). It pays to cross-check such claims. The element strontium had not been discovered at that time and the name celestine was even further in the future.

The first analyses of natural strontium sulphate were published by Martin Heinrich Klaproth (1797: pp. 92–98), who described "Schwefelsäuren Strontianits [strontium sulphate]" from Frankstown in Pennsylvania in the second volume of his *Contributions to the Chemical Knowledge of Minerals*. Bell's Mill near



EXPLICATION MORALE
DU JEU
DE CARTES;
ANECDOTE
CURIEUSE ET INTERESSANTE,
Sous le nom de *Louis* BRAS-DE-FER,
engagé au Service du ROI.

A BRUXELLES.

M. DCC. LXXVIII.

Figure 4. The title page of Louis Bras-der-Fer's volume which claims to describe early celestine (RRuff, 2022).

Frankstown in Blair County, Pennsylvania is considered to be the type locality. The name celestine was subsequently suggested by Abraham Gottlieb Werner, who was fascinated by mineral classification and nomenclature, but left the task of publication to colleagues. In his *Textbook of Mineralogy*, Emmerling (1799: p. 859) notes:

> Mr. Werner added the name celestine, which was taken from its colour, and now also means this for the other species.

The Editor would be pleased to hear from any reader who can shed light on this strange story. A practical joke, perhaps? If so, as readers who are familiar with story of texasite and the aptly named W. W. Crook III (1977) will be aware, it would not be an isolated case. It may be a delusion in the same vein as 'crazy old Randolph Kirkpatrick' (Assistant Keeper at the British Museum, no less) and his 'numinous nummulosphere' (Gould, 1980). But there is probably a more innocent explanation. Such puzzles add some human interest to mineralogy. A pdf of Louis Bras-de-Fer's possibly apocryphal volume is currently available as a free download on the RRuff (2022) website.

Returning to JRS 25, short articles by Peter Briscoe, John Chapman and colleagues describe the rare and rather nondescript species fraipontite and prosopite from localities in Yorkshire. To paraphrase Robert Hazen: most minerals that remain to be discovered are white and poorly crystallised.

It is hoped that readers have had an opportunity to look at the anaglyph images produced by John Chapman as a supplement to JRS 24. Such images provide an exciting way to appreciate specimens, especially when they are combined with image-stacking techniques.

The technique of 'stacking' together images acquired at tiny depth increments is commonly used to improve the depth of field in images of small specimens. One of the less desirable aspects of this method is that all the elements appear to be in a flat plane. There is little concept of the real three-dimensional appearance of the specimen.

When a mineral is studied using a stereomicroscope each eye views the specimen at an angle of between about four and six degrees from the vertical. The eye-brain complex fuses the separate images into a three-dimensional impression which has depth information.

Three-dimensional imaging (3D for short) is a way of regaining the same depth information by combining two two-dimensional images. In combination with image-stacking it is possible to produce images that have an extended depth of field, providing unrivalled detail. It is possible (with an appropriate choice of optical systems) to view specimens at a combination of magnification, resolution and depth of field that is higher than the best modern research stereomicroscopes can achieve. And those images can be shared.

It may be worth recording that 3D can be generated in several different ways, which have their own drawbacks and benefits. The three principal techniques are:

1) The left and right images can be printed or viewed on a computer screen side by side. In this format all the natural colours of the specimen are retained. Some people can 'free-view' the image pairs but most require an optical aid (such as the viewer supplied many years ago by *The Mineralogical Record*). A disadvantage of this technique is that individual images in the pairs cannot be more than about 65 mm across (the interpupillary distance) as few people have the ability to make their eyesight diverge.

2) The left and right images can be combined in a single frame, printed in complementary colours, in an anaglyph. Usually, these colours are red and cyan, though yellow and purple can also be used. A disadvantage of anaglyphs is that they do not produce a correct colour impression of shades that are similar to the anaglyph spectacle filters. An advantage is that the image can be enlarged to view the smallest features that the system can resolve. Inexpensive red-cyan spectacles are all that is required for viewing (Fig. 5).

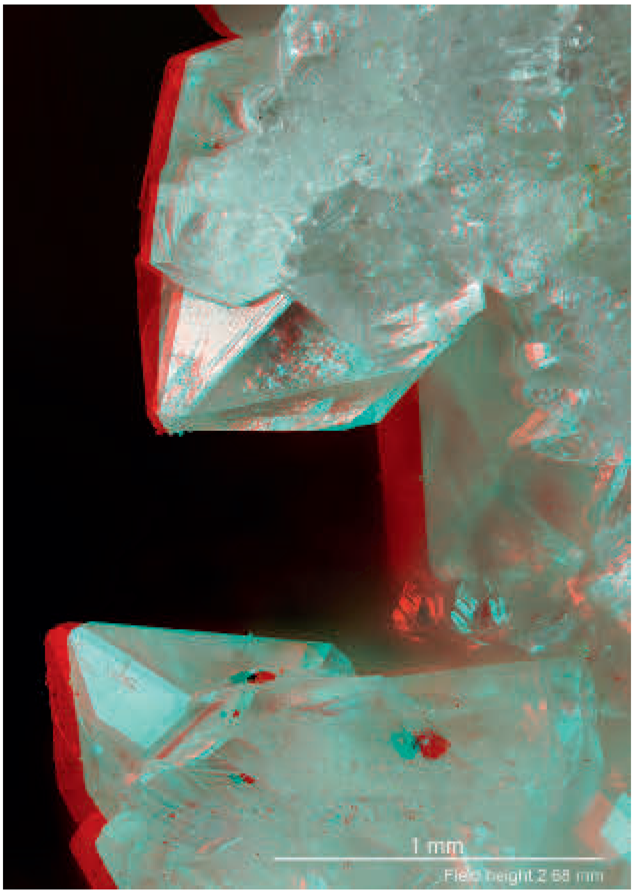


Figure 5. A red-cyan anaglyph image of pseudohexagonal witherite from Lead Mines Clough, Anglezarke, Lancashire (see Alderton *et al*., this issue). The resolution and depth of field are significantly better than could be achieved with a conventional stereomicroscope, and when viewed with red-cyan spectacles it is possible to differentiate between inclusions and surface encrustations (see bottom crystal group). Specimen AZ(HC)02 in the Harry Critchley Collection. Photo John Chapman.

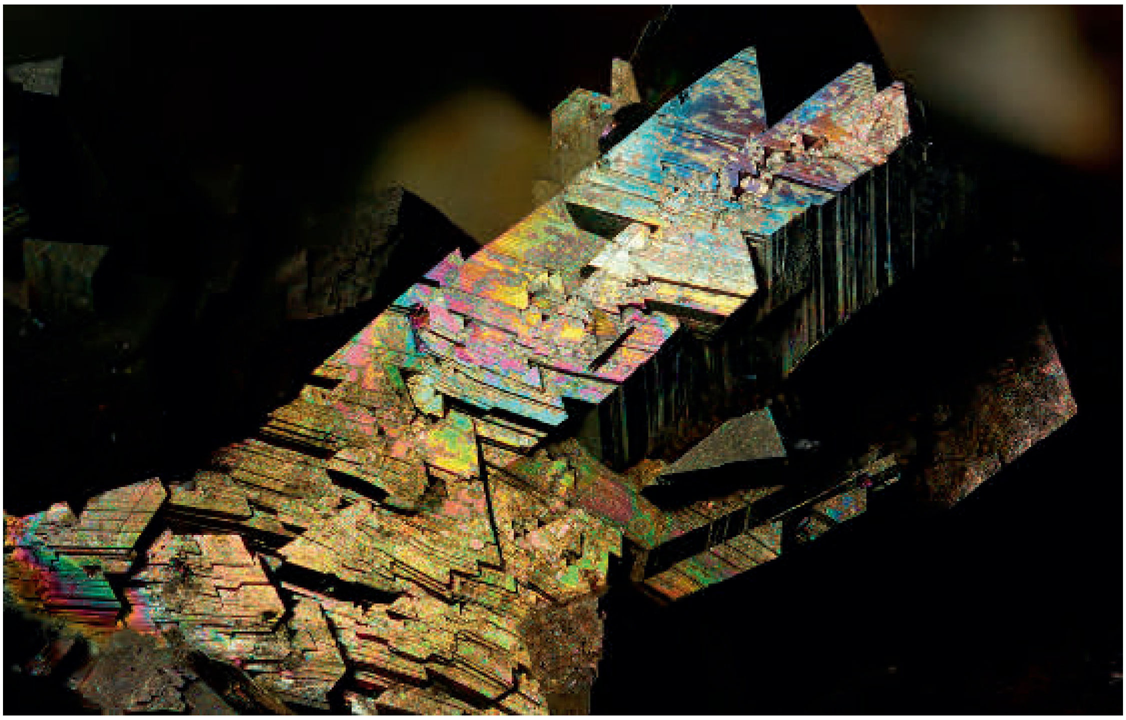


Figure 6. Marcasite from Temple Meads Opencast, Leeds, West Yorkshire. The field of view is 3.5 mm across. Photo John Chapman.

3) The right and left images can be superimposed and either projected or shown on a 3D television screen. In this technique, the images are separated by either polarising spectacles or 'shutter glasses', which use LCD technology to flip viewing from left to right in synchrony with the output. The action is so rapid that it cannot be seen, and this method is currently considered to be the best available. The natural colour of the specimen is preserved and the screen size allows reasonably close scrutiny.

The image that is reproduced here (Fig. 5) is one of a number which are available to accompany the articles in this journal on the Russell Society website.

Readers with an interest in printing may be aware that there are colours which can be shown in RGB on a computer screen but cannot be printed in CYMK. A so-called out-of-gamut error. The green pyromorphite from Coldstones Quarry described in this issue is particularly challenging and two images have been added to the website to show the mineral in its true colours.

To conclude this Editorial, readers may recall that JRS 21 contains an account of the minerals of the Yorkshire coalfield (Bateman *et al.*, 2018). Remarkably little of mineralogical note is preserved from the billions of tonnes of material that were moved by Britain's coal industry. A marcasite specimen from the Temple Meads Opencast near Leeds appeared in a recent collection sale (Fig. 6). This huge opencast site, a few miles from the Editor's home, is now completely restored. It produced several million tonnes of coal in the second half of the twentieth century, but there does not appear to be a single mineralogical record. The information base on British mineralogy, although deep and detailed in places, has huge gaps and a great deal remains for the interested researcher to contribute. That thought is as good as any to sign off the current Editor's tenure.

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PONDERING THE DISCOVERY OF AERATED PONDEROUS SPAR: THE TYPE LOCALITY AND EARLY HISTORY OF WITHERITE

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The first scientific descriptions of the barium carbonate witherite date from the 1780s. Uncertainty about the site of the original discovery, which seems to be the result of deliberate misdirection, is entrenched in the scientific literature. Detailed study of early publications, the key characters involved in the discovery and contemporary mineral collections shows that Anglezarke near Chorley in Lancashire, rather than Alston Moor, is the type locality. Anglezarke is known to have produced witherite from at least 1700, but the first definite report of the mineral from Alston Moor dates from 1809. Other important early localities include St Asaph in Flintshire, Arkengarthdale in North Yorkshire, Dufton in Cumbria, Fallowfield Mine in Northumberland and Snailbeach in Shropshire.

INTRODUCTION

Witherite, ideally $BaCO_3$, is unusually abundant in the epithermal orebodies in and around the Pennine blocks in northern England. It has a long and interesting history. Early accounts include conflicting assertions about its properties, uses and the site which provided the original specimens. Unravelling these claims and counterclaims is the principal objective of this article.

The International Mineralogical Association has no record of the type locality for witherite, but many mineralogical textbooks and internet sites favour Alston Moor. For example, Clark (1993: p. 756) lists the type locality as “Alston Moor, Cumbria, England”, on the basis of Abraham Gottlob Werner’s *Mineral System* (published by Hoffmann, 1789), in which the name “Witherit” was first proposed. The type locality is listed as “Alston Moor, Cumbria” by Clark *et al.* (1995) in their account of the *Mineral Species and Varieties Originally Described from the British Isles*. The online database Mindat currently claims Brownley Hill Mine near Nenthead in Cumbria without any supporting evidence (Mindat, 2022).

A number of twentieth-century studies attempted to determine the truth about witherite (Fowles, 1927; Zeman, 1950; Selwyn Turner, 1963; Williamson, 1963), but their conclusions are contradictory. Incomplete analysis of contemporary data is the most common cause of error. The underlying problem is essentially one of doubt: firstly, doubt surrounding Withering’s original assertion that the material he studied came from Alston Moor (Withering, 1784); and secondly, doubt surrounding James Watt Jnr’s claim that Withering was mistaken in attributing his material to Alston Moor and that it actually came from Anglezarke (Watt, 1790a). The discovery of witherite at Wellhope on Alston Moor in the first decade of the nineteenth century added to the uncertainty, and later finds of outstanding crystal specimens from a number of workings in the area caused further confusion.

Accounts published in the years immediately following Withering’s original description record several different localities for ‘aerated terra ponderosa’ the name most commonly used at the time for witherite. Unfortunately, the same name was also applied to the chemically similar carbonate minerals strontianite and strontium-bearing aragonite. Clear distinctions between these species did not emerge until the end of the eighteenth century, and this adds further to the complexity.

This narrative is the culmination of many years of detailed study of the original references, archives and collections. It describes all of the important early witherite localities and makes a critical analysis of previous accounts. The occurrence of witherite on Alston Moor is described in numerous references (e.g. Symes and Young, 2008; Tindle, 2008) but there is no modern description of the mineralisation at Anglezarke. An account of the minerals at Lead Mines Clough, the largest deposit on Anglezarke Moor, is included in a complementary article in this issue (Alderton *et al.*, 2022).

The spelling of locality names varies in early references and in the data preserved in archives. The currently recognised spellings of locations, particularly Alston Moor, Anglezarke, Arkengarthdale, Hexham, Leadhills, St Asaph and Wellhope, are used herein, but the original spellings are retained in quotations. It is hoped the reader will forgive the absence of [*sic*] in every case.

PREVIOUS REVIEWS

In textbooks of mineralogy the type locality for witherite is listed either as Alston Moor or, less commonly, as Anglezarke near Chorley in Lancashire. This information typically forms part of the preamble to a scientific description of the species, and simply repeats earlier claims. Mineralogical articles which deal specifically with the type locality (Fowles, 1927; Selwyn Turner, 1963), favour Alston Moor, however, studies of industrial history which include information about witherite favour Anglezarke (Williamson, 1963; Gill, 1987).

Among mineralogical texts, Miers (1902: p. 410) is substantially correct, noting that crystals were found in the mines on Alston Moor but that "the mineral discovered and analysed by Withering in 1783 was a fibrous variety from Anglesark in Lancashire". Rudler (1905) also reports that witherite was discovered on Anglezarke Moor, stating that it was found by James Watt. James Watt (1736–1819), the famous engineer, had nothing to do with the discovery but his son, James Watt Jnr (1769–1848), is integral to the story.

Two twentieth-century mineralogical articles which attempted to determine the type locality are responsible for most of the confusion. Fowles (1927: p. 309), records:

> "it is usually stated in treatises on chemistry that witherite (native barium carbonate) was discovered by Dr. Withering on the Lead Hills (or at Leadhills) in Scotland",

but that Aikin and Aikin (1807: p. 490) had suggested "the mineral described by Withering came from Anglezark in the north of Lancashire". Fowles was aware that "a similar statement appears in *Mineralogy* by Miers, 1902, p. 410". Rather than investigating the discrepancy he concluded:

> "it is obvious that both localities cannot be correct, and if Withering's own paper is to be taken as the authority (Phil. Trans., 1784, 74, 293), and I cannot find that he ever amended it, then both are wrong, for he twice states that the mineral he examined came from a lead mine at Alston Moor in Cumberland".

There is no evidence that Withering had any connection with the mines at Leadhills, but Fowles is correct in stating that it is "usually stated in treatises on chemistry [that witherite was discovered at Leadhills]", because many chemistry texts report this. Immediately prior to Fowles' article, Roscoe and Schorlemmer (1923: p. 631) noted the witherite "was discovered at Leadhills in Scotland by Withering in the year 1783". It is important, therefore, to determine the origin of this statement.

The earliest reference linking Withering, witherite and Scotland is Crell (1784). Lorenz Crell, a German chemist, in the second issue of the *Chemische Annalen* (p. 388), which was dedicated to the recently deceased Torbern Bergmann, records:

> "Withering found Heavy Earth [this could refer to barium or strontium in this context] with Air Acid [carbonate in this context] in an agglutinated mass at Leadhill [*sic*] in Scotland during the summer of 1783".

Withering (1783) provided no provenance for the specimens in his English translation of Bergman's *Sciagraphia Regni Mineralis*, but the locality is listed as Alston Moor in his account of the mineral, published in the next year (Withering, 1784: p. 293). It is unclear whether Bergman genuinely thought that Leadhills was the original source or Crell added the information posthumously. Regardless of the precise details, the claim that Leadhills is the type locality for witherite is the result of a confusion with strontium-bearing aragonite (which is discussed more fully in the following text).

Fowles (1927: p. 309) concluded that Withering's original paper (Withering, 1784), which twice states that the mineral he examined came from Alston Moor in Cumberland, must be taken as the authority. He appears to have been unaware of James Watt Jnr's article (Watt, 1790a) which indicates that Withering was misinformed, and that the witherite specimens were from Anglezarke near Chorley in Lancashire.

Surprisingly, Fowles' research is not cited by Selwyn-Turner (1963). In a brief article on the history of witherite important early descriptions are reviewed but too much reliance is placed on assumptions, as for example "Withering's change of mind about the provenance of his material appears to have been no more than one of belief". It is clear that Selwyn-Turner's knowledge of the timing of contemporary mineralogical discoveries was limited. This is particularly evident in his statement:

> "Watt's authority for denying the occurrence of witherite in Alston Moor was unreliable, its occurrence there being well known (Miers, 1902, p. 410; Dunham and Dines, 1945, pp. 24-26)".

The occurrence of witherite on Alston Moor was certainly well known by the mid-twentieth century as a result of the discovery of the deposits at Nentsberry Haggs Mine. There is, however, no independent published evidence that witherite was known from anywhere on Alston Moor in the 1790s. Selwyn-Turner (1963) concludes:

> "no final solution to the problem seems possible, but the claims of Anglezark rest on more shaky foundation than those of Alston Moor".

In the same year that Selwyn-Turner published his research, a paper describing the early history of witherite appeared in the rather less accessible *Mining Magazine* (Williamson, 1963). Its conclusion is altogether different. It has been overlooked by mineralogists but it is cited by Gill (1987) in his excellent historical review of the Anglezarke lead mines.

The uncertainty about the type locality for witherite extends to recent studies. In a review of the world's best specimen localities, Cook (2007) notes that the type locality for witherite is "the Alston Moor district", but provides no corroboration. His article makes no mention of Anglezarke whatsoever.

In *Minerals of Northern England*, a key modern reference, Symes and Young (2008: p. 123) include an overview of the history of witherite, highlighting the unique abundance of barium carbonate minerals in the

Northern Pennine Orefield. Although they cite Williamson's (1963) account of the Anglezarke mines and note the involvement of James Watt Jnr (Watt, 1790a,b) in the early debate, they state:

> "Watt considered that it was known on 'good authority' that no witherite had been found on Alston Moor. However, this claim is not credible and it is now accepted that the type locality is Alston Moor, although the precise locality remains unknown. It is probable that no final completely convincing solution will be possible, but as Selwyn-Turner, writing in the *Mineralogical Magazine* in 1963, concludes: 'the claims of Anglezarke rest on a more shaky foundation than that of Alston Moor'".

This analysis is mirrored in another key reference, *Minerals of Britain and Ireland* (Tindle, 2008: p. 533), which states:

> "Alston Moor is generally accepted as the type locality" but continues "although Anglezark Moor mine, east of the Liverpool waterworks, near Chorley, Lancashire, is also a contender ([Selwyn-]Turner 1963)".

Bridges (2009) came out in support of Alston Moor, but his analysis is based on a misinterpretation of Jenny Uglow's popular account of *The Lunar Men* (2002). As a demonstration of how easily the truth can be twisted it is worth studying a statement in Uglow (2002: p. 303) whose otherwise fine account of the Midlands-based Lunar Society provided some of the inspiration for this investigation. Describing the discovery of witherite, Uglow notes that in Matthew Boulton's collection of minerals:

> "One of these, a glassy milky-white mineral with pyramidal crystals, found in a Cumberland lead mine caught Withering's attention. Peering at it closely, he was sure he had found a 'terra ponderosa aerata' (barium carbonate), which Bergman had said was not to be found in its native state, but only as barytes (barium sulphate, or 'heavy spar'). Withering's experiments proved him wrong. Two years on he published his findings and much later Werner listed this as witherite".

There are subtle but crucial errors in this statement. First and foremost, "a glassy milky-white mineral with pyramidal crystals" is not an accurate description of the cream-coloured, massive, radiating witherite described in Withering's early publications. In presenting a popular narrative, Uglow has inadvertently used a description of perfect crystals of witherite, such as those discovered much later at Fallowfield Mine and on Alston Moor. There is no evidence these were known to Withering, Boulton or any other members of the Lunar Society at the time. Secondly, Bergman does not state that barium carbonate was not to be found in its native state, merely that he had not come across an example of it.

The database Mindat, which has become the principal online source of mineralogical information, wrongly records the type locality for witherite as Brownley Hill Mine in Cumbria (Mindat, 2022). The first reference to witherite at this locality is due to Thomson (1835), half a century after witherite was first described. The reason that this locality has been chosen is unclear, but it requires correction. Several entries in Wikipedia, which suggest that Cumberland is the type locality, also require revision.

In the course of this research countless historical inaccuracies have been identified and a few previously overlooked sources of information have been uncovered. Notable amongst these is Köhler's[1] (1790) *Message from the Mine at Anglezark, England, where the Acidic Earth or Witherite has Broken. From the Memoranda of the Literary and Philosophical Society of Manchester, by the Author Mr. James Watt Junior, Translated and Communicated with some Changes.* This article, broadly a translation of Watt (1790a), illustrates the remarkable speed at which scientific knowledge was disseminated at the time. The most important aspect of this study is that it records a clear case of misdirection designed to protect vested interests in the supply of an unusual mineral. This concealment was so effective that it led Köhler (1790: p. 217) to remark, that mineral dealers had been able to keep the true locality secret by convincing British mineralogists that the source was Alston Moor.

A few years later Klaproth (1801a: pp. 224–225) provided this informative statement:

> "The reason, why the geognostic situation and the true native place of witherite (falsely stated to be Alston-Moor, in Cumberland) continued for some time misunderstood, was the concealment practised by the miners ... and perhaps also to the base interestedness of the usurious dealers in fossils".

More than two centuries later Alston Moor is still commonly described as the original source. This is probably because the mines on Alston Moor were subsequently to become a source of barium carbonate in quantities far greater than anyone involved in the original description of witherite could have imagined.

EARLY HISTORY

In any historical analysis it is important to understand the state of contemporary scientific knowledge. Most scientific historians trace the modern concept of a chemical element to Antoine Lavoisier's *Traité Élémentaire de Chimie* which was published in 1789. It includes a description of compounds of the element barium, which was first recognised by Carl Wilhelm Scheele in 1774, in a short list of irreducible species (Partington, 1962: p. 213). Strontium does not appear in the list as it was not clearly separated from barium until the 1790s (Partington, 1942; 1951). Thus, an eighteenth-

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[1] Alexander Wilhelm Köhler (1756–1832) was public teacher of mining rights at the Bergakademie Freiberg and an Honorary Member of the Leipzig Economic Society (Wikipedia, 2021a). He served as Mayor of Freiberg. He edited the *Bergmännisches Journal* from 1789 to 1791 and jointly with his son-in-law Christian August Siegfried Hoffmann from 1792 to 1794.

century reference to 'terra ponderosa' could describe a mineral containing either barium or strontium[2].

The mineral we now know as witherite was first described by the Birmingham-based physician William Withering[3] as "TERRA PONDEROSA aerata" in a footnote to his English translation of Torbern Bergman's *Sciagraphia Regni Mineralis* (Withering, 1783: p. 28). In this account Withering provided no locality details, simply recording:

> "I have lately discovered a specimen of TERRA PONDEROSA aerata got out of a mine in this kingdom. It is very pure and in a large mass".

Torbern Bergman (1782: p. 45) was aware of the properties of artificial terra ponderosa aërata (barium carbonate). Along with Carl Wilhelm Scheele and Johan Gottlieb Gahn he had prepared numerous barium compounds but stated that the carbonate had not been found in nature at the time (see Withering, 1783: p. 28). In a scientific description of natural barium carbonate, which was published shortly thereafter, Withering (1784: p. 293) recorded that "This substance was got out of a lead-mine at Alston-Moor, in Cumberland".

In the first few years after the discovery, British mineralogists appear to have relied on specimens and information provided by Withering. For example, Kirwan (1784) notes:

> "Dr. Withering presented me with a very pure specimen of this species from Alston Moor, in Cumberland. It much resembles alum, but its texture is striated: its specific gravity is 4.331".

This is repeated in Nicholson (1787: p. 163):

> "Ponderous Earth, combined with the aerial acid, has been found at Alston Moor, in Cumberland. It resembles alum, but is of a striated texture, and its specific gravity is, 4.331".

In continental Europe a different story emerged. A year after Withering's description, Martin Heinrich Klaproth (1785: p. 217) noted that in his 'last publication', Bergman mentioned that "Schwererde" [heavy earth] mixed with air acid [carbonate in this context] was found in Scotland. In this context, Bergman's 'last publication' refers to notes edited and published posthumously by Lorenz Crell in *Chemische Annalen*. According to Crell (1784: p. 388), Bergman stated that Withering had found heavy earth united with air acid at Leadhills in Scotland during the summer of 1783. Bergman went on to record that he had not yet received the samples promised by Withering but had received a sample from Dr. Schwediauer[4] provided by Prof. Black[5] (Crell, 1784: p. 388). In hindsight, there are several possibilities for unintended error in this sequence of events.

It is unclear whether Bergman had mentioned Leadhills in his notes, or whether Crell (1784) added that detail. It should, however, be noted that Withering's (1784) paper citing "Alston Moor" was read on April 22, 1784, and that Bergman died on July 8, 1784. Therefore, Bergman may have written his notes in 1783 after Withering had announced the discovery of natural "TERRA PONDEROSA Aerata" to the scientific community but before his later paper which provided the locality details. Bergman may, therefore, have obtained his locality information from Schwediauer or Black, but whether either knew the original source is unclear. It is nonetheless interesting that Joseph Black, working in Edinburgh, appears to have had access to this new substance, or something similar, at about the same time as Withering.

Surprisingly, Bergman's *A Dissertation on Elective Attractions*, published in the month of his death and rapidly translated into English (Bergmann, 1785: pp. 180−184) suggests that he was unfamiliar with naturally occurring barium carbonate in any form. However, the translator notes (p. 368) that Bergman had received a sample "from this country [England]" shortly before his death.

Klaproth, who was fascinated by the newly discovered mineral, stated that Eversmann[6] had brought a sample from England back to Germany. Eversmann

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[2] Chemical knowledge was advancing rapidly at the time and in the first years of the nineteenth century James Sowerby (1806: p. 31) was able to record that the strontium sulphate celestine was present in many British collectors' cabinets labelled either as 'sulphate of baryte' or 'sulphate of lime' in the eighteenth century.

[3] William Withering (1741−1799) is best known as a physician for the discovery of the digitalis, and as a botanist for an early flora of Britain which earned him the title "The English Linnaeus". He was a member of the Lunar Society, but his somewhat prickly disposition meant he had few close friends (Peck and Wilkinson, 1950).

[4] Franz Xavier Schwediauer (1748−1824) was an Austrian-born chemist, botanist and physician who settled in London in the mid-1770s (Larousse, 1875: sections on Schwediauer and Swediaur). He practiced medicine in both London and Edinburgh. Alongside Bentham he translated Bergman's *An Essay on the Usefulness of Chemistry* into English. He later changed his name to Francis Swediaur and was a business associate of Matthew Boulton in France from 1791. Margolis (1988) speculated that it was Swediaur's association with Withering that may have led to his acquaintance with Boulton.

[5] Joseph Black (1728−1799) was Professor of Chemistry at the University of Edinburgh and predecessor to Thomas Charles Hope, who took on the role in 1795. Black worked closely with James Watt. Black's experiments on carbonates of magnesium and calcium, conducted in 1756, led to the discovery of fixed air (carbon dioxide) and carbonic acid (Black, 1777). There is no direct evidence that he experimented with barium carbonate prior to the work of Withering.

[6] Friedrich August Alexander Eversmann (1759−1837) was a Prussian technologist, mining clerk and publicist. As factory commissioner of the County of Mark in west Prussia he travelled during 1784 through the industrial regions of England promoting the economic development of the metal goods industry. He was responsible for the procurement of the first James Watt steam engine for pumping a coal mine in Prussia in 1786 (Wikipedia, 2021b) and is likely to have met Matthew Boulton.

received the sample from John Gilbert[7], agent for the Duke of Bridgewater's coal mines at Worsley[8] in Lancashire (Klaproth, 1785: p. 218). Gilbert is said to have found the sample, a rounded mass, in the mountains of Lancashire near the border with Yorkshire but suspecting that it contained valuable metals he did not give a precise locality. Klaproth (1785) went on to report that Gilbert had shared similar samples with a number of well known Englishmen including William Withering, Richard Kirwan[9], Joseph Priestley[10] and James Watt[11]

In the early years of chemistry information passed from Britain to continental Europe and back, often acquiring an additional commentary in the process. Klaproth's (1785) work was known to the French chemist, Balthazar-Georges Sage (1740–1824), who contributed his own observations. Sage (1788) notes that Klaproth questioned Bergman's analyses of the material from Leadhills, which contained only 8 parts of heavy earth and 16 parts calcareous earth.

With hindsight, it is likely that Bergman's material from Leadhills was not witherite, but the confusingly named 'stronites', a pale green strontium- and lead-bearing aragonite, first collected from "the Mines at Leadhills" by Revd John Walker[12] in 1761 (Walker, 1822: p. 90–91) but not identified at the time and later erroneously stated to be strontianite (Livingstone, 2002: footnote to p. 21). This is consistent with Bergman's analysis which returned ⅔ calcareous earth and ⅓ of heavy earth (which is entirely wrong for witherite) and also with what is now known about the crystal chemistry of aragonite, in which strontium commonly replaces calcium. The 'heavy earth' would have been impossible for Bergman to properly characterise because strontium had not been separated from barium at the time of the experiments. Furthermore, 'stronites' would have been accessible to Joseph Black who, like Walker, was based in Edinburgh.

Sage (1788) reported that the aerated heavy spar [*le spath pesante aéré*] studied by Klaproth was from coal mines in Lancashire [*des mines de charbon de Lancashire*] and occurred in round masses the size of a man's head. This almost certainly refers to the lead mines at Anglezarke. He recorded that the material investigated by Withering, Priestley and Watt was from the same locality, but claimed that Black had received heavy spar from "a lead mine at Alston-moor". The foundation for this claim is uncertain, it may have been added by Sage to fit in with his own narrative[13].

Sage went on to report his own experiments on aerated heavy spar from 'Alston Moor', based on samples provided by Charles Francis Greville (1749–1809), whose extensive collection of minerals was acquired by the British Museum [later the Natural History Museum] shortly after his death (Wilson, 1994: p. 78). Greville's specimen was described by Sage (1788) as:

> "striated and half transparent; it was six inches long, and the ends were covered with pale yellow ochre".

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[7] John Gilbert (1724–1795) was land agent for Francis Egerton, the third Duke of Bridgewater, from about 1758 (Wikipedia, 2021c). At age 12 or 13 he was apprenticed to Matthew Boulton's father and would almost certainly have had some contact with Matthew Boulton himself from an early age. Gilbert appears to have been knowledgeable in terms of mining and raw materials, because he set up a pencil factory in Worsley supplied by the Duke's mines near Keswick and developed the first deep salt mine at Marston Mill in Cheshire. He also worked with James Brindley in engineering a canal from Worsley to Manchester, which was completed in 1761.

[8] Gabriel Jars (1732–1769), a French industrial spy, toured England and Scotland in 1765 documenting the methods of mining and productions. His observations were published posthumously (Jars, 1774; 1780; 1781). He visited the Duke of Bridgewater's coal mines at Worsley, but made no mention of other mineral deposits in the neighbouring hills. He provided an account of some of the mines on Alston Moor, but does not record any mineral substance resembling witherite.

[9] Richard Kirwan (1733–1812) was an Irish chemist, meteorologist, and geologist. Kirwan published his *Elements of Mineralogy* in 1784 within which he described (p. 53) "Ponderous Earth combined with the Aerial Acid" based on a specimen from "Alston Moor, in Cumberland" presented to him by Withering. In the second edition Kirwan (1794: p. 134) makes no mention of Alston Moor, but instead refers in detail to the occurrence at Anglezarke in Lancashire, as described by Watt (1790). Kirwan also mentions Argyllshire as a source, but this is presumably in relation to strontianite.

[10] Joseph Priestley (1733–1804) was an English theologian, chemist and philosopher. He was a member of the Lunar Society along with Matthew Boulton, William Withering James Watt and Josiah Wedgewood. He conducted experiments with "terra ponderosa aerata" in the process of investigating the properties of fixed air (Priestley, 1788; 1790; 1794) but correspondence between him and Wedgewood shows that in 1787 he was having great difficulty in obtaining samples (Bolton, 1892: pp. 84–86). Priestley (1788) did not mention the source of his material, but he did reference (p. 152) the excellent analysis provided by Withering. He also mentioned Dr Withering examining some of the liquors for him in other experiments (p. 151) which suggests that the two men consulted closely. Priestley (1794) provided lectures at New College, Hackney, London and in lecture 20 (pp. 81-84) he covered "Terra Ponderosa", and more specifically "terra ponderosa aerata" and the fact that heat alone will not reduce it of its fixed air, but that steam is required when it is red hot.

[11] James Watt (1736–1819) was a Scottish inventor, mechanical engineer and chemist (Wikipedia, 2021d). In the mid-1770s he became involved with the industrialist Matthew Boulton in Birmingham. It is interesting that it was Watt's son, James Watt Jnr (1769–1848), who is better known in relation to the history of witherite even though he was only twenty years of age when he read his two instructive papers on the subject (Watt, 1790a,b). His knowledge on this subject appears to coincide with him moving to Manchester in 1788. Klaproth (1785) was clearly referring to James Watt senior (his son would have been just sixteen years of age in 1785), in relation to the specimens of terra ponderosa aerata he received, but it does not appear that Watt conducted any on his own experiments on this substance. It is interesting that Klaproth (1785) suggests that Dr Black received material from a different locality because Black and Watt were good friends from the mid-1750s (Wikipedia, 2021d).

[12] Revd John Walker (1731–1803) was Professor of Natural History at the University of Edinburgh. Predominately a botanist his natural history classes included much on minerals after he became professor (Wilson, 1994). His personal mineral collection was removed from its place in the University Museum following his death by the trustees of his estate in 1804 and was said to have been acquired by the Scottish mineralogist Robert Jameson (1774–1854) whose collection was donated to the Royal Scottish Museum in 1855 (Cleevely, 1983 and DNB in Wilson, 1994: p. 177). A superb account of John Walker is provided by Eddy (2008).

[13] An English translation of Sage's (1788) work, published in 1789, is littered with errors.

It is not known how Greville acquired his specimen but it was clearly substantial. It cannot be traced in the Greville Collection at The Natural History Museum, London (referred to as NHM from now on) and may have ended up in one of the French museums. It should be noted that Sage's description is a good match to contemporary specimens from Anglezarke, and it seems probable that Greville was misled in his attribution to Alston Moor.

At the end of the eighteenth century, discoveries were being made by many different groups of scientists, scrabbling to find compounds with beneficial properties or industrial uses and occasionally isolating new chemical elements. Numerous investigations of the medicinal properties of barium compounds followed Withering's discovery. Adair Crawford (1748/9–1795) took a leading role in this research. In trying to find new sources of terra ponderosa aërata for his work at St Thomas' Hospital in London, Crawford (1789) reported that a batch of "aerated barytes ... sold at Strontean, in Scotland" possessed "different properties from the terra ponderosa of Scheele and Bergman" and proposed that it was probably a "new species of earth which has not hitherto been sufficiently examined".

For comparison, he obtained a sample of true terra ponderosa aërata from William Babington[14] who was already of the opinion that the Scottish mineral was different (Crawford, 1789: p. 356). Crawford's (1789: p. 357) description of the 'Strontean mineral' as of a "greenish cast" confirms that it was not witherite, but the related mineral now known as strontianite.

Thomas Charles Hope (1766–1844), who succeeded Joseph Black as Professor of Chemistry at Edinburgh, showed that strontium and barium were similar but distinct chemical elements in a careful series of experiments in the 1790s (Hope, 1794; 1798). A further decade of intensive experimentation passed before Sir Humphry Davy isolated elemental strontium and barium using the newly devised method of electrolysis in 1808 (Davy, 1812). Livingstone (2002: pp. 130–132) provides a detailed account of the early history of strontianite.

The physical and chemical similarities between witherite, strontianite, and strontium-bearing aragonite and the use of the term 'aerated terra ponderosa' to describe all of these minerals, must be borne in mind in interpretations of the early literature. It is possible to unravel most mistakes retrospectively. Specimens which many previous authors and historians have assumed to be witherite, including Bergman's mineral from Leadhills, Crawford's "aerated barytes ... sold at Strontean, in Scotland" and Black's Scottish 'heavy earth', did not contain barium, but the yet-to-be-isolated element strontium. In 1787 when Joseph Priestley wrote to Wedgewood regarding the scarcity of terra ponderosa aërata he mentioned that he had heard that there was plenty of it in Scotland (Bolton, 1892: p. 85). It is quite clear that it was strontianite that had been found there.

Any early reference to witherite from Scotland must be treated with suspicion. The Revd John Walker's classification of minerals, published in 1787, is vague and does not mention barium carbonate or any equivalent. Walker later claimed, in an account of his life in mineralogy [original date unknown, believed to be circa 1797 (Eddy, 2008: p. 85), but published posthumously (Walker, 1822: p. 90)], to have collected the mineral which became known as strontianite "in great plenty" from Strontian in Argyllshire in 1764, and that he had (p. 91) "observed it but very sparingly, three years before, in the Mines at Leadhills". There is no mention of witherite in Walker's account, and Robert Jameson who, as editor of the *Edinburgh Philosophical Journal*, helped to posthumously publish his manuscript in 1822, did not record any Scottish occurrences in his *System of Mineralogy* (Jameson, 1820: p. 397). Much later, Heddle (1901: p. 142) noted that witherite had "not yet been detected in Scotland". The first reliable account of a Scottish specimen is from the deep workings at Glencrieff Mine, Wanlockhead (Brown, 1919), although it must have been encountered at Hilderston Mine at a much earlier date (Meikle, 1994).

In 1790, James Watt Jnr (1769–1848), son of the famous industrialist and a former student of Werner, claimed that Withering's "Aerated Barytes" was from "Anglezark" in Lancashire, not Alston Moor. Watt's study is key to unravelling the early claims and counterclaims about the type locality. In a description of witherite he records (Watt, 1790a):

> "However he [Withering] was misinformed as to the place from whence his specimen came, which he supposed to be Alston Moore, where I have good authority for advancing, that none has been found. He has since informed me that he believes it came from the same mine of Anglezark, which forms the subject of the present paper".

James Watt Jnr's *Some account of a Mine in which the Aerated Barytes is found* (Watt, 1790a) is a very detailed work, and in contrast to the studies by other scientists it includes observations made on two short visits to Anglezarke. It is of significance that William Withering made no attempt to correct Watt in later letters or publications[15] (e.g. Withering, 1822: pp. 61–62). Köhler (1790: p. 217) in his translation of Watt (1790a) implied that Withering had been provided with the original locality information second or third

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[14] William Babington (1756–1833) was an Anglo-Irish physician and mineralogist of high regard who was engaged by John Stuart, third Earl of Bute, to arrange his extensive mineral collection (Wilson, 1994). Babington purchased much of Bute's collection, upon his death in 1792, and based his most important works, *A Systematic Arrangement of Minerals* (1795) and *A New System of Mineralogy in the Form of a Catalogue* (1799) on its contents (Wilson, 1994). He is known to have received specimens from Philip Rashleigh in 1794 (RIC archive No. RASH/1/33). Once he completed his mineralogical publications, he sold his portion of the "Butean Collection" for £3,000 to John St Aubyn (1758–1839) in around 1799 (Wilson, 1994).

hand. So why did Withering attribute his mineral to Alston Moor?

Withering (1784) records:

> “I first saw it [witherite] in the valuable collection of my worthy and ingenious friend MATTHEW BOULTON, Esq. at Soho; who, when he picked it up, conjectured from its weight that it contained something metallic” [and that] “Mr. Boulton, with his usual benevolence, presented me with a piece of it, part of which accompanies this paper, for the inspection of the Members of the Royal Society”.

This suggests that the original specimen and the contextual information was provided by Matthew Boulton (1728–1809). Boulton, an industrialist and business partner of James Watt Snr, was an avid mineral collector (unlike Withering) and used his involvement with mining companies to acquire specimens. He also obtained specimens from other members of the Lunar Society, many of whom shared similar interests (Uglow, 2002).

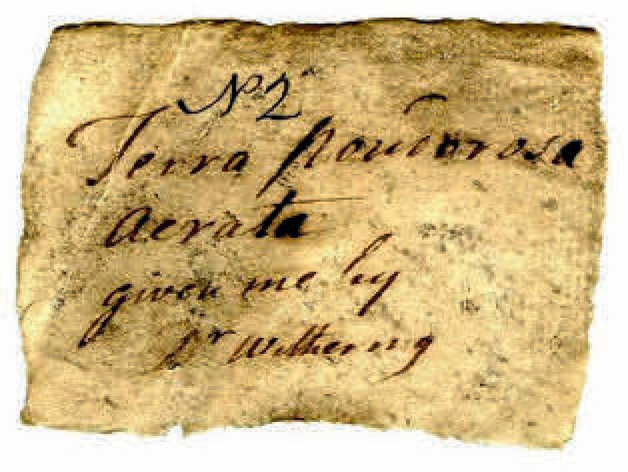
Boulton’s mineral collection is preserved at The Lapworth Museum of Geology at the University of Birmingham. It includes five witherite specimens (Starkey, 2011a). None have any locality data, although a label accompanying one of the specimens, in Boulton’s hand (Starkey, 2011b: p. 20), contradicts Withering’s assertion in that it suggests Withering gave the specimen to Boulton (Fig. 1).

With regard to Boulton’s specimen, Withering (1874: p. 293) wrote:

> “about two years ago [i.e. about 1782] I saw it in his possession; and partly from its appearance, being different from any calcareous spar I had seen, and partly from its great weight, I suspected it to be the spatum ponderosum”.
>
> “A few experiments made at the moment confirmed my suspicions, at least so far as to shew that it contained a large proportion of the terra ponderosa united to fixed air; but I did not then flatter myself that it would prove so pure as I afterwards found it to be”.

He went on to describe it as:

> “not much unlike that of a lump of alum; but upon closer inspection, it seems to be composed of slender spiculae in close contact, but more or less diverging. It may be cut with a knife. Its specific gravity is from 4,300 to 4,338”.



N^{o}2
Terra Ponderosa
Aerata
given me by
D^{r} Withering

Figure 1. Faded label from the collection of Matthew Boulton (1728–1809) at The Lapworth Museum of Geology, written in Boulton’s own hand, recording: “N^{o}2 Terra Ponderosa Aerata given me by D^{r} Withering”. Roy Starkey photograph reproduced courtesy of Birmingham Museums Trust.

Three of Boulton’s specimens are figured by Starkey (2011a: p. 69). They are massive and cream coloured with a somewhat fibrous structure. They are not obviously nodular and lack well formed crystals. All of these features are consistent with Withering’s description. Two of Boulton’s specimens have an ochreous, weathered, surface crust several millimetres in thickness (Figs 2 and 3). A third specimen (Fig. 4) is a small solid mass of cream-coloured witherite. All of these specimens have strong similarities to modern well provenanced witherite from Anglezarke (see Alderton *et al*., 2022: fig. 28 and Figs 29–30 herein).

The description of the specimen that Withering gave to Richard Kirwan (1784) is also consistent with those in Boulton’s collection: “It much resembles alum, but its texture is striated”.

Figure 2. Compact somewhat fibrous witherite, 70 × 50 × 25 mm, with an orange-brown ochreous surface layer. Specimen 1993G03.1026 in the Matthew Boulton Collection at The Lapworth Museum of Geology. Roy Starkey photograph reproduced courtesy of Birmingham Museums Trust.

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[15] It should also be noted that by 1790 Withering’s health was poor. Ever since his days as a medical student in Edinburgh he had suffered with chest infections. In 1790, he had a severe attack of pleurisy and fever and was unable to work between February and April; the same thing happened in May 1791 when he spent a month in bed. This was a troubled year in Birmingham with riots during which his friend Joseph Priestley’s house was burnt down. Withering resigned his post at the General Hospital in 1792 due to failing health. It may be that he failed to correct the geographical origin of witherite for health reasons. His botanical studies took precedence in the last years of his life.

Figure 3. Compact somewhat fibrous witherite, 120 × 70 × 70 mm, with an orange-brown ochreous surface layer. Specimen 1993G03.1027 in the Matthew Boulton Collection at The Lapworth Museum of Geology. Roy Starkey photograph reproduced courtesy of Birmingham Museums Trust.

Matthew Boulton's letters, which are preserved in the archives at Birmingham Library, are of crucial importance to this investigation. On 12 November 1789, Boulton wrote to his son, Matthew Robinson Boulton (1770–1842), at Bad Langensaltza (Thuringia, Germany):

> "I have sent you a bit of terra ponderosa airata [*sic*], for an account of which I refer you to Dr. Withering's annalisis [*sic*], published in the Philosophical Transaction of our Royal Society publish'd about five or six years ago. That stone is now found to be a cure for cancerous and all scrofulous disorders, by takeing [*sic*] about ten drops of saturated sollution [*sic*] of it in marine acid once or twice a day; this use of it was discover'd by Dr. Crawford of London , who lately published a book on Heat and Fire" (Birmingham archive: MS 3782/12/57/38).

Thus, witherite was thought to have considerable medicinal value. Further letters show that Boulton had access to a supply, for on 1 February 1790 he wrote:

Figure 4. Massive lamellar witherite, 40 × 30 × 15 mm. Specimen 1993G03.1030 in the Matthew Boulton Collection at The Lapworth Museum of Geology. Roy Starkey photograph reproduced courtesy of Birmingham Museums Trust.

> "I have now got a pretty good stock of terra ponderosa aerata, some of which I will send you by the way of Holland" (Birmingham archive: MS 3782/12/57/41).

On 8 March 1790 he wrote:

> "I am glad you have got the fossills [*sic*], &c., safe. I have also sent you another box full of terra ponderosa aerata; it is consign'd to Messrs. Isnel & Martin at Amsterdam, to be forwarded to you by the dilligence [*sic*] to Langensaltza" (Birmingham archive: MS 3782/12/57/42).

Boulton did not divulge the source (either the supplier or the locality) of his specimens, perhaps with good reason. There was considerable demand for witherite, not just as a chemical curiosity (as stated by Watt, 1790a: p. 599) but also because of its growing significance in the preparation of medicine (Crawford, 1789). It was quite common for dealers to conceal the exact source of their material to prevent competitors from bypassing them and to protect their supplier, especially if the material had been gathered illicitly. Köhler's (1790: p. 217) remark that he was surprised that dealers had been able to keep the locality secret for so long may relate specifically to Boulton, but it is unlikely that the full truth will ever emerge.

Matthew Boulton was one of the leading mineral collectors in England in the second half of the eighteenth century, but he has never been considered to be a mineral dealer. His letters show that he supplied several boxes of witherite to Germany in 1789 and 1790 and as he provided material to Withering in 1782 he appears to have had access to specimens over a prolonged period. Whether he was a major distributor is not known, but witherite was obtained illicitly from Anglezarke at the time: firstly, in about 1782, by two Frenchmen who, according to Parkes (1823: p. 327) stayed in Chorley for a number of days, visited the lead mines, filled two boxes with the spar and sent it off by carrier before leaving town; and secondly, by a local man called James Smithels who collected witherite under cover of darkness (Parkes, 1823: p. 328).

It is unclear if any of Boulton's specimens were destined for Köhler in Freiberg, Saxony, but after translating Watt's (1790a) detailed account of the mine at Anglezarke (Köhler, 1790) he would presumably have been on the lookout for material. Much remains to be discovered about the individuals involved in this trade.

Regardless of the details of the supply chain, witherite specimens were distributed widely across continental Europe in the last decades of the eighteenth century. The French chemist Antoine François, Comte de Fourcroy, published experiments on carbonate of baryte, reputedly from Alston Moor, in 1796. Boulton had business ties with France: in 1786 he had visited the country accompanied by his business partner James Watt and in 1791 he attempted to win a lucrative contract to provide coinage (Margolis, 1988). It is worth noting that his agent in France, Dr Francis Swediaur, was the same Dr Schwediauer [as noted earlier he changed his name] who provided the samples of aerated terra ponderosa to Bergman (Crell, 1784: p. 388) from Joseph Black.

Boulton certainly provided specimens of witherite to British mineral collectors, most notably Philip Rashleigh (1729–1811). The Royal Institute of Cornwall archives has a list of eleven specimens (not all witherite) with a note that:

> "The above were presented to Philip Rashleigh with several other curious Minerals by Mathew Boulton Esq. Oct. 1785" (RIC archive No. RASH/1/46).

At least one of the specimens was an example of the newly discovered substance because Rashleigh's manuscript catalogue, which is preserved along with most of his collection at the Royal Cornwall Museum in Truro, records:

> "No. 1. Ponderous Earth combined with Aerial Acid part of the Stone from which Dr. Wethering [*sic*] made his Experiments Alston Moor – Boulton".

As a result of his business interests, Boulton spent time in Cornwall. He lived at Cusgarne House in Gwennap from around 1779 into the 1780s, and must, at some point, have become acquainted with Rashleigh. The wording of Rashleigh's catalogue implies that his specimen was part of the original specimen analysed by William Withering in 1783 which was claimed to be from Alston Moor (Withering, 1784), but it is not known whether Boulton provided Rashleigh with the locality details, or whether Rashleigh recorded them on the basis of Withering's publication.

It is interesting to note, however, that Rashleigh later changed his opinion as to where this specimen originated. On 21 April 1804, in a letter to James Sowerby, he wrote:

> "The Carbonate of Barytes from Arkendale is of a deeper Yellow than what I have seen from Anglesark, I have a small piece of the original very near White" (NHM, London, General Library, Sowerby Archive: Rashleigh: 47/8),

which clearly indicates he had come to believe that the original locality was Anglezarke. At the time, Sowerby had just begun publishing *British Mineralogy* (Sowerby 1804; 1806; 1809; 1811; 1817) and Plate 76 (Sowerby, 1804) illustrates a new discovery from Arkengarthdale. Rashleigh's letter goes on to note:

> "The Carbonate of Bartyes [*sic*] in double Hexahedral Crystals is new to me, & being mixed with Lead Ore is an addition to it";

which implies that Sowerby had sent him a sample from Arkengarthdale. There are no illustrations of witherite from Anglezarke in Sowerby (1804; 1806; 1809; 1811; 1817), perhaps because it was not considered aesthetically pleasing or unusual enough to warrant inclusion. Indeed, it is clear from an earlier letter from Sowerby to Rashleigh (dated 2 April 1804) that it was the first time that witherite had been found in such distinct crystals:

> "I am glad to add another rarity for you Crystalized Carbonate of Barytes very lately found; and known to only 2 or 3 persons. It is immatative [*sic*] of quartz." (Cornwall Record Office, Truro: Rashleigh Archive: DDR/5757/2/23).

It is unfortunate that no witherite specimens can be traced in the Rashleigh Collection at the Royal Cornwall Museum. The collection had been split prior to the purchase by the Royal Institution of Cornwall in 1902. It is possible that the witherite specimens may have ended up in the part of the collection subsequently purchased from Arthur Rashleigh by Arthur Russell in 1923 (Russell, 1952: p. 104). If found, it would be expected that at least one specimen would be similar in appearance to those preserved in Boulton's collection at The Lapworth Museum of Geology.

WITHERITE AND POTTERY

It is occasionally claimed that Josiah Wedgewood (1730–1795), another of the 'Lunar Men', experimented with carbonate of baryte, either in the body of his pottery, or as glaze. Uglow (2002: p. 298) states:

> "since 1772 he [Wedgewood] had identified the materials he needed: the feldspar, moorstone and the elusive 'spath fusible', carbonate of barium. He finally discovered great masses in the lead mines near Matlock on an expedition with his father-in-law Richard in 1774 and with this he achieved a fine white body".

The date, 1774, which is nine years earlier than Withering's identification, and the reference to Matlock in Derbyshire eliminate any possibility that 'spath fusible' is witherite[16]. The term may refer to fluorite, baryte or feldspar (de Fourestier, 1999). The error appears to have entered the literature in a nineteenth century biography of Wedgewood as a result of a misunderstanding of early mineral names. In common with other blunders associated with witherite it has proved difficult to correct.

In a preface to *The Life of Josiah Wedgewood from his Private Correspondence and Family Papers*, Meteyard (1865: p. xix) states:

> "On many points of scientific interest we gain great light. We approximate to a date for the invention of the mortar-material, and we trace Wedgewood's unwearied search amongst spars of all kinds for the **terra ponderosa**, or carbonate of barytes. In this search he was aided by Dr. Fothergill, Dr. Darwin, Mr. Vigor of Manchester, Mr. Whitehurst of Derby,

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[16] In their review of the minerals of the Peak District, Ford *et al.* (1993: p. 35) note that witherite has occasionally been mentioned in association with Derbyshire but in all cases the mineral has turned out to be baryte.

> and even Brindley. But Bentley was the friend who procured for him at last some true specimens, probably from the mines of Anglezarke in Lancashire".

The last sentence is a cause of considerable confusion, but several other errors should also be highlighted. The term 'terra ponderosa' was used to describe minerals containing barium (and to a lesser extent strontium) by Torbern Bergman from 1779 (Cullen, 1784: p. 28). It does not refer specifically to the carbonate, which was described as terra ponderosa aërata. Bergman's experiments, which were undertaken in about 1774 (and translated by Cullen, 1784), suggest that he had produced terra ponderosa aërata [barium carbonate] chemically (Bergman, 1782: p. 62), although the analyses (Cullen, 1784: p. 29) indicate that it contained a considerable amount of water. It seems reasonably certain that he had not come across natural terra ponderosa aërata [i.e. witherite] as in *Sciagraphia Regni Mineralis* (Bergman, 1782: p. 45) he records:

> "BARIUM *sulphate* has a place among the earths; nitrate a lot of natural places to meet with and yet none was found, which also applies to the carbonate".

Bergman sometimes also referred to the baryte, the marmor metallicum of Cronstedt, as "spathum ponderosum" (Cullen, 1784: p. 28). William Withering used the same terms as Bergman (1782), i.e. "TERRA PONDEROSA *aërata*". It is absolutely clear, therefore, that Wedgewood was not searching specifically for witherite, but more generally for dense barium minerals.

Meteyard's (1865: p. xix) claim that Bentley's specimens were "probably from the mines of Anglezarke" is particularly unhelpful. There is no primary evidence to support this contention, but historians including Gill (1987: p. 60) have used it to claim that Wedgewood had experimented with samples from Anglezarke:

> "During the middle of the eighteenth century, the witherite deposit attracted the attention of Josiah Wedgewood, who was experimenting with "cawk" as a body material for the production of Jasper ware. One sample was described as "cawk aerated from near Chorley, Lancashire" and, to maintain secrecy about its nature, it was crushed before being transported to Etruria".

Watt (1790b: p. 616) sheds some light on the confusion. In order to test the theory that "the fixed air might be expelled from the Aerated Barytes [witherite] by a strong heat alone" he sent some to Wedgewood's son, Josiah Wedgewood Jnr (1769–1843). Watt asked him to expose it to the greatest possible heat in one of his father's furnaces. He obliged, but the results proved surprising:

> "I have exposed to a very strong heat for thirty-six hours, two ounces of the Aerated Barytes [witherite], but have not been able to weigh it since, from an effect having taken place which I did not expect. Some part of the Barytes appears to have begun to vitrify with the matter of the cup in which it was exposed and has formed a greenish substance, which sticks pretty fast to the Vessel and in one place has corroded it so much as to have formed a small hole exactly in the way that Fluor does. As I was not very careful in picking the pieces I suppose the greenish colour to have been owing to some impurities [Watt considered this to have been caused by ochreous water within the specimens]. This experiment has however proved that a long continued heat does not expel the whole of the fixed air if it does any part of it, for the burnt Barytes immediately upon coming out of the oven effervesced strongly with the Marine Acid and dissolved exactly in the same manner as the crude. The heat it has undergone was 110º of my Father's Thermometer".

This implies that neither Josiah Wedgewood, father or son, had previously experimented with witherite a contention which is supported by correspondence between Joseph Priestley and Wedgewood Snr in 1787 within which Priestley asks if Wedgewood could provide him with a pound or two of terra ponderosa aërata, but he replied that he had none in his possession (Bolton, 1892: pp. 84–86). Furthermore, Wedgewood Jnr's remarks appear to describe the discovery that barium carbonate (witherite) had the potential to form a glaze.

Meteyard (1865; 1866) appears to have been unaware of James Watt Jnr's publications (Watt, 1790a,b), relying instead on Samuel Parkes' detailed accounts of the mines of Anglezarke (Parkes, 1807; 1815; 1823), without giving him any credit. Parkes (1823: p. 317) explained that Wedgewood [i.e. Josiah Wedgewood Snr] derived great profit incorporating sulphate of barytes in his jasperware. Meteyard's (1866: p. 9) somehow mistook this for 'carbonate of baryta' [witherite]:

> "after a series of long extended experiments, resulted in Mr. Wedgewood's finest discovery, his crowning feat, as a philosophic chemist, that of the use of the Terra ponderosa, the Spath fusible of the French chemists, or the carbonate of baryta, and ultimately its sulphate, in the body of pottery".

Wedgewood was an experimenter, but not an analyst. He trialled new materials for use in ceramics from as early as 1766 (Meteyard, 1866: p. 11). In mid-1773 he began to focus his attention on heavy (barium containing) compounds for use in porcelain. Wedgewood refers to "some portion of the spaith fusible or terra ponderosa" as a constituent of the fine white terra cotta body (Meteyard, 1866: p. 315), but nowhere is barium carbonate mentioned. Parkes (1815: p. 193) contention that he used baryte is supported by modern analyses which show barium sulphate was the secret ingredient (e.g. Cuthbertson, 2012). An excellent explanation of Wedgewood's experiments with barium compounds provided by Elliott (2006: p. 21) which records that baryte was used in jasperware until the 1930s. The lead in the baryte acted as flux to such an extent that pure baryte is rarely used nowadays as it is of little benefit.

Wedgewood's attention was directed toward Derbyshire as a source of compact, massive, white baryte known locally as cauk and sometimes spelled caulk or cawk (Historic England, 2021). Pilkington (1784: pp. 169–173) provides an excellent account of the different forms of cauk found in Derbyshire and also notes that "Dr. Whithering [*sic*]" had been conducting experiments on the different types.

The fact that the mine at Anglezarke had lain idle for a long period before 1781 makes the possibility of a visit by Wedgewood and any connection between his pottery witherite extremely unlikely. As with much else in the history of witherite, errors have been introduced in later narratives. It should be added that barium carbonate was eventually, and still is, used as a glaze in pottery (e.g. Ceramic Arts Network, 2021). Barium oxide is the reactive ingredient but it is commonly added as a carbonate. In enamels, barium carbonate promotes brilliancy, increases the intensity of the colour and gives a high gloss, improved co-efficient of expansion, elasticity and greater resistance to organic acids (Anon., 1940).

WITHERITE IN HISTORIC COLLECTIONS

Historic collections and their catalogues offer an insight into the availability of mineral specimens from localities at different points in time. The older the collection, the more likely it is to have suffered damage and loss, but the significance of the specimens that remain and any associated documentation is often much greater. Several large mineral collections were assembled by wealthy collectors broadly contemporaneously with Matthew Boulton and William Withering.

One of the earliest extant mineral collections belonged to the London physician and anatomist William Hunter (1718–1783). His collection formed the basis of the Hunterian Museum in Glasgow. In 1813, the Hunterian Museum had just one specimen of witherite on display, from Anglezarke in Lancashire (Laskey, 1813: p. 42). As Hunter died in 1783, this specimen is unlikely to have been part of his original collection and was probably added to the museum collection in the intervening years.

An early collection with a strong bias towards the north of England was assembled by the Revd Clayton Mourdant Cracherode (1730–1799). Cracherode's collection contains much material from "Alston moor, Cumberland" and it is documented in a handwritten manuscript catalogue preserved at the NHM, London (Special Collections Library: MSS CRA). There are three pages of specimens listed under "Terra Ponderosa", but none relate specifically to witherite. Specimen number 27, however, is interesting:

> "27. Green aerated Barytes, with white Barytes, from Scotland".

This is clearly strontianite and suggests that Cracherode's catalogue was produced before the name strontianite, coined by Sulzer in 1791, came into popular use. The absence of any specimens of witherite shows that it was difficult, even for someone with an association with the north of England, to obtain specimens.

Philip Rashleigh's (1729–1811) remarkable collection which was formerly housed in his stately home at Menabilly, near Fowey in Cornwall included a specimen of witherite directly attributable to Boulton, originally thought to be from Alston Moor, but about which Rashleigh later changed his opinion [*vide supra*]. It included one other specimen:

> "No. 21. Aerated Terra Ponderosa or Witherite – from Anglesark A".

The letter "A" indicates that it is was given to Rashleigh by Stanesby Alchorne (1727–1800), an English botanist (Sara Chambers, *personal communication*, 2016). It is not known for certain when Alchorne provided Rashleigh with the specimen, but RIC archive document No. RASH/1/26 notes that Philip Rashleigh sent 24 "minerals for Mr. Alchorn" in February 1792. Perhaps this was part of an exchange. The date corresponds with the use of "Witherite", which was proposed in Hoffmann (1789), and is before 1800, the year in which Alchorne died. Unfortunately, the specimen cannot be traced in the collections at Royal Cornwall Museum[17].

Rashleigh published two pioneering works on British mineralogy, *Specimens of British Minerals Selected from the Cabinet of Philip Rashleigh*, in 1797 and 1802. Neither feature barium carbonate. Perhaps the specimens were not considered aesthetic enough to warrant illustration.

The Anglo-Irish physician and mineralogist William Babington (1757–1833) assembled a substantial mineral collection based largely on specimens purchased from the Earl of Bute (1713–1792). He used the collection as a basis for two publications (Babington, 1795; 1799). The second work, *A New System of Mineralogy in the Form of a Catalogue*, was dedicated to Sir John St Aubyn, Bart (1758–1839) who had recently purchased the collection from Babington for the sum of £3,000 (Wilson, 1994: p. 70). It provides a valuable account of the witherite specimens that were available in the late eighteenth century.

Babington (1799: pp. 31–32) described four specimens of "Carbonate of Baryt", one with well formed

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[17] Prior to being purchased by the Royal Cornwall Museum Philip Rashleigh's collection was inherited by his nephew William Rashleigh (1777–1855) who, at some point, provided an apparently random selection of minerals to his son Jonathan Rashleigh (1820–1905). It is possible that the two witherite specimens were amongst those that went to Jonathan Rashleigh, which were eventually tracked down and purchased by Arthur Russell in 1923 (Russell, 1952).

crystals and three massive. Three of the specimens are attributed to "Anglesark near Chorley, Lancashire", the fourth is not provenanced.

The crystallised form (variety I) is described as:

> "I. b 1. In hexhedral prismatic crystals, of a dull white colour, terminated by hexahedral pyramids; lining a cavity in a compact mass of the same interspersed with yellow pyrites.
> Anglesark near Chorley, Lancashire".

The massive material (variety II) was either fibrous or compact. Two of the specimens had a fibrous texture:

> "II. a 1. Of a fibrous texture, semitransparent, and of a water colour, the fibres running nearly parallel, and having one side covered by a cellular ochry incrustation.
> Same place".

> "III, a 2. The same, composed of fibres diverging from different centres and without incrustation.
> Same place".

The compact specimen is described as:

> "IV. c 1. Of a compact texture, with white opake sulphate of baryt, and yellow sulphuret of iron".

At about the same time, St Aubyn purchased the collection of Richard Greene (1716–1793) of Lichfield for £100 (Wilson, 1994: p. 81). He continued to add to his collection which was housed at Lime Grove in Putney as, although his family's history was deeply rooted in the West Country, he found his Cornish estates at Clowance and St Michael's Mount rather uninspiring (Shepherd, 2009). At the time it was common for the gentry to house their collections in London as it was easier show them off. St Aubyn employed the French mineralogist and exile from the Revolution, Jacques-Louis Count de Bournon (1751–1825) to order and arrange his minerals, but the project was not finished before St Aubyn relocated the collection to his country estate at Crowan in Cornwall (Currey, 1975) between 1806 and 1807 (Shepherd, 2009: pp. 51–52). By that time much of the collection had been catalogued. Transcriptions of de Bournon's descriptions of St Aubyn's witherite specimens were available online on the Plymouth City Museum and Art Gallery website until 2020[18].

Prior to his death, St Aubyn reorganised his collections and sold off part of his estate. He employed the mineral dealer Isiah Deck to organise the dispersal of his mineral collection (Wilson, 1994). Deck wrote (as noted by Wilson, 1994) in a copy of Babington's 1799 catalogue of the Butean Collection:

> "In 1834 I had the [job of making an] arrangement of Sir John's whole collection, of which I formed two complete small collections; one for Lady St. Aubyn and another for Mrs. Parnell, his daughter. A very beautiful and extensive collection I formed for the museum at Devonport, and the duplicates were brought to the hammer, most of which I purchased".

Thus, the bulk of the collection passed to the Civil and Military Library at Devonport [one of St Aubyn's many estates was Stoke Damerel]. In 1924, the Devonport collections were transferred to Plymouth City Museum. According to Currey (1975: p. 133) a collection of duplicate specimens was donated to the museum at Saffron Walden near which St Aubyn resided for many years [at Shortgrove Hall]. However, as Deck lived in Cambridge, just 18 miles from Saffron Walden, those specimens are more probably the ones that he acquired at auction.

Three of de Bournon's (1815) witherite entries are transcribed, all of which are listed as from "Anglesark". One of the entries refers to the "preceding No. 5" implying that at least six specimens were present. In total there are seven specimens of witherite linked to St Aubyn documented in the The Box Plymouth Collection, but the original de Bournon labels affixed to some of the specimens indicate that there may originally have been at least nine (Fig. 5). St Aubyn clearly acquired additional specimens after Babington produced his publication (Babington, 1799). One of the specimens is not provenanced, but the remainder are from Anglezarke.

The Box Plymouth specimen number PLYMG 1924.1.943x (Figs 5 and 6) is not dissimilar in appearance to those preserved in Matthew Boulton's collection. It is probably specimen number "II. a 1" in Babington (1799). It was described by de Bournon (translated from French) as a:

> "Very beautiful piece of aerated heavy spar, greyish white and with a very beautiful semi-transparency, analogous to that of chalcedony. Its texture is striated, like that of the preceding pieces, but the striae are much finer, closer together and almost parallel. On one of the two extremities, perpendicular in the direction of the striae, they are very visibly detached from each other, so that they can be very easily seen and even counted. The other extremity is covered by a thin layer, made up of the combination of an immensity of small irregular layers of sulphuric heavy spar, coloured an ochreous brown yellow and separated from the aerated heavy spar by a small vein of dull white sulphuric heavy spar. ... from Anglesark".

Specimen number PLYMG 1924.1.941x which has the old label "B 5A" attached has some of the largest witherite crystals (up to approximately 8 mm in length) known from Anglezarke (Fig. 7). It was described by de Bournon (translated from French) as:

> "Piece of aerated heavy spar, in a cavity of which are large crystals belonging to the variety described

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[18] The webpage link http://plymhearts.org/wp-content/uploads/2016/03/St-Aubyn-mineral-catalogues.pdf was broken when the museum rebranded as The Box Plymouth but will hopefully be reinstated at some time in the future.

Figure 5. Witherite from Anglezarke, 75 mm across, in the St Aubyn Collection. The distinctively patterned handwritten label (inset left) is by Count de Bournon who curated the collection while it was in London. The code 'B 9' indicates that it was the ninth specimen in the grouping 'B', probably referring to 'Barium'. The other handwritten label (inset right) indicates that this was the first example of the seventh species in the fourth order and is believed to relate to a classification system which was in use when the specimen first entered the Devonport Collection. It seems likely that the fourth order was barium minerals and the seventh species was witherite. Specimen PLYMG 1924.1.943x from the collection of The Box Plymouth. Roy Starkey photograph reproduced with permission from The Box Plymouth.

> in the preceding No.5. They are semi-transparent and of a slightly greyish white. The same piece has another cavity in which the crystals have long prisms and without any replacement plane for their summit. ... the same [i.e. "from Anglesark"]".

Specimen number PLYMG 1924.1.939x which is number "B 2" was described by de Bournon (translated from French) as:

Figure 6. The reverse side of the specimen shown in Figure 5. Note the fibrous texture and ochreous crust on the right-hand side. The catalogue number 682 refers to an old institutional system. Roy Starkey photograph reproduced with permission from The Box Plymouth.

> "Quite a sizeable piece of aerated heavy spar, showing a large cavity, adorned with very beautiful, large crystals of the same substance, displaying the two pyramids of the dodecahedron separated by a long intermediary prism, which produces a regular long hexahedron prism terminated by two hexahedron pyramids with triangular isosceles planes, analogous to a similar variety in rock crystal, but differing from it in the measurement of the angles of the pyramids. The faces of the pyramid make a solid angle of 146º 15' with those of the prism. As with the rock crystal also, the sides of the prism are very often striated along their width. This comes from the direction of the superimposing layers being absolutely the same. Sometimes, too, again similarly to rock crystal, the prism becomes imperceptibly thinner as it approaches the pyramids and in that case it is strongly striated. Some of these crystals are dull white, others greyish white and with a very weak semi-transparency. The aerated heavy spar

Figure 7. Witherite from Anglezarke, 72 mm in length, with an early St Aubyn Collection number 'B 5/A', handwritten by Count de Bournon who curated the collection while it was in London. Specimen PLYMG 1924.1.941x from the collection of The Box Plymouth. Roy Starkey photograph reproduced with permission from The Box Plymouth.

> which contains these crystals is partly dull white and opaque and partly greyish white with a semi-transparency. It is penetrated, here and there, by some specks of pyrites; its exterior surface is coloured a yellowish brown by an iron-rich ochre which stains it. This piece is one of the most beautiful that I have seen of this substance. ...
> from Anglesark".

There are several further St Aubyn collection specimens, for which de Bournon catalogue entries have not been traced. Specimen No. PLYMG 1924.1.938x (Fig. 8) is a solid mass of white sparry witherite with a small crystal lined cavity. The edge of the specimen has a vein of brown sphalerite. It is recorded in the early museum catalogues as from Anglezarke. Specimen No. PLYMG 1924.1.942x (Fig. 9) displays a typical crystal lined cavity within massive white witherite containing patches of minor brown sphalerite. The reverse of the specimen (Fig. 10) reveals a transition to cream-coloured fibrous witherite with an etched matt texture and partial ochreous overgrowth. It is also from Anglezarke. Specimen No. PLYMG 1924.1.944x is a thin specimen of crystallised witherite displaying a mottled rusty surface coating and is also from Anglezarke.

Figure 8. Witherite with sphalerite from Anglezarke, 62 mm across, in the St Aubyn Collection. A small cavity contains pyramidal crystals. The handwritten label is believed to relate to a classification system that was in use when the specimen first entered the Devonport Collection (as noted in the caption for Fig. 5). Specimen PLYMG 1924.1.938x from the collection of The Box Plymouth. Roy Starkey photograph reproduced with permission from The Box Plymouth.

Figure 9. Massive laminar witherite from Anglezarke, 76 mm across, in the St Aubyn Collection. The central cavity contains small elongated pseudohexagonal pyramidal crystals. The handwritten label is believed to relate to a classification system that was in use when the specimen first entered the Devonport Collection (as noted in the caption for Fig. 5). Specimen PLYMG 1924.1.942x from the collection of The Box Plymouth. Roy Starkey photograph reproduced with permission from The Box Plymouth.

The collection of Sir Abraham Hume (1749–1838), another important mineral collector from this period, is preserved at the Sedgwick Museum of Earth Sciences at the University of Cambridge. It too was catalogued by Count de Bournon in at least six beautifully presented volumes (de Bournon, 1813–1814). The catalogues, which are written in French, remain with the collection (Sedgwick Museum of Earth Sciences, University of Cambridge, Reference DDF Boxes 801–802). They provide an insight into the mineralogical material that was available before 1814. Hume continued to expand

Figure 10. Massive witherite from Anglezarke, 76 mm across, in the St Aubyn Collection. The reverse side of the specimen illustrated as Figure 9, showing conspicuous ochreous staining. Specimen PLYMG 1924.1.942x from the collection of The Box Plymouth. Roy Starkey photograph reproduced with permission from The Box Plymouth.

his collection after that date, but the additional specimens are catalogued in a different hand and can be distinguished.

The volume of Hume’s catalogue entitled:

> ‘‘BARYTE. STRONTHIAN. QUARTZ. CALCÉDOINE. AGATE. SARDOINE. JASPE. CORNALINES. CHRYSOPRASE. BOIS AGATISÉ. PECHSTEIN. OPALE. FELDSPATH. ANDALOUSITE”,

includes descriptions of thirteen specimens of “Baryte Carbonatée” [witherite] (pp. 216–219). The first nine are written neatly in de Bournon’s handwriting. The last four post-1814 additions are also recorded in French, but the handwriting is scruffier and the final two specimens are recorded in the margin at the bottom of the page.

The post-1814 handwriting is that of John Henry Heuland (1778–1856), the foremost British mineral dealer of the early nineteenth century (Russell, 1950; Cooper, 2001). Specimen numbers 11 and 12 are specifically recorded as from ‘‘M^{r} Heuland’s own Collection”. As de Bournon had a great dislike of Heuland (Cooper, 2001: p. 17) he would have been incensed to see his immaculate catalogue defaced in this way.

Of the nine specimens documented by de Bournon, five are from Anglezarke ‘‘d’Anglesark” in Lancashire, two are from Alston Moor ‘‘d’alton more, en Northumberland”, one is from Derbyshire and one is unprovenanced. The additional specimens added by Heuland include one from ‘‘Lancashire”, one from ‘‘Yorkshire” and two that are not provenanced.

The catalogue pages provide considerable descriptive detail, which is particularly useful in assessing whether specimens have been mixed up. This is particularly important as some specimens can no longer be traced and those that remain do not always match their descriptions. Perhaps the best example is specimen No. 10 for which Heuland’s catalogue entry can be translated:

> “Beautiful piece of barium carbonate [witherite] in long hexagonal prisms terminated by a triangular top covered by a white limestone, with crystals modified [altered] to the heavy spar [baryte]”.

Two specimens accompany the label with Hume specimen No. 10 (University of Cambridge Department of Mineralogy and Petrology No. 1653 but with no Sedgwick Museum of Earth Sciences number assigned), but neither matches the catalogue entry. One is a small (30 × 30 mm) tabular baryte crystal with no identification number and the other a small prismatic calcite crystal. The whereabouts of the original specimen is unknown.

The Hume Collection specimens from Anglezarke and Alston Moor are of particular interest to this discussion. Of the five specimens from Anglezarke, only two can be identified. The first of these, Hume Collection No. 2, is a small mass of witherite with squat euhedral pyramidal crystals and a prominent matt white overgrowth of baryte (Fig. 11). De Bournon’s description of this specimen can be translated as:

> “No. 2
> Group of barium carbonate crystals with its pyramids separated by a short intermediate prism crystals are embedded by a very thin layer, and a dull white, of barium sulphate without gangue From Lancashire - to anglesark”.

The second Anglezarke specimen, Hume Collection No. 5, consists of an aggregate of large fudge coloured prismatic crystals with a chalky white surface coating probably of baryte (Fig. 12). This specimen bears a strong resemblance to more modern specimens from Cox’s Vein at Nentsberry Haggs Mine. The relatively modern typed No. 5 label affixed to it rather than Hume’s original handwritten number label suggests that the original specimen was misplaced, and a similar number attached to a more recent specimen. De Bournon’s original description can be translated:

> “No. 5
> Aggregation of barium carbonate belonging to the 2nd amendment without gangue - from anglesark”. [The second amendment is a] “replacement of the solid angle from the top by a plane perpendicular to the axis”.

The specimen does not correspond with this description and the sheer size of the crystals relative to all other specimens in contemporary collections casts further

Figure 11. Tabular witherite crystals, with a white surface coating of baryte, from Anglezarke. The specimen is 60 mm across and retains an original Hume Collection No. 2 affixed by Count de Bournon. Specimen CAMSM 13513 in the Sedgwick Museum of Earth Sciences. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

Figure 12. Witherite with a coating of chalky baryte, 50 mm across, with data that indicates it is from Anglezarke, but which may have been mixed up and has certainly been re-labelled with a later 'Count de Bournon' No. 5. Specimen with an old institutional No. 1648 in the Sedgwick Museum of Earth Sciences. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

doubt on its authenticity. De Bournon would most certainly have mentioned this but does not. Other Hume specimens are missing from the Sedgwick Museum suggesting that the collection has suffered periods of curatorial neglect in the last 200 years.

Both of the specimens from Alston Moor remain in the collection. The first, Hume Collection No. 4, is small with distinct pyramidal crystals with a thin surface coating of baryte (Fig. 13). De Bournon's description can be translated as:

> "No. 4
> Group of barium carbonate crystals belonging to the variety of the previous piece, and the crystals are coated with an encrustation of dull white barium sulphate this piece has the same substance as gangue is from Alton more, in Northumberland".
> "2nd modification; replacement of the solid angle from the top by a plane perpendicular to the axis".

The second specimen from Alston Moor, Hume Collection No. 6, is much larger and is in places a distinctive cream colour (Fig. 14). The witherite is compact but made up of elongated prismatic crystals. De Bournon's description can be translated as:

> "No. 6
> A piece of massive barium carbonate containing a large number of crystals of this substance, among which several show the following modification [the description continues for several pages describing the crystal forms in great detail]. A piece shows some traces of brown zinc sulphide - from alton more".

Figure 13. Witherite as pyramidal crystals with a thin surface coating of baryte from Alston Moor. The specimen retains an original Hume Collection No. 4 affixed by Count de Bournon. Specimen with an old institutional No. 1647 in the Sedgwick Museum of Earth Sciences. The field of view 40 mm across. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

Of the other witherite specimens in Hume's collection only one is described as fibrous: "No. 7 Baryte Carbonatee en masse fibreuse – D'Anglesark". Although it is no longer identifiable the fact that only one of the five specimens recorded by de Bournon from Anglezarke is described as a fibrous mass indicates that the majority of specimens were better crystallised than Boulton's, although the crystals are generally quite small.

Figure 14. Witherite from Alston Moor, 90 mm across, with minor surface alteration to baryte at the top right. The specimen retains an original Hume Collection No. 6 affixed by Count de Bournon. Specimen CAMSM 13514 in the Sedgwick Museum of Earth Sciences. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

Figure 15. Massive witherite from Lancashire, 90 mm from top to bottom. Specimen No. 12 in the Hume Collection, with an earlier Heuland Collection No. 6439. Specimen CAMSM 13142 in the Sedgwick Museum of Earth Sciences. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

Finally, Hume Collection No. 12 is also of interest (Fig. 15). It was from "Mr Heuland's own collection" and is listed as very rare ("très rare") and from "Lancashire". Heuland's original collection label is still affixed to this specimen therefore we can be confident of its heritage. It is consistent with other samples from Anglezarke and the remark "très rare" provides an indication that such specimens were becoming more difficult to obtain in the early nineteenth century.

During his time in London, Count de Bournon also curated the collection of the Rt Hon. Charles Francis Greville (1749–1809) at Paddington Green. De Bournon assisted Greville from 1794 to 1806 but left suddenly when Greville tired of him of breaking his specimens and keeping the best pieces (Cooper, 2001: p. 17). De Bournon does not appear to have produced a detailed catalogue of Greville's specimens. He did, however, ensure that they were all carefully labelled. Greville died intestate and it was necessary to liquidate his estate for division among his heirs (Wilson, 1994). William Babington, William Wollaston, Charles Hatchett and four others appraised Greville's mineral collection on behalf of the British Museum. They concluded that it was:

> "equal in most, and in many parts superior, to any similar collection which any of us have had the opportunity of viewing in this or other countries".

Their valuation for the entire collection (roughly 14,800 specimens) was £13,727 which was paid by Parliament (Wilson, 1994: p. 78). De Bournon stated that the collection was "far superior" to the existing museum holdings (Wilson, 1994). Greville's collection is now preserved at the NHM, London, but no catalogue is known to have survived.

Fortunately, de Bournon documented Greville's witherite specimens as an "observation" (following his description of specimen No. B2) in St Aubyn's catalogue which is preserved at The Box Plymouth. It almost certainly pre-dates 1806 when the two parted ways.

> "Observation: I have seen in M.Gréville's cabinet a piece of aerated heavy spar in which the two pyramids of the dodecahedron are separated by just a very short intermediary prism. The same cabinet also contains other varieties which are very rare and which, for that reason, I am going to describe:
>
> 1. Three varieties without intermediary prism, with a short prism and a long prism in which the solid angle of the summit is replaced by another small, very obtuse, hexagonal pyramid, of which the planes face those of the first pyramid and make with them a solid angle, which seemed to me to be 140º. The solid angle of the summit of this small pyramid, taken on the centre of two of its opposing faces is, therefore, 147º-30'.
>
> 2. The same three preceding varieties, in which the planes of the upper small pyramid become rounded so as to give the crystal the appearance as if the first pyramid had its summit replaced by a single plane.
>
> 3. The variety with elongated prism, in which the planes of the upper pyramid come down lower and are rounded, in such a way that the crystal has the appearance of a hexahedron prism of which the terminal faces would be rounded and of which the edges which join these faces to those of the prism would each be replaced by a plane making a solid angle of 146º-15' with the faces of the prism".

Unfortunately, no locality details are provided, but de Bournon's "observation" followed on from one of St Aubyn's Anglezarke specimens. Oddly, de Bournon's descriptions do not match Sage's (1788) account of a specimen provided to him by Greville which was reputedly from Alston Moor. Sadly, no witherite specimens can now be identified in Greville's collection at the NHM.

In 1805, the Derbyshire-based mineral dealer White Watson (1760–1835) organised a large auction of mineral specimens in Bakewell. His auction catalogue (Watson, 1805) featured 1,339 individual specimens in 30 lots. Fifteen specimens containing "*Carbonate of Baryte*" (numbered individually as: 524; 525; 526; 528; 529; 530; 531; 532; 535; 535; 537; 537 a; 537 b; 555; 970) are listed, predominantly within lots described as "A SYSTEMATIC COLLECTION".

Of these specimens, eight are described as from "Lancashire", four from "Yorkshire", one specifically as from “Anglezark” and two with no details. There are no specimens from Alston Moor.

Watson was employed by Lady Georgiana Cavendish, Duchess of Devonshire (1757–1806) to organise her extensive mineral collection at Chiswick, London and at Chatsworth House, Derbyshire. In 1804, he produced “Catalog C”, “Catalogue of a Systematic Collection of British Fossils” based on specimens at Chatsworth (Cooper, 2005: p. 261). Cooper reported that Catalog C described several specimens of witherite from Anglezarke in Lancashire, but that the only witherite specimens so far identified in her collection were from Arkengarthdale in Yorkshire.

Joseph Dawson (1740–1813) a wealthy ironmaster who lived at Bradford in Yorkshire amassed an extensive collection of mineral specimens including a considerable number from northern England (Pacey, 2003). Dawson’s manuscript catalogue, mostly completed in 1810 with additions until he died in 1813, is preserved at Cliffe Castle, Keighley and provides a wealth of important data. It documents an impressive 17 specimens of carbonate of barytes: eleven from Arkengarthdale; three from Anglezarke; two from Derbyshire; and one from Germany (Dawson, 1810–1813: p. 178). One further specimen is recorded in his cabinet collection as from Arkengarthdale. Dawson’s collection included specimens from Alston Moor and the absence of any witherite from this area is noteworthy. Dawson’s three witherite specimens from Anglezarke are described as “Grey & Lamellar”, “Grey & Radiated” and “Grey & Compact”, all descriptions typical of the material studied by Withering.

At around the same time, Lady Henrietta Antonia Clive, Countess of Powis (1758–1830) was assembling a systematic collection of minerals. Lady Clive’s manuscript collection catalogues (Vol. 1, *Catalogue of Earthy Minerals*; Vol. 2, *Catalogue of Metallic Minerals*), dated 1817, are preserved at Amgueddfa Cymru. There are two entries under “Witherite” in the *Catalogue of Earthy Minerals* both of which (numbers 155 and 155_1) are listed as from “Anglesea”. Although neither specimen can be traced the catalogue entries are useful because they suggest once again that specimens from Anglezarke [“Anglesea” is clearly a typographic error] were far more common than those from Alston Moor prior to 1817.

Lady Anna Grosvenor’s, née Wilbraham (c.1791–c.1860s) collection, also at Amgueddfa Cymru, follows suit. A single, nondescript, 45 × 40 × 30 mm specimen of massive, pale cream coloured witherite with a matt crust on the upper surface is preserved with two old handwritten labels [possibly there were originally two separate specimens] both stating “Anglesark”.

Mary Morland Buckland (1797–1857), wife of Revd William Buckland, also assembled a fine mineral collection. It was presented to the Oxford University Museum of Natural History (OUMNH) in 1996/7 and contains a single specimen of witherite. The specimen (OUMNH No. 29403) has two typed labels (“Witherite” and “568”) and is recorded on the museum label as from “Anglezarke, Chorley, Lancashire, England”. It is a 90 × 70 mm fragment of massive translucent witherite.

Sir Arthur Russell had a knack for rediscovering historic mineral collections, which he often subsequently acquired (Starkey, 2022). His collection at the NHM, London includes a sizable mass of compact fibrous witherite (Fig. 16) from the collection of George Croker Fox (1784–1850). Fox’s original handwritten label documents the specimen as “Witherite (Carbonate of Barytes) Anglezark, Lancashire”. A similar but smaller specimen (BM.1964,R6720) is accompanied by an unidentified handwritten label which records “Aerated Barytes or Witherite from Anglesark, Lancashire”. Russell’s collection has no late eighteenth to early nineteenth century witherite from Alston Moor, his remarkable specimens from that area were mostly collected in the early twentieth century.

Charles Hampden Turner (1773–1856), a businessman from Surrey, purchased Jacob Forster’s (1739–1806) private collection from Forster’s nephew, John Henry Heuland, in 1820. Heuland had modified the collection somewhat and commissioned Armand Lévy to catalogue it in 1827 but progress was slow and eventually Heuland lost patience. The catalogue was completed by E. Brookes and published as Levy (1837). Volume 1 includes descriptions of eight specimens of witherite (pp. 186–188). Astonishingly, six are listed as from Alston Moor, one from Snailbak [Snailbeach], Shropshire and one from Steinbauer Mine, Neuberg, Haute-Styrie. This contrasts with every other contemporary collection, where it was rare to find even one Alston Moor witherite.

Figure 16. Compact fibrous witherite from “Anglezark, Lancashire”, 80 × 40 × 20 mm, with a George Croker Fox label. Specimen BM.1964,R6723 in the Russell Collection at the Natural History Museum, London. Tom Cotterell photograph reproduced courtesy of the NHM, London.

Witherite specimens from Arkengarthdale in Yorkshire and Dufton in Westmorland were available from the early decades of the nineteenth century and from the 1820s world class crystals of witherite were being extracted from Fallowfield Mine. It is possible that the witherite part of the collection was kept as Forster had assembled it, and therefore that it pre-dates 1806, and that Forster was unaware that the early claims of specimens from Alston Moor were false.

Turner’s collection was acquired by Henry Ludlam (1822−1880) who later bequeathed it to the Museum of Practical Geology, Jermyn Street, London. It was subsequently transferred to the NHM. Seventeen witherite specimens are recorded in the Ludlam Collection on the NHM online data portal (Scott and Smith, 2021). Seven are from Alston Moor, two of which are specifically listed as Blea Gill and Balgill [i.e. Blagill, the type locality for barytocalcite]. The Ludlam Collection does not include any witherite specimens from Anglezarke.

Strangely, however, Heuland was able to provide witherite specimens from Anglezarke to a contemporary collector: the London-based Isaac Walker (1794−1853). Walker had a specimen recorded as:

> “324____H____1842
> Acicular Carbo=
> =nate of Barytes
> Anglesark
> | Lancashire”.

That specimen now forms part of the Russell Collection (BM.1964,R6722) at the NHM. It is a fist-sized mass of compact divergent masses of fibrous witherite partly coated in white baryte (Fig. 17). It is atypical of Anglezarke and draws Heuland’s provenance into question.

Further evidence that Heuland occasionally mislabelled specimens is provided by another specimen in Russell’s collection, accession number BM.1964,R6798, which was also part of Walker’s collection. It was originally labelled as:

> “H____973____1839
> Dodecahedral Carbo=
> =nate of Barytes
> [P]ost Lady Aylesford
> [Col]l
> Cumberland”.

Russell’s personal label notes:

> “Witherite crystals on crystals of calcite (the specimen seems to have been slightly treated with acid) Danby Level, Whaw, Arkengarth Dale, Yorkshire. No 2086 Louisa Countess of Aylesford Collection. Lady Aylesford paid £12 for this specimen at a Henry Heuland sale in 18[left blank]. On the disposal of her collection by Heuland [in] 1839 the specimen was bought by Isaac Walker from the sale of who’s collection by S. Henson in 1911 I obtained it for 30/-. The locality is wrongly given as Cumberland on the Walker label”.

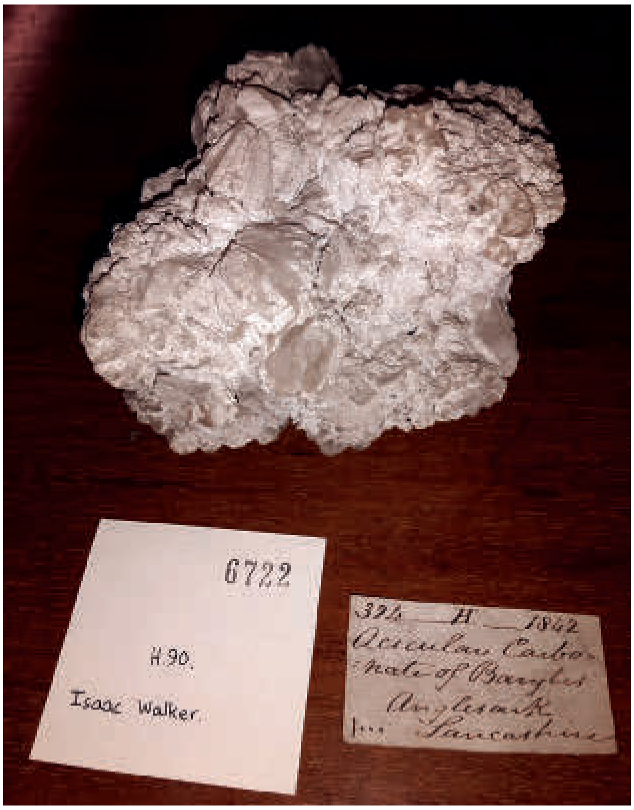

Figure 17. Witherite with a white baryte frosting accompanied by a label stating “Anglesark, Lancashire” from the collection of Isaac Walker. Walker’s label records that the specimen was purchased from Heuland (H) in 1842. The symbol “|” in the bottom left-hand hand corner indicates that it cost 8/- [the symbols |=5/- and ... =3/-] (see Starkey, 2022: p. 127). Tom Cotterell photograph reproduced courtesy of the NHM, London.

The amount Lady Aylesford paid is equivalent to over £1,000 today. The amount that Russell paid is equivalent to just £100, a rare example of deflation in the price of minerals.

The Allan-Greg Collection at the NHM is an amalgamation of the collections of Thomas Allan (1777−1833) of Lanfine, Edinburgh and Robert Hyde Greg (1795−1875) of Manchester. It is a useful barometer of British localities in the first half of the nineteenth century. Robert Hyde Greg purchased the Allan Collection in 1835. Greg’s son, Robert Philips Greg (1826−1906), continued to add to his father’s collection which was used as the basis for the *Manual of the Mineralogy of Great Britain and Ireland* (Greg and Lettsom, 1858). It was purchased by the British Museum (Natural History) in 1860. The beautifully presented manuscript catalogue preserved with the collection documents the specimens in order of acquisition. A total of 34 witherite specimens are listed.

The first (earliest) specimen in the Allan-Greg Collection catalogue (registered as BM 89680) is unusual, but unfortunately it has no provenance. It is a small (25 × 25 × 10 mm) aggregate of slightly friable white radiating prismatic crystals with some of the pyramidal terminations coated with chalky white baryte. A note in the catalogue records that it was “given me by D^{r}. Henry”. Dr Henry could be Dr William Henry

(1774–1836), the Manchester based chemist, whose son, William Charles Henry, married Thomas Allan's daughter Margaret (Farrar and Farrar, 1968), or, his father, the surgeon and apothecary Thomas Henry (1734–1816), who was President of the Manchester Literary and Philosophical Society. The latter probably acquired the material as Bucholz (1792) records that Thomas Henry the younger investigated witherite, but perhaps it was his son who gave the specimen to Allan. The association with Manchester suggests Anglezarke as the most likely source. It has similarities with one of the forms of Anglezarke witherite described by Watt (1790a: p. 607):

> "a number of small Crystals radiated in the form of a star from a centre; these Crystals were about half and inch in length, very thin, and appeared to be hexagonal columns rounded to a point".

Specimen two in the Allan-Greg Collection is from Arkengarthdale and has typical bipyramidal crystals. Specimen three is the only example from Alston Moor and the accompanying crystal illustration shows a distinctive barrel-shaped pseudohexagonal prism. This habit is a good match to that illustrated by Sowerby (1817: Plate 453) (Fig. 18). It is described in the catalogue as "very indistinctly pronounced, but the form which is also one of composition, may be traced, in white translucent crystalline concretions, Alstone". Unfortunately, the specimen itself can no longer be traced.

Figure 18. Plate 453, the only illustration of witherite from Alston Moor in James Sowerby's *British Mineralogy*. The accompanying text (Sowerby, 1817: p. 93) records: "The specimens are from Alstone moor, and are in groups more or less confused, and in a great variety of directions; they are commonly covered with very small rounded prisms of Sulphate of Barytes, apparently produced by their partial decomposition".

Specimens four to nine, twelve and thirteen are from Dufton in Cumberland. Specimen ten (BM 89685), a "compact fibrous variety, translucent, and of a greyish white colour", is recorded in Thomas Allan's handwriting as "the variety called Witherite, after D^{r} Withering who first analysed it, from Anglezarke in Lancashire". The actual specimen is a massive, fudge-coloured, fibrous aggregate (approximately 80 × 50 × 40 mm) with an opaque white and orange-brown surface weathering crust (baryte with ochre), all features which are typical of Withering's original description. Specimen eleven (BM 89686) is also from Anglezarke and is massive and fibrous but a less usual yellow-orange colour. A note in the margin of the catalogue indicates that it was acquired in 1824. This provides a useful chronological marker as it shows that specimens one to ten were acquired before 1824. It is approximately 80 × 70 × 50 mm.

A further twenty specimens are from Fallowfield Mine, six of these were "presented by Mr. Charlton in 1833". The remainder were obtained by Robert Hyde Greg in, or after, 1852.

The limited number of specimens from Anglezarke, Alston Moor and Arkengarthdale compared with significant numbers from Dufton and Fallowfield Mine provides a useful indication of the availability of witherite until the acquisition of the collection by the British Museum (Natural History) in 1860. The acquisitions between 1824 and 1852 are almost all from Dufton and Fallowfield Mine, with one presumably recycled specimen from Anglezarke.

William Burrows (b. *ca* 1791, *fl.* 1828–1877), an Alston-based mineral dealer who supplied many mineral specimens to the British Museum (Cooper, 2006: p. 80), would have had access to new discoveries in Alston Moor. It is surprising, therefore, that he sold just one specimen of witherite to the museum in 1866. Labelled simply as "Alston Moor, Cumberland" it is a massive to slightly fibrous white to very pale cream witherite cementing fragments of brown limestone (Fig. 19). That the British Museum purchased such a poor specimen is an indication of the rarity of witherite from Alston Moor in the first half of the nineteenth century. It is also noteworthy that the locality information is vague.

Bristol Museum & Art Gallery whose collections date to the foundation of the Bristol Institute during the 1820s, have very few specimens from either Anglezarke or Alston Moor. The collections were damaged by bombing during the Second World War, but the early collection catalogues remain intact. One early collection purchased by the Bristol Institute in 1832 belonged to Johann S. Miller (ca 1779–1830). His neatly presented

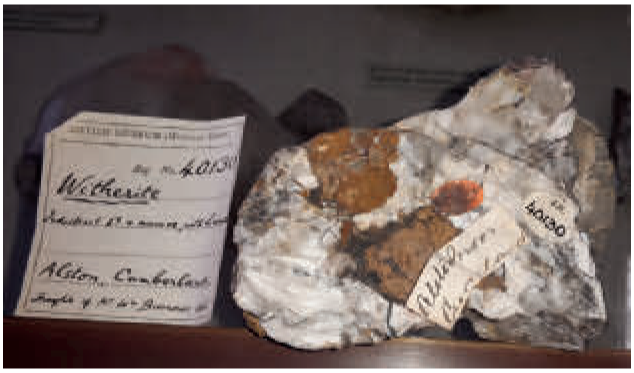

Figure 19. Witherite on brown limestone, 90 mm across, from Alston Moor. Sold by William Burrows of Alston to the British Museum (Natural History) in 1866. Specimen BM 40130 in the collection of the Natural History Museum, London. Tom Cotterell photograph reproduced courtesy of the NHM, London.

handwritten catalogue contains a blank page entitled "Witherite" indicating that he failed to acquire any examples of the mineral. The only specimen of witherite from "Anglesark Mine" in the Bristol Museum & Art Gallery Collection is from the B. V. Cooper Collection, which was acquired in 1982. Cooper's small handwritten specimen label documents that it was "kindly presented by Eric Richardson 1966". It is likely to be a twentieth-century specimen.

In Edinburgh, the early collections of National Museums Scotland (formerly the Industrial Museum of Scotland and later the Royal Scottish Museum) were catalogued in 1854. No specimens from either Anglezarke, or Alston Moor are documented (Peter Davidson, *personal communication*, 2018). However, two specimens of witherite from Anglezarke recorded as "Old Museum Specimen found unregistered" were accessioned in 1984 and 2013 (G.1984.41.118 and G.2013.18.21). Both specimens are accompanied by old handwritten labels. The appearance of both specimens, in particular G.2013.18.21, as compact masses of pale cream coloured fibrous witherite with a partial ochreous crust is consistent with material in Matthew Boulton's collection. There is a strong possibility that these specimens are pre-1854 and they probably date from the late eighteenth century.

The oldest specimen of witherite from Alston Moor in the collections at National Museums Scotland is from the Dudgeon Collection obtained in 1890 (Peter Davidson, *personal communication*, 2018). Patrick Dudgeon (1817–1895) probably acquired it in the middle of the nineteenth century.

In Ireland, Stokes (1807, p. 76) described a specimen (No. 650) in the collection at Trinity College, Dublin which might be one of the earliest known examples from Alston Moor. The description recalls the illustration by James Sowerby (Plate 453 in Sowerby, 1817) which is reproduced as Figure 18:

> "Witherite crystallized in low six-sided prisms, a great number of which are confusedly group together; from Alston-more, in Cumberland".

The Trinity College Collection was re-catalogued and amended by Apjohn (1850). Specimen No. 650 appears to have been renumbered as 1150, which is described as "A globular mass consisting in great part of numerous six-sided prisms, rough on the surface, and confusedly grouped. Alston Moor, Cumberland". It can no longer be traced in the modern collection (Patrick Wyse Jackson, *personal communication*, 2018), however, specimen No. 652, which was renumbered as 1148, is described as:

> "Massive, with something of a radiated structure, translucent, and of a yellowish tinge of colour. Anglesark, Lancashire".

Additional specimens recorded by Apjohn (1850) include three from "Arkindale, Yorkshire" and one reputed to be from Derbyshire (Patrick Wyse Jackson *personal communication*, 2017).

Henry James Brooke (1771–1857), the crystallographer, who worked with John George Children on the description of barytocalcite (Brooke and Children, 1824) does not appear to have had any specimens of witherite from Alston Moor. Brooke's collection is preserved at the Sedgwick Museum, Cambridge. Likewise, the Oxford University Museum of Natural History (OUMNH) does not have any specimens from Alston Moor which pre-date the late nineteenth century.

ANGLEZARKE OR ALSTON MOOR?

Despite contemporary evidence that the first specimens of witherite were not from Alston Moor (Watt, 1790a; Köhler, 1790; Bucholz, 1792), Withering's original claim that it was the type locality is entrenched in the scientific literature and has proved exceedingly difficult to dislodge. In such a situation it is crucial that all of the evidence for and against the claimed first occurrence is assessed carefully. The next section of this article reassesses written accounts of the early history of witherite in relation to the two possible sources.

Witherite from Alston Moor

As witherite is now known to be abundant on Alston Moor (see, for example, the list of localities provided by Young, 1985), it is natural to ask where was it first identified? Witherite was characterised as a new species in the 1780s and Matthew Boulton was shipping boxes of it to Germany in 1790. If it was from Alston Moor, the source would have been difficult to conceal.

In this context it is interesting to note that the claim that Alston Moor was the original source had disappeared from key mineralogical references by the first decade of the nineteenth century. All references to Alston Moor were removed from the second and third editions of *Elements of Mineralogy* (Kirwan, 1794: p. 134; 1810: p. 122) which simply states "this substance, as found at Anglesark in Lancashire, is described by Mr. Watt, Jun". Haüy (1801: p. 312) reports:

> "The carbonate of barytes was discovered by Dr. Withering, and has been given the name of witherit by the famous Werner. It is found in England, not in Alston-Moore, as we had thought, but Anglesarck, in the county of Lancashire, in a lead mine".

Werner's *Handbuch der Mineralogie*, compiled by Ludwig (1803: p. 168), describes "witherit" from Anglezarke near Chorley in Lancashire with no mention of Alston Moor. Jameson (1804) likewise states:

> "it [witherite] is found at Anglesark in Lancashire; other localities have been mentioned, but they are doubtful".

Kidd (1809, p. 86) describes "carbonate of baryt" (or witherite) as "being met with in a lead mine at Anglesark in Lancashire", and being employed for the purposes of destroying rats in Cumberland, but does not specifically mention Alston Moor.

James Sowerby, the doyen of early nineteenth century mineralogy in Britain (Henderson, 2015), states in volume I of *British Mineralogy* (Sowerby, 1804: pp. 157–158) that, "Carbonate of Barium" was first found at "Anglesark in Lancashire only, but has since been observed at several other places". These 'other' places, which supplied the first well crystallised British specimens, included Arkengarthdale in Yorkshire (figured by Sowerby, 1804: Plate 76; Sowerby, 1806: Plate 127), and Dufton in Westmoreland[19] (Sowerby, 1809: Plate 239).

The significance of Sowerby's mineralogical work lies in the fact that his *British Mineralogy* publications spanned 13 years. We therefore know that when he figured a fine, crystallised, specimen of witherite from "*Alstone moor*" (Sowerby, 1817: TAB CCCCLIII; see Fig. 18) that he regarded this as a significant new discovery [his figure was engraved on April 1, 1812]. Indeed, he states (p. 93) "it remains that the present rare and unexpected variety should be shown".

The earliest independent and reliable account of witherite from Alston Moor appears in Westgarth Forster's *A Treatise on a Section of the Strata, Commencing near Newcastle Upon Tyne, and Concluding on the West Side of the Mountain of Cross-Fell. With Remarks on Mineral Veins in General* (Forster, 1809: footnote to p. 85):

> "There is a vein in Welhope, in the county of Northumberland, belonging to Colonel Beaumont, containing the common cauk spar, or barytes, in the upper beds, which changed its matrix in the great limestone, and contained the aerated or carbonated barytes. It lies mostly in the cavities or shakes of the vein, in round balls; and, when broke, it is striated, as diverging from the centre".

Although heralded as a pioneer of English geology because of his detailed descriptions of the strata of northern England, much of Westgarth Forster's work was copied from earlier volumes, particularly Williams' *The Natural History of the Mineral Kingdom*, which was published in 1789 (Forbes, 2015). The modern fixation with originality was less embedded in the scientific conventions of the period but the fact that the information appears as a footnote suggests that it was a recent observation made by Forster himself. No earlier claim of witherite from Wellhope has been found.

Forster would certainly have had first-hand knowledge of the local mines. He lived in the village of Garrigill, on the edge of Alston Moor, and was mining agent for the Coalcleugh area (of the Beaumont Estate) between 1797 and 1808 (Fairbairn, 1993: p. 24). He included much more detailed lists of the mines in the second edition of his *Treatise* (Forster, 1821). There are two 'witherite' localities. Mine No. 7 (p. 217) under the heading "List of Lead Mines, in the two Allendales, In the Manor of Hexham, and County of Northumberland, Belonging to Colonel and Mrs. Beaumont" is:

> "Welhope Head, one mile and a half N.W. of Coalcleugh; Lead, with Sulphate and Witherite or Carbonate of Barytes, in Strata, from the High Slate Sill to the bottom of the Great Lime-stone".

Mine No. 64 (p. 300) under the heading "A list of Lead Mines, Which are, or have been, worked in the Manor of Alston, in the County of Cumberland" is:

> "Slote, alias Bunker's Hill, one mile and quarter E. of Alston: some Lead, with Witherite or Carbonate of Barytes, and Calc Sinter, in the Coal Sills".

The so called 'witherite' at this second locality is likely to be barytocalcite, which was not recognised as a new species for another three years. The occurrence at Wellhope Head, however, is undoubtedly genuine.

Why then, after Forster (1809; 1821) described the occurrence at 'Welhope', did specimens not begin to appear in contemporary collections? No authentic specimens from the early nineteenth century have been located by the author. The only possibility is specimen No. 650 in the collection at Trinity College, Dublin (Stokes, 1807: p. 76), which is no longer traceable (Patrick Wyse Jackson, *personal communication*, 2018).

Alston Moor was a busy place in the eighteenth and nineteenth centuries, with mines in nearly every valley. The specimens that made their way out from the area were often poorly located. They are commonly labelled "Cumberland" or "Northumberland". It might be that restrictions placed on miners to prevent them from being 'distracted' from their work limited production or that dealers falsified locality information to protect their sources. Nonetheless, the miners commonly claimed they had a customary right to collect and sell spar and

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[19] Old spellings of the former county commonly include a second e; this was subsequently dropped.

there was a thriving trade in mineral specimens, with several shops in Alston. It seems most probable that the rare and comparatively drab witherite was overshadowed by the abundance of colourful and beautifully crystallised fluorite as Sopwith (1833: p. 110) records:

> "only a very small proportion of them [i.e. mineral specimens] are the product of veins in this manor, by far the most beautiful and abundant of these specimens being found in the mines of Weardale and Allendale".

Whatever the reason, many discoveries (other than new and exciting colours of fluorite) took an inordinately long time to reach the cabinets of collectors and the scientific community.

An interesting example is provided by barytocalcite, which was described as a new species by Brooke and Children (1824) without locality details. Shortly afterwards, Brewster (1824) claimed that "The only habitat of this mineral is Alston Moor, in Cumberland", but thirty-four years passed before the precise locality was revealed! In their *Manual of the Mineralogy of Great Britain and Ireland*, Greg and Lettsom (1858: p. 50) record barytocalcite:

> "At Bleagill, Alston Moor, Cumberland, in attached crystals and massive, in veins in mountain limestone. It is a plentiful mineral there. The crystals are usually greyish-white, and semi-transparent. From half an inch to an inch in length generally speaking, but crystals 2 inches long are sometimes met with. These large crystals are coated over with a deposit of barytes".

The deposit had been worked long before barytocalcite was identified as a distinct species. Dunham (1948: p. 147) notes that the name Blagill was probably derived from "Bleigill", suggesting a German connection, perhaps in relation to Wallace's (1890: p. 109) statement that the Alston Moor mines were held under lease in 1359 to one Tilman of Cologne. Blagill was certainly leased by the London Lead Company at the end of the seventeenth century and was in production from at least 1700 (Fairbairn, 1993).

It is surprising, therefore, that Forster (1821) makes no mention of barium mineralisation in his description of Blagill. However, he records (p. 289) 'witherite' in the Coal Sills at "Mine No. 64", Slote, also known as Bunker's Hill, which Dunham (1948: p. 146) included as part of the Blagill sett. As noted in the foregoing text, Forster's 'witherite[20]' is probably barytocalcite. Indeed, Dunham (1948: p. 147) noted that on the basis of price realised per ton the 'witherite' produced at Blagill during the late nineteenth century was mostly barytocalcite.

Returning to the occurrence of witherite on Alston Moor, it is worth noting that Forster's (1809) publication was, at first, overlooked by the scientific community. Bakewell (1815) records:

> "if the present paper have no other merit than that of making Mr. Forster's section more generally known, it will render an acceptable service to English geologists, and do some justice to a person whose labours have not been sufficiently appretiated [*sic*]".

Robert Bakewell visited Northumberland and Durham in the summer of 1813 and added to some of Forster's observations. He appears to have seen specimens of witherite and includes details of their dimensions (Bakewell, 1815: p. 92):

> "The carbonate of barytes is principally found in large detached balls, which have a radiated diverging structure. I have seen some of them not less than ten inches in diameter. ... Mr. Forster relates a striking change in the barytic spar as it passes through different strata at Welhope in Northumberland. The vein in the sandstone strata contains sulphate of barytes (caulk) ; but when it enters the great limestone, the carbonate of barytes becomes the matrix".

It is, once again, surprising that no examples of these considerable (10 inches = 25.4 cm) spherical aggregates of witherite are known to have survived[21].

On 18 March 1814, Nathaniel Winch read *Observations on the Geology of Northumberland and Durham* to the Geological Society. This provides additional details of the occurrence of witherite, which Winch (1817: p. 87) describes as:

> "Forming crystallized balls of a dirty white colour, and striated fracture, radiating from a center", and as "irregular 6-sided prisms without pyramids, and perfectly transparent, occurring occasionally in the center of the balls above mentioned ; from the Welhope mines in the great limestone, where the veins in the upper sills bear heavy spar".

The paper goes on to note that witherite was found as "irregular stalactitical minute crystals, opake and white ; from Aldstone mines" and "Incrusting fragments of galena, blende and limestone ; white and opake ; from Aldstone moor". Winch (1817) also reports witherite from Arkengarthdale and Dufton but does not mention Anglezarke, perhaps because Lancashire was beyond the geographical remit of his study.

With the exception of this cluster of papers, specific mention of witherite from Alston Moor is rare. Thomas Thomson, for example, made a personal tour of Alston Moor in the summer of 1813. He visited a number of the mines but does not record witherite (Thomson, 1814). He

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[20] Witherite does occur at Blagill, but it is much less common than barytocalcite.

[21] Despite his description of specimens from Alston Moor, it should be noted that Bakewell believed that witherite was first discovered at Anglezarke as he records: "The mine at Anglesark, in Lancashire, where it was first obtained, has ceased to be worked" (Bakewell, 1819: p. 459).

appears to have remained oblivious to its presence as the only locality listed in *A System of Chemistry* is at "Anglesark in Lancashire" from which Thomson and Cooper (1818: p. 307) record witherite crystals as:

> "very small and rare ... hence their primitive form has not been ascertained ... They are six-sided prisms, terminated by six-sided pyramids, or double six-sided pyramids".

Thus, despite the descriptions of witherite by Forster (1809; 1821), Bakewell (1815), Winch (1817) and Sowerby (1817) contemporary specimens from Alston Moor are exceptionally rare. A good indication is provided by the Allan-Greg Collection, purchased by the British Museum (Natural History) in 1860, which has just one Alston Moor witherite in a total of thirty-four specimens.

A review of the principal witherite localities on Alston Moor is useful in an analysis of the history of the mineral. 'Welhope' and 'Welhope Head' (Forster, 1809; 1821), refer to a complex of mines on Wellhope Moor. Witherite, barytocalcite or both are known from at least six localities in the Wellhope Burn catchment (Young, 1985), but Wellhope Mine itself is probably the only contemporary working with the stratigraphic range to support Forster's (1809) statement in relation to vertical zonation in barium mineralisation from the upper beds down to the Great Limestone.

Wellhopehead Vein was an important target for early miners. The name refers to the structure formed by the northward merging of the Brownley Hill and Brownley Hill North veins, which were worked at neighbouring Brownley Hill Mine. The vein extends northeast from the county boundary across Wellhope Moor and is known as Scraithole Vein where it crosses into West Allendale. Fairbairn (2000: p. 30) reports that "Wellhopehead Vein = Scraithole Vein" was worked from early times on the west side of Wellhope Burn. Production statistics from 1763 to 1815 indicate that it was a medium-sized operation (6,899 tons of lead ore) with later output (from 1808 to 1815) combined with Hearty Cleugh Mine.

Dunham (1967: p. 193) suggests that the earliest workings, a series of shafts sunk from surface, are probably ancient. Wellhopehead Shaft [NY 7844 4581] and Coke shafts [around NY 7874 4608], probably reached the Slate Sills and have coarse baryte on the dumps (Dunham, 1967: p. 193). This is consistent with Forster's (1809) description which notes that the upper beds contained "the common cauk spar, or sulphate of barytes". However, witherite is abundant around an open shaft 200 m southwest of Wellhopehead Shaft on the continuation of Wellhopehead Vein in Cumbria (Clarke, 2008). Thus, Wellhopehead cannot be discounted as an early source of witherite on purely topographic grounds.

A number of levels were driven from Wellhope Burn to test the vein in depth. Fairbairn (1993: p. 24) records Wellhope Head Mine was begun by Mr Joseph Dickinson around 1800. It is unclear whether significant workings existed at this horizon before Dickinson commenced his operations, but it seems possible that Dickinson's workings produced the witherite reported by Forster (1809).

Wellhope Top Level was driven beneath the Firestone Sill [from NY 784 466] directly towards Wellhopehead Vein but according to Dunham (1967: p. 193) no stopes are shown above this level on mine plans. The dumps contain baryte with witherite (showing partial alteration to baryte) and a little sphalerite. A drift known as the Middle Level has been driven in shale beneath the Pattinson Sill, but uncertainty surrounds when this development took place. Dunham (1967: p. 193) records that the reverse gradient in the Middle Level suggests that it was probably started from a rise from Wellhope Low Level and driven towards the southeast. It is also unclear if Wellhope Low Level [NY 7796 4793], which was begun in the early nineteenth century (Fairbairn, 2000), and encountered what we now know as First and Second Sun veins and Treloar Vein, continued all the way to Wellhopehead Vein.

In depth, the First and Second Sun veins and Treloar Vein contained considerable quantities of witherite and sphalerite. Dunham (1990: p. 155) records that the early workings on these veins had been abandoned before the beginning of the nineteenth century. He notes:

> "on the first there was a sump to the bottom of the Great Limestone and the vein had also been opened out in the Low Coal Sill. There was also a sump to the bottom of the Great Limestone on Treloar Vein".

These early workings were later incorporated into the substantial workings of Nentsberry Haggs Mine (also described as Haggs Mine or Nentsberry Mine) which were eventually accessible via Wellhope Shaft [NY 7787 4664], sunk in 1925, and via a crosscut from the Nent valley. Dunham (1990: p. 155) describes the vein-complex at Nentsberry Haggs Mine as a striking example of mineral zoning in a lateral sense. At the intersection of the ENE trending First and Second Sun, Treloar and High Raise veins with Sincay, Cox, Dupont and Liverick veins the lodestuff was galena-rich with subsidiary sphalerite and pyrite in a gangue dominated by ankerite and quartz with some barium minerals. In three directions (NE, SE and SW) away from the intersection the veins became progressively poorer in galena and dominated by barium minerals. Some vertical zonation in the barium mineralisation, with baryte at higher levels and witherite in the Great Limestone, similar to that recorded by Forster (1809) at Wellhope, is likely.

In the early nineteenth century, mining companies avoided the barium and zinc-bearing veins on Alston Moor in favour of those that were rich in lead. Development at Wellhope appears to have ceased when rich lead veins were discovered across the county boundary at Brownley Hill Mine. Mining only resumed in earnest at the end of the century when the value of zinc and barium minerals had risen sufficiently to make the deposits profitable. It is these later workings that produced the fine witherite specimens from Nentberry Haggs Mine.

Barium mineralisation in the Great Limestone at Brownley Hill Mine is restricted to a small area on High Cross Vein near Holmes' Rise which was opened up in the second quarter of the nineteenth century (Green *et al.*, 2000). This rules out any possibility that it is the type locality for witherite, despite claims to the contrary[22] (Mindat, 2022). At Brownley Hill Mine, witherite occurs as stacks of thin pseudohexagonal crystals, exceptionally to 30 mm, with multiple re-entrants, and less commonly as small pseudohexagonal pyramids. It is commonly associated with alstonite in a matrix which includes pink baryte and is entirely unlike any early nineteenth century witherite specimen. Access to the area must have been restricted by the late nineteenth century because, as noted in a letter to L. J. Spencer at the British Museum in 1909 by Mr Jacob Walton [grandson of the mine manager, also Jacob Walton, at the time of the original discovery], no specimens of alstonite had been found at the mine for over fifty years (Spencer, 1910). The rediscovery of the 'alstonite area' at Brownley Hill Mine by explorers in the late 1980s is described in Young *et al.* (1990).

Thomas Thomson gave the first account of witherite from Brownley Hill Mine in a paper which describes five new barium minerals, almost all of which have subsequently proved to be mixtures (Thomson, 1835). The third of these, "Sulphato-Carbonate of Barytes", is described as follows:

> "This mineral occurs in Brownley Hill Mine, in the County of Cumberland. I first saw it in a collection of minerals exposed for sale in Glasgow in November 1834, by Mr. Cowper, a mineral dealer from Alsten Muir. Colour, snow white. ... The specimen consists of cengeries of very large six-sided prisms, terminated by low six-sided pyramids".

Thomson's chemical analysis is consistent with witherite contaminated by baryte, an interpretation confirmed in a later study by James Johnston (1837: pp. 375−376) who analysed one of Thomson's specimens and found it to be "carbonate of baryta nearly pure".

The Warington W. Smyth Collection, which was acquired by Arthur Russell, included specimens of witherite from Tailor's Grove Mine, Alston Moor (BM.1964,R6593 and BM.1964,R6594). They display crystallised witherite with a surface coating of baryte which has been subsequently weathered, probably on a mine dump. On the label, Smyth noted that he bought the specimens at Alston in 1848.

The NHM purchased a specimen with stacked platy pseudohexagonal witherite crystals from the dealer Francis Henry Butler in 1890 (Fig. 20). Although the crystals have some similarities to well provenanced specimens from Holmes' Rise at Brownley Hill Mine, the matrix is not characteristic of that locality and there is no associated alstonite. There are similarities to the unlocated specimen illustrated by James Sowerby (see Fig. 18), and to platy witherite from Scraithole Mine, Carrshield, Northumberland.

The witherite deposits at Nentsberry Haggs Mine were worked between 1894 and 1916 when a total of 1,600 tonnes was produced (Collins, 1972: p. 28), but it was only when the Vieille Montagne Company commenced large-scale redevelopment at Nenthead in the 1920s that exceptional witherite specimens reached collections. Arthur Russell gained access to the mine in January 1931 and collected many fine specimens including a superb 100 × 88 mm specimen with crystals to 33 × 23 mm (BM.1964,R6641). Bancroft (1973) considered it to be the finest specimen of witherite ever collected. The habit, prismatic pseudohexagonal crystals with a slight surface coating of baryte, was unique to a large cavity on Liverick Vein, in the crosscut between Treloar and the High Raise veins. Similar specimens are represented in the Robert [Bob] J. King (1923−2013) Collection preserved at Amgueddfa Cymru, and are variously labelled as Treloar Vein, Nentsberry Mine (NMW 83.41G.M.5466); Carr's Vein, Haggs Mine

Figure 20. Platy hexagonal witherite crystals to 20 mm on sphalerite-galena matrix from "Alston, Cumberland". Sold by Francis Henry Butler to the British Museum (Natural History) in 1890. An old collection number "131" overlaps a price label for 10/-, which was roughly a day's wages for a skilled tradesperson at the time. Specimen BM 65726 in the collection of the Natural History Museum, London. Tom Cotterell photograph reproduced courtesy of the NHM, London.

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[22] Mindat (2022) cites Green *et al.* (2000) as the key reference to the mineralogy of Brownley Hill Mine: this article notes the occurrence of witherite at Holmes' Rise but makes no claim that it is the type locality.

(NMW 83.41G.M.5446); and simply Nentsberry Mine (Fig. 21).

Nentsberry Haggs Mine also produced a small number of pseudohexagonal pyramids similar to the classic crystals from Fallowfield Mine. These crystals, rarely associated with alstonite, were collected by Lancelot Liverick, in September 1931, from Cox's Vein and given to Arthur Russell. The finest example in Russell's collection displays an aggregate of large grey pyramidal crystals one of which is doubly terminated and 80 mm in length (Fig. 22). A similar, but slightly bruised, crystal aggregate was presented to OUMNH by J. M. Edmunds in 1932 (OUMNH No. 19164). Earlier, in 1930, Russell had collected fudge-coloured pseudohexagonal prisms to over 50 mm from Cox's Vein.

Similar fudge-coloured coarse hexagonal prismatic crystals in the King Collection at Amgueddfa Cymru are labelled as from Carr's Vein (Fig. 23). King acquired many of his Nentsberry Haggs specimens in 1947 as part of the Raymond Walsh Collection. Unbeknown to King,

Figure 21. An aggregate of snow-white hexagonal prismatic witherite crystals up to 30 mm in length, partially replaced by baryte, from Nentsberry Haggs Mine on the Cumbria-Northumberland border. Specimen NMW 83.41G.M.5469 in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K9008). Tom Cotterell photograph reproduced with permission from Amgueddfa Cymru.

Figure 22. Bipyramidal witherite crystals from Cox's Vein, Nentsberry Haggs Mine, Northumberland, the largest 80 mm across. Specimen No. BM.1964,R6626 in the Russell Collection at the Natural History Museum, London. Tom Cotterell photograph reproduced courtesy of the NHM, London.

Figure 23. An aggregate of fudge-coloured pseudohexagonal prismatic witherite crystals to 45 mm, erroneously labelled Carr's Vein [the specimen is almost certainly from Cox's Vein], Nentsberry Haggs Mine, on the Cumbria-Northumberland border. Specimen NMW 83.41G.M.5445 in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K459/1942), collected by Raymond Walsh in 1942. Tom Cotterell photograph reproduced with permission from Amgueddfa Cymru.

his friend and collecting partner Walsh had acted as a spy for Nazi Germany while visiting mines across Britain during the war years. Walsh fled Britain shortly after the war leaving his collection behind.

There is good reason to believe that the specimens from ‘Carr’s Vein’ collected by Walsh in 1942 are from another part of the mine. Carr’s Vein was one of the first to be encountered in the driving of the Nentsberry Haggs Level from the southwest and does not contain any significant barium mineralisation. The fudge-coloured coarse hexagonal prismatic witherite crystals in aggregates labelled as from Carr’s Vein are identical to some of Arthur Russell’s specimens from Cox’s Vein and the frosted snow-white hexagonal prismatic witherite crystals to specimens from the large cavity on Liverick Vein.

The King Collection also includes large corroded hexagonal prismatic witherite crystals altering to baryte from High Raise Vein (collected in 1947) and fudge coloured radiating witherite in broken nodules from Admiralty Flats (collected in 1941 and 1947) (Fig. 24). This habit is not dissimilar to the fibrous variety from Anglezarke although the Lancashire specimens tend to have an ochreous crust.

In the 1970s, collectors gained access to the Admiralty Flats in Nentsberry Haggs Mine and discovered large (10 cm or more) pitted pseudohexagonal partially corroded prismatic crystals with surface alteration to baryte (Fig. 25). These specimens, similar to those collected by Bob King in High Raise Vein, are unique to the locality.

Figure 24. Fudge-coloured witherite forming a 70 mm diameter spherical aggregate with a radiating internal structure on the broken surface from Admiralty Flats, Nentsberry Haggs Mine, on the Cumbria-Northumberland border. Specimen NMW 83.41G.M.5442 in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K454/279/1947), collected in 1947. Tom Cotterell photograph reproduced with permission from Amgueddfa Cymru.

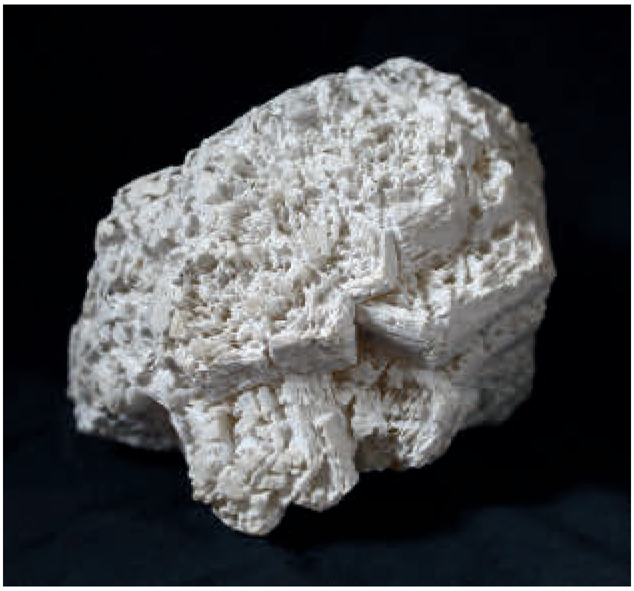

Figure 25. Pitted group of baryte-coated pseudohexagonal witherite crystals, 100 mm across, from Admiralty Flats, Nentsberry Haggs Mine, on the Cumbria-Northumberland border. Formerly in the David Hacker Collection. Photo Tom Cotterell.

Commercial extraction of ‘witherite’ took place at Blagill Mine from 1880 up to 1896. The product was low-grade indicating that it was largely barytocalcite. Production was only in relatively small quantities: the only year in which output exceeded 200 tons was 1887 when 812 tons were sold (Wilson *et al*., 1922: p. 40). Some witherite was also produced at Nentsberry Haggs Mine (called Nentsbury Mine in Wilson *et al*., 1922), but the intimate growth of baryte, witherite and sphalerite provided a poor product. As a consequence, it was never regarded as an important source of barium compounds (Wilson *et al*., 1922) and no detailed records of production have survived.

Elsewhere on Alston Moor, witherite has been found in small isolated deposits on Scaleburn Vein and Boundary Cross Vein at Rampgill Mine near Nenthead in Cumbria and at Scraithole Mine just over the county boundary in Northumberland. On Scaleburn Vein witherite occurs as coarsely crystalline white to pale cream-coloured masses and rare crude pseudohexagonal crystals up to 15 mm long, partly replaced by baryte (Bunting, 1994). On Boundary Cross Vein[23] lustrous pseudohexagonal pyramids up to 150 mm across and smaller crystals with curved faces and surface replacement by drusy baryte were found. The mineralisation was in a small area of infill and could not be traced *in situ* (Bridges and Green, 2006). At Scraithole Mine, witherite occurs large masses and thin pseudohexagonal crystals up to about 20 mm, occasionally overgrown by barytocalcite (Green and Briscoe, 2002).

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[23] Described by Bridges and Green (2006) as Bounder End Cross Vein.

Witherite from Anglezarke

Detailed historical accounts of the Anglezarke mines are provided by Williamson (1963) and Gill (1987). They produced lead in the late seventeenth century but were closed in 1694 following a dispute between Lady Margaret Standish, the widow of Sir Richard Standish, and a number of lesser gentry (Williamson, 1963: p. 133). Lead was mined between 1731 and 1732 and the Clitheroe Mining Company had some involvement between 1753 and 1766 (Kerr, 1875). The most active period was between 1781 and 1790 when Sir Frank Standish worked the mines (Williamson, 1963). This coincides with the identification of barium carbonate as a new species and an illicit trade in specimens. Gill (1987: p. 61) records that there was a final phase of mining in the 1820s when John Thompson, an iron merchant, from Wallgate, Wigan, took out a 21 years' lease. He surrendered the lease in November 1837 having invested heavily with no return.

Witherite was known from Anglezarke in the late seventeenth century. Its peculiar properties were reported by Charles Leigh a "Dr of Physick" at Oxford (Leigh, 1700). Leigh did not understand the chemistry of the 'spar', but his description is sufficiently detailed that there can be no doubt that he had investigated barium carbonate eighty-three years before Withering unravelled its chemistry. This is overlooked in most studies of the early history of witherite, but noted by James Watt Jnr (Watt, 1790a,b), Alexander Köhler (Köhler, 1790), Samuel Parkes (Parkes, 1815), Iain Williamson (Williamson, 1963) and Mike C. Gill (Gill, 1987).

James Watt Jnr's accounts (Watt, 1790a,b) provide the key evidence that witherite was originally from Anglezarke. He claimed that Withering had been "misinformed" in attributing the 'terra ponderosa aërata' to Alston Moor and also recorded that Withering had:

> "since informed me that he believes it [witherite] came from the same mine of Anglezark, which forms the subject of the present paper" (Watt, 1790a).

There is no evidence to suggest that Withering disputed Watt's claim and his son later recorded that his father was confused regarding the source of the material he described as "*Aerated* Terra Ponderosa", at first supposing that it came from Alston Moor in Cumberland, but that James Watt Jnr had proved that it was the produce of the mine of Anglezarke near Chorley (Withering, 1822: p. 61)

James Watt Jnr's (1790a) paper is a remarkable piece of work, not least because he was just twenty years of age when it was read before the Manchester Literary and Philosophical Society on 30 November 1789. It remains the most detailed account of the geology of the Anglezarke mines. Unfortunately, it has diverted the attention of mineralogical historians from Watt's second paper *On the Effects Produced by Different Combinations of the Terra Ponderosa given to Animals* (Watt, 1790b), which follows it in the same volume. This rather gruesome piece of research demonstrates how dramatically scientific study has changed since the late eighteenth century. It opens with the statement "At the Time of writing the foregoing Paper, I consulted Dr. Leigh's *Natural History of Lancashire, Cheshire, &c.*". As Leigh's publication is not mentioned in Watt's predominantly mineralogical first paper it has been overlooked by most historians of mineralogy.

Leigh's account reveals that a "Sparr" was known at Anglezarke in the late seventeenth century and used for "medicinal" purposes. The description of the mineral, its applications, and source leaves absolutely no doubt that it refers to witherite:

> "There are different Kinds of these Sparrs ; as to their internal Qualities, some if taken inwardly will Vomit, and Purge most violently, as that in the Lead Mines near Andlesack [Anglezarke] in Lancashire" (Leigh, 1700: p. 70).

Despite recommending the "Sparr" for its medicinal properties there was no understanding of the true reason that it induced vomiting. Leigh's (1700) statement:

> "and this no doubt consists in a great measure of Salt and Sulphur, which I will take to be the reason that it is Emetic. But the Nature of this Spar will be more fully made out from the subsequent Instances, and the first is by Calcination, in which you may easily discover that a Pound of this will yield a Dram of Arsenic at the least, lying betwixt the Lamellæ of the Spar. Whence therefore this comes to be of so Poisonous a Nature is plainly evident",

is a reflection of the parlous state of knowledge before the foundation of the modern science of chemistry. Chemical knowledge had improved by the late eighteenth century and Watt (1790b: p. 611) realised that the substance was aerated barytes (witherite) and that Leigh's explanation of its effects was incorrect. Watt (1790a: p. 607) also noted that an advertisement for the sale of muriated terra ponderosa mentioning that the aerated barytes, from which that salt was derived, frequently contains a quantity of arsenic was also mistaken. In the early eighteenth century the word 'arsenic' was used to describe a variety of poisonous mineral substances.

Watt (1790b: p. 611) recounted that the miners at Anglezarke had told him that they used aerated barytes to poison rats. He also noted that "Poisons, when properly administered, are generally esteemed the most efficacious remedies" (Watt, 1790b: p. 612), a maxim which had been established for millennia (it is occasionally correct). This goes some way to account for the early medical interest.

Watt (1790a: p. 605) noted that because witherite was found near to the surface and had little intrinsic value in the early years of mining, great quantities had been thrown onto the dumps or stacked underground. He described it as varying in colour from pale greyish white to milk white, occasionally with a slight yellowish tinge caused by the presence of iron. The most common form was as masses rounded on the outside, or globular, with a radial internal structure. He went on to record four 'crystal habits':

> "small Crystals radiated in the form of a star from the centre ; these Crystals were about half and inch in length, very thin, and appeared to be hexagonal columns rounded to a point. The other varieties were the six-sided column, pointed with a pyramid of the same number of faces ; also the double six-sided, and the double four-sided pyramid".

Watt's descriptions are a close match to early specimens of witherite (Figs 2–10) and to some of the recent material collected at Lead Mines Clough (Alderton *et al*., 2022), and the timing of his publication is closely coincident with the first description of the mineral.

The chemist Samuel Parkes, who subsequently described the Anglezarke mines (Parkes, 1807, 1815, 1823), was aware of Leigh's (1700) paper (Parkes, 1815: p. 200; pp. 219–220) but did not give it much credit. Parkes' contributions to the literature on the Anglezarke mines in the early nineteenth century, must be considered carefully and in full with respect to the early history of witherite.

In his initial publication, Parkes (1807: p. 97) noted that:

> "Carbonate of barytes was first discovered by Dr. Withering of Birmingham, in the lead mines of Alston Moor, Cumberland ; and for a long time afterwards it was found only there and at Anglezark, three miles to the east of Chorley, in Lancashire".

In a later and more detailed work, Parkes (1815: p. 200) made an attempt to decipher the early history of witherite, recording that in 1784:

> "Dr. Withering, a physician of Birmingham, announced that among the minerals in Mr. Bolton's [*sic*] cabinet he had discovered a specimen of native carbonate of barytes, which was found in a lead-mine on Alstone moor, in the county of Cumberland" (Parkes, 1815: pp. 198–199);

and that:

> "not long after this discovery of Dr. Withering's, it was found that a similar mineral existed in abundance in the lead-mines of Anglezark in Lancashire ; and while these mines were worked, the chemists of Europe might have been supplied with any quantity of this native carbonate" .

According to Parkes (1815), the only other known occurrences of carbonate of barytes were one district in Scotland [probably a reference to the Strontian lead mines (Parkes, 1823: pp. 327–328)], and Sweden. Interestingly, by the time the second edition of his later work was published, Parkes (1823: p. 324) had amended his position with regard to witherite:

> "at one time no carbonate of barytes was found any where in these kingdoms, except in the lead-mines of Anglezark in the hundred of Salford in the county of Lancaster";

noting that a similar mineral had subsequently been found in varying degrees of purity at:

> "Aldstone in Cumberland; at Dufton and other places in the county of Durham; at Merton Fell in Westmoreland; and at Snailback mine in Shropshire".

Parkes (1823: p. 324) went to great lengths to discover more about the occurrence at Anglezarke:

> "Conceiving that this mineral product might probably be usefully employed in some of our manufactures, if an abundant supply could be procured, I determined to go to the mines to make the necessary inquiries; which I did in the autumn of 1810".

On inquiring in Chorley he was surprised by the remoteness of the mines, finding that:

> "the mines are in so obscure a part of the country that it would be necessary for me to take a guide with me; and I was so happy as to meet with a gentleman of fortune in the town, who very kindly offered to accompany me and conduct me thither" (Parkes, 1815: p. 203).

Parkes (1815) records that he obtained detailed information about the history of the mines from Banister Derbyshire, a local man of nearly seventy years of age. Derbyshire said that the mines were in full production before 1710 but were closed and then reopened by Sir Thomas Standish the father of the current owner. The number of shafts suggested that a large quantity of lead ore had been raised. In about 1780 (1781 according to Watt, 1790a: p. 605) the mines were re-opened by direction of Sir Frank Standish who decided to drain the workings using levels driven from the foot of the hills. Unfortunately, his workforce conspired to defraud him and in about 1790, after spending thousands of pounds on the venture, he closed the mines. At the time of Parkes' visit they lay in ruins.

The story of lead mining was but part of the tale. According to Parkes' guide, the quantity of carbonate of barytes, known to the miners as 'spar', was immense, five to one compared with the lead ore, but it was left in the mine as it was thought to have no value. However, it did have a value and Parkes recounts that in about 1782 two Frenchmen arrived in Chorley. They were in the town some days without the nature of their business being suspected till it was discovered that they had been at the lead mines and filled two boxes with the spar which they secured with great care and sent off by carrier:

> "At this, Mr Tatham, the steward of Sir Frank Standish, immediately took an alarm; and having given strict orders that in future no one should be

> suffered to take away any of the spar, set himself to make every inquiry he could into its nature; to learn, if possible, to what uses these foreigners intended putting it; and whether some methods might not be discovered for consuming it in this country. In prosecuting these objects of inquiry, however, he never succeeded" (Parkes, 1823: p. 327).

Parkes (1823: pp. 327–328) goes on to report that:

> "following the papers on the carbonate of barytes published by Dr Withering and Mr Crawford in the Philosophical Transactions attention was drawn to the mine. All of the chemists of Europe wanted this newly discovered mineral so that its real nature and properties were every where soon understood. But during this investigation, in which every chemist who was fortunate enough to procure specimens was probably engaged nothing new occurred at the mine".

Unbeknown to Standish, a local man by the name James Smithels, who occupied a cottage and forty acres of his land, was illicitly selling carbonate of barytes. Smithels and his wife collected spar from the old spoil heaps on moonlit nights, packed it into boxes, and delivered them to a carrier in Chorley who took them to Liverpool. From there they were shipped to a middleman on the continent, though their final destination could not be traced (Parkes, 1823: p. 328).

A neighbouring farmer reported Smithels to Standish, but Standish was unable to establish how much witherite had been sold, the price paid, or where the mineral had been sent. Smithels passed this information to Alexander Gerrard, another local farmer, with the claim that he had sold a very large quantity of the spar for which he received five guineas per ton and that it had been shipped from Liverpool to Germany where it was used in porcelain manufacture (Parkes, 1823: p. 330).

The fact that Matthew Boulton had access to enough witherite to send "boxes of terra ponderosa aerata" to his son in Germany in 1790 (Birmingham Archive, MS 3782/12/57/42) suggests that he was involved in this illicit trade. Were this true, it would provide a very good reason for misdirecting the curious to Alston Moor.

The mines at Anglezarke closed in about 1790 and from then on it appears that access to specimens became restricted. Mawe (1802: p. 131) in his account of the mines north of Derbyshire described disused lead mines near Chorley as having produced witherite from workings sunk in grit or sandstone before they ceased operation about 15 years ago. Mawe also indicated that the old workings were filled in or flooded. Some material must have remained in circulation as White Watson auctioned numerous witherite specimens from "Lancashire" in pre-assembled 'systematic' mineral collections (Watson, 1805).

Citing Jameson (1804) in a paper read in December 1811, Arthur Aikin (1817: p. 438) noted that the only thoroughly ascertained locality for witherite was Anglezarke in the county of Lancashire, where it was first discovered by Mr James Watt. Jameson (1804) actually stated (pp. 573–576):

> "according to the observations of Mr. Watt, jun. a scholar of Werner it is found at Anglesark in Lancashire; other localities have been mentioned, but they are doubtful".

Aikin was either conservative in his judgement or poorly read as localities on Alston Moor, in Arkengarthdale and in Flintshire were known by 1811.

Phillips' (1816: p. 172) description of witherite is intriguing. It states that it was:

> "discovered by Dr. Withering, who first noticed it at Anglesark in Lancashire, in a vein, with sulphuret of lead, and some of the ores of zinc, traversing a stratified mountain, composed of beds of sandstone, slate, and coal ; the carbonate of Barytes is chiefly found in the lower part of the vein, the sulphate nearer the surface : the carbonate occurs in this vein in globular masses, having a radiated structure".

Zonation from baryte near the surface to witherite at depth is the opposite of the geological circumstances reported by Watt (1790a) and Brongniart (1807: p. 256) but echoes Forster's (1809) account of the occurrence at Wellhope on Alston Moor. Robert Allan's revision of Phillips (1837: p. 188) notes witherite was:

> "found by Dr Withering, at Anglesark in Lancashire, in a vein, with sulphuret of lead and some of the ores of zinc, in globular concretions having a radiated structure".

It is also recorded in veins in the north of England but without any specific mention of Alston Moor.

In 1839, Wallis published (pp. 13–14) *Dr. Taylor's Cheap and Efficacious Method of Destroying Rats* which noted that carbonated barytes "may be procured in large quantities at the lead mines belonging to Sir Frank Standish, Bart. at Anglezark, near Chorley, in Lancashire". It was also noted that "it may be purchased at a cheap rate, from the collectors of minerals". It is unclear who Dr Taylor was and there are clear errors in the volume as Sir Frank Standish had died in 1812 and no mining was going on at Anglezarke by 1839. Standish was succeeded by a distant relative, Frank Hall, who obtained the right to change his surname to Frank Hall Standish but was prevented from obtaining the baronetcy which was extinguished. This suggests that Dr Taylor's original observations date from the period before 1812.

The *Manual of the Mineralogy of Great Britain and Ireland*, the key nineteenth-century reference to British mineralogy, considers Anglezarke to be the type locality for witherite, noting that "Anglezarke near Chorley" was where "this species was first discovered" (Greg and Lettsom, 1858: pp. 47–48). Withering's original analysis is republished but listed from Anglezarke rather than Alston Moor as originally claimed.

De Rance (1873: p. 66) was quite specific as to where on Anglezarke Moor the "carbonate of baryta was first discovered by Dr. Withering", describing it at one of several shafts in the Kinderscout-grit at Stronstrey Bank. However, Williamson (1963: p. 136) notes that De Rance (1873) omitted to state the source of this data and no other reference has been found to corroborate it.

Arthur Russell and Max Hey collected witherite from Anglezarke in the early twentieth century. Hey presented three specimens of witherite from "Anglezarke lead mine" to the NHM in 1936 (BM.1936,1252, BM.1936,1253 and BM.1936,1254). All three specimens are weathered, one is split in two revealing small crystals in cavities in more massive white witherite with a dirty or orange-brown surface weathering; another is massive with aggregates of small crystals in cavities with spots of galena, the whole specimen coated with an orange weathering crust; the third specimen is fibrous and quite delicate (naturally etched). Hey's specimens are similar to material in the St Aubyn and Hume collections recorded as from Anglezarke. The presence of an ochreous crust on exposed surfaces is notable. A single specimen which Russell collected from the dumps (Fig. 26) is similar to the crystallised specimens in the St Aubyn Collection (Figs 7–9).

The King Collection at Amgueddfa Cymru includes one large specimen of witherite from "Anglezarke Moor mine" (Fig. 27). King's handwritten catalogue does not record how he acquired it, but the absence of a date suggests that he did not collect it himself.

In King's reserve collection, specimens RJK1206, RJK1207 and RJK1208 are large fragments broken from the registered specimen, showing the same massive compact cream to fudge-coloured fibrous structure and a smooth waterworn surface; they are labelled "Anglezarke". Specimen RJK3238 is a rounded weathered mass of compact fibrous cream-coloured witherite with a thin partial crust of white baryte and rusty ochre, labelled "Anglezarke Moor". It also appears to have been somewhat smoothed by water. The appearance of these samples suggests that they were collected in the twentieth century.

Figure 26. Witherite from mine dumps at Anglezarke, 45 mm across, collected by Arthur Russell in the first half of the twentieth century. Specimen BM.1964,R6721 in the Russell Collection at the Natural History Museum, London. Tom Cotterell photograph reproduced courtesy of the NHM, London.

Figure 27. Pale fudge-coloured compact fibrous witherite from "Anglezarke Moor mine", 120 × 80 × 50 mm, with a waterworn surface on the reverse. Specimen NMW 83.41G.M.5438 in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K1840). Tom Cotterell photograph reproduced with permission from Amgueddfa Cymru.

Williamson (1963) records witherite as "fairly common" on the dumps at Lead Mines Clough (Fig. 28), Stronsay [*sic*] Bank and White Coppice. The workings in Lead Mines Clough are the only ones where "any considerable amount of mining" was done (Price *et al.*, 1963: p. 97) and almost certainly correspond to the site described by Watt (1790a). They are likely, therefore, to be the type locality for witherite.

Witherite is relatively common on the dump from Old or Sun Vein [SD 6300 1638] in Lead Mines Clough. A detailed description of the mineralogy of the site is included in a complementary article in this journal (Alderton *et al.*, 2022). Witherite occurs as replacements of baryte, vein breccias and massive radiating vein fills (this last habit is the only one that is commonly represented in collections). Baryte is also common and oxidation in relatively acidic conditions has produced a variety of supergene minerals. Two recent witherite specimens (Figs 29 and 30) provide a useful comparison with the material described in this study and additional examples are illustrated in Alderton *et al.* (2022).

OTHER EARLY LOCALITIES

Witherite was reported from a number of British localities in the first half of the nineteenth century. A survey is useful as old-time specimens in many institutional collections have become mixed up over time. The variation in habit and association provide further support for the conclusion that Anglezarke is the type locality.

Figure 28. A vein section, 160 × 80 × 80 mm, collected during research carried out by Iain Williamson in the early 1960s at Lead Mines Clough, Anglezarke, Lancashire. The principal vein fill is massive witherite with a coarse radiating texture. There is a small mass of slightly altered compact laminar baryte which appears to represent one wall of the vein (top right) and a larger mass of baryte which has been almost completely replaced by witherite on the other wall (bottom left). Specimen No. 5500 in the Harry Critchley Collection. Photo David Green.

Figure 29. Witherite with a compact radiating structure and brown surface coating of fine-grained iron-stained baryte from Lead Mines Clough, Anglezarke, Lancashire. A grey area to the right of the number contains marcasite and a little pyrite. Specimen No. 5357, 50 mm from top to bottom, in the Harry Critchley Collection. Originally in the Mike Bayley Collection (No. 3352.5) with a catalogue entry which indicates it was collected at Lead Mines Clough (Neil Hubbard, *personal communication*, 2022). Photo David Green.

Figure 31. Pyramidal witherite crystals with a fine white baryte coating, 110 mm across, from Pennant Mine, St Asaph, Flintshire. Specimen NMW 83.41G.M.5437, in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K5829-1952). David Green photograph reproduced with permission from Amgueddfa Cymru.

One of the earliest records of witherite in the British Isles is from north Wales, but the precise locality is lost. In a biographical article, Withering's son (1822: p. 62) notes:

Figure 30. Massive radiating witherite, with minute chalcopyrite and marcasite inclusions and a patchy orange-brown ochreous surface coating, from Lead Mines Clough, Anglezarke, Lancashire. A small cavity contains millimetre-size pyramidal crystals. Specimen No. M2100, 40 × 50 mm, formerly in the Keith Snell Collection. Photo David Green.

> "in Wales it [witherite] is reported to have been found in a mine opened in 1786, on Cefn-meriadog Rocks, in the Parish of St. Asaph, preserving its radiated appearance".

This locality is about seven miles WSW of the better known occurrence at Pennant Mine. Witherite was described from the vicinity of St Asaph as early as 1790 (Köhler, 1790: p. 217: cited by Brochant, 1800–1802, pp. 613–617 as "Napione[24], *Berg. J.*, 1790, p. 217"). Dr Thomson, a Professor at Oxford, stated that Chevalier de Napion had found large quantities there. Indeed, the only British locality other than Anglezarke listed by Brongniart (1807: p. 256) is St Asaph in Flintshire.

The first specific reference to Pennant Mine is in Davies (1810), which records "barytes united with carbonic acid, the terra ponderosa aërata, at Pennant, between St Asaph and Holywell". Pennant Mine produced witherite between 1875 and 1891 and the extensive dumps and old underground workings were reworked in 1913 (Carruthers *et al.*, 1915: pp. 67–68). Despite an annual output of 200–300 tons during the first phase of operations very few specimens from the locality survive (Fig. 31).

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[24] Chevalier Napion is mentioned in a letter from John Hawkins to Philip Rashleigh dated 28 November 1792 as having found "Aerated Barites" in North Wales two years ago. No precise locality is given.

Mines in the Yorkshire Dales supplied some of the first well crystallised British witherite. The most detailed early account is provided by Sowerby (1804: pp. 157–158) on the basis of specimens provided in 1803 by the Revd J. Harriman and Mr W. Watson from lead mines in Arkengarthdale managed by Frederick Hall (Fig. 32). Sowerby described the crystals as the "largest I have seen, and ... very rare at present", a statement which adds to the evidence that they were small and uncommon at Anglezarke.

Frederick Hall subsequently provided Sowerby with specimens including a radiating spray of what is claimed to be "Carbonate of Barytes" figured as Plate 109[25] and an exceptional aggregate of hexagonal bipyramidal crystals figured as Plate 127 (Fig. 33). The latter specimen was subsequently acquired by Lady Elizabeth Anne Coxe Hippisley (1760–1843) and is preserved in the Russell Collection (BM.1964,R6797) at the NHM. Lady Elizabeth's label records "Carbonate of Barytes from Arkindale [*sic*] ... Sowerby Tab. CXXVII. Very Scarce".

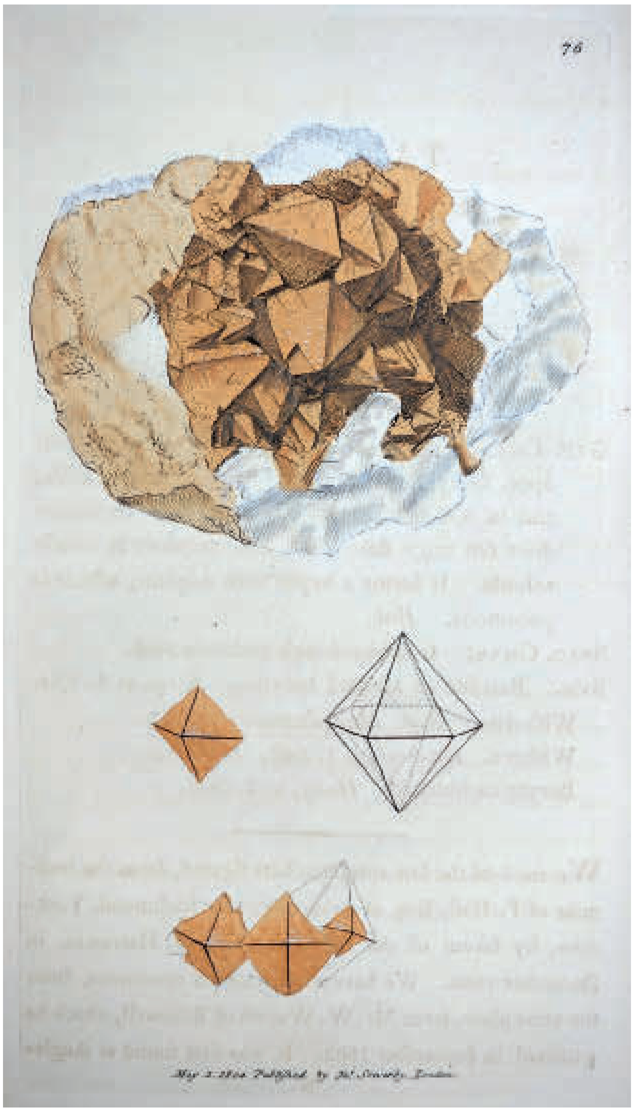

Figure 32. Plate 76, witherite from Arkengarthdale, from volume one of James Sowerby's *British Mineralogy*. The accompanying text (Sowerby, 1804: pp. 157–158) notes that: "We received the fine specimen here figured, from the lead-mine of F. Hall, Esq. at Arkendale, near Richmond, Yorkshire, by favour of our friend the Rev. J. Harriman, in December 1803. It was first found at Anglesark in Lancashire only but has since been observed at several other places". In a later description of another baryte specimen from Arkengarthdale, Sowerby (1809: p. 135) wrote that this was "the best specimen of crystallized Carbonate of Barytes, *tab. 76*" known. The lower sketches show how the crystals described by Watt (1790a) as 'four-sided pyramids' relate to the bipyramidal habit.

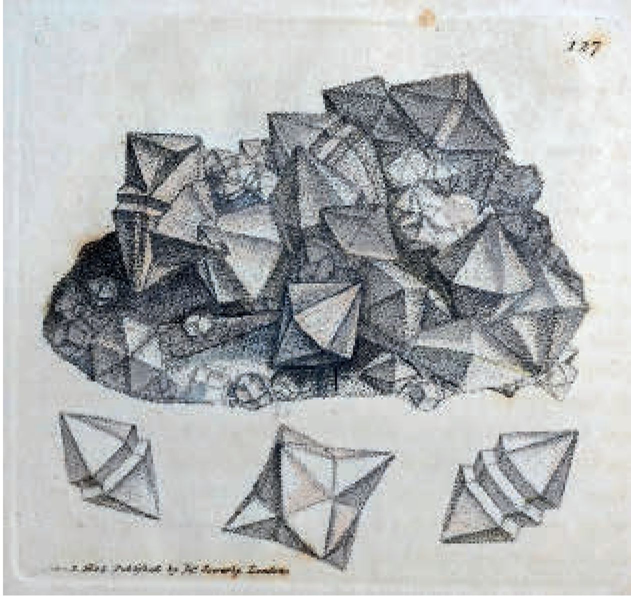

Figure 33. Plate 127, witherite from Arkengarthdale, from volume two of James Sowerby's *British Mineralogy*. The accompanying text (Sowerby, 1806: pp. 49–50) notes that: "We are obliged to F. Hall, Esq., of Arkendale, near Richmond, Yorkshire, for the superb specimen from part of which this figure was taken ... The Carbonate of Barytes has, in this specimen, a tendency to crystallise in groups, in a stellated manner: see *the middle figure*. The whole of the Carbonate of Barytes is chiefly formed on Carbonate of Lime, and is partly covered with Sulphate of Barytes in fine spiculæ ...".

Until the end of the eighteenth century the mines in Arkengarthdale were mostly worked from shafts. Horse levels were begun to drain the workings and improve productivity at the beginning of the nineteenth century (Tyson, 1986). Frederick Hall, of Easterby Hall and Company, the driving force behind many of these ventures, moved into Scar House between Langthwaite and Whaw when the leases for Arkengarthdale and nearby New Forest and Hope were signed in December 1801. His fortunes fluctuated: in 1811 only Frederick Hall and his brother Walter remained with the company, but by 1812 they had attracted new shareholders including Sir John Coxe Hippisley, Lady Elizabeth's husband.

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[25] This unusual specimen is unlike any other witherite subsequently found in Arkengarthdale, but has a strong similarity to radiating sprays of strontianite. Weathered but otherwise similar strontianite specimens could be seen *in situ* near the head of Turf Moor Hush a mile southwest of Frederick Hall's home at Scar House in the 1980s. Similar specimens are known from the Old Gang and Lownathwaite mines (Wood, 1993).

At some point Lady Elizabeth's specimen acquired a more specific provenance as Dunham and Wilson (1985: p. 93) record:

> "[a] beautiful example from Danby Level being preserved in the Lady Anne Cox Hippesley [*sic*] Collection (part of the Russell Collection)".

The basis for this claim is unclear: witherite is known from Danby[26] Level, but not usually associated with calcite and well crystallised specimens on calcite have been found at other nearby localities.

The W. Watson who provided James Sowerby with the specimens from Arkengarthdale is the well known Derbyshire-based mineral dealer White Watson (1760–1835). Watson must have had a significant number of specimens as he auctioned a lot of "Carbonate of Baryte" (Watson, 1805: p. 72) from "Yorkshire". They are described as "crystallized" (No. 535, 3rd lot), "crystallized in Octahedrons" (No. 537, 3rd lot), "crystallized in double hexagonal pyramids" (537 a, 26th lot) and "crystallized" (No. 537 b, 16th lot) a good fit with Sowerby's figures of specimens from Arkengarthdale.

A Yorkshire specimen is recorded as No. 651 by Stokes (1807: p. 76) in the collection at Trinity College, Dublin:

> "Witherite crystallized in six-sided pyramids confusedly grouped, on Calcareous Spar, with an argillaceous stone underneath; from Arkendale, in Yorkshire".

A manuscript catalogue compiled by the Bradford-based collector Joseph Dawson (1740–1813) details an impressive eleven specimens of "carbonate of baryte" from Arkengarthdale (Dawson 1810–1813). One further specimen is recorded in his cabinet collection from the same area (David Green, *personal communication*, 2017). The specimens are quite varied with catalogue descriptions including, "White & Yellow", "White & Translucent", "Grey & Striated", "Grey & Radiated", "White & Crystallized", "Beautifully Crystallized on Galena" and "Crystallized". Joseph Dawson knew Frederick Hall and it is likely that he provided the specimens. Unfortunately, less than half can now be identified and many of those that remain have become separated from their original labels.

Yorkshire witherite is briefly noted by Davy (1812: p. 192) "there is a mineral substance found in Cumberland, Yorkshire, and other parts of Britain, called Witherite, or carbonate of baryta". Nathaniel Winch (1817: p. 87) documented witherite from the "Arkendale mines", describing "dodecahedral crystals formed of two hexahedral pyramids of a pale wine-yellow colour", and "Massive [witherite], of a wine yellow colour". His descriptions are heavily reliant on Sowerby's *British Mineralogy*, and the caveat about the supposed occurrence of "elongated hexahedral pyramids or spiculæ of a chalky white colour" (Sowerby's Plate 109), which are probably strontianite, must be borne in mind. Witherite must have been abundant in some of the levels being worked at the time as Winch goes on to record "witherite is the common matrix to lead ore in Arkendale, it occurs only rarely further to the north". This comment reinforces its perceived rarity on Alston Moor in the early nineteenth century.

Yorkshire specimens were supplanted to such an extent by the spectacular examples from Fallowfield Mine in Northumberland that they are mentioned only briefly by Greg and Lettsom (1858: pp. 47–48). Witherite, nonetheless, is widespread in the county. In Swaledale, Bradley (1862: p. 11) describes "carbonate and sulphate of baryta" as one of the chief constituents of the gangue.

Barium carbonate was worked on a small scale, at Virgin Moss Mine in Wensleydale where eight tons were returned in 1887 (Carruthers *et al.*, 1915: p. 42). Small (1977: p. 179) notes that "twelve tons of witherite was mined from Lucky String on the Old Rake Vein System" in 1892. A small quantity may also have been produced at Lolly Mine in Nidderdale and Barras High Level in Swaledale.

Summarising the distribution in the mineral deposits of the Askrigg Block, Dunham and Wilson (1985: pp. 92–93) record:

> "It is almost certain that before oxidation damaged the deposits, there were major concentrations in the Old Rake, Friarfold and Surrender veins. Witherite was the principal gangue mineral in the deep workings of Sir Francis Level at the A.D. Mines and some was produced from Barras High Level nearby. At Virgin Moss Mine, flots carrying massive witherite were found ... Other localities include Whitaside, Victoria, Cobscar Rake and ... Lolly Mine (enclosing yellow fluorite crystals) and Providence Prosperous. The mineral is normally a distinct yellow colour on a fresh face, but also occurs white and massive. In cavities mamillary [*sic*] growths are found to be incipient pseudo-hexagonal crystals; fully developed crystals in this form are occasionally found".

Well crystallised witherite occurs at numerous localities in Swaledale. Radiating aggregates of columnar crystals up to 50 mm across have been found at Lanehead Mine at the western extremity of the North Swaledale Mineral Belt. To the east, small pseudohexagonal pyramids occur at Beldi Hill and Swinnergill and across a substantial vertical range at the Lownathwaite mines, where crystalline specimens are recorded from Priscilla Level by Wood (1993: p. 19). Witherite is

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[26] Possibly named for William Danby Jnr (1752–1833) a wealthy and eccentric landowner who lived at Swinton Park, Masham, Yorkshire and had a "richly furnished museum of minerals" (Wikipedia, 2021e). The Danby family had been involved in lead mining in the Yorkshire Dales and coal mining on Masham Moor (Tyson, 2007) for centuries. William was the last of the line.

common *in situ* in the sections of Old Rake Vein still accessible via Sir Francis Level (Wood, 1993) where thin tabular pseudohexagonal crystals up to about 15 mm have been found. It is abundant as compact massive radiating masses and pseudohexagonal pyramids up to about 20 mm at Bunton Hush and is locally present in some of the veins cut by Hard Level. Spoil heaps along Forefield Rake have occasionally produced unaltered pyramidal crystals with complex re-entrants up to 30 mm long, not unlike those from Fallowfield Mine.

Baryte coated witherite crystals on specimens to large hand size occur at Danby Level in Arkengarthdale. Witherite is widely distributed in the area and is common at the nearby Moulds levels. Isolated but damaged pseudohexagonal crystals up to 90 mm are known from Sleigill, a northern tributary of Arkle Beck (Fig. 34). Crusts of pyramidal crystals to about 20 mm, substantially replaced by baryte, are common at the nearby Fell End mines, particularly around Wellington Shaft.

Witherite is found further to the east at Feldom and Sorrowful Hill (Dunham and Wilson, 1985), but the most notable occurrence is at Forcett Quarry near East Layton where Young *et al*. (2012) record:

> "Witherite typically forms compact radiating crystalline masses of a white to pale cream colour ... These are typically up to around 15 cm across, though a few masses up to 0.5 m across have also been seen. Locally the witherite assumes a compact massive crystalline form, apparently devoid of the otherwise typical radiating structure. Much more rarely, cavities in such material are lined with euhedral witherite crystals up to about 10 mm across which comprise pseudohexagonal prisms with pyramidal terminations. Some specimens of witherite exhibit small irregular cavities up to 15 mm across suggestive of corrosion or dissolution. Many of the witherite masses are overgrown by coarse-grained crystalline baryte, which appears to have formed by alteration of the underlying witherite. In these instances the baryte typically occurs as spear shaped crystals in which (110) and (001) faces are prominent, a morphology considered by Dunham and Wilson (1985) to be characteristic of the mineral where formed secondarily from an original barium carbonate mineral".

Figure 34. Pyramidal witherite with pinkish calcite in the base and minor surface alteration to baryte, 90 mm across, from Washy Green Level, Sleigill, Arkengarthdale, North Yorkshire. David Green collection and photo.

Localities on the high ground between Swaledale and Wensleydale include Whitaside Mine, where masses of radiating witherite to 30 cm across and pseudohexagonal crystals to 20 mm occur. Similar masses occur at Virgin Moss Mine where "A flat containing pure witherite was ... cut" (Dunham and Wilson, 1985: p. 172). There does not appear to be any previous record of the isolated pseudohexagonal prisms with flat terminations from the adjoining workings of Brownfield Mine or of pseudohexagonal bipyramids, with fine surface alteration to baryte, from Wet Grooves Mine.

Dunham and Wilson (1985) record that witherite begins to die out further to the south in the Askrigg Block, where it becomes a "mineralogical curiosity". It occurs sparingly at Grassington Moor in Wharfedale (Fig. 35) and at the Prosperous-Providence mines near Greenhow.

Kendall and Wroot (1924: p. 856) record colourless globular stellate masses at Lolly Mine (Fig. 36) in Nidderdale, from where a small quantity of witherite is said to have been shipped to Germany (Raistrick, 1973; Dunham and Wilson, 1985). Arthur Russell collected two witherite specimens from Cononley Mine near

Figure 35. Pale brown witherite overgrown by a thick crust of drusy white baryte, 45 mm across, from Taylor's Shaft on Coalgrove Beck Vein, Grassington, North Yorkshire. Collected by Harry Edmond while exploring the Duke of Devonshire's mines with a view to reopening in the 1950s. David Green collection and photo.

Figure 36. Section of a compact spheroidal witherite mass, 100 × 70 mm, from Ramsgill [i.e. Lolly] Mine in Nidderdale, North Yorkshire. Collected by Harry Edmond in the 1950s. David Green collection and photo.

Skipton in surveys on behalf of the Ministry of Supply at the end of the First World War (Roy Starkey, *personal communication*, 2020). The crystals at this locality are pseudohexagonal tablets.

Large quantities of witherite were discovered at Dufton in Westmorland (modern-day Cumbria) immediately prior to 1 October 1807, when James Sowerby produced an illustration of a "wedge-shaped fragment" (Fig. 37). This was part of a larger spherical mass and in the accompanying text Sowerby (1809: p. 77) noted that he had seen "balls pretty perfect, from one to three or four inches in diameter". The Dufton witherite is typically darker in colour than specimens from elsewhere. The specimen figured by Sowerby is beige, and Winch (1817: p. 87) describes clove-brown witherite with a striated texture attached to galena. The source was probably Dufton Fell Mine which was worked by the London Lead Company in the early part of the nineteenth century (Dunham, 1990: p. 112).

There are other historic localities in the immediate area. Parkes (1823: p. 324) noted witherite "at Merton Fell in Westmoreland". This probably refers to Murton Mine in Scordale, where (jointly with nearby Hilton Mine) seventy tons of witherite was produced in 1896 (Dunham, 1990: p. 115). In the early twentieth century, some effort was expended in attempts to reach the Carbonate Shake at Murton Mine where reserves of witherite remain in place, but the ground was too dangerous and the company gave up (Tyler, 2013). Witherite specimens from Hilton and Murton are surprisingly rare in collections. Spheroidal masses up to about 70 mm across are known from surface exposures, and iron-stained pseudohexagonal pyramids up to about 25 mm were found in the levels below the Whin Sill at Hilton Mine when access was available in the early 1980s (Peter Briscoe, *personal communication*, 2021).

The King Collection at Amgueddfa Cymru includes a fudge-coloured banded nodular mass, 35 mm in thickness, from Silverband Mine on Great Dun Fell (NMW 83.41G.M.5478). Witherite also occurs at the remote workings of Stakebeck Mine (Young, 1985) and at Loppysike Vein on Great Dun Fell (Dunham, 1985). It is present across a wide area of the escarpment north of Dufton and small quantities were mined at Flushiemere and Lunehead mines a little to the east (Young, 1985).

Figure 37. Plate 239, witherite from Dufton (rear specimen), from volume three of James Sowerby's *British Mineralogy*. The accompanying text (Sowerby, 1809: pp. 77–78) notes that: "SULPHATE OF BARYTES has been represented in *tab*. 96 of a globular form, and I believe it was thought almost a distinguishing character of the substance. Since Carbonate of Barytes has occurred in globular forms also it becomes necessary to show the distinction, as we do not know that it has been before observed by any author. According to a specimen I have received from Dufton in Westmorland, which is a rather wedge-shaped fragment-see *the back figure*-they may be tolerably large, as this fragment, which seems to have been part of a ball, being near six inches long ... The fractured parts have something of a columnar radiation; but very indistinctly and massively incorporated and the fracture is otherwise small or largish, irregularly splintery, without any sign of internal crystallisation fracture".

Witherite was reported in the lower part of "Snailbach" [i.e. Snailbeach] Mine in Shropshire as irregular white to slightly yellowish masses up to several hundredweights in a thick baryte vein (Aikin, 1817). It seems to have been known for some years before Aikin's account as a letter from John Hawkins to Philip Rashleigh, dated 28 November 1792, records:

> "I cannot precisely tell you where Raspe[27] found the Aerated Barites. Chevalier Napion found it two years ago in North Wales. Raspe's spot is not far from Minsterly in Shropshire." (County Records Office, Truro, Rashleigh Papers: DDR 5757/1/74).

Witherite was found at Snailbeach until the early twentieth century, but crystals are rare. Starkey (2018: p. 271 and 274) figured several specimens and noted that some have distinctive inclusions of hydrocarbons, although these are not present in every specimen from the locality. Elsewhere in the South Shropshire Orefield witherite occurs with baryte, calcite and barytocalcite at Rorrington Mine, near Chirbury (Starkey *et al.*, 1994) and Tankerville Mine, Shelve (Neil Hubbard, *personal communication*, 2022).

Fallowfield Mine north of Hexham in Northumberland is widely regarded as the source of the world's finest witherite (Figs 38 and 39). Specimens are remarkable for their perfection size and aesthetic quality.

The mine was worked as early as 1611 (Smith, 1923; Dunham, 1948; Wilson, 2010) and was one of the most important lead producers in northern England in the seventeenth and eighteenth centuries. A rough plan accompanying a report by John Armstrong dated 14 August 1734 shows four levels: 15 fm; 40 fm; and two lower levels extending for about 1,300 yds (Smith, 1923: p. 21). The abundant presence barium minerals was recognised early in the mine's history, but witherite is not specifically noted until about 1821. An anonymous report, dated 1766, (reproduced in part in Smith, 1923: p. 24) described the deposit as follows:

> "She is a strong vein running E. and W., or rather two veins, E. of the engine against the north cheek is a soft dowk part shivery, next to that a strong cawk, or spar, a yard or more wide, which is joined on the south side by a strong rider mixed with spar several yards wide, the southmost part of which is all or mostly spar, in which lies ore in ribs of 4, 5, or 6 ins. wide. This spary part is 1½ - 2 yds. Wide, but instead of the rib the spar is some times flowered with ore. In some places opposite the little limestone on sun cheek the vein seems to form a sort of flat and that spary bearing part of the vein flutters in among the riders towards the North cheek."

In this context 'cawk' probably refers to both witherite and baryte, as was the custom in mining until much later (e.g. Bradley, 1862). The report goes on to note that the mines produced 1,000 bings (400 tons) of

Figure 38. Elongated bipyramidal witherite crystals, up to 41 mm in length, on drusy alstonite from Fallowfield Mine, Hexham, Northumberland. Specimen in the Gail and Jim Spann Collection, formerly in the collections of Lindsay Greenbank, Ralph Sutcliffe, Richard Barstow and the NHM, London to whom it was supplied by Elizabeth Gilmore (ca 1892). Tom Spann photograph, reproduced with permission.

Figure 39. Pyramidal pseudohexagonal witherite with a little well crystallised alstonite, 45 mm from top to bottom, from Fallowfield Mine, Hexham, Northumberland. John Hall Collection. Photo © John Hall.

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[27] Rudolf Erich Raspe (1736–1794) the German librarian and scientist best known for *The Surprising Adventures of Baron Munchausen*.

lead and employed 100 miners in 1765 (Smith, 1923: p. 22).

Shortly afterwards, Wallis (1769: p. 121) described Fallowfield Mine as exceedingly rich. At the time of his account, steam power was being used to pump out formerly flooded workings and the mine employed about eighty men. Wallis (1769: pp. 122–125) provided unusually clear (for the period) descriptions of the minerals, but none of these correspond to witherite.

By 1799 the vein had been explored by numerous additional levels and shafts (Smith, 1923: p. 22). Bailey and Culley (1813: pp. 18–19) note that Fallowfield produced a small quantity of lead ore, but no barium minerals are mentioned. In Mackenzie (1825: p. 301), the mine is described as having:

> "a rich metallic vein, from which great quantities of lead ore were formerly extracted; and it is reported, the workings are to be renewed when the heir of the late Sir William Blackett, Bart. Of Matfen, is of age".

Again, there is no record of barium minerals, and the wording suggests that mining operations were in abeyance.

The first definite record of Fallowfield witherite is in a *List of Donations to the Library and Museum of the Cambridge Philosophical Society*, on 10 December 1821 which notes "Crystallized Carbonate of Barytes from Fallowfield – Northumberland R. Lyon, Esq." (Anon., 1822). It seems reasonable to assume that well crystallised witherite was recognised at about that time. If fine specimens had come onto the collector market before 1817 James Sowerby would surely have illustrated them in his *British Mineralogy*.

Phillips (1823) briefly mentions the witherite occurrence at "Fallowfield mine, Hexam". The lack of detail is suggestive of a new discovery. Specimen quality gradually improved as the mine became better known to the mineralogical world and Johnston (1835: p. 2) notes:

> "the lead-mine of Fallowfield near Hexham, in Northumberland, is known to modern collectors of minerals as the locality where the finest specimens of crystallized carbonate of barytes have yet been obtained".

Such specimens were available in quantity by 1838 when R. Stokoe and B. Leadbeater presented a considerable number to the British Museum (Natural History).

In 1845, Jacob Walton and John Cowper acquired Fallowfield Mine and commercial extraction of witherite began (Wilson, 2010). Jacob Walton (d. 1863) was a mining entrepreneur (Cooper, 2006, p. 108) and John Cowper Jnr was the son of John Cowper Snr one of the most important and successful mineral dealers in Alston, who provided the specimen of the new "bicalcareo-carbonate of barytes" to Thomas Thomson (Cooper, 2006: p. 108). According to a section at Allenheads Estate Office (Dunham, 1948: p. 327), when Walton and Cowper took control of the mine the main development was on the 45-fathom (180 ft. O.D.); and 69-fathom (0 to 10 ft. O.D.) levels. The mine remained in the Walton family until it closed in 1912 (Dunham, 1948: p. 327).

Initially, witherite mining focused on the removal of sections of vein where the gangue had been left in place. New levels driven for witherite are shown on the section described by Dunham (1948: p. 327) at 300, 230, 175, 120 and 80 ft. O.D. This clearly demonstrates that the witherite was abundant in the upper parts of the vein, well above the level that had been reached by the lead-mining operations.

The workings clearly remained productive as in 1847, William Hutton (1797–1860) donated specimens of witherite and alstonite from Fallowfield Mine to the Natural History Society of Northumbria (their collection now forms part of the Great North Museum: Hancock). Greg and Lettsom (1858: p. 48) report that Fallowfield Mine had produced "the finest crystals yet known ... They are frequently very perfect, and are occasionally remarkable for their size". They go on to record a wide variety of crystal forms and combinations, up to 5 inches long, and note that the largest crystals are often coated with a white deposit of baryte.

Some of the finest crystallised specimens from Fallowfield passed through the hands of the Alston-based mineral dealers Patrick (ca. 1833–1892) and Peter Gilmore (1855–1892). In 1887, Peter Gilmore offered the British Museum (Natural History):

> "The largest Witherite ever found at Fallowfield which measures in length nearly 18 inches & has 3 different formations large flat toped [*sic*] xls, pointed & doubly terminated upon pink Alstonite & dogtooth Calcite and well worth £50 but can take £20 for it clear of damage".

The museum offered Gilmore £15, which he accepted to keep specimen in the country (Cooper, 2006: pp. 136–137).

Fallowfield continued to produce fine specimens of witherite until it closed in 1912. The total recorded production from 1855–1912 is 98,986 tons of witherite but Dunham (1948: p. 327) estimates the true figure as about 105,000 tons if estimates of early gaps in the records from 1846 to 1854 are included. Unlike most of the other notable Pennine occurrences, zinc minerals, particularly sphalerite, are uncommon with witherite at Fallowfield Mine (see for example Dunham, 1990: pp. 263–272).

Settlingstones Mine, between Haydon Bridge and Hexham, has the distinction of being Britain's largest witherite producer. It was a relatively late discovery, producing 363,814 tons of barium carbonate between 1873 and 1941 (Dunham, 1948: p. 324). Originally a lead mine (Wallis, 1769: p. 121), the gangue changed to witherite when the workings cut through a cross vein in 1873 (Symes and Young, 2008). It seems unlikely that any specimens were obtained before that date. The mine is probably best known for yellow-brown lustrous drusy crusts of tabular pseudohexagonal crystals (Figs 40 and 41), which are occasionally overgrown by harmotome.

Barium minerals, including witherite, were known in the Durham coalfield at the beginning of the twentieth century (e.g. Spencer, 1910). Substantial witherite veins (up to 6.5 m thick though more typically 1.2 to 1.6 m) were discovered in about 1928 at Morrison (South Moor) Colliery (Collins, 1972). They were remarkably pure and together with two smaller deposits at Craighead Colliery, produced 56,773 tonnes of witherite between 1932 and 1944. Ushaw Moor Colliery, which produced about 19,000 tonnes, and New Brancepeth Colliery, where the veins were mostly baryte but production included 1,000 tonnes of witherite, are probably the best known specimen localities.

Warrington W. Smyth (1817−1890) was one of the first people to identify witherite in the Central Wales Orefield (Smyth, 1848). One of Smyth's original specimens from Pen-y-Clun Mine, north of Llanidloes is preserved at Amgueddfa Cymru (NMW 00.20G.M.1). Witherite occurs as aggregates of thin platy hexagonal crystals (Fig. 42) to 20 mm (Morgan and Starkey, 1991) and as compact fibrous masses. Despite its abundance the deposit was never considered commercially viable (Carruthers *et al.*, 1915: p. 69). Bryn-y-Tail Mine on the same lode to the west of Pen-y-Clun was worked for barytes by a German company in about 1865 (Carruthers *et al.*, 1915: p. 70). Witherite is not mentioned but it occurs on the dumps as grey-white compact masses. South of Llanidloes cream-coloured masses of compact fibrous witherite are known from Gorn Mine where it appears to be more abundant than baryte (Carruthers *et al.*, 1915: p. 69). Further north, at Cwm Orog Mine near Llangynog, platy witherite crystals are overgrown by thin crusts of baryte.

Figure 40. Dense aggregate of lustrous pale fudge-coloured witherite crystals, 100 mm across, from Settlingstones Mine, Fourstones, Northumberland. Specimen NMW 83.41G.M.5480 in the collection of Amgueddfa Cymru, formerly in the King Collection (No. K999). Tom Cotterell photograph reproduced with permission from Amgueddfa Cymru.

Figure 41. Stacked pseudohexagonal witherite on a 75 × 50 mm specimen from Settlingstones Mine, Fourstones, Northumberland. Former Richard W. Barstow specimen in the John Hall Collection. Photo © John Hall.

In south Wales, witherite was reported in the Llantrisant area in Triassic breccia in a by-pass road cutting south of the town (Bowler and Kingston, 1971). The site, between Mwyndy Cross and Cefn-parc Farm produced large tabular pseudohexagonal witherite crystals often with an orange surface coating which were initially misidentified as celestine (T. M. Thomas specimens donated to Amgueddfa Cymru in 1967).

Figure 42. Thin tabular pseudohexagonal witherite, 12 mm across, from Pen-y-clun Mine, Llanidloes, Powys. Roy E. Starkey Collection, No. RES 2830-17. Photo Michael P. Cooper.

Subsequent investigations by local collectors identified abundant witherite in the neighbouring lead mines notably old dumps near Rhiwsaeson and a single specimen at Parc Mine near Cefn-parc Farm. Widening of the earlier road cutting in the late 1980s produced further fine large witherite crystals (Fig. 43) but they are not mentioned in Alabaster's (1990) detailed account of the exposure.

More recently, witherite has been found in some abundance in shallow-dipping veins cutting Neoproterozoic basement rocks at Dolyhir Quarry in the Welsh borders (Todhunter, 2002; Cotterell *et al.*, 2011). Radiating masses of highly elongated prismatic crystals occur on specimens to large hand size.

Witherite is occasionally claimed from localities in Derbyshire. In addition to the vague references in the foregoing text, witherite is noted by Mello (1875), Stokes (1879) and Hughes (1952). In every case it has turned out to be baryte (Ford *et al.*, 1993: p. 35). White Watson's catalogue (Watson, 1805) featured four lots (1, 19, 25 and 27) comprising comprehensive suites of geological specimens illustrative of the geological and mineralogical products of Derbyshire. None include carbonate of barytes.

Specimen No. 8 in Count de Bournon's catalogue of Sir Abraham Hume's extensive collection is described as large crystals of carbonate of baryte from Derbyshire. That specimen is extant in the collections at the Sedgwick Museum of Earth Sciences (No. CAMSM14588) but is atypical of Derbyshire (Fig. 44).

Figure 43. Altered sheaf-like group of tabular pseudohexagonal witherite on calcite, 30 mm across, from the Llantrisant bypass, Llantrisant, Glamorgan. Ian E. Jones Collection. Michael P. Cooper photo reproduced with permission from Amgueddfa Cymru.

Figure 44. Weathered and fractured witherite, 80 mm across, said to be from Derbyshire. The specimen retains an original Hume Collection No. 8, affixed by Count de Bournon. Specimen CAMSM 14588 in the Sedgwick Museum of Earth Sciences. Tom Cotterell photograph reproduced courtesy of the Sedgwick Museum of Earth Sciences.

Apjohn (1850) recorded a specimen of witherite from Derbyshire in the Trinity College Collection in Dublin (Patrick Wyse Jackson, *personal communication*, 2017). Other witherite specimens purporting to be from Derbyshire include a single specimen in the King Collection at Amgueddfa Cymru (NMW 83.41G.M.5433) accompanied by a handwritten label stating:

> "Witherite. said by J. Hodson to be from a vein at Cromford Moor".

The specimen is a small (28 × 18 × 13 mm) mass of compact fibrous pale-cream coloured witherite that contains minute inclusions of what seem to be coal[28] (black) and sphalerite (orange-brown) at one end. The label is suggestive of a mid-twentieth century specimen but unusually (for the King Collection) it does not have one of Bob King's own handwritten number labels affixed to it, nor is there a museum number label attached.

Two similar-sized specimens from 'Derbyshire' are preserved in the collections at the Royal Albert Memorial Museum in Exeter. One (No. 52/2009.54) is accompanied by a small square brown card label stating in biro "BARYTOCALCITE CASTLETON". It appears to be massive to slightly fibrous witherite. The second specimen (No. 52/2009.53) has a strong visual similarity to barytocalcite and is accompanied by a similar square card label stating "WITHERITE CASTLETON". Both were donated by Fran Caseley and collected by Graham

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[28] In this context it is interesting to note that coal can be found embedded in barium minerals at Cononley Mine in Yorkshire.

Hayward. The barytocalcite has strong similarities to specimens from Blagill, near Alston. Neither is from Derbyshire.

CONCLUSION

This study provides compelling evidence that the contemporary accounts of Watt (1790a), Köhler (1790) and Bucholz (1792), which claim that the source of the barium carbonate analysed by William Withering and others in the latter part of the eighteenth century was Anglezarke near Chorley in Lancashire, are correct. The most likely motivation for what appears to be deliberate misdirection to Alston Moor in the original mineral description is to protect the supply of a valuable commodity (and perhaps even to hide the fact that it was being collected from the mine owner until the lead-mining operations were abandoned in 1790).

Although it can be concluded with some confidence that the type locality for witherite is at Anglezarke, the claim that the original specimens came from Alston Moor has been bolstered by two later studies (Fowles, 1927; Selwyn Turner, 1963) and the fact that the deep deposits on Alston Moor produced some of the world's finest witherite specimens in the first half of the twentieth century. This study shows that the first reliable report of witherite from Alston Moor is from Wellhope twenty-five years after Withering's original description (Forster, 1809). Very few early specimens from Alston Moor found their way into collections in the first half of the nineteenth century. Their rarity is such that the author would be pleased to know of any further examples.

Early catalogues and the associated specimens in a number of British museums were key to unravelling the mystery. Unfortunately, many have been mixed up, a problem which would not have arisen if small labels had been fixed to the specimens. The holotype specimen of witherite cannot be located. The specimens with the best claim to be designated as neotypes are probably in the Matthew Boulton Collection at The Lapworth Museum of Geology (see Figs 1–4). A comparison with well provenanced specimens shows that the ochreous surface layer on two of these is characteristic of Anglezarke, but unlike Alston Moor (Alderton *et al*., 2022).

Matthew Boulton's involvement in the supply of specimens and the distribution of witherite to Europe is a fascinating side story which warrants further investigation. No evidence as to whether he was directly responsible for the deception, or unwittingly duped into believing that his material was from Alston Moor, has emerged.

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A REVIEW OF THE MINERALS OF LEAD MINES CLOUGH, ANGLEZARKE, CHORLEY, LANCASHIRE: THE TYPE LOCALITY FOR WITHERITE

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Lead-zinc-copper mineralisation in a baryte or witherite gangue fills fractures in the Fletcher Bank Grit at Lead Mines Clough in the parish of Anglezarke, Lancashire. The workings are the largest on Anglezarke Moor and almost certainly the type locality for witherite. There are three distinct primary assemblages. The first consists of simple veins containing early galena in compact laminar baryte with minor chalcopyrite, sphalerite, iron sulphides and a little witherite. It is followed by a complex witherite-dominated assemblage which consists of early sphalerite-rich replacements of baryte with later vein breccias in the less competent lithologies and massive vein fills in the more competent sandstones. The most recent primary assemblage is dominated by open-textured baryte. The supergene assemblage includes aragonite, anglesite, baryte, cerussite, hydrozincite, leadhillite, pyromorphite, malachite, smithsonite, sulphur, and iron and manganese oxides and oxyhydroxides. Secondary marcasite and pyrite are common as drusy encrustations on aragonite and smithsonite, and indicate a late-stage reversion to reducing conditions. It seems likely that post-mining alteration of the secondary iron sulphides produced the ochreous encrustations that are common at the site.

INTRODUCTION

Witherite is abundant in low-temperature lead-zinc-copper deposits at Anglezarke near Chorley in Lancashire. A historical study, which shows that witherite was originally discovered at one of the Anglezarke mines and not on Alston Moor as is commonly supposed, is published in this journal (Cotterell, 2022). The only working that could have produced witherite in the quantities that are known to have been traded in the late eighteenth century is Lead Mines Clough (Price *et al.*, 1963). It is almost certainly the type locality.

This description complements the research reported in Cotterell (2022). Some early witherite specimens have become dissociated from their original labels after more than two centuries in collections and a summary of the distinguishing features and characteristic associations at Lead Mines Clough facilitates a meaningful assessment of provenance.

Unfortunately, it was not possible to gain permission for fieldwork at the site during the recent pandemic. This study is based on specimens in the collections of the late Harry Critchley and Keith Snell, respected Russell Society members who had a particular interest in the locality. It concentrates on witherite and also includes descriptions of the associated minerals.

LOCATION

Anglezarke Moor forms the northernmost part of an isolated area of high ground on the western edge of the Pennine hills between Blackburn, Bolton and Preston. There are trials for lead along Dean Black Brook to the east of the small settlement of White Coppice, and on Stronstrey Bank, but the only site where "any considerable amount of mining has been done" (Price *et al.*, 1963: p. 97) is in Lead Mines Clough, a steep-sided valley which extends SSW from the moor to the Yarrow Reservoir. The principal workings are clustered at about 200 m above Ordnance Datum on the east side of the valley (Fig. 1).

All of the specimens from the Keith Snell Collection are labelled with the grid reference SD 630 164. This indicates that they were collected from the only major

Figure 1. A sketch map showing the location of Lead Mines Clough in the parish of Anglezarke to the east of Chorley in Lancashire. The spoil heap for the principal working on Old or Sun Vein is marked with a pick-and-shovel symbol; two nearby shafts (black circles with crosses) show the direction of the vein. Other trials on Anglezarke Moor are indicated by black circles. Alance Bridge crosses an arm of the Yarrow Reservoir at bottom-centre of the plan. The grid squares are in Ordnance Survey 100 km square SD.

spoil heap in Lead Mines Clough, on Old or Sun Vein, about 500 m northeast of Alance Bridge (Fig. 2). Specimens in the Harry Critchley Collection are mostly from the same site, although a few were obtained from small grass-covered shaft dumps on the vein to the east (see Fig. 1) when post-holes were being excavated in the late 1990s.

HISTORY

The history of lead mining in the parish of Anglezarke is summarised by Williamson (1963) and Gill (1987). The most important contemporary description of the workings was read before the Manchester Literary and Philosophical Society late in 1789 by James Watt Jnr (Watt, 1790). The mineralogical history, with a particular focus on witherite, is described by Cotterell (2022) in this journal. There is no benefit in repeating this information, and a short summary is all that is included here.

Recent archaeological studies show that galena was known in the area as early as 1800 BCE (Barrowclough, 2014). Documentary evidence shows that the Anglezarke mines were active in the late seventeenth century, closing in about 1694 following a dispute between Lady Margaret Standish and a number of lesser gentry (Williamson, 1963: p. 133). The mines were active in 1731 and 1732, and the Clitheroe Mining Company raised some ore between 1753 and 1766 (Kerr, 1875).

The most productive period of mining was between 1781 and 1790 when Sir Frank Standish raised a little less than 100 tons of ore (Price *et al*., 1963; Williamson, 1963). This coincides with the first scientific description of witherite and an illicit but lucrative trade in specimens (Withering, 1784; Watt 1790; Cotterell, 2022). Lead Mines Clough may be an early example of a locality where the value of the spar (witherite for chemical research and medicinal use) exceeded the value of the ore. An attempt to rework the deposits in the 1820s and 1830s, under the direction of John Thompson, an iron merchant from Wigan, met with no success (Gill, 1987: p. 61) and the mines have been abandoned since that time.

GEOLOGY

Lead Mines Clough follows a minor NNE–SSW trending fault in Namurian rocks of the Millstone Grit Group on the western side of the Rossendale Anticline (British Geological Survey, 1982). The sequence is dominated by deltaic conglomerates, sandstones, siltstones, shales and mudstones, which are exposed sporadically in the steep-sided valley. Thin coals associated with fireclays and seatearths show that terrestrial floras developed in swampy conditions during periods of emergence. Black shales with abundant goniatite fossils were deposited in shallow water during brief marine transgressions. All of these lithologies are recorded within two hundred metres of the mine site on a large scale plan produced by Iain Williamson and colleagues in the 1960s (Wigan College, n.d.)

The mineral veins are best developed in fractures in the more competent units of the Marsdenian Fletcher Bank Grit. The principal lode, Old or Sun Vein, strikes ENE–WSW immediately to the east of the Brinscall Fault (British Geological Survey, 1982) and is described by Price *et al*. (1963: p. 97) as follows:

> “The principal lode seems to have been the Old or Sun Vein, which can apparently be traced for about a quarter mile by a line of pits trending E. 15ºN. Near the surface it was found to hade at a small angle to the north, but it flattened considerably in depth. It varied in width from 6 to 36 in, and consisted mainly of galena with some blende, accompanied by witherite, barytes, iron pyrites and a little calcite as gangue minerals. The part of the vein richest in galena was in gritstone, the shale beds containing mainly blende and pyrites. The vein was irregular, the ore occurring in ‘nodules’ and ‘clusters’ and, where wide, in a breccia of sandstone and shale. The witherite was present in greater quantities towards the surface, being mixed with barytes in depth and entirely replaced by it in the lower levels”.

This short account, which is based on field slips and other unpublished records held by the Geological Survey and the few published accounts of the site [principally

Figure 2. The principal spoil heap on Old or Sun Vein in Lead Mines Clough, now cut in two by an unmetalled road, as it stood in the summer of 2022. Photo Christine Critchley.

the contemporary description by James Watt Jnr (1790)], is the most detailed modern synopsis of the mineralisation. Price *et al*. (1963) record four subsidiary veins, and the maps produced during Iain Williamson's research in the 1960s plot more than ten, mostly "interpolated from old plans" (Wigan College, n.d.).

A detailed geological commentary is beyond the scope of this study, which is entirely collection based, but it is worth recording that clasts in vein breccia include angular fragments of fine-grained well bedded micaceous sandstone, siltstone, grey shale, mudstone and rarely black vitreous coal. It is also worth noting that although the coarser sandstone is typically made up of rounded quartz grains, authigenic quartz overgrowths are not unusual and near to fractures recrystallisation has occasionally produced small volumes of sandstone dominated by millimetre-size transparent euhedral quartz crystals in a frothy siliceous cement.

MINERALS

The minerals found at Lead Mines Clough are listed alphabetically in the following text. Species with subtitles in capitals have been identified beyond reasonable doubt but a degree of uncertainty remains for those with subtitles listed in lower case. Identifications of the common minerals are visual, supported where appropriate by simple wet chemistry. The less common species have been examined by energy-dispersive spectrometry (EDS) on a scanning electron microscope (SEM) and in some instances by X-ray powder diffraction (XRD).

The descriptions are based on approximately two hundred collection specimens obtained on about a dozen separate field visits (about 150 from the Harry Critchley Collection and 50 from the Keith Snell Collection) and a significant amount of unregistered material (ca 300 specimens retained by Harry Critchley) which had been put aside in field boxes to be examined when time allowed.

Uncatalogued material was assigned a unique temporary number beginning with the letters AZ as part of this research. This allowed analyses and images to be related back to the relevant specimens.

Allophane, $(Al_2O_3)(SiO_2)_{1.3-2}\cdot 2.5-3H_2O$

Glassy, translucent, white to pale blue crusts with pale brown lath-like cerussite in a cavity in altered witherite-rich matrix (see Fig. 13) have an appearance and composition which are consistent with copper- and lead-bearing allophane. Analyses by EDS indicate there is some replacement of the silica in the ideal formula by copper- and lead-bearing molecular species but this is not unusual in allophane from supergene environments. A bright pale blue fluorescence is excited by longwave ultraviolet light (Fig. 3).

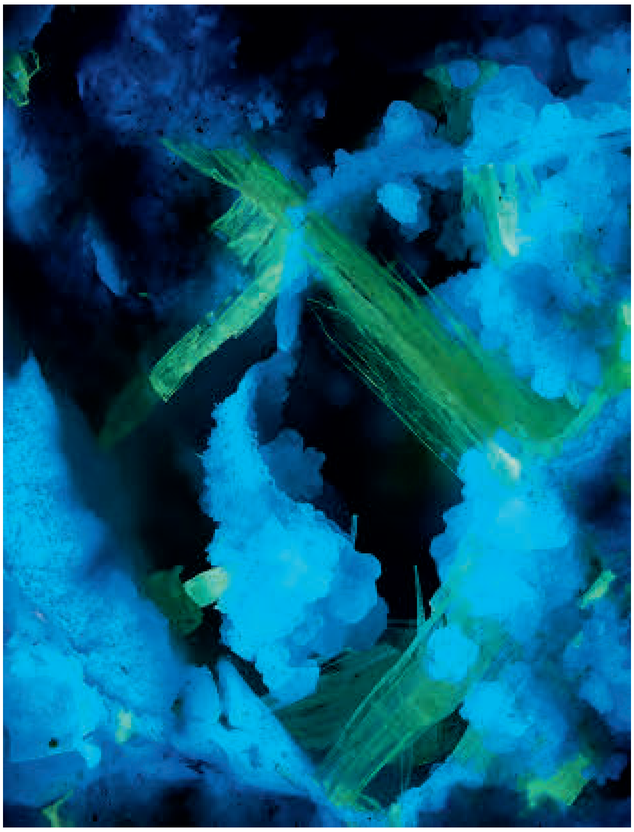

Figure 3. Copper- and lead-rich allophane with lath-like cerussite crystals up to 2 mm in length illuminated in longwave ultraviolet light to show the distinctive pale blue (allophane) and yellow (cerussite) fluorescence colours. Miniature specimen AZ(HC)12 in the Harry Critchley Collection. Photo John Chapman.

ALMANDINE, $Fe^{2+}_3Al_2(SiO_4)_3$

Transparent to translucent pink to purple crystals and crystal fragments, up to 0.7 mm across, with a conchoidal fracture and vitreous lustre are preserved on three specimens in the Harry Critchley Collection. Energy-dispersive X-ray analysis indicates that they are magnesium-bearing almandine (rather than the tentative visual identification of fluorite).

There is no indication that the almandine, or quartz with which it is associated, have any genetic relationship to the vein mineralisation. The quartz appears to have formed authigenically but, as garnet-group minerals are not generally regarded as authigenic, the almandine is likely to be detrital.

ALSTONITE, $BaCa(CO_3)_2$

A remarkably rich specimen of massive alstonite containing small crystal-lined cavities was shown to one of the authors (DG) in 2008 by the late Keith Snell. It has not been traced in this study, but a small fragment (16 × 8 × 7 mm) which appears to be from the same piece [the label records that it was “donated by Keith Snell”] is preserved in the Harry Critchley Collection. On this specimen, sharply pointed translucent pseudohexagonal alstonite pyramids up to 0.4 mm in length line cavities in massive alstonite (Fig. 4). In exposed cavities the crystals are coated by fine-grained baryte or aragonite, possibly as a result of recent alteration in the mine spoil, but in well sealed cavities the crystals are sharp and lustrous.

Figure 4. Pointed pseudohexagonal alstonite pyramids in massive alstonite. A tiny fragment detached from specimen AZ(HC)23 in the Harry Critchley Collection. The field of view is 558 µm across. SEM image by Jeremy Poole.

Alstonite was identified by XRD supported by EDS which showed that barium and calcium were the only major elements present with an atomic number greater than 10.

ANGLESITE, $PbSO_4$

Anglesite is typically found within, or in very close proximity to, masses of oxidising galena. It occurs as drusy crusts of colourless, transparent, blocky prismatic to tabular crystals, typically no more than about 0.2 mm in length, in fractures in galena. Transparent elongated prismatic crystals, up to 2 mm in length (Fig. 5) are occasionally present in cavities in the surrounding oxidation rinds.

Anglesite is commonly associated with pale yellow pyramidal sulphur and rarely overgrown by powdery bindheimite in fractures in galena. It is occasionally associated with cerussite and leadhillite in cavities and fractures near the edge of oxidising galena masses and with cerussite in fractures in the surrounding baryte.

Analyses of radiating sprays of white acicular crystals up to about 0.3 mm across on two specimens in the Harry Critchley Collection (tentatively identified as dundasite) by EDS detected lead and sulphur (but no aluminium). They are probably anglesite, although other supergene lead minerals containing oxidised sulphur species cannot be completely ruled out.

ARAGONITE, $CaCO_3$

Bright white acicular aragonite forms dense crusts in cavities in witherite-rich matrix. The individual crystallites rarely exceed 0.1 mm in length and the radiating clusters are no more than about 0.3 mm across but they

Figure 5. Transparent blocky prismatic anglesite crystals, the largest 1.5 mm in length, in a cavity surrounding a partly oxidised mass of galena. Specimen AZ039 in the David Green Collection. Photo John Chapman.

occasionally dominate the linings of the cavities in which they occur (Figs 6 and 7). Aragonite sometimes occurs as a direct overgrowth on witherite but is more usually found on the diamond-shaped drusy baryte which lines cavities in massive witherite. It coats pyramidal alstonite crystals where cavities have been exposed to alteration in the mine spoil. Aragonite is commonly associated with smithsonite and may be overgrown by late-stage secondary iron sulphides (marcasite or pyrite) or the brown iron oxyhydroxide films which form when they decompose.

The identification is based on wet chemistry and analysis by EDS, which differentiate the crystal sprays from other carbonates except calcite, together with comparisons with similar sprays which have been confirmed by XRD at other witherite-dominated assemblages in the Pennines, all of which have proved to be aragonite.

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

Aurichalcite occurs rarely as clusters of pale sky-blue to greenish blue lath-like crystals in partly oxidised witherite veinstone (see Fig. 30). It is also found as sparse isolated pale blue-green to turquoise-blue spherules, up to about 0.5 mm in diameter, on otherwise unaltered lustrous pyramidal witherite.

Figure 6. Radiating spherulites and occasional bow-ties of white acicular aragonite in a cavity lined with minute diamond-shaped baryte crystals in massive lamellar witherite. Slightly oxidised sphalerite is overgrown by an unidentified brown coating, and the whole assemblage is scattered with late-stage secondary marcasite. Specimen AZ005 formerly in the Keith Snell Collection. The field of view is 2.2 mm across. Photo John Chapman.

BARYTE, $BaSO_4$

Baryte is abundant at the mines and trials on Anglezarke Moor and it commonly infills joints in local sandstones (Wigan College, n.d.). Primary baryte occurs in two distinct assemblages: compact early baryte with a range of sulphide minerals including abundant galena, and open-textured late-stage baryte composed of interlocking crystals without any associated sulphides except residual galena.

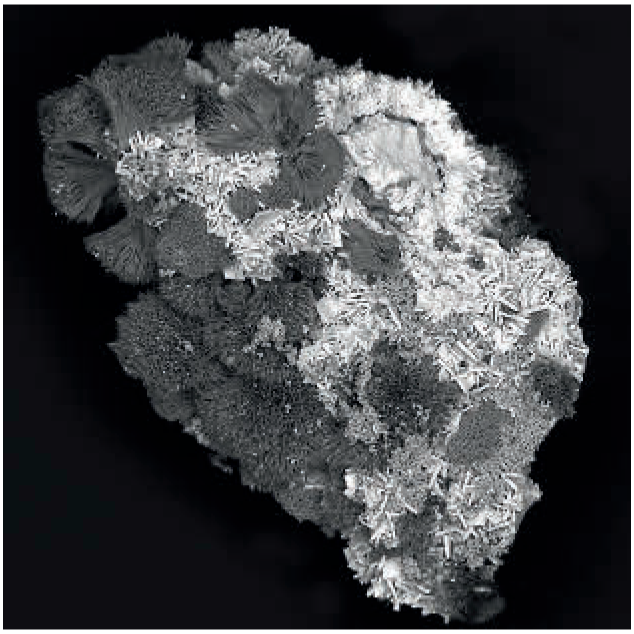

Figure 7. Back-scattered electron image of radiating acicular aragonite (dark) overgrowing euhedral diamond-shaped baryte (bright white) with a little etched massive witherite (top centre-right also white). A 1.2 mm fragment detached from specimen AZ005 formerly in the Keith Snell Collection (see Fig. 6). SEM image by David Alderton.

The early primary baryte is compact and white with a laminar structure. It commonly encloses idiomorphic galena, lesser chalcopyrite, iron sulphides, sphalerite and minor witherite; contains occasional cavities lined with cockscomb crystals (Fig. 8); and is typically found in symmetrical fissure veins in coarse sandstone. It predates the major phase of witherite deposition.

The start of the sulphate-alteration process which generates at least some of the late-stage open-textured baryte is commonly visible in massive witherite where hairline fractures are commonly delineated by fine-grained baryte; cavities are lined with drusy crusts of diamond-shaped crystals (Fig. 9); and baryte pseudomorphs after witherite are common. As witherite destabilises it is replaced by interlocking baryte crystal aggregates. Some specimens contain relict radiating structures or pyramidal pseudomorphs which indicate direct replacement of earlier witherite (Fig. 10), but these structures have been obliterated by Ostwald ripening in coarser baryte aggregates.

Cylindrical tubes in some open-textured baryte suggest more distal formation perhaps by fluid mixing. In these cases the baryte is unlikely to have formed as a direct replacement but witherite remains a possible source of the barium-rich solutions.

Witherite from the spoil heap is commonly coated by thin porcellaneous post-mining crusts of fine-grained baryte stained orange-brown by iron oxyhydroxides (Cotterell, 2022). The crusts, which seem to have developed in an interaction between witherite and the acidic sulphate-rich solutions generated by the destabilisation of iron sulphides, form a seal around the relatively reactive carbonate. Supergene coralloidal baryte (Fig. 11) which occasionally overgrows iron oxyhydroxides in cavities and fractures in witherite appears to have formed in a similar manner.

Figure 8. Jumbled iron-stained baryte sheaves lining a cavity in laminar vein baryte. Specimen AZ004 formerly in the Keith Snell Collection. The field of view is 6 mm across. Photo John Chapman.

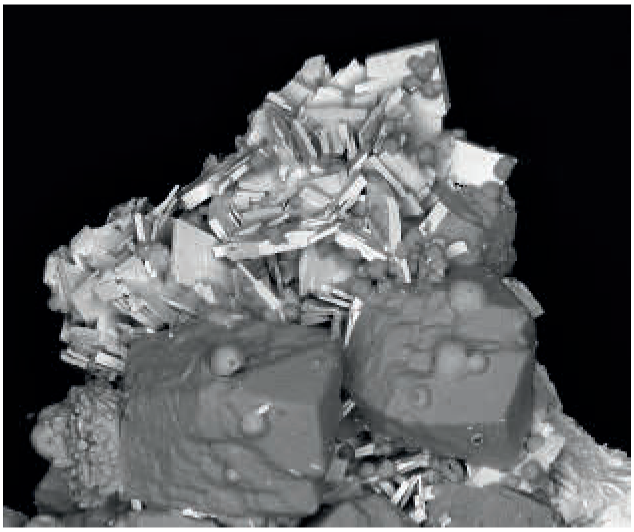

Figure 9. Back-scattered electron image of diamond-shaped baryte crystals lining a cavity in massive witherite. The baryte is overgrown by spheroidal masses of an unidentified barium manganese oxide and associated with two well formed blocky calcite crystals encrusted in zinc-bearing iron oxyhydroxide (cf. Fig. 12). A fragment detached from specimen AZ010 formerly in the Keith Snell Collection. The field of view is 1 mm across. SEM image by David Alderton.

Figure 10. Drusy baryte pseudomorphs after witherite in a matrix of open-textured baryte. The pseudomorphous structures on this specimen, which is 40 mm from top to bottom, clearly indicate direct replacement of witherite by baryte. Specimen AZ(HC)01 in the Harry Critchley Collection. Photo David Green.

Figure 11. White coralloidal supergene baryte (identified by EDS) overgrowing iron-stained witherite and late-stage secondary marcasite. Specimen AZ002 formerly in the Keith Snell Collection. The field of view is 2.5 mm across. Photo John Chapman.

Bindheimite, $Pb_2Sb_2^{5+}O_7$

Analysis by EDS reveals that tiny pale yellow powdery patches associated with anglesite only contain lead and antimony (with an atomic number >10). They are probably best described as the poorly defined lead antimony oxide 'bindheimite', which is mostly synonymous with the recently described pyrochlore-group mineral oxyplumboroméite (Atencio *et al*., 2010; Christy *et al*., 2013).

CALCITE, $CaCO_3$

Calcite is recorded as a minor component of the primary mineralisation by Price *et al.* (1963). Translucent primary calcite, which can be distinguished by its well developed rhombohedral cleavage, is occasionally found as irregular masses in witherite. Blocky prismatic crystals with shallow rhombohedral terminations, typically less than 1 mm in length, are sometimes associated with diamond-shaped baryte in cavities in witherite. They often have a thin preferential overgrowth of a brown zinc-bearing iron oxyhydroxide and may also be encrusted by black spherulitic manganese oxides and late-stage secondary marcasite or pyrite (Fig. 12).

CERUSSITE, $PbCO_3$

Colourless to white cerussite crystals, generally less than a millimetre in length, with a wide range of tabular, blocky and prismatic habits occur rarely in cavities and

Figure 12. Blocky prismatic calcite with shallow rhombohedral terminations on drusy diamond-shaped baryte. The calcite has a preferential overgrowth of an unidentified brown iron oxyhydroxide, possibly zinc-sorbed goethite, a black spherulitic barium manganese oxide and rare clusters of secondary marcasite (cf. Fig. 9). Specimen AZ010 formerly in the Keith Snell Collection. The field of view is 4 mm across. Photo John Chapman.

fractures in and around partly altered galena masses. Unlike anglesite, which is restricted to baryte veinstone, cerussite is occasionally found around masses of oxidised galena in witherite.

Unusual pale brown pointed lath-like cerussite crystals (Fig. 13), similar to the recently described specimens from Whitwell Quarry in Derbyshire (Briscoe *et al.*, 2021), have been identified by EDS (with carbonate confirmed by wet chemistry). They are associated with copper-bearing allophane and minute hexagonal scales of an unidentified zinc aluminium silicate, possibly fraipontite, on a small number of specimens in the Harry Critchley Collection.

CHALCOPYRITE, $CuFeS_2$

Minute idiomorphic chalcopyrite crystals occur as sparse inclusions in primary baryte and witherite. They become larger and more abundant in the last stages of witherite formation. The crystals are brassy yellow when unoxidised, occasionally tarnished metallic blue to purple, but most commonly partly to completely pseudomorphed by goethite.

A chalcopyrite-rich vein cuts massive witherite on a single specimen (Fig. 14). It may represent a copper-rich episode of mineralisation at the end of witherite deposition, but it is unwise to extrapolate from a single example.

Figure 14. A veinlet containing abundant idiomorphic chalcopyrite and witherite cutting massive witherite. Specimen B126 formerly in the Keith Snell Collection. The field of view is 12 mm across. Photo John Chapman.

Figure 13. Lath-like pale brown cerussite crystals up to 2 mm in length on glassy pale blue copper- and lead-rich allophane. Miniature specimen AZ(HC)12 in the Harry Critchley Collection. Photo John Chapman.

GALENA, PbS

Galena was the principal target of the mining operations on Anglezarke Moor and small masses are reasonably common on the spoil heaps in Lead Mines Clough. Galena is typically early in the primary paragenesis, often crystallising directly on sandstone wall-rock (Price *et al.*, 1963). It is commonly associated with chalcopyrite, iron sulphides and sphalerite in early laminar baryte, less common in the later complex witherite-dominated assemblage and occurs as remnant masses in the open-textured late-stage baryte.

Although it occasionally appears to be idiomorphic, galena is most common as broken anhedral fragments derived from the earlier galena-baryte mineralisation in the witherite-dominated assemblage. A leached specimen in the Harry Critchley Collection consists of a broken mass of centimetre-size crudely cuboctahedral crystals with deeply pitted surfaces overgrown by dark brown sphalerite.

GOETHITE, α-$Fe^{3+}O(OH)$

Goethite is the natural end-point of most supergene alteration sequences that involve the ‘moist oxidation’ of iron minerals (Cornell and Schwertmann, 2003). It is conspicuous and abundant at most near-surface trials on Anglezarke Moor, presumably as a result of the oxidation of iron sulphides. Sharp goethite pseudomorphs after chalcopyrite are occasionally present in cavities in witherite, but no goethite pseudomorphs after either marcasite or pyrite have been identified.

Brown coatings and dendritic crusts in cavities in witherite lined with aragonite, baryte and smithsonite (Fig. 15) appear to be zinc-sorbed goethite but are too thin to properly characterise with the techniques available to this study. The post-mining crusts which surround broken fragments of witherite in the spoil heaps

Figure 15. The stepped rhombohedral terminations of a typical three-sided subparallel bundle of smithsonite crystals coated in a crudely dendritic iron oxyhydroxide crust. Specimen AZ012 formerly in the Keith Snell Collection. The field of view is 0.9 mm across. Photo John Chapman.

probably owe their orange-brown colour to similar material. Iron oxyhydroxides are a complex group of minerals and although most are likely to be goethite they merit more detailed study.

Hydroniumjarosite, $(H_3O)Fe^{3+}_3(SO_4)_2(OH)_6$

An analysis of a yellow-brown powdery crust around recently oxidised marcasite by EDS identified iron and sulphur in approximately the correct ratio for a 'jarosite' (*sensu lato*). The absence of potassium or sodium rules out jarosite and natrojarosite. A process of elimination suggests hydroniumjarosite but ammoniojarosite cannot be excluded by these results alone.

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

Hydrozincite is always the last zinc-bearing mineral in the supergene paragenesis. It generally appears to have formed by post-mining oxidation in spoil. Inconspicuous pale blue-white films can almost always be identified on, in and around slightly oxidised sphalerite. Bright white hydrozincite crusts up to several millimetres in thickness are common in cavities in sphalerite-rich veinstone (Fig. 16) and sometimes completely cover the external surfaces of broken veinstone blocks (see Fig. 41).

Hydrozincite crusts are usually made up of minute lath-like crystals. Transverse sections often reveal a radiating or foliated internal structure. Powdery white hydrozincite often fills the voids around relatively unoxidised euhedral sphalerite where the surrounding witherite has been dissolved by acidic solutions. In the presence of oxidising chalcopyrite the crusts and infills sometimes develop a pale green tint. Hydrozincite is always later than smithsonite. The two minerals typically coexist (see Fig. 41), but smithsonite which has been exposed on the outer surfaces of blocks in the mine spoil may be completely replaced by hydrozincite.

Figure 16. Mammilliary hydrozincite as a bright white late-stage coating in a cavity lined with drusy diamond-shaped baryte in sphalerite-rich witherite veinstone. Specimen AZ007 formerly in the Keith Snell Collection. The field of view is 2.5 mm across. Photo John Chapman.

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

Leadhillite occurs in tiny cavities and thin fractures close to the outer edges of partly oxidised galena masses on a handful of specimens. The colourless to white blocky to tabular pseudohexagonal crystals do not exceed 0.2 mm. Leadhillite is the only supergene mineral present in some of the cavities in which it occurs but is associated with anglesite or cerussite or both in others. If all three minerals are present anglesite is generally overgrown by leadhillite, which is in turn overgrown and sometimes partly replaced by cerussite (Fig. 17).

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

Malachite is rare and inconspicuous. It occurs as spherulitic aggregates, sometimes close to oxidised chalcopyrite, in partly oxidised witherite veinstone (Fig. 18) and, in common with aurichalcite, as sparse scattered spheroidal masses on unaltered lustrous witherite.

MANGANESE OXIDES

Two visually distinct manganese oxides are present on the specimens examined in this study: dull black coatings which occasionally develop into spheroidal masses (see Figs 9 and 12) and aggregates of ragged metallic brown laths. Analyses by EDS show that the sooty black coatings and spherulites are a barium manganese oxide. They are likely to be either hollandite or romanèchite, most probably the latter which is common in supergene environments, but insufficient material is available for determination by XRD.

The ragged metallic brown flakes are typically less than a micrometre in thickness and have visual similarities to lagalyite, ranciéite and todorokite. Calcium and manganese with minor sodium were

Figure 17. Backscattered electron image of blocky anglesite crystals overgrown by a few relatively large pseudohexagonal leadhillite crystals and smaller but more abundant prismatic cerussite twinned along the elongation direction. A fragment from specimen B416 formerly in the Keith Snell Collection. The field of view is 700 µm across. SEM image by Jeremy Poole.

identified by EDS in analyses of material on a specimen in the Keith Snell Collection. This is consistent with ranciéite or lagalyite, but the matrix also registered through the thin crystals and the results cannot be regarded as reliable. Sodium (with minor calcium and barium in one case and minor calcium in another) and manganese in elemental ratios that are consistent with todorokite were identified in analyses of similar looking but more substantial crystal clusters, removed from their underlying matrix, on a specimen in the Harry Critchley Collection.

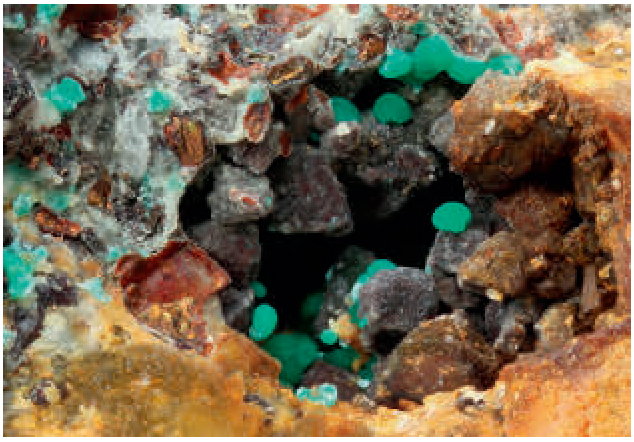

Figure 18. Spherulitic malachite, with minor aurichalcite on the left-hand side, in a cavity containing sphenoidal chalcopyrite which is overgrown and partly cemented by minutely drusy baryte. Specimen B126 formerly in the Keith Snell Collection. The field of view is 2.5 mm across. Photo John Chapman.

MARCASITE, FeS_2

Aggregates of millimetre-size twinned interlocking pyramidal marcasite crystals have been leached from enclosing carbonates using dilute mineral acid on specimens in the Harry Critchley Collection (Fig. 19). A specimen from one of the field boxes, with broken fragments of well crystallised marcasite in a witherite-calcite matrix, is probably representative of the original veinstone and suggests that the main phase of marcasite formation pre-dates brecciation.

In addition to the primary assemblage, marcasite is common as late-stage secondary (supergene) crystal aggregates, some with an open dendritic structure, others compact with drusy crystal surfaces. They commonly overgrow aragonite, baryte and smithsonite in cavities in lamellar witherite and appear to represent a local reversion to reducing conditions which post-dates the formation of smithsonite but pre-dates dump-formed hydrozincite.

Figure 19. Well formed marcasite crystals with characteristic twinning leached from enclosing carbonate. Miniature specimen AZ(HC)14 in the Harry Critchley Collection. The field of view is 5.5 mm across. Photo John Chapman.

PYRITE, FeS_2

The record of "pyrites" in Price *et al*. (1963) probably refers to marcasite [*vide supra*] which is much more common than pyrite on the specimens examined in this study. Saccharoidal overgrowths on acid-etched marcasite crystal groups are mostly minute distorted pyrite crystals (Fig. 20). Sharp octahedral pyrite crystals, rarely more than 0.1 mm on edge, are sparsely scattered on calcite or witherite on a few specimens in the Harry Critchley Collection (Fig. 21).

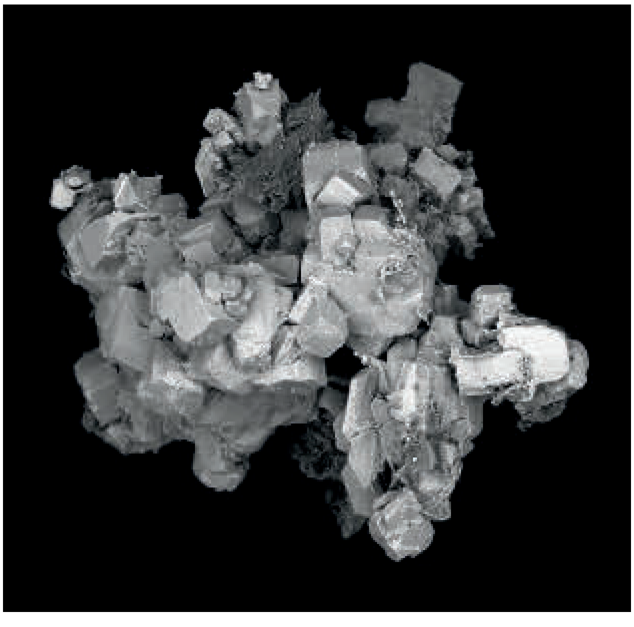

Figure 20. Blocky distorted pyrite up to 50 µm on edge in a sulphide latticework removed from the surface of a large marcasite crystal (see Fig. 19). A tiny fragment detached from miniature specimen AZ(HC)14 in the Harry Critchley Collection. SEM image by Jeremy Poole.

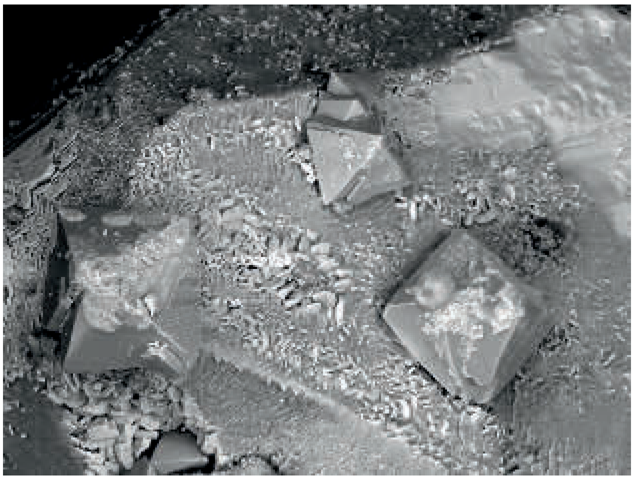

Figure 21. Octahedral pyrite crystals on the surface of a bipyramidal witherite crystal coated in a thin crust of minute tabular baryte (which has a brown-stained appearance under the optical microscope). A tiny fragment of miniature specimen AZ(HC)17 in the Harry Critchley Collection. The field of view is 164 µm across. SEM image by Jeremy Poole.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$

Pyromorphite occurs as dense crusts of colourless transparent crystals, typically less than 0.1 mm in length and a few tens of micrometres across, in cavities in open-textured primary baryte. The absence of contrast between the crystals and matrix, and their small size, make the crystal habit difficult to discern under a stereomicroscope. Elongated hexagonal prisms with pinacoidal terminations are easily resolved by scanning electron microscopy (Fig. 22).

Figure 22. Back-scattered electron image of hexagonal-prismatic pyromorphite (bright white) overgrowing equant late-stage baryte (pale grey), with preferential sculpting on some crystal faces. A fragment detached from specimen AZ024 formerly in the Keith Snell Collection. The field of view is 700 µm across. SEM image by David Alderton.

▲ Figure 23

Figure 24 ▼

▼ Figure 25

▼ Figure 26

Pyromorphite was identified by EDS on two specimens in the Keith Snell Collection which were labelled 'hemimorphite'. Its composition is close to end-member: vanadium and arsenic are absent and calcium substitution for lead is minor.

QUARTZ, SiO_2

The wall-rocks at Lead Mines Clough include coarse poorly sorted sandstones made up of rounded quartz grains. Authigenic overgrowths are sometimes present and, in a few instances, local alteration has produced a lithology dominated by transparent euhedral crystals, typically about 0.5 mm in length, with pyramidal terminations and short prism faces in a fine-grained siliceous cement. In some cases recrystallisation is so pervasive that no indication of the original sandstone remains. The alteration is not related to the formation of the lead-zinc-copper deposits. There is no sign of recrystallisation in most of the sandstone wall-rock along the selvedges of veins or in the sandstone clasts in mineralised breccias and no quartz of any sort is present in the veins themselves.

SMITHSONITE, $ZnCO_3$

Smithsonite is abundant in cavities in sphalerite-rich witherite. It occurs as groups of sub-parallel colourless to white, pale grey, yellow-brown, orange-brown, grey-brown and black crystals which commonly have minutely stepped surfaces (Fig. 23). Crystals are often acutely rhombohedral (Fig. 24) and occasionally form curved wheat-sheaf or bow-tie aggregates (Figs 25 and 26). Spheroidal aggregates, which occasionally reach 3 mm across, may be colour zoned with white, grey, brown and black bands. Smithsonite is commonly overgrown by secondary marcasite or pyrite, iron oxyhydroxides (see Figs 15 and 41) and post-mining hydrozincite (see Fig. 41), by which it is occasionally replaced.

SPHALERITE, ZnS

Figure 27. Translucent dark brown to orange-yellow idiomorphic sphalerite in massive witherite. Specimen B261 formerly in the Keith Snell Collection. The field of view is 9 mm across. Photo John Chapman.

Brown sphalerite is a minor component of the sulphide assemblage in early laminar vein baryte. Euhedral sphalerite is often abundantly intergrown with witherite in the early barium carbonate replacement mineralisation. Dark brown to pale yellow plane-faced crystals up to a few millimetres across are often completely enclosed in medium-grained witherite (Fig. 27). Rarely, minute dark euhedral sphalerite crystals with a little fine-grained witherite form sharp pseudomorphs after earlier baryte. Sphalerite is widespread in the later witherite vein breccias and compact radiating vein fills, but not in the same abundance as the early replacement assemblage. It does not occur in late-stage open-textured baryte

Strontianite, $SrCO_3$

Sprays of white acicular crystals in witherite, the largest 15 mm across, which dissolve with effervescence in acid and give a positive (crimson) flame test for strontium, are probably strontianite (Neil Hubbard, *personal communication*, 2022).

SULPHUR, S_8

Drusy pale yellow crusts of blocky to steeply pyramidal sulphur crystals are often associated with anglesite in fractures in massive galena. A narrow rim of minutely crystalline sulphur occasionally surrounds partly oxidised masses of galena in iron-stained baryte matrix.

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Figure 23. Brown subparallel sheaves of smithsonite with stepped rhombohedral terminations on baryte. Specimen AZ012 formerly in the Keith Snell Collection. The field of view is 2 mm across. Photo John Chapman.

Figure 24. Subparallel aggregates of acutely rhombohedral smithsonite on bright white diamond-shaped baryte. Specimen AZ018 formerly in the Keith Snell Collection. The field of view is 1 mm across. Photo John Chapman.

Figure 25. Curved wheat-sheaf aggregate of translucent pale brown smithsonite on baryte. Specimen AZ018 formerly in the Keith Snell Collection. The field of view is 0.8 mm across. Photo John Chapman.

Figure 26. Asymmetric bow-tie aggregate of pale brown smithsonite on baryte. Specimen AZ018 formerly in the Keith Snell Collection. The field of view is 0.8 mm across. Photo John Chapman.

WITHERITE, $BaCO_3$

Witherite specimens from 'Anglezarke' are preserved in a few late-eighteenth and early-nineteenth century collections (Cotterell, 2022) but the absence of well crystallised hand specimens (as compared with the 'classic' localities in northern England) and abundance of unstable marcasite have combined to make the locality unpopular with twentieth-century collectors. Modern collections occasionally include a broken radiating mass (the most spectacular incarnation of witherite at the locality) but little else.

Historic specimens sometimes appear to have been mixed up with material from other locations (Cotterell, 2022). This study documents the distinguishing features and characteristic associations of witherite from Lead Mines Clough to support meaningful assessments of provenance.

Witherite occurs in three distinct assemblages on the specimens examined in this study. It commonly replaces earlier laminar baryte, it is the dominant vein mineral in later breccias and occurs as massive radiating vein fills in sandstone (the variety most commonly represented in collections).

Some witherite replacements are perfectly pseudomorphous and easily mistaken for massive baryte (see Figs 34 and 37). They can be distinguished by their rather greasy lustre and effervescence in dilute acid. Others consist of jumbled granular witherite with sphalerite and grey micritic debris and are easily mistaken for wall-rock clasts (see Fig. 36). Small areas with relict lamellar structures provide the only indication of the former presence of baryte in these cases.

Witherite veins without any obvious internal structure commonly surround brecciated fragments of less competent fine-grained wall-rocks and witherite-sphalerite replacements of baryte (see Fig. 36). Unlike the earlier replacement witherite, they contain no micritic debris and comparatively little primary sphalerite.

Most witherite specimens from Anglezarke in mineral collections, past and present, are white to pale grey or pale yellow-brown masses with a radiating structure on broken faces (Fig. 28). Further examples from the Harry Critchley and Keith Snell collections are illustrated in Cotterell (2022: figs 28, 29 and 30). The weathered outer surfaces are commonly coated in a patchy orange-brown crust, which may infiltrate a few millimetres into the specimen. It appears to have been produced by acidic solutions generated by the rapid destabilisation of iron sulphides in the dumps and, together with the coarse radiating structure, is a useful distinguishing characteristic of specimens from the site.

The crystal habits on the specimens examined in this study correspond closely with those described by Watt (1790) and with historic specimens figured by Cotterell (2022). Millimetre-size pseudohexagonal pyramids are common. The crystals are usually dull and opaque due to supergene alteration (Figs 29 and 30) but retain their

Figure 28. A typical broken fragment, 60 mm across, of massive radiating witherite (nodular on the reverse) with orange-brown iron staining. One of a number of similar fragments from a field box retained by Harry Critchley containing material awaiting further study. There are strong similarities with specimens in the Matthew Boulton Collection which have perhaps the best claim to be chosen as neotypes for witherite (Cotterell, 2022). Specimen AZ066 in the David Green Collection. Photo David Green.

lustre and transparency in well sealed cavities (Fig. 31). Less common crystal habits include thin pseudohexagonal plates (Fig. 32) and columnar crystals with flat terminations (Fig. 33).

There is no evidence that any of the veins in Lead Mines Clough ever produced the large (>2 cm) cyclic pseudohexagonal twins that are characteristic of classic witherite localities in northern England. Claimed specimens of this sort in old collections are almost certainly mislabelled.

UNIDENTIFIED MINERALS

Uncertainties in the identifications of some of the minerals listed in the foregoing text, including allophane, bindheimite, hydroniumjarosite, strontianite and various iron and manganese oxides and oxyhydroxides, are reflected in the subheadings, which are listed in lower case.

Tentative identifications, which proved incorrect when specimens were analysed, include dundasite (which is probably anglesite), fluorite (which is actually almandine) and hemimorphite (which is variously baryte, calcite and pyromorphite).

A few problematic phases remain to be characterised. A brown mineral, which preferentially overgrows and encrusts calcite and is insoluble in dilute acid may be zinc-sorbed goethite as EDS shows that it contains iron and minor zinc. Hexagonal scales on allophane (<0.1 mm across the flat faces) contain aluminium, silicon and zinc. They are probably fraipontite but are too thin for EDS to generate reliable indications of the elemental proportions. Sparse radiating clusters of a pale azure blue supergene mineral with partly oxidised chalcopyrite and galena in witherite veinstone are likely to be linarite. The crystals are less than 0.1 mm in length and would be difficult to characterise (and entirely destroyed) using the techniques available to this study. Sparse aggregates of a feathery turquoise-blue supergene copper zinc sulphate (possibly serpierite) and a green copper sulphate (probably brochantite) are also restricted to tiny crystals or thin crusts and require further study.

DISCUSSION

The first scientific description of witherite is based on specimens from the parish of Anglezarke in Lancashire (Cotterell, 2022). There are a number of trials on Anglezarke Moor (see Fig. 1) but the only important workings are on Old or Sun Vein in Lead Mines Clough (Price *et al*., 1963: p. 97), which is almost certainly the type locality.

The claim by de Rance (1873) that the original specimens were found at Stronstrey Bank is entirely unsupported. A line of bell pits extends southwest–northeast for about 200 m from SD 6218 1756 to SD 6232 1769 across the flank of Hurst Hill at the southern end of Stronstrey Bank. Witherite is recorded by Williamson (1963) and noted on a map produced during his research (Wigan College, n.d.). Abundant open-textured baryte and goethite, galena and traces of lead secondary minerals were observed on a field visit to this site in 2018 (Peter Briscoe, *personal communication*, 2022). Witherite is restricted to relict patches in baryte. The workings are small and shallow and there is no indication that they could have supplied witherite in the quantities that are known to have been traded in the late eighteenth century (Cotterell, 2022).

Witherite is also recorded along a line of bell pits which extend for 160 m southwest–northeast from SD 6338 1897 to SD 6349 1909 north of Dean Black Brook near Drinkwaters (Williamson, 1963; Wigan College, n.d.). At this locality open textured baryte occurs with galena and a little anglesite, cerussite and sulphur in a yellow clay gouge but witherite is rare.

The status of type locality increases the scientific importance of any site and makes a description of its minerals desirable. Price *et al.* (1963) provide a brief summary of the primary mineralisation at Lead Mines Clough but record no details of the supergene assemblage. The current entry in the online database Mindat (2022) includes only three species. The lack of a modern descriptive account is compounded by the impression generated by public collections which preserve occasional specimens of massive radiating witherite but little else (Cotterell, 2022).

Unfortunately, material gathered during Iain Williamson's research in the 1960s, which was preserved in the mineral collection at Wigan College, has been dispersed. The collections at a number of small local museums have suffered similar fates (Don Alderson, *personal communication*, 1995). The current research is based on the private collections of two former Russell Society members and shows the value of a systematic approach, detailed labels and careful documentation.

Primary Mineralisation

The primary mineralisation consists of two simple baryte dominated assemblages which bookend texturally complex witherite.

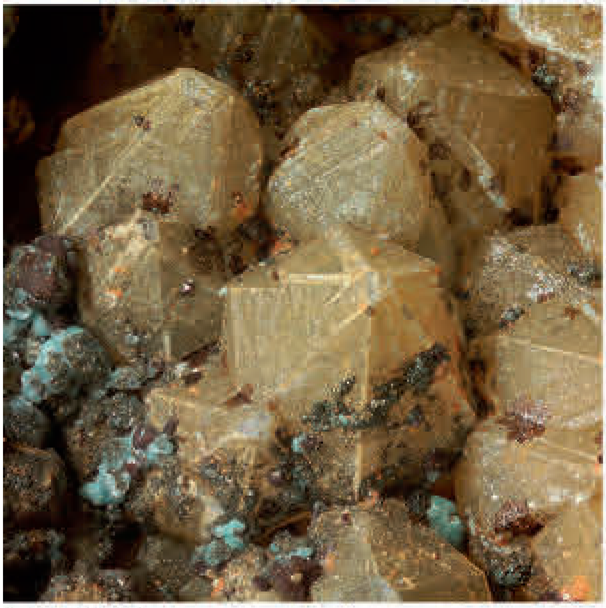
In the absence of *in situ* observations any assessment of the paragenesis can only be provisional, but those specimens which record more than one episode of primary mineralisation, together with the paragenetic overlaps between different specimens, are sufficient to establish a tentative chronology. The three major primary assemblages are:

1. Symmetrical vein fills containing compact laminar baryte, galena, minor chalcopyrite, sphalerite and iron sulphides, with a little witherite of uncertain affinity.

2. Witherite-dominated mineralisation with the following texturally distinct elements:

    a. witherite replacements of laminar baryte often with abundant sphalerite and minor late stage chalcopyrite;
    b. relatively pure witherite vein breccias with minor sphalerite and chalcopyrite in shale and siltstone;

▲ Figure 29



▲ Figure 30

▲ Figure 31

▼ Figure 32

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Figure 29. Translucent grey pseudohexagonal witherite. Specimen AZ019 formerly in the Keith Snell Collection. The field of view is 2.9 mm across. Photo John Chapman.

Figure 30. Opaque pseudohexagonal witherite pyramids, the edges picked out in a slightly lighter colour, with surface encrustations of aurichalcite, goethite and marcasite. Specimen AZ022 formerly in the Keith Snell Collection. The field of view is 2 mm across. Photo John Chapman.

Figure 31. Lustrous transparent pseudohexagonal witherite with prominent pyramid and small prism faces. Specimen AZ(HC)02 in the Harry Critchley Collection. The terminal crystal is 0.2 mm across. Photo John Chapman.

Figure 32. Platy pseudohexagonal witherite crystals up to 4.5 mm across coated in drusy baryte with the witherite revealed in the broken section at top-centre. The crystals are on the outside of a block of massive witherite coated in hydrozincite. Specimen AZ075 in the David Green Collection. Photo John Chapman.

c. massive radiating witherite vein fills with minor sphalerite and late-stage chalcopyrite in coarse sandstone.

3. Open-textured interlocking tabular baryte enclosing minor (possibly remnant) galena without other associated sulphides.

In addition to ubiquitous barium, the chemistry of these assemblages is:

1. Sulphate dominated with lead, minor copper, iron, zinc, carbonate and sulphide.
2. Carbonate dominated with abundant early zinc, probable iron[1], and minor late-stage copper sulphides.
3. Sulphate dominated.

They were deposited in the order 1–[2a–2b,2c]–3. The mineralogical and chemical differences between the major assemblages (1, 2 and 3) are substantial and suggest that they formed in separate events from fluids with distinct and different compositions.

Figure 33. Prismatic columnar pseudohexagonal witherite up to 5 mm in length coated in iron-stained drusy baryte with the underlying witherite revealed in the broken section at bottom-right. Specimen AZ076 in the David Green Collection. Photo John Chapman.

Early galena-baryte veins (assemblage 1) are widespread in the Anglezarke area (Price *et al.*, 1963; Wigan College, n.d.) and common around the periphery of the Askrigg Block. They are almost certainly distal elements of the Pennine suite (Dunham and Wilson, 1985).

Three texturally distinct witherite-dominated assemblages, labelled 2a, 2b and 2c, have been identified in this study (Figs 34–37). Witherite, often with abundant euhedral sphalerite (assemblage 2a), post-dates and commonly replaces baryte. It appears to have formed in an interaction between early baryte (assemblage 1) and zinc-rich carbonating fluids.

Vein breccias and massive radiating fracture fills (assemblages 2b and 2c) post-date the replacement witherite. Both consist of relatively pure witherite with a little sphalerite and late-stage chalcopyrite. There appears to be some lithological control: the breccias are restricted to the less competent siltstone and mudstone beds and the fracture fills to the thick competent sandstones. Although they do not overlap on any specimen examined in this study it seems likely that both crystallised rapidly from carbonating solutions in the same event. Simple gravitational collapse in a lode with a staircase geometry, perhaps supplemented by crystallisation pressure produced by supersaturated solutions, appears the most likely brecciation mechanism.

The late-stage open-textured interlocking tabular baryte (assemblage 3) is almost certainly the result of the alteration of barium carbonates in assemblage 2 by invasive sulphate-rich solutions. Such baryte[2] is very common at localities where witherite has been altered by

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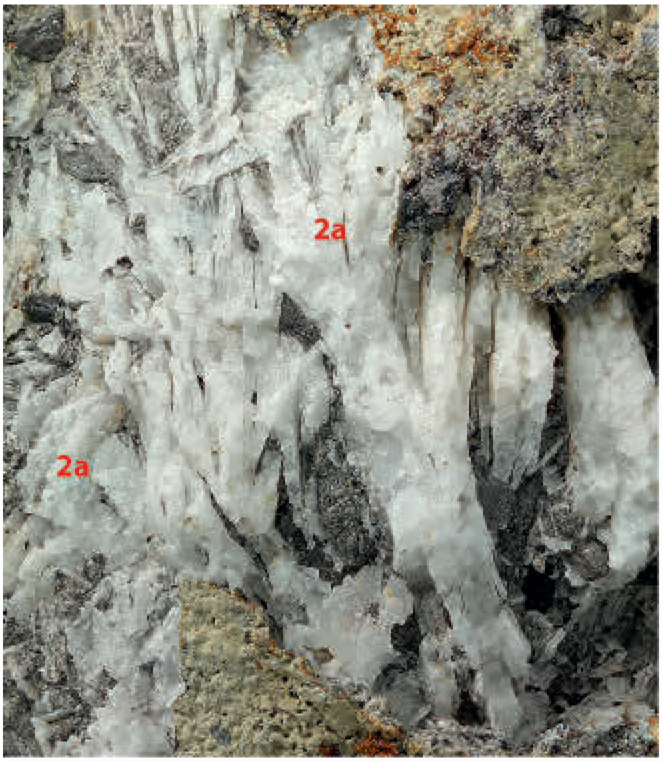
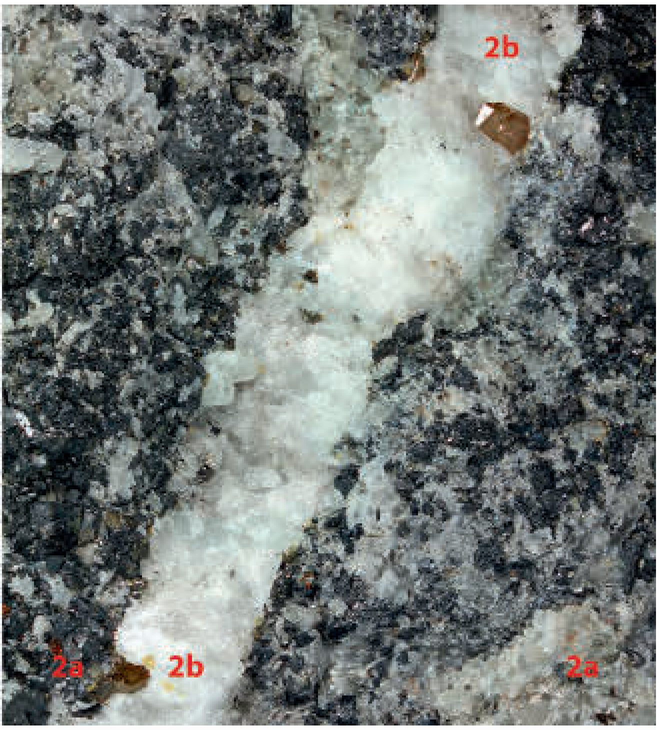
[1] Although iron sulphides are present on a number of the specimens it has not been possible to determine which assemblage the well crystallised marcasite belongs to with certainty.

[2] The term ‘secondary baryte’, which is commonly used to refer to open-textured late-stage baryte that has formed as a result of the alteration of witherite, is avoided here because of the potential for confusion with supergene baryte. It should also be noted that the presence of open-textured tabular baryte does not necessarily imply alteration from witherite, there are many examples of deposits where such baryte is abundant and there is no indication of the former presence of witherite.





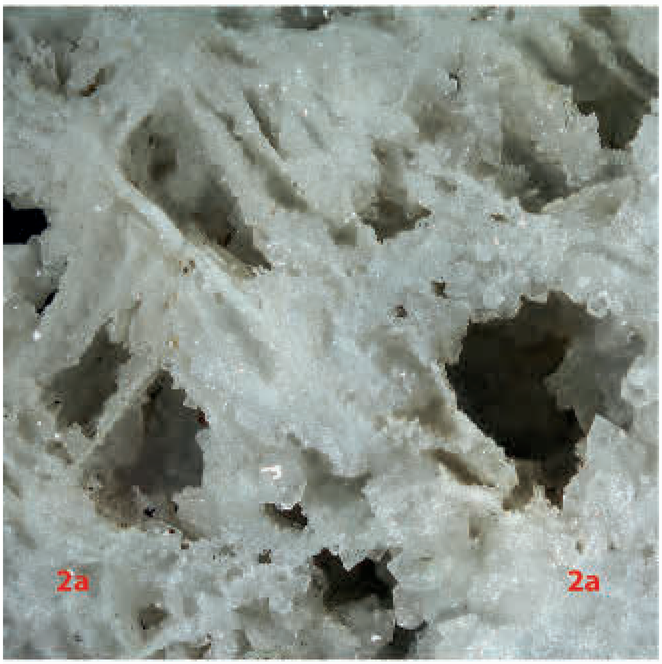


Figure 34 (*top left*). Granular witherite (assemblage 2a) replacing bladed baryte. Specimen AZ030 in the David Green Collection. The field of view is 10 mm across. Photo John Chapman.

Figure 35 (*bottom left*). Lamellar witherite (assemblage 2a) with cavities lined with pyramidal crystals and occasional crystalline curtains which may indicate the former positions of thin tabular baryte crystals. Specimen AZ(HC)02 in the Harry Critchley Collection. The field of view is 21 mm across. Photo John Chapman.

Figure 36 (*top right*). Breccia in which a vein of witherite with minor honey-yellow sphalerite and traces of chalcopyrite (assemblage 2b) cuts through an earlier witherite-sphalerite clast (assemblage 2a). The field of view is 6 mm across. Specimen AZ033 in the David Green Collection. Photo John Chapman.

Figure 37 (*bottom right*). Lamellar witherite replacing baryte (assemblage 2a) on the cheek of a vein in coarse sandstone overgrown by massive radiating witherite (assemblage 2c). Specimen No. 5500 in the Harry Critchley Collection. Photo David Green.

sulphate-bearing fluids in the Askrigg and Alston blocks (Dunham and Wilson, 1985; Dunham, 1990). The baryte occasionally encloses resistant galena from the earlier assemblages, but no other sulphides are present. Oxidising solutions and the access provided by the open texture has removed any chalcopyrite, marcasite and sphalerite, remnant or otherwise, that might have been present. The presence of pseudomorphs (see Fig. 10) shows that some specimens are direct replacements of earlier witherite. In other cases there is no indication of the former presence of the carbonate, and cylindrical tubes surrounded by baryte crystals suggest formation in open voids by fluid mixing.

In the absence of isotopic and fluid inclusion data any analysis of the origin of the mineralisation is purely speculative. The position of the deposit next to the major Brinscall Fault provides an obvious conduit for mineralising fluids. If the early galena-baryte veins are part of the widespread Pennine suite, the sulphate is likely to have a Lower Carboniferous evaporite source and the lead and other base-metals are probably derived from deeply buried metal-rich shales (Dunham and Wilson, 1985; Dunham, 1990). Deposition in the early Permian at a depth of at least 2 km from basinal metal-rich fluids channelled along the Brinscall Fault is likely. The origin of the carbonating solutions is less clear, the relative motion of fault-bounded blocks may have provided pathways for carbonate-rich karstic fluids or, in common with the sulphates, they may have a source in Lower Carboniferous evaporites. The later sulphate-rich fluids which altered the witherite back to baryte probably have their origin in calcium sulphate evaporites which are common in the basal Carboniferous and nearby Permian–Triassic sedimentary basins.

Witherite is a particular focus of this study and the witherite-dominated assemblage deserves comparison with other Pennine localities. Previous studies have highlighted the remarkable abundance of witherite in and around the Alston and Askrigg blocks (Dunham and Wilson, 1985; Dunham, 1990). It occurs at a wide range of stratigraphic horizons, from the base of the Carboniferous (at Murton Mine in Scordale) to the Westphalian (veins in the Durham Coalfield). Some deposits are associated with ‘centres of mineralisation’ (as at the Old Gang Mines in Swaledale) but many of the most important are peripheral (as at the Fallowfield and Settlingstones mines in Northumberland). Major changes in the witherite content of veins are associated with cross-cutting faults at some localities, but this is not usually the case. An association with coal has occasionally been remarked upon, but it is not universal. Some deposits are concentrated at particular horizons (as suggested by Watt, 1790 at Anglezarke), but most have an extensive vertical range. The observation that witherite at Anglezarke is replaced by baryte in depth (Watt, 1790; Price *et al.*, 1963) is unusual in a Pennine context. At most localities the reverse is true and witherite is replaced by open-textured baryte near to the surface.

Pennine witherite deposits are a heterogeneous group which do not fit into a single unifying template. Cotterell (2022) highlights the differences between witherite specimens from Anglezarke and other localities. This comparative analysis can be extended to the primary assemblage as a whole.

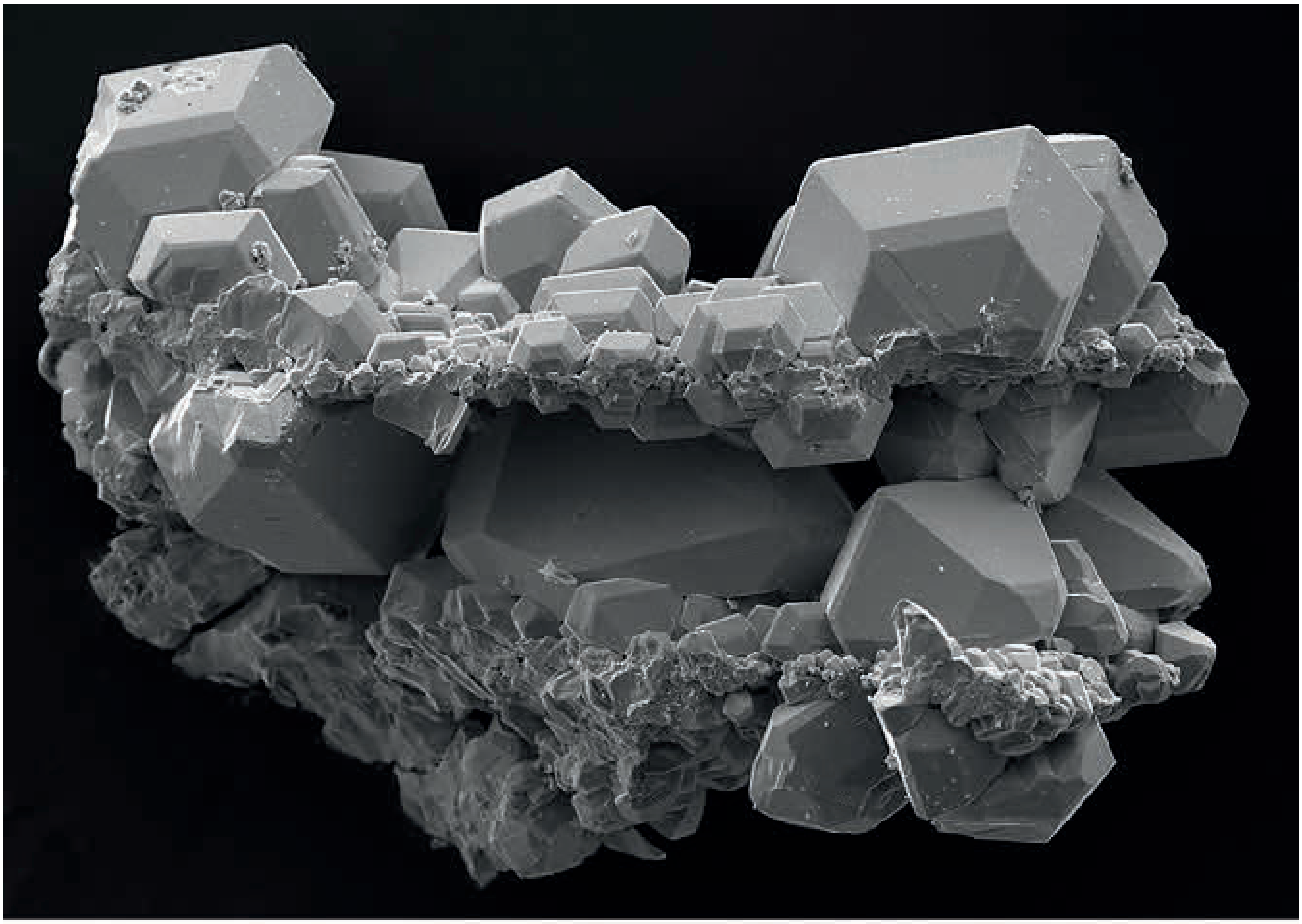
Pseudomorphous replacements of baryte by witherite or witherite and sphalerite are common (but not always obvious) at Lead Mines Clough. Witherite replacement of baryte has been documented at a few other Pennine deposits, but it is relatively unusual (Bridges and Green, 2006). Experimental studies suggest that rapid pseudomorphous replacement of baryte by witherite in carbonating solutions requires temperatures of more than 200ºC (Rendón-Angeles *et al.*, 2008). This exceeds the maximum temperatures recorded in fluid inclusion studies in the Askrigg Block (Dunham and Wilson, 1985). A lower temperature alteration over a much longer time period is more likely in the current context. Recent experiments have shown partial conversion of powdered baryte to witherite in potassium carbonate solution at 80ºC in a relatively short time scale (Steve Plant, *personal communication*, 2022).

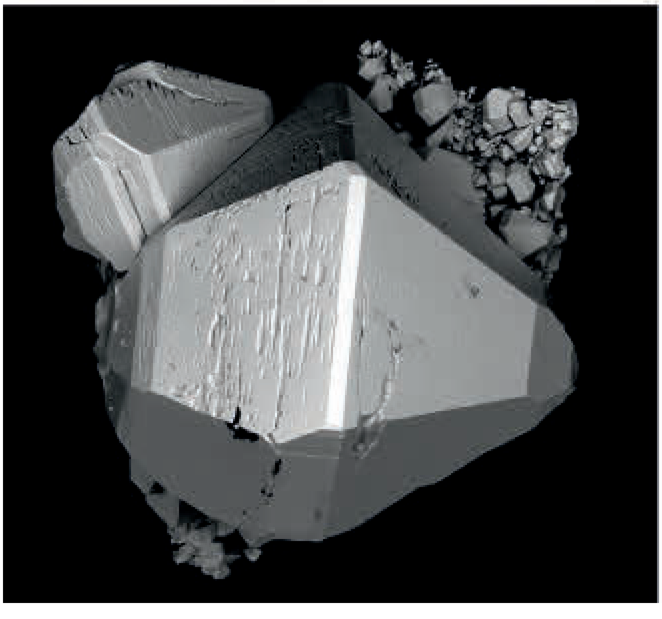
The association between sphalerite and witherite, particularly in the early replacement assemblage, has similarities to some localities (e.g. Nentsberry Haggs Mine on Alston Moor), but it is not a general feature of Pennine deposits. Witherite-dominated vein breccias are abundant at Lead Mines Clough, but not generally recorded at other Pennine deposits, possibly because thin veins in siltstone and mudstone wall-rocks were not tried at most Pennine lead mines. Massive compact witherite (assemblage 2c) is fairly common at Lead Mines Clough. The specimens are relatively coarse and do not develop into the perfect spheroidal aggregates that characterise some Pennine occurrences.

The surfaces of most witherite crystals from Lead Mines Clough have been subject to alteration by oxidising solutions. Rarely, well sealed cavities contain minute gemmy crystals, a few tens to a few hundred micrometres across. The individual crystals in these cavities are difficult to resolve, even under a stereomicroscope, due their small size and the general lack of contrast (see Fig. 31). Their true morphological variability can be appreciated in the images generated by scanning electron microscopy (Figs 38–40). Although they are somewhat pseudohexagonal, the crystals are not miniature versions of the cyclic twins that are well known at other Pennine deposits.

The only uncommon primary mineral recorded in this study is the barium calcium carbonate alstonite, which has been identified on two specimens from the same small block. Although it is well known from deposits in and around the Alston Block, this is the first record of alstonite from the mid-Pennines. It is not possible to assign a definite paragenetic position, but localised crystallisation from carbonating solutions (assemblage 2) appears likely.

Authigenic alteration of the coarse sandstone wall-rock has produced small volumes of jumbled euhedral





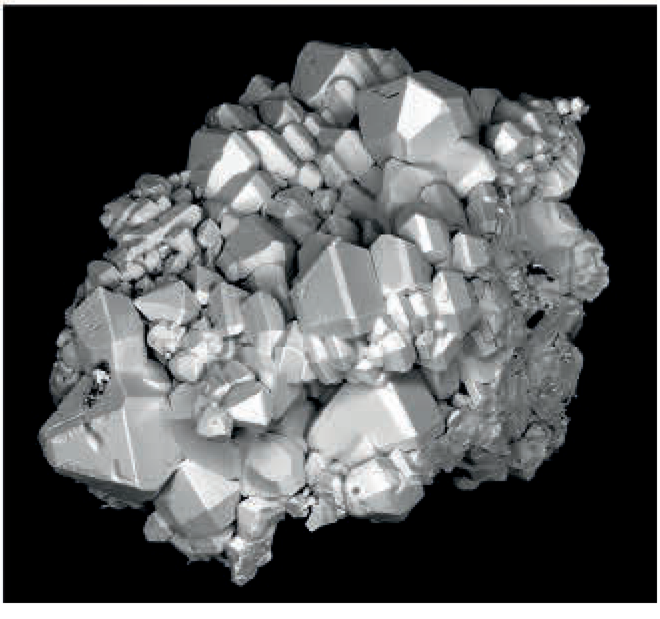


Figure 38 (*top*). Complex pseudohexagonal witherite crystals up to 200 μm across. The horizontal planar structures appear to be the last vestiges of tabular baryte, completely replaced by crystalline witherite. A fragment of specimen AZ(HC)02 in the Harry Critchley Collection. SEM image by Stephen Moreton.

Figure 39 (*bottom left*). Pseudohexagonal witherite with a blocky bipyramidal habit. A fragment of specimen AZ072 in the David Green Collection. The principal crystal is 400 μm across. SEM image by Jeremy Poole.

Figure 40 (*bottom right*). Part of a witherite 'curtain', 800 μm across. A fragment of specimen AZ072 in the David Green Collection. SEM image by Jeremy Poole.

quartz in the matrix of some specimens. This assemblage does not appear to be associated with the vein mineralisation, but is mentioned in passing as, in addition to almandine, it contains other unidentified phases and deserves further study.

Pennine witherite also deserves further study. Trace element, fluid inclusion and isotopic analyses would be helpful in determining its affinities. Any model at a regional scale would have to address its abundance in and around the Askrigg and Alston Blocks and absence in the Derbyshire dome. If such a project was considered worthwhile, the authors would be happy to contribute well provenanced specimens from Lead Mines Clough.

As a speculative aside, it is interesting to note that the primary mineralisation at Lead Mines Clough is at a relatively high level in a thick basinal Carboniferous sequence. It is not a large deposit [though the dismissive assessment of its economic potential in Wilson *et al.* (1922: p. 63) is not justified], but in view of its location close to a large structural fault, which appears to have acted as a conduit for mineralising solutions, it does not seem impossible that larger deposits might be concealed more deeply within the sequence.

Supergene Minerals

Although much of the mined deposit was above the water table, there is no evidence that the supergene assemblage at Lead Mines Clough was of any economic importance[3]. The compact vein fills and fine-grained wall-rocks provided a reasonably effective barrier to percolating fluids and the primary sulphides are relatively unoxidised. Supergene minerals are, nonetheless, widespread and include most of the species that would be expected in a Pennine lead-zinc-copper deposit.

Lead-bearing supergene species include anglesite, bindheimite, cerussite, leadhillite, pyromorphite and possibly linarite. This short list is quite diverse for a Pennine locality. It probably reflects the differing micro-environments that developed in a deposit containing chemically reactive (witherite-dominated) and passive (baryte-dominated) assemblages in relatively inert siliceous wall-rock.

Anglesite and cerussite are the most widespread lead-bearing species, but neither could be described as common. Anglesite occurs with sulphur in cavities and fractures in galena and is very occasionally present in the surrounding matrix. This association almost certainly reflects oxidation in solutions containing Fe^{3+} ions generated by the oxidation of iron sulphides (Williams, 1990: p. 44). Acidic solutions generated by the rapid destabilisation of iron sulphides may also explain the rarity of cerussite (Bridges, 2015).

Pyromorphite is restricted to cavities in open-textured baryte without any associated carbonate (which would stabilise cerussite). This association has similarities to other Pennine occurrences where pyromorphite occurs in baryte dominated veins in siliceous wall-rocks (Tindle, 2008; Green and Tindle, 2022) and to the bell pits on nearby Stronstrey Bank, where traces of pyromorphite occur in gossanous baryte-rich veinstone.

Minute pseudohexagonal leadhillite crystals overgrow anglesite and are overgrown by cerussite in cavities and fractures in and around oxidising galena. This is consistent with an oxidation sequence which begins at a low $p(CO_2)$ in a well sealed micro-environment where anglesite is stable. As alteration allows more access to invasive solutions the $p(CO_2)$ increases and leadhillite and then cerussite become stable (see Briscoe *et al.*, 2021). Leadhillite is rare in the Pennine orefields. It has been reported as colourless to white hexagonal prisms up to 1 mm across in oxidised galena-baryte matrix from Closehouse Mine, Lunedale (Young *et al.*, 1994) and as clusters of hexagonal platy crystals associated with galena and limonite from Middlegrove Vein near Killhope (Bridges and Young, 1998). There do not appear to be any previous records in the mid-Pennines.

Zinc carbonates are widespread and relatively abundant at Lead Mines Clough. Smithsonite is common in cavities in witherite veinstone. Hydrozincite is abundant as crusts on and around sphalerite-bearing material in the spoil heaps. Their distribution is controlled by the carbonate ion activity (Williams, 1990; Bridges, 2015). Smithsonite forms over an extended period at the relatively high $p(CO_2)$ values that develop within oxidation zones whereas hydrozincite forms rapidly in near-surface environments at $p(CO_2)$ values close to atmospheric (Fig. 41).

The absence of the common zinc silicate hemimorphite is intriguing as the wall-rock is siliceous and at least one supergene silicate (allophane) has been identified. Material tentatively identified as hemimorphite has proved to be either pyromorphite (Keith Snell Collection), botryoidal supergene calcite or drusy baryte (Harry Critchley Collection).

The presence of secondary marcasite on smithsonite in cavities in witherite shows there was a localised reversion to reducing conditions at a late stage in the alteration of the deposit. Much of the supergene marcasite has subsequently oxidised, generating thin brown coatings on the surrounding minerals and perhaps contributing iron oxyhydroxides to the orange-brown crusts which surround witherite in the mine spoil. The dominance of marcasite over pyrite provides evidence that the supergene solutions were relatively acidic as marcasite only crystallises at a $pH<5$ (Kitchaev and Ceder, 2016).

Further investigation of the rather nondescript iron oxyhydroxide and manganese oxide coatings which are

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[3] By contrast, Wilson *et al.* (1922: p. 63) record that at one of the trials near White Coppice lead ore was principally in the form of anglesite.

Figure 41. White etched smithsonite, partly coated with a crudely dendritic iron oxyhydroxide, on the outer surface of a block of witherite veinstone coated in bright blue-white hydrozincite. Specimen AZ075 in the David Green Collection. The field of view is 3.6 mm across. Photo John Chapman.

abundant at Lead Mines Clough would be worthwhile. The only manganese oxide that can be claimed with any degree of confidence in this study is todorokite. The other species remain to be properly characterised. The same comment applies to the iron oxyhydroxide coatings, particularly the zinc-bearing iron oxyhydroxide crusts on calcite, which are quite variable in colour and may not all be limonitic goethite (Cornell and Schwertmann, 2003).

Chalcopyrite is reasonably common in the witherite dominated primary assemblage. It is commonly replaced by goethite, but distinct supergene copper minerals are rare. They are restricted to isolated spots of malachite and aurichalcite and traces of copper-bearing hydrozincite. It seems likely that the iron in chalcopyrite oxidised to Fe^{3+} and precipitated as goethite (which is extremely insoluble in oxidising environments), while the copper ions were carried away in solution.

CONCLUSION

This study of the minerals of Lead Mines Clough is based on the collections of two former Russell Society members. It considerably increases the number of species recorded from the site. Witherite is of particular interest as research published in this journal shows that the first scientific description of the species was based on specimens from Anglezarke (Cotterell, 2022). The workings in Lead Mines Clough are the only credible source of witherite in the quantities that were traded in the late eighteenth century and they are almost certainly the type locality.

The mineralisation is hosted by fractures in the footwall of the Brinscall Fault and it is probably a distal component of the low-temperature early Permian Pennine suite. There are three distinct primary assemblages. Simple symmetrical baryte-galena veins are followed by complex witherite-dominated mineralisation which has been altered by sulphate-bearing solutions to form open-textured baryte.

Oxidation in relatively acidic conditions has produced a variety of supergene minerals including aragonite, anglesite, aurichalcite, baryte, cerussite, hydrozincite, iron oxyhydroxides, leadhillite, malachite, manganese oxides, pyromorphite, smithsonite and sulphur. Most of these minerals are reported from Lead Mines Clough for the first time, the record of leadhillite appears to be the first in the mid-Pennines and that of pyromorphite may be the first in Lancashire.

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should note that this is an entirely collection-based study; permission to collect at the locality must be obtained through the appropriate channels.

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LEAD-BEARING APATITE-SUPERGROUP MINERALS FROM LEADHILLS–WANLOCKHEAD, SOUTHERN SCOTLAND

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Analyses of lead-bearing apatite-supergroup minerals from the Leadhills–Wanlockhead mining district in southern Scotland are reported. The visual distinctions used by collectors to label specimens (well crystallised, colourful and blocky = pyromorphite; pale coloured and massive to acicular = phosphohedyphane; brown and botryoidal = vanadinite) are useful guides but not entirely reliable. A complete and continuous solid solution exists between end-member pyromorphite and end-member phosphohedyphane, but there is a gap between pyromorphite–phosphohedyphane and vanadinite. Limited data suggest that the solid solution between phosphohedyphane and hydroxylapatite is also incomplete. There are strong similarities in the compositions of lead-bearing apatite-supergroup minerals at Leadhills–Wanlockhead and Whitwell Quarry in Derbyshire. At both localities, calcium and phosphate replace lead and vanadate in vanadinite in a coupled homovalent substitution which can be written: $^{M(1)}\mathbf{Pb}^{2+} + 2^{T}\mathbf{VO}_4^{3-} \leftrightarrow {}^{M(1)}\mathbf{Ca}^{2+} + 2^{T}\mathbf{PO}_4^{3-}$**.**

INTRODUCTION

The Leadhills–Wanlockhead mining district straddles the border between the former counties of Lanarkshire (now South Lanarkshire) and Dumfries (now Dumfries and Galloway) in southern Scotland. The geology is described by Floyd *et al*. (2002) and summarised by Floyd (2003). The primary mineralisation is hosted by fractures in poorly sorted sandstones of the Upper Ordovician Portpatrick Formation. Extensive and deep oxidation has produced a complex assemblage of lead-, zinc- and copper-bearing secondary minerals for which the deposits are famous (Heddle, 1901a,b; Brown, 1919, 1927; Gillanders, 1991; Livingstone, 2002; Tindle, 2008).

Lead-bearing apatite-supergroup minerals are an important component of the supergene assemblage and they have been studied since the beginning of the nineteenth century. Pyromorphite is widespread and abundant and there are significant local occurrences of hydroxylapatite, phosphohedyphane and vanadinite (Temple, 1954). These minerals have structural formulae that can be written:

$$M(1)_2M(2)_3(TO_4)_3X.$$

The $M(1)$ and $M(2)$ cation sites are crystallographically distinct. They may contain the same element [as in pyromorphite, ideally $Pb_5(PO_4)_3Cl$] or different elements [as in phosphohedyphane, ideally $Ca_2Pb_3(PO_4)_3Cl$]. Species defining M-site cations include Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^{+}, Ce^{3+}, La^{3+}, Y^{3+} and Bi^{3+}. Species defining T-site anions include arsenate, borate, phosphate, silicate, sulphate and vanadate. Carbonate is widely recognised as an important T-site anion (Pan and Fleet, 2002) but it is never dominant and all carbonate-apatite species names have been discredited (Pasero *et al*., 2010). Charge-balancing X anions occupy flexible channel sites parallel to the c-axis: the most common are F^{-}, OH^{-} or Cl^{-}, but vacancies, water, carbonate, oxide and sulphide may also be present.

The compositions of fifteen lead-apatite crystal fragments (each distinguished by a three digit number prefixed by the letter P) are reported in this investigation. Locality details and short descriptions are provided in Table 1.

ANALYSIS

Millimetre-size fragments were detached from the specimens, embedded in epoxy resin, and ground and polished to produce a ‘survey slide’ suitable for microprobe analysis. Analyses were made by wavelength-dispersive X-ray spectrometry at an accelerating voltage of 20 kV and beam current of 20 nA with a 10 µm defocused beam and matrix-appropriate standards. Aluminium, arsenic, barium, calcium, chlorine, cobalt, copper, iron, lead, magnesium, manganese, phosphorus, strontium, titanium, silicon, sulphur, vanadium and zinc were sought.

It is impractical to include a complete tabulation of wt% oxides for 100 analyses, each with eighteen individual determinations plus the totals and correction for halogen content, in a publication such as this. A spreadsheet is available as ‘deposited material’ on the Russell Society website. Although homogeneous looking crystal fragments were selected, there is significant variation in composition in some of the datasets. A summary of the species identified in each of the grains is provided in Table 2.

ANALYSIS	DESCRIPTION
P208	Brown spheroidal aggregates labelled ‘vanadinite from Leadhills’; almost certainly from High Pirn Mine, Whyte’s Cleuch, Wanlockhead. Manchester Museum Collection (accession number N08579).
P224	Pale brown spheroidal ‘vanadinite’ from Glencrieff Mine, Whyte’s Cleuch, Wanlockhead. Richard Bell Collection.
P225	Brown spheroidal ‘vanadinite’ aggregates on white crustose matrix from Belton Grain Vein, Whyte’s Cleuch, Wanlockhead. Peter Briscoe Collection with an old Andrew Seager Collection label.
P226	White crustose matrix on the specimen from Belton Grain Vein, Whyte’s Cleuch, Wanlockhead sampled as P225. Peter Briscoe Collection with an old Andrew Seager Collection label.
P227	Botryoidal greenish material from New Cove Mine, Whyte’s Cleuch, Wanlockhead. Tim Neall Collection (collection number NCVA52).
P228	Botryoidal pale brown material from New Cove Mine, Whyte’s Cleuch, Wanlockhead. Tim Neall Collection (collection number NCVA52).
P229	A layered massive white crustose phase with a conspicuously low density from New Cove Mine, Whyte’s Cleuch, Wanlockhead. Tim Neall Collection (collection number NCV20).
P230	Botryoidal white material from High Pirn Mine, Whyte’s Cleuch, Wanlockhead Tim Neall Collection (collection number HPM14).
P231	Botryoidal pale green material from New Cove Mine, Whyte’s Cleuch, Wanlockhead. Tim Neall Collection (collection number NCVA67).
P232	Pale greenish buff material from Lady Anne Hopetoun Shaft [NS 880 142], near the intersection of Brow and Hopeful veins, Leadhills. Tim Neall Collection (collection number LAH9993).
P233	Pale buff material from Lady Anne Hopetoun Shaft [NS 880 142], near the intersection of Brow and Hopeful veins, Leadhills. Tim Neall Collection (collection number NCVJ200).
P234	Pale greenish botryoidal material almost certainly from High Pirn Mine, Whyte’s Cleuch, Wanlockhead. Manchester Museum Collection (accession number N05822).
P235	Well formed yellow-green crystals from Glengonnar Shaft [NS 882 138], Leadhills. David Green Collection (collected 1987).
P254	Matrix to pale brown vanadinite from Glencrieff Mine, Whyte’s Cleuch, Wanlockhead, also sampled as P224. Richard Bell Collection.
P255	Well formed bright yellow crystals from a shaft dump on Horner’s Vein [NS 882 138], Leadhills. David Green Collection (collected 1987).

Table 1. List of the studied specimens with a description of the material sampled for analysis by wavelength-dispersive X-ray spectrometry. The information is summarised from notes made in 2006, it has not been possible to re-examine any of the specimens recently.

ANALYSIS	RESULT
P208	Vanadinite
P224	Phosphohedyphane Pyromorphite Vanadinite
P225	Phosphohedyphane Vanadinite
P226	Phosphohedyphane
P227	Phosphohedyphane
P228	Vanadinite
P229	Hydroxylapatite
P230	Hydroxylapatite Phosphohedyphane
P231	Phosphohedyphane
P232	Phosphohedyphane
P233	Phosphohedyphane
P234	Phosphohedyphane Pyromorphite
P235	Pyromorphite
P254	Phosphohedyphane
P255	Phosphohedyphane Pyromorphite

Table 2. Minerals identified by wavelength-dispersive X-ray spectrometry in the analysed fragments (see Table 1 for descriptions). These detailed results are supported by XRD but this technique is not suitable for species-level identifications in all cases.

Calcium, chlorine, lead and phosphorus are present in almost all of the analyses. Vanadium is a major constituent of vanadinite but otherwise present in either minor-element or trace-element quantities (conventionally, trace elements are present at <0.1 wt% and minor elements between 0.1 and 1 wt%). Arsenic and silicon are typically present in minor-element quantities, the maximum concentration of the former being 1.4 wt% As_2O_5 and the latter 2.1 wt% SiO_2.

The maximum barium, cobalt, iron, magnesium, manganese, sodium, strontium, sulphur and titanium concentrations are all <0.2 wt% with means $\leqslant$0.02 wt%. These elements have no individual effect on the empirical formulae (to one decimal place) and are dealt with as trace elements. Slightly more zinc is present but with a maximum of 0.19 wt% ZnO and a mean of 0.04 wt% this is also considered to be a trace element. Copper is generally present in trace-element quantities (<0.1 wt%) but reaches more than 2 wt% CuO in two analyses of phosphohedyphane from Lady Anne Hopetoun Shaft. These anomalous copper contents are due to contamination by ‘chrysocolla’ (see Green and Tindle, 2022) and they are excluded from the discussion. There is evidence that four further datasets (two ‘vanadinite’ and two ‘phosphohedyphane’) are fine-scale intergrowths with other minerals and they are also excluded.

A plot of calcium–lead versus phosphate–vanadate ratios for the remaining compositions (Fig. 1) shows that they can be divided into four groups:

1. End-member pyromorphite.
2. Calcium-rich pyromorphite and phosphohedyphane.
3. Calcium- and phosphate-rich vanadinite.
4. Hydroxylapatite (in two subgroups, one close to end-member composition, the other lead and chloride rich).

There are minor differences in the ways that the empirical formulae were calculated and each of the groups is examined separately. The datasets in groups one and three are 'well behaved', with no evidence of the presence of undetected elements, and the calculations follow the recommendations of Pasero *et al*. (2010); group two includes some datasets which require correction for undetected elements (mostly carbonate which cannot be detected by electron-beam techniques); group four requires correction for undetected carbonate and structural vacancies. The methods used to correct the group two and four formulae are described by Green and Tindle (2022).

Group One

Nine analyses of a yellow-green crystal fragment from Glengonnar Shaft, Leadhills (P235) are close to end-member pyromorphite. The mean empirical formula, calculated on the basis of nine atoms per formula unit [using method 4(a) of Pasero *et al*. (2010)] and rounded to two decimal places, is:

$$\mathrm{Pb_{4.82}Ca_{0.12}}M^{2+}_{0.02}\mathrm{[(PO_4)_{2.84},(AsO_4)_{0.02},(SiO_4)_{0.09}]Cl_{1.09}},$$

where M^{2+} is included as a placeholder for divalent cations and sodium.

The sum of divalent cations at the *M*(1) and *M*(2) sites is 4.96±0.06; the *T*-site anions sum to 2.95±0.05; and chloride in the channel site is 1.09±0.04. Calcium substitution is minor and there are no other significant *M*-site substitutions. *T*-site occupancies are all within ±3% of 3.0, which Pasero *et al*. (2010) use as a barometer of reliable data. The *T*-site contains minor silicate and arsenate, but negligible vanadate. The *X*-site occupancy is a little higher than ideal, but slight non-stoichiometry at this site is not unusual.

There are no obvious patterns in the trace-element data, and the charge imbalance of −0.11±0.24 does not give cause for concern.

Group Two

Ten fragments have mean empirical formulae that lie within the phosphohedyphane composition field (although there is often significant zonation and some of the fifty or so individual analyses which contribute to

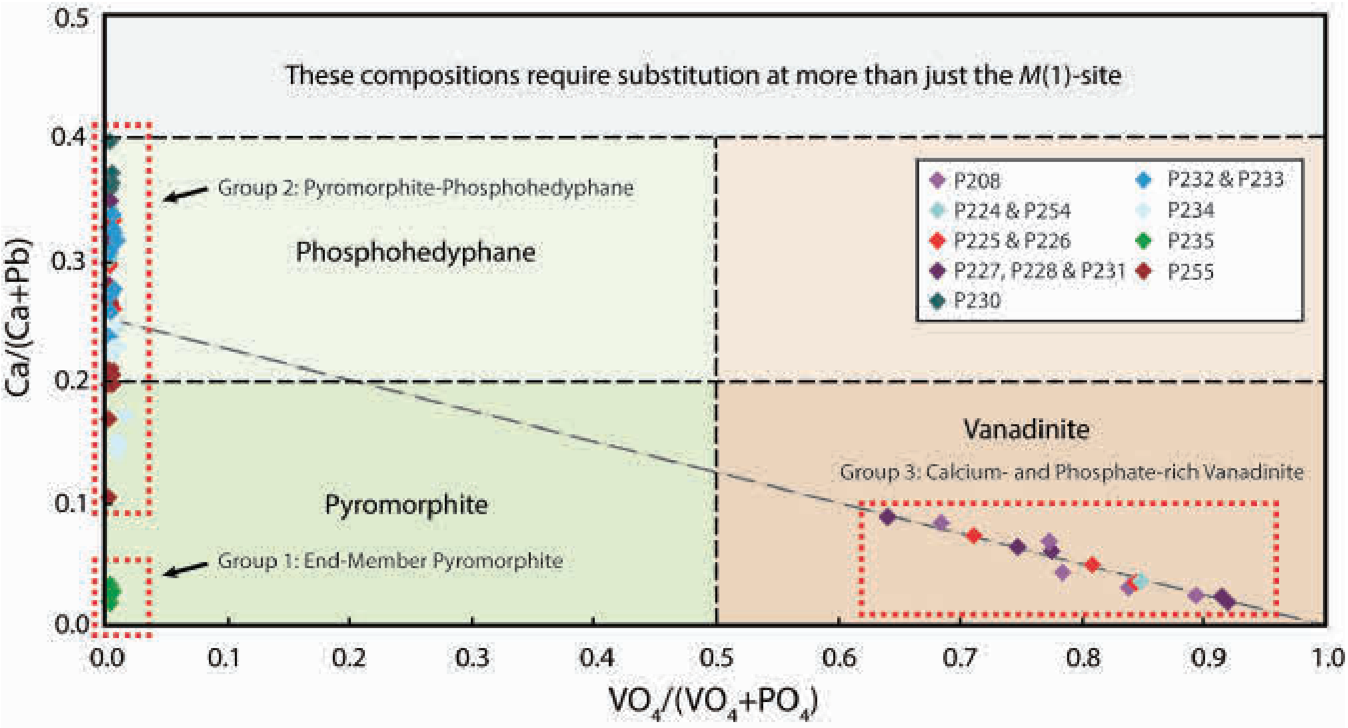

Figure 1. Analyses of phosphohedyphane, pyromorphite and vanadinite (coloured diamonds) from Leadhills–Wanlockhead. Species boundaries are indicated by black dashed lines. Compositions at the bottom-left and bottom-right corners correspond to end-member pyromorphite and vanadinite, ideally $\mathrm{Pb_5(PO_4)_3Cl}$ and $\mathrm{Pb_5(VO_4)_3Cl}$, respectively. The point at the top-left of the phosphohedyphane field is end-member phosphohedyphane, ideally $\mathrm{Ca_2Pb_3(PO_4)_3Cl}$. The analyses are divided into three groups, enclosed in dashed red boxes on the diagram, each of which is discussed separately in the accompanying text. A fourth group (hydroxylapatite) is above the top of the diagram and is not shown. Localities are: P208 and P230, High Pirn Mine; P224 and P254, Glencrieff Mine; P225 and P226, Belton Grain Vein; P227, P228 and P231, New Cove Mine; P232 and P233, Lady Anne Hopetoun Shaft; P234, 'Leadhills' assumed to be High Pirn Mine; P255, Horner's Vein.

the averages are calcium-rich pyromorphite). Mean empirical formulae, excluding any intergrown vanadinite or hydroxylapatite, are listed in Table 3.

Although it is not necessary in every case, for consistency all of the formulae listed in Table 3 have been subject to the same correction procedure. The most extreme corrections (which are necessary to produce credible charge balanced formulae) involve additions of 0.25 divalent *M*-site cations per formula unit, or 0.24 *T*-site carbonate and 0.36 *X*-site hydroxyl groups per formula unit. The adjustments (all of which are small) are discussed in more detail in Green and Tindle (2022).

The mean group-two minor-element content at the *M*- and *T*-sites is greater than in groups one, three and four. Unlike groups one and three, the *X*-site chloride content is typically less than 1.0.

Group Three

Fourteen analyses of four separate fragments of vanadinite fall within the vanadinite composition field. The mean empirical formula calculated on the basis of nine atoms per formula unit [method 4(a) of Pasero *et al*. (2010)] and rounded to two decimal places is:

$$\mathrm{Pb_{4.66}Ca_{0.24}}M^{2+}_{0.02}\mathrm{[(VO_4)_{2.36},(PO_4)_{0.52},(AsO_4)_{0.04},(SiO_4)_{0.03}]Cl_{1.10}},$$

where M^{2+} is included as a placeholder for divalent cations and sodium.

The sum of divalent cations at the *M*(1) and *M*(2) sites is 4.94±0.09; the *T*-site anions sum to 2.96±0.07; and chlorine in the channel site is 1.10±0.08. Calcium substitution at the *M*-sites varies from a little less than 5 to a little more than 22 mol%. Phosphate substitution at the *T*-site, varies from 7.8 to 32.2 mol%. There is a clear relationship between the two, which is discussed in the next section of the article. The *T*-site occupancies are all within ±3% of 3.0, which Pasero *et al*. (2010) use as a barometer of reliable data. Silicate substitution at the *T*-site averages less than 1 mol% and mean arsenate is 1.7 mol%. The *X*-site occupancy is a little higher than ideal, but slight non-stoichiometry at this site is not unusual.

There are no obvious patterns in the trace-element data and the charge imbalance of −0.13±0.33 does not give cause for concern.

Group Four

The hydroxylapatite data can be divided into two subgroups, one close to end-member composition and the other lead and chloride rich. Neither is included in Figure 1 as the compositions are beyond the range of Ca/(Ca+Pb) values that can be plotted.

The first subgroup of five analyses of a white crustose mineral from New Cove Vein (P229) are all close to end-member hydroxylapatite. The mean empirical formula, calculated following the procedure outlined in Green and Tindle (2022), is:

$$\mathrm{Pb_{0.17}Ca_{4.60}}M^{2+}_{0.03}\square_{0.20}\mathrm{[(PO_4)_{2.55},(SiO_4)_{0.03}(CO_3)_{0.41}](Cl_{0.01},OH_{0.99})},$$

where the open-square symbol, □, represents a structural vacancy. The sum of divalent cations at the *M*(1) and *M*(2) sites is 5.01±0.02; the *T*-site anions sum to 3.00±0.02; and chlorine plus hydroxyl and the channel site are 1.00. This is very close to ideal apatite-supergroup stoichiometry (but readers should note that small adjustments have been made at every structural site).

Two analyses, in which hydroxylapatite with significant *M*-site lead is intergrown with phosphohedyphane (P230), are discussed in the next section of the article.

ANALYSIS	MEAN EMPIRICAL FORMULA
P225	$\mathrm{Pb_{3.34}Ca_{1.60}}M^{2+}_{0.06}\mathrm{[(PO_4)_{2.76},(AsO_4)_{0.04}(SiO_4)_{0.35}(CO_3)_{0.15}](OH_{0.12},Cl_{0.88})}$
P226	$\mathrm{Pb_{3.33}Ca_{1.40}}M^{2+}_{0.05}\mathrm{[(PO_4)_{2.72},(AsO_4)_{0.03}(SiO_4)_{0.08}(CO_3)_{0.12}](OH_{0.13},Cl_{0.87})}$
P227	$\mathrm{Pb_{3.42}Ca_{1.50}}M^{2+}_{0.07}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.70},(AsO_4)_{0.07}(SiO_4)_{0.07}(CO_3)_{0.24}](OH_{0.19},Cl_{0.81})}$
P230	$\mathrm{Pb_{3.10}Ca_{1.85}}M^{2+}_{0.05}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.90},(AsO_4)_{0.01}(SiO_4)_{0.02}(CO_3)_{0.06}](OH_{0.16},Cl_{0.84})}$
P231	$\mathrm{Pb_{3.34}Ca_{1.62}}M^{2+}_{0.04}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.82},(AsO_4)_{0.01}(SiO_4)_{0.07}(CO_3)_{0.06}](OH_{0.06},Cl_{0.94})}$
P232	$\mathrm{Pb_{3.33}Ca_{1.60}}M^{2+}_{0.04}\mathrm{[(VO_4)_{0.02},(PO_4)_{2.64},(SiO_4)_{0.12}(CO_3)_{0.24}](OH_{0.36},Cl_{0.64})}$
P233	$\mathrm{Pb_{3.73}Ca_{1.25}}M^{2+}_{0.06}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.43},(AsO_4)_{0.02}(SiO_4)_{0.35}(CO_3)_{0.15}](OH_{0.32},Cl_{0.68})}$
P234	$\mathrm{Pb_{3.87}Ca_{0.89}}M^{2+}_{0.02}M^{2+}_{0.20}\mathrm{[(VO_4)_{0.02},(PO_4)_{2.86},(SiO_4)_{0.03}]Cl_{1.07}}$
P254	$\mathrm{Pb_{3.24}Ca_{1.47}}M^{2+}_{0.04}M^{2+}_{0.25}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.97},(SiO_4)_{0.02}]Cl_{0.99}}$
P255	$\mathrm{Pb_{3.79}Ca_{1.00}}M^{2+}_{0.07}M^{2+}_{0.17}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.80},(SiO_4)_{0.12}]Cl_{0.96}}$

Table 3. Mean empirical formulae for phosphohedyphane in the samples listed in Table 1. The means only include the compositions that lie within group two in Figure 1. Intergrown vanadinite and hydroxylapatite (which are present in sample numbers P224, P225 and P230) are excluded. Small additive corrections follow the procedure outlined in Green and Tindle (2022).

DISCUSSION

The approach used in calculating the empirical formula for groups two and four is described by Green and Tindle (2022) and it is not considered further here. This discussion concentrates on the compositions of lead-apatites from Leadhills–Wanlockhead and makes comparisons, where appropriate, with Whitwell Quarry in Derbyshire (Briscoe *et al.*, 2021).

Despite its international importance (e.g. Livingstone, 2002; Starkey, 2022), there is no comprehensive modern review of the minerals of the Leadhills–Wanlockhead district. This account relies on a baseline study, conducted in the early 1950s, which summarises nineteenth and early twentieth century investigations and includes the only detailed topographic survey of the mine dumps (Temple, 1954).

The results summarised in Table 2 show that there is fine-scale chemical zonation in many homogeneous looking crystal fragments. The visual distinctions used by collectors to label specimens (well crystallised, colourful and blocky = pyromorphite; pale coloured and massive to acicular = phosphohedyphane; brown and botryoidal = vanadinite) are not entirely reliable. Phosphohedyphane and pyromorphite; phosphohedyphane and hydroxylapatite; and pyromorphite-phosphohedyphane and vanadinite commonly occur as fine-scale intergrowths.

There are strong similarities between the major-element compositions of the lead-apatites at Leadhills–Wanlockhead and Whitwell Quarry, particularly with respect to the chemical substitutions in vanadinite (cf. Briscoe *et al.*, 2021: p. 115). The principal difference between the two localities is in the abundance of pyromorphite at Leadhills–Wanlockhead and its almost complete absence at Whitwell Quarry. This is probably a reflection of the host lithologies. The reactive dolostone wall-rock at Whitwell Quarry appears to have maintained a uniformly high calcium ion activity during supergene oxidation, strongly favouring phosphohedyphane. The siliceous sequence at Leadhills–Wanlockhead did not act in the same way.

In a survey of the supergene mineralisation at Leadhills–Wanlockhead, Temple (1954: p. 83) records:

> "Pyromorphite, together with cerussite, is the commonest secondary mineral in the district, and is present on the majority of the old dumps, particularly good localities being the High Pirn Mine on the Belton Grain Vein, and the shallow workings on the Sarrowcole Vein. The pyromorphite occurs in two forms, one having hexagonal crystals and being either green, yellow, or orange in colour, generally formed in small cavities, and associated with galena and cerussite, whilst the second form is usually massive, varying in colour from black to white, and often pseudomorphously replacing galena or cerussite. The latter variety may crystallize in small radiating aggregates of hexagonal crystals, white to yellow-green in colour, numerous examples occurring on the dumps in Whyte's Cleuch".

Analyses revealed chemical and structural differences between the two types of pyromorphite and Temple (1954: p. 88) concluded:

> "This brief survey of the pyromorphites therefore reveals that the group is divisible on a structural basis, into two groups, one characterised by hexagonal crystal form, the other commonly massive but also present as hexagonal crystals. The structural difference between the two groups is attributed to the presence of calcium in the second group, whilst minor structural variations are due to several other elements, of which arsenic and vanadium are predominant".

> "A complete series between pyromorphite ... and calcium rich pyromorphite probably exists. The name polysphaerite ... has priority in the nomenclature of the calcium rich variety, and it is suggested that the structural differences between the two groups allow the retention of the name polysphaerite[1] as the end member of a series in which calcium substitutes for lead in pyromorphite".

This is supported by more recent research at the National Museum of Scotland which also indicates that 'pyromorphite' is divided into two types, one mostly massive and containing between about 7 and 9.5 wt% CaO and the other well crystallised and containing very little calcium (Livingstone, 2002: p. 123).

The data published in this article is in agreement with previous studies, though the range of calcium substitution in pyromorphite–phosphohedyphane is greater than indicated by either Temple (1954) or Livingstone (2002). The maximum of 10.6 wt% CaO from New Cove Mine is very close to end-member phosphohedyphane. Most of the sixty or so analyses of pyromorphite–phosphohedyphane contain between 5 and 9 wt% CaO (Temple's second group), but there are enough data points outside this region to show that there is a complete and continuous solid solution between the two minerals at the scales examined in this study (Fig. 1).

Well formed yellow-green crystals from Glengonnar Shaft (P235) are very close to end-member pyromorphite but well crystallised yellow crystals from Horner's Vein near Leadhills (P255) have strong compositional zonation. The corrected empirical formulae for the most lead- and calcium-rich compositions from this locality are:

$$\mathrm{Pb_{4.24}Ca_{0.49}}M^{2+}_{0.20}\mathrm{[(VO_4)_{0.01},(PO_4)_{2.79},(AsO_4)_{0.13},(SiO_4)_{0.03}]Cl_{1.05}},\text{ and}$$

$$\mathrm{Pb_{3.55}Ca_{1.36}}M^{2+}_{0.15}\mathrm{[(VO_4)_{0.00},(PO_4)_{2.82},(AsO_4)_{0.04},(SiO_4)_{0.15}]Cl_{0.92}}.$$

The first of these (with $\mathrm{Pb_{4.24}Ca_{0.49}}$) is well within the pyromorphite field and the second (with $\mathrm{Pb_{3.55}Ca_{1.36}}$) is well within the phosphohedyphane field (Fig. 1). Colour

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[1] The polysphaerite and calcium-rich pyromorphite would now be described as phosphohedyphane, which was characterised as a new species in the first decade of this century (Kampf *et al.*, 2006).

and form, therefore, do not always reliably differentiate pyromorphite from phosphohedyphane.

The same observation extends to topographic schemes which assume that phosphohedyphane is restricted to localities in and around Whyte's Cleuch and pyromorphite dominates elsewhere. In addition to the zoned pyromorphite–phosphohedyphane from Horner's Vein (which is near Leadhills), two specimens from Lady Anne Hopetoun Shaft on the Leadhills side of the county boundary (P232 and P233) are well within the phosphohedyphane composition field with mean empirical formulae:

$Pb_{3.33}Ca_{1.60}M^{2+}_{0.04}[(VO_4)_{0.02},(PO_4)_{2.64},(SiO_4)_{0.12},(CO_3)_{0.24}](OH_{0.36},Cl_{0.64})$, and

$Pb_{3.73}Ca_{1.25}M^{2+}_{0.06}[(VO_4)_{0.01},(PO_4)_{2.43},(AsO_4)_{0.02},(SiO_4)_{0.35},(CO_3)_{0.15}](OH_{0.32},Cl_{0.68})$.

These examples, together with a record from Broad Law northeast of Leadhills (Temple, 1954: p. 86), and the authors' unpublished EDS data show that phosphohedyphane is widely distributed at Leadhills–Wanlockhead.

Measured minor-element and trace-element M^{2+}, with a global mean of 0.052 atoms per formula unit, is more concentrated in phosphohedyphane than pyromorphite, vanadinite or hydroxylapatite. Silicate, with a mean of 0.085 atoms per formula unit, is also present in significantly higher concentrations. Intermediate pyromorphite–phosphohedyphane tends to contain more minor and trace elements than compositions close to end-member pyromorphite or phosphohedyphane.

The distribution of minor and trace *M*-site cations is surprisingly random at the scales investigated in this study (typically about a hundred micrometres between data points). There are few obvious correlations within or between any of the datasets. It might be expected, for example, that there would be some relationship between the concentrations of the group-two elements calcium and strontium, but there is no evidence that this is the case. A similar observation was made in a detailed study of lead-apatites from Germany (Markl *et al.*, 2014) where large and seemingly random variations in trace-element concentrations are also noted. The reasons for these variations remain to be explored: exsolution textures have been reported in lead-apatites and repeated dissolution-precipitation is undoubtedly involved in the formation of some crystals.

Most of the vanadinite specimens analysed in this study contain a significant amount of calcium. Calcium substitution in vanadate-bearing lead-apatites from Wanlockhead has been investigated since the nineteenth century. Temple (1954: p. 97) notes:

> "A calcium bearing variety of vanadinite was described from Wanlockhead by Frenzel (1881, in Dana, 1951, p.897), 3.25% calcium oxide being present",

and goes on to discuss a calcium-bearing pyromorphite–vanadinite intermediate which was given the name 'collieite' (Collie, 1889; Cotterell *et al.*, 2022).

Livingstone (1994b) records "an unexpected coupled substitution of Ca and P" in vanadinite from Wanlockhead. This detailed account appears to be the first report of this type of coupled substitution in vanadinite from any worldwide locality.

Plotting formula calcium (x) against formula phosphate (y) for the vanadinite in this study reveals a linear relationship (Fig. 2) which can be expressed:

$$y = 0.49x - 0.01.$$

The errors in the slope and intercept are 0.49±0.03 and −0.01±0.02, respectively. This can be expressed as a coupled homovalent substitution in which calcium and phosphate replace lead and vanadate:

$$^{M(1)}Pb^{2+} + 2^{T}VO_4^{3-} \leftrightarrow {}^{M(1)}Ca^{2+} + 2^{T}PO_4^{3-}.$$

The calcium–lead exchange is assigned to the *M*(1) site because lead partitions into the larger *M*(2) site in the apatite structure.

A statistically identical relationship is reported in vanadinite from Whitwell Quarry by Briscoe *et al.* (2021: pp. 115–116). The fact that the same substitution has been identified in vanadinite from both of these localities reinforces the similarities in their supergene geochemistry. A minor discrepancy between the details of the analysis published by Livingstone (1994b) and this study is discussed in the Appendix.

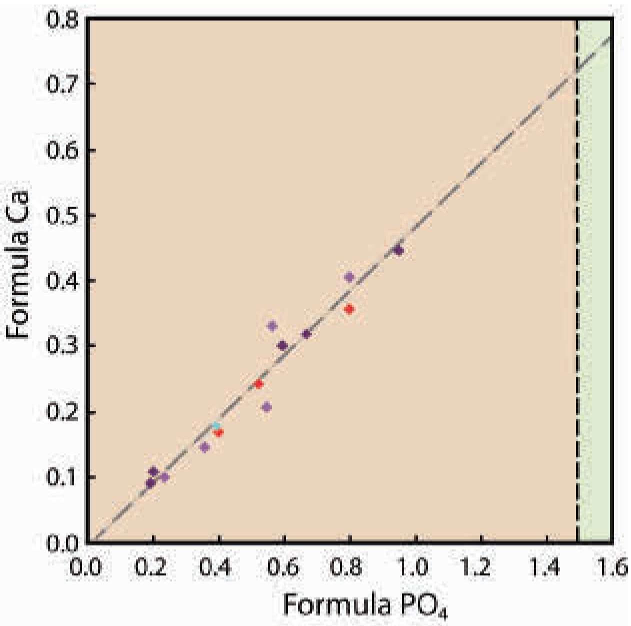

Figure 2. Plot of formula calcium versus formula phosphate for fourteen analyses of vanadinite from Wanlockhead (see Fig. 1 for localities). There is a clear linear trend ($r^2 = 0.95$) with a slope of 0.49±0.03.

The simple whole-number ratio involved in the substitution, in which one *M*(1)-site calcium ion and two *T*-site phosphate groups replace one *M*(1)-site lead ion and two *T*-site vanadate groups, is one of the most interesting results of these analyses. It deserves further investigation.

The absence of any compositions along the substitution vector with ${}^{T}PO_4^{3-}$ >2 atoms per formula unit (if the Whitwell data are also included) provides evidence of a 'miscibility gap' in the chemical system[2], an interpretation which is reinforced by the observation that vanadinite is closely associated (and occasionally intergrown) with phosphohedyphane and lead-rich hydroxylapatite, neither of which contain more than a trace of vanadate, at both Leadhills–Wanlockhead and Whitwell Quarry (Livingstone, 1994a,b; Briscoe *et al.*, 2021).

The Leadhills–Wanlockhead district is known for lead-rich hydroxylapatite (Temple, 1954, 1956: Tindle, 2008). A dirty white crust from New Cove Mine (P229) has a mean empirical formula:

$$Ca_{4.60}Pb_{0.17}M^{2+}_{0.03}\square_{0.20}[(PO_4)_{2.55},(CO_3)_{0.41},(SiO_4)_{0.03}](Cl_{0.01},OH_{0.99}).$$

It contains negligible *X*-site chloride[3] and very little *M*-site lead, and is much closer to end-member composition than any previously reported lead-bearing hydroxylapatite from the area (Livingstone, 1994a,b). The presence of such a phase was predicted by Temple (1954: p. 89):

> "The association of polysphaerite with apatite may indicate that the ultimate end of the calcium for lead substitution in pyromorphite is a calcium phosphate, the chloride group having been lost".

Such material may be more common than this single set of analyses suggests. Most of the lead-rich hydroxylapatite previously reported from Leadhills–Wanlockhead is as white crusts on spectacular specimens of vanadinite (which must have formed in relatively lead-rich microenvironments). Dirty white crusts without closely associated lead-apatites, such as specimen P229, may have been overlooked.

Lead-rich hydroxylapatite is intimately intergrown with phosphohedyphane in a white crust (with associated vanadinite) on specimen P230. Phosphohedyphane on this specimen contains up to 10.6 wt% CaO, which is very close to the theoretical maximum (with *M*(1) fully occupied by calcium). The formulae of the intergrown hydroxylapatite crystallites are:

$$Ca_{3.26}Pb_{1.57}M^{2+}_{0.03}\square_{0.14}[(PO_4)_{2.69},(SiO_4)_{0.02}(CO_3)_{0.28}](Cl_{0.30},OH_{0.70}), \text{ and}$$

$$Ca_{3.00}Pb_{1.81}M^{2+}_{0.02}\square_{0.17}[(PO_4)_{2.62},(SiO_4)_{0.02}(CO_3)_{0.35}](Cl_{0.49},OH_{0.51}).$$

The most plumbian of these compositions contains more lead than any previously reported hydroxylapatite from Leadhills–Wanlockhead.

A general comparison of formula calcium with formula chlorine across the whole dataset (hydroxylapatite, phosphohedyphane, pyromorphite and vanadinite) reveals that compositions with less calcium generally contain more chloride but without any well defined numerical relationship.

The arsenate content of the lead-apatites (which reaches a maximum of 1.4 wt% As_2O_5 in vanadinite from Belton Grain Vein) is generally in the minor to trace element range, reinforcing the general impression that arsenic is relatively unimportant in the supergene system at Leadhills–Wanlockhead (Temple, 1954: pp. 90–96). Arsenate concentrations are elevated in the area around Whyte's Cleuch where Temple (1954: p. 94) records:

> "Mimetite, $Pb_5(AsO_4)_3Cl$, has been recorded from two localities the High Pirn Mine on the Belton Grain Vein, and the dumps by the side of the road near the Glencrieff mine. A specimen (551.7) from the former locality exhibits barrel shaped crystals of mimetite (var. campylite), associated with pyromorphite and plumbogummite".

In this context it should be noted that the X-ray powder diffraction patterns of calcium- and vanadate-rich pyromorphite (collieite) can be mistaken for mimetite (Cotterell *et al.*, 2022), and that Temple's description of specimen 557.1 has strong similarities with material from the Caldbeck Fells. More detailed studies of the lead-apatites from this area are needed to establish the paragenetic position of any arsenate-bearing phases. They should ideally include analyses by electron-beam techniques as well as X-ray diffractometry.

CONCLUSIONS

The principal conclusions of this study of the compositions of lead-bearing apatite-supergroup minerals from Leadhills–Wanlockhead are conveniently summarised as a list:

1. The distinctions used by collectors to label lead-bearing apatite-supergroup minerals from Leadhills–Wanlockhead (well crystallised, colourful and blocky = pyromorphite; pale coloured and massive to acicular = phosphohedyphane; brown and botryoidal = vanadinite) are not entirely reliable.
2. Homogeneous looking crystal fragments are commonly zoned and may be intergrowths of several different species.
3. There is a complete and continuous solid solution between end-member phosphohedyphane and end-member pyromorphite.

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[2] It should be noted that the solid solutions between end-member mimetite, pyromorphite and vanadinite (in the absence of calcium) are complete and continuous (Baker, 1966). The gap appears in the phosphohedyphane-pyromorphite-vanadinite fields in low-temperature supergene assemblages if and only if calcium is introduced into the system (Briscoe *et al.*, 2021).

[3] Fluorine was not sought in these analyses, but it was not detected in the earlier energy-dispersive X-ray analysis and is not thought to be a major *X*-site substituent in this specimen.

4. Phosphohedyphane cannot be identified solely on the basis of its appearance (white to pale green and massive) or locality (Whyte's Cleuch).
5. Phosphohedyphane (particularly the compositions with intermediate amounts of calcium) typically contains more minor and trace elements than other lead-apatites.
6. There is a compositional gap between vanadate-bearing lead-apatites (mostly vanadinite) and phosphate-dominated lead apatites (pyromorphite–phosphohedyphane).
7. Calcium and phosphate replace lead and vanadate in vanadinite in a coupled substitution which can be expressed ${}^{M(1)}\mathrm{Pb}^{2+} + 2{}^{T}\mathrm{VO}_4^{3-} \leftrightarrow {}^{M(1)}\mathrm{Ca}^{2+} + 2{}^{T}\mathrm{PO}_4^{3-}$.
8. There is a broadly antithetical relationship between calcium (and calculated carbonate) and chlorine.
9. There is a compositional gap between phosphohedyphane and lead-rich hydroxylapatite.
10. Arsenate is generally present in minor to trace element quantities in lead-apatites from Leadhills−Wanlockhead and appears to be relatively unimportant in the supergene system.

There are strong similarities between the supergene assemblages at Leadhills−Wanlockhead and Whitwell Quarry in Derbyshire. The quantitatively identical coupled substitution of calcium and phosphate for lead and vanadate in vanadinite from both localities is intriguing. The principal difference between the two sites is the relative abundance of pyromorphite at Leadhills−Wanlockhead and its comparative absence at Whitwell Quarry. This is probably a reflection of differences in the wall-rock lithologies.

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APPENDIX

Livingstone (1994b) reported "an average Ca/P ratio of 0.36" in an analysis of the coupled calcium and phosphate for lead and vanadate substitution in vanadinite from Wanlockhead, a value which is significantly less than the 0.49±0.03 determined by linear regression of the data published in this article.

The empirical formulae reported in Livingstone (1994b) are calculated on the basis of twelve equivalent oxygen atoms and are not directly comparable with this study or with general apatite-supergroup formulae, which are calculated on the basis of thirteen equivalent oxygen atoms or nine atoms per formula unit (see Green and Tindle, 2022). Reworking the data on the basis of nine atoms per formula unit (the method used in this study, and recommended by Pasero *et al.*, 2010) yields a mean empirical formula:

$$Pb_{5.00}Ca_{0.16}[(VO_4)_{2.54},(PO_4)_{0.41}]Cl_{0.90},$$

for the eighteen analyses listed in Livingstone (1994b). The *M*-site cation sum is 5.16±0.10; the *T*-site anion sum is 2.95±0.10; and *X*-site chlorine is 0.90±0.04. There is a small but significant over-determination of *M*-site cations in these analyses.

Regression of the reworked data reveals a linear relationship between formula calcium and formula phosphate ($r^2 = 0.94$) with a slope of 0.40±0.03 and an intercept of 0.00±0.01. This is higher than the reported value of 0.36, but significantly lower than the regressions for the coupled substitutions in vanadinite from Whitwell Quarry (Briscoe *et al.*, 2021) and Wanlockhead (this study) of 0.46±0.03 and 0.49±0.03, respectively.

The measured calcium substitution in phosphohedyphane in the current dataset (Fig. 1) lies within expected bounds of up to almost exactly two atoms per formula unit (Kampf *et al.*, 2006), and this suggests that the calcium determinations are correct or very nearly so. The data give no reason to doubt the phosphate values. A possible reason for the difference between the two sets of regression statistics is a small systematic under-determination (*c.* 25%) of calcium in Livingstone's datasets.

TECHNICAL NOTE:
CALCULATING THE EMPIRICAL FORMULAE OF LEAD-BEARING APATITE-SUPERGROUP MINERALS

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A method of calculating the empirical formulae of lead-bearing apatite-supergroup minerals is outlined. The likely levels of random and systematic error are assessed, the possibility of miscalculation due to mixtures or inclusions evaluated, and formulae based on incomplete datasets are subjected to small corrections. Charge balance is used as a basis for the corrections and their efficacy is assessed by comparison with ideal apatite-supergroup stoichiometries. The importance of explicitly considering structural vacancies (written using the open-square symbol, □) in some calculations is emphasised. There is no universally reliable approach to calculating apatite-supergroup formulae from the data generated by electron-beam techniques. Techniques for correcting the local charge imbalance produced by *T*-site carbonate are compared.

INTRODUCTION

Empirical formulae are widely used to express the composition of minerals. They communicate the relationships between chemical components more clearly than the tables of oxide sums generated by electron-beam analysis but require thoughtful computation.

This article considers methods of calculating the empirical formulae of lead-bearing apatite-supergroup minerals using datasets on hydroxylapatite, pyromorphite and phosphohedyphane from Leadhills–Wanlockhead in southern Scotland (Green and Tindle, 2022a). It describes the adjustments that were needed, in a minority of cases, to produce credible and consistent formulae. The general approach is outlined in the body of the text and illustrative calculations are included as an Appendix.

Reliable lead-apatite formulae are challenging to calculate from the oxide totals produced by electron-beam techniques for two principal reasons: the range of potential substitution is surprisingly complex, and datasets are commonly incomplete (Eusden *et al*., 2002; Markl *et al*., 2014; Ondrejka *et al*., 2020). The techniques for calculating formulae described in Pasero *et al*. (2010: p. 173) are almost always sufficient for the common lead-apatites (mimetite, pyromorphite and vanadinite), but additional adjustments are often required for phosphohedyphane and lead-rich hydroxylapatite.

The likely level of systematic error in the datasets examined in this article are estimated using analyses of grains of end-member composition. If datasets return stoichiometries that differ from ideal values by significantly more than the estimated systematic errors, and oxide sums are less than 100 wt%, it is assumed that the dataset is incomplete. A simple ionic model of charge balance is used to make corrections. If they produce a stoichiometry that is close to ideal they are considered reasonable. If they do not produce a sensible stoichiometry the possibility that inclusions, intergrowths or vacancies are present is considered.

The procedures outlined in this article have been used to calculate the empirical formulae of lead-bearing apatite-supergroup minerals in recent descriptions of the supergene assemblages at Whitwell Quarry in Derbyshire (Briscoe *et al*., 2021), Leadhills–Wanlockhead in southern Scotland (Green and Tindle, 2022a) and Coldstones Quarry in North Yorkshire (Green and Tindle, 2022b). They are not without objection: statistical analyses of quantities calculated on differing bases are not strictly reliable; charge balance can be challenged as a basis for additive corrections; and the *X*-site in apatite supergroup minerals may be more flexible than the limits imposed here. The adjustments are, nonetheless, considered worthwhile as there has been little exploration of methods to mitigate problems associated with undetected elements (particularly *T*-site carbonate ions) in discussions of the composition of lead-bearing apatite-supergroup minerals.

In an ideal scenario the calculations would be a prelude to further experimentation. The examples discussed in this article are an attempt to get the best from old datasets where additional experimentation is no longer possible.

APATITE-SUPERGROUP CHEMISTRY

The most comprehensive recent discussion of the apatite supergroup is due to Pasero *et al*. (2010). Apatite-supergroup minerals have a flexible structure with a general formula that can be written:

$$M(1)_2M(2)_3(TO_4)_3X.$$

There are two crystallographically distinct *M*-sites: *M*(1) and *M*(2). Species defining *M*-site cations include Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^{+}, Ce^{3+}, La^{3+}, Y^{3+} and Bi^{3+}. Species defining *T*-site anions include arsenate, borate, phosphate, silicate, sulphate and vanadate. Carbonate is widely recognised as an important *T*-site anion (e.g. Ivanova *et al*., 2001; Pan and Fleet, 2002) but it is never dominant and all carbonate-apatite species names have been discredited (Burke, 2008; Pasero *et al*., 2010). The charge-balancing *X*-site anions, which occupy channels parallel to the *c*-axis, are commonly F^{-}, OH^{-} or Cl^{-}. Vacancies, neutral water and divalent oxide, carbonate and sulphide ions may also occupy this relatively flexible site. In apatite-supergroup minerals with relatively small *X*-site anions, notably fluorapatite, the *X*-site occupancy can significantly exceed 1.0 (Chakhmouradian *et al*., 2017). Carbonate substitution is described as A-type if it replaces *X*-site anions and B-type if it replaces *T*-site anions.

Barium, chromium, cobalt, copper, rare-earth elements, nickel, silver, thorium, uranium and zinc may be present in small but significant quantities in lead-apatites (Temple, 1954; Markl *et al*., 2014; Ondrejka *et al*., 2020; Briscoe *et al*., 2021; Green and Tindle, 2022a). The difficulty of gathering complete, dependable and consistent datasets in a mineral group that can include half of the elements in the periodic table is considerable. Routine determinations by electron microprobe do not usually measure more than about twenty individual elements and they are unable to provide reliable analyses of light elements such as boron, carbon, lithium and oxygen.

EMPIRICAL FORMULAE

Empirical formulae are calculated using one of two procedures in the earth sciences. Petrologists working with common rock forming minerals (mostly silicates) typically follow the method outlined in Deer *et al*. (2013), which bases formulae on a particular number of equivalent oxygen atoms. Mineralogists and crystallographers commonly use structure refinements to look for reliable site sums and base calculations on an appropriate number of atoms per formula unit. Three different methods of reducing electron-beam data on the basis of site sums are outlined in Pasero *et al*. (2010: p. 173) and a fourth is used by Chakhmouradian *et al*. (2017) and Ondrejka *et al*. (2020). They do not produce identical formulae. The procedural variability is illustrated using a suitable (well behaved) apatite-supergroup dataset in the first set of calculations in the Appendix.

For minerals or mineral groups in which substitutions are limited, matrix corrections are straightforward, and no light elements are present, formulae accurate to one or two decimal places can be calculated from datasets generated by electron-beam techniques with relative ease. If forty or fifty different elements may be present and matrix corrections are challenging, as with lead-bearing members of the apatite supergroup (e.g. Markl *et al*., 2014), it would be unusual, even with modern instrumentation, to obtain complete and accurate empirical formulae.

Problems associated with incomplete *X*-site data are highlighted in a recent article which shows that standard calculations can result in discrepancies of up to 4% in the coefficients of empirical formulae as a result of undetected hydroxyl (Ketcham, 2015). It is important to note that the molar proportions of the elements in the formulae calculated by Ketcham are correct; the coefficients are not comparable because they are not normalised on the same basis. This problem is noted in Pasero *et al*. (2010) which recommends the addition of a suitable amount of calculated H_2O if total (F + Cl) is significantly less than 1.0[1].

Modern studies avoid the problems associated with undetected elements in flexible *X*-sites by excluding them from calculations if (F + Cl) is significantly different from 1.0. Markl *et al*. (2014) circumvent the problem by calculating lead-apatite formulae on the basis of eight atoms per formula unit at the *M*- and *T*-sites [method 4.1(b) of Pasero *et al*. (2010)]. The tacit assumption is that the *M*- and *T*-site sums are complete and reliable, but the presence of significant undetected *T*-site carbonate in phosphohedyphane and lead-bearing hydroxylapatite (Livingstone 1994a,b; Ondrejka *et al*., 2020) shows that it is not always defensible.

Ondrejka *et al*. (2020) circumvent the '*T*-site carbonate problem' by basing calculations on five *M*-site atoms per formula unit. The *T*-site is backfilled with carbonate and the *X*-site with hydroxyl to produce an ideal stoichiometry. This approach is reliant on complete and accurate *M*-site sums. It does not allow for the possible presence of *M*-site vacancies which may partially charge compensate for carbonate substitution at the *T*-site (Ivanova *et al*., 2001; Biagioni *et al*., 2019). The resultant formulae often have a significant charge imbalance.

CALCULATION AND CORRECTION

Although procedures have been established to assign elements to particular structural sites and assess the presence of vacancies in a few mineral groups (e.g. Zolotarev *et al*., 2007), there is no general method for correcting empirical formulae based on incomplete datasets. If the structural chemistry of the phase in question is unknown there is little that can be done except to test for simple whole-number elemental ratios and check the oxide totals for the possibility of undetected elements. It may be tempting to assign 'water by difference' if there is reasonable evidence that no other

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[1] The possibility that the *X*-site occupancy might exceed 1.0 is not discussed in this context in Pasero *et al*. (2010), although formulae with significantly higher occupancies (up to 2.0) occasionally appear (e.g. Livingstone, 1994a). A short summary with a particular focus on fluorapatite is included in Chakhmouradian *et al*. (2017: p. 189).

light elements are present, but calculations based on 'residuals' are not usually reliable.

If minerals have been identified to group level, as is the case with the lead-apatites described here (where identifications were confirmed by X-ray powder diffraction), additional constraints can be placed on the calculations. The formulae should be consistent with the general structural formula (and therefore stoichiometry) of the mineral group, and if a simple ionic model is appropriate the charges on the anionic and cationic constituents should balance to within reasonable errors. If either of these conditions is not met a knowledge of probable substitutions, with the constraint that any additions should not increase the corrected oxide sum to more than 100 wt%, can be used as a basis for small additive corrections.

Before corrections are made it is important to consider other potential sources of error. Possible reasons for divergences between calculated formulae and true compositions include:

1. Random errors, particularly in elements that are present at low concentrations.
2. Calibration problems if there is a slight error in the composition of the reference material being used.
3. Volatilisation problems due to ion migration if the mineral is beam-sensitive.
4. Spectral interferences.
5. Specimen specific issues resulting from poor preparation of grain mounts (e.g. due to surface roughness), inclusions, heterogeneities or intergrowths.
6. Matrix-related calculation errors.
7. Incorrect assignment of ionic speciation (or oxidation number).
8. Genuinely non-stoichiometric formulae.
9. Undetected elements.
10. The presence of structural vacancies (written explicitly in chemical formulae using the open square symbol, □).

Although small amounts of undetected elements are likely to be a problem in many lead-apatite datasets, especially in specimens that have crystallised in chemically complex environments, it is unwise to appeal to the last two possibilities before attempts have been made to characterise the others.

Random counting errors are inconsequential in modern microprobe analysis, but pseudo-random systematic errors, which result from surface roughness or other heterogeneities, can be significant (Shirley and Jarochowska, 2022). They are minimised by careful selection, preparation and inspection of grain mounts. Defocusing the electron beam minimises volatilisation and ion migration, and neither sodium nor fluorine (the two principal offenders) are present in significant quantities in any of the current datasets. Spectral interferences such as the well known P on F peak problem can be important in some apatite-supergroup analyses but are of no concern for the major elements listed here. Matrix corrections are problematic in lead-apatites (e.g. Markl *et al*., 2014) but are minimised by using matrix-appropriate standards in the current datasets.

Issues associated with ionic speciation include the possibility that phosphorus might not be entirely present as PO_4^{3-} (another possibility being HPO_4^{2-}) and silicon may not be entirely SiO_4^{4-}. They are difficult to assess without evidence from complimentary analytical techniques such as vibrational spectroscopy, but there is no evidence of unusual ionic speciation in the supergene lead-apatites from Leadhills–Wanlockhead. *X*-site occupancies can increase up to at least 1.2 and possibly more in fluorapatite (Mason *et al*., 2009; Chakhmouradian *et al*., 2017), but there is no evidence that lead-apatites (which typically contain large charge balancing chloride ions) are highly non-stoichiometric.

Reasonable bounds to systematic errors resulting from matrix correction problems and random and pseudo-random errors can be estimated on the basis of statistical analyses of data gathered from well prepared grains of near end-member composition from geochemically simple supergene environments. Such analyses suggest that a deviation of more than about 0.1 atoms per formula unit at any structural site[2] is unlikely to be entirely due to systematic errors (second set of calculations in the Appendix). This criterion is in accord with the recommendation in Pasero *et al*. (2010: p. 173) which considers deviations of more than about 3% in *T*-site anion sums to be cause for concern.

In the datasets examined in this article, additive corrections for undetected elements are only considered appropriate if stoichiometric discrepancies significantly exceed 0.1 atoms per formula unit, oxide totals are less than 100 wt%, and there is an imbalance of more than about ±0.2 electron charges per formula unit. Charge balance is used as a basis for correction because it characterises the error and helps to determine the minimum addition to put it right. Further proportionate additions to increase oxide totals to 100.0 wt% are difficult to justify due to the inaccuracy of the residuals, potential flexibility of the *X*-site, and possible presence of neutral molecular species (Mason *et al*., 2009). The corrections are generally small (a few wt% at the very most). Large corrections cannot be justified as they would have a significant impact on the matrix-related calculations used to generate the original datasets.

The datasets were examined on a grain-by-grain basis to identify statistically significant negative and positive excesses. The correction for a dataset with a small negative charge excess (a pyromorphite–phosphohedyphane intermediate from Leadhills–Wanlockhead) is shown in the third set of calculations in the Appendix.

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[2] The *X*-site is the most flexible in lead-apatites and there is limited evidence that the site occupancy can exceed 1.1 atoms per formula unit in some circumstances.

The mean charge imbalance is −0.52±0.05 per formula unit. The presence of small amounts of undetected univalent, divalent and trivalent *M*-site cations are the most probable reason for the discrepancy. As the amounts and valencies of these ionic species are not known they are represented in the corrected empirical formula by an additional 0.25 M^{2+} per formula unit. An adjustment of this magnitude appears reasonable. Ondrejka *et al.* (2020) found that phosphohedyphane from Slovakia contains up to 0.1 REE^{3+} per formula unit. If REE^{3+} were present at this level at Leadhills–Wanlockhead they would account for most of the imbalance without the need for any other addition.

Two datasets with positive charge excesses (both also pyromorphite–phosphohedyphane intermediates from Leadhills–Wanlockhead) are examined in the fourth set of calculations in the Appendix. Comparison with other analyses (Livingstone, 1994a,b) indicates that the excess is probably due to undetected carbonate and hydroxyl and therefore the *X*-site is filled with hydroxyl to the ideal stoichiometric value of 1.0, and additional carbonate is added at the *T*-site to produce a charge balanced formula[3]. In the most extreme case this adds an extra 0.24 carbonate and 0.36 hydroxyl groups per formula unit. The corrections generate stoichiometries that are very close to the ideal apatite-supergroup values of 5, 3 and 1 and also appear reasonable. If the *X*-site occupancy is allowed to increase to significantly more than the ideal value of 1.0 [as in the carbonatite calcium apatites studied by Chakhmouradian *et al.* (2017), where occupancies of up to 1.6 are reported] the resultant formulae have *T*-site occupancies that are significantly less than the ideal value of 3.0 (Pasero *et al.*, 2010). Since this adjustment generates non-stoichiometric formulae it has less appeal. Unlike calcium-bearing fluorapatites, there is no indication that chloride-rich lead-apatites are highly non-stoichiometric.

As the datasets described in the foregoing text, with positive and negative balance errors, were gathered one after the other under the same conditions on mineral grains prepared using the same technique with very similar compositions (all are pyromorphite–phosphohedyphane intermediates from Leadhills–Wanlockhead) it is unlikely that the errors are the result of systematic matrix-related effects. Such errors might favour positive or negative imbalances, but not both. Undetected elements are the most probable reason for the deviations from expected apatite-supergroup stoichiometries.

The fact that the corrections generate empirical formulae with close to ideal stoichiometries might lead the sceptic to conclude that any dataset could be corrected in this way. This is not so. A data point with a large charge imbalance and anomalously high aluminium, copper and silicon is examined in the fifth set of calculations in the Appendix. All of the anomalous elements are potential substituents in lead-bearing apatite-supergroup minerals, but it is impossible to make a sensible additive correction. In this case the discrepancy is almost certainly due to admixed ‘chrysocolla’ (a poorly crystalline phase which was not detected by X-ray diffractometry). Datasets, therefore, must be examined on individual basis.

The sixth set of calculations in the Appendix consider the empirical formula of hydroxylapatite from Leadhills–Wanlockhead. The dataset is of interest because the correction requires a large addition of carbonate into a relatively pure calcium apatite. If divalent carbonate replaces trivalent phosphate, ${}^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{T}\mathrm{CO}_3^{2-}$, it must be integrated into the structure in a way that preserves local charge balance. In the corrections involving phosphohedyphane (the fourth set of calculations in the Appendix) most or all of the local imbalance could be mitigated by heterovalent substitutions involving compensating silicate or sodium ions[4]. In the absence of these elements some other mechanism must be considered. One possibility is the heterovalent $2{}^{T}\mathrm{CO}_3^{2-} + {}^{M}\square \leftrightarrow 2{}^{T}\mathrm{PO}_4^{3-} + {}^{M}\mathrm{Ca}^{2+}$ substitution, which has been shown to preserve local charge balance in synthetic calcium apatites (Ivanova *et al.*, 2001). Adding one *M*-site vacancy for every two carbonate groups generates a formula with an almost ideal apatite-supergroup stoichiometry:

$$\mathrm{Pb}_{0.17}\mathrm{Ca}_{4.60}M^{2+}_{0.03}\square_{0.20}[(\mathrm{PO}_4)_{2.55},(\mathrm{SiO}_4)_{0.03},(\mathrm{CO}_3)_{0.41}](\mathrm{OH}_{0.99},\mathrm{Cl}_{0.01},),$$

as long as the *M*-site vacancies are explicitly included.

The corrected hydroxylapatite formula is of interest because it provides a credible example of an *M*-site sum that is significantly less than 5.00 (4.80 measured *M*-site cations, plus 0.2 calculated vacancies). It has already been established that measured *X*-site and *T*-site sums can deviate from the ideal values of 3.00 and 1.00 in lead-apatites due to undetected hydroxyl and carbonate (Markl *et al.*, 2014; Ondrejka *et al.*, 2020). The potential presence of *M*-site vacancies casts doubt on *M*-site sums. Thus, none of the methods of calculating empirical formulae outlined in Pasero *et al.* (2010) can be guaranteed to be reliable for lead-bearing hydroxylapatite from Leadhills–Wanlockhead. This last analysis brings the discussion of the approach used to calculate formulae in recent publications in the *Journal of the Russell Society* (Briscoe *et al.*, 2021; Green and Tindle, 2022a) to a close.

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[3] The alternative procedure, filling the *T*-site to exactly 3.00 and adding ions to the *X*-site to produce charge balance, also produces credible formulae. The choice is arbitrary, although calculated stoichiometric deviations for the trivalent *T*-site anions are clearly going to be less than those for univalent *X*-site anions.

[4] It is important to note that although this is possible, it is not necessarily the case. The presence of limited *M*-site vacancies, or a somewhat non-stoichiometric *X*-site occupancy, or both, in phosphohedyphane from Leadhills–Wanlockhead cannot be ruled out.

A different approach to the addition of *M*-site vacancies to produce local charge balance has been adopted in other studies and a brief examination of two of these adjustment techniques is useful.

The corrections outlined above include the tacit assumption that site sums do not vary by more than about 0.1 atoms per formula unit from the ideal values of 5, 3 and 1. This appears to be generally true of the *T*-site cations in apatite-supergroup minerals (Pasero *et al*., 2010), but there is more leeway for variation in the charge-balancing anions at the relatively flexible *X*-site. In particular, the substitution:

$$^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{T}\mathrm{CO}_3^{2-} + {}^{X}\mathrm{F}^{-},$$

can undoubtedly raise the *X*-site occupancy to *c*. 1.2 atoms per formula unit where carbonate replaces phosphate in fluorapatite (Mason *et al*., 2009). Extending the analogy, it may be that a substitution of the form:

$$^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{T}\mathrm{CO}_3^{2-} + {}^{X}\mathrm{OH}^{-},$$

could play a similar role in hydroxylapatite or more generally in any carbonate-bearing lead-apatite. Although it is not discussed explicitly, this mechanism is used by Livingstone (1994a) to correct the formula of a lead-rich hydroxylapatite from Wanlockhead, where a combination of analytical techniques produced:

$$(\mathrm{Ca}_{4.39},\mathrm{Pb}_{0.61})_{\Sigma=5.00}[(\mathrm{PO}_4)_{2.76},(\mathrm{CO}_3)_{0.22}]_{\Sigma=2.98}(\mathrm{OH}_{0.85},\mathrm{F}_{0.37},\mathrm{Cl}_{0.06})_{\Sigma=1.28}\cdot 0.75\mathrm{H}_2\mathrm{O},$$

on the basis of five *M*-site cations. In this formula, the *X*-site sum exceeds 2.0 if neutral water molecules are included. This appears unreasonably high. Non-stoichiometry of this magnitude was the principal reason that the $^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{T}\mathrm{CO}_3^{2-} + {}^{X}\mathrm{OH}^{-}$ substitution was rejected as the principal charge balance mechanism in lead-bearing hydroxylapatite in this study.

If the carbonate content in Livingstone (1994a) is allowed to vary a little, and the substitution, $2^{T}\mathrm{CO}_3^{2-} + {}^{M}\square \leftrightarrow 2^{T}\mathrm{PO}_4^{3-} + {}^{M}\mathrm{Ca}^{2+}$, used in this study maintains charge balance, the formula can be re-calculated as:

$$(\mathrm{Ca}_{4.24},\mathrm{Pb}_{0.59},\square_{0.17})_{\Sigma=5.00}[(\mathrm{PO}_4)_{2.67},(\mathrm{CO}_3)_{0.33}]_{\Sigma=3.00}(\mathrm{OH}_{0.58},\mathrm{F}_{0.36},\mathrm{Cl}_{0.06})_{\Sigma=1.00}.$$

Site occupancies (including vacancies) sum to the ideal values of 5, 3 and 1 with excess water assumed to be interstitial. It might be argued that since the carbonate and water contents are measured they should not be treated in this manner, but as the differences are small, and the carbonate and water determinations were not made on exactly the same material as the electron-beam analyses, the formula appears credible.

The final part of this discussion examines empirical formulae calculated on the basis of five *M*-site cations and an ideal stoichiometry without considering charge balance. Five formulae listed in Ondrejka *et al*. (2020: p. 355) are tabulated in the seventh set of calculations in the Appendix. Those with significant calculated *T*-site carbonate have large charge imbalances (up to +0.7 electron charges per formula unit). This shows that calculations based on assumed stoichiometries, which ignore charge balance, can produce unreasonable results. Adjustments are needed to produce credible formulae.

The question of how to make the corrections naturally arises. It may be that a flexible *X*-site can accommodate extra charge balancing hydroxyl ions, as implied by Livingstone (1994a) and shown by Chakhmouradian *et al*. (2017) for carbonatite fluorapatites. As discussed in the foregoing text, however, an *X*-site occupancy of ~1.7, in a formula with more than 0.5 chloride ions (which are relatively large) appears unlikely. The presence of *M*-site vacancies as a result of a coupled $2^{T}\mathrm{CO}_3^{2-} + {}^{M}\square \leftrightarrow 2^{T}\mathrm{PO}_4^{3-} + {}^{M}\mathrm{Ca}^{2+}$ substitution appears more reasonable.

In summary, two different procedures which produce charge balanced formulae for carbonate-bearing apatite-supergroup minerals are outlined in the last part of this discussion. In fluorapatites, the occupancy of the charge balancing *X*-site increases to accommodate sufficient anionic charge to compensate for the reduced *T*-site charge (Chakhmouradian *et al*., 2017). This mechanism does not appear to extend to chloride and lead-rich apatites from low-temperature supergene environments such as Whitwell Quarry and Leadhills–Wanlockhead, where charge compensation probably involves coupled heterovalent substitutions such as:

$$2^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{T}\mathrm{SiO}_4^{4-} + {}^{T}\mathrm{CO}_3^{2-}\ ,$$

$$^{M}\mathrm{Ca}^{2+} + {}^{T}\mathrm{PO}_4^{3-} \leftrightarrow {}^{M}\mathrm{Na}^{+} + {}^{T}\mathrm{CO}_3^{2-},\ \text{and particularly}$$

$$2^{T}\mathrm{CO}_3^{2-} + {}^{M}\square \leftrightarrow 2^{T}\mathrm{PO}_4^{3-} + {}^{M}\mathrm{Ca}^{2+}.$$

There is, nonetheless, a possibility that an increased *X*-site occupancy has some effect on charge balance. Pyromorphite from Coldstones Quarry, for example, has a small chloride ion excess [1.08 atoms per formula unit compared to the ideal value of 1.0 (Green and Tindle, 2022b)], which may be charge balancing.

One of the functions of a journal such as this is to highlight problems that would benefit from study by techniques that are not generally available to the amateur community. The substitution of carbonate into lead-apatites is one such problem. Phosphohedyphane and lead-rich hydroxylapatite from Leadhills–Wanlockhead provide an ideal test-bed for an examination of the character and extent of substitutions in natural material. Specimens are readily available in most large institutional collections (e.g. Cotterell and Skotnicki, 2022) and would repay further study.

Structural trends in apatite-supergroup minerals are complex and still not well understood (e.g. Hazrah and Antao, 2022). It would be interesting to establish the 'free X-site volume' as a function of composition in carbonate-bearing lead-apatites and their geometric capacity for charge balance. It might be that the differing geometries of planar carbonate and the otherwise generally tetrahedral occupants of the T-site increase the free volume in such a way that ${}^{T}CO_3^{2-}$ and ${}^{X}OH^-$ behave as a compound entity, ${}^{T,X}[CO_3^{2-}\ OH^-]$, in some cases.

This article is a simple exploration of the assessment and correction of empirical formulae of lead-bearing apatite-supergroup minerals using datasets gathered by electron-beam techniques. The calculations explore a variety of "what ifs". It is important to note that additional experimentation is required to assess whether the corrected formulae represent true compositions.

CONCLUSIONS

Empirical formulae are commonly calculated from data gathered by electron-beam techniques in mineralogy. A careful assessment of the method is worthwhile. Undetected elements, flexible sites and vacancies present problems in calculating reliable apatite-supergroup formulae, especially where heterovalent substitutions are suspected. The procedures proposed here are not without objection, but they offer a pragmatic approach in an area where multiple sources of error combine to generate problems without exact analytic solutions.

Fortunately, most lead-apatite datasets produce stoichiometric formulae without any need for correction. Introducing small additive corrections due to undetected elements produces unique and defensible charge balanced empirical formulae in many of the remaining cases. Allowing vacancies (the algebraic equivalent of negative numbers) to populate particular sites on the basis of known heterogeneous substitutions also yields defensible improvements. If further mathematical exploration is allowed it is easy to make unjustified corrections.

The principal practical difficulties discussed in this article are twofold: firstly how to estimate the likely levels of random and systematic error and secondly how to calculate the most reasonable empirical formulae. The calculations outlined in the discussion suggest that no combination of the ideal M-site, T-site and X-site sums of 5, 3, and 1 atoms per formula unit provide a universally reliable basis for calculating empirical formulae.

The presence of significant (undetected) T-site carbonate presents a particular problem. The substitution of divalent carbonate for trivalent phosphate must preserve local charge balance. In carbonate-rich lead-apatites, the substitution probably involves M-site vacancies. Such vacancies are often omitted from empirical formulae, but in lead-apatites (and other minerals with well known structures) an explicit recognition of their presence is useful.

At a practical level, corrections are only justified if discrepancies due to undetected elements or vacancies significantly exceed the best estimate of other errors. The fact that corrections outlined in the foregoing text generate formulae with site occupancies that are close to the ideal apatite-supergroup M-, T- and X-site occupancies of 5, 3 and 1, and identify errors due to inclusions and intergrowths, suggest that they have some merit.

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APPENDIX

The following sets of example calculations use datasets that were gathered one after the other by wavelength-dispersive spectrometry on an electron microprobe in 2006. Millimetre-size homogeneous samples were arranged and embedded in epoxy resin on a 48 mm glass probe slide. They were ground and polished to produce a 'survey slide' suitable for microprobe analysis. Measurements were made using an accelerating voltage of 20 kV, beam current of 20 nA and a 10 µm defocused beam with matrix-appropriate standards. The elements aluminium, arsenic, barium, calcium, chlorine, cobalt, copper, fluorine, iron, lead, magnesium, manganese, phosphorus, strontium, titanium, silicon, sulphur, vanadium and zinc were sought.

1. TRUSTED TECHNIQUES

As noted in the first paragraphs of the main article, empirical formulae are calculated using one of two procedures in the earth sciences. Many petrological investigations use the method outlined in Deer *et al.* (2013: pp. 485–486), and after correcting oxygen totals for halogen content calculate empirical formulae based on 26 equivalent oxygen atoms for apatite-supergroup minerals ($Z = 1$). In mineralogy it is more usual to report such data based on 13 equivalent oxygen atoms ($Z = 2$). To take pyromorphite as an example, this produces a formula of the form $Pb_5(PO_4)_3Cl$, rather than the $Pb_{10}(PO_4)_6Cl_2$ preferred by petrologists[5].

Calculations with reliable *X*-site sums can also be normalised to nine atoms per formula unit. This is the basis for some of the calculations outlined in this article and many of the apatite-supergroup formulae reported in Briscoe *et al.* (2021). If the *X*-site contains undetected elements (as is commonly the case with phosphohedyphane and hydroxylapatite) a correction procedure which backfills with 'hydroxyl' and renormalises as described in Ketcham (2015) may be appropriate [this is a variant of method 4(a) of Pasero *et al.* (2010) which includes calculated hydroxyl]. Alternatively, formulae may be calculated on the basis of eight *M*- and *T*-site anions (Markl *et al.*, 2014) [method 4(b) of Pasero *et al.* (2010)]. If the *T*-site sum is also thought to be unreliable, formulae may be calculated on the basis of five *M*-site cations (Ondrejka *et al.*, 2020), and if the opposite is suspected and the *M*-site sum is thought to be unreliable, formulae may be calculated on the basis of three *T*-site anions [method 4(c) of Pasero *et al.* (2010)].

Calculations based on thirteen equivalent oxygen atoms do not necessarily yield the same formulae as those based on nine atoms per formula unit. The mean empirical formula calculated using the technique outlined in Deer *et al.* (2013) on the basis of thirteen equivalent oxygen atoms for near end-member pyromorphite from Glengonnar Shaft at Leadhills is:

$$Pb_{4.883}Ca_{0.125}[(PO_4)_{2.877},(AsO_4)_{0.017}, (SiO_4)_{0.092}]Cl_{1.100}.$$

The same calculation based on nine atoms per formula unit yields:

$$Pb_{4.821}Ca_{0.123}[(PO_4)_{2.840},(AsO_4)_{0.017}, (SiO_4)_{0.091}]Cl_{1.086}.$$

The differences result from an *X*-site occupancy which is slightly more than 1.0. The stoichiometric ratios of the elements in the two formulae are, however, identical. The latter are obtained from the former by multiplying by 0.987.

The calculation on the basis of eight *M*- and *T*-site atoms per formula unit [method 4b of Pasero *et al.*, (2010)], which is used by Markl *et al.* (2014) yields:

$$Pb_{4.874}Ca_{0.125}\ [(PO_4)_{2.871},(AsO_4)_{0.017},(SiO_4)_{0.092}]Cl_{1.098}.$$

Five *M*-site cations per formula unit (Ondrejka *et al.*, 2020), produces:

$$Pb_{4.859}Ca_{0.124}\ [(PO_4)_{2.862},(AsO_4)_{0.017},(SiO_4)_{0.092}]Cl_{1.094}.$$

This last calculation is reliant on the accuracy of the cation sum at a single structural site, as are similar calculations based on three *T*-site anions [method 4c of Pasero *et al.*, (2010)]. Neither can be recommended for well behaved datasets, although they may have a part to play in identifying non-stoichiometric site occupancies, vacancies or undetected elements.

The coefficients in the formulae above are reported to three decimal places to show the mathematical variation that calculations using different assumptions generate. It is important to note that this level of accuracy is not justified. In reality, the major elements are probably only accurate to one decimal place. Formulae are reported to two decimal places in the remainder of this article and in recent studies using these datasets (Briscoe *et al.*, 2021; Green and Tindle, 2022a,b) so that the contributions of minor elements can be explicitly included.

There are deviations from ideal apatite-supergroup stoichiometry and small charge imbalances (the difference between the sum of the formal charges on the anionic and cationic components) in all of the formulae. The sign, magnitude and variance of the deviations provide crude but useful assessments of the reliability of the datasets.

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[5] Note that calculations made on a different basis, as for example Livingstone (1994b) in which the vanadinite formulae are calculated on the basis of *twelve* equivalent oxygen atoms, do not produce coefficients that can be compared with ideal apatite-supergroup formulae. The molecular proportions in such formulae are not wrong, but their basis must be borne in mind if comparisons are made.

Summary: a dataset which generates acceptable empirical formulae using procedures based on: 13 equivalent oxygen atoms; 9 'atoms' per formula unit; 8 *M*- and *T*-site cations and anions per formula unit; 5 *M*-site cations atoms per formula unit; and 3 *T*-site anions per formula unit. Most of the datasets gathered in the current study are similarly 'well behaved'.

2. END-MEMBER STANDARDS

Lead-bearing apatite-supergroup minerals present significant analytical problems for electron-beam techniques (Eusden *et al*., 2002; Markl *et al*., 2014). Strong matrix effects generate systematic errors that are not easy to fully correct using the standard ZAF or φρz models (Markl *et al*., 2014). They can be mitigated by using matrix-matched calibration standards (as in this study), but not entirely eliminated.

Well crystallised grains with end-member XRD patterns from localities with relatively simple supergene assemblages were chosen to test the reliability of the datasets examined in this study. The nearest of these to ideal end-member pyromorphite is from Coldstones Quarry near Greenhow in North Yorkshire (Green and Tindle, 2022b). The mean empirical formula on the basis of nine atoms per formula unit is:

$$\mathrm{Pb}_{4.92}\mathrm{Ca}_{0.05}M^{2+}_{0.01}[(\mathrm{PO}_4)_{2.92},(\mathrm{SiO}_4)_{0.02}]\mathrm{Cl}_{1.08},$$

where M^{2+} is included as a 'placeholder' for traces of divalent species plus sodium which are present at less than 0.01 atoms per formula unit. The formula is close to the ideal $\mathrm{Pb}_5(\mathrm{PO}_4)_3\mathrm{Cl}$: the *M*-site cations sum to 4.98±0.07 (ideally 5.00); the *T*-site anions sum to 2.94±0.04 (ideally 3.00); and chlorine at the *X*-site is 1.08±0.04 (ideally 1.00). The oxide sum (corrected for O=Cl as described in Deer *et al*., 2013: pp. 485−486) is 99.7±1.1 wt%, which is close to the expected value of 100 wt%.

This analysis and similar measurements of the compositions of near end-member vanadinite and mimetite allow an estimate of the overall reliability of the instrumentation. There are small deviations from ideal apatite-supergroup stoichiometry, particularly at the *X*-site, which is slightly 'over full' in this example, but as charge balance is excellent at +0.04 per formula unit and the oxide sum is close to 100 wt% additive corrections cannot be justified. The *X*-site is relatively flexible in apatite-supergroup minerals (Mason *et al*., 2009; Chakhmouradian *et al*., 2017) and an *X*-site occupancy within 10% of the ideal value of 1.0 gives little cause for concern.

Regardless of the precise reason for the discrepancies, the calculations provide pragmatic constraints on those deviations that can be regarded as significant (i.e. in need of correction) and those that cannot be differentiated from random and systematic errors, or genuine non-stoichiometry. This and other similar analyses suggest that a deviation of more than about 0.1 atoms per formula unit at any site with a charge balance error of more than ±0.2 per formula unit, is significant. This is an extension of the '3% *T*-site deviation rule' recommended by Pasero *et al*. (2010: p. 173) as an indication of unreliable datasets.

Summary: a well behaved dataset which generates a near end-member formula and (with other similar analyses) provides a basis for differentiating deviations due to undetected elements from experimental errors and genuinely non-stoichiometric compositions.

3. NEGATIVE CHARGE EXCESS

Specimen P254 from Glencrieff Mine, Wanlockhead has a mean empirical formula calculated on the basis of nine atoms per formula unit:

$$\mathrm{Pb}_{3.34}\mathrm{Ca}_{1.51}M^{2+}_{0.05}[(\mathrm{VO}_4)_{0.01},(\mathrm{PO}_4)_{3.06},(\mathrm{SiO}_4)_{0.02}]\mathrm{Cl}_{1.01}.$$

The *M*-site cation sum is 4.89±0.03; the *T*-site anions sum to 3.09±0.04; and chlorine in the channel site is 1.01±0.06. The stoichiometry is at the edge of the acceptable range (3% deviation at the *T*-site) and the charge balance error of −0.52±0.05 per formula unit, which is the result of high *T*-site and low *M*-site sums, makes a correction desirable. The mean oxide sum, 96.6 wt%, is less than ideal, and allows a small additive correction.

The dataset was chosen as an example because it cannot be credibly corrected by adjusting the occupancy of the *X*-site [which is very close to the ideal value of 1.0 but would have to increase to *c*. 1.5 (Cl + OH)]. It is similarly impossible to adjust it using the procedures outlined in Ketcham (2015). Furthermore, the formula must be examined holistically and not just on the basis of the *T*-site sum, which is within 3% of the ideal value (cf. Pasero *et al*., 2010).

The approach adopted in this study is to adjust to a charge balanced formula by adding extra M^{2+}. An additional 0.25 M^{2+} per formula unit produces:

$$\mathrm{Pb}_{3.24}\mathrm{Ca}_{1.47}M^{2+}_{0.04}M^{2+}_{0.25}[(\mathrm{VO}_4)_{0.01},(\mathrm{PO}_4)_{2.97},(\mathrm{SiO}_4)_{0.02}]\mathrm{Cl}_{0.99},$$

renormalised to nine atoms per formula unit. The additional M^{2+} is indicated in red to show that it is calculated rather than measured. Checking the stoichiometry: the *M*-site cations now sum to 5.00±0.02; the *T*-site anions to 3.00±0.04; and chlorine in the channel site to 0.99±0.06. This is very close to the ideal apatite-supergroup formula.

It is reasonable to ask whether this adjustment is defensible. The maximum measured minor and trace element M^{2+} per formula unit (based on ten measured elements) in the phosphohedyphane analyses from Leadhills−Wanlockhead is about 0.1 per formula unit (Green and Tindle, 2022a). The adjustment, therefore, is larger than the largest measured values. It does not, however, compromise the oxide totals, which with a mean of 96.6 wt% are low. The measured dataset includes univalent sodium and all of the divalent species-defining apatite-supergroup cations, but does not include bismuth, chromium, rare-earth elements or uranium, which are commonly present in lead-bearing apatite-supergroup minerals (Temple, 1954; Markl *et al.*, 2014; Ondrejka *et al.*, 2020). The additional '0.25 M^{2+} equivalent' per formula unit would be rather less if the undetermined elements were largely trivalent. Rare earth elements on their own could account for most of the balance error if they were present at the levels measured by Ondrejka *et al.* (2020) in phosphohedyphane from Slovakia.

It should be noted that 'subtractive corrections' are unrealistic. They would require a subtraction of more than half of the *X*-site chlorine or the loss of 0.18 *T*-site cations per formula unit, neither of which is consistent with apatite-supergroup stoichiometry or the accuracy of the instrumentation.

Summary: a dataset for which a small additive *M*-site correction produces a defensible stoichiometry.

4. POSITIVE CHARGE EXCESS

Specimens P232 and P233 from Lady Anne Hopetoun Shaft, Leadhills have mean empirical formulae calculated on the basis nine atoms per formula unit:

$Pb_{3.57}Ca_{1.72}M^{2+}_{0.05}[(VO_4)_{0.02},(PO_4)_{2.83},(SiO_4)_{0.13}]Cl_{0.68}$, and
$Pb_{3.94}Ca_{1.31}M^{2+}_{0.06}[(VO_4)_{0.01},(PO_4)_{2.57},(AsO_4)_{0.02},(SiO_4)_{0.37}]Cl_{0.72}$.

The *M*-site cation sums[6] are 5.33±0.04 and 5.25±0.05; the *T*-site anion sums are 2.98±0.02 and 2.96±0.02; and chlorine in the channel site is 0.68±0.02 and 0.72±0.03. The formulae have charge imbalances of +0.97±0.14 and +0.66±0.22 per formula unit. The errors are in the opposite sense to the previous dataset and represent an excess of cation charge. The low *X*-site total invites the approach outlined by Ketcham (2015), backfilling with hydroxyl and renormalising, but filling the *X*-site with hydroxyl is insufficient to produce a balanced formula, and does not generate an acceptable stoichiometry.

Previous studies (e.g. Livingstone, 1994a,b) have shown that lead-rich hydroxylapatites from Leadhills–Wanlockhead contain carbonate at the *T*-site and its presence in phosphohedyphane has recently been confirmed by Ondrejka *et al.* (2020). Filling the *X*-site with hydroxyl, adding suitable carbonate to the *T*-site to produce charge balance, and renormalising to nine atoms per formula unit yields:

$Pb_{3.33}Ca_{1.60}M^{2+}_{0.04}[(VO_4)_{0.02},(PO_4)_{2.64},(SiO_4)_{0.12},\mathbf{(CO_3)_{0.24}}](\mathbf{OH_{0.36}},Cl_{0.64})$, and

$Pb_{3.73}Ca_{1.25}M^{2+}_{0.06}[(VO_4)_{0.01},(PO_4)_{2.43},(AsO_4)_{0.02},(SiO_4)_{0.35},\mathbf{(CO_3)_{0.15}}](\mathbf{OH_{0.32}},Cl_{0.68})$.

The additional carbonate and hydroxyl are **indicated in blue** to show that they are calculated rather than measured. The *M*-site cation sums are 4.97±0.02 and 5.03±0.03; the *T*-site anion sums are 3.02±0.01 and 2.96±0.02; and chlorine plus hydroxyl in the channel site are exactly 1.00.

The fact that charge balance criteria produce credible empirical formulae that are close to the ideal apatite-supergroup stoichiometry shows the merit of this approach. The alternative scheme which charge compensates by increasing the *X*-site occupancy to more than 1.0 produces non-stoichiometric formulae with *T*-site deviations of more than 3%.

Summary: two datasets for which small additive *T*- and *X*-site corrections produce formulae with defensible stoichiometries. Calculations are made so that the *X*-site occupancy is 1.00 and the *T*-site is allowed to vary, in both cases the *T*-site deviation is less than 3% as recommended by Pasero *et al.* (2010).

5. INCLUSION ERRORS

Two data points with anomalously high copper contents were recorded on a specimen from Lady Anne Hopetoun Shaft at Leadhills. The highest value of nearly 4.0 wt% CuO correlated with the highest silicon and aluminium contents of any of the datasets. The empirical formula calculated on the basis of nine atoms per formula unit is:

$Pb_{3.06}Ca_{1.35}Cu_{0.56}Al_{0.07}M^{2+}_{0.06}[(VO_4)_{0.01},(PO_4)_{2.21},(SiO_4)_{1.04}]Cl_{0.64}$,

The *M*-site cation sum is 5.10; the *T*-site anion sum is 3.26; and chlorine in the channel site is 0.64. None of these are acceptable.

This dataset cannot be adjusted to produce a charge balanced empirical formula with an apatite-supergroup stoichiometry by adding elements to the *M*- *T*- and *X*-sites within the limitation that oxide totals must sum to less than 100 wt%. Removing the anomalous copper and aluminium and balancing silicon does, however, result in a formula which can then be corrected to an ideal apatite-supergroup stoichiometry (a carbonate-bearing phosphohedyphane). The most reasonable explanation for the anomalous data, therefore, is the presence of a small amount of admixed 'chrysocolla'[7]. As chrysocolla does not produce an intense diffraction pattern it is easy to see how it might have been missed in analyses of grains by X-ray powder diffraction.

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[6] Differences in the last decimal place between quoted cation sums and those obtained by adding the coefficients in the formulae are due to rounding errors.

[7] Chrysocolla, *sensu lato*, is known from numerous localities at Leadhills–Wanlockhead (e.g. Temple, 1954: p. 60), but to the authors' knowledge, none of the specimens have been confirmed by PXRD. Indeed powder patterns that are supposed to be characteristic of chrysocolla (published by the Joint Commission on Powder Diffraction Standards) are widely variable. Material which is labelled as 'chrysocolla' is usually better described as a 'copper-bearing aluminosilicate gel'. However the term is retained here for convenience and continuity.

Summary: a dataset for which a small additive corrections do not produce a defensible stoichiometry, but with a composition that can be explained by the presence of admixed chrysocolla.

6. LOCAL CHARGE BALANCE

Specimen P229, a white crustose mineral from New Cove Vein, Whyte's Cleuch, Wanlockhead, has a composition close to end-member hydroxylapatite. As the *X*-site elements cannot be determined by wavelength-dispersive spectrometry, the initial calculations are based on *M*- and *T*-site occupancies of 5.00 and 3.00 [method 4(b) of Pasero *et al*. (2010)]. This produces a mean empirical formula:

$$\mathrm{Pb_{0.18}Ca_{4.96}}M^{2+}_{0.03}\mathrm{[(PO_4)_{2.76},(SiO_4)_{0.04}]Cl_{0.01}}.$$

The *M*-site cation sum is 5.17±0.05; the *T*-site anions sum to 2.79±0.04; and chlorine in the channel site is 0.01±0.01. The charge balance error is +1.948±0.23 per formula unit. In this case, the simplest approach to correction is to follow assumptions made in the fourth set calculations (above) and add hydroxyl to fill the *X*-site to 1.00 and the remaining anions as *T*-site carbonate to produce charge balance. This produces an empirical formula:

$$\mathrm{Pb_{0.17}Ca_{4.70}}M^{2+}_{0.03}\mathrm{[(PO_4)_{2.61},(SiO_4)_{0.03},(CO_3)_{0.43}](OH_{0.99},Cl_{0.01})},$$

with calculated **additions in blue**, which is nearer to the ideal apatite-supergroup stoichiometry. The *M*-site cation sum is now 4.92±0.02; the *T*-site anions sum to 3.07±0.02; and chlorine plus hydroxyl at the channel site is exactly 1.00. This is not entirely satisfactory as there are deviations from the ideal stoichiometry at the *M*- and *T*-sites.

A significant improvement can be made by considering the implications of replacing trivalent phosphate with divalent carbonate in the apatite structure. The heterovalent substitution ${}^{T}\mathrm{PO_4^{3-}} \leftrightarrow {}^{T}\mathrm{CO_3^{2-}}$ requires a mechanism which preserves local charge balance. In the carbonate which is added into the phosphohedyphane analyses in the fourth set of calculations (listed above) it is possible that coupled substitutions of the form:

$$2{}^{T}\mathrm{PO_4^{3-}} \leftrightarrow {}^{T}\mathrm{SiO_4^{4-}} + {}^{T}\mathrm{CO_3^{2-}}\text{ or,}$$

$${}^{M}\mathrm{Ca^{2+}} + {}^{T}\mathrm{PO_4^{3-}} \leftrightarrow {}^{M}\mathrm{Na^{+}} + {}^{T}\mathrm{CO_3^{2-}},$$

mitigate most or all of this local imbalance[8]. There is insufficient silicate or sodium in the hydroxylapatite for either of these substitutions to play a significant balancing role. An alternative heterovalent substitution that has been established in synthetic calcium apatites (Ivanova *et al*., 2001) is:

$$2{}^{T}\mathrm{CO_3^{2-}} + {}^{M}\square \leftrightarrow 2{}^{T}\mathrm{PO_4^{3-}} + {}^{M}\mathrm{Ca^{2+}},$$

where the open-square symbol, □, represents a structural vacancy (at the *M*-site in this case). Adding vacancies at the *M*-site on the basis of this substitution yields:

$$\mathrm{Pb_{0.17}Ca_{4.60}}M^{2+}_{0.03}{>}\square_{0.20}\mathrm{[(PO_4)_{2.55},(SiO_4)_{0.03},(CO_3)_{0.41}]}$$
$$\mathrm{(OH_{0.99},Cl_{0.01},)},$$

with calculated **additions in blue**. The *M*-site cation sum (including vacancies) is now 5.01±0.02; the *T*-site anions sum to 3.00±0.02; and chlorine plus hydroxyl at the channel site are exactly 1.00. This additional correction, which introduces sufficient *M*-site vacancies to produce local charge balance, generates an ideal apatite-supergroup stoichiometry as long as the vacancies are included explicitly in the empirical formula.

It is impossible to be certain that this correction is appropriate on the basis of the available data. Although their presence is well established, Pasero *et al*. (2010: p. 173) do not regard structural vacancies as a significant issue in calculations of the empirical formulae of apatite-supergroup minerals. A credible formula can be generated if the *X*-site occupancy is allowed to increase up to ~1.2 and there is a charge-balancing substitution of the form ${}^{T}\mathrm{PO_4^{3-}} \leftrightarrow {}^{T}\mathrm{CO_3^{2-}} + {}^{X}\mathrm{OH^{-}}$. Such non-stoichiometric formulae have been proposed by Mason *et al*. (2009) in calcium-bearing fluorapatite, but similar proposals in lead-bearing hydroxylapatite require unusually large *X*-site occupancies.

Adding half of the carbonate into the *X*-site as an A-type substitution makes the stoichiometry worse and can be discounted for that reason alone. Hydroxylapatite, however, is a complex phase. Exchanging $\mathrm{PO_4}$ for $\mathrm{HPO_4}$ can generate non-stoichiometric compositions of the form $\mathrm{Ca_{5-\mathit{x}}(PO_4)_{3-\mathit{x}}(HPO_4)_{\mathit{x}}(OH)_{1-\mathit{x}}}$ (where x is between 0 and 0.5). This type of substitution, which is briefly noted in the main body of the text, is characteristic of biogenic hydroxylapatite and is unlikely to be associated with abiogenic formation.

Regardless of the details of this particular calculation, the potential presence of significant but unknown amounts of *M*-site vacancies highlights a problem in calculating formulae based on an *M*-site sum of 5.00, as proposed by Ondrejka *et al*. (2020), even using a dataset in which every possible *M*-site element has been determined. The potential for discrepancies generated by heterogeneous coupled substitutions of the form $2{}^{T}\mathrm{CO_3^{2-}} + {}^{M}\square \leftrightarrow 2{}^{T}\mathrm{PO_4^{3-}} + {}^{M}\mathrm{Ca^{2+}}$ is clear.

Summary: a dataset in which the character of the heterogeneous carbonate for phosphate substitution must be considered to produce a credible empirical formula. A stoichiometric addition of charge balancing anions at the *X*- and *T*-sites and the addition of *M*-site vacancies on the basis of a known hydroxylapatite substitution provides a credible stoichiometric formula. A non-stoichiometric formula with an increased *X*-site occupancy cannot be entirely discounted.

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[8] Although it is possible to appeal to these coupled heterovalent substitutions, there are no definite correlations in the minor-element data to support them, *M*-site vacancies may also be present.

	1	2	3	4	5
Uranium	0.004	0.000	0.003	0.020	0.011
Aluminium	0.069	0.011	0.005	0.000	0.000
REE	0.062	0.070	0.097	0.083	0.012
Calcium	2.457	2.460	1.226	1.479	1.411
Lead	2.272	2.330	3.654	3.401	3.508
M^{2+}	0.104	0.126	0.013	0.012	0.057
Na+K	0.029	0.003	0.000	0.000	0.000
***M*-site sum**	4.997	5.000	4.998	4.995	4.999
***M*-site charge**	10.104	10.078	10.104	10.113	10.032
Sulphate	0.011	0.010	0.026	0.032	0.025
Phosphate	2.856	2.888	2.754	2.432	2.269
Arsenate	0.000	0.000	0.000	0.044	0.041
Vanadate	0.000	0.000	0.000	0.000	0.000
Carbonate	>0.073	>0.092	>0.204	>0.471	>0.653
Silicate	0.061	0.010	0.016	0.022	0.012
***T*-Site sum**	3.001	3.000	3.000	3.001	3.000
***T*-site charge**	8.980	8.908	8.786	8.522	8.334
***X*-site charge**	>1.000	>1.000	>1.000	>1.000	>1.000
Anion charge	9.980	9.908	9.786	9.522	9.334
Balance Error	**0.124**	**0.170**	**0.318**	**0.591**	**0.698**

Table 1. Five analyses of phosphohedyphane from Slovakia in which apatite-supergroup stoichiometry has been used to correct the empirical formulae to site-occupancies of 5, 3 and 1, backfilling the *T*-site with carbonate (**calculated value >in blue**) and the *X*-site with hydroxyl (Ondrejka *et al*., 2020: p. 354). Calculated charge imbalances, based on simple ionic assumptions, are listed in **bold face.**

7. CHARGE BALANCE AS A TEST OF STOICHIOMETRIC FORMULAE

A simple ionic approach can be used to test empirical formulae that are based on assumed stoichiometries. Five representative formulae listed in Ondrejka *et al*. (2020), calculated on the basis of an *M*-site sum of 5.00 and an assumed *T*-site sum of 3.00 and *X*-site sum of 1.00 are listed in Table 1. The charge imbalances, calculated as electron charges per formula unit, are included in bold face. Analyses one and two, without much carbonate, are reasonable. Analyses four and five, in which significant divalent carbonate replaces trivalent phosphate, give cause for concern. In these cases (assuming that a simple ionic model is appropriate) there is insufficient anionic charge.

The foregoing discussions suggest that the charge imbalance can be mitigated by the substitution $2\,{}^{T}\mathrm{CO}_3^{2-} + {}^{M}\square \leftrightarrow 2\,{}^{T}\mathrm{PO}_4^{3-} + {}^{M}\mathrm{Ca}^{2+}$. The possibility that carbonate (rather than hydroxyl) occupies the *X*-site, can be ruled out by the accompanying Raman spectra, which distinguish A- and B-site substitution. Mitigating the imbalance using a flexible *X*-site yields a formula with an *X*-site occupancy of ~1.7, which appears unreasonably high in a channel site which also contains more than 0.5 chloride ions (with large ionic radii) per formula unit.

Summary: a dataset which shows the importance checking that formulae adjusted to an assumed stoichiometry are charge balanced.

A RE-EXAMINATION OF 'COLLIEITE' FROM WANLOCKHEAD, DUMFRIES AND GALLOWAY

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Contemporary mineralogists suggested that collieite, a black botryoidal mineral from Wanlockhead, Dumfries and Galloway, was a calcium- and vanadate-rich variety of pyromorphite. More recent analyses have identified similarly labelled material as mottramite or a mixture of phosphohedyphane and manganese oxides. An investigation of a fragment of the original specimen, preserved at the Natural History Museum in London, reveals a banded structure in which layers of grey-black and pale green phosphohedyphane with minor yellow to orange-brown zinc-rich mottramite are overgrown by a dark outer layer containing mottramite and vanadinite. The original analysis is interpreted as a mixture of approximately 10 wt% mottramite, 20 wt% end-member vanadinite and 70 wt% lead-rich phosphohedyphane.

INTRODUCTION

The Leadhills–Wanlockhead mining district in southern Scotland is famous for lead-, zinc- and copper-bearing supergene minerals (Heddle, 1901a,b; Brown, 1919, 1927; Gillanders, 1991; Livingstone, 2002; Tindle, 2008). It is the type locality for caledonite, lanarkite, leadhillite, plattnerite and susannite, which were described in the nineteenth century, and chenite, macphersonite, mattheddleite and scotlandite, which were characterised more recently (Livingstone, 2002: pp. 188–189). Some claimed species including 'collieite', which is discussed in this article, have not stood the test of time.

The name collieite was proposed in 1927 by Robert Brown (1864–1941) in honour of John Norman Collie (1859–1942) a distinguished chemist and mountaineer who reported two analyses of a black botryoidal mineral from Wanlockhead in 1889. The published composition and density are in keeping with Collie's suggestion that the mineral is a calcium- and vanadate-rich variety of pyromorphite, but more recent analyses of a specimen in the Heddle Collection have suggested that it is mottramite (Livingstone, 2002: p. 124). This study was catalysed by the discovery of a 'collieite' specimen at Amgueddfa Cymru which proved to be a mixture of phosphohedyphane and poorly characterised manganese oxides together with recent research (Green and Tindle, 2022a,b) which suggests that the composition proposed by Collie (1889) is unlikely to represent a homogeneous phase. In short, collieite is ripe for re-examination.

COLLIEITE

In 1889, John Norman Collie published a short paper "On some Leadhills Minerals" in the *Journal of the Chemical Society*. It includes analyses of a number of rare supergene minerals from the Leadhills–Wanlockhead mining district. Collie had collected some of the minerals himself and the remainder were supplied by "Dr. Wilson, of Wanlockhead, Leadhills"[1] via "Professor Letts of Belfast"[2]. Collie (1889: p. 91) noted that two of the minerals had not been reported previously. One of these is a lead-rich variety of aragonite[3], and the other, in Collie's own words:

> "*Calcium vanado-pyromorphite*, or pyromorphite containing calcium and vanadic acid, with a small quantity of copper hydroxide".

The mineral is described (Collie, 1889: pp. 94–95) as follows:

> "This new mineral occurs in black botryoidal masses, and is unlike either pyromorphite or vanadinite in appearance. The fracture is uneven or conchoidal; it fuses easily before the blowpipe, leaving a brown granule, which when broken shows a crystalline structure. It dissolves readily in hydrochloric acid when warm, and leaves a slight residue of a brown colour, which consists chiefly of an oxide of iron. Two analyses were made:

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[1] This is probably Dr John Wilson (1838–1905) a supplier of specimens to Matthew Forster Heddle (Johnston, 2015: p. 143) who moved to Wanlockhead from the Liberton area of Edinburgh at some time between 1868 and 1871 (Graham Tulloch, *personal communication*, 2022).

[2] Edmund Albert Letts (1852–1918) a pioneering analytical chemist at Queen's College, Belfast (Burns and Walker, 2015).

[3] In reality, lead-bearing aragonite had been known from Leadhills–Wanlockhead since the eighteenth century (Cotterell, 2022).

	I[4].	II.
$Pb_3(PO_4)_2$	52.0	–
$Pb_3(VO_4)_2$	19.2	–
$Ca_3(PO_4)_2$	15.8	–
$PbCl_2$	11.4	10.7
$Cu(OH)_2$	1.6	1.4
Insoluble residue	0.6	0.5

> The specific gravity is 6.9–7.0.
>
> The mineral is therefore a pyromorphite in which calcium replaces lead, and vanadic acid replaces phosphoric acid. The amount of water (0·4 per cent.) which the mineral loses when it is heated is just enough to combine with the oxide of copper, and as there is an insufficient amount of acid to unite with all the bases present, this is rendered probable. Unfortunately there was only a very small quantity of the mineral, so no further analyses could be made”.

The mineral attracted the interest of the doyen of Scottish mineralogy, Matthew Forster Heddle (1828−1897), who, like Collie, was an accomplished mountaineer (Johnston, 2014, 2015). Heddle repeated much of Collie's original description in *The Mineralogy of Scotland* and concluded (Heddle, 1901b: p 161):

> “The mineral is therefore a Pyromorphite in which calcium replaces lead, and Vanadic acid replaces phosphoric acid”.

Despite the fact that it appeared to be an intermediate between two well defined species, Robert Brown thought that the mineral was sufficiently distinctive to merit a name and proposed ‘collieite’ in honour of John Norman Collie (Brown, 1927). The name is recorded in Leonard James Spencer's *Second Supplementary list of British Minerals*, but not as a valid species (Spencer, 1931). The first edition of *Hey's Mineral Index* also lists collieite as a variety rather than a species (Hey, 1950).

The beginnings of a dissenting narrative can be traced to the early 1950s when A. K. Temple made a detailed survey of the minerals of the Leadhills−Wanlockhead mining district. He examined a specimen of ‘collieite’ (number 522.10 in the Heddle Collection) at the National Museum of Scotland by X-ray diffraction, found that it was a member of the descloizite group, and concluded (for that reason) that it was not the mineral that had been analysed by Collie (Temple, 1954).

In an update of Spencer's supplementary lists of British minerals, Macpherson (1983) maintained the orthodox position, describing collieite as a calcium- and vanadate-rich variety of pyromorphite. However, Livingstone (2002: p. 124) noted that the black hemispheres on Heddle's collieite specimen (522.10) from Belton Grain Vein were mottramite. There is no reason to doubt any of these claims, but they have led to confusion which is encapsulated in Tindle (2008: p. 156) as follows:

> “Collieite has been described as a calcium-, vanadium-rich variety of pyromorphite, apatite group, but examination of a black hemispherical sample from Belton Grain vein, Wanlockhead shows it to be mottramite”.

The current research was prompted by the discovery of a ‘collieite’ specimen in the King Collection (NMW 83.41G.M.8430; K1494) at Amgueddfa Cymru. The associated catalogue records: “Collieite, on smithsonite” from “Beltongrain vein, High Pirn Mine, Wanlockhead, Dumfriesshire”.

Norman Collie provided several minerals to Henry Francis Harwood (1886−1974), part of whose collection was later acquired by Bob King, but this particular specimen appears to have been purchased from “Messrs Rogers [or possibly Rayners]” in 1958. The ‘collieite’ is rather nondescript: a PXRD analysis (NMW X-3826) produced a weak pattern with some diffraction peaks that are consistent with phosphohedyphane and others that remain to be identified. When it was sampled, areas of hard black material with a conchoidal fracture and a soft powdery black material with ‘onion-skin’ layering were exposed. Both appear to be manganese oxides. Therefore, King's ‘collieite’ is a mixture of phosphohedyphane with one or more poorly crystallised manganese oxides. The underlying green ‘smithsonite’ is phosphohedyphane (NMW X-3825), a misidentification which mirrors similar mistakes described by Cotterell and Skotnicki (2022).

As well as calcium- and vanadate-rich pyromorphite and mottramite, the name collieite has been applied to manganese-stained phosphohedyphane. The only reasonable explanation is that similar looking but different black botryoidal minerals from Leadhills–Wanlockhead have been labelled ‘collieite’. This poses a problem as to the identity of the original material.

ANALYSIS

The original analyses are of importance in unravelling the mystery surrounding collieite because they provide constraints on the species that could be present. The chemical data must be considered in context because even the best late-nineteenth century schemes of quantitative semi-micro analysis could fail to detect one or more minor elements.

The measured density of the original mineral, 6.9−7 g cm^{-3}, is consistent with the lead-apatites pyromorphite (7.04 g cm^{-3}) and vanadinite (6.88 g cm^{-3}) but not with mottramite (5.9 g cm^{-3}) or end-member phosphohedyphane (5.92 g cm^{-3}). Density could be measured with reasonable precision by the last quarter of the nineteenth century and systematic errors (due to bubbles, inclusions and air pockets) mostly led to underestimates. This measurement alone precludes the possibility that the original specimen was pure mottramite or end-member phosphohedyphane.

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[4] Toward the end of his article, Collie notes that all of the chemical analyses marked with the Roman numeral I were made by a Mr Wheeler, who is presumed to have been one of Prof. Letts' students at Queen's College, Belfast.

Calculating empirical formulae from the original datasets following the method outlined in Green and Tindle (2022a) yields:

$$Pb_{4.03}Ca_{0.74}Cu_{0.21}\ [(PO_4)_{2.15},(VO_4)_{0.66},(SiO_4)_{0.13}]Cl_{1.07}, \text{ and}$$

$$Pb_{4.06}Ca_{0.75}Cu_{0.19}[(PO_4)_{2.20},(VO_4)_{0.68},\ (SiO_4)_{0.11}]Cl_{1.02},$$

on the basis of nine atoms per formula unit with the assumption that the small amount of insoluble residue reported in the analyses is iron-stained silica. The *M*-site cation sums (including copper) are 4.98 and 5.00; the *T*-site anion sums (including silica) are 2.95 and 2.98; and *X*-site chlorine is 1.07 and 1.02. These compare remarkably well with the ideal site sums of 5, 3 and 1 for apatite-supergroup minerals (Pasero *et al*., 2010). Both formulae, therefore, are consistent with calcium- and vanadate-rich pyromorphite (with some copper and silicate substitution), as suggested by Collie (1889) and Heddle (1901b).

Modern analyses of lead-apatites from Leadhills–Wanlockhead (Green and Tindle, 2022a,b) add constraints that were unknown to earlier researchers. The first is that the collieite formula lies at a point in composition space well away from any reliably measured lead-apatite from Leadhills–Wanlockhead. The second is that the concentration of copper is much greater than would be expected in lead-apatite from the area.

The fact that collieite lies within a 'compositional gap' (see Fig. 3) suggests that it is a mixture which the analytical techniques of the late-nineteenth century were unable to resolve. Recent research has shown that there is substantial variation on a micrometre-scale in the composition of pyromorphite–phosphohedyphane from localities in and around Whyte's Cleuch and that vanadinite and phosphohedyphane often occur as intimate intergrowths. The chemical variation in all three species extends within well defined limits and large areas of composition space are empty (Temple, 1954; Livingstone, 1994; Green and Tindle, 2022b).

The high concentration of copper is consistent with the presence of admixed mottramite. Mottramite is an occasional associate of lead-apatites at Leadhills–Wanlockhead (Tindle, 2008; Starkey, 2022: p. 130) and its presence would explain the black colour of the botryoidal masses.

Subtracting sufficient copper, lead and vanadate from the totals so that all of the copper is present as mottramite has relatively little effect on the empirical formulae of the remaining lead-apatite. The calculated formulae after this adjustment are:

$$Pb_{4.10}Ca_{0.80}[(PO_4)_{2.32},(VO_4)_{0.48},(SiO_4)_{0.14}]Cl_{1.14}, \text{ and}$$

$$Pb_{4.13}Ca_{0.80}[(PO_4)_{2.34},(VO_4)_{0.51},(SiO_4)_{0.11}]Cl_{1.08},$$

on the basis of nine atoms per formula unit. The *M*-site cation sums are 4.90 and 4.94; the *T*-site anion sums are 2.95 and 2.98; and *X*-site chlorine is 1.14 and 1.08, respectively. These remain near to the ideal values of 5, 3 and 1 (Pasero *et al*., 2010). Thus, the copper in the original analyses is consistent with the presence of about 7 wt% admixed mottramite.

One of the difficulties of a 'forensic' investigation such as this is that the material evidence has often been lost or discarded. The project had reached an impasse when a chance enquiry revealed that a small part of the original specimen was still extant (Fig. 1).

In 1922, Collie, who by then was Head of Chemistry at University College, London, donated a suite of twenty-six specimens from 'Leadhills' to the British Museum (Natural History). Four of the specimens were collected by Collie himself in the late 1870s and the remainder were obtained from John Wilson of Wanlockhead via Edmund Albert Letts in the late 1880s.

Specimen BM 1922,1209 was originally registered as pyromorphite and the accompanying label (Fig. 2) reads:

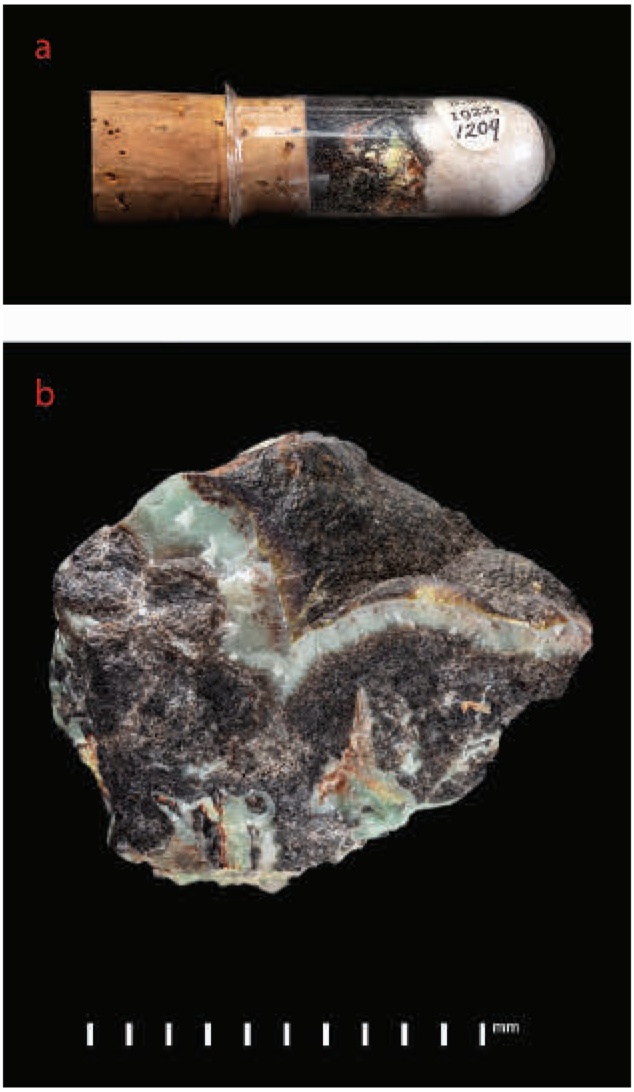
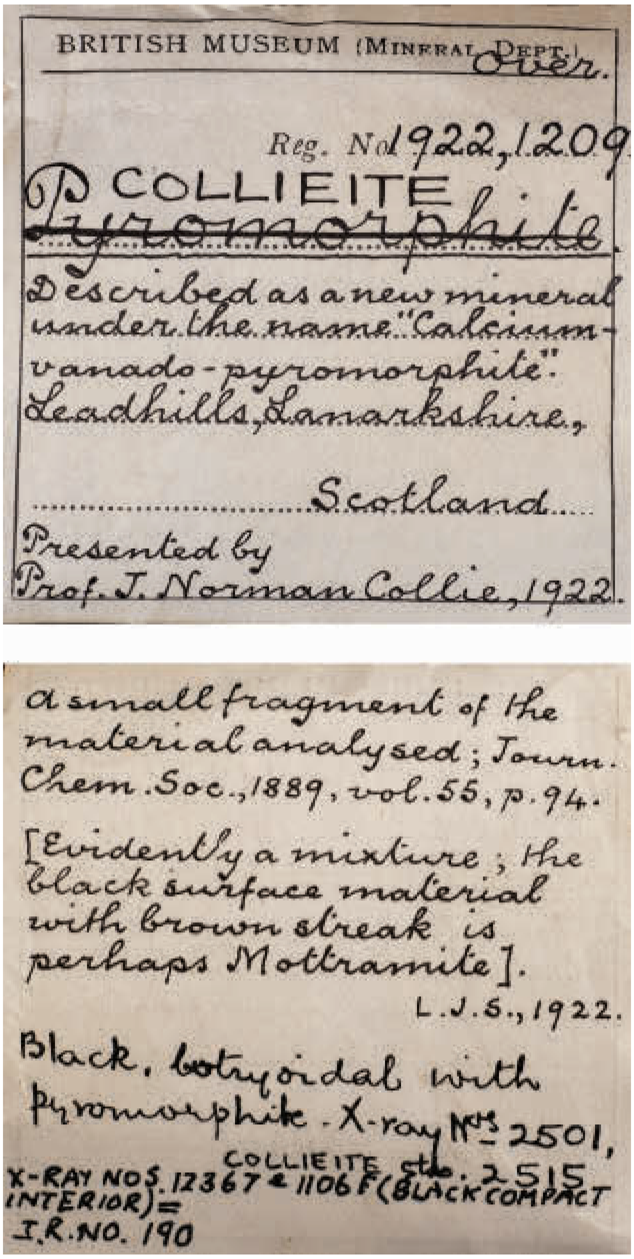


Figure 1. Part of the original collieite specimen (BM 1922,1209): a) as stored with label in a test tube; b) the major fragment, 12 mm across, showing a complex layered structure. Photos © Trustees of the Natural History Museum.



BRITISH MUSEUM (MINERAL DEPT.) Over.

Reg. No1922,1209

COLLIEITE

~~Pyromorphite~~

Described as a new mineral under the name "Calcium-vanado-pyromorphite".
Leadhills, Lanarkshire,
Scotland

Presented by
Prof. J. Norman Collie, 1922.

a small fragment of the material analysed; Journ. Chem. Soc., 1889, vol. 55, p. 94.
[Evidently a mixture; the black surface material with brown streak is perhaps Mottramite].
L.J.S., 1922.

Black, botryoidal with pyromorphite. X-ray Nos 2501,
COLLIEITE etc. 2515
X-RAY NOS. 12367 & 1106F (BLACK COMPACT INTERIOR) =
I.R. NO. 190

Figure 2. The back and front of the principal label associated with the collieite specimen (BM 1922,1209) which Norman Collie donated to the British Museum (Natural History), with contemporary observations by L. J. Spencer and later analytical notes. Photos © Trustees of the Natural History Museum.

> "Described as a new mineral under the name "Calcium vanado-pyromorphite" ... a small fragment of the material analysed".

Leonard James Spencer (1870–1959) examined the specimen in the year it was registered and noted that it was:

> "Evidently a mixture; the black surface material with a brown streak is perhaps Mottramite".

Spencer's observation that collieite was a mixture with a surface layer containing mottramite is consistent with the interpretation outlined above.

An archive associated with the specimen includes several analyses that were made after it was registered in the museum collection. In 1941, two X-ray powder diffraction patterns were collected using different characteristic radiation. Notes accompanying the first of these (X2501) record "not mottramite, but close in pattern to mimetite spacing however much < pyromorphite"; notes accompanying the second (X2515) record "spacings much < pyromorphite". Further notes, dating from 1967, are somewhat contradictory, they list collieite as "near pyromorphite" with a cryptic note "matches D F Ball material". The inconsistencies in the archival data and confusion in the published literature provided a good case for a re-examination of the specimen.

The remaining fragment (Fig. 1) has an outer black layer, typically about 200 µm thick, overgrowing a very thin yellow layer which rests, in turn, on a thicker pale green layer, typically 1–1.2 mm thick, containing a band of dark orange-brown blebs. A thick grey-black layer beneath the green layer completes the cross-section. It is immediately clear that the sample contains more than one mineral.

Dealing with the layers from the inside out, qualitative analyses by energy-dispersive spectrometry (EDS) indicate that the innermost grey-black layer and the overlying pale green layer are phosphohedyphane. In common with the analyses reported in Green and Tindle (2022a,b) neither of these layers contains any significant copper or vanadium. The thin yellow layer has a composition that is consistent with an intergrowth of zinc-bearing mottramite and phosphohedyphane and the outer black layer a composition that is consistent with a fine-scale intergrowth of mottramite and vanadinite. The dark orange-brown blebs in the green phosphohedyphane also appear to be a fine-scale intergrowth of mottramite and phosphohedyphane.

DISCUSSION

A careful examination of the published data (Collie, 1889), together with a reconnaissance analysis of the original specimen by EDS, shows that 'collieite' is a complex banded intergrowth of phosphohedyphane, mottramite and vanadinite. The approximate contributions of each these minerals to the original analyses are shown (alongside typical compositions of lead-apatites from Leadhills–Wanlockhead) in Figure 3.

If Collie's density measurements and chemical analyses are reliable, the inner black and pale green layers in the original analysed fragments were a pyromorphite–phosphohedyphane intermediate with an average composition that can be described as lead-rich phosphohedyphane (see Fig. 3). This average almost certainly disguises a substantial variation in lead: calcium ratios (Green and Tindle, 2022b).

Some zinc was detected by EDS in the mottramite in this study, but it is not reported in the published chemical analyses. Therefore, the estimate of about 7 wt% admixed mottramite, based solely on the copper

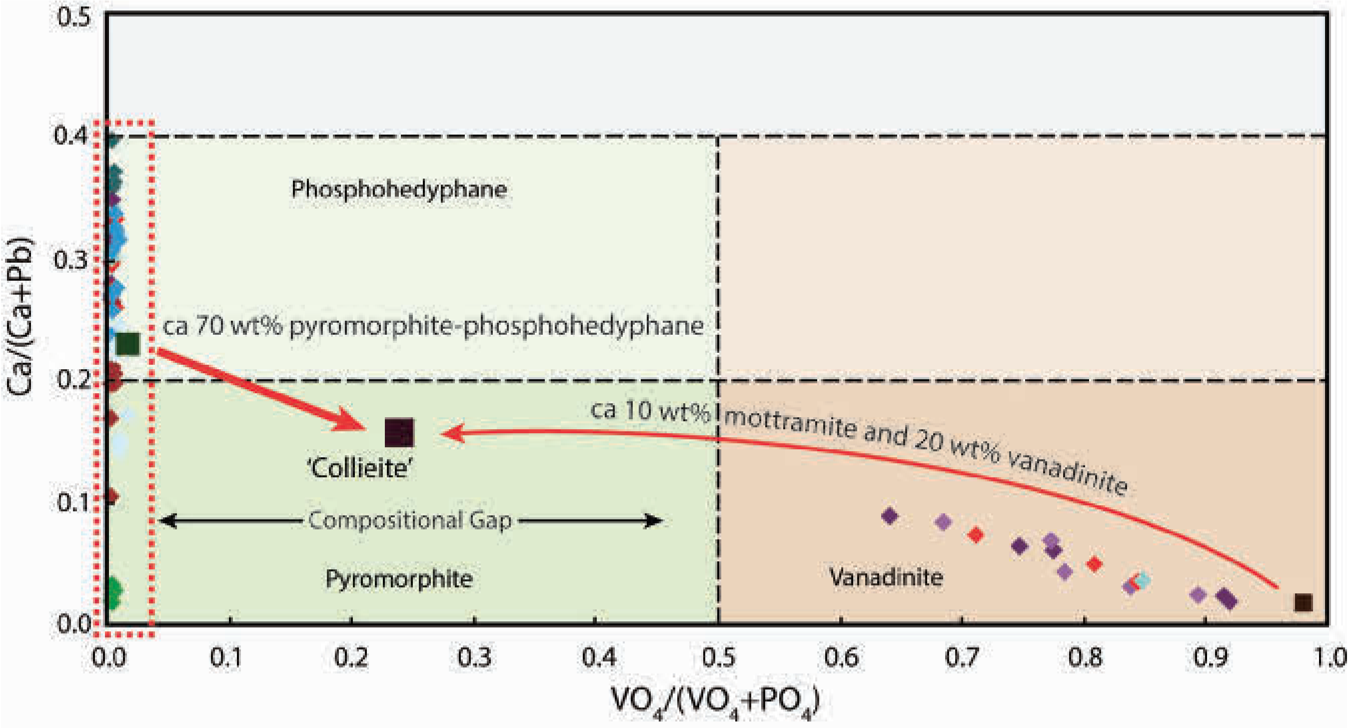


Figure 3. Typical compositions of phosphohedyphane, pyromorphite and vanadinite (various coloured diamonds) from Leadhills–Wanlockhead (see Green and Tindle, 2022a,b), with the composition of collieite (Collie, 1889) indicated by a large black square. An examination of a fragment of the original specimen suggests that the original collieite chemical analyses, determined by traditional wet chemistry, represent an intergrowth of several different minerals. Their compositions are illustrated on the diagram by the dark green square (middle-left), which represents pyromorphite–phosphohedyphane (contributing ca 70 wt% with an average lead-rich phosphohedyphane composition) and the smaller brown square (bottom-right), which represents zinc-bearing mottramite and end-member vanadinite (contributing ca 10 wt% and 20 wt%, respectively).

content, is a lower bound. For this reason, the estimated mottramite content of the original analysed specimens have been increased to 10 wt%.

The vanadinite which is intergrown with mottramite in the outer layer of the specimen does not contain any detectable calcium or phosphate and is therefore close to end-member composition. The remaining vanadate in the collieite analyses can, therefore, be apportioned as end-member vanadinite.

Taken together these data suggest that the original collieite samples were a mixture containing approximately 10 wt% zinc-bearing mottramite, 20 wt% end-member vanadinite and 70 wt% lead-rich phosphohedyphane (see Fig. 3).

The research prompted a search for similar looking specimens. Botryoidal black material from Wanlockhead in the Russell Collection at the NHM has been identified as a mixture of pale grey vanadinite and dark mottramite (Starkey, 2022: p. 130). This is very similar in appearance and composition to the outer collieite layer. A duplicate specimen, misidentified as 'plattnerite', from Wanlockhead in the reserve collection at the NHM proved to have a very similar layered structure to collieite[5]. It includes pyromorphite of close to end-member composition in the innermost layer, some very tiny aggregates of a lead-manganese oxide, and has a rather more complex chemistry than BM 1922,1209, with measurable arsenic, chromium and zinc.

A few observations remain to be explained. The dark grey-black colour of the innermost band of phosphohedyphane in the collieite aggregate is unusual as phosphohedyphane is usually pale pastel green at Wanlockhead (Cotterell and Skotnicki, 2022). The colour may be due to the presence of manganese oxides at concentrations below the detection limit of the EDS system. The fact that mottramite is not noted on any of the X-ray powder photographs is also surprising, especially in view of L. J. Spencer's note that the black surface material was possibly mottramite. The most likely reason is that material from the dark inner layer of the specimen was sampled.

CONCLUSION

Two competing narratives have developed around collieite. One follows the original author and most subsequent researchers and suggests that it is a calcium- and vanadate-bearing variety of pyromorphite. The other describes it as a variety of mottramite. This study shows that both are partly correct. Collieite is a layered intergrowth of lead-rich phosphohedyphane, end-member vanadinite and mottramite in the approximate ratio 70:20:10.

This excursion into a backwater in the history of mineralogy shows the importance of maintaining well

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[5] Now registered in the collection as BM 2022,10.

curated collections and the value of applying the results of a general study (the composition of lead apatites from Leadhills–Wanlockhead) to a particular problem (the identity of collieite). Although the remaining fragment of the original collieite specimen has a volume of less than a cubic centimetre it was more than sufficient to confirm the hypotheses about its chemistry and mineralogical composition using modern analytical techniques.

ACKNOWLEDGEMENTS

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PHOSPHOHEDYPHANE FROM WANLOCKHEAD: A COMMON BUT WIDELY MISIDENTIFIED SPECIES

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Phosphohedyphane has been identified by powder X-ray diffraction and energy-dispersive X-ray analysis on old specimens in the collection of Amgueddfa Cymru. Despite diverse mislabelling, all of the grey-green massive to crustose or botryoidal material examined in this study is phosphohedyphane from Whyte's Cleuch near Wanlockhead, Dumfries and Galloway. These observations raise more general questions about the reliability of information associated with historic specimens.

INTRODUCTION

Mineralogy as a scientific study places considerable reliance on well provenanced specimens. Historic collections have a valuable role to play and remain as important today as when they were assembled. Contemporary specimens have recently been used to show that the type locality for witherite is at Anglezarke in Lancashire and not Alston Moor as was commonly supposed (Cotterell, 2022).

It is common for specimens in old collections to become mixed up or separated from their original data over time. It has occasionally been argued that such specimens have little or no worth and should be deaccessioned or otherwise eliminated from public collections. Such arguments were used to good effect by collectors including Sir Arthur Russell (Starkey, 2022) and Richard Barstow (Starkey and Cooper, 2010) to obtain fine specimens for a fraction of their true value.

In many cases, experienced curators and collectors can be reasonably sure of the provenance of material by careful visual inspection. It is useful to support observational data with analytical investigations. This article describes the application of 'forensic' techniques to a poorly characterised group of specimens in the collection of Amgueddfa Cymru.

ANALYSIS

In 2015, the authors examined a group of green minerals from the collections at Amgueddfa Cymru with identifications or provenance that were considered suspect. Colour was chosen as a simple characteristic to produce a group of manageable size. Seven of the specimens are relevant to this article (Table 1). The material of interest is a pale lime-green to pale greyish green phase, often with a distinctive 'waterworn' appearance or smooth surface texture (Figs 1–6). Despite their striking visual similarities, the specimens had been identified as apatite, pyromorphite or smithsonite and the labels suggested several different localities, or provided no data at all.

Geochemical processes commonly produce similar assemblages at different localities and mineral species may mimic each other's colour and morphology. The original data could have been correct, but curatorial instinct suggested otherwise. One of the benefits of a well resourced department with large and diverse collection is that it is possible to compare anomalous groups with well provenanced material and subject the specimens to confirmatory analyses.

The analytical survey used powder X-ray diffraction (PXRD) to characterise the specimens. They all produced similar diffraction patterns which proprietary software identified as the rare apatite-supergroup mineral caracolite [ideally $Na_3Pb_2(SO_4)_3Cl$]. This seemed highly unlikely. Search algorithms occasionally return erroneous results, especially in attempts to distinguish structurally similar minerals, and therefore the composition of residual powder was investigated by energy-dispersive X-ray spectrometry on a scanning electron microscope (SEM EDS). The unidentified phase contained lead, oxygen, phosphorus, calcium and chlorine, but neither sodium nor sulphur was present. This suggested the structurally similar apatite-supergroup mineral phosphohedyphane, the powder-diffraction pattern for which was absent from the pattern-matching database. When the *d*-values were checked it became clear that all of the unidentified specimens were phosphohedyphane.

Phosphohedyphane, ideally $Ca_2Pb_3(PO_4)_3Cl$, is an apatite-supergroup mineral which was described as a new species from the Capitana Mine, Las Animas Mining District, Copiapœ Province, Atacama, Chile (Kampf *et al.*, 2006). It is a member of the hedyphane group and is structurally related to caracolite, which has a very similar powder diffraction pattern.

DISCUSSION

Although it is much less common than pyromorphite, phosphohedyphane has been identified at a considerable number of localities since it was characterised in 2006

Accession number	Previous identification	Original provenance	PXRD no.	SEM EDS
NMW 88.185.2 [ex. G. T. Clark[a]] (Fig. 1).	Apatite	Unrecorded	NMW X-3165	No
NMW 14.311.GR.190 [ex. F. J. North[b]]	Smithsonite on quartz	Unrecorded	NMW X-3107	Yes
NMW 83.41G.M.8324 [ex. R. J. King Coll.[d] and ex. H. F. Harwood Coll.] (Fig. 2).	Pyromorphite	Leadhills	NMW X-3162	No
NMW 18.95.GR.320 [ex. Rippon Coll.[c]] (Fig. 3).	Smithsonite on quartz	Cumberland	NMW X-3112	Yes
NMW 18.95.GR.331 [ex. Rippon Coll.[c]] (Fig. 4).	Smithsonite on chalcedony	Cumberland	NMW X-3115	No
NMW 18.95.GR.234 [ex. Rippon Coll.[c]] (Fig. 5).	Pyromorphite	Leadhills, Mourne Mountains	NMW X-3164	No
NMW 83.41G.M.8386 [ex. R .J. King Coll.[d]] (Fig. 6).	Vanadinite [on a green mineral which isn't described]	Belton Grain Mine, Wanlockhead	NMW X-3167	No

Table 1. Phosphohedyphane specimens identified during this study. Details of the original collectors are as follows:

[a] George Thomas Clark (1809−1898) of Talygarn Manor, near Llantrisant who donated a small number of mineral specimens to Cardiff Museum in 1888 which were incorporated into the National Museum of Wales when it was founded in 1907.
[b] Frederick John North (1889−1968) first Keeper of Geology at Amgueddfa Cymru from 1914−1959.
[c] Robert Henry Fernando Rippon (1836−1917) an English zoologist, entomologist, illustrator and musician with an obsession for collecting. His scientific collections were purchased by Lord Rhondda [David Alfred Thomas] of Llanwern House, Newport and gifted to the National Museum of Wales in 1918. He died in the same year. Rippon's insect collection amounted to over 100,000 specimens, but his mineral collection was a more modest 3,000 specimens. The geological material included much from the collection of his friend Colonel John Wilson Rimington (1832−1909) but was largely of poor quality and only 428 specimens were accessioned in the museum's collection the remainder going into educational collections.
[d] Robert Joseph (Bob) King (1923−2013) a dedicated mineral collector who acquired many older collections. In 1974 he inherited the better half of a large and historically important mineral collection belonging to Professor Henry Francis Harwood (1886−1974). The King Collection was purchased by Amgueddfa Cymru in 1983.

(Mindat, 2022). There are two important occurrences in the British Isles: the lead mines at Leadhills–Wanlockhead, particularly localities around Whyte's Cleuch, Dumfries and Galloway (Tindle, 2008; Green and Tindle, 2022a,b); and Whitwell Quarry in Derbyshire (Tindle, 2008: p. 391; Starkey, 2018; Briscoe *et al*., 2021).

(*Facing Page*)
Figure 1. 'Apatite', locality unrecorded. Ex Cardiff Museum Collection, donated by G. T. Clark in about 1888. NMW 88.185.2. Analysis by PXRD indicates that the green mineral is phosphohedyphane. The specimen is 60 mm across.
Figure 2. 'Pyromorphite' from Leadhills, South Lanarkshire (formerly Lanarkshire). Bob King Collection No. K8752; NMW 83.41G.M.8324. Analysis by PXRD indicates that the green mineral is phosphohedyphane. The specimen is 68 mm from top to bottom.

Figure 3. 'Smithsonite' on quartz from "Cumberland". Ex Rippon Collection, donated by Lord Rhondda in 1918. NMW 18.95.GR.320. The number on the card label (723) does not match that of a typed label affixed to the specimen (No. 1097). Analysis by PXRD indicates that the green mineral is phosphohedyphane. The specimen is 26 mm from top to bottom.

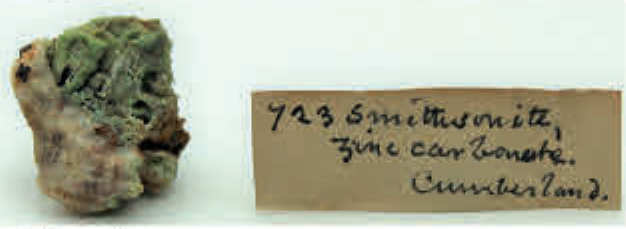
Figure 4. 'Smithsonite' on chalcedony from "Cumberland". Ex Rippon Collection, donated by Lord Rhondda in 1918. NMW 18.95.GR.331. The number on the card label (723 – which is the same as for specimen NMW 18.95.GR.320) does not match that of a typed label affixed to the specimen (No. 28516). Analysis by PXRD indicates that the green mineral is phosphohedyphane. The specimen is 34 mm from top to bottom.

Figure 5. Pyromorphite coating galena from "Leadhills, Mourne Mountains [*sic*]". Ex Rippon Collection, donated by Lord Rhondda in 1918. NMW 18.95.GR.234. The number on the card label (493) does not match that of a damaged typed label affixed to the specimen. Analysis by PXRD indicates that the green mineral is a pyromorphite-phosphohedyphane intermediate. The specimen is 45 mm from top to bottom.

Figure 6. Vanadinite (beige spherules) on green phosphohedyphane from High Pirn Mine, Wanlockhead, Dumfries and Galloway. Bob King Collection No. K894; NMW 83.41G.M.8386. The specimen is 62 mm from top to bottom.

▲ Figure 1

▲ Figure 2



▲ Figure 3

▲ Figure 4

▲ Figure 5 ▼ Figure 6

Figures 1 to 6. Specimens from the collections of Amgueddfa Cymru described in Table 1. Photos Tom Cotterell.

As the occurrence at Whitwell Quarry was not discovered until 1985, and phosphohedyphane is associated with baryte and galena in a dolostone host, it can be discounted as a potential source of the pieces at Amgueddfa Cymru, all of which date from the nineteenth or early twentieth century and are associated with vein quartz. Massive white, yellow, pale green and mid-green material identical in appearance to the phosphohedyphane on the study specimens is abundant at Whyte's Cleuch. It is present on the dumps of New Glencrieff Mine and is found on spoil heaps all the way up the valley as far as the High Pirn Mine. It is sometimes associated with globular brown vanadinite and white crustose hydroxylapatite in the area around High Pirn Mine.

Confusion with Smithsonite

It seems likely that the green crusts on the specimens mislabelled as calamine or smithsonite (Table 1; see Figs 3 and 4) were originally identified on the basis of their appearance. The erroneous identifications are probably the result of an uncritical examination of the mineralogical literature. In the first description of vanadinite from Wanlockhead, Johnston (1831) describes the associated green mineral as 'calamine' (a name applied to both smithsonite and hemimorphite at the time). In the *Mineralogy of Great Britain and Ireland*, Greg and Lettsom (1858: p. 409) note that vanadinite:

> "Has been found both formerly and again lately among the old heaps at the Hegh-pirn [*sic*] of the Susannah mine [*sic*] at Wanlock Head [Wanlockhead], in Dumfriesshire ... on common and cupreous calamine".

This description confuses the High Pirn and Susanna mines (which are separate localities in different mineral liberties) and provides an erroneous identification of the matrix and a credible but false reason for its green colour (the presence of copper). Modern studies show that the white to green material associated with vanadinite is invariably either phosphohedyphane (the 'cupreous calamine' and some of the 'common calamine') or lead-rich hydroxylapatite (the rest of the 'common calamine') (Temple, 1954; Livingstone, 1994a,b; Green and Tindle, 2022a,b).

The confusion with 'calamine' is surprising. A simple acid test would rule out the presence of smithsonite and hemimorphite: smithsonite dissolves with effervescence in hydrochloric acid and hemimorphite gelatinises; phosphohedyphane and pyromorphite, on the other hand, are almost insoluble.

Specimens of vanadinite were known to collectors (though not properly characterised as such) much earlier than 1831. James Sowerby (1817: Plate 543) illustrated 'Phosphate of Lead', almost certainly from Belton Grain Vein at Wanlockhead[1] (Fig. 7). The upper specimen on Sowerby's plate is described as having "the appearance of Calamine, but is distinguishable by its greater weight, colour, and fusibility" (Sowerby therefore realised that it was not hemimorphite or smithsonite). Its colour and botryoidal habit are strongly suggestive of phosphohedyphane. The lower specimen, which is described as "a rare variety from the same place", is clearly vanadinite.

In this context it is also worthwhile recording that Heddle (1901a,b) made no claim of smithsonite from any of the mines at Leadhills–Wanlockhead; his references to 'calamine' refer exclusively to hemimorphite [see parenthetic additions in Heddle (1923, 1924)]. The first claim of smithsonite from the Leadhills–Wanlockhead district in 'Heddle' appears in the supplement to the second edition by J. G. Goodchild, where it is listed 'on the authority of the Geological Survey' (Heddle, 1924: p. 198).

Figure 7. Plate 543, "Phosphate of Lead" from Leadhills from volume five of James Sowerby's *British Mineralogy*. The accompanying text (Sowerby, 1817: p. 267) notes that: "These varieties of Phosphate of Lead should not be passed over, as they, as well as the Carbonates, no doubt, have occasionally been, by many miners who look for Lead, supposing it only of consequence when like Galena ... The crystallized Phosphates are better known, and being more attracting as curiosities, were preferred in collections. The upper specimen is from the Lead Hills; it has much the appearance of Calamine, but is distinguishable by its greater weight, colour, and fusibility. The lower fine specimen is a rare variety from the same place; its colour is very novel; the matrix is principally Quartz".

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[1] The proximity of the mining villages of Leadhills and Wanlockhead, either side of Wanlock Dod, has resulted in old specimens being labelled interchangeably from both settlements. In general, Leadhills gets more mentions than Wanlockhead and is often used in an inclusive sense to describe any locality in the Leadhills–Wanlockhead mining district.

Confusion with Pyromorphite

Many old-time mid-green crustose specimens from the area around Whyte's Cleuch are labelled pyromorphite (see Fig. 5). This error is much more reasonable. Chemical analysis was sufficiently advanced by the late nineteenth century to provide accurate quantitative data (e.g. Collie, 1889), but an understanding of site-specific substitution in the apatite supergroup is relatively recent (Pasero *et al.*, 2010). There was no reason for contemporary mineralogists to suspect that 'calcium-bearing pyromorphite' should be regarded as a distinct species.

In a survey of the mineralisation in the Leadhills–Wanlockhead district, Temple (1954) established that 'calcium-bearing pyromorphite' had a distinctive powder diffraction pattern (that of the mineral now known as phosphohedyphane). Most of the specimens are from Whyte's Cleuch, although one example from Broad Law northeast of Leadhills is noted (Temple, 1954: p. 86) and several further localities are recorded by Green and Tindle (2022a,b).

Misattributions

The incorrect attributions or lack of provenance on the specimens examined in this study are partly a reflection of their age (when locality data was less valued) and they have been compounded by poor curatorial practice. Some have lost their associated labels. The best defence against such against disorder is provided by small permanent labels fixed directly to the pieces themselves.

The claim that specimen NMW 18.95.GR.234 (see Fig. 5) is from the Mourne Mountains is clearly in error and can be discounted immediately. The specimens in the Rippon Collection labelled 'Cumberland' (see Figs 3 and 4) were probably assumed to be from one of the pyromorphite localities in the Caldbeck Fells (Cooper and Stanley, 1990). Specimens from the Caldbeck Fells are commonly confused with Leadhills–Wanlockhead in old collections. The type specimen of mattheddleite, for example, was accompanied by data which suggested it was from the Caldbeck Fells, but was re-assigned by the authors to the Leadhills–Wanlockhead district (Livingstone *et al.*, 1987). Traces of a mineral that falls just within the composition field of phosphohedyphane have been identified at the outcrop of the Roughton Gill South Vein in higher Roughton Gill (Green *et al.*, 2008), but no similar material was noted in a detailed survey of the main Roughton Gill Mine (Bridges *et al.*, 2011), and there is no indication that phosphohedyphane is present in substantial quantities at any other site in the Caldbeck Fells.

The unifying characteristics of the specimens examined in this study are the presence of fairly thick crusts or solid aggregates of phosphohedyphane with massive vein quartz, encasing relict primary galena, or with scattered globular vanadinite. These features are characteristic of localities in and around Whyte's Cleuch.

The Matrix for Vanadinite

The identification of phosphohedyphane on the seven questionable specimens at Amgueddfa Cymru and their attribution to Whyte's Cleuch prompted a re-examination of specimens from nearby localities. Six specimens in the R. J. (Bob) King Collection [NMW 83.41G.M.8381; 8382; 8388; 8390 (Fig. 8); 8391(Fig. 9); 8393] were investigated. White to pale green supergene crusts and boxworks overgrow quartz veinstone and are overgrown by globular aggregates of vanadinite on these specimens. An analysis of crusts showing a colour change from white at the base to pale green on the upper surface on specimen NMW 83.41G.M.8391 reveal they are a mixture of 'apatite' and phosphohedyphane (NMW X-3827).

Bob King inherited the specimens in question from Henry Francis Harwood in 1974. Two are registered as from Belton Grain Mine [Wanlockhead], one from Beltongrain, High Pirn Mine [Wanlockhead], two from Wanlockhead and the last specimen from Leadhills. Harwood's original labels reveal that four were labelled "Wanlockhead" and two "Leadhills". The attributions to Belton Grain Mine appear to have been made after King acquired the specimens. Published records relating to vanadinite in Scotland support these attributions, although they would have been better documented as from 'Belton Grain Vein at High Pirn Mine' and it would have been helpful if the reasoning had been explained.

In the mid-1990s, Livingstone (1994a) described a chalky white lead-rich hydroxlyapatite intimately associated with globular vanadinite from the lead

Figure 8. Vanadinite (beige spherules) on a thin pale grey-green crust of phosphohedyphane coating partially oxidised galena. Beltongrain [Vein], High Pirn Mine, Wanlockhead, Dumfries and Galloway, Scotland. Henry Francis Harwood Collection then Bob King Collection No. K6305; NMW 83.41G.M.8390. The label attached to this specimen is 25 mm in length. Photo Tom Cotterell.

Figure 9. Vanadinite (beige spherules) on pale green to white phosphohedyphane from Beltongrain [Vein], High Pirn Mine, Wanlockhead, Dumfries and Galloway. Henry Francis Harwood Collection and then Bob King Collection No. K6306; now NMW 83.41G.M.8391. The specimen is 89 mm from top to bottom. Photo Tom Cotterell.

mines at Wanlockhead in Scotland. Chemical analyses produced an empirical formula:

$$(Ca_{8.78}Pb_{1.22})_{\Sigma=10}[(PO_4)_{5.53}(CO_3)_{0.44}]_{\Sigma=5.97}(OH_{1.70}F_{0.73}Cl_{0.13})_{\Sigma=2.56}\cdot 1.5H_2O,$$

on the basis of ten *M*-site cations (*Z*=1). This is consistent with carbonate- and lead-bearing hydroxylapatite[2]. A specimen of vanadinite in the R. J. King collection (NMW 83.41G.M.8387) labelled “Beltongrain [vein], High Pirn Mine, Wanlockhead, Dumfries & Galloway” matches Livingstone’s description (Fig. 10). The specimen was formerly part of the Harwood Collection and was previously labelled as from “Belton Grain Vein”. Analysis of the white material by PXRD (no. NMW X-3752) confirm that it is a calcium apatite [undifferentiated between hydroxylapatite, fluorapatite or chlorapatite].

Figure 10. Vanadinite (beige spherules) scattered on porous, silky white stalactitic ‘apatite’. Beltongrain [Vein], High Pirn Mine, Wanlockhead, Dumfries and Galloway. Henry Francis Harwood Collection then Bob King Collection No. K6302; NMW 83.41G.M.8387. The specimen is 90 mm from top to bottom. Photo Tom Cotterell.

Unlike phosphohedyphane, old-time vanadinite specimens from Belton Grain Vein are highly prized by collectors of classic British minerals. They are usually correctly provenanced owing to their rarity and distinctive appearance, but old labels commonly misidentify the minerals in the matrix.

The recent discovery of a closely similar assemblage of minerals at Whitwell Quarry in Derbyshire (Briscoe *et al*., 2021) shows the potential risks associated with reassigning the provenance of specimens. It must be done with care: old labels should not be discarded, but new ones added and the reason for the changes recorded. In this instance it is clear that none of the specimens are from Whitwell Quarry, but distinctions can blur over time.

CONCLUSION

Crustose material on old-time specimens from Whyte’s Cleuch near Wanlockhead is commonly misidentified. Colour and form provide a useful guide: white crusts with vanadinite may be lead-rich hydroxylapatite or phosphohedyphane or a mixture of the two; smooth botryoidal stalactitic crusts in pale shades of green, mint-green, yellow-green or blue-green are

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[2] The formula has an extraordinarily high *X*-site occupancy. There is some evidence that the *X*-site occupancy may exceed the ideal stoichiometric value in apatite-supergroup minerals (Green and Tindle, 2022a,b), but even if the neutral water is discounted, the *X*-site occupancy is very high. It is likely that the calculations have omitted *M*-site vacancies and there is a small error in the *T*-site anion sum as discussed in Green and Tindle (2022a).

usually phosphohedyphane. Analyses, ideally by powder X-ray diffraction supported by energy-dispersive X-ray spectrometry, are required to differentiate phosphohedyphane and pyromorphite, but confusions with hemimorphite (and smithsonite) can be eliminated by simple acid tests.

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THE COMPOSITION OF PYROMORPHITE FROM COLDSTONES QUARRY, GREENHOW, NORTH YORKSHIRE

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Pyromorphite of near end-member composition occurs in fractures in Namurian sandstones at Coldstones Quarry, Greenhow, North Yorkshire. Green prismatic crystals up to about 3 mm in length are associated with baryte and quartz. The empirical formula, $Pb_{4.92}Ca_{0.05}M^{2+}_{0.01}[(PO_4)_{2.92}(SiO_4)_{0.02}]Cl_{1.08}$, is very close to ideal end-member composition. The absence of any major substituents reflects crystallisation in a geochemically simple supergene environment.

INTRODUCTION

Coldstones Quarry [SE 125 641] produces aggregate from the thick Lower Carboniferous limestones of the Coldstones Dome at a hill-top site near the village of Greenhow. It is well known for low-temperature Pennine-type lead-zinc mineralisation and has been a regular venue for Russell Society field trips for many years. Two major veins, Coldstones Sun Vein and Garnet Vein, cross the site and numerous smaller structures are sporadically exposed.

The principal primary minerals are baryte, calcite, fluorite and galena. Sphalerite, which was abundant before the deposits were exposed to supergene oxidation, has been replaced by hemimorphite and smithsonite. Cerussite is the most widespread lead-bearing supergene mineral. Anglesite is well known (and prized by collectors), but it is uncommon and for the most part restricted to pockets in massive galena. Other supergene minerals which have been identified include aurichalcite, bindheimite, cinnabar, doyleite, goethite, gypsum, hydrozincite, malachite, otavite, prosopite, rosasite and sulphur. These combine to make Coldstones Quarry one of the most diverse and interesting mineral localities in the Yorkshire Pennines (Young *et al.*, 1989; 1997; authors' unpublished data).

ANALYSIS

In 2006 the authors made a reconnaissance study of the composition of lead-bearing apatite-supergroup minerals from the British Isles in preparation for the publication of *Minerals of Britain and Ireland* (Tindle, 2008). The principal objectives were to differentiate pyromorphite and mimetite at localities where there was little previous data and to establish the composition of 'calcium-rich pyromorphite' which had been investigated by X-ray powder diffraction and produced powder patterns that were difficult to interpret[1].

A pyromorphite specimen from Coldstones Quarry (accessioned as N14684 at Manchester Museum) was chosen as a 'standard' because the powder pattern was close to those published for pyromorphite and energy-dispersive X-ray spectrometry had only revealed the presence of lead, phosphorus and chlorine. It was one of a number of specimens which were selected to test whether the analyses and subsequent calculations would generate reasonable stoichiometries.

A millimetre-size crystal fragment was embedded in epoxy resin and ground and polished for analysis. Measurements were made at an accelerating voltage of 20 kV and beam current of 20 nA, with a 10 μm defocused beam and matrix-appropriate standards. Five independent analyses are listed in Table 1.

The principal elements present with an atomic number greater than 10 are lead, phosphorus and chlorine. The tabulated summary includes calcium which is present at between 0.1 and 0.3 wt% CaO, and silicon at between 0.1 and 0.2 wt% SiO_2. All other elements are either below detection limits or present at much less than 0.1 wt%.

A detailed discussion of the crystal chemistry and stoichiometry of lead apatites, the experimental procedure, and the techniques used to calculate empirical formulae, is given in Green and Tindle (2022a,b) and there is no benefit in repeating it here. The mean empirical formula, calculated on the basis of nine atoms per formula unit and rounded to two decimal places, is:

$$Pb_{4.92}Ca_{0.05}M^{2+}_{0.01}[(PO_4)_{2.92}(SiO_4)_{0.02}]Cl_{1.08},$$

where M^{2+} is a placeholder for traces of divalent species plus sodium.

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[1] At the time the study was initiated phosphohedyphane had not been characterised as a new species (Kampf *et al.*, 2006). It is worth noting, however, that pyromorphite with a 'complex diffraction pattern' but without substantial calcium substitution has been reported from Old Rake Vein in the North Swaledale Mineral Belt (Small, 1977).

No.	CaO	PbO	SiO_2	P_2O_5	Cl	Total	O=Cl	Total
P205	0.11	82.23	0.11	15.41	2.89	100.90	0.65	100.25
P205	0.10	81.65	0.09	15.09	2.81	99.78	0.63	99.14
P205	0.19	81.86	0.10	15.17	2.77	100.18	0.63	99.55
P205	0.29	82.23	0.10	15.74	2.90	101.43	0.66	100.77
P205	0.27	82.06	0.14	15.74	2.99	101.39	0.67	100.72
Mean	0.13	81.91	0.10	15.22	2.82	100.29	0.64	99.65

Table 1. Five analyses of pyromorphite from Coldstones Quarry including all of the elements detected at mean concentrations of >0.1 wt%. Other elements which were sought include aluminium, arsenic, barium, cobalt, copper, iron, magnesium, manganese, sodium, strontium, sulphur, titanium, vanadium and zinc. All of these are present at maximum values of <0.1 wt% with mean values of $\leqslant$0.02 wt%. They have no effect on the empirical formulae to two decimal places and are best dealt with as 'trace elements', but are included in the totals. The penultimate column O=Cl is the compensation required in the calculations because the cations are reported as neutral oxides (Deer *et al*., 2013).

The formula is very close to ideal apatite-supergroup stoichiometry: the sum of divalent cations at the $M(1)$ and $M(2)$ sites is 4.98±0.07 (ideally 5.00); the T-site anion sum is 2.94±0.04 (ideally 3.00); and the X-site chlorine sum is 1.08±0.04 (ideally 1.00). The oxide sum (corrected for O=Cl as described in Deer *et al*., 2013: pp. 485–486) is 99.7±1.1 wt%, which is very close to the expected 100 wt%.

DISCUSSION

Pyromorphite from Coldstones Quarry is very close to ideal end-member composition. This probably reflects alteration in a geochemically simple supergene environment. There is minor substitution of calcium for lead and of silicate for phosphate. Traces of barium, cobalt, copper, iron, magnesium, sodium, strontium and zinc are included as $M^{2+}_{0.01}$ in the mean empirical formula, but none of these elements is present in amounts that are significant at two decimal places. Arsenic was detected in two of the five analyses, but the mean value corresponds to 0.003 arsenate anions per formula unit. Vanadium was below the detection limit in every case. The mean charge imbalance of 0.04±0.15 is not statistically different from the expected value of zero. Taken together these data suggest that the empirical formula is reliable (Pasero *et al*., 2010; Green and Tindle, 2022a). The only slight deviation from ideal apatite-supergroup stoichiometry is a small but statistically significant excess of chloride ions, but it does not give cause for concern as it is at the relatively flexible X-site (Mason *et al*., 2009).

Pyromorphite is uncommon in Pennine lead deposits (Dunham and Wilson, 1985). The material described in this article was discovered on a Russell Society visit in June 1998. The field trip report (Critchley, 1998) records:

> "It was on this level [the upper southwest bench], just as we were getting to the shales, that Christine Critchley picked up a small piece of gritstone which looked green. On closer inspection this was identified as pyromorphite. A rapid look around enabled us to find three more pieces and then that was that. Simon [Broad] said that it had never been found in the quarry before, a 'first' that made our day! The bright green pyromorphite was on what looked like a quartz base on the gritstone and the bits of baryte attached suggested that it had come from the edge of a baryte vein in the grit. The crystals were well formed hexagonal prisms up to about 2mm".

A specimen collected on that day is illustrated in Figure 1.

Subsequent fieldwork by Simon Broad, the Assistant Manager at the time, traced the specimens to a small vein in alternating fine- and coarse-grained siliciclastic rocks of the Namurian Millstone Grit Group exposed on the top bench of the quarry. These rocks surround the massive limestones of the Coldstones Dome. A medium-grained yellow-brown sandstone unit, at least 3 m thick, contained a thin fracture filled with curved platy baryte, brown iron oxyhydroxides and patches of well crystallised dark green pyromorphite. The fragment that

Figure 1. Prismatic pyromorphite crystals up to 3 mm in length in a fracture in Namurian sandstone from Coldstones Quarry, Greenhow, North Yorkshire. Harry Critchley Collection. Photo John Chapman.

was analysed in this study (and a number of specimens now preserved in the mineral collection at Manchester Museum with accession numbers N14420; N14684–N14686; N14694 and N15393) are from this locality.

Pyromorphite is widespread but generally rather sparse in the area around Greenhow. An early report of "Phosphate of Lead" is included in Nathaniel Winch's *Observations on the Geology of Northumberland and Durham*. Winch (1817: p. 84) notes pyromorphite:

> "Of a siskin green colour, crystallized in small 6-sided prisms, terminated by 6 planed acuminations, forming clusters in light yellowish brown marly earth: from Surside mines, Netherdale, Yorkshire".

Netherdale is an early synonym of Nidderdale and the "Surside mines" almost certainly refer to the Sunside mines in the Greenhow lead mining field (Gill, 1998). Dark green pyromorphite is present in oxidised veinstone on the large spoil heaps outside the Gillfield and Cockhill levels in Brandstone Beck (David McCallum, *personal communication*, 2015). Colourless, yellow and pale green crystals have also been found along Greenhow Rake, on spoil heaps near the intersection of Waterhole Vein and Green Grooves Vein to the north of Greenhow, and in siliceous matrix from the fluorspar workings on Galloway Vein to the south of the village. Surprisingly, Dunham and Wilson (1985) do not mention any of the pyromorphite localities around Greenhow in their account of mineralisation in the Askrigg Block, but they note good specimens from Merryfield Vein in Ashfold Side Beck, about 2 km to the north. Dark green crystalline masses made up of aggregates of blocky prismatic crystals up to about 5 mm long are found in dark brown clay at this locality (Tim Smith, *personal communication*, 2014).

The pyromorphite occurrences in thick sandstones around Greenhow, together with localities in chert and silicified limestone in the North Swaledale Mineral Belt (Small, 1977, 1982; Dunham and Wilson, 1985; Charles Lamb, *personal communication*, 2018) are the richest in the Yorkshire Pennines. They illustrate a strong tendency toward formation in baryte-dominated mineral deposits in siliceous wall-rocks, probably because the carbonate ion activity is sufficiently depressed in these environments to stabilise pyromorphite rather than cerussite (Bridges, 2015).

Although pyromorphite appears to have an aversion to high carbonate environments in the Pennines it has been found associated with massive galena collected from clay-filled gulphs in carbonate host rocks at Coldstones Quarry (Neil Hubbard, *personal communication*, 1998). In these specimens it seems likely that a local barrier to fluids in equilibrium with the carbonate host-rocks (possibly phosphate-bearing glacial clay) allowed a micro-environment to develop in which pyromorphite was more stable than cerussite (Fig. 2).

CONCLUSION

Pyromorphite from Coldstones Quarry is very close to ideal end-member composition. The only minor substitutions are calcium for lead and silicate for phosphate. A small group of specimens with well formed dark green prismatic crystals to 3 mm collected in 1998 from a thin vein in Namurian sandstone are among the few examples that have been collected from the site. This underlines the importance of regular fieldwork and careful curation of specimens and their associated data. The distribution of pyromorphite at Coldstones Quarry illustrates a general tendency for pyromorphite to form in baryte-dominated deposits in siliceous wall-rocks in the mineral deposits of the Askrigg Block.

ACKNOWLEDGEMENTS

The staff at Coldstones Quarry have welcomed scientific societies of all sorts for many years. The authors would like to thank Bob Orange, the quarry manager, who was kind enough to allow visits from the mid-1980s on; Simon Broad, the assistant manager, whose persistence led to the discovery of the vein *in situ*; and Shirley Everett who continued the tradition. Harry Critchley is thanked for donating one of the specimens collected on a Russell Society field trip to Manchester Museum and Neil Hubbard for donating another specimen (N16254) which showed that pyromorphite is not entirely restricted to the siliciclastic units at Coldstones Quarry.

Figure 2. Drusy pyromorphite overgrowing and replacing blocky vee-twinned cerussite on galena with minor fluorite from Coldstones Quarry, Greenhow, North Yorkshire. Harry Critchley Collection (obtained from Midland Minerals). Photo John Chapman.

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ALEXANDER THOMS:
A BIOGRAPHICAL STUDY

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Alexander Thoms (1837–1925) was one of Matthew Forster Heddle's closest friends. He was responsible for bringing Heddle's masterpiece, *The Mineralogy of Scotland*, to publication and married his beloved daughter Clementina. Although he published very little, Thoms was well regarded as natural scientist. He was a mainstay of the St Andrews Literary and Philosophical Society and his remarkable mineral collection is preserved at The Hunterian Museum in Glasgow. Thoms' family, early life, career in India, friendship with Heddle and philanthropic work are described and there is a short introduction to his interest in mineralogy.

INTRODUCTION

Admirers of Matthew Forster Heddle (Johnston, 2014, 2015, 2022) may have a passing familiarity with Alexander Thoms[2] who was responsible for the posthumous completion and publication of *The Mineralogy of Scotland* (Heddle, 1901). Thoms dedicated the book to Heddle's eldest daughter Clementina, whom he married in 1898 shortly after Heddle's death. Little is recorded of Thoms' life and his philanthropic and scientific achievements. This article provides the biographical context for a study of Thoms' collections, which are described in a complementary article in this journal (McMullen, 2022).

FAMILY HISTORY

Alexander Thoms' paternal grandfather, also Alexander (*c.* 1740–1809), was a textile merchant who owned three country estates including West Clepington just north of Dundee. He was involved in the administration of the town and was Provost[3] twice between 1794 and 1800.

Thoms' father, John (1794–1888) was the second of Alexander's six sons. He and his brother James (1797–1859) were involved in shipping and textile manufacture. Cloth work was a lucrative business in the first half of the nineteenth century. Dundee had overtaken Leeds as the largest linen manufactory in Britain by 1840 and its population tripled between 1800 and 1850. Thoms' ships imported the raw materials for cloth production and exported the finished goods.

Thoms' mother, Barbara (née Wise) (1806–1884) was from a prosperous local family. Her father, Thomas Wise (1755–1819) was a physician and owned the Claremont Estate in Jamaica. On his return to Scotland he married Anne Chalmers and bought the Hillbank Estate, north of Dundee. They had six children between 1796 and 1806, Barbara being the youngest and the only daughter.

John and Barbara Thoms had twelve children, of whom Alexander, born 9 November 1837, was the eldest son. The family moved to Mylnefield House near Longforgan, west of Dundee, in 1844, and remained there for the next seven years. Here the young Thoms learned about estate management and country pursuits. He visited the nearby Kingoodie quarries, which produced the stone for London's docks, and saw the opening of the Perth to Dundee railway, which passed between Mylnefield and the Firth of Tay.

By 1851, John had accumulated sufficient wealth to purchase the Pitscottie Estate in Fife and retire from active trading. He moved to the douce antiquity of St Andrews where he bought Seaview[4], a mansion in large grounds linking the Scores to North Street. Financial security gave the family the time to engage in local culture. John was elected a member of the prestigious St Andrews Literary and Philosophical Society in 1856. Its members consisted of university professors, clergymen, landed gentlemen and civic leaders. Matthew Forster Heddle, the new Assistant Professor of Chemistry, was elected in the following year. It must have been soon after this that young Alexander Thoms met the man who would become his closest friend.

CAREER

Four of Thoms' uncles (on his mother's side) pursued careers in Bengal. Thomas A. Wise (1802–1889) was a doctor and educational administrator with the East India Company who retired to Edinburgh in 1852. In later life he donated his Indian and Nepalese artefacts to Dundee College[5], and a remarkable collection of maps of the

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[1] Matthew Forster Heddle's great-great-grandson and biographer (see Johnston, 2014; 2015).

[2] Alexander, a popular name in the Thoms family, is a source of confusion in genealogical research. In this article, the name Thoms refers to Alexander Thoms (1837–1925) unless otherwise stated.

[3] In Scotland the Provost is civic head of a town council; Dundee was a town (and Royal Burgh) until 1889 when it was granted the status of city.

[4] Seaview was purchased by the University in 1933 and demolished to make way for St Salvator's Hall, the students' residence.

[5] The Wise Collection is currently held in the McManus, Dundee's Art Gallery and Museum.

Himalaya to the India Office Library, now the British Library (Lange, 2020).

Three other uncles, led by Josiah P. Wise (1803–1879), were involved in the indigo business. Until it was replaced by synthetic dyes in the late nineteenth century, indigo was an exceptionally valuable crop, being the only source of a fast brilliant blue. Josiah P. Wise went to Bengal around 1824/5 and became very successful. By 1857 "Indigo production in Dacca and the neighbouring districts in eastern Bengal was all but monopolised by J. P. Wise", according to Kling (1966). This was to influence Alexander Thoms' choice of career.

Thoms was about fifteen when his family moved to St Andrews. An inscription in a book from his personal library, which reads:

> "to Mr. Alexander Thoms as an expression of esteem, for excellent ability, diligence in the prosecution of his studies, and an amiable disposition. From his tutor, Robert Bell M. A. St Andrews 27 July 1855"[6],

suggests he was privately educated. As a young member of a successful, outward-looking commercial family it is not surprising that when Josiah Wise visited Scotland in 1858 he encouraged his nephew to join the family business. Thoms was in his early twenties when he travelled to Bengal. After gaining experience in the field, he became manager of several of Wise's concerns (groups of indigo factories) in Mymensingh and Phulbari. At that time, the indigo business was mired in controversy. The unfair pressure it put on local farmers led to the so-called Blue Mutiny, which began in 1859. Josiah Wise was the lead representative of the Indigo Planters' Association and gave evidence to the Indigo Commission between 1859 and 1861 but it seems he could see the problematic nature of the business and began a gradual withdrawal soon thereafter. He diversified into tea planting, a trade he had entered in 1856 after acquiring plantations in Cachar, Assam.

By 1869, Thoms was general manager of Wise's indigo concerns, and from 1870 he operated from his uncle's headquarters in Dacca (Dakha), attending to contracts, sales, land deals, finances and taxation. In 1873, Wise retired to Rostellan Castle near Cork, Ireland, leaving Thoms to manage all his businesses in India.

Thoms was a trustee of Wise's will, and when he died in 1879 had responsibility for managing and disposing of his assets in India. Thoms continued in this role after he returned to Scotland, expanding and consolidating the tea plantations around the Joyling name, which was the last Wise business to be sold in 1888.

The career Thoms had pursued as J. P. Wise's lieutenant in India gave him the business and financial acumen which he would later use for the benefit of the Church of Scotland, voluntary organisations, the City of St Andrews and his great friend Matthew Forster Heddle.

RETURN TO ST ANDREWS

In 1878, Thoms left India and returned to St Andrews. He purchased 7 Playfair Terrace (Fig.1) and, in 1879, married Mary Watson Wemyss (1849–1880), the daughter of a retired Edinburgh surgeon. Mary soon became pregnant, but she and her infant son died in March 1880 following a traumatic confinement. In September 1884, Thoms married Jane Fowler (1855–1890), the daughter of a church minister and a son, also Alexander, was born in June 1885. Jane suffered a catastrophic heart attack in September 1890 while the family was travelling through Perthshire, leaving Thoms widowed once again, with a five-year-old son to take care of.

Thoms' father John died at Seaview in 1888, at the grand old age of 93. At the time of his second wife's death Thoms was managing the dispersal of the family estates,

Figure 1. The stone-built 7 Playfair Terrace, which Thoms purchased on his return to St Andrews and where he lived for the rest of his life. Photo Hamish Johnston.

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[6] This volume, Edward Lucett's *Rovings in the Pacific, from 1837 to 1849*, is currently held in St Andrews University Special Collections (s G478.L8).

particularly the feuing of Clepington, which was gradually disappearing beneath the expanding suburbs of Dundee. The various financial settlements and transactions and his ownership of other properties provided a significant income, which was increasingly devoted to philanthropic endeavours.

FRIENDSHIP WITH HEDDLE

Thoms and Heddle were good friends by the early 1880s. Heddle took Thoms under his wing and encouraged his scientific studies, particularly in mineralogy (Fig. 2). In 1883, ahead of his retirement from the Chair of Chemistry at St Andrews University, Heddle accepted a lucrative contract in South Africa as geologist, assayer and adviser to Lisbon-Berlyn (Transvaal) Gold Fields Ltd. It was almost certainly Thoms who negotiated his remuneration, which included a valuable annuity. A man of strong principles, Heddle exposed the company when, after arriving at the properties, it became clear they had exaggerated their claims. He was sued for breach of contract and return of all monies paid. Heddle fought and won the case. Although, as Heddle had predicted, the company collapsed, the annuity emerged intact. Heddle subsequently benefited from Thoms' financial advice when his younger son Stuart, who had emigrated to America in 1892 to take up farming, acquired property there.

In 1886, Thoms was elected a member of the St Andrews Literary and Philosophical Society. The Society was in decline at the time, and was in danger of being wound up, but Thoms' appointment as Secretary in March 1888 generated a significant revival. Thoms re-established regular programmes of talks on up-to-date topics delivered by noteworthy speakers, including Heddle, J. G. Goodchild (1844–1906) of the British Geological Survey, and Ramsay Traquair (1840–1912), palaeontologist, of the Edinburgh Museum. In 1894, to maintain interest, Thoms presented *A Brief Account of the Origin and Work of the Literary and Philosophical Society of St Andrews During the Last 56 years* which, at Heddle's suggestion, was later published.

By the end of the 1880s, Heddle's health, which had worsened in the years before his retirement, had deteriorated further. He wanted his mineral collection to go, in its entirety, to a prestigious museum. In 1890, his friend Patrick Dudgeon (1817–1895) entered into negotiations with the British Museum, but they were unsuccessful because it would not take the entire collection. Thoms took over, with the aim of keeping

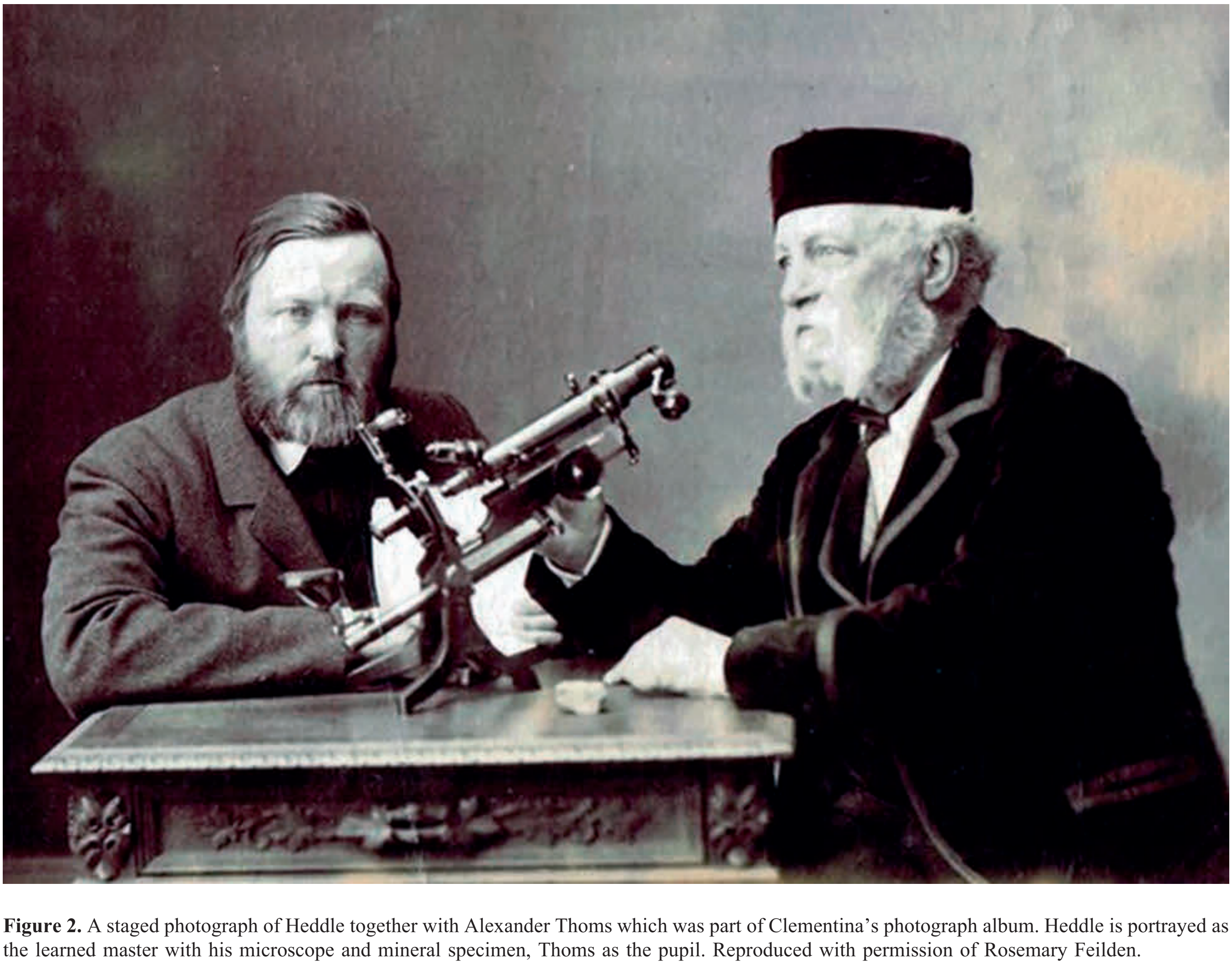

Figure 2. A staged photograph of Heddle together with Alexander Thoms which was part of Clementina's photograph album. Heddle is portrayed as the learned master with his microscope and mineral specimen, Thoms as the pupil. Reproduced with permission of Rosemary Feilden.

the collection in St Andrews. He secured the agreement of the St Andrews Literary and Philosophical Society to accept it, part by gift, part by purchase, knowing that this would require the University, which owned the museum, to construct an extension. The plan was abandoned when the University failed to raise the necessary funds. Thoms was unusually forthright in his condemnation (StALPS, 1891), recording:

> "for reasons I consider to be wholly unworthy of such an educational board this grand collection has now been offered to Edinburgh where it has been received with the highest gratitude".

A man of extensive experience, Thoms had anticipated the outcome and separately reached an agreement with the Edinburgh Museum of Science and Art (now the National Museum of Scotland), who were pleased to agree to Heddle's conditions: the payment of 'a thousand pounds for a thousand specimens', the remainder being donated, and that Heddle would help to integrate the collection with that of his long-time friend and collecting partner Patrick Dudgeon in display cabinets to be constructed to his own design. Heddle's collection was integrated with Dudgeon's and the new mineral gallery opened to great acclaim in September 1895.

In the last years of his life Heddle worked tirelessly on *The Mineralogy of Scotland* but the many precise drawings of crystals absorbed too much time and the work was incomplete when he died in November 1897. In his will Heddle appointed a committee, led by Thoms, to complete and publish the work. The principal editor was J. G. Goodchild who concentrated on the text. Goodchild had helped Heddle organise and label the collection at the Edinburgh Museum and developed a good understanding of his thinking, style and intentions. Goodchild's son, Wilbert (1870–1944), completed the remaining crystal drawings. James Currie (1863–1930), a wealthy shipowner recognised for his expertise in botany and mineralogy, dealt with locality details and provided a chapter on Scottish pseudomorphs[7]. Thoms wrote the introductory memoir which describes Heddle, and compiled the lists of minerals found in each Scottish county. Although not alluded to in Heddle's manuscript, Thoms judged it advisable to place on record Heddle's view that he had identified diamonds at Ben Hope in Sutherland, a notion that was only dismissed in the first decade of this century (Faithfull, 2007). *The Mineralogy of Scotland* was completed by the end of 1900 and published in two volumes by David Douglas of Edinburgh in the next year.

Over the years Thoms had become very close to Heddle and his family. Heddle's wife Mary died in 1891, after which Clementina, the eldest daughter, returned to run the household. Her father's death in November 1897 allowed her to put her own interests first and she married Thoms in April 1898. Thoms dedicated *The Mineralogy of Scotland* to her. Clementina was Thoms' third wife but his misfortunes were not over: their son was stillborn on 14 February 1899. The couple seem, nonetheless, to have had a successful relationship: faded photographs, dating from the first decades of the twentieth century show the family on holiday together (Fig. 3).

As Secretary, Thoms continued to be the driving force behind the St Andrews Literary and Philosophical Society. The most important issue in the early 1900s was the future of the museum. The Society could no longer manage the collection adequately, and in 1903/4 Thoms instigated negotiations which transferred ownership to the University. Although the Society continued to hold meetings, their frequency became erratic and attendance declined. In an attempt to reverse its fortunes Thoms secured Archibald Geikie, Britain's foremost geologist, as President. Geikie was elected in 1901, and re-elected twice more. Despite these efforts the decline could not be reversed, and in February 1916 Thoms called a meeting at which it was decided that the Society was moribund and should be wound up. The minute books, other papers and residual funds passed to the University.

PHILANTHROPY

The involvement with *The Mineralogy of Scotland* was but one of Thoms' philanthropic endeavours. A committed and practical Christian he devoted himself to good works in his later years. He campaigned energetically on behalf of the Church of Scotland and the St Andrews Memorial Cottage Hospital.

Thoms had become an elder of St Leonard's Church in 1884, and its Treasurer in 1888. He was much involved in controversial events that began in 1899 when the University terminated the arrangement under which the St Leonard's congregation had used St Salvator's College Church after its own place of worship fell into disrepair in 1759. The ruined building stood adjacent to the Thoms-owned St Leonard's House, and the Parish wanted to repair and enlarge it by acquiring some of their land. The matter went to the courts on several occasions in 1899 and 1900, and eventually a decision was taken to build a new church in Hepburn Gardens. Although he had been in dispute with the Parish, Thoms was central to the new church project. He made substantial financial contributions and after the church opened in 1904 Thoms and Clementina donated a silver baptismal bowl and silver communion set in memory of their stillborn son.

The spread of the gospel worldwide was close to Thoms' heart. The National Bible Society of Scotland provided Bible translations in support of church missions abroad and Thoms was its Treasurer from the 1890s onward. Failing eyesight forced him to resign as church Treasurer in 1921 but throughout his life he spared neither time nor money in support of the church and its work. Thoms was personally devout but noted for his lack of ostentation. He attended daily services until the end of his life.

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[7] After Currie's death in 1930 his wife donated his extensive mineral collection to Edinburgh University. It is now in the Cockburn Museum.

Figure 3. A faded photograph, thought to date from the 1900s, showing, from left to right, Katie Heddle, Ethel Marshall (née Heddle), William Marshall (front), Alexander Thoms (rear), Cecilia Thomson (née Heddle), Clementina Thoms (née Heddle) and Matilda 'Tillie' Johnston (née Heddle). Copyright private collection.

Thoms' philanthropy is best illustrated in his work for the St Andrews Cottage Hospital. At the beginning of the twentieth century he became fully engaged with the planning, construction and management of a replacement hospital. In March 1901, land was acquired in Abbey Park and a new eighteen bed hospital was begun. In May 1901, Thoms was elected as one of four Hospital trustees. Thoms and Clementina paid for the furnishings in the six bed children's ward, which opened in August 1902. Thoms continued his involvement through membership of the management committee, serving continuously and paying daily hospital visits for the remainder of his life. He was pleased to contribute time and money to any scheme that would benefit the hospital and the committee chose him to represent them when the Prince of Wales (later King Edward VIII) was invited to St Andrews to receive the freedom of the city in September 1922.

Thoms died at the age of 88 on 26 December 1925 at his home in Playfair Terrace. He is buried in the St Andrews Eastern Cemetery (Fig. 4). A stained-glass memorial window in St Leonard's church was commissioned by Clementina and dedicated in October 1926. Clementina died in 1942. In due course, four more stained-glass windows were dedicated to Heddle and Thoms family members.

NATURAL PHILOSOPHY

Thoms' wide interest in 'natural philosophy' is shown by the subjects of his talks to the St Andrews Literary and Philosophical Society. He described the behaviour of Bengal rivers and their tendency to deviate westwards, a phenomenon that affected landowners, some as gainers, others as losers; and also spoke about a visit to the Nainital in the Himalayas in 1875; the geology of the Ben Cruachan area; the geology of Glen Urquhart; and Darwinism. His wide experience of travel in foreign lands led to his election as a Fellow of the Royal Geographical Society (FRGS).

It was, however, as a mineralogist that Thoms received his greatest scientific recognition. In January 1905 he was elected a Fellow of the Royal Society of Edinburgh (FRSE). He was proposed by four eminent members: Ben Peach (1842–1926) and John Horne (1848–1928), the two geologists who resolved the controversy over the geology of northwest Scotland; Robert Kidston (1852–1924), a pioneering palaeobotanist; and James Currie (1863–1930), who had served on the committee which published *The Mineralogy of Scotland*.

Thoms had been interested in mineralogy during his time in India, and presented specimens to the St Andrews Literary and Philosophical Society museum including

Figure 4. Thoms is laid to rest in the St Andrews Eastern Cemetery with his first wife and child (beneath the carved angel). His third wife, Heddle's daughter Clementina, is commemorated by the simple stone at right angles. St Regulus Tower, about which Thoms had written, is in the background. Photo Hamish Johnston.

garnet sand, said to contain gold, from the Soobunsiri River, Assam, and coal from the Joyling Tea Garden, Assam. Following his return to Scotland in 1878, he began to accumulate a mineral collection, no doubt encouraged by his friendship with Heddle, who described Thoms as "... my dear old student and ever constant friend ..." in his will. Thoms' collections, which eventually included more than 5000 mineral specimens, 1500 agates and a comprehensive set of wooden crystal models are described in more detail in a complementary article (McMullen, 2022).

Unlike the prolific Heddle, Thoms' only scientific paper is a brief note about the blocks used to build St Regulus Tower (see Fig. 4) in St Andrews (Thoms, 1913). In this article he challenged a study by David Henry which stated that the stone had come from northern England. Using chemical and optical techniques Thoms showed it was a local contact-metamorphosed sandstone. In his analysis of the problem he referred to Heddle and Archibald Geikie, and secured the support of the Director of the Geological Survey.

In 1922 Thoms presented his collection of minerals and rock sections, together with apparatus and equipment, to University College Dundee. His choice probably reflected his family's origins in that city, and his disappointment over the failure of St Andrews University to properly engage with the proposed acquisition of the Heddle Collection in the early 1890s. Thoms made a further gift in 1925 and authorised a reprint of *The Mineralogy of Scotland*, the cost of which was met by the College Council.

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ALEXANDER THOMS:
HIS COLLECTIONS AND MINERALOGICAL LEGACY

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Alexander Thoms' (1837–1925) collections and contributions to mineralogy have been overshadowed by those of his friend and mentor Matthew Forster Heddle. Thoms is best known for his role in bringing *The Mineralogy of Scotland* to publication after Heddle's death, but this considerably underestimates his mineralogical legacy. He donated a set of wooden crystal models made to illustrate René Just Haüy's groundbreaking work on crystallography to the Edinburgh Museum of Science and Art (now the National Museum of Scotland) in 1915. His collection of more than 1500 agates includes specimens figured in *The Mineralogy of Scotland* and, in a Scottish context, is second only to Heddle's in importance. His collection of more than 5300 mineral specimens includes a fine suite from Leadhills–Wanlockhead in southern Scotland and features specimens from many other classic localities. It was donated to University College, Dundee in 1922. In 1989, following a major review of Earth Science teaching in the UK, it was transferred to the Hunterian Museum at the University of Glasgow.

INTRODUCTION

Alexander Thoms is probably most familiar to British mineralogists and collectors as a result of his involvement in the posthumous publication of *The Mineralogy of Scotland*. He was one of Matthew Forster Heddle's closest friends and is the author of the biographical sketch that appears in the introduction to Heddle's masterpiece. Thoms' personal contributions to mineralogy, and the collections he assembled, have been overlooked. The most extensive description of his life and mineralogical legacy extends to just two paragraphs in the 'Miscellaneous Collectors' chapter of *Minerals of Scotland* (Livingstone, 2002: p. 81).

A biographical study, summarising Thoms' family background, early life, career in India, friendship with Heddle and philanthropic work, is included as a complementary article in this journal (Johnston, 2022). This narrative concentrates on Thoms' contributions to mineralogy, particularly the collections that he assembled.

MINERALOGICAL LEGACY

Thoms' interest in mineralogy was nurtured by his friendship with Heddle, whose daughter, Clementina, he eventually married. In a long and eventful life he accumulated a worldwide mineral collection, a collection of agates, a historically important set of early wooden crystal models, several important handwritten nineteenth-century manuscripts and miscellaneous scientific instruments.

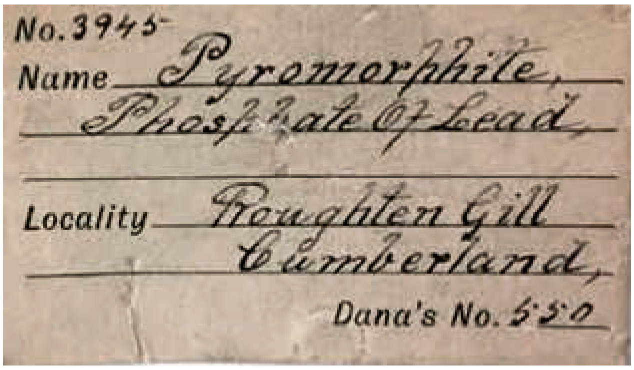
Thoms' mineral and agate collections are catalogued in two handsome registers which record a unique accession number, details of the storage location, the species present, their composition, Dana number and miscellaneous locality information. They form the largest part of his legacy.

Minerals

Thoms' mineral collection, which is now preserved at the Hunterian Museum in Glasgow, is the most important part of his mineralogical legacy. He acquired specimens over a period of more than forty years from his return to St Andrews in 1878 until the early 1920s. His catalogue has more than 5300 entries and includes microcline (315), muscovite (458) and baryte (719) specimens which are mentioned by Heddle in *The Mineralogy of Scotland*.

It is perhaps unsurprising, as Thoms was Heddle's 'student' (Fig. 1), that the collection includes a considerable number of representative study specimens and has a somewhat systematic focus. The chemical composition is prominently recorded on Thoms' labels (Fig. 2) and occupies the central column of his collection catalogue. A classification number, following Dana's System (1837; 1892), is recorded in the bottom right-hand corner of the labels and in a left-hand column in his collection register.

Figure 1. A staged photograph of Heddle together with Alexander Thoms. Heddle is portrayed as the learned master with his microscope and mineral specimen, Thoms as the student. Reproduced with permission from Rosemary Feilden.



No.3945

Name Pyromorphite,

Phosphate Of Lead,

Locality Roughten Gill

Cumberland,

Dana's No. 550

Figure 2. A small printed pro-forma label from Thoms' collection which records an accession number, the species name, chemical composition, locality and Dana number. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

The right-hand column on each page in the catalogue is given over to locality data, but the entries are commonly vague or absent. There is generally no record of how and from whom the individual specimens were acquired. Thoms did not permanently fix the registration numbers to his specimens, relying instead on the numbered labels in trays with the specimens. This was undoubtedly his single biggest mistake and has resulted in a significant loss of information.

In 1922, despite a long association with St Andrews, Thoms decided to donate his collection to University College, Dundee. The decision seems to have been influenced by his displeasure at the University of St Andrews' attitude to the Heddle Collection, which it failed to acquire in the early 1890s (Johnston, 2022). Regardless of the precise motivation, the *Dundee Courier* (1922) recorded:

> "Mr. Alex. Thoms, of St Andrews has presented to the College his valuable collection of minerals. The importance of the gift cannot be overestimated. The collection is well known to Scottish geologists, and contains more than 5,000 specimens of minerals, together with many rock-collections and much valuable working apparatus for the scientific study of the subject. The collection owed its origins to the most distinguished Scottish geologist the late Professor Heddle, of St Andrews but it has grown to its present magnitude under the assiduous labours of Mr. Thoms himself, who has devoted the work of a lifetime to its building up and its arrangement and cataloguing. As an epitome of Scottish geology it is almost unique in the country, and is unsurpassed by any except the more important of our national collections".

It was clearly a significant addition to University College and was later incorporated into the teaching collection at the Department of Geology at Dundee University, which received its Charter in 1967.

In the mid-1980s, the government decided to streamline geological teaching in the UK and the Universities' Funding Council recommended significant closures and amalgamations. The Department of Geology at Dundee University was subsumed into the University of Glasgow and in 1989 its collections were transferred to the Hunterian Museum.

The collection had suffered some degradation by that time and in a short description Livingstone (2002: p. 81) notes:

> "[Thoms'] considerably depleted collection went to the Hunterian Museum via the geology department of Dundee University, where it was formerly housed. Highlights include a 20 cm Japanese stibnite specimen, tetrahedrite after bournonite, a 15 cm specimen enriched with bournonite, and a good representative Leadhills–Wanlockhead suite. From Bryce-Wright, Thoms acquired mendipite from the type area. Matlockite, gold in matrix from Landlord's Brae[1], Wanlockhead and a large euhedral schorl are also notable".

Although the localities recorded in the collection register are often imprecise or absent, and many specimens have become dissociated from their labels, careful analysis, curation and conservation of the specimens after they were transferred to the Hunterian has preserved the information that remained and begun to reveal the importance of the collection.

For example, the only full-page photographic plate reproduced in *The Mineralogy of Scotland*, apart from the frontispiece portrait, is of radiating crystals of actinolite from Ord Ban, Loch an Eilean [*sic* as in the figure caption], Inverness-shire (Heddle, 1901b, 1924). The image, which faces page 35 in volume 2, illustrates a text entry for actinolite (which Heddle considered to be a variety of hornblende) from Inverness-shire:

> "Strathspey, at Ordban, near Loch an Eilein [*sic* as in the text], rarely, in magnificent clusters of stellate groups (M'Tier) and plumose groupings".

The specimen was recently rediscovered in the Alexander Thoms Collection (Fig. 3).

Agates

Heddle and Thoms collected agates at many Scottish sites including Birkhill and Balmerino in Fife and Scurdie Ness and Usan in Angus (Johnston, 2014, 2015). Heddle left the bulk of his personal collection of agates, which he always considered to be separate to his mineral collection, to Thoms. In 1898, Thoms donated a thousand of Heddle's specimens, which had been prepared to describe the structure and origin of agates in *The Mineralogy of Scotland*, to the Edinburgh Museum of Science and Art. This generous act ensured that all of Heddle's important collections were kept together at a single institution.

Thoms' personal agate collection, consisting of 1541 catalogued specimens, includes the counterparts to some of the specimens in Heddle's collection (Fig. 4). Indeed, a few of his specimens were better than Heddle's, and some are figured in *The Mineralogy of Scotland* (Fig. 5).

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[1] This interesting specimen (GLAHM: 100272) is described by Lauder (1878).

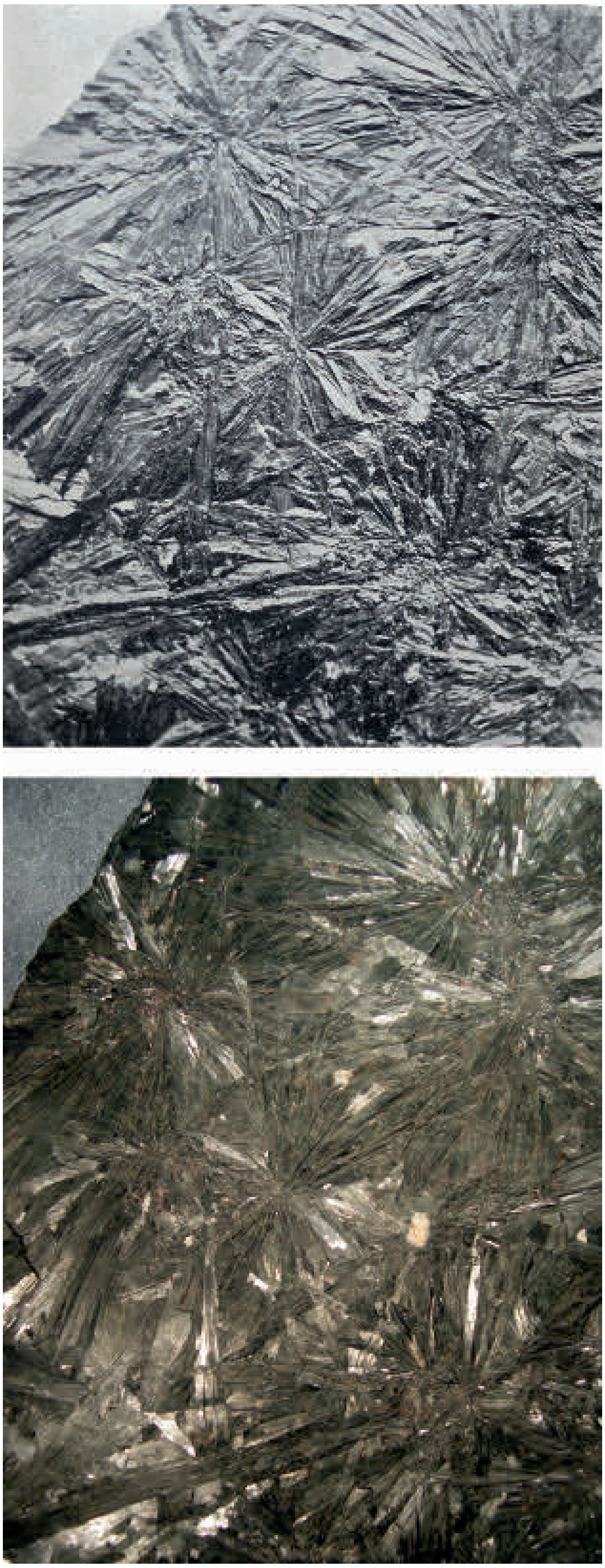


Figure 3. Radiating crystals of actinolite from Ord Ban, Loch an Eilean, Inverness-shire (Heddle, 1901b, 1924). The original plate from *The Mineralogy of Scotland* (top) faces page 35 in volume 2 and illustrates a text entry for actinolite. The modern photograph (bottom) shows approximately the same area of a specimen in the Alexander Thoms Collection (GLAHM: 100684). Photo John Faithfull © The Hunterian, University of Glasgow.

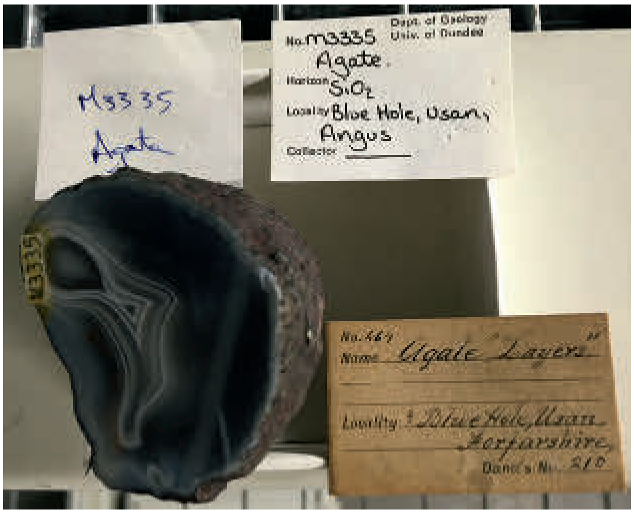


Figure 4. An agate half nodule from the famous Blue Hole, Usan, Angus with Thoms' brown label (No. 464) in his own hand, and a later label (M3335) from the Department of Geology at Dundee University. This specimen is the counterpart to a half nodule in the Heddle Collection at the National Museum of Scotland. Alexander Thoms Collection. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

Crystal Models

In 1915, Thoms presented a set of wooden crystal models to the Edinburgh Museum (Fig. 6). They are one of a small number of sets made by Beloeuf of Paris to illustrate René Just Haüy's classic four volume *Traité de Minéralogie* (1801) [they also provide a useful supplement to the updated two volume *Traité de Crystallographie*, published in 1822]. The importance of Haüy's work extends far beyond mineralogy, it is central to solid-state physics and the models are of exceptional scientific importance (Kunz, 1918; Leonardo, 2013).

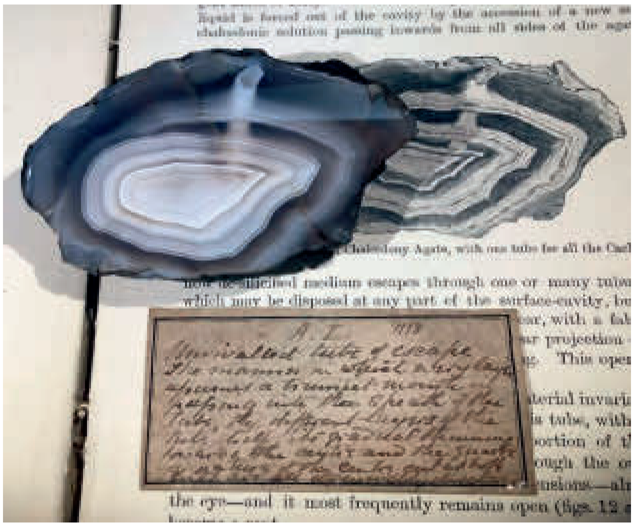


Figure 5. One of Thoms' agate specimens, which was used to illustrate the origin of agates in *The Mineralogy of Scotland* (Heddle, 1901a: p. 65) (GLAHM: 111215). The label in Heddle's handwriting records an "unrivalled example of a tube of escape". Alexander Thoms Collection. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

Figure 6. The entire Thoms' crystal model collection at the National Museum of Scotland (G.1915-11:1–888), arranged for inspection by Jane Insley and Valerie McCathern (in photo). Reproduced with permission from the National Museums of Scotland.

Beloeuf of Paris was Haüy's last official carpenter. They produced at least five sets of crystal models in light hardwood between 1813 and 1818. Thoms' set is one of three that are known to have survived. The models are beautifully crafted, typically about 50 mm in their maximum dimension, and generally in excellent condition (Fig. 7), although some of the paper labels have become detached in storage.

Unfortunately, no record of how, where and when Thoms acquired the collection has been found. They may have belonged to Heddle, who had an excellent practical knowledge of crystallography and included a large number of crystals drawings in *The Mineralogy of Scotland*, but if this is the case they must have passed through other hands as they were manufactured before Heddle was born.

Manuscripts and Ephemera

Some of Thoms' books are now in the special collections section of the library at the University of St Andrews, but his catalogues and the handwritten manuscripts which he inherited from Heddle were donated to University College, Dundee along with his minerals in 1922. The most historically important manuscript is a handwritten notebook which records mineralogical lectures given by Alexander Rose (1781–1860) (Fig. 8).

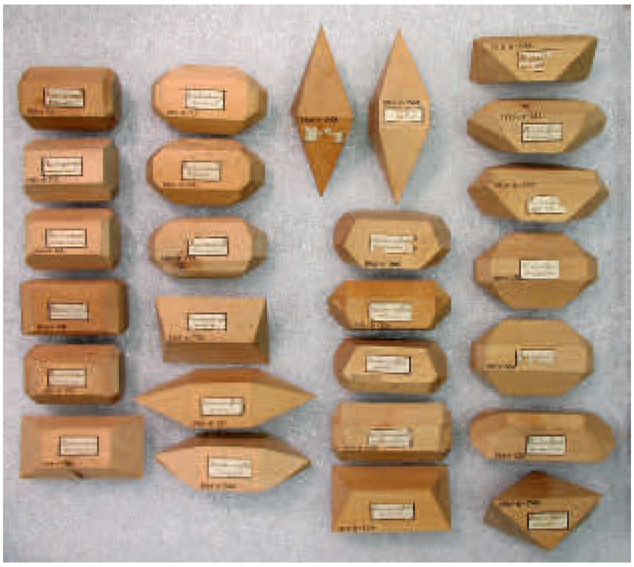


Figure 7. A selection of Thoms' crystal models, the largest about 60 mm in length, with individual paper labels recording the crystal name and handwritten accession numbers dating from 1915. Reproduced with permission from the National Museums of Scotland.

Rose had a remarkable life. He was one of Scotland's leading instrument makers, Professor of Geology and Mineralogy at 'Queen's College', Edinburgh (a lecturing association) and a well regarded mineral dealer. Rose was well liked by his students, indeed the Edinburgh Geological Society can trace its origins to his lecture courses, and he was acquainted with Heddle.

The notebook records some of Rose's mineralogical lectures. It includes descriptions of mineral species with notes on their chemical and physical properties, thumbnail crystal drawings and localities where they could be found (Fig. 9). It would certainly have been of use to Heddle in his compilation of *The Mineralogy of Scotland*.

In addition to the notebook, which has an uncertain history, Thoms acquired the majority of the apparatus

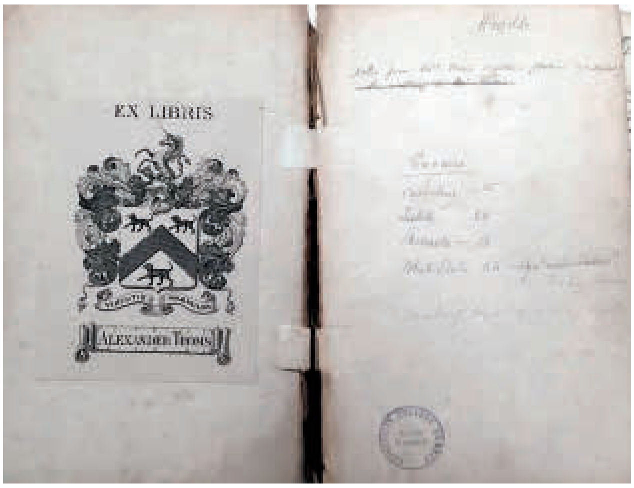
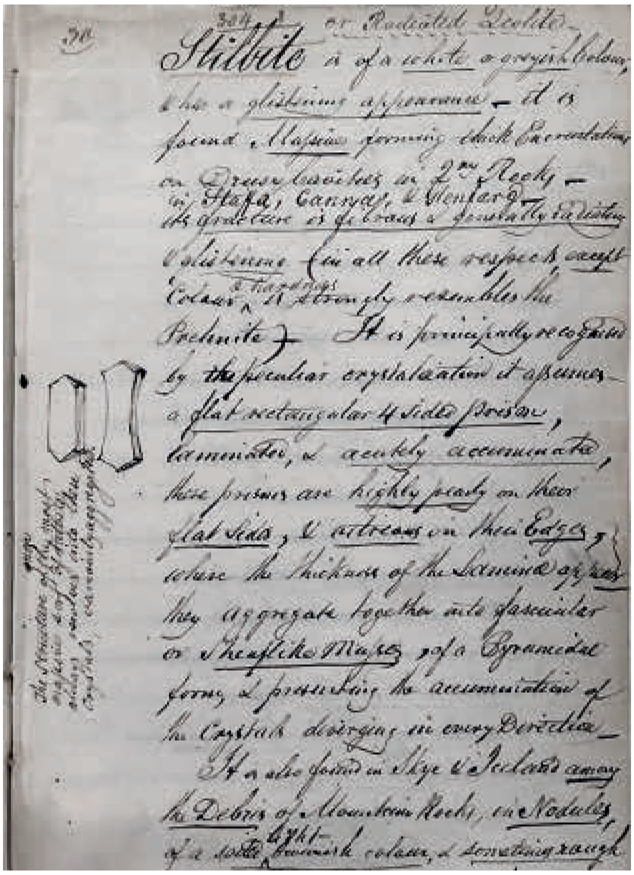


Figure 8. A notebook which Heddle (faint pencil signature top-right) bequeathed to Thoms (with Thoms' bookplate including his family crest and motto "honour is the reward of virtue") with details of mineralogical lectures given by Alexander Rose. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.



30

304 or Radiated Zeolite

Stilbite is of a white or greyish colour, & has a glistening appearance — It is found Massive forming thick Encrustations on Druse cavities in 2nd Rocks — in Staffa, Canna, & Glenfarg — its fracture is foliated & generally radiating & glistening (in all these respects except Colour & hardness) it strongly resembles the Prehnite — It is principally recognised by the peculiar crystalisation it assumes — a flat rectangular 4 sided prism, terminated, & acutely acuminated, these prisms are highly pearly on their flat sides, & vitreous on their Edges, where the thickness of the Laminæ appears they aggregate together into fascicular or Sheaflike Masses of a Pyramidal form, & presenting the accumination of the Crystals diverging in every Direction — It is also found in Skye & Iceland among the Debris of Mountain Rocks, in Nodules of a white light brownish colour, & sometimes rough

Figure 9. A page from the notebook (see Fig. 8) with notes from a lecture in which Alexander Rose described the mineral stilbite, including a sketch showing the characteristic crystal habits. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

and instruments which Heddle had used in his mineralogical research and his extensive collection of thin sections. The instruments would almost certainly have included the original apparatus which Heddle designed for the microscopic examination of crystals at different angles (Heddle, 1889; Johnston, 2015), but it is not known to have survived. One of the petrographic microscopes was sold soon after Heddle died (Thoms probably had one already), but Thoms retained the thin sections and donated them to University College, Dundee in 1922. They were later transferred to the Hunterian Museum, together with Heddle's handwritten catalogue, and a selection are illustrated in Starkey and Finch (2019: pp. 65–66) and in Johnston (2015).

DISCUSSION

Thoms is best known for his role in bringing *The Mineralogy of Scotland* to publication; he also garnered support for the later reprint, the first volume of which was published in 1923 and the second in 1924 (Heddle, 1901a,b; 1923, 1924). For this alone he deserves an honoured place in the history of mineralogy. His material legacy, which has been overlooked until recently, makes up a significant element of the mineralogical holdings at both the National Museum of Scotland and the Hunterian Museum. Without his generosity both institutions would be considerably poorer. It is perhaps easiest to deal with the major collections in reverse order, beginning with the crystal models.

The ideas that René Just Haüy developed at the beginning of the nineteenth century form the basis of the science of crystallography and the collection of crystal models at NMS is of international importance. It would be interesting to trace its path from early nineteenth century Paris to Scotland. As Thoms had negotiated the transfer of Heddle's minerals and subsequently donated his agate collection to the Edinburgh Museum of Science and Art, it is tempting to suggest that the models had also belonged to Heddle and that Thoms was simply putting them with the rest of his collections in their rightful place. Unfortunately, no evidence of their previous provenance has come to light but, since Heddle (b. 1828) and Haüy (d. 1822) do not overlap, they must have had other owners. Possibilities include Sir David Brewster (1781–1868), who conducted important research in crystallography and was Principal of the University of St Andrews between 1837 and 1859; Thomas Brown (1774–1853) who was one of Heddle's mentors; and Alexander Rose (1781–1860) who was Professor of Geology and Mineralogy at 'Queen's College', Edinburgh and knew Heddle in his formative years. The latter seems most likely as Rose was well travelled and included a great deal of crystallography in his lectures (Livingstone, 2002: pp. 50–51; Cooper, 2006).

Thoms' agate collection dates from a golden age when localities such as the Blue Hole near Usan were productive. Some of his specimens provided critical evidence for early theories of agate formation (see Fig. 5). The collection is second only to Heddle's in importance. It deserves further study.

The mineral collection is the principal element of Thoms' scientific legacy and the assessment of the Dundee Courier (1922) that it was "unsurpassed by any except the more important of our national collections" is probably fair. Thoms' is not a once-in-a-generation collection of the sort assembled by Sir Arthur Russell (Starkey, 2022), but a fine collection nonetheless, with important specimens and locality suites.

There is a preponderance of what might be described as study specimens in the early material. This probably reflects Thoms' position as Heddle's pupil (see Fig. 1). Many of these specimens appear to have been chosen to illustrate the physical and chemical properties of common minerals. Fine specimens and less common species begin to appear as Thoms' interests developed and he retained an interest in worldwide minerals throughout his life (Fig. 10).

Acquisition pathways are difficult to trace as details are rarely recorded in the catalogue. Friends and colleagues certainly gave some specimens, but less than one percent are associated with a definite name and few of these names appear more than once (see Appendix). The 'named specimens' appear to represent

Figure 10. Interpenetrating stibnite, 140 mm across, one of several fine specimens from Ichinokawa Mine, Ehime, Japan (GLAHM: 100464). Alexander Thoms Collection. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

sporadic donations from a broad social network. In addition to Matthew Forster Heddle, contributors include relatives such as Stuart Heddle, T. Johnston, William Marshall, William Traill and A. Watson Wemyss; academics such as Prof. Thomas Purdie (Heddle's successor at St Andrews), Prof. James D. Forbes (Principal of the University of Edinburgh), Dr Allen Thomson, (physiologist at the University of Edinburgh) and J. G. Goodchild (of the British Geological Survey); naturalists such as Dr John Wilson (one of Heddle's main contacts at Leadhills–Wanlockhead) and John Harvie-Brown (the ornithologist who accompanied Heddle on voyages around the Scottish islands); and civic leaders such as Sir Edward Buck (the grand old man of Indian agriculture) and Arthur J. Balfour (Secretary of State for Scotland and later Prime Minister).

Although there are no records in the catalogue, it is clear that Thoms regularly purchased specimens. There are numerous labels from late nineteenth and early twentieth century dealers, including the London-based Bryce Wrights, Francis Henry Butler, Richard Talling and Thomas Doulton Russell (Cooper, 2006); as well as F. Krantz of Bonn and A. E. Foote of Philadelphia. He seems to have developed a preference for classic display specimens exemplified by bournonite from Herodsfoot Mine, Cornwall (Fig. 11), fluorite from White's Level, Middlehope Shield Mine, Weardale, Co. Durham (Fig. 12) and 'campylite' from Dry Gill Mine, Caldbeck Fells, Cumbria (Fig. 13).

The suite from Leadhills–Wanlockhead in southern Scotland is particularly fine. It includes the primary minerals that were encountered at deeper levels in the mines in the late nineteenth and early twentieth centuries and a number of excellent examples of the supergene minerals for which the district is famous, and which must have been 'old-time specimens' by the time Thoms acquired them (Figs 14–16). A wide range of other Scottish specimens (e.g. Fig. 17) make up a considerable proportion of the collection.

This year is the centenary of Thoms' donation to Dundee College and a short commentary on the fate of his collection in that time is worthwhile. Educational establishments have a mixed record of long-term collection care. Donations to schools are almost always catastrophic. Universities have a better record, but sometimes prioritise destructive research and teaching over conservation and preservation. Thoms' collection, although somewhat depleted during its years in Dundee (Livingstone, 2002), has fared better than many.

Its prospects improved significantly in the late 1980s when it was transferred to the Hunterian Museum which has a dedicated curator of mineralogy. The rationalisation of teaching in UK universities in the late 1980s had a positive impact on the care of collections for a short while. As part of the programme, collection centres were set up at the Sedgwick Museum, Cambridge; Oxford University Museum; the Lapworth Museum, Birmingham; Manchester Museum; and the Hunterian Museum at the University of Glasgow. A number of new posts were created and members of staff appointed. Sadly, the promises of 'posts in perpetuity' proved hollow and when Liston (2011) examined the impact of the programme twenty years after its inception, his analysis was bleak:

> "No matter what conditions are made, what safeguards are laid down, they can all be forgotten with a simple change of management ... and any collection can become a collection in crisis".

In difficult times it is worthwhile recording actions that can help to protect material. If there is one lesson to be learned from Thoms' collection it is the need for a permanent link between specimens and the associated labels and catalogue entries. Simply recording the accession number on the specimen label invites disaster. It is vital that a number is permanently glued to an unobtrusive part of the specimen. In a public collection, this simple expedient ensures data security and hedges against future uncertainties[2].

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[2] Note however that in a private collection, which is almost certain to be broken up at some point in the future, a glued label including an abbreviated locality and grid reference should be regarded as the minimum standard.

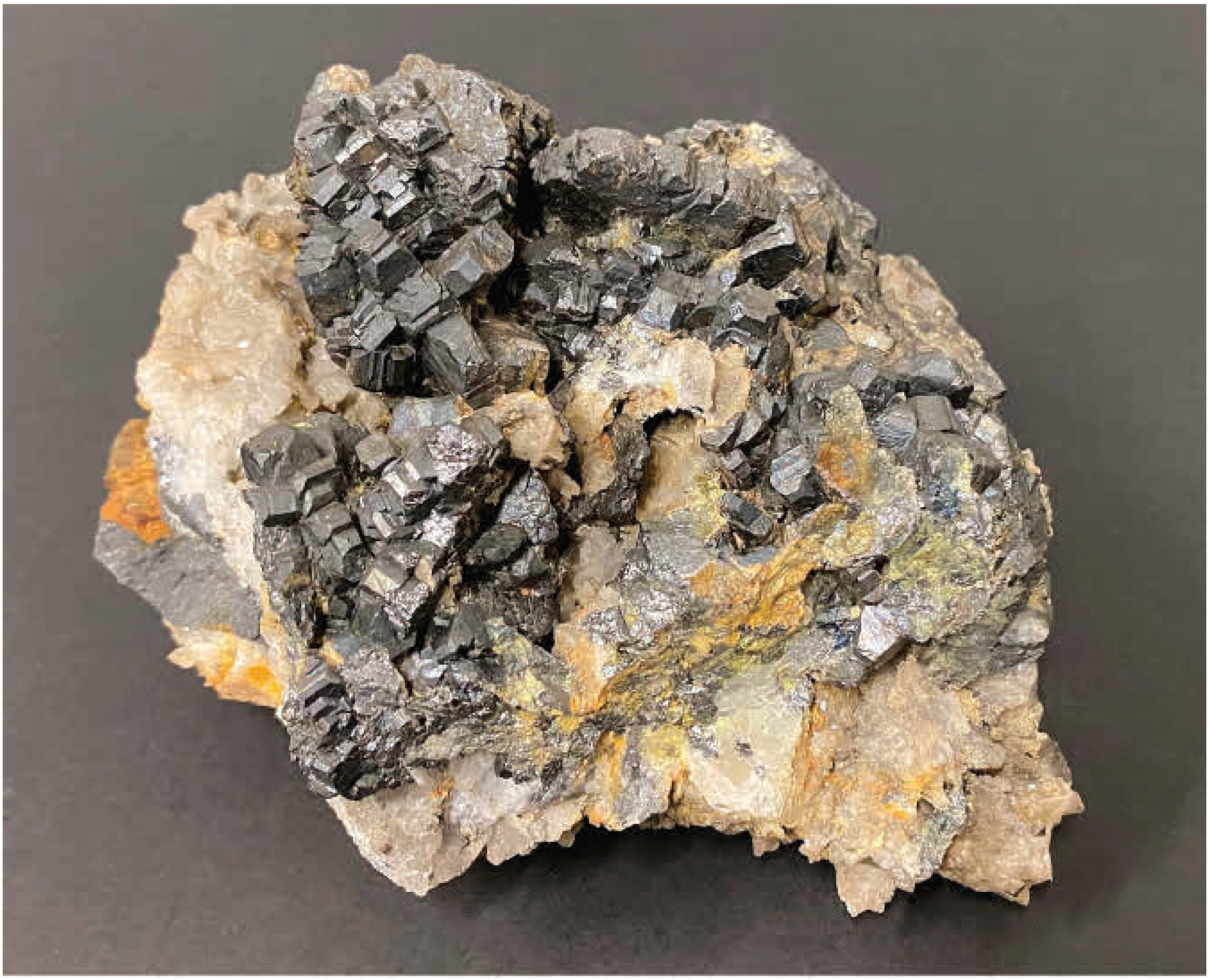

Figure 13. Campylite from Dry Gill Mine, Caldbeck Fells, Cumbria (GLAHM: 100460). Alexander Thoms Collection. The specimen is 70 mm across. Photo Erika Anderson © The Hunterian, University of Glasgow.

Figure 14. Honey-coloured tabular crystals, possibly of macphersonite, with greenish epitaxial susannite and slightly altered caledonite from the Leadhills–Wanlockhead district in southern Scotland (GLAHM: 100287). Alexander Thoms Collection. The specimen is 70 mm across. Photo John Faithfull © The Hunterian, University of Glasgow.

CONCLUSION

Alexander Thoms (1837–1925) made considerable contributions to mineralogy. He was a close friend of Matthew Forster Heddle and had a central role in bringing *The Mineralogy of Scotland* to publication.

(*facing page*)

Figure 11. (*top*). Bournonite on quartz with minor tetrahedrite from Herodsfoot Mine, Liskeard, Cornwall (GLAHM: 100439). Alexander Thoms Collection. The specimen is 150 mm across. Photo Erika Anderson © The Hunterian, University of Glasgow.

Figure 12 (*bottom*). Fluorite, almost certainly from White's Level, Middlehope Shield Mine, Weardale, Co. Durham (see Fisher, 2006) (GLAHM: 134366). Alexander Thoms Collection. The specimen is 110 mm across. Photo Erika Anderson © The Hunterian, University of Glasgow.

Figure 15. Radiating grey-white lanarkite with leadhillite from the Leadhills–Wanlockhead district in southern Scotland (GLAHM: 100291). The specimen is 150 mm from top to bottom. Alexander Thoms Collection. Photo John Faithfull © The Hunterian, University of Glasgow.

Figure 16. Caledonite from Brown's Vein, Leadhills, Lanarkshire (GLAHM: 100787). Alexander Thoms Collection. Photo Michael McMullen reproduced by courtesy of The Hunterian, University of Glasgow.

Figure 17. Vesuvianite on an undifferentiated garnet-group mineral, 100 mm across, from Delnabo Quarry, Glen Gairn, Ballater, Aberdeenshire. Thoms' catalogue No. 2847. Specimen and photo Michael McMullen.

He donated Heddle's agate collection to the Edinburgh Museum of Science and Art (now the National Museum of Scotland) shortly after Heddle's death and added a historically important set of wooden crystal models, which had been cut to illustrate René Just Haüy's groundbreaking work on crystallography, in 1915.

Thoms donated his remaining personal collections to University College, Dundee in 1922 and they were eventually integrated into the teaching collections in the Department of Geology at Dundee University. In 1989, following a review in Earth Science teaching in the UK, they were transferred to the Hunterian Museum at the University of Glasgow.

Thoms' agate collection of more than 1500 specimens includes specimens figured in *The Mineralogy of Scotland* and is second only to Heddle's in importance. His main collection of more than 5300 mineral specimens includes fine suites from Leadhills–Wanlockhead in southern Scotland, the Caldbeck Fells, Cumbria, and southwest England. Both have significant potential for further research and deserve to be better known.

ACKNOWLEDGEMENTS

Thanks are due to Hamish H. Johnston, great-great-grandson of Matthew Forster Heddle, for his painstaking original research and guidance in completing this work. John Faithfull, former Curator of Mineralogy and Petrology, Hunterian Museum, University of Glasgow is thanked for allowing the author access to the Thoms Collection. Erika Anderson, the current curator, is thanked for supplying photographs at very short notice. Peter Davidson, Senior Curator of Mineralogy, Natural Sciences Department, National Museums of Scotland, provided additional information as did Robert Neller, collections officer at Haslemere Educational Museum. The referees are thanked for helpful suggestions which improved the manuscript.

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THE *GEOGNOSY AND MINERALOGY OF SCOTLAND* A UNIQUE WORK BY MATTHEW FORSTER HEDDLE

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The core content of the *Geognosy and Mineralogy of Scotland* by Matthew Forster Heddle (1828–1897) consists of approximately 520 pages describing the mineralogy and geology of Shetland, Orkney, Caithness and Sutherland. It was originally published between 1878 and 1884 as a series of articles in the *Mineralogical Magazine*. The information is remarkable in its breadth and depth. Information about geology, geomorphology, history, petrology and topography is interspersed with careful descriptions of sites of mineralogical interest supported by detailed maps, chemical analyses and crystal drawings. Heddle originally intended to describe the whole of Scotland in this fashion, but his ambitions exceeded the pecuniary limitations of the Mineralogical Society and he was only able to cover the far-northern counties. Not content to let the work go to waste, he gathered the original articles together and had them repaginated. He appears to have acted as publisher and distributor of the resultant book and commonly included a selection of his other mineralogical papers with orders. As a result, most copies of the *Geognosy and Mineralogy of Scotland* are unique.

INTRODUCTION

Matthew Forster Heddle (Johnston, 2014; 2015) is best known to mineralogists for *The Mineralogy of Scotland*, a remarkable description of the mineralogy of his native land which was published posthumously in 1901. This article records one of his less well known publications, the *Geognosy and Mineralogy of Scotland*. To the bibliophile and historian, copies of the *Geognosy* are among the most fascinating of nineteenth century texts: they are uncommon (indeed it is not known how many were produced) and no two are alike.

The core content of the *Geognosy* consists of papers which describe the geology and mineralogy of Shetland, Orkney, Caithness and Sutherland, bound with a title page which is dated 1878. The pages are numbered consecutively[2] (and therefore, they are not reprints in the strict sense) but they are otherwise faithful reproductions of papers published between 1878 and 1884 in the *Mineralogical Magazine*. Most copies also include a selection of reprints of Heddle's other mineralogical papers, bound in one or two volumes.

The *Geognosy* is little known and even the most ardent bibliophile would be unlikely to have more than a single copy. This study was conceived after the author acquired copies which had belonged Clementina (1860–1942), Heddle's eldest daughter, and Patrick Dudgeon (1817–1895), his closest friend, during genealogical research. A comparison between these two presentation copies and other examples revealed substantial differences in content, which suggested that the *Geognosy* was not a conventional nineteenth-century mineral book.

THE *GEOGNOSY*

In 1878, *Mineralogical Magazine* published the first of a series of articles by Matthew Forster Heddle which describe *The County Geognosy and Mineralogy of Scotland*. Each of these articles is a broadly topographic description of the geology and mineralogy of a well defined area. In the first of the papers, Heddle (1878a: p 9) records:

> "The chapters of this work purport to be the chronicles of our present state of our knowledge of the mineralogy of the northern portion of the kingdom ... The geognosy and lithology are treated of to such an extent only as, in the first place, to explain the position of the minerals; and, in the second, to aid future investigators in their explorations".
>
> "In these chapters, in order to do full justice to the work of others, the authority for, and the original discoverer of every locality mentioned, will be quoted, wherever known".
>
> "The author, having attempted to visit every known mineral locality to the north of the Forth and Clyde, and having succeeded in this attempt with less than half-a-dozen exceptions, is able in most cases to authenticate, or the opposite, as the case may be, the statements of previous observers". ...
>
> "This record is the result of some five-and-twenty summers of persistent exploration, and of many winters of equally persistent analytical research. In the hope that it may serve as a mineralogical guide book, the localities are given with a fulness [*sic*] of description, and precision of detail which aims at leading the collector, if not to the spot itself, at least to within half-a-mile of it".

These introductory remarks make it clear that Heddle's aim was to provide a topographic guide to the mineralogy of Scotland. He had visited almost all of the then known mineral localities north of the Midland Valley, tramped across or sailed around much of northern Scotland, and was intent on summarising the results of his investigations. He was aware of the

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[1] Heddle's great-great-grandson and biographer (see Johnston, 2014; 2015).

[2] With a number of pagination errors which are recorded in the next section of the text.

unsavoury practices of some contemporary mineral dealers and went on to note:

> "If the tenth part of the money which is thrown away, – the word is used purposely, – upon the rivalrous hoarding up of specimens, were expended in individual exploration of different parts of the country, followed up by judicious and well directed analytical investigation of rocks, and of alteration products, the following results would probably be attained".
>
> "Geologists would no longer characterise mineralogy as being a repulsive study, inasmuch as it was but the "dry bones of a science," destitute even of the lineaments of life. Mineralogists would no longer speak of the false application of the word science to that which, founded not on known laws, was speculative and theoretical, – propped on the one side by false chemistry, and on the other by unsound physics".
>
> "Museums in the country would become more numerous; and the present rivalry of secretiveness would give place to a rivalry in the sending the best, or at least the second best specimens to one or other of the three metropolitan museums, – such being the only sure way of attaining to anything worthy of being called truly national collections".

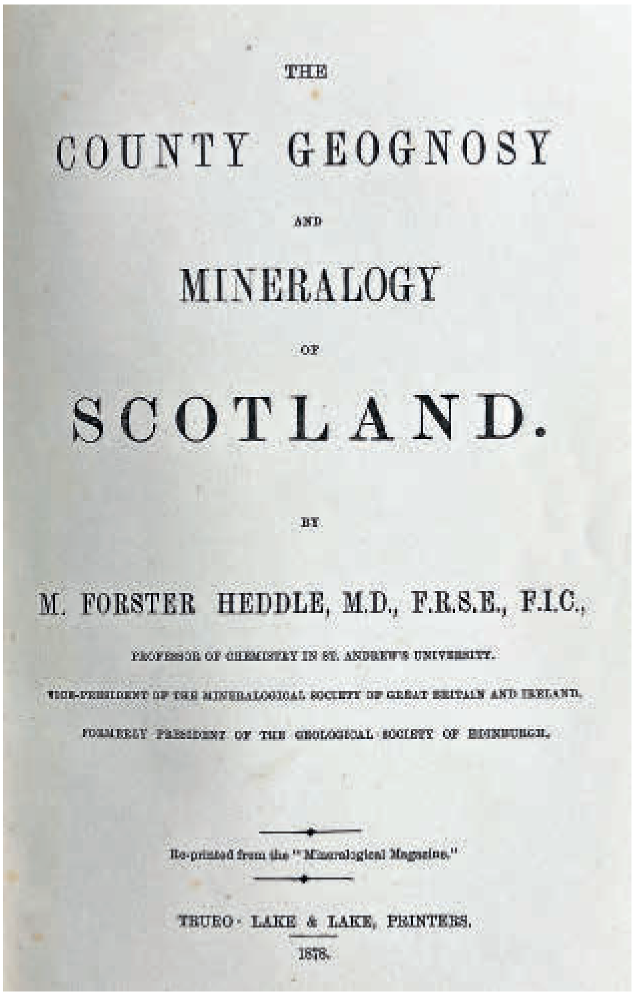
Heddle had set himself a huge task and decided it would be accomplished as follows:

> "Probably the most scientific manner of treating of the mineralogy of a county would be to commence with the consideration of the minerals occurring in the oldest rock, – working from that gradually upward".
>
> "Inasmuch, however, as such a plan would be difficult of execution from the older rocks occurring in several counties, I shall adopt the simpler one of locality; taking the counties in order of their occurrence from north to south".

During the next six years, a series of topographic papers appeared in the *Mineralogical Magazine.* They describe Shetland (Heddle, 1878a,b,c; 1879b) with a geological map (Heddle, 1879a); Orkney (Heddle, 1879c; 1880a); Caithness (Heddle, 1880b); and Sutherland (Heddle, 1881a,b; 1882b; 1883a,b; 1884) also with a geological map (Heddle, 1882a).

It is clear that Heddle felt he was at the start of an important project and even as he published the first of the papers he envisaged their eventual appearance in book form[3]. They would be gathered together as *The County Geognosy and Mineralogy of Scotland*. The title page appears to have been printed at the same time as the first paper (Fig. 1).

Copies of the book have dividers between some of the chapters in a similar format to the main title page except that they do not include the word 'County'. Part II, which describes Fetlar, is dated 1878; Part V, which describes Orkney, and Part VIII, which describes Sutherland (Fig. 2), are both dated 1880. There are no title pages for Part III which describes part of the Mainland of Shetland and Part IV, which describes the remainder of the Mainland plus some outlying islands. Those for Parts VI and VII which describe the southern Orkney Islands and the county of Caithness, are also absent.



THE

COUNTY GEOGNOSY

AND

MINERALOGY

OF

SCOTLAND.

BY

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FORMERLY PRESIDENT OF THE GEOLOGICAL SOCIETY OF EDINBURGH.

Re-printed from the "Mineralogical Magazine."

TRURO · LAKE & LAKE, PRINTERS.

1878.

Figure 1. The main title page for *The County Geognosy and Mineralogy of Scotland* by Matthew Forster Heddle. The date of 1878, the fact that the printer is listed as Lake and Lake of Truro [they were replaced in 1882 after J. H. Collins resigned as Editor], and the fact that Heddle is listed as Vice-President of the Mineralogical Society [Henry Clifton Sorby was President in 1878 and Heddle was Vice President; Heddle became President in 1879 and held the post until 1881 when he was replaced by Wilfred Hudleston] indicate that this page was printed in 1878 and that from the start Heddle intended to gather the papers into a book. Photo Hamish Johnston.

The inconsistency in the dates of publication gives some difficulty in producing a satisfactory bibliographic reference for the *Geognosy*. The core 'county paper' content was published in the *Mineralogical Magazine* between 1878 and 1884 and the approach adopted in this article is to refer to *The County Geognosy and Mineralogy of Scotland* as Heddle (1878–1884), even though the main title page only uses the date 1878. This is not entirely satisfactory as the earliest copy known to the

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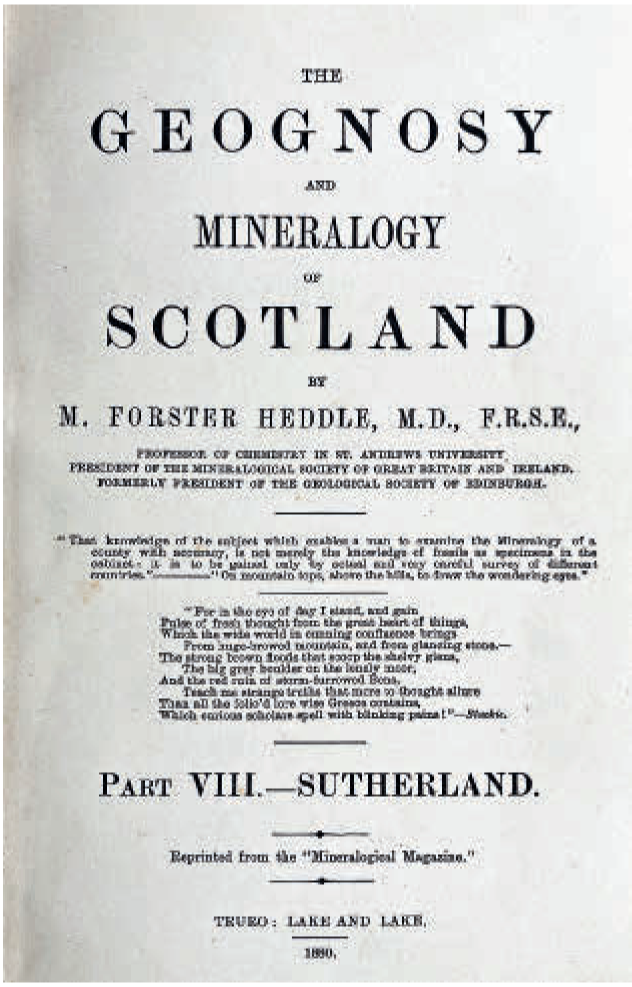
[3] The first paper is unusual in that it begins with a Preface, a form of words which is normal in a book but very unusual in an article in a scientific journal, where the opening remarks typically form an Introduction.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"That knowledge of the subject which enables a man to examine the Mineralogy of a county with accuracy, is not merely the knowledge of fossils as specimens in the cabinet: it is to be gained only by actual and very careful survey of different countries."——"On mountain tops, above the hills, to draw the wondering eyes."

"For in the eye of day I stand, and gain
Pulse of fresh thought from the great heart of things,
Which the wide world in cunning confluence brings
From huge-browed mountain, and from glancing stone,—
The strong brown floods that sweep the shelvy plains,
The big grey boulder on the lonely moor,
And the red ruin of storm-furrowed Bens,
Teach me strange truths that more to thought allure
Than all the folio'd lore wise Greece contains,
Which curious scholars spell with blinking pains!"—*Blackie.*

PART VIII.—SUTHERLAND.

Reprinted from the "Mineralogical Magazine."

TRURO: LAKE AND LAKE,
1880.

Figure 2. The title page for Part VIII of *The County Geognosy and Mineralogy of Scotland*. Surprisingly, the word county is omitted. Heddle is listed as President of the Mineralogical Society, an office he held between 1879 and 1881. The date is 1880. Photo Hamish Johnston.

author is limited to Shetland and includes only those papers published in 1878 and 1879, and most of the other copies contain papers published before or after the years 1878–1884. Such volumes can only be dealt with on an individual basis.

Heddle was able to gain publicity for the project as it developed. In 1882 the *Geological Magazine* carried a detailed review of the first eight parts (Anon., 1882b). It concludes:

> –"In his descriptions of minerals and mineral localities, Professor Heddle is most patient and painstaking; but his accounts of the scenery and geognosy of the different areas are most attractive to the geological reader. He hurries us onward from point to point and scene to scene, hardly allowing us time to take breath. His style is often a little high-pitched perhaps, but never flat or uninteresting. ... The mass of the work is of course interesting only to the mineralogical student, to whom the book in its completed form will become an absolute necessity. But much of it is interesting not only to British geologists in general, but to all those who love nature and nature's interpreters and we trust that the author will find time and opportunity to complete a work so worthily begun".

Surprisingly, for a book review, there is no information about the publisher or how a reader might obtain a copy. It seems likely that the volume in question had been bound by Heddle himself in an attempt to garner support for the *Geognosy* project which had begun to falter as its ambition exceeded the pecuniary limitations and scientific remit of the Mineralogical Society.

In 1880 the Mineralogical Society was in financial crisis. Accounts for the year ending 1880 reveal a substantial increase in its debt to Lake and Lake of Truro who printed the *Mineralogical Magazine* (Anon., 1881: p. iii). Matters were further complicated by the resignation of Joseph Collins[4], who had acted both as general secretary and editor, on 15 February 1881. There was no suggestion of impropriety, Collins had taken a position at the Rio Tinto mines in Spain and could no longer function in either role. Robert H. Scott (1833–1916) was appointed as General Secretary and he and Heddle (who was President), together with Arthur H. Church (1834–1915), Wilfred H. Hudleston (1828–1909) and Frederick W. Rudler (1840–1915) formed the Editing Committee. It seems that the volume of colour illustrations, many of which were Heddle's, were responsible for the high printing costs. At the Annual General Meeting on 2 September 1881 (when Wilfred Hudleston succeeded Heddle as President) it was decided (Anon., 1881: p. i):

> "That the authors of all papers which are printed in the Magazine shall in future defray one third of the cost of all such coloured illustrations of their papers as have been approved by the Editing Committee".

The Society reduced the number of journals it produced from four to three per year in response to the debt, and the minutes of a meeting on 24 October 1882 record a better financial position. They also note that the journal (to which Heddle was chief contributor) needed 'careful supervision'. Reading between the lines it appears that there were tensions between Heddle and some of the other Society members. It may be these that signalled the beginning of the end for the *Geognosy*. In his anniversary address on 23 October 1883, Hudleston (1883: pp. xxii–xxiii) recorded:

> "It is only fair to admit that Dr. Heddle has been mainly instrumental in keeping us before the public in respect of publication, and if severer critics maintain that portions of his papers are not mineralogical, scarcely indeed scientific, it should be borne in mind that but for these papers the Journal would have been very attenuated indeed. There can be no doubt that Dr. Heddle's papers, and

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[4] Joseph Henry Collins (1841–1916) is commonly credited as the driving force behind the foundation of the Mineralogical Society (Anon., 1881: p. iv). He spent much of his life in Cornwall, but was chief chemist and metallurgist for the Rio Tinto mines in Spain between 1881 and 1884. In 2008, the Mineralogical Society established an annual award, The Collins Medal, to recognise the lifetime contributions of scientists to pure or applied aspects of mineral science, in his honour.

more especially his maps, have helped us in more ways than one".

Successive presidential addresses wondered if the Society (and by extension Heddle's geognostic papers) were straying too far into the territory of the Geological Society. In this context, it should be noted that at the time considerable tension was centred around what has become known as the Highlands Controversy. A lithology described in Heddle's Sutherland papers as the 'Logan Rock' was at the heart of the then unresolved dispute (Johnston, 2015).

Heddle's final geognostic paper: "The Geognosy and Mineralogy of Scotland (Ross and Cromarty). Part I., The Islands" (Anon., 1885: p. xi) was read at the Mineralogical Society on 9 December 1884 but not subsequently published. Sadly, the manuscript has disappeared. By the time the paper was read it had been decided that although the Mineralogical Society would continue to publish Heddle's mineralogical papers, it was no longer willing to support the more wide ranging *Geognosy*. In a holograph letter bound into one of the copies of the *Geognosy* Heddle states "As the Min Soc thinks (or its Council at least) these papers too geologic they have ceased to publish them".

Although Heddle wrote no further geognostic papers he decided to consolidate those that had been published into book form. He had suffered from financial problems throughout his professional life, but had just returned from a contract with the Lisbon-Berlyn (Transvaal) Gold Fields Ltd, and in November 1884 had defeated the company's court action against him, guaranteeing both earnings and annuity (Johnston, 2015). This financial certainty would have made the project more attractive.

Heddle arranged for the original papers to be repaginated[5]. In the book, each appears as previously printed except the first two Sutherland papers which are linked seamlessly at pp. 266–7, the title page for the second paper being omitted. A number of mistakes were made in the process: the text on pages 44–46 is repeated verbatim on pages 47–49; page numbers 99–137 are repeated; and there is a gap between pages 164 and 205.

DISCUSSION

The information contained within the county *Geognosy* papers is remarkable in its breadth and scope. They were published at a time when Heddle was also writing his "Chapters on the Mineralogy of Scotland", for the *Transactions of the Royal Society of Edinburgh*[6]. These publications provided the feedstock for *The Mineralogy of Scotland*, but contain far more detail than Heddle's posthumous masterpiece. It is hard not to be impressed with the quantity and variety of information and observation. Discussions of geology, geomorphology, history, petrology and topography are interspersed with careful descriptions of sites of mineralogical interest, many supported by detailed chemical and petrographic analysis, and goniometric measurement. This level of detail would be difficult to emulate with modern analytical equipment and transport, that it was accomplished in the mid-nineteenth century is extraordinary.

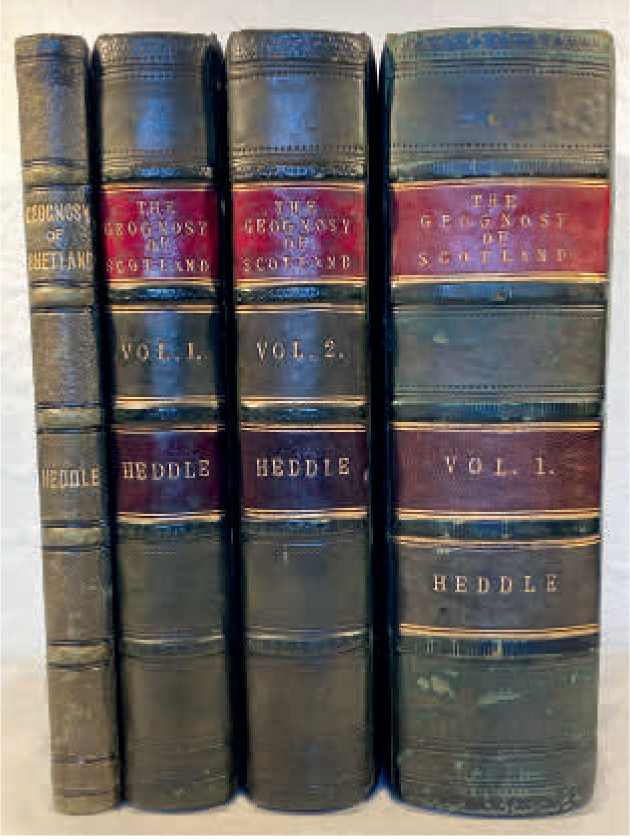

Figure 3. Three copies of the *Geognosy*. The version on the left contains only those papers related to Shetland. The middle version has the complete core content plus a selection of Heddle's other reprints bound in two volumes. The version on the right has same core content plus a different selection of reprints bound in a single volume. Photo Hamish Johnston.

In bibliographic terms, much of the interest of the *Geognosy* is in its variability. No two copies are alike (Fig. 3). The shortest example of which the author is aware contains only the geognostic papers relating to the Shetland Islands. All of others examined to date contain the core geognostic content published in the *Mineralogical Magazine* between 1878 and 1884 plus a selection Heddle's other scientific reprints.

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[5] The *Mineralogical Magazine* was printed by Lake and Lake of Truro between 1876 and 1882 (while J. H. Collins was Editor). After Collins' resignation it was transferred to Williams and Strahan of 7 Lawrence Lane, Cheapside (Anon., 1882a). The new printers obtained the plates for Heddle's first set of papers, and as far as possible they maintained the original format and typography in the last three Sutherland papers. It is presumed that Heddle used the original Lake and Lake title pages, printed in 1878 and 1880, and omitted to credit Williams and Strahan for reasons of cost.

[6] These were extensively reviewed with occasional additions in the *Mineralogical Magazine*. A full list is provided in Johnston (2015: p. 262).

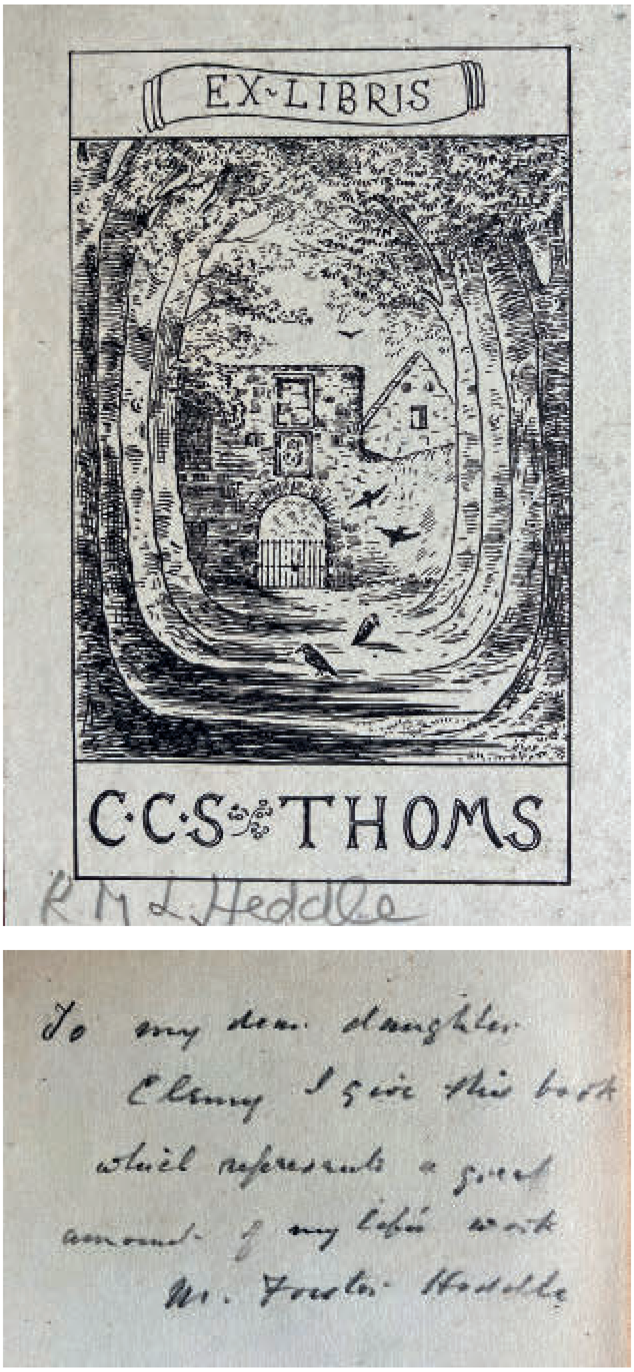
Twenty-nine of the sixty or so scientific papers that Heddle produced are included in versions known to the author. The earliest paper dates from 1857 and the latest from 1892. The number of extra papers in the books examined during this study are 4, 9, 9, 13, 16 and 19. The last two (and longest) are the copies that Heddle gave to his friend Patrick Dudgeon (Fig. 4) and his eldest daughter Clementina (Fig. 5). An unexamined copy digitised by the University of Michigan has 15 extra papers.

It seems likely that most of the copies were collated by Heddle and dispatched unbound. The core content, which consists of 520 printed pages plus the associated plates, must have occupied a considerable space in his study. An undated holograph letter in a copy examined by the author notes that Heddle had sent "Volume 1 of my *Geognosy of Scotland* and some chaff which you may care to bind up with it". The 'chaff' included nine of Heddle's other papers. If this was normal practice it explains the variation in content, the lack of consistency in binding, and the fact that some copies are bound as one volume and others as two. Heddle would have been able

1 vol 21/-

With life-long good wishes
from
M. F. H
author

Figure 4. The bookplate and dedication "With life-long good wishes" in the copy of the *Geognosy* that Heddle gave to his friend, Patrick Dudgeon. Photo Hamish Johnston.



R M L Heddle

To my dear daughter
Clemy I give this book
which represents a great
amount of my life's work
M. Forster Heddle

Figure 5. The bookplate and dedication "To my dear daughter Clemy I give this book which represents a great amount of my life's work" in the copy of the *Geognosy* that Heddle gave to his eldest daughter, Clementina. Photo Hamish Johnston.

to add additional material according to the interests of the buyer (or provide a personal selection for a presentation copy) but would have been constrained by the availability (and size) of reprints.

Interestingly, a single presentation volume in a contemporary binding, which includes Heddle's final published geognosy paper from 1884, has 'Volume 1' tooled on its spine. This suggests that at the time Heddle still felt there was a possibility that further geognostic papers might be produced. A subsequent presentation copy, bound in two volumes, includes a paper from 1885, by which time Heddle must have realised that there would be no more papers in the series. Despite this disappointment, Heddle continued to make the books available: some copies include reprints of papers published as late as 1892. They probably remained available almost up to his death in 1897.

The author would be pleased to hear from any reader who owns, or knows of, a copy of Heddle's *Geognosy*. Any information will be added to a comprehensive table, which will be shared with contributors, and uploaded as supplementary material onto the Russell Society website.

CONCLUSION

Surviving copies show that the *Geognosy and Mineralogy of Scotland* is not a conventional text. It was assembled by Heddle himself over a considerable period of time (and with a varied content) either as a token of affection for family and friends or as a result of a request from an interested third party. It is not known how many copies were produced, but the run is likely to have been small. The book is much less common than *The Mineralogy of Scotland*. Catalogue entries indicate that institutions usually take the 1878 and 1880 title pages at face value. Given their rarity it is likely that few owners, institutional or otherwise, realise that their copy is unique.

ACKNOWLEDGEMENTS

The author would like to thank those who commented on the first draft. A non-mineralogist, he is particularly grateful to David Green for providing technical assessments of Heddle's work, and for suggesting additional material that has enriched the paper, but which the author had omitted for fear of making it too long.

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PETER MURRAY, NATURALIST, PHYSICIAN AND PHILANTHROPIST: A FORGOTTEN YORKSHIRE COLLECTOR

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Peter Murray (30 March 1782 – 27 February 1864) was a physician with strong religious convictions and wide interests in natural history. He studied under the mineralogist Robert Jameson and the chemist Thomas Charles Hope at the University of Edinburgh, and was on friendly terms with prominent scientific figures of the late eighteenth and early nineteenth centuries, including Sir Humphry Davy, Sir Joseph Banks, William Smith and John Phillips. His most important contribution to mineralogy was the first description of strontium minerals in Yorkshire. Minerals containing the newly discovered element were of considerable scientific interest in the early nineteenth century. Murray identified celestine in the Permian rocks around Knaresborough in 1811 and reported the first English strontianite at Merryfield Mine near Pateley Bridge in 1825. Strontianite specimens from Murray's collection, preserved at the Natural History Museum in London, are among the finest from the British Isles. Murray retired to the seaside town of Scarborough in 1827. He wrote a number of accounts of the minerals found in the cliffs and took particular pride in the eponymous scarbroite. He was appointed to various curatorial roles (including Curator of Mineralogy) at the Rotunda Museum and was Vice-President of the Scarborough Philosophical Society (later the Scarborough Philosophical and Archæological Society) for many years.

INTRODUCTION

This article began as a footnote in a topographic study of strontium minerals in Yorkshire. The first indication that strontium minerals had been identified in the county is in the Minute Book of the Geological Society (Anon., 1817), where it is noted that in 1811 "Dr Murray of Harrogate" discovered celestine in the banks of the River Nidd near Knaresborough. Murray subsequently reported the first English strontianite at Merryfield Mine near Pateley Bridge. These discoveries suggested he might be a worthwhile subject for research. Investigations in libraries, archives and museums gradually revealed the life of a forgotten collector.

Murray was a prominent figure in nineteenth-century Yorkshire. He took on civic duties, championed good causes, and was a member of many scientific, municipal and religious organisations. The Revd Robert Balgarnie[1], who moved to Scarborough in 1851, compiled a biography: "*The Beloved Physician;*" *A memoir of Peter Murray, M.D., of Belle Vue, Scarborough* in the months following Murray's death. Although Balgarnie observed that Murray's principal interests were in philanthropy, science and religion, he recorded little of his scientific work and hardly mentioned his wide ranging collections and long involvement with the county's philosophical societies. Indeed, the biography is somewhat evangelical in nature and occasionally harbours a degree of hostility toward science (Balgarnie, 1864: p. 144):

> "Why give time and thought to science and withhold them from religion? What will it avail, though you be learned in all knowledge, and yet know not Him whom to know is life eternal".

This may be a reflection of the religious zeitgeist in the aftermath of Darwin's challenge to the biblical interpretation of the creation. Regardless of his motivation, Balgarnie does not provide a rounded picture Murray's life. Fortunately, information about his scientific interests can be garnered from a few published works, society records and donations to institutional collections.

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[1] The Revd Robert Balgarnie (1826–1899) was a Scottish preacher who arrived in Scarborough in 1851. He became Minister of the Bar Church and later the South Cliff Church and was involved with Murray in several charitable undertakings (Anon. 1901: pp. 104–108). His best known work is a biography of the Victorian industrialist Sir Titus Salt (Balgarnie, 1877).

BIOGRAPHY

Murray's life can be divided into four periods: his childhood in Jamaica and England is the stuff of historical fiction; at the University of Edinburgh, and shortly thereafter, he met some of the great scientists of the late eighteenth and early nineteenth centuries; he built an excellent professional reputation in medical practice in Knaresborough, reporting the occurrences of celestine and strontianite while he was physician in the town; a long and productive retirement, with many geological diversions, in the fashionable resort town of Scarborough followed. Murray was a central figure in many societies and institutions, particularly the Scarborough Philosophical Society, which completed the iconic Rotunda Museum in 1829. This study concentrates on his scientific activities, particularly in mineralogy, which was one of his passions.

Early Years

Peter Murray was born at Montego Bay in Jamaica on 30 March 1782. His mother Mary (née Wilmer) was the eldest daughter of John Wilmer, a successful merchant who had amassed a considerable fortune, and his wife Elizabeth. Mary had two sisters: Elizabeth, named after her mother, who would become Peter's guardian; and Grizell, who married Alexander Grant in 1782. Foster and Green (1888) summarise the lives of many generations of the Wilmer family, though their description of Peter Murray and his immediate relatives is brief.

Peter's father, Patrick Murray, was a Quaker, whose ancestry lay with the Scottish clan of Murray[2]. He was born at Kirkcudbright in southern Scotland to William Murray and his wife Sarah. Several members of his extended family had business interests in Jamaica. Patrick qualified as a physician, married Mary Wilmer in 1774, and the couple set off for the island to seek their fortune.

The loss of several children had a profound effect on Mary's well-being and she was in poor health while she was expecting Peter. Patrick hoped that a child might bring them together as a family, but it was not to be. Mary lived to see Peter christened on 27 April 1782, but died on 1 May of that year. Thus, Peter never knew his mother. Patrick engaged a Mrs Buchanan to look after his son. He was well cared for in those first critical years, but eighteenth-century Jamaica was no place for a delicate child. Peter was sole heir to a large fortune, and the Wilmer family asked Patrick to entrust them with his care and education.

In 1786, Peter was sent to live with his maternal grandmother Elizabeth, widow of the late John Wilmer (a wealthy silk merchant d. 22 January 1764, aged 67). Elizabeth had married Major John Sinclair in the year her husband died and the couple were very wealthy. Murray was accompanied by Mrs Buchanan, his nurse Mrs Mackenzie, and a servant, John. The eighty-day voyage to England formed his earliest recollection, he had no memory of his father, or the time that they time spent in Jamaica in later life. He came into the care of his grandmother on 26 July 1786 at the age of four.

The first few months in England were spent in luxury, but clouds had been gathering around the Wilmer family finances for some time. Elizabeth had inherited a fine mansion house, other property, and a considerable fortune, but her second husband had extravagant tastes. They were within the family's means until Major Sinclair decided to underwrite the ambitions of a nephew who wished to secure a seat in Parliament. These were the days of 'rotten boroughs', when fortunes were spent acquiring sufficient influence to become an MP. The venture ruined the family. Their mansion house and other properties were sold to pay outstanding debts and they had to move from London, in much reduced circumstances, to rented properties in Yorkshire (first at Beverley, then in Scarborough, and finally in York). It was in York, at a house in Skeldergate, that Major Sinclair died on 23 November 1787.

Murray's formal education began while the family were in Scarborough. He learned to read and write and began studying Latin and natural history. Many years later he recalled that his first half guinea was spent purchasing the second edition of *Bewick's Quadrupeds*, a beautifully engraved natural history of mammals[3].

The family returned to London after Major Sinclair's death as it was thought Peter would receive a more satisfactory education there. He was sent to an expensive school, but its ethos was unsuited to an intelligent and sensitive child. The unhappy experience came to an end in 1793 when Elizabeth Sinclair died. With the death of his grandmother Peter found himself in the care of his aunt Elizabeth, who decided that a more suitable education could be had in the quiet and respectable university town of St Andrews.

University Studies: St Andrews and Edinburgh

A brief note in Murray's handwriting records the start of the next chapter in his life: "Removed to St. Andrew's [*sic*] with my beloved Aunt Wilmer, also with my father, now in a very broken state mentally and bodily. There, with my cousin, Miss Faussett, we remained in happiness and contentment till 1799" (Balgarnie, 1864: p. 23).

It appears Patrick Murray, Peter's father, returned from Jamaica after the death of his mother-in-law (Balgarnie, 1864: p. 19), but the loss of his wife, failure of his business ventures and the maladies that

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[2] In later life, Peter kept a square of the Murray tartan with a sprig of juniper in his drawing-room as a reminder of his Scottish ancestry.

[3] Thomas Bewick (1753–1828) was one of Northumberland's greatest artists. A wood engraver and naturalist, his work is celebrated by the Bewick Society. He is best known for his *Illustrations of British Birds* which remains in print to this day (Bewick Society, 2018).

afflicted Jamaica in the late eighteenth century had sapped his health and spirit. For a time he lived with Elizabeth, who supported him from her modest annuity, but he does not figure in Balgarnie's biography any further. He returned to Kirkcudbright, where he lived for more than 30 years, dying in August 1829 at the age of 85 (York Herald, 1829; Anon., 1829: p. 477). He was laid to rest in St Cuthbert's Church with his mother and father. There is no indication that father and son were estranged, and the lack of any further reference in Balgarnie's biography is surprising.

Murray began his 'university education' at St Andrews in 1794 at the age of twelve. In 1798 he sufficiently impressed members of the newly formed Edinburgh 'Academy of Physics' (effectively a dissenting student society) to be elected as a member for an essay on marine zoophytes (which include the animals now known as bryozoans). He regularly explored the country around St Andrews, talking long walks, gathering specimens, and jotting down ideas.

After completing the course of study at St Andrews, Murray moved with his aunt to Edinburgh, and on 31 October 1799, enrolled at the university. Attendance lists record that a Mr Murray from Jamaica registered for the natural history course in that year. Murray is listed as a student of philosophy rather than of medicine (Eddy, 2016); he may have been too young to register as a medic, or as yet undecided on medicine as a career.

There were a remarkable number of outstanding academics at the university in *fin de siècle* Edinburgh, and it provided a first-rate education. Thomas Charles Hope (1766–1844) had just succeeded the renowned Joseph Black (1728–1799) to the Chair of Chemistry. Robert Jameson (1774–1854), whose contributions to mineralogy are well known, had taken over most of the natural history teaching from the Reverend John Walker (1731–1803). Murray recorded:

> "I specially applied myself to chemistry, botany and mineralogy. In the two latter studies I had an instructor, and most intimate friend, in Mr. John Murray, the very able public lecturer ... I became, also, a not inactive member of the Natural History Society, where I was associated, to my honour and advantage, with Dr. Kennedy, the well-known coadjutor with Sir James Hall, in establishing, by rigid analysis, the identity of basalt with lava. Besides Dr. Kennedy, I was then intimate with other members of the society, since of high celebrity; as Henry, now Lord Brougham, Sir George Mackenzie, [and] Professor Jameson, the assistant of the good Dr. Walker, professor of natural history".

Murray continued to take long walks, usually on Saturday, to clear his mind and search for botanical and geological specimens. It was probably on one of these explorations that he found the quartz crystals subsequently described by James Sowerby (1804: p. 89):

> "The regular dodecaëdral crystal of quartz is somewhat rare. I at present know of no certain habitat for it in Great Britain, excepting at Craig Lackart [Craiglockhart], about 3 miles from Edinburgh, from whence I have an irregular group given me by Dr. P. Murray, who gathered it himself."

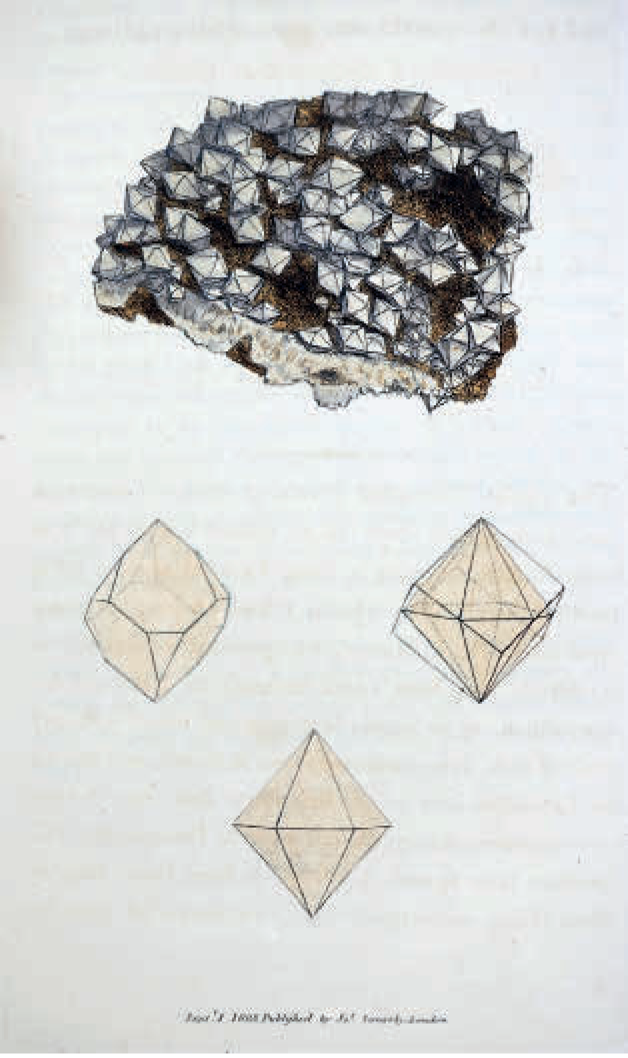

Figure 1. Plate 42 from James Sowerby's classic *British Mineralogy*, showing the bipyramidal habit of quartz crystals (bottom figure) which Peter Murray collected at Craig Lackart (Craiglockhart) near Edinburgh during his studies at the university. The figured specimen is from Cader Idris in Gwynedd.

Sowerby went on to note that similar material could be found in Lancashire, Devon and around Bristol, but the specimen figured on Plate 42, facing his commentary, is from Cader Idris in Wales (Fig. 1).

Murray's medical doctorate is recorded in the University of Edinburgh's *Laureation and Degrees Album* on 24 June 1802. He had earned the qualification at the age of twenty, and as his youth was a disadvantage in setting up in practice he moved from Edinburgh to London to gain some experience. He was received in London by Dr Maxwell Garthshore[4], a highly regarded

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[4] Maxwell Garthshore was born in Kirkcudbright (Patrick Murray's home town) on 28 October 1732, he died in London on 1 March 1812, a wealthy and highly respected physician (Anon., 1812; Ewart, 1830).

physician and friend of his father. Dr Garthshore provided an introduction to Sir Humphry Davy, President of the Royal Institution, who gave Murray free use of his laboratory for chemical experimentation. He was also introduced to Sir Joseph Banks, President of the Royal Society and a close friend of Garthshore (Ewart, 1830), in whose library he was encouraged to study. Employment was obtained as assistant physician at the Finsbury Dispensary, a job in which he encountered patients with diverse and distressing maladies. By the end of his time in London, Murray was acquainted with some of the great minds of the late eighteenth and early nineteenth centuries, and well equipped for the role of physician in provincial Yorkshire.

Medical Practice in Knaresborough

The salary at the dispensary was small and, although the position provided valuable experience, Murray was anxious for financial independence. He had relied on his aunt's modest income for most of his life. An opportunity to practice in Knaresborough came up in a chance conversation in 1803. Soon after he received a competing offer to set up in Scarborough. The choice proved difficult, but it was at Castle Ings in Knaresborough (on Permian limestone overlooking the River Nidd) that Murray set up his practice late in 1803 (Kellett, 1991; 2013).

No suitable house was available in the town, and in May 1804 Murray and his aunt moved into a cottage close to a chalybeate spring in nearby Harrogate. The next eight years were spent shuttling between Harrogate and Knaresborough. By the end of that time, many of the local gentry, notably Sir Thomas Slingsby[5] and Edward Lascelles[6], could be counted among his friends. The latter was so impressed with the young doctor that he offered him the position of family physician. Murray declined, as it would mean a separation from his aunt Elizabeth, but he stayed in touch with the Lascelles family, at whose country seat, Harewood House, he met with his old friend Sir Humphry Davy.

The journey between Harrogate and Knaresborough was tiresome, but not without interest. Murray sent several specimens of gypsum from a quarry on the banks of the River Nidd between Harrogate and Knaresborough to his old friend James Sowerby and they are figured on Plate 234 of *British Mineralogy* (Fig. 2). He became interested in the medicinal properties of a nearby 'sulphur spring'. The site (Bilton Spa) now lies forgotten in woodland on the south bank of the Nidd, but it was of importance in the nineteenth century when the emergent middle classes visited the area to 'take the waters'. Granville (1841: p. 89) records:

> "For all the measures adopted in restoring Knaresborough to its present state of usefulness, and for having roused the inhabitants of that town from their previous apathy respecting it, the public are indebted to Mr. Calvert of Knaresborough, who published, in 1836, a small historical and descriptive account of the Spa. Dr. Murray, also, by analyzing the water, contributed to give it publicity".

The curative properties of natural waters became a national obsession at a time when medical knowledge was inadequate. Murray was a strong advocate and by 1812 he was sufficiently well known to be mentioned by

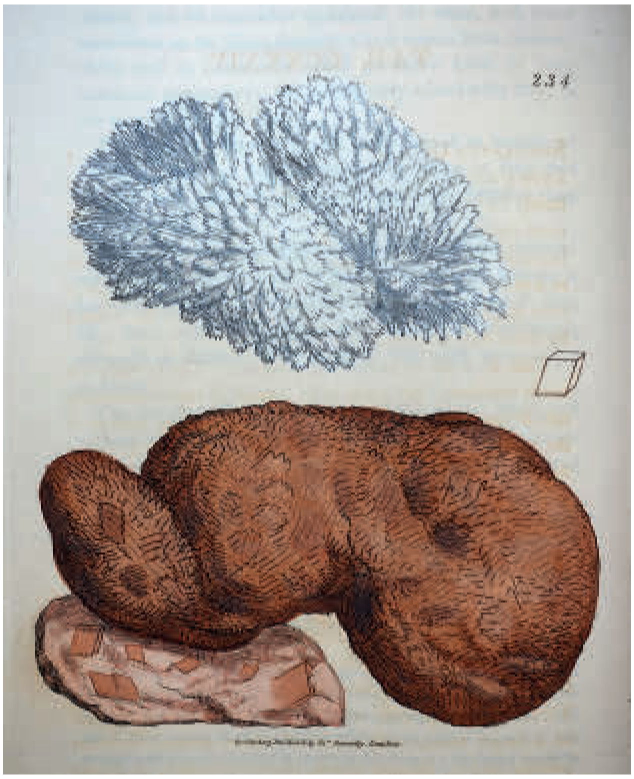

Figure 2. Plate 234 from James Sowerby's classic *British Mineralogy*, showing gypsum from Derbyshire (top specimen) and Bilton near Knaresborough, the latter supplied by Peter Murray (bottom specimens). The accompanying commentary (Sowerby 1809: p. 67) notes:

> "The *under specimen* might be considered as a red or rose-coloured Gypsum. They are often coloured with red Oxide of Iron, in varying degrees. This specimen appears of an uncommon form; the crystals ... lie horizontally; and it would seem as if the whole was a sort of Stalagmite, having fallen into this form in a particular state".
>
> "I received this specimen by favour of my kind friend Dr. P. Murray, from the limestone quarry at Bilton in Yorkshire, along with another very instructive one, part of a larger mass, with a vein of whiter striated Gypsum passing into it, holding almost orange-coloured, or deeper tinged perhaps, primitive rhombs within it ... This variety is sometimes compact and hard enough to be turned and polished for ornaments"

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[5] Sir Thomas Slingsby (1775−1835) of Scriven the ninth Baronet who served as High Sheriff of Yorkshire.

[6] Edward Lascelles (1740−1820) a Member of Parliament and plantation owner who was raised to the peerage as Baron Lascelles in 1796 and became Viscount Lascelles and first Earl of Harewood in 1812.

the writer Barbara Hofland (1770–1844), in comic verse (Hofland, 1812):

> "I obey'd the loud mandate of Gen'ral O'Flurry,
> And this morning consulted with one Doctor Murray
> Who sans ruffles, sans wig and sans avis supercilious,
> Has pronounc'd on my case and declares I am bilious"

It was in his explorations of the woodland along the banks of the Nidd that Murray discovered celestine. Strontium minerals had a measure of scientific novelty in the early nineteenth century. Murray had the good fortune to have met many of the key players in the discovery of the element. The Revd Dr John Walker, who held the Regius Chair in Natural History at the University of Edinburgh from 1779 until 1803, identified the mineral now known as strontianite. Walker visited Strontian in 1764 on a tour of the Highlands and found "that singular substance, since called the Strontianite, in great plenty" (Walker, 1822). By the time that Murray was a student at Edinburgh, it was known that strontianite contained a 'new species of earth' [i.e. strontium oxide] (Crawford, 1790). He would undoubtedly have been aware of the detailed investigations of Thomas Charles Hope, who was Professor of Chemistry at the University of Edinburgh from 1799, which proved strontium was a distinct chemical element with properties between calcium and barium. Murray also knew Sir Humphry Davy, who was familiar with the first British discoveries of celestine in the area around Bristol, and isolated metallic strontium by electrolysis in 1808 (Partington, 1942; 1951).

The earliest report of the discovery of celestine in Yorkshire appears in a summary of a meeting of the Geological Society of London on 1 November 1811. The minutes record that a letter describing "sulphate of strontian" in limestone from the banks of the River Nidd near Knaresborough, was received from Dr Murray of Harrogate (Anon., 1817: p. 445). The recipient was James Sowerby, an active member of the Society who Murray had known for some time [*vide supra*]. Sowerby was engaged in the production of *British Mineralogy*, a beautifully illustrated compendium of the minerals of the British Isles (Conklin, 1995; Henderson, 2015). Murray's letter was accompanied by a specimen and on 6 December of that year Sowerby donated it to the Geological Society (Anon. 1814: p. 540). Subsequent correspondence between Murray and Edward Daniel Clarke (1769–1822), Professor of Mineralogy at the University of Cambridge, dated 8 May 1813, preserved at the Natural History Museum[7], shows that the discovery generated some scientific interest (Roy Starkey, *personal communication*, 2021).

Celestine is illustrated on Plate 444 of *British Mineralogy* (Fig. 3). The associated commentary (Sowerby, 1817: pp. 75–76) begins with the observation that rocks of similar age and appearance commonly contain the same minerals. The first British discoveries of celestine were made in the area around Bristol in the 1790s (Levere *et al.*, 2017; Starkey, 2018; Tom Cotterell, *personal communication*, 2018), and Sowerby notes:

> "my highly esteemed and ingenious friend Dr. Murray of Harrowgate [*sic*], in company with Sir Thomas Slingsby, bart., discovered Sulphate of Strontian similar to that of Bristol, on the banks of the river Nidd, near Knaresborough, in an apparently similar rock ... It is thus that the same deposit or formation of rock may be known by a similarity of substances".

The announcement was not without controversy: just nine days after part 71 of *British Mineralogy* was issued,

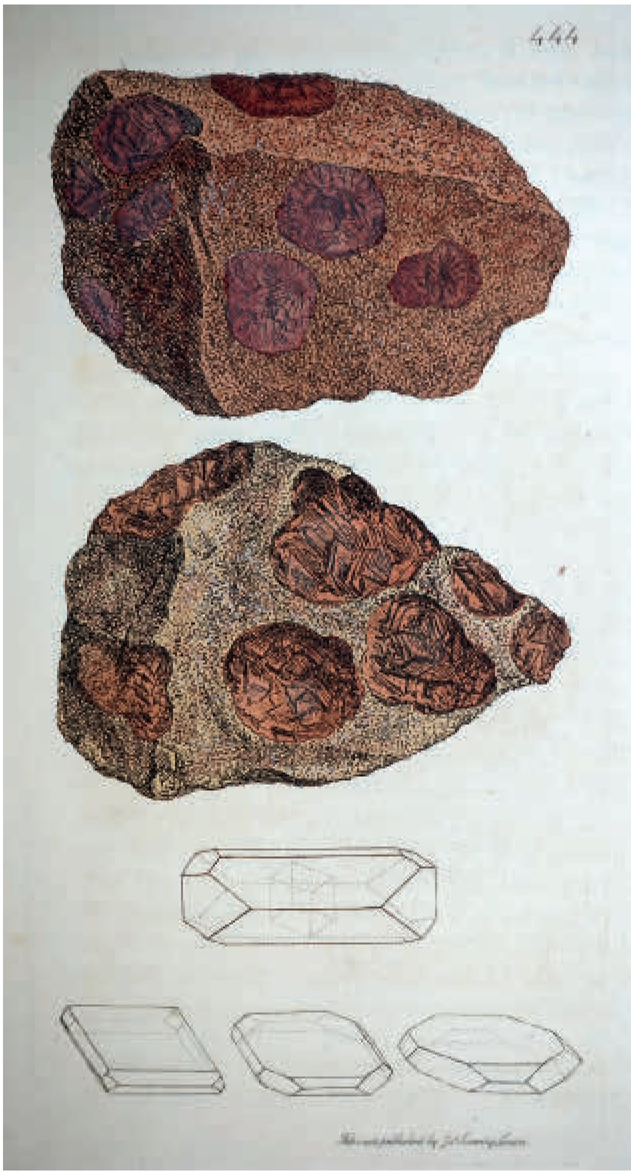

Figure 3. Plate 444 from James Sowerby's classic *British Mineralogy*, showing celestine, probably from the area around Bristol, but with one crystal drawing of a specimen from the banks of the Nidd near Knaresborough. Readers should note that *British Mineralogy* was issued to subscribers in parts, which were bound only after each volume was complete; although volume five is dated 1817, Plate 444 was issued five years before, in part 71, on 1 February 1812 (Conklin, 1995).

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[7] A small exercise book with seven pages of notes in the Russell Archive: NHM archive reference MIN MSS Rus Box 4.

the mineral surveyor John Farey asserted that the celestine had been found eight miles away near the village of Kirk Hammerton (Farey, 1812). Despite Farey's claims, there is no reason to doubt the locality on the banks of the River Nidd near Knaresborough. Celestine is widespread in the Permian rocks in this part of Yorkshire and (as suggested by Farey) is also probably present in the overlying Triassic strata.

Although Sowerby provided the first published description of celestine from Knaresborough, and credited Murray with the discovery, his text suggests the specimens figured in Plate 444 are from the area around Bristol. One of the crystal drawings, however, definitely relates to a Knaresborough specimen. It was provided by William Danby[8], and Sowerby notes:

> "Just as I was executing these [drawings], my good friend W. Danby, esq. sent me a specimen from near Knaresborough with elongated crystals, much resembling the Nutfield Sulphate of Barytes, but of a pale blue colour and smaller. I add a figure of the form with the nucleus".

Murray's specimen came into the care of the British Museum in 1911 (Fig. 4). It is unlike anything figured in *British Mineralogy*. Indeed, none of the Knaresborough specimens that were later donated to the Natural History Museum and other institutional collections bear much resemblance to Sowerby's illustrations.

Returning to more prosaic matters, Murray wanted to live nearer to his practice in Knaresborough and in 1812 a suitable property became available. He took up residence with his aunt Elizabeth at The Red House in Bond End[9]. He was so devoted to his aunt that he broke off an engagement to the only daughter of a wealthy friend out of a sense of responsibility, declaring that he would not marry while she was alive. His natural benevolence led him toward the church. Balgarnie (1864: p. 66) notes:

> "In his professional visits he endeavoured to combine the Christian with the physician; while ministering to the body he also ministered to the soul".

Murray and the local pastor founded the Knaresborough Dispensary for the benefit of the needy poor. For some years he was its sole medical attendant and would not charge people who could not afford to pay. Fortunately, his professional practice prospered alongside this charitable work and the household finances improved still further when a second aunt, Grizell Grant, lost her husband and came to live in Knaresborough.

Sulphate of Strontian found [illegible]
the banks of the River Nidd near
Knaresborough by D. P. Murray.
Presented to the Geological Society
by James Sowerby.

Figure 4. The specimen which Murray sent to Sowerby in 1811 (BM 1911,616) with a label which records "Sulphate of Strontian found in the banks of the River Nidd near Knaresborough by Dr P. Murray. Presented to the Geological Society by James Sowerby". The 70 × 80 mm section of white to pale blue celestine is unlike any of the specimens illustrated by Sowerby in Figure 3. Photos © Trustees of the Natural History Museum.

As Murray's scientific reputation grew his skills as a chemist were sought, notably in the trial of a man who was alleged to have poisoned his brother-in-law to gain possession of his property. Murray was able to provide conclusive evidence of arsenic in the dead man's stomach and the accused was sentenced to death.

These same chemical skills were employed in mineralogy and Murray became known "for his analyses of various new minerals, particularly the Yorkshire combinations of Strontia (Celestina Strontia), which he was the first to discover in that part of the country" (Balgarnie, 1864: p. 61).

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[8] William Danby (1752–1833) of Swinton Park near Masham, Yorkshire was a wealthy collector. He made several donations to the Geological Society's cabinet of minerals (Anon., 1821); was Vice-President of the Yorkshire Philosophical Society, to which he made many important donations; and had a fine library and mineral museum (Cooper, 1888). He would almost certainly have been acquainted with Murray.

[9] The Red House still exists, behind the World's End pub, just north of the bridge which carries the A59 over the River Nidd in Knaresborough. The name is presumed to reflect its red brick construction. Most early houses in Knaresborough, and its ruined castle, are of natural yellow-brown stone.

The earliest report of the discovery of strontianite in Yorkshire[10] appears in one of a series of letters in the archives of the Yorkshire Philosophical Society, which was established in 1822. The letters were re-discovered in the Second World War and published with commentaries by Sidney Melmore (1894–1969) in *The North Western Naturalist* (Melmore, 1942). They include correspondence between Peter Murray and James Atkinson (1759–1839), the Vice-President of the Yorkshire Philosophical Society, dated 12 December 1824 (Melmore, 1943):

> "I have great pleasure in offering for the acceptance of the York Philosophical Society, some specimens of a New Yorkshire Mineral, the Carbonate of Strontites from the neighbourhood of Pateley Bridge. Indeed this may also be called a new English mineral, as hitherto it has only occurred at *Strontian* in *Argyleshire*; and the Sulphate merely has been found at Bristol & Knaresbrough [*sic*]. I have accompanied these little specimens with their analysis in which as well as colour & crystallization, they differ most materially from the Scottish Strontianite. I have sent a short notice upon the Carbonates & upon the various Sulphates which I have detected near my own town to the Edinburgh Phil. Journal & probably it will appear in the January number".

A summary of the mineralogical discoveries duly appeared as the tenth of a series of articles of 'scientific intelligence' in *The Edinburgh Philosophical Journal* (Murray, 1825: pp. 175–176) and, with minor alterations, in the *York Herald* on 15 January 1825. Two strontium-bearing mineral species are recorded as 'lately discovered': the first English occurrence of the carbonate (strontianite) from the Merryfield mines near Pateley Bridge, and several localities for the sulphate (celestine) on the banks of the River Nidd near Knaresborough and Bilton:

> "10. *Strontites in Yorkshire*.—Most of the native combinations of strontites have of late been found by Dr Peter Murray in the West Riding of the county of York, in the vicinity of Knaresborough and Pately [*sic*] Bridge.—The *carbonate* has, for the first time in England, been observed at the lead-mine of Merryfield, near Pately, in veins and nests, associated with galena and sulphate of barytes in calcareous grit. Two varieties have been met with: one compact, semitransparent, and of the most splendent white colour, resembling some kinds of arragonite [*sic*], and contains in the 100 parts, 55 of Strontian, 4 Carbonate of Lime, 2 of Alumina, Sulphate of Barytes 1, Water and Carbonic Acid 32; the other is beautifully crystallised in prisms, of a greyish-white colour, and in many specimens impressing calcareous spar, and, when analysed, has been found to contain in 100 parts, 1 of Water, 33 of Carbonic Acid, 6 of Lime, and 60 of Strontian.—Of the *sulphate*, three varieties have been noticed upon the banks of the Nidd, near Knaresborough. The *foliated sulphat* [*sic*] of Professor Jameson finely crystallised, of a delicate blue colour, and well meriting the name of Celestine, in magnesian limestone, resting upon the new red sandstone, and containing a small percentage of carbonate of lime, varying in different specimens. The *compact sulphate*, of a snowy white, occurs with the former in spheroidal or reniform pieces, containing 7 per cent. of carbonate of lime— The *radiated sulphat*, of a yellowish or reddish-white colour, is found at Bilton, upon the opposite bank of the river, in the new red sandstone formation, accompanied by several varieties of gypsum. This sandstone greatly varies within very narrow limits, extremely compact and hard where inclosing the strontites, and then becoming almost amygdaloidal, with nodules of quartz, on one hand; and on the other passing into a soft red marl, containing gypsum".

Murray presented four "Specimens of Minerals from Knaresborough" to the Yorkshire Philosophical Society in 1822 (Yorkshire Philosophical Society, 1823: p. 28); "Sulphate of Strontian, Knaresbro" and "Two varieties of Carbonate of Strontian: Merryfield Mine, Pately [*sic*]" in the next year (Yorkshire Philosophical Society, 1824: pp. 10–11 and p. 14); and two further specimens of "Carbonate of Strontian and Barytes, from Merryfield Lead mines" in January 1825 (Yorkshire Philosophical Society, 1826: p. 18). A number of specimens of strontianite from Merryfield Mine (e.g. Figs 5 and 6) and celestine from Knaresborough remain in the collection of the Yorkshire Museum, but unfortunately none can be attributed with certainty to Murray.

As Murray grew older, the workload and responsibility of medical practice began to take its toll and in

Figure 5. Strontianite (45 × 60 mm) from Pateley Bridge with a very early accession number, YORYM: M846, in the collection of the Yorkshire Museum. This might be one of the specimens to which Murray refers in his letter to the Vice President of the Yorkshire Philosophical Society (it is one of four similar pieces catalogued under this number) but unfortunately the acquisition details can no longer be traced. Photo John Chapman.

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[10] Readers may wish, however, to consider plate 109 in Sowerby (1806), which is described as "Crystallized Carbonate of Barytes" (i.e. witherite). It is from Arkengarthdale in North Yorkshire. In many years of exploration no similar witherite has been found in the area. Strontianite, on the other hand, is widespread as radiating crystal groups in north Swaledale. Could it be the first illustration of Yorkshire strontianite?

Figure 6. Small sprays of strontianite associated with baryte in two distinct crystal habits, cubic fluorite, pyrite and sphalerite from Pateley Bridge. Accessioned relatively recently, YORYM: 2007.9678, but almost certainly dating from the 1820s, it shows the paragenetic sequence at Merryfield Mine. The field of view is 30 mm across. Photo John Chapman.

1826 his health deteriorated. He realised that something needed to be done, and after some soul-searching decided to leave Knaresborough and move to the coastal town of Scarborough to live in semi-retirement. He had become a valued and respected member of the local community and the subscription to mark his retirement reached two hundred guineas[11].

A presentation in recognition of his services to the local community was arranged as a commemoration. The *Yorkshire Gazette* recorded the event on 6 January 1827:

> "a handsome Silver Tureen, Ladle, and Salver of the value of 200 guineas [was presented] to Dr. Murray on the occasion of his leaving the town, after a residence of upwards of twenty years".

The article went on to quote part of Sir Thomas Slingsby's speech, which gives an impression of the esteem in which Murray was held:

> "Those who have had the pleasure of living in your society must long regret [the loss] of a companion with every amiable and gentleman-like quality, and adorned with every variety of scientific, useful, and elegant knowledge; and far, far higher praise than that,—the poor will long lament their benefactor and their friend".

The house move offered an opportunity to refine Murray's collections and, with characteristic generosity, "eight specimens of Strontian and Barytes" were donated to the collection of the Newcastle Literary and Philosophical Society in October 1826 (Tyne Mercury, 1826). Soon thereafter a "brass symbol of Isis ... found at Aldborough, the ancient Isurium"[12] and "47 fossils from the chalk of Norwich and Cambridgeshire" were presented to the Yorkshire Philosophical Society (Yorkshire Philosophical Society, 1829: p. 23, p. 39 and p. 50).

Retirement in Scarborough

Murray and his aunts moved to Belle Vue[13], a fine house on the edge of Scarborough, in 1827. They had maintained strong connections with the area while they lived in Knaresborough, subscribing to books such as John Cole's *Graphic and Historical Sketches of Scarborough* (1822)[14]. Murray began his education in the town and it was where his aunt Grizell was married. Belle Vue is described in the sixth edition of *Cole's Scarborough Guide* (1834) as:

> "the residence of Dr. Murray; aptly so named as occupying one of the finest of situations for a mixed and beautiful prospect".

Murray could not fully relinquish medical practice. Many former patients sought his services. He was content to continue in a less demanding role and, in an extension of his interests in the benefits of spa waters (see Granville, 1841), took an interest in the health benefits of bathing in seawater (which was a common belief in the eighteenth century and developed into something of a Victorian obsession). He is listed as physician at the "General Sea-Bathing Infirmary" in the third edition of *Theakston's Guide to Scarborough* (1847).

In the early years of his retirement Murray devoted himself principally to philanthropy and science. In his professional life in Knaresborough he had resisted public speaking, feeling it was inconsistent with his position as a physician. In Scarborough he developed into a popular public speaker (in particular on the hustings where he advocated political reform) and as a scientific lecturer.

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[11] Using the Retail Price Index as a measure of inflation, 200 guineas in 1826 corresponds to about £25,500 in 2017 (Clark, 2011).

[12] The Roman settlement of Isurium Brigantum, near Boroughbridge in North Yorkshire.

[13] 'Belle Vue' was the residence of John Bell (*d.* 11 August 1829) in the early 1820s. It is identified on the 1:1056 town plan of 1852 (Ordnance Survey, 1852), but was demolished in about 1882 to allow for expansion of the railway.

[14] John Cole (1792–1848) was a popular lecturer, author, and bookseller, who produced many works about Scarborough in the 1820s and early 1830s. Despite his exceptional talent and enthusiasm he had little regard for pecuniary matters and died in poverty (Baker, 1882).

Geological study was encouraged in fashionable nineteenth-century Scarborough. Notable collectors in the town included Thomas Hinderwell (1744–1825), William Bean (1787–1866), and John Williamson (1784–1877). Shops "on the Cliff, in Long-Room-Street, and in Newborough-Street" sold minerals and fossils (Cole, 1834: p. 65) and they were popular with visitors to the town (Jaspars *et al.*, 2022).

Pebbles from Scarborough's beaches are described by Hill (1748: pp. 333–337) and are conspicuous in Joseph Dawson's collection catalogue[15], which was completed in 1813 (Dawson, 1810–1813; Pacey, 2003). The first book specifically devoted to the minerals and fossils of the area was completed by the Revd Frederick Kendall (1816), a suspected arsonist whose colourful life is charted in Torrens (2004). Writing a year later, the Revd George Young (1817: pp. 778–779) recorded:

> "precious stones of all sorts are washed down by the rains or floods, and are often picked up on the beach. Among these are many beautiful specimens of agate, jasper, jasper-agate, mocha, chalcedony, carnelian, onyx, and flint variegated like Egyptian agate".

George Young subsequently collaborated with the artist William Bird on *A Geological Survey of the Yorkshire Coast*. Published in 1822 it quickly became the standard guide.

By the late 1820s Scarborough had become a centre for geological investigation. William Smith and his nephew John Phillips had strong links with the town from 1820 onward and both were actively engaged in research. Smith is regarded as the 'Father of English Geology' and his seminal work mapping the strata needs no introduction (Torrens, 2003). Phillips (whose life is charted in Morrell, 2005) was engaged in fieldwork that would lead to the *Illustrations of the Geology of Yorkshire* (Phillips, 1829; 1836).

Mineralogy was also in the ascendant. In 1829, William Vernon (later Vernon Harcourt), the first President of the Yorkshire Philosophical Society, announced the discovery of a new mineral which he named "scarbröite" (Fig. 7) after the site of its discovery at White Nab in the South Bay (Yorkshire Philosophical Society, 1829; Vernon, 1829).

Geological enquiry coalesced around the Scarborough Philosophical Society which developed plans to build a museum on a circular design suggested by William Smith. The aim was to provide a focus for scientifically minded members of the community and an attraction for visitors. Funds were raised by subscription. Murray's contribution of £25 (to which a further £5 was subsequently added), was one of the larger amounts and entitled him to the privileged status of 'Proprietary Shareholder'.

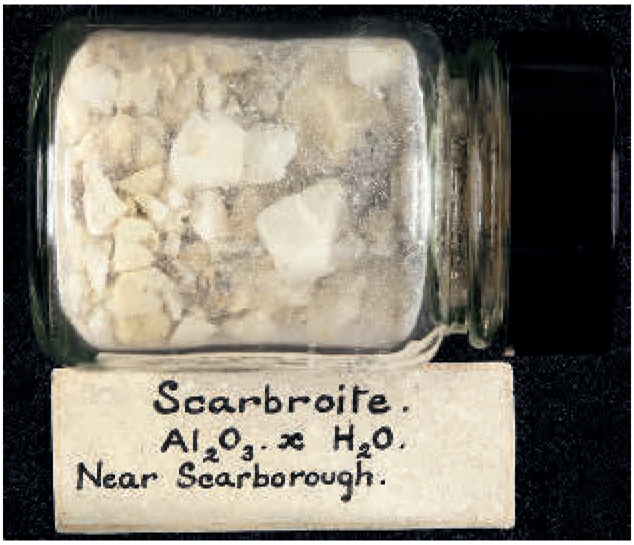

Figure 7. Scarbroite in the collection of the Yorkshire Museum, YORYM: 2007.5567. The mineral was announced in a communication to the Yorkshire Philosophical Society on 6 January 1829 (Yorkshire Philosophical Society, 1829: p. 34). In the original description (Vernon, 1829), the name is written with a diaeresis on the letter o. Scarbröite is phonetically correct as the vowel sounds are separate, but the diaeresis has been abandoned in modern publications. The correct spelling and typography is currently given as scarbroite (CNMNC, 2022), and the name is unaccountably omitted from the recent IMA-approved review of the use of diacritical marks in mineral names (Burke, 2008). The formula on the label, is the early but incorrect $Al_2O_3{\cdot}xH_2O$, the ideal formula was later shown to be $Al_5(CO_3)(OH)_{13}{\cdot}5H_2O$ (CNMNC, 2022). Photo John Chapman.

The foundations were laid on 9 April 1828 and the building opened on 31 August 1829. John Williamson was appointed Keeper of the Museum, a position he retained until his retirement, and Murray was chosen, in very distinguished company, as its first Curator of Mineralogy and Geology. He donated minerals, fossils and books from his personal collection, and was able to solicit specimens from other collectors (Fig. 8). The first report of the Society records "the splendid foundations laid in geology by the munificence of Mr Duesbury and Mr Williamson, [and] in mineralogy by Mr Duesbury and Dr Murray" (Scarborough Philosophical Society, 1830) [16].

Much of what is known of Murray's scientific life from 1830 onward is charted in the annual reports of the Scarborough Philosophical Society (1830–1854) and of

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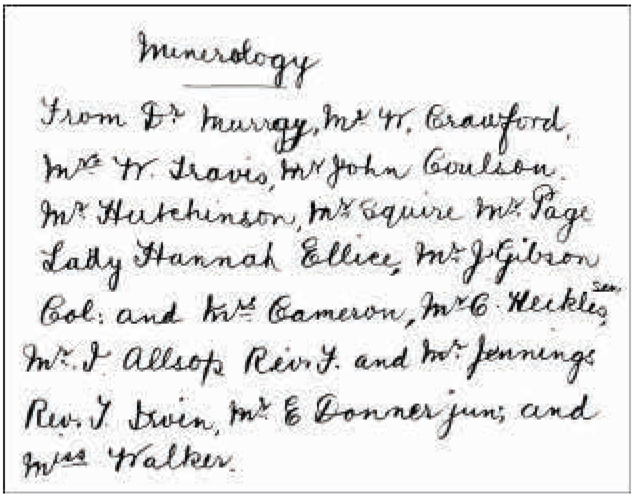
[15] Joseph Dawson (1740–1813) was one of the founders of the Low Moor Ironworks near Bradford. He had wide interests in mineralogy and chemistry, and applied scientific principles to the production of iron. His mineral collection, now held at Cliffe Castle in Keighley, is accompanied by a manuscript catalogue, and includes a number of specimens from the beaches at Scarborough (Dawson, 1810–1813; Pacey, 2003).

[16] Thomas Duesbery (also written Duesbury) of Beverley presented the collection of minerals, rocks and fossils assembled by his late uncle, the noted Scarborough historian Thomas Hinderwell (1744–1825), to the society. The society purchased John Williamson's extensive and valuable fossil collection for £75 (Scarborough Philosophical Society, 1830).



Minerology

From Dr Murray, Mr W. Crawford, Mrs W. Travis, Mr John Coulson. Mr Hutchinson, Mr Squire Mr Page Lady Hannah Ellice, Mr J Gibson Col: and Mrs Cameron, Mr C. Heckles sen. Mr J Allsop Rev J. and Mrs Jennings Rev. J. Dunn, Mr E Donner jun: and Miss Walker.

Figure 8. Handwritten records from the first report of the Scarborough Philosophical Society in 1830 recording donations of minerals from Mr W. Crawford, Mrs W. Travis, Mr John Coulson, Mr Hutchinson, Mr Squire, Mr Page, Lady Hannah Ellice, Mr J. Gibson, Col. and Mrs Cameron, Mr C. Heckles sen., Mr J. Allsop, Rev. J. and Mrs Jennings, Rev. J. Dunn, Mr E. Donner jun. and Miss Walker. There was clearly a thriving interest in the local area.

the Scarborough Philosophical and Archæological Society (1855–1865) thereafter. He served in several curatorial roles at the museum and as Vice-President of the Society. His contributions to the collections were substantial (and are listed in the Appendix).

Murray's involvement with the Scarborough Philosophical Society is only part of his legacy. He became President of the Scarborough branch of the British and Foreign Bible Society after the death of Thomas Hinderwell; was for many years President of the Scarborough Lancasterian Schools; and was one of the founders of the Scarborough Mechanics' Institute. He had links with many scientific institutions, conducted independent research, and his large and varied personal collection became sufficiently well known that scientific visitors to Scarborough often came with letters of introduction in the hope of inspecting it[17] (Balgarnie, 1864: p. 91; Phillips, 1875).

Murray kept in contact with friends from his university days, including the physician and scientist Thomas Stewart Traill (1781–1862). He provided one of the testimonials for Traill's successful application for the position of Professor of Medical Jurisprudence in 1832 in Liverpool (Wellcome Collection, 2021: p. 22):

> "I HEREBY certify, That I have been on terms of intimate for upwards of thirty years, with Dr THOMAS STEWART TRAILL, which friendship first commenced when a Student of Medicine at Edinburgh; and that ever since I have entertained the highest regard for his character as a man, and for his talents as a Physician and Natural Philosopher".

Traill was an avid mineral collector and his manuscript catalogue, which is now part of the archive associated with the Russell Collection at the Natural History Museum, records six specimens of celestine from the banks of the Nidd near Knaresborough and three specimens of strontianite from Merryfield Mine near Pateley Bridge (Roy Starkey, *personal communication*, 2020). These are almost certain to have come from Murray.

The cliffs around Scarborough provided opportunities for research in mineralogy and palaeontology. Combining his love of geology and botany, Murray contributed an account of the plant fossils of the "Coal Formation of the Third Secondary Limestone, near Scarborough" to *The Edinburgh New Philosophical Journal* (Murray, 1828). This deposit has become known as the 'Gristhorpe Plant Bed' (Wilson, 1968). It is of Middle Jurassic Bajocian age and of note because of the excellent preservation and diversity of the plant fossils. Murray's account shows he was aware of the importance of the developing science of stratigraphy; his interpretation of the deposit notes:

> "the vast excellency and usefulness are shewn [*sic*] of the plan laid down by M. Brongniart, in France, and Mr William Smith, in England, who shew that similar fossils characterise similar formations, and thus give us the means of determining the nature and place of any strata".

Many visits were made to collect from the cliffs, and in an account by the brilliant palaeontologist Gideon Mantell (1838: p. 401), Murray's generosity shines through:

> "Along the coast under Gristhorp cliffs, a seam of shale, but a few inches in thickness, may be traced for miles; and, from its abounding in leaves of ferns, equiseta, cycadeæ, and of a great many other plants, it is chiselled out by collectors, to obtain specimens. The beauty and variety of these fossil plants are shown in this extensive series presented to me by Dr. Peter Murray, and Mr. Williamson of Scarborough".

The only mention of minerals at Gristhorpe in Murray's article is of veins of calcite. Despite his interest in strontium minerals it is unlikely that the "Strontian"[18], described from this area (and also in the oolite near Scarborough), in the second edition of *A Geological Survey of the Yorkshire Coast* (Young and Bird, 1828: p. 92), was found by Murray. There are no records of strontium minerals in any of his articles on the area (see Murray, 1854).

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[17] In his description of fossil plants from the Yorkshire Coast, Sir Charles J. F. Bunbury (1851: p. 179) records: "To the liberality and kindness of Dr. Murray I am especially indebted ... and I wish publically [*sic*] to express my obligations to him".

[18] Although the first description: "Strontian likewise occurs [at Gristhorpe], but in small quantity; and the same mineral has been found in the oolite near Scarborough" in Young and Bird (1828: p. 92) does not make it clear which strontium-bearing mineral is being described, a subsequent note in the same volume shows that it is celestine: "sulphate of strontian [is found in] our oolitic rocks (see p. 92)" (Young and Bird, 1828: p. 172).

Murray achieved a measure of scientific immortality in the names of two fossil plants from Gristhorpe. The first of these is *Solenites murrayana* Lindl. & Hutton (Lindley and Hutton, 1833–1835: p. 109):

> "We therefore distinguish it as a peculiar genus for which the name *Solenites* has been suggested by its fistular structure Dr Murray is fully entitled to have it bear his name in addition in commemoration of his having been both the discoverer of the fossil and the determiner of its affinity".

The species was subsequently transferred to the genus *Czekanowskia*. With the introduction of the International Code of Botanical Nomenclature, *Czekanowskia murrayana* (Lindl. & Hutton) Heer, was shown to be a synonym of *Flabellaria viminea* Phillips, which has priority. The genus *Solenites* was subsequently revived and the species has become *Solenites vimineus* (Phillips) Harris.

Although it no longer bears his name, the description of *Solenites murrayana* is of scientific importance because it was the first time that a fossil plant was examined by transmitted light under an optical microscope. It has been claimed that Lindley and Hutton were the first to employ the technique, but in his original article, Murray (1828: p. 312) noted:

> "The vegetable nature of these curious impressions is remarkably shewn [*sic*] by the scarcely fossilized state of one of the varieties, apparently a fern allied to the genus Isoëtes [*Solenites murrayana*], which, when detached from the imbedding stony mass, still retains elasticity and flexibility, and burns like a piece of charred wood. Others yet preserve, even in their clay bed, much of their original colour, a dull red resembling that of some fuci; and portions of such leaflets maybe peeled away,—are perfectly flexible and combustible,—and are actually semi-transparent and striated, and afford most pleasing and curious objects for a microscope. They are, however, so completely carbonized, as not to yield either tannin or resinous matter, in the experiments which I have instituted".

The exceptional preservation is described by Lindley and Hutton (1833–1835: p. 106), who used a chemical technique to enhance the transparency of fragments:

> "Considering however their flexible state it occurred to us that if it were possible to separate the tissue from the carbonaceous matter by some powerful solvent the transparency of the specimens might be restored and some insight obtained into their anatomical structure. Accordingly upon plunging them into boiling nitric acid in a few moments a dark crust peeled away in flakes and presently the centre part became amber coloured and transparent when washed and placed beneath a microscope it was found that all the foreign matter which had rendered the specimen opaque was separated".

Murray has been luckier with the second fossil plant species named for him: *Pecopteris murrayana* (Brongn.) (Fig. 9). It was described by the 'Father of Palaeobotany', Adolphe-Théodore Brongniart (1801–1876), in 1836. The locality is recorded as "Scarborough on the coast of Yorkshire (Murray)" where Brongniart notes (p. 358):

Figure 9. The original drawings of *Pecopteris murrayana* from Gristhorpe near Scarborough, Plate 126 in part 10 of the first volume the *Histoire des Végétaux Fossiles* (Brongniart, 1828–1837).

> "*Les nombreux échantillons de cette Fougère, que j'ai reçus du docteur Murray de Scarborough, me permettent cle rapporter presque avec certitude à un même type spécifique des formes assez différentes*"[19]

In the 1840s, it became clear to Brongniart that the genus *Pecopteris* was limited to the Palaeozoic, appearing in the Devonian, flourishing throughout the Carboniferous, and dying out in the Permian. In 1849, he created a new genus, *Coniopteris*[20], for Jurassic plants with similar leaves and *P. murrayana* became *Coniopteris murrayana* Brongn. Later researchers, notably A. C. Seward at the University of Cambridge, considered *C. murrayana* and various other species to be variants of *C. hymenophylloides* (Brongn.), which had priority as it was described in an earlier part of the *Histoire des Végétaux Fossiles* (see Seward, 1910). More modern texts (e.g. Harris, 1961; van Konijnenburg-van Cittert and Morgans, 1999) retain *C. murrayana* as a valid species.

The curators of the Rotunda Museum changed frequently in its early years and Isaac Stickney had succeeded Peter Murray as Curator of Mineralogy and Geology by the time of the second annual report. The Council once again noted the "very valuable donations of ... Dr. Murray", whose specimens formed the basis of

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[19] Translated from the French as: "The numerous specimens of this fern, which I received from Dr. Murray of Scarborough, permit me to report with certainty to the same specific type rather different forms".

[20] The name *Coniopteris* should be replaced by *Polystichites*, which has priority under the rules of the International Code of Botanical Nomenclature, however, the latter term fell out of use in the nineteenth century whereas *Coniopteris* remained widespread in palaeobotany. A proposal has therefore been made to retain *Coniopteris* (Doweld, 2013).

the mineral collection (Scarborough Philosophical Society, 1832).

Murray made many further contributions throughout his life. He gave ten shillings toward the purchase of a box of foreign insects in 1833, and when meteorological observations were begun in September of that year, the rain gauge was located in his garden and the rainfall data recorded by his servant Peter Hawkridge. The composition of the rainwater was of some interest and Murray used his chemical skills to prove that it contained salt when the wind blew off the sea (Scarborough Philosophical Society, 1834):

> "THE presence of saline matter occasionally, in the rain which falls at Scarborough, has been proved by a series of experiments, instituted by Dr. MURRAY; whereby muriatic acid and lime have been detected in the rain water, carefully collected when the wind blew from the East or North-East; and the quantity so found was proportioned to the force of the blast, or its nearness to the Eastern point. Muriate of soda, and muriate of lime, were also detected, by slow evaporation; but no trace either of iodine, or of potash. The ordinary rain water is, at Scarborough, peculiarly free from the impregnation of muriatic acid".

In his early years in Scarborough, Murray retained an interest in minerals from the area around Knaresborough, acquiring specimens of celestine from a locality on Scotton Moor, to the west of the town, in the early 1830s. He donated "Sulphate of strontian, from Scotton, near Knaresborough" to the Yorkshire Museum in 1833 (Yorkshire Philosophical Society, 1834) and in the next year, a donation of 59 specimens to the University of Durham, included two more celestine specimens from Scotton Moor (Durham County Advertiser, 1834). Sadly, very few of the early mineral specimens at the Rotunda Museum have survived with details of their original donors, but an early specimen from Scotton Moor, with an old handwritten label, can only be from Murray (Fig. 10).

Figure 10. Celestine vein section, with an old label glued to the base "201. Sulphate of Strontian or Celestine, Scotton Moor, Knasebro' [*sic*]". Now accessioned as 1011.55.GM535 at the Rotunda Museum but clearly a very early specimen and, given the locality, almost certainly from Peter Murray. Photo Jim Middleton.

Murray was much in demand as a lecturer. He spoke at the Scarborough Mechanics' Institute on such diverse topics as "Astronomy, with illustrations"; "Mining and Metals"; and "The Materials in the District, used in Buildings and the Arts" (Balgarnie, 1864: p. 88). The relationship between the Mechanics' Institute[21], which Murray had helped to found in 1830 (Popple, 1958), and the Scarborough Philosophical Society of which he was Vice-President for three years in that decade (Scarborough Philosophical Society, 1835; 1836; 1837) exposes a paternalistic egalitarianism that is characteristic of the period. The *Report of the Scarborough Philosophical Society* for 1834 notes:

> "The Council having afforded an opportunity for all the members of the Mechanics' Institute, with their families, to examine the collection [at the Rotunda Museum], upwards of three hundred availed themselves of the offer. Although the funds of the Society were not benefited by the latter admission, they were not injured by it, and the Council had much pleasure in affording an intellectual feast, without sacrifice on their part, to the members of a kindred, though somewhat humbler, institution. Every endeavour to raise the character of this class of society, tends to the furtherance of science and the developement [*sic*] of genius; as a very large proportion of the most active scientific labourers have arisen from the humbler ranks of life".

The Rotunda Museum continued to build its collections and the *Report of the Scarborough Philosophical Society* for 1835 notes[22, 23]:

> "The mineralogical department has been enriched by the present of a box of Minerals, from North America, by our former munificent benefactor, Miss Currer; and a foundation has been laid, of a botanical collection, by the son of the Keeper of the Museum, (William Williamson) who has presented his valuable collection of plants, the result of much arduous labour, to the Institution".

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[21] The Scarborough Mechanics' Institute was established at a meeting held at the Freemasons' Lodge on 12 November 1830 by J. B. Baker, a chemist and author, with the assistance of Peter Murray and the Revd B. Evans (Balgarnie, 1864: pp. 87–89; Popple, 1958: pp. 38–39).

[22] Miss Currer is Frances Mary Richardson Currer (1785–1861) of Eshton Hall, Gargrave. A book collector and possible benefactor of the Brontë sisters, who also had connections with Scarborough (see Jaspars *et al*., 2022) she made generous contributions to the Scarborough Philosophical Society for many years (Lee, 2004).

[23] William Crawford Williamson (1816–1895) became Professor of Natural History at Owen's College, which later became the Victoria University of Manchester. An expert palaeobotanist, he was elected FRS in 1854 and won the Royal Medal in 1874.

The same volume records that Murray, then Vice-President of the Society, donated "Sulphate of Strontia, in broad tabular Prisms, from the red Marl, Bilton Banks, Knaresboro'" (Scarborough Philosophical Society, 1835).

Late in 1835 it became clear that corruption was widespread on Scarborough Town Council. The councillors failed to attend to their civic duties, organised extravagant junkets and paid excessive rents to a select group of cronies; all at the town's expense. An election was called for 28 December 1835 and the offending officers were removed. Murray, who (amongst his many positions) was Chairman of the Society for the Protection and Extension of Civil and Religious Liberty, did not shirk from civic duty and was returned as one of the replacement councillors (Binns, 2001).

Murray's aunt Grizell died on 26 January 1837 at the age of 81. This left Murray, his aunt Elizabeth, and four servants at Belle Vue. The household over the next thirty years is recorded in census returns, which show that Murray had sufficient means to maintain a staff of four servants. Peter Hawkridge, who had joined at the age of twelve in Knaresborough, remained with Murray for the whole of his life.

According to Balgarnie (1839: p. 91), Murray donated a large piece of jet and a suite of fossil plants to the British Museum in 1839 and was thanked by the trustees "for this desirable addition to the National collections"; however, a history of the Department of Geology (there was no separate Department of Mineralogy until 1857) records that the "Lower Jurassic plant-remains from Yorkshire, were purchased from Dr. Peter Murray of Scarborough" (British Museum, 1904: p. 205 and p. 314). This is unusual, as Murray normally made donations to institutional collections. In the same year he donated a specimen labelled scarbroite (but later identified by X-ray diffractometry as kaolinite). At about the same time, new cabinets (to which Murray subscribed the sum of £5) were installed to better display the geological collection at the Rotunda Museum.

Returning to civic responsibilities, Murray, in his role as President of the Scarborough Lancasterian Schools, became caught up in an acrimonious financial disagreement dating from before he had any involvement with the institution and of which he had little knowledge. The dispute seems to have hinged on whether money was given or lent by certain of the trustees. An extended series of letters, with complaints and commentaries were published (Davies, 1840; 1842; 1843). Peppered with repressed resentment, these works are about as near as nineteenth-century gentlemen came to a rant. Murray seems to have dealt with the grievances in as fair a way as he was able, and even the author (Davies, 1840: p. 90) comments that:

> "great allowances should be made for the amiable and kind-hearted President, Dr. Murray, whose benevolent tendencies are so well known and justly appreciated".

Murray continued to give lectures, one of which, to the Hull Literary and Philosophical Society[24] in January 1841, described "the Minerals of Yorkshire, with a very general Sketch of its Geological Structure" (Hull Packet, 1840). Murray was Curator of Mineralogy at the Rotunda Museum at the time, and he remained in the post for three years (the maximum duration a curatorial post could be occupied under the rules of the society); he then took the role of Curator of Medals and Coins, numismatics being another of his many interests (Scarborough Philosophical Society, 1841; 1842; 1843a,b; 1845; 1846). He donated a "Polished piece of Heliotrope originally forming part of the Mosaic pavement of the High Altar at the Cathedral of St. Andrews" in 1841 (Scarborough Philosophical Society, 1842), which may have been acquired during his studies at the university in the last years of the eighteenth century.

The *Report of the Scarborough Philosophical Society* for 1841 records visits by three geological luminaries: the Revd Adam Sedgwick (1785–1873), Richard Owen (1804–1892) and Roderick Impey Murchison (1792–1871). Their principal concerns are likely to have been palaeontological or stratigraphical in nature, but with regard to the museum, Baker (1882: p. 373) notes that Sedgwick was impressed and commented:

> "after having seen most of the local collections in Europe, he had met with none so complete and well adapted to the purposes of the student as this".

Sedgwick was familiar with the geology of the Yorkshire coast, blaming his loss of visual acuity in later life on a chip of rock acquired while hammering at Robin Hood's Bay. He had surveyed the Magnesian Limestone between Nottinghamshire and Northumberland in the early 1820s and reported several localities for celestine around Knaresborough and Ripon (Sedgwick, 1835). This is certain to have interested Murray, and although no evidence has been uncovered in this study, it would be surprising if the two did not meet[25].

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[24] The Hull Literary and Philosophical Society opened a museum on 15 July 1823, a year after it was founded. It had an extensive and important geological collection which was destroyed by bombing on 24 June 1943. The Hull Museum had acquired the collections of Malton Museum in 1932, and a portion of these survive (Boyd, 1983; Edwards, 1984). There are no records of any donation by Peter Murray, but specimens were donated by the Scarborough Philosophical Society (Edwards, 1984).

[25] The Revd James Sedgwick (1794–1869), one of Adam Sedgwick's brothers, became Vicar at Scalby near Scarborough in 1840 (Clark and Hughes, 1890; Park, 2017). Given Murray's strong religious and geological interests they would almost certainly have been acquainted.

The same can be said of Richard Owen, who coined the term *Dinosauria* in 1842. Owen was aware that giant fossil bones had been found in the cliffs near Scarborough and made passing mention of his visit to Scarborough Museum, where they were on display (Owen, 1841). They had been recorded by William Crawford Williamson in 1837 (Whyte *et al*., 2010), but Owen gave no credit to Williamson in his publications. The same is true of dinosaur teeth from the Malton area. Whyte *et al*. (2010: p. 196) record:

> "The earliest records of dinosaurs from the Upper Jurassic 'marine formations' are teeth attributed to *Megalosaurus bucklandi* from the Coralline Oolite Formation (Oxfordian) of the Malton area ... It is probably these teeth that Owen (1841) suggested might belong to *Cetiosaurus* but, by the next year, he was referring to them as *Megalosaurus* (Owen 1842). These are the joint second record of dinosaurs from Yorkshire and the first to actually be placed within the Dinosauria".

Owen has become notorious for giving insufficient credit to fellow scientists and is described as "a most deceitful and odious man" by Freeman (2007). His first publication on the *Dinosauria* records *Megalosaurus* teeth in "private collections in the town of Malton" (Owen, 1842: p. 110), and this is repeated in a detailed account of *Megalosaurus bucklandi* (Owen, 1856: p. 26). By 1840, Murray had amassed one of the finest fossil collections in Yorkshire and was commonly consulted by visiting academics (Phillips, 1853; 1875). The collection certainly contained dinosaur material as in 1849 Murray donated:

> "a tooth of the Megalosaurus from the Malton Oolite ... not only unique as a Yorkshire Fossil, but in regard to size and the extent of fang preserved, ... the most characteristic specimen known"[26] (Yorkshire Philosophical Society, 1850: p. 9).

to the Yorkshire Philosophical Society. This remarkable specimen was recently on display in the 'Yorkshire's Jurassic World' exhibition at the Yorkshire Museum. The fact that the specimen was regarded as unique and characteristically Megalosaurid[27] at least allows for the possibility that Owen had seen it and recognised its importance on his visit to Scarborough. Apart from the short and the until now overlooked entry in the *Annual Report of the Council of the Yorkshire Philosophical Society* for 1850, it was not described in the scientific literature until 1875, more than ten years after Murray's death (Whyte *et al*., 2010).

It is of course, possible that Owen had seen the specimen (or others) in Malton, where there were important early collections (Edwards, 1983). Unfortunately the date it was acquired by Murray is not recorded.

Murray retained strong connections with the Yorkshire Philosophical Society, which had established itself as one of the country's leading provincial institutions by the early 1840s. In 1847 "remarkable donations to the Geological collection" included "the remains of Gyrosteus mirabilis *Agassiz*, (a gigantic osseous fish) from the Lias of Whitby, presented by Dr. Murray, of Scarborough" (Yorkshire Philosophical Society, 1848: p. 11).

In the same year, William Bean, a friend and fellow collector who must have known of Murray's early interest in zoophytes, named a newly discovered fan bryozoan *Flustra murrayana* after "Dr. Murray, a scientific and zealous naturalist of Scarborough" (Bean in Johnston, 1847: p. 347). As with the fossil plants, the genus *Flustra* has been revised. In a re-evaluation of the cheilostomatous bryozoa, Levinsen (1909) created the genus *Dendrobeania*. The name *Dendrobeania murrayana* (Johnston, 1847) honours both William Bean and Peter Murray. *Dendrobeania* remains in current use (Bock and Gordon, 2018), and currently includes about thirty-five species of bryozoa.

Murray's aunt, Elizabeth Wilmer, died at the grand old age of 94 on 24 February 1849. The loss had a profound impact (Balgarnie, 1864) and seems to have increased his devotion to the church. His philanthropic endeavours continued and despite advancing years he was one of the physicians who (along with Robert Balgarnie) helped to set up the free Scarborough Dispensary in Vernon Place in 1851. A plaster bust (Fig. 11), in the collection of Scarborough Museum may date from about this time.

The breadth of Murray's interests is shown by the fact that (among many other positions) he was President of the Scarborough Archaeological Society at the time of his aunt's death (Hull Packet, 1849). In the summer of that year he took an extended continental tour, which provided material for a lecture entitled "Scenes and Impressions in a Tour on the Continent". Two years later he made an archaeological tour of Ireland and shortly thereafter:

> "A meeting of the members of the Scarborough Archaeological Society took place on Tuesday evening at the residence of the president, Dr. Murray. ... Dr. Murray gave a very interesting and graphic account of his observations during a recent tour through Ireland, commenting on the antiquities and traditions of various localities in the true spirit of an archaeologist" (Hull Packet, 1851).

The involvement with the Archaeological Society was providential. The Philosophical Society found itself in more-than-usual financial difficulty in the late 1840s and early 1850s (no reports being printed in the years 1847 or 1848). The Rotunda Museum was on a precarious financial footing, and the ambitions of members

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[26] The Malton Oolite is an ooidal limestone of Oxfordian age (Jurassic) which is locally present in the Coralline Oolite Formation to the west of the Malton.

[27] The tooth is currently regarded as being from a theropod dinosaur, but its precise phylogeny is uncertain.

Figure 11. A plaster bust of Peter Murray in the collections of Scarborough Museum. According to the *Biographical Dictionary of Sculptors in Britain* (Roscoe *et al*., 2018), the bust is by Joseph Theakston (1772–1842); however there may be some confusion about the date as the same work notes that it was made in 1851, nine years after Theakston's death.

frequently outstripped pecuniary resources[28]. Mr Micawber, who arrived in the national consciousness at about this time, would have been familiar with the situation!

Murray was keen that the museum should prosper, and a merger between the Scarborough Philosophical Society and the Scarborough Archæological Society was proposed as a way to increase income and spread costs. The Philosophical Society effectively absorbed the Archæological Society in 1854, and the first publication of the joint body, the *Twenty-Third Report of the Scarborough Philosophical and Archæological Society*, appeared in 1855.

There was a strong desire from members of both societies for proper scientific meetings, at which papers could be given and recorded in print (Scarborough Philosophical Society, 1854); in this Murray played a pivotal role:

> "In conclusion your Committee are glad to state that what had been so long a matter of complaint in their reports, is this year to some extent removed. For this the Society is much indebted to the energy and talents of their Vice-President, Dr. Murray, under whose auspices the scientific meetings of the Society have been renewed, and to whom they are indebted for two valuable papers, which have been published among the Society's transactions. They trust that the meetings commenced with so much promise will not be suffered to decline, but the Committee would remind the members that they cannot unaided sustain the scientific character of the Society, and they beg that the talents, as well us the money of the various members may not be withheld in their efforts to place the Scarborough Philosophical and Archæological Society in that position amongst similar institutions which it must be the wish of all to see it occupy".

The valuable papers noted in the foregoing paragraph (Murray, 1853a,b), are incorporated into the *Twenty-Third Report of the Scarborough Philosophical and Archæological Society* (1855) under the title *Proceedings of the Scarborough Philosophical and Archæological Society*. They demonstrate Murray's interest in marine biology. The first includes a description of a rare bramble shark, *Echinorhinus brucus*, which was caught near Scarborough and appears to be the largest recorded example of the species. The second describes an unusual species of octopus found on the shore near Filey.

The scientific meetings continued for some years and, on 28 March 1854, Murray contributed an account of 'The Minerals of Scarborough'. He noted the occurrence of aragonite at Pudding Hole[29], at the southeast end of Gristhorpe Cliff, described gypsum from several localities in the neighbourhood of Scarborough, and commented on the rare mineral scarbroite.

The aragonite specimens are described as encrustations in fissures in calcareous sandstone. Murray was interested in why aragonite rather than the more common polymorph calcite had formed, and reported some chemical analyses which he had made at the request of John Phillips:

> "Now, as both are carbonates of lime, (of calcium, if we must employ learned names), what is the cause of such a difference in crystalization [*sic*]. It has been supposed to depend on a small quantity of strontia being often present; but this cannot be the case, for that earth is not an invariable constituent, as

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[28] Significant interest was charged on debts incurred in the early years. In the late 1840s the annual salary of the Museum Keeper, John Williamson, which had been set at a meagre £30 for many years, was reduced to £20 (Scarborough Philosophical Society, 1849; 1850). In this context it is worthwhile recording that the average annual earnings in the UK were £32.69, £34.15 and £36.10 in 1830, 1840 and 1850, respectively (Clark, 2011).

[29] Pudding Hole is marked at about TA 0955 8348 on the beach below Gristhorpe Cliff on the first series six-inch map (Ordnance Survey, 1854), but in a slightly different position in more modern versions.

> is the case with our Scarborough specimen, for several years ago Professor Phillips wished me to test it for strontia, in consequence of my discoveries and analyses of the lovely Yorkshire strontianites from Pately [*sic*], and the celestines from Knaresborough, but I did not discover any in the Pudding Hole Arragonite [*sic*]—merely carbonic acid, lime, and water".

Modern thermodynamic studies show that aragonite is metastable with respect to calcite in all normal conditions, but the difference between the free energies of formation of the two minerals is small. Early precipitation of strontianite can produce nuclei around which aragonite crystallises. As Murray's analyses did not reveal any strontium it is more likely that Mg^{2+} ions in solution, which inhibit the nucleation of calcite, allowed the ion activity product to increase sufficiently for aragonite to form (White and Culver, 2012). The description also confirms that early claims of strontium minerals from the cliffs at Gristhorpe in Young and Bird (1828) are not based on analyses by Murray.

After a discussion of worldwide occurrences of aragonite and its use in carvings, Murray went on to describe local occurrences of gypsum:

> "This brief notice of modern alabaster naturally leads me to the transparent crystallized sulphate of lime—SELENITE, or Sparry Gypsum—called by the older naturalists, *Glacies Mar, Lapis Specularis*, from its divisibility into extremely thin laminæ, so thin as to have been employed by the Ancients for giving light, or for shewing objects as in bee-hives, which were sometimes made partly of thin Selenite that the insects might be seen at their work. So, if we pass on from Pudding Hole, along the splendid bay of Gristhorpe, to its northern end, we come to a rough insulated rock, where, among the loose shingly shell, very small and delicate but well-formed prisms of Selenite occur, as they do plentifully among the Oxford clay, and behind our Castle, and among the Speeton clay, and which are of every day formation, by the decomposition of sulphuret of iron or pyrites, where the sulphuric acid, generated by the oxygen and water, seizes on the lime so abundantly offered, and rapidly crystalizes [*sic*] in these little transparent prisms. And, again, by a never-ending decomposition and reproduction, we see the pyrites themselves, after, in some places, giving rise to new forms and combinations, becoming produced by the disintegration of clay iron-stone of our great oolite, or lias, etc. By the action of water, especially sea water, a superabundance of sulphuric acid combining with the oxide or carbonate of iron forms sulphate of iron, and that in turn changes into a sulphuret; and, in the water or debris of the alum shale, we often detect a very impure sulphate of alum or clay, not the alum of commerce".

This text illustrates Murray's knowledge of chemistry and the role played by pyrite in the formation of ephemeral species such as gypsum and melanterite.

The final part of the article describes scarbroite, a mineral that excited the attention of collectors because of its rarity:

> "SCARBROITE, so very interesting to all collectors, especially from its limited locality, which is chiefly in the interstices of our great oolite in its various strata, particularly on this side of the White Nab, and also in the clay iron-stones Nodules, at the celebrated plant-bed at Redcliff, I strongly suspect is another instance of the very recent if not continual production of a mineral. Be this as it may, Scarbroite was first determined to be a separate mineral by the Revd W. J. Harcourt, and is composed of Alumina and Silex. As I said before, Scarbroite is most acceptable to all collectors, and particularly so to foreigners. A valuable correspondent and liberal contributor to my cabinet, Mr. Markoe, of Washington, who holds so important a station in the United States, and was one of the leading founders of their National Institute (of which I have the honour of being an honorary member), requested me to send him as many specimens as possible of Scarbroite, as peculiarly welcome additions to the collections of his scientific friends in the United States. By-the-bye, any gentleman who unluckily cannot find the Scarbroite, or who has not time to spare for the search, may be supplied to order, with pieces of any size, *fresh made*, by certain clever dealers at Whitby, though probably, they will not find these specimens to agree with the analysis of Mr. Harcourt—being, as I understand, mainly composed of Spanish White."

The bluntness of the final sentence shows Murray's attitude to falsification. The truth was important! There is some disagreement about the composition, but most references describe 'Spanish White' as a generic term for a pigment based on chalk with the addition of small quantities of more expensive pigments (with higher refractive indices) to increase its whiteness (Eastaugh *et al.*, 2008). Analyses by X-ray diffraction would readily distinguish it from scarbroite.

The assertion that scarbroite is a relatively recent mineral fits with modern interpretations (King, 1982), but the claim that it occurs in clay-ironstone nodules (where the white mineral is usually either kaolinite or dickite) is mistaken as is the assumption (common to many other nineteenth-century texts) that scarbroite is an aluminium silicate (see Fig. 7).

The final part of the discussion shows that Murray assembled some of his collection by exchange. Francis Markoe Jr (1801–1871/2) of Washington DC was one of the most important collectors in the United States in the middle of the nineteenth century (Canfield, 1923), and would have been a valuable correspondent. Murray and Markoe may have been put in contact by George W. Featherstonhaugh (1780–1866), a British-American geologist and geographer who grew up in Scarborough and was in regular contact with the Scarborough Philosophical Society.

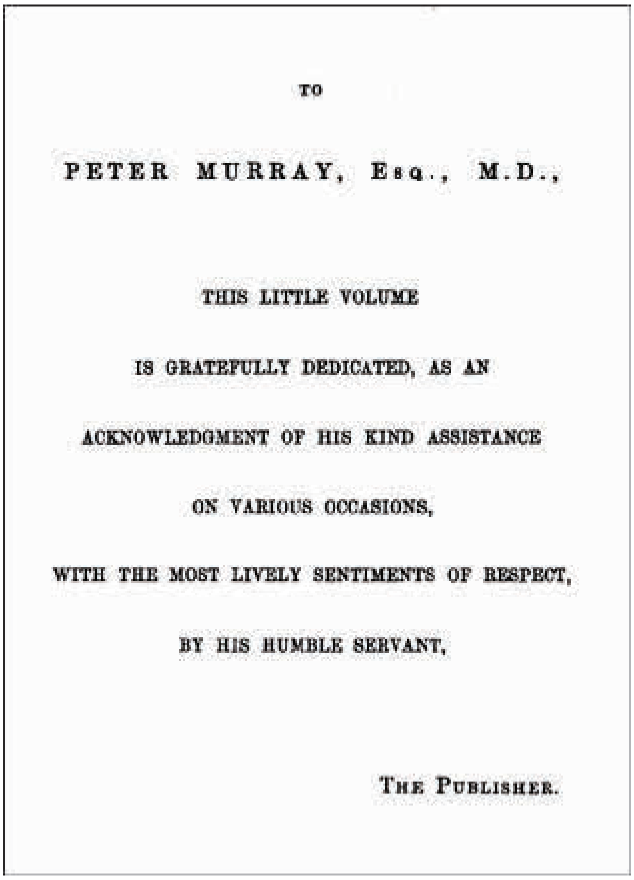
In the autumn of his life Murray's habit of walking remained. Indeed it was to this, and to God, that he attributed his health and vitality. Robert Balgarnie (1864: p. 109) records that he collected "Flowers in the woods, fossils in quarries, minerals in the cliffs, pebbles by the sea shore [and that] all these objects afforded him real enjoyment". He also notes that: "On his return from his walks he dined. No visitors were admitted after five o'clock. Unless to preside at a public meeting, the evenings were spent either in examining his collections of coins, shells, &c., or in reading".

Murray remained Vice-President of the Scarborough Philosophical and Archæological Society until his death in 1864. He contributed funds to a sea-water aquarium which became a considerable attraction at the Rotunda Museum and helped secure its financial future.

In 1859, he was honoured by a portrait (Fig. 12). The cost of £50, which was raised by public subscription, provides an indication of his standing. The painting was presented by Sir J. V. B. Johnstone [President of the Scarborough Philosophical Society for many years and one of the two Members of Parliament for Scarborough (Craig, 1977)] at a ceremony on 25 June 1859, and accepted by the Mayor on behalf of the town. The Town Hall, as it appeared after the ceremony, is described in the eighth edition of *Theakston's Guide to Scarborough*, (Theakston and Carter, 1860):

> "A portrait of George III., painted by Stewartson, is suspended over the chair; and the room is also graced by portraits of the late Mr. Bartholomew Johnson, a celebrated musician of Scarborough, who attained the age of 103 years, painted by the late J. Jackson, Esq., B.A.; and of Peter Murray, Esq., M.D., an esteemed inhabitant still resident here, painted by Mr. Crighton".

Figure 12. Portrait of Peter Murray by Hugh Ford Crighton (1824–1886). Reproduced by courtesy of Scarborough Museum Trust.



TO

PETER MURRAY, Esq., M.D.,

THIS LITTLE VOLUME

IS GRATEFULLY DEDICATED, AS AN

ACKNOWLEDGMENT OF HIS KIND ASSISTANCE

ON VARIOUS OCCASIONS,

WITH THE MOST LIVELY SENTIMENTS OF RESPECT,

BY HIS HUMBLE SERVANT,

THE PUBLISHER.

Figure 13. The dedication to Peter Murray in the introduction to the eighth edition of *Theakston's Guide to Scarborough* (Theakston and Carter, 1860).

It is worthwhile making a diversion into *Theakston's Guides to Scarborough*, which were extremely popular and ran through numerous editions in the mid nineteenth century, as Murray almost certainly had an involvement in the text (Fig. 13). Few modern guides compare to Theakston's publications in the breadth of their ambition. The various editions squarely target 'Renaissance Man' and have the improving qualities that characterise the Victorian period. Every aspect of the local area that might interest the educated visitor is described (Fig. 14).

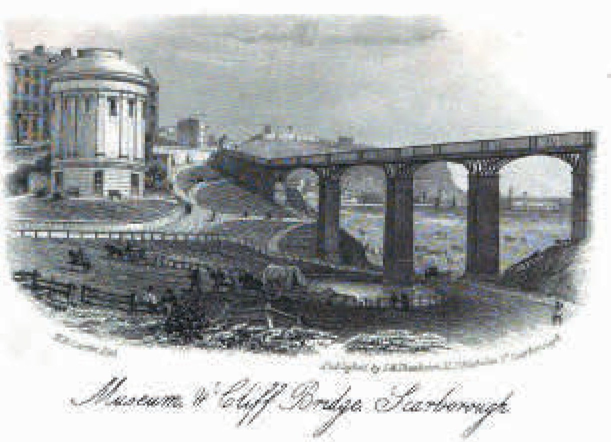


Figure 14. An illustration of the iconic Rotunda Museum in Scarborough by the artist Henry Barlow Carter (1804–1868) taken from the eighth edition of *Theakston's Guide to Scarborough*.

In total, ten pages of the guide are given over to the local geology: with notes on fossils, rocks and minerals. Parts of that text have strong similarities to Murray's previous geological papers (Murray, 1828; 1854) and the section on minerals has been copied almost verbatim (Theakston and Carter, 1860: pp. 129–131). Murray must have had a hand in the text, which begins with a description of pebbles from local boulder clay:

> "The diluvium, which overspreads all these strata, offers a source whence a collection of minerals, surprising in extent and variety, might be readily obtained, the products of the primitive and transition rocks of the north of England, or south of Scotland, brought here in rolled pieces, by some mighty inundation, flowing apparently from north-east to south-west. We may enumerate several kinds of granite, especially that from Shapfell, in Cumberland, so well known by its large crystals of red felspar; and another equally marked by the size of the mica; also a dark coloured gneiss, containing garnets; mica slate, likewise with garnets; a pale-red syenite clay, and hornstone porphyry; compact felspar; adularia, in small crystals, in a granite; chatoyane [*sic*] felspar, chiefly reflecting the blue rays; dialtage [*sic*] rock; chlorite slate; greywacke; serpentine from Portsoy, in Banffshire; schorl rock; quartz rock; amethystine quartz; olivine, in trap or amygdaloid; galena, in metalliferous limestone; the nodular radiated magnesian limestone of Sunderland; acicular stilbite, in amygdaloidal greenstone; epidote; and *one* instance of heulandite; beautiful specimens of compact radiated green prehnite, strangely here called beryl, are sometimes found in rolled pieces; as are also mica, black and white hornblende, massive or disseminated; agates, either veined or dendritic; and often, particularly the green, mochas, of very great beauty; along with many varieties of hornstone, red jasper, and heliotrope".

This extends the observations Murray published in 1828 and is of topographic interest even today as it reports minerals such as heulandite, prehnite and stilbite which are rare and little known in Yorkshire.

The next paragraph records:

> "On the north sands, immediately beyond the first brook, black magnetic iron-sand occurs plentifully, containing titanium, and probably nickel, and of which the origin is singularly obscure. The ferruginous particles are easily separable from the common sand, by means of an ordinary loadstone [*sic*]. Masses of calcareous spar are found in the Kelloways formation, behind the castle; also gypsum, in most minute and delicate prisms. Calcareous sinter is also seen abundantly, lining fissures in the limestone rocks, along the coast; and in some places as at Claughton, accompanied with *calc tufa*, prettily arborized, or with arragonite [*sic*], in thin mammillated veins, as in the calcareous grit, at Newbegin Wyke [now Newbiggin Wyke]".

The magnetic material is clearly magnetite, and the presence of titanium in the black sand suggests the common detrital mineral ilmenite. The incorrect spelling of aragonite (cf. Murray, 1854) adds further evidence that Murray was the author.

No account of the local minerals could fail to mention scarbroite:

> "An interesting mineral, named by the Revd Canon Harcourt, "Scarbroite," occurs in the fissures of the grey shelly limestone of the lower oolitic series, at the White Nab. It is a hydrosilicate of alumina; and, from its locale, is much prized by foreign collectors. It is nearly allied to the rare allophane, recently detected by Mr. Morris, of Kensington, in the chalk at Charlton, in Kent".

Although Murray did not quite make the connection, his note of the discovery of allophane in Kent and its similarity to scarbroite is more than coincidental. The erroneous description of scarbroite as a 'hydrosilicate' in nineteenth-century texts is almost certainly due to admixed allophane, which is now known to be common at the type locality (Ryback, 1988). The Mr Morris in the text is Prof. John Morris (1810–1886) who had reported the first British occurrence of allophane three years earlier (Morris, 1857); he was well known in Scarborough due to his interest in the fossils of the Yorkshire Coast.

The guide goes on to reprise the comments made by Murray in 1854 about local occurrences of gypsum and makes specific mention of the formation of 'green vitriol', the mineral melanterite, during the natural oxidation of pyrite:

> "Gypsum, or sulphate of lime, is one of those minerals which are forming every day before our eyes, as in the aluminous shale, when it is continually deposited, in thin prisms, from the decomposition of the pyritous limestone; the sulphuric acid being yielded by the sulphuret of iron. In the same way, at many places along the beach, the sulphate of iron, or green vitriol, is generated by the decomposed pyrites, and hence some light may be thrown upon the productions of our chalybeate springs".

Two final paragraphs summarise the iron-bearing minerals found in the local area, and include a mention of the unusual geodes known as eagle-stones or aetites:

> "Septaria of argillaceous ironstone abounds in irregularly disposed layers in the lias, and are scattered everywhere along the sands; when broken, they present either some organic relics, or are divided, as their name implies, into numberless septa, usually filled up with calcareous spar, iron glance, or semi-liquid bitumen".
>
> "Connected with these, is the *ætites*, or eagle-stone, sometimes rounded, at others multiangular, and containing a nucleus, occasionally so detached as to rattle, when the stone, which is argillaceous iron, is shaken. Clay ironstone occurs in extensive beds, also in the inferior oolite formation, as for instance, just beyond the Spa, the nodular kidney-shaped hæmatite is very common. Iron pyrites, either massive or cock's-comb, or radiated, is found in detached pieces, or accompanying most of the stratifications".

In addition to its mineralogical observations, the eighth edition of *Theakston's Guide* contains a palaeontological conundrum: it notes a fossil starfish "*Ophuira Murrayana*", presumably named for Murray, from Jurassic marl near the town (Theakston and Carter, 1860: p. 127). Of this species there is not a single further record.

The affection in which Murray was held at the end of his life is underscored by the fact that the way-fare connecting Londesborough and Westover roads was named Murray Street in 1861. He was one of very few Scarborough residents to be honoured by a street name during his lifetime.

In 1863, Murray donated four celestine specimens from the area around Knaresborough; and two specimens of strontianite, and a calcite on galena and baryte from Merryfield Mine near Pateley Bridge, to the British Museum. They appear to have been among the finest pieces in his collection (Figs 15 and 16). By this time his health was deteriorating, but his scientific interest remained. He was involved in the cleaning and re-display of the mineral collection, which was inspected by Prof. John Morris in that year (Scarborough Philosophical and Archæological Society, 1864):

> "The Mineralogical cases have been cleaned, and the specimens re-arranged,—the thanks of the Society being especially due to Prof. Morris, of London, for kindly inspecting and correcting their classification".

It may be that Morris took Murray's donation to the British Museum and brought the last recorded donation which involved Murray to the Rotunda Museum. This was from "W.T. Waller, Greenwich through Dr. Murray" and included a "Piece of Black Jack" (*Scarborough Philosophical and Archæological Society*, 1864).

Murray died within a month of his eighty-second birthday on 27 February 1864 and was laid to rest in the eastern portion of Scarborough Cemetery (now Dean Road and Manor Road Cemetery) on 5 March of that year. The inscription on a simple gravestone reads:

Figure 15. Strontianite on cockscomb baryte from Merryfield Mine near Pateley Bridge, North Yorkshire. Specimen BM 35334 in the collection of the Natural History Museum, London. The label indicates that it was one of the specimens Murray donated in 1863, shortly before his death. Photo © Trustees of the Natural History Museum.

Figure 16. Celestine from Bilton on the banks of the River Nidd near Knaresborough. Specimen BM 35336 in the collection of the Natural History Museum, London An associated label indicates that it was one of the pieces Murray donated shortly before his death in 1863. Photo © Trustees of the Natural History Museum.

IN MEMORY OF

PETER MURRAY, M. D.

WHO DIED FEBRUARY 27TH

1864

AGED 81 YEARS.

Murray's will was proved at the District Registry attached to Her Majesty's Court of Probate at York on 7 June 1864. The executors were William Collins of Knaresborough, William Edward Woodall of Scarborough and Frederick Elliston (also known as Elstone) who lived in Middlesex. Murray's effects are listed as under £2,000, most of which were divided between his servants. The principal beneficiary was Peter Hawkridge. An obituary was included in the *Yorkshire Gazette* for 5 March 1864, but Murray's scientific achievements only merit two sentences:

> "In his connection with the Scarbro' Philosophical Society, Dr. Murray has been well known for many years, to the lovers of natural science both at home and abroad. In the departments, especially of geology and botany, his attainments vere [*sic*] considerable, and he has, at various times, been the entertainer or the guest of many of our distinguished savans [*sic*]."

Of his scientific accomplishments, Balgarnie (1864: p. 139) records:

> "*As a Man of Science*, he could not be regarded as original or profound, but his knowledge was extensive, well arranged, and exact. In a letter recently received from the eminent naturalist, Mr. Waterton[30], he says, "Dr. Murray was an amiable gentleman, a sound philosopher, and a valuable friend; thousands now living can bear testimony to this." In former years he was a contributor to various medical and scientific journals. Abundant evidence is supplied in the foregoing pages of his scientific

> attainments, and yet so great was his humility, that however uninformed his friends might be, he always seemed to place himself in the position of a learner rather than of a teacher".

The record in the *Thirty-Third Report of the Scarborough Philosophical & Archæological Society* (1865: pp. 7–8) is surprisingly brief:

> "Your Committee have to mention with deep regret the removal, by death, of a number of the most influential members, among others, the venerable Dr. Murray, whose close connection with the Society from its commencement, and continued and liberal support both pecuniary and as a donor of many valuable objects of interest in most of the departments of Natural Science, have rendered his removal a serious misfortune to the well-being of the institution".

The collections that Murray assembled over a long and eventful life are hardly mentioned. The *Annual Report of the Council of the Yorkshire Philosophical Society* is also brief (Yorkshire Philosophical Society, 1865: pp. 14–15):

> "In 1864 the Society has again lost one of those Honorary Members whose connection with it dates back almost to the period of its foundation, in the person of Dr. Peter Murray, of Scarborough. Dr. Murray was well known as a collector of fossils, and was a liberal donor to the Geological Collection of the Museum during the earlier years of its existence",

but at least records that Murray was a collector.

DISCUSSION

Peter Murray appears to have been a man of great integrity. His wide circle of friends included some of the great scientific minds of the early nineteenth century. He made extensive donations to public museums, was an excellent lecturer, an active member of many scientific societies[31] and is regularly mentioned in contemporary newspapers. He was honoured for his contributions to life in Knaresborough (where friends paid for a handsome Silver Tureen, Ladle, and Salver to mark his retirement) and Scarborough (where a portrait and bust were commissioned). A number of exceptional fossil and mineral specimens have been located in this study, and many more must lie undiscovered in museum drawers. Why then is he so little known? Unlike many of his contemporaries he has (as of mid-2022) no entry in either the *Oxford Dictionary of National Biography*, or that more modern barometer of celebrity *Wikipedia*.

Most of Murray's scientific observations are recorded in obscure publications. He appears to have shunned the limelight. In later years he almost certainly acted as ghost-writer for the geological content of Theakston's popular guides but only received roundabout credit in the dedication (see Fig. 13). His most important mineralogical discoveries, celestine and strontianite from Yorkshire, are noted without attribution in the *Manual of the Mineralogy of Great Britain and Ireland* (Greg and Lettsom, 1858) the key nineteenth century guide to British topographic mineralogy. His biography and obituaries play down his scientific achievements and despite a long involvement in many local societies, historical accounts of Scarborough (e.g. Baker, 1882; Binns, 2001) and Knaresborough (e.g. Calvert, 1844) barely mention him.

Despite his numerous donations Murray has also been forgotten as a collector: there is no mention of him among the nineteenth-century mineral collectors noted by Peter Embrey in his foreword to the 1977 reprint of *Manual of the Mineralogy of Great Britain and Ireland* or, indeed, in any biographical work on British mineral collectors of which the authors are aware. This pattern extends into other areas of natural history. He was the first person to report the examination of plant fossils by transmitted light under an optical microscope (Murray, 1828), but credit is usually given to the later work of Lindley and Hutton. The bramble shark caught off Scarborough (Murray, 1853a), is the largest and heaviest example of the species on record, but has been missed by subsequent researchers (e.g. Shark Trust, 2010). The plant fossil *Solenites murrayana* has been renamed, and the fossil brittle star *Ophiura murrayana* vanished without trace. His collections included a theropod tooth which is perhaps the most important dinosaur fossil ever collected in Yorkshire, but despite a label which records that it was presented to the Yorkshire Museum by Dr Murray, he does not figure in any historical account of the Dinosauria.

It may be that the breadth of his interests, which encompassed almost every field of scientific endeavour from archaeology to zoology, diluted his contributions. The evangelical character of his biography which downplays his scientific accomplishments is another factor. The celebrity of some of his contemporaries has probably also had an adverse effect. Important and interesting figures vie for the attention of scientific historians in nineteenth-century Scarborough: the most notable is William Smith, the 'Father of English Geology', and the list also includes William Bean, John Cole, Thomas Hinderwell, Frederick Kendall, John Leckenby, John Phillips and John and William Williamson. In this company Peter Murray has been overlooked. The evidence assembled here shows that he was a capable analyst who was able to support his mineralogical discoveries with quantitative chemical data and that his fossil and mineral collections included material of exceptional quality. This last point begs questions about the current disposition of his specimens.

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[30] Charles Waterton (1782–1865) was an eccentric environmentalist and explorer who lived at Walton Hall near Wakefield, West Yorkshire.

[31] Balgarnie notes that he subscribed to 37 different societies and many of these were scientific in nature.

Collection

Murray made numerous donations to public institutions during his lifetime. Most of his mineralogical donations feature strontium minerals from Yorkshire, but the diversity of his collection can be extrapolated from the specimens he gave to the Rotunda Museum over many years and to Durham University in 1834 (listed in the Appendix). They include a considerable number of unusual species from a wide range of locations. Records summarised in the foregoing text show that he also presented mineral specimens to the British Museum [now the Natural History Museum (NHM), London]; the Geological Society (whose collection was transferred to the NHM in 1911); the Yorkshire Philosophical Society (whose collection now forms part of the Yorkshire Museum in York) and the Newcastle Literary and Philosophical Society. These known records almost certainly underestimate his true contribution.

The British Museum acquired Murray's finest strontianite and celestine specimens shortly before his death (see Figs 15 and 16). Together with a mislabelled scarbroite and a very early celestine from the Geological Society's cabinet (see Fig. 4), these are the only minerals that have been traced with absolute certainty to Murray in this study. The quality of the strontianite from Merryfield Mine can be judged by the fact that one of the specimens is among the handful chosen to represent the minerals of the Yorkshire Pennines in *Minerals of Northern England* (Symes and Young, 2008: p. 174). A celestine specimen from Bilton near Knaresborough (BM 35337), has a descriptive label in a rather scruffy cursive script (Fig. 17). A second well crystallised blue celestine (BM 35336) has a similar label which records that it supplied the material for one of the analyses published by Murray in 1825. The specimen from Scotton Moor which Murray donated to the British Museum was exchanged with the US National Museum in 1890.

The labels with material at the NHM (see Fig. 17) are of value in assessing specimens in other collections. Scarborough Museum has a celestine specimen with a faded paper label that indicates it is from "Scotton Moor, Knasbro'" (see Fig. 10). The specimen label has the number 201, suggesting that it was part of a larger collection, and the cursive script has some stylistic similarities to the handwriting on Murray's labels at the NHM. It is almost certain to be from Murray, as he is the only recorded donor of celestine from Knaresborough to the Rotunda Museum (Scarborough Philosophical Society, 1830–1864). Scarborough Museum also has three unlocated strontianite specimens which are undoubtedly from Merryfield Mine near Pateley Bridge. They are very similar in appearance and paragenesis to the specimens that Murray donated to the British Museum in 1863 and also seem likely to be part of his legacy.

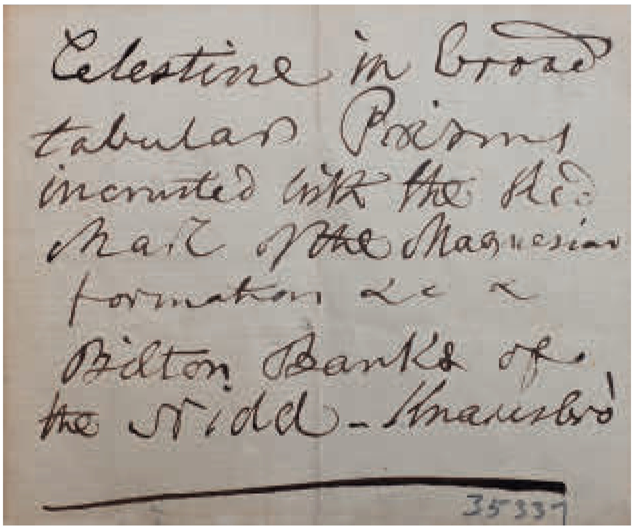
Celestine in broad
tabular Prisms
incrusted with the Red
Marl of the Magnesian
formation &c &
Bilton Banks of
the Nidd - Knaresbro'
35337

Figure 17. A descriptive label in Murray's rather scruffy and varied cursive script describing celestine from Bilton on the south bank of the River Nidd near Knaresborough. Specimen BM 35337 in the collection of the Natural History Museum, London. Photo © Trustees of the Natural History Museum.

There are a number of Merryfield strontianite specimens in the collection of the Yorkshire Museum (see Figs 5 and 6), some of which are certain to have come from Murray given his numerous recorded donations, but time has eroded the associated data. Mineralogy was popular in early nineteenth century Yorkshire and Merryfield specimens were also donated by John Bland, William Danby (1752–1833), John Phillips (1800–1874), Mrs Roddam and William West (1792–1851). A similar analysis applies to the Knaresborough celestine specimens which Murray donated to the museum, which cannot be traced with certainty.

The question of what happened to the residual specimens after Murray's death remains. In his will, Murray bequeathed most of his worldly goods, including his 'fossils', to his butler Peter Hawkridge. Hawkridge had contributed a number of zoological specimens (mostly bird skins) to the Rotunda Museum in the early years and is thanked in the *First Report of the Scarborough Philosophical Society* (1830) for geological specimens. A joint donation with John Williamson of "Specimens of Arragonite [*sic*], found to the south of Gristhorpe Bay" (Scarborough Philosophical Society, 1836) shows he had a passing interest in minerals.

A short note in the 'collections and information lost and found' section of the *Newsletter of the Geological Curators' Group* suggests that some of Murray's specimens were sold to the Museum of Victoria in Melbourne, Australia by the dealer Robert Damon[32] (Torrens, 1977). It is not known whether the sale included minerals but, if so, none are recorded in the museum database (Dermot Henry, *personal communication*, 2018).

A contemporary account of local collections (Phillips, 1875: pp. 193–194) records:

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[32] Robert Damon (1815–1889) lived in Weymouth, Dorset and was an important and active dealer in minerals and fossils from 1851 until 1888 (Cooper, 2006: pp. 114–117).

> "Formerly the fine and well arranged cabinets of Mr. Bean and Mr. Williamson and Dr. Murray were freely open for study; but of those collections only one remains on the coast (in the Scarborough Museum), the others must be looked for divided among distant localities. Mr. Leckenby, indeed, in a considerable degree remedied this unfortunate dispersion by wisely and liberally amassing a splendid series of selected specimens, including many of those which belonged to Mr. Bean and Dr. Murray; and these have now found an honoured residence in the Geological Museum of Cambridge".

This suggests that Hawkridge passed the best of Murray's remaining geological specimens to John Leckenby. Leckenby (1814–1877), who moved to Scarborough in 1837, was a collector and naturalist (e.g. Leckenby, 1864). He had amassed a fine collection by the early 1850s when Phillips (1853: p. 127) notes:

> "Among private cabinets on the coast we may signalize [*sic*] Mr. Bean's, rich in all branches of marine zoology and palaeontology. Dr. Murray and Mr. Leckenby at Scarborough and Mr. Ripley at Whitby, are liberal possessors of many choice things".

Fossils which had been part of Murray's collection definitely found their way to Cambridge University in the Leckenby Collection, which it purchased in 1871 (Clark and Hughes, 1890; Woods, 1891; Shipley, 1913). There are no definite records that any of Murray's minerals arrived with the fossils, but celestine specimens now preserved at the Sedgwick Museum, are likely to have belonged to him. Three specimens are listed in volume five of an early accession register (p. 241), which describes phosphates and sulphates:

> "[36]6 A mass of fibrous celestine from the magnesian limestone Scotton Moor near Knaresborough
> [36]7 A mass of white-granular celestine in magnesian limestone Scotton Moor
> [36]8 Crystalline celestine from the Red Marl on the south bank of the Nidd Knaresborough".

Two are illustrated with their labels in Figures 18 and 19. Although Murray's handwriting (as an old man) on his labels at the NHM (see Fig. 17) is rather scruffy and variable, there are similarities with the labels at the Sedgwick Museum.

A note in the *Newsletter of the Geological Curators' Group* suggests that in 1885 some geological material remained in the possession of Mrs Mary Hawkridge (1809–1896) (Pyrah in Torrens, 1978). Although this is possible, no further evidence has emerged in this study. Mary Hawkridge was the widow of Peter Hawkridge (1805–1882), she was descended from the Bean family [her mother was Mary Bean (1779–1846)] and was related to Murray's friend William Bean. Mary married Peter Hawkridge in 1864 shortly after Murray's death and the couple moved to Stourton Villa. Peter Hawkridge died there on 12 November 1882, but no mention is made of a collection or any other specific item in his will, which was proved at the York Probate Registry on 31 January 1883. It simply records that his wife should inherit all of his possessions. It seems probable that Peter Hawkridge disposed of most of Murray's geological specimens after

Figure 18. Celestine from Scotton Moor, Knaresborough, a locality which has a strong association with Murray [*vide infra*], in the collection of the Sedgwick Museum, University of Cambridge. The formation of the letters, for example the letter S is similar to labels in Murray's hand at the NHM (see Fig. 17). Photo Peter Briscoe.

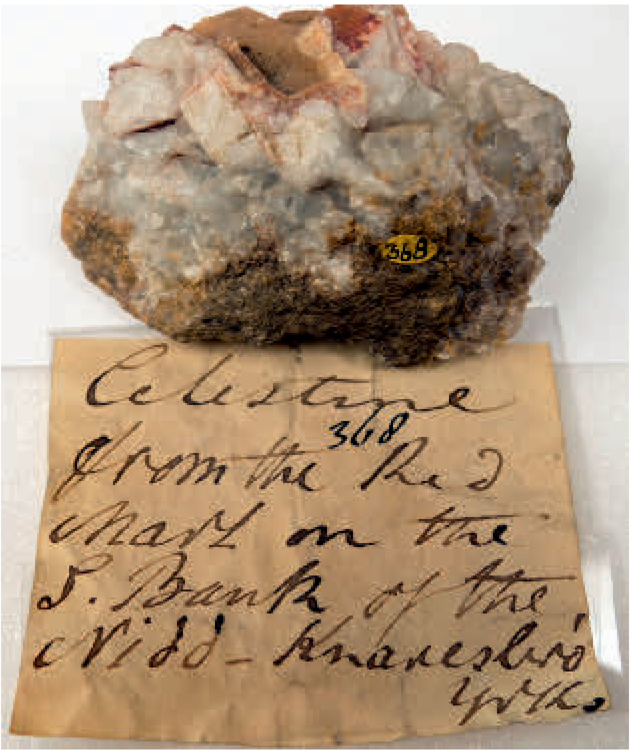

Figure 19. Celestine from the Red Marl on south bank of the River Nidd at Knaresborough, a locality which has a strong association with Murray [*vide infra*], in the collection of the Sedgwick Museum, University of Cambridge. The formation of the letters and words in 'Red Marl' for example is very similar to labels in Murray's hand at the NHM (see Fig. 17). Photo Peter Briscoe.

his death, some specimens passing to John Leckenby others being sold by Robert Damon. Mary Hawkridge died on 14 December 1896 and her will was proved at York on 15 February 1897, but it contains no reference to minerals.

Given Murray's generosity, the specimens identified in this study almost certainly underestimate his contribution to institutional collections. Further specimens must lie hidden in museum drawers, but poor curation in the nineteenth and early twentieth centuries has resulted in almost complete information loss. Old specimens of strontianite from Merryfield Mine, celestine from Knaresborough and scarbroite from Scarborough in museum collections should be checked carefully. There is, for example, a specimen of strontianite from Merryfield Mine in Bristol Museum which was donated by 'Dr M." (Tom Cotterell, *personal communication*, 2019). This may well refer to Murray.

It is perhaps worthwhile reflecting that there is no guarantee that any collection, even one of considerable merit, will survive much beyond the lifespan of its owner. None of the fine mineral collections that were assembled in nineteenth-century Yorkshire has survived intact to the present day.

Mineral Localities

In a mineralogical account such as this it is worthwhile examining how the early localities and the specimens they produced compare with later British discoveries. Three important locations emerge in this study: Merryfield Mine near Pateley Bridge (for strontianite); the Permian rocks around Knaresborough (for celestine); and the shore and cliffs around White Nab near Scarborough (for scarbroite). A discussion of these localities in the context of two further centuries of research and exploration allow a retrospective evaluation of Murray's contributions to mineralogy.

The easiest of these is strontianite. In their description of Murray's specimen from Merryfield Mine, Symes and Young (2008: p. 174) note: "Strontianite is known from several mines in the Askrigg Pennines, though specimens of this quality are rare". Few fine specimens of any kind survive from the heyday of lead mining in Yorkshire. Representative strontianite specimens (including one of a pale green colour) have been found on mine dumps in Ashfoldside Beck, near Pateley Bridge (Mike Wood, *personal communication*, 1993), but they do not compare to the large well crystallised examples that were obtained while the deposits were being worked. In recent years, strontianite has been reported from other localities in the Yorkshire Pennines (Young, 1987; Wood, 1993). The best are well crystallised, but Murray's Merryfield specimens set the standard. They are second only to the best from the type locality at Strontian in Argyll in the British Isles.

Murray's celestine specimens from the Permian rocks around Knaresborough include the largest crystals the authors are aware of from northern England, but do not compare with the best from localities in the area around Bristol and near Yate (Starkey, 2018). The finest specimen at the NHM (see Fig. 16), displays attractive pale blue crystals, and is described in Murray's handwriting as "remarkably large well defined Prisms very Similar to those from Mazzara in Sicily". It is certainly of regional importance.

Celestine was found at three separate localities near Knaresborough between 1811 and 1835. It is probably a residual mineral formed as a result of the dissolution of strontium-bearing calcium sulphate evaporites of the Edlington Formation. As the area is now mostly built over the specimens have some historical interest. Murray's descriptions are not sufficiently precise to locate the original sites with absolute certainty but, together with modern geological maps, they are useful in narrowing the possibilities.

In the Nidd Gorge, Carboniferous (Namurian) sandstone and shale are unconformably overlain by late Permian dolostone and marl. Celestine is restricted to the Permian strata. Dolostones of the Cadeby Formation (formerly the Lower Magnesian Limestone) form the elongated ridge on which Knaresborough is built. The overlying rocks of the Edlington Formation (formerly the Middle Permian Marls) are typically soft, red-brown, calcareous mudstones or siltstones with some residual gypsum. They overlap the Cadeby Formation to the north and west, where they rest unconformably on the Carboniferous basement. The Edlington Formation is overlain and overlapped by dolomitic limestone of the Brotherton Formation (formerly the Upper Magnesian Limestone), which also rests directly on the Carboniferous basement in places (British Geological Survey, 1987). An illustrated description of the geology, with detailed notes on almost every exposure in the Nidd Gorge is provided by Cooper (2008). It makes no mention of celestine.

Murray's first report of celestine in "magnesian limestone, resting upon the new red sandstone" on the north bank of the River Nidd (i.e. the opposite bank to Bilton; Murray, 1825), describes the rocks in which the celestine occurs:

> "This sandstone greatly varies within very narrow limits, extremely compact and hard where inclosing the strontites, and then becoming almost amygdaloidal, with nodules of quartz, on one hand; and on the other passing into a soft red marl, containing gypsum".

This rules out the Namurian sandstones which, although reddened near the unconformity, do not contain gypsum and would never be described as "new red sandstone". The only reasonable interpretation is that it refers to the Edlington Formation, and therefore that the magnesian limestone resting on the sandstone is the Brotherton Formation. The first place that this sequence is exposed in the Nidd Gorge is in a faulted block about 1 km to the southeast of the Low Bridge (British Geological Survey, 1987). The north bank of the river [in the loop between SE 356 556 and SE 361 557] seems the most likely site. This area is now occupied by private housing.

Murray also describes celestine "at Bilton .... in the new red sandstone formation" (Murray, 1825), and later in the "red Marl [at] Bilton Banks, Knaresboro'" (Scarborough Philosophical Society, 1835). This almost certainly refers to the Edlington Formation, and is probably the site noted in Baines (1822):

> "At a little distance from Knaresbro' near the river side, and almost opposite the mansion of Sir Thos. Slingsby, Bart. is a bed of Strontian earth, which is very rare, if not unique, in this kingdom".

Sir Thomas lived at Scriven Hall, a fine mansion house which was demolished in 1952 after a disastrous fire (Kellett, 1991). Rocks of the Edlington Formation lie below much of Mackintosh Park to the west of the High Bridge at Knaresborough and extend along south side of the Nidd valley along 'Bilton Banks', below Bilton Hall, directly opposite the site of Sir Thomas's mansion. The area is now a public park with few obvious exposures.

The celestine from Scotton Moor must have been discovered after the other localities in the Nidd Gorge as it is not mentioned in Murray (1825). Scotton Moor is relatively extensive and references to it in contemporary mineralogical texts and on labels are vague. The most likely site is somewhere along Scotton Banks below the site of the Iron Age settlement on Gates Hill [SE 332 580]. In a description of Knaresborough Spa (Granville, 1841: p. 93) records "veins of celestine, both blue and white, occasionally finely crystallized" at "a place just beneath the ancient encampment". This information seems likely to have come from Murray who Granville met while he lived in Scarborough. Most of the Iron Age settlement on Gates Hill has now been developed for housing and what remains of Scotton Banks is steep and densely wooded with little exposure.

Murray had a particular fondness for scarbroite, which receives honoured mention in all of his accounts of the minerals of the Scarborough area (Murray, 1828, 1854; Theakston and Carter, 1860). The cliffs near White Nab in South Bay are the type locality, which confers an added scientific importance, especially as scarbroite remains a relatively uncommon mineral (Tindle, 2008).

Murray seems to have assumed that all of the white powdery material found in fractures in the rock near the type locality were scarbroite. In this he was misled by the original chemical analyses (Vernon, 1829) which indicated that scarbroite was an aluminium silicate. Many subsequent analyses of natural material have reported significant amounts of silica (e.g. Duffin and Goodyear, 1960; King, 1982), but this is now known to be due to contamination by allophane. Modern studies show that scarbroite is a basic aluminium carbonate with a layer structure and an ideal formula $Al_5(CO_3)(OH)_{13}\cdot 5H_2O$ (CNMNC, 2022).

A number of minerals that are very similar in appearance to scarbroite occur in joints in the sandstone in the Scarborough cliffs. The late George Ryback (1936–2003) recorded basaluminite, alumohydrocalcite and allophane (Ryback, 1988). He subsequently identified para-alumohydrocalcite (by infrared spectroscopy and X-ray diffraction) on specimens collected by Richard Tayler (Richard Tayler, *personal communication*, 2018). Duffin and Goodyear (1960) reported gibbsite and small amounts of kaolinite, and they also identified a more hydrous phase, hydroscarbroite[33], following detailed structural studies of material from the type area. The mineralisation in joints in the sandstone at White Nab is much more complex than originally thought.

It is not surprising, therefore, that there was confusion among nineteenth-century collectors. The specimen which Murray donated to the British Museum in 1839 has subsequently been shown to be kaolinite, and the mineral described by Murray from the clay-ironstone nodules at Redcliff (and similar material described by Greg and Lettsom, 1858) is probably dickite (Tayler in King, 1982).

Science and Religious Belief

Murray lived in a period when there was a transition between what has been called 'scriptural geology' with interpretations that are consistent with a biblical narrative and modern empirical geology. Given his religious conviction (Balgarnie, 1864), a discussion of the relationship between faith and science is worthwhile.

Religious conviction and scientific curiosity were seen as complementary virtues during most of Murray's lifetime. An elegant and persuasive summary of the prevailing viewpoint is provided by William Paley (1743–1805) in *Natural Theology: or, Evidences of the Existence and Attributes of the Deity; Collected from the Appearances of Nature* (1802). The argument is essentially that careful study of nature can reveal God's power, wisdom and goodness; a philosophy that had a particularly strong resonance with the Protestant tradition in Britain. This appears to have been Murray's attitude as Balgarnie (1864: p. 144) notes:

> "To him, science was a handmaid of religion, and the various objects in nature were but visible symbols of an omnipresent God".

The number of clerics who occupied prominent geological positions in the early nineteenth century

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[33] Hydroscarbroite, $Al_{14}(CO_3)_3(OH)_{36}\cdot nH_2O$, was proposed as a more hydrous species as a result of detailed XRD studies of scarbroite from the type locality, some samples of which contained an unknown phase that dehydrated irreversibly in normal laboratory conditions to scarbroite (Duffin and Goodyear, 1960). Further research is required to establish hydroscarbroite as a valid mineral species (CNMNC, 2022).

(Johns, 1975) shows that geology was an appropriate activity for a man of faith. Murray's strong religious convictions do not appear to have caused an existential clash with his varied geological interests. Balgarnie's (1864: p. 69) rhetorical question: "Did religion abate his devotion to scientific pursuits?" is answered: "Every new discovery was so much tribute brought from the field of science and laid on the altar for Christ".

The beginning of what Thomas Henry Huxley and other agnostics came to characterise as the conflict between science and religion is commonly traced to 1860 and the now-famous evolutionary debate with Bishop Samuel Wilberforce at the meeting of the British Association for the Advancement of Science in Oxford. Its roots go back further: the literal truth of the Bible had been the subject of some geological debate from the middle of the eighteenth century. The hostility between creationists and evolutionists does not seem to have impinged on Murray and was not seen as a major threat to the authority of the Church in his lifetime. That position was occupied by 'biblical criticism', which required the Bible to be examined in the same way as any other historical document (e.g. Cosslett, 1984).

Geological controversies which played out in Murray's lifetime include the neptunist–plutonist debate, and the battle between the catastrophists and uniformitarians. When Murray was a student in Edinburgh, the rival theories of neptunism and plutonism were at the centre of geological argument. The neptunists followed the Revd John Walker (1731–1803), at the University of Edinburgh; Johan Gottschalk Wallerius (1709–1785) in Sweden; and particularly Abraham Gottlob Werner (1749–1817) in Germany, in the belief that the Earth had originally consisted largely of fluid, and that rocks formed by sedimentation and precipitation. The plutonist cause was espoused by James Hutton (1726–1797), who lived in Edinburgh, and his advocate the Revd John Playfair (1748–1819), who was Professor of Mathematics and later of Natural Philosophy. The plutonists argued that many rocks were emplaced in a molten state, and that uplift generated by internal heat and pressure balanced the slow sedimentary processes of weathering and erosion[34].

Given the geographical locations of the principal combatants, it is no surprise that the debate was particularly fierce in *fin de siècle* Edinburgh (Bretsky, 1983; Dean, 1992). Robert Jameson, one of Murray's tutors, who succeeded John Walker to the Chair in Natural History in 1803, had studied under Werner at the Mining Academy in Frieberg and held strongly to Wernerian views (Hartley, 2001). The chemist John Murray (1778–1820), who Peter Murray described as a "most intimate friend" (Balgarnie, 1864), was also a committed Wernerian[35]. It might be tempting to assume, therefore, that Peter Murray fell into the Wernerian camp, but there is no evidence for this. If anything his views seem to have aligned with the plutonists. He records an affiliation "with Dr. Kennedy, the well-known coadjutor with Sir James Hall, in establishing, by rigid analysis, the identity of basalt with lava"[36] (Balgarnie, 1864); and was a friend of Sir George Mackenzie (1740–1848), an enthusiastic supporter of Hutton's geological theories[37].

Basalt gave rise to much speculation in the late eighteenth century; in 1776, James Keir conjectured that the "great native crystals of *basaltes*, such as those which form the Giant's Causeway, or the pillars of Staffa" formed by the slow cooling of vitreous lava (Keir, 1776: p. 539). The Edinburgh Wernerians argued against an igneous origin. The fact that Murray describes basalt as an igneous rock places him with the plutonists.

Although there is little direct evidence of Murray's view of the neptunist–plutonist controversy, there can be no doubt where he stood in the battle between catastrophism and uniformitarianism[38], which entered into nineteenth-century public consciousness in a way that no other geological debate ever had. The catastrophists believed that the Earth was shaped by cataclysmic events, the sub-text to their position being that these could include one or more floods of biblical proportion. The uniformitarians believed the geology could be explained by gradual changes over enormous spans of time, a position that sat less well with religious dogma. Murray's description of the geology of the coast near Scarborough in *The Edinburgh New Philosophical Journal* (1828) gives an insight into his personal view of Holy Writ and its relationship with natural philosophy:

> "Had geology conferred no other benefit upon society than this, of guiding the miner in the true

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[34] James Hutton published his essay on the *Theory of the Earth* in 1788 in the first volume of the *Transactions of the Royal Society of Edinburgh* and after encouragement from his friends extended it to produce a two volume book in 1795.

[35] John Murray wrote *A Comparative View of the Huttonian and Neptunian Systems of Geology: In Answer to the Illustrations of the Huttonian Theory of the Earth, by Professor Playfair* in 1802, the year in which Peter Murray graduated. This comparison of the Huttonian and Wernerian systems strongly favours the latter.

[36] Robert Kennedy worked with Sir James Hall to prove that basalt crystallised from a molten state; Hall was a committed Huttonian and his experiments disproved a key neptunist assertion that basalt was sedimentary in origin. Hartley (2001 p. 176) notes that very little is known about Kennedy.

[37] The strained relationship between Sir George Mackenzie and Robert Jameson is charted in Hartley (2001). It reached comic proportions when a play that Sir George had written about his geological travels in Iceland closed on the first night due to disruption caused by Wernerians.

[38] Retrospective analyses almost all use these 'labels', but they hardly feature in contemporary debate. The words catastrophism and uniformitarianism were coined in 1837 by William Whewell in a *History of the Inductive Sciences*.

> and right path to his subterranean treasures, and warning the enthusiastic speculator from pursuing a fleeting shadow, it would have been entitled to a place among those sciences which demand the attention and respect of mankind. But of a far higher character is the strong confirming light which it reflects upon the historical records of Holy Writ, which tell of a sudden and universal flow of waters overwhelming the whole surface of the earth".

Murray's account also includes observations on the minerals and rocks of the local area, which he interpreted as evidence of the biblical flood:

> "Geology demonstrates, by many irrefragable marks, everywhere to be seen, that a mighty inundation has actually passed over all lands, apparently from north to south, at no very remote period, and covering the more solid beds of rock with a varied deposition of clay and sand, intermingled with rounded pieces of stone detached from masses at vast distances, and of a very different nature from any in the immediate vicinity".

These observations were published some years before the major challenge to catastrophist theories, which came in the early 1830s in Charles Lyell's popular *Principles of Geology* (1830–1833). Lyell championed the uniformitarian cause and his arguments gave additional importance to the way in which geological specimens were ordered and interpreted in museums. The *Report of the Scarborough Philosophical Society* for 1839 makes tangential reference to the debate, and strikes a more conciliatory note than Murray's account of ten years earlier:

> "A good geological collection like the Scarborough one, enables the student to arrange and combine; yet, the Science itself being in its infancy, it will require a modest, sober, and a master hand to arrange and systematize the data and phenomena of the conflicting theories now before the Public, and to harmonize them with the Bible History".

By the second quarter of the nineteenth century it was clear to most geologists that the literal interpretation of Genesis, and the famously detailed chronology worked out by Archbishop Ussher, was untenable. Catastrophism was in retreat, although it remained a widespread belief. Devout Christian geologists, notably Adam Sedgwick, William Buckland, Thomas Chalmers and Hugh Miller, occupied important positions. It was not until the mid-nineteenth century that the uniformitarian viewpoint prevailed[39].

The eighth edition of *Theakston's Guide to Scarborough* (Theakston and Carter, 1860) still interprets the local geology through a catastrophist prism. There can be little doubt of Murray's influence in this. The geological diversity of material from what is now recognised as glacial boulder clay[40] is considered to be evidence of a "mighty inundation", an antediluvian interpretation which echoes Murray's paper of 1828, and suggests he remained wedded to the Biblical interpretation to the end of his life.

CONCLUSION

This article sheds light on a 'natural philosopher' who deserves to be better known. He exemplifies nineteenth-century propriety, charity and moderation, and its links with Christian belief. Throughout a long and busy life Peter Murray worked for his own improvement and in the service of his fellows. His contributions to charity were diverse and substantial, he wrote scientific papers, used his chemical skills in research, and was a prominent and energetic member of religious, civic and scientific societies. He seems to have been honest and fair in dealing with difficult situations but had little tolerance of corruption. He was well liked in the spa town of Knaresborough, where he had a medical practice between 1803 and 1826, and in Scarborough where he had a long and productive retirement. His scientific interests were wide ranging, extending (in true Renaissance fashion) from archaeology to zoology. Geology was particularly prominent and there is no indication of any conflict between it and his Christian beliefs.

He would, we are sure, be pleased that the Rotunda Museum has survived, though the issues of funding created by the recent austerity crisis might generate a sense of déjà vu: *plus ça change, plus c'est la même chose*. What he would make of present-day Scarborough, a town of contrasts in which nineteenth-century splendour is juxtaposed with twenty-first-century tat, and where people still sleep rough on the streets, is left for the reader to judge.

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[39] The gradualist credo went on to cause its own problems. In the evolution of geological ideas in the late twentieth century there was strong resistance in some quarters to the idea that catastrophic events, such as the asteroid impact that caused the mass extinction at the end of the Cretaceous period, could play a central role in geology.

[40] Despite his confidence in Biblical interpretations of geological features, even Buckland, author of a *Bridgewater Treatise* and possibly the last great diluvialist, became convinced that glacial action rather than Noachian deluge was responsible for much of the boulder clay that covered Britain after engaging in field investigations with Louis Agassiz in 1840.

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APPENDIX – DONATIONS TO MUSEUMS

Peter Murray made numerous donations to public collections during a long and eventful life. They provide an indication of the breadth of his interests and the diversity of his collections. Sadly, with the exception of the specimens now at the Natural History Museum in London, very few of the specimens can now be traced [*vide supra*]. Fortunately, although specimens cannot now be traced with certainty, Murray's donations to the Scarborough Philosophical Society (SPS) and later the Scarborough Philosophical and Archæological Society (SPAS) are recorded in various annual reports which are summarised in Tables 1 and 2.

A donation to Durham University (which cannot now be traced) is recorded in Table 3. It features numerous strontium minerals (specimens 1, 9, 10, 21, 23, 27, 50, 52 and 54), many from his Yorkshire discoveries. The specimens from the area around Edinburgh were probably collected during Murray's time at the university there and those from the Yorkshire coast are also probably self collected. The excellent contacts between the Yorkshire Philosophical Society and mineralogists in Cornwall, who made many donations in the 1820s, may go some way to explain the abundance of Cornish material. Specimens from foreign localities are likely to have arrived in Murray's collection by exchange from dealers. Most of the species are easy to identify, but the nature of 'rhoetirite' from Shetland is unknown.

DESCRIPTION (AS A DIRECT QUOTATION)	REFERENCE
[Mineral specimens]	(SPS, 1830)
[Fossil Specimens]	(SPS, 1830)
Turritella, from the Lias. Several specimens of Fossil Plants, lower sandstone and shale, Scarborough.	(SPS, 1832)
Fossil Fish, from Barrow on Soar, Leicestershire.	(SPS, 1832)
3 Specimens of Transition Slate, and Limestone, with Fossils, from Plymouth.	(SPS, 1832)
Paludina from the Hasting beds. Fossil Fish with an Astacus, from the Chalk.	(SPS, 1832)
Chromate of Iron, from Shetland.	(SPS, 1832)
Sulphate of Alum, Castle-Hill, Newhaven.	(SPS, 1832)
Actynolite, from New-South-Shetland.	(SPS, 1832)
Serpentine and Steatite, from the Lizard Rock, Cornwall. Serpentine containing Diallage, Cornwall. Calc Tufa, from near the Cataract of Niagara.	(SPS, 1832)
Specimen of Granite, Hayton Quarries; Polypothecia Clavillata, from the Chalk; Lignite, from the Plastic Clay, Devonshire; Trigonia, from Lyme, Dorset; Specimen of the old red Sandstone, &c.	(SPS, 1834)
Specimen of Opal;−Crystals of Carbonate of Lime, from Kingston Cave, County of Tipperary, Ireland.	(SPS, 1834)
Solenites Murrayana;—several Fossils from the Cornbrash;—Fossil Plant *(Neuropteris)* new species.	(SPS, 1835)
Sulphate of Strontia, in broad tabular Prisms, from the red Marl, Bilton Banks, Knaresboro'; — specimen of Siliceous Sinter, from the boiling Springs of Reikholt, Iceland.	(SPS, 1835)
Specimen of Arragonite [*sic*], found to the south of Gristhorpe Bay.	(SPS, 1836)
Beautiful Trigonia, from Weymouth; Cryolite of a snow-white colour, from Greenland.	(SPS, 1837)
Crania from Hampton Wick, near Bath. Trilobite, from the Silurian Rocks, Sweden.	(SPS, 1840)
Specimen of the Scales of the Holoptychus, from the Burdie-house Limestone.	(SPS, 1840)
Stalactitical Incrustations on Calc Tufa, from a Cave in Bermuda. Collection of small Corals from the Crag.	(SPS, 1841)
Polished piece of Heliotrope originally forming part of the Mosaic pavement of the High Altar at the Cathedral of St. Andrews.	(SPS, 1842)
Trochus from the Speeton Shale. Stem of Cycadeæ. A Polished Slab of Silicious Turbinolia. Orthoceratite from Kinnekulle, South of Sweden. Specimen of Fossil Fish from the Schistose Beds of Caithness.	(SPS, 1843*a*)
Fusus parilis, Pecton Madisonii, Ostrea stellæformis, from the Tertiary of America. Ammonites Greenovi. Three specimens of Fossil Fruits, from Malton. Six specimens of rare Minerals, from America.	(SPS, 1847)
Piece of Black Jack, Do., Joss Stick China, Fossil Tooth, Corr. Oolite, Kernal or Seed	(SPAS, 1864)

Table 1. Geological donations made by Peter Murray to the collection of the Rotunda Museum between 1829 and 1864, as recorded in the annual reports of the Scarborough Philosophical Society (SPS) and the Scarborough Philosophical and Archæological Society (SPAS). With the exception of the first two entries in square parentheses, the descriptions are direct quotes from the Annual Reports. They occasionally include non-geological items.

DESCRIPTION (AS A DIRECT QUOTATION)	REFERENCE	SUBJECT
[Books]	(SPS, 1830)	Library
Beautiful specimens of the Unio Cariosus, and Unio Purpureus, from the river Ohio:− eight specimens of the Testacell maugii.	(SPS, 1834)	Conchology
Firman of the Ottoman Porte; specimen of the Nutmeg, (Myristica Moschtata); Pouch, from Hudson's Bay.	(SPS, 1834)	Anthropology
A beautiful specimen, in full plumage, of the Northern Diver, (*Colymbus Glacialis*).	(SPS, 1835)	Zoology
2 fine specimens of Terebratulæ;— 1 Unio Cariosus.	(SPS, 1835)	Conchology
Ball made from the Ashes collected in a Roman British Cemetery, at Aldborough — Isurium Brigantum.	(SPS, 1835)	Antiquities
Several Arrows used by the Natives of Guiana [sic] for killing fish.	(SPS, 1835)	Anthropology
Specimen of the Velvet Crab, *(Cancer Velutinus.)*	(SPS, 1836)	Zoology
Unio Signatus and Anodon Latimarginatus, from Para, South America.	(SPS, 1837)	Conchology
Silver Penny of one of the Edwards.	(SPS, 1837)	Numismatics
1 Pair of Bustards. *(Otis tarda.)* Male and Female.	(SPS, 1840)	Zoology
1 Neritina Puligera. Achatina Perdis, from Accara, Gold Coast.	(SPS, 1841)	Conchology
Specimen of Scalaria.	(SPS, 1843b)	Conchology
Unio delphinus. Orbicula, *Lamellosa and Variabilis*.	(SPS, 1845)	Conchology
Opossum, *(Didelphis Vulpina.)*	(SPS, 1847)	Zoology
Sawfish Shark.	(SPS, 1854)	Zoology
Hancock and Alder on the Nudibranchiate Mollusca.	(SPAS, 1855)	Library
70 volumes of the Edinburgh Philosophical Transactions. The entire series from 1819 to 1854.	(SPAS, 1858)	Library

Table 2. Non geological donations made by Peter Murray to the collection of the Rotunda Museum between 1829 and 1864, as recorded in the Annual Reports of the Scarborough Philosophical Society (SPS) and the Scarborough Philosophical and Archæological Society (SPAS). With the exception of the entry in square parentheses, the descriptions are direct quotes from the Annual Reports.

NO.	DESCRIPTION (AS A DIRECT QUOTATION)
1	Brewsterite—*Strontian Lead Mines, Argyllshire.*
2	Shorl in Quartz—*Scotland.*
3	Small grained Granite with White Topazes—*St Michael's Mount, Cornw*.
4	Common Fibrous Gypsum—*Ripon, Yorkshire*.
5	Steatite—*Chapell Quarry, Fifeshire*.
6	Wolfram in Quartz—*Cornwall*.
7	Sulphuret of Molybdenum—*Bohemia*.
8	Olive Pitch Stone—*Scotland*.
9	Strontianite in Mountain Limestone—*Lead Mines, Pately, Yorkshire.*
10	Celestine—*Barasia*.
11	Chlorite disseminated in Calc. Spar—*Siberia*.
12	Mesotype or Thompsonite—*Kilpatrick*.
13	Black Mica in Felspar—*Siberia*.
14	Granular Augite—*Arendahl, Norway*.
15	Scapolite, &c—*Arendahl, Norway*.
16	Grenatite, in Mica Slate—*St Gothard, Switzerland.*
17	Epidote in Prisms, or Granular Augite—*Arendahl, Norway*.
18	Compact Epidote—*Siberia*.
19	Colophonite—*Arendahl, Norway*.
20	Compact White Felspar—*Scotland*.
21	Sulphate of Strontia, with Native Sulphur— *Mazzara, Sicily*.
22	Sulphate of Barytes—*Pately, Yorkshire.*
23	White Sulphate of Strontia, in Magnesian Limestone—*Banks of the Nidd, Knaresborough*.
24	Common Obsidian—*Isle of Ascension*.
25	Alum Rock—*Siberia.*
26	Zircon in Sienite—*Christiana*.
27	Carbonate of Strontia with Galena and Sulphate of Barytes—*Strontian Lead Mines, Argyleshire*.
28	Granite—*Haytor, Cornwall.*
29	Radiated Zeolite—*Greenland.*
30	Grey Manganese in Prisms—*Salisbury Crags, near Edinburgh*.
31	Salmon-coloured Compact Gypsum Red Marl—*Knaresborough, Yorksh*.
32	Massive Red Oxide of Copper
33	Blue Oxide of Copper—*Cornwall*.
34	Hornblende passing into Actynolite—*Unst, Shetland.*
35	Shorl Rock
36	Axinite—*Lands End*.
37	Common Tremolite—*Scotland*.
38	Jet—*From the Hard Shale of the Upper Lias, Whitby, Yorkshire*.
39	Zircon Sienite—*Norway*.
40	Wollastonite[...]—*Castle Rock, Edinburgh*.
41	Chatoyant Adularia, with Hornblende a bouldered Nodule—*From the Sea Coast of Scarborough*.
42	Amethystine Quartz—*Cornwall*.
43	Rhoetirite—*Shetland*.
44	Stilbite, with Mesole—*Faroe*.
45	Calc. Sinter—*From the Magnesian Limestone in the Dropping Well, Knaresborough*.
46	Pyritic Ball—*Lias, Whitby*.
47	Common Serpentine—*Banffshire*.
48	Septarium—*From the Lias, Yorkshire*.
49	Prehnite—*Frisky, Dumbarton*.
50	Celestine or Sulphate of Strontia, in Magnesian Limestone—*Scotton Moor, near Knaresborough*.
51	Quartz Chrystals [*sic*] or Granite—*Siberia*.
52	S. of Strontia in Chrystals [*sic*], nearly of the primary form, Red Marl—*Knaresborough, Yorkshire*.
53	Garnets in Mica Slate—*Loch Tay Head*.
54	Celestine in Magnesian Limestone—*Scotton Moor, near Knaresborough*.
55	Vitreous Copper, with the Green Oxide—*Cornwall*.
56	Subsulphate of Alumine, from a layer of Ochry Clay upon the Chalk—*Newhaven, Sussex*.
57	Malachite—*Siberia*.
58	Apophyllite of the Valley of Fassa—*Tyrol*.
59	Antrimolite, Var. of Mesotype—*Antrim, Ireland*.

Table 3. Murray's donation to Durham University in 1834 (Durham County Advertiser, 1834).

PROSOPITE FROM COPPERTHWAITE VEIN, SWALEDALE, NORTH YORKSHIRE: A SECOND BRITISH OCCURRENCE

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The rare calcium aluminofluoride prosopite occurs as supergene infills in cavities in laminar baryte at Copperthwaite Vein northeast of Reeth in Swaledale, North Yorkshire. It occurs as powdery masses, intimately associated with fraipontite, which overgrow cinnabar, smithsonite and supergene fluorite. It appears to have formed in acidic aluminium-rich fluids saturated with respect to fluorite.

INTRODUCTION

Prosopite, ideally $CaAl_2F_4(OH)_4$, was first recorded from the Altenberg tin-tungsten deposit in Saxony (Charpentier, 1799; Scheerer, 1853). It is a rare mineral which is most commonly found as an alteration product of topaz in greisens, or with other aluminofluorides in cryolite-bearing pegmatites. The only British record is in fluorite veinstone at Coldstones Quarry near Greenhow, North Yorkshire (Young *et al*., 1997).

A complementary article in this journal describes the distribution of the zinc-bearing aluminosilicate fraipontite in the Yorkshire Pennines (Chapman *et al*., 2022). The first British specimens of this uncommon mineral were identified by George Ryback (1936–2003) at Copperthwaite Vein in Swaledale (Ryback and Tandy, 1992). As the geological context of the discovery was not recorded, collectors were asked if they had any unidentified white powdery minerals from this locality. A specimen in the Peter Briscoe Collection proved to be a mixture of fraipontite and prosopite.

LOCALITY

Copperthwaite Vein[1] is exposed as an east–west trending mineralised shatter belt up to about 50 m wide with several productive oreshoots and flat-type replacements in the Underset and Main limestones below Fremington Edge. It extends to the east across Marrick Moor as a curviform fissure in the Main Chert and Richmond Chert.

Dunham and Wilson (1985: p. 146) suggest the Romans may have exploited the deposit but the first documentary evidence of mining dates from the twelfth century, when ledgers record that lead from Copperthwaite was used in the construction of a priory near Marrick. Even at that early period the workings were regarded as ancient, as it was recorded that the vein had produced lead "from time out of minde [*sic*]" (Gill, 2001: p. 138). As lead mining developed in Swaledale, the western section of the vein below Fremington Edge was worked as part of the Fremington or Grinton liberty and the eastern section on Marrick Moor as an outlying part of the Hurst mines. The vein was worked sporadically until the late nineteenth century but the later operations were comparatively unproductive.

The principal primary gangue minerals are baryte and calcite, and there is a little local fluorite (Chapman *et al*., 2019; Green and Chapman, 2019). Galena is the principal primary ore mineral and Dunham and Wilson (1985) record minor sphalerite.

Oxidation is deep and extensive. Most of the sphalerite has been altered to hemimorphite and smithsonite. Cellular limonite-stained hemimorphite is present on almost every spoil heap. Smithsonite occurs more locally as grey lenticular crystals, and white to yellow-green botryoidal crusts. White silky hydrozincite, white powdery fraipontite and brick-red cinnabar are occasionally associated with these supergene minerals.

Cerussite is the most abundant lead-bearing supergene mineral. It occurs as colourless to white prismatic crystals up to about 8 mm in length. Anglesite is occasionally present as inconspicuous millimetre-size colourless crystals in cavities and fractures in massive galena. Pyromorphite occurs as photosensitive yellow to

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[1] The name Copperthwaite is probably a corruption of Cowperthwaite. Cowper is a local family surname and thwaite refers to a clearing in a wooded area. There is no evidence it refers to the presence of copper minerals (Dunham and Wilson, 1985).

Figure 1. Bright white infills of powdery prosopite (analysis CPT02) with white fraipontite (analysis CPT04) on the broken face of a 50 × 50 × 30 mm specimen of massive baryte from Copperthwaite Vein, Reeth, Swaledale, North Yorkshire. Peter Briscoe Collection. Photo David Green.

green crusts (Charles Lamb, *personal communication*, 2019). Energy-dispersive X-ray spectrometry (EDS) reveals it is very close to end-member composition (David Alderton, *personal communication*, 2022). Dunham and Wilson (1985) record traces of malachite, but supergene copper minerals are rare.

PROSOPITE

Prosopite was identified on a hand specimen and small associated fragment found in a field bag (possibly from the Keith Snell Collection) in stock belonging to Peter Briscoe. The origin of the specimen is unclear, a scrap of paper simply records: "Cinnabar [from] Copperthwaite, NZ 0595 0023, Reeth".

The larger specimen (Fig. 1) consists of laminar baryte veinstone with a broken face exposing small cavities lined with powdery brick-red cinnabar. Traces of resinous brown to black sphalerite remain and there are a few patches of slightly oxidised galena. Cavities on the broken face are lined with colourless fluorite, brick-red cinnabar and poorly formed white to pale brown smithsonite, and partially infilled by white powdery material. The small fragment has similar patches of white powdery material infilling cavities lined with brick-red cinnabar (Fig. 2).

Figure 2. Prosopite intimately intergrown with white powdery fraipontite on brick-red cinnabar from Copperthwaite Vein, Reeth, Swaledale, North Yorkshire. The field of view is 9.5 mm across. David Green Collection. Photo John Chapman.

The difficulties in characterising white powdery phases from the Yorkshire Pennines are summarised in a complementary article (Chapman *et al*., 2022) which notes that the only unambiguous identification technique is X-ray diffractometry (XRD). Analyses were carried out on a Riguku Miniflex 600 X-ray powder diffractometer using CuKα radiation.

Energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM) was subsequently used to differentiate prosopite from fraipontite. A number of small powdery fragments were removed from the specimens illustrated in Figures 1 and 2. There were no obvious visual distinctions between these subsamples, but two contained major zinc, aluminium and silicon (and are largely fraipontite) while several others contained calcium, aluminium and fluorine (and are largely prosopite).

DISCUSSION

The occurrence at Copperthwaite Vein has similarities with the only other British record of prosopite at Coldstones Quarry near Pateley Bridge, which is described by Young *et al*. (1997: p. 896) as follows:

> "At Coldstones Quarry prosopite occurs as white to pale blue-tinted chalky or soft earthy masses up to 10 mm across, always associated with minerals of undoubted supergene origin. Identification was by IR, EDA and powder XRD. Examination by SEM showed the prosopite to consist of aggregates of prismatic crystals 1−5 µm long ... It is most commonly found embedded in thick, pale brown, often somewhat spongy encrustations on massive fluorite and on 1−3 cm fluorite cubes. Such crusts consist of variable mixtures of smithsonite, halloysite-10 Å, and several not fully characterized aluminium hydroxide and/or silicate phases (some possibly amorphous); the prosopite may be replacing the original components. Similar patches of prosopite occur in irregular open cavities within the encrustations or within the fluorite veinstone. These are lined with iron-stained smithsonite which, together with traces of cinnabar, probably represent original masses of sphalerite. Here prosopite clearly postdates smithsonite. There seems little doubt that all of the prosopite at this locality is of supergene origin. On the specimens examined, prosopite is quite abundant, though its distribution in the vein may be restricted".

At both localities, prosopite is associated with smithsonite and cinnabar. At Coldstones Quarry it fills cavities in fluorite, at Copperthwaite Vein it occurs in cavities in laminar baryte some of which contain supergene fluorite (Fig. 3).

The intimate association between prosopite and fraipontite at Copperthwaite Vein shows that they formed in similar conditions. Chapman *et al*. (2022) suggest fraipontite forms when acidic solutions produced by the destabilisation of primary marcasite leach zinc and aluminium from the surrounding rock. Fraipontite is deposited in solutions with high aluminium and zinc ion activities as the pH evolves back towards neutral. Similar conditions, with a local supply of calcium and fluoride ions from the dissolution of primary fluorite, appear to favour the formation of prosopite.

The presence of supergene fluorite in some of the cavities that contain prosopite at Copperthwaite Vein (see Fig. 3) shows that solutions were saturated with respect to calcium fluoride. The formation of aluminofluoride minerals in solutions buffered by fluorite is almost certainly governed by the aluminium ion activity, which is strongly pH dependent. Acidic conditions (pH 4 to 5) are suggested by Bridges and Green (2005) in a discussion of the formation of the chemically similar mineral gearksutite, ideally $CaAlF_4(OH)\cdot H_2O$, in a similar supergene environment in Derbyshire.

Supergene aluminofluorides are probably more common in the Pennine Orefields than current records suggest. Gearksutite has been identified at the Old Gang Mines in Swaledale, North Yorkshire with gypsum and ktenasite (Green, 2003) and at Ball Eye Opencast near Cromford in Derbyshire (Bridges and Green, 2005). Prosopite occurs at Coldstones Quarry near Greenhow in North Yorkshire (Young *et al*., 1997) and at Copperthwaite Vein. Both are easily overlooked. They typically occur as nondescript powdery masses and are

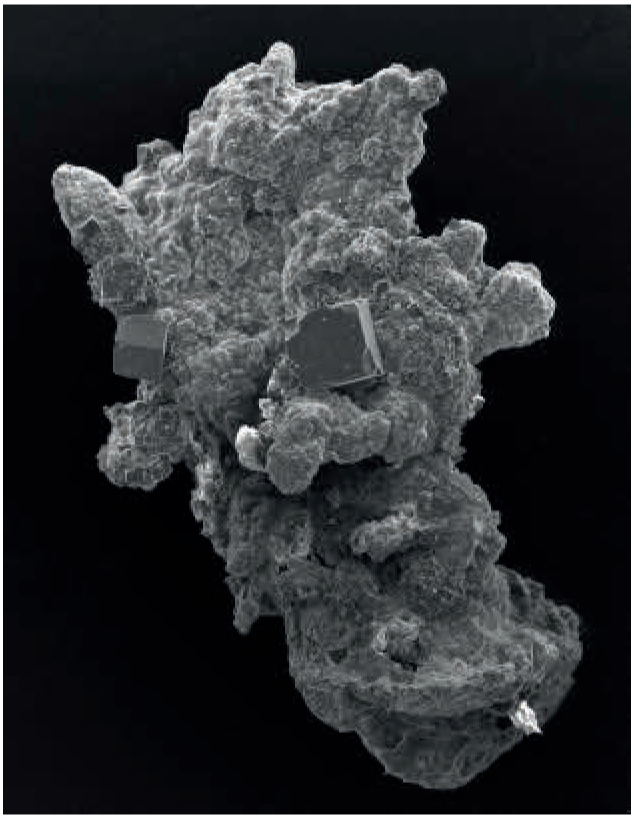

Figure 3. Supergene fluorite cubes (confirmed by EDS at two points) associated with powdery masses of fraipontite (confirmed by EDS on the projecting mass just below main fluorite cube) overgrowing smithsonite (difficult to differentiate from fraipontite in this image but confirmed by EDS near the top of the field) from Copperthwaite Vein, Reeth, Swaledale, North Yorkshire. The field of view is 1.2 mm across. Peter Briscoe Collection. SEM image by David Alderton.

vulnerable to aggressive cleaning regimes. The authors would be pleased to know of similar specimens in readers' collections.

CONCLUSION

At Copperthwaite Vein prosopite occurs as white powdery aggregates in intimate association with fraipontite in cavities lined with cinnabar, smithsonite and supergene fluorite in baryte veinstone. This is the second British report of the mineral and the second record in a low-temperature lead-zinc orebody in the Yorkshire Pennines.

ACKNOWLEDGEMENTS

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FRAIPONTITE FROM THE YORKSHIRE PENNINES

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Fraipontite localities in the Yorkshire Pennines are reviewed and new occurrences at Buckden Gavel Mine in Wharfedale and Providence Mine in Swaledale reported. Fraipontite occurs as white to pale green and brown masses intimately intergrown with gibbsite and opaline silica at Buckden Gavel Mine. It forms white porcellaneous masses in cavities lined with smithsonite and hemimorphite at Providence Mine. In both cases it is found in limonitic matrix in oxidised replacement deposits. Previously reported localities at Virgin Moss Mine in Wensleydale and Copperthwaite Vein in Swaledale are discussed.

INTRODUCTION

Fraipontite, ideally $(Zn,Al)_3[(Si,Al)_2O_5](OH)_4$, is an uncommon member of the kaolinite-serpentine group of minerals. The name honours Julien Fraipont (1857–1910) and his son Charles (1883–1946), who held professorial positions at the University of Liège (Cesàro, 1927). Fraipontite is typically reported from the oxidation zones of zinc-rich orebodies, where it is occasionally present in sufficient quantities to be worked as an ore (Boni and Mondillo, 2015; Arfè *et al.*, 2017). It usually occurs as nondescript porcellaneous masses and infills, but well formed pearly micro-crystals have been reported at a few localities.

The first British fraipontite was identified in 1967 on material collected at Copperthwaite Vein in Swaledale, North Yorkshire (Ryback and Tandy, 1992). It has subsequently been reported from Virgin Moss Mine in Wensleydale, North Yorkshire (Young *et al.*, 1992); Machen Quarry near Caerphilly, Mid Glamorgan (Goulding and Price, 1995; Plant and Jones, 1995); and Silver Gill in the Caldbeck Fells, Cumbria (Green *et al.*, 2005). Thin hexagonal crystals from Lead Mines Clough, Anglezarke, Lancashire may be fraipontite but require further analysis (Alderton *et al.*, 2022).

This study was initiated by the discovery of two specimens labelled as ‘fraipontite’ from Buckden Gavel Mine in the collection of the late Keith Snell, a former Russell Society member with a keen interest in Yorkshire minerals. One proved to be a misidentification of hydrozincite but the other was confirmed as fraipontite by X-ray diffractometry. This prompted a search for further material. A specimen from the workings of Providence Mine was identified and additional examples from Copperthwaite Vein and Virgin Moss Mine came to light.

ANALYSIS

Fraipontite can be confused with many other species including dickite, doyleite, halloysite, hydrozincite, gibbsite, kaolinite, prosopite, saponite, sauconite and zaccagnaite (if white), limonitic goethite or other iron oxyhydroxides (if brown) and chrysocolla (if blue-green). There is no simple method of differentiating all of these species, although the carbonates such as hydrozincite can be distinguished by their effervescence in acids.

Powder X-ray diffractometry (XRD) is the most reliable method of differentiating fraipontite from the other white, brown and blue-green minerals with which it can be confused. Analyses were carried out on a Riguku Miniflex 600 X-ray powder diffractometer using CuKα radiation in this study.

Energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM) is helpful in revealing the relationships between fraipontite and any associated phases. The presence of zinc, aluminium and silicon in EDS data eliminates most possible confusions. Standardless EDS analyses were carried on several different SEMs in this study.

LOCALITIES

This survey is restricted to localities in the Askrigg Block of the North Pennine Orefield (Dunham and Wilson, 1985). The localities are described alphabetically.

Buckden Gavel Mine

Buckden Gavel Mine worked a complex north–south trending vein system which crosses the western flank of Buckden Pike in Upper Wharfedale (Northern Mine

Figure 1. White to very pale green and inconspicuous brown fraipontite, 45 × 30 mm, replacing dolomitic limestone from Buckden Gavel Mine, Wharfedale, North Yorkshire. Specimen LB 3890, formerly in the Keith Snell Collection. Photo David Green.

Research Society, 1980; Dunham and Wilson, 1985). The principal access to the nineteenth century workings, Higgs or Buckden Gavel Level, was driven as a cross-cut at the base of the Main Limestone from the head of Buckden Gill [SD 9554 7814]. Mineralisation was encountered 465 m from the portal. The mine exploited irregular replacements in dolomitised limestone at three main horizons.

The most abundant primary minerals are baryte, calcite and galena. Minor fluorite is recorded by Dunham and Wilson (1985: p. 189) and cellular barytocalcite is locally present (authors' unpublished data). Primary iron sulphides and sphalerite were probably abundant before the deposits were attacked by oxidising groundwater. The former presence of marcasite is betrayed by sharp goethite pseudomorphs.

The supergene assemblage is dominated by limonitic goethite. Anglesite, cerussite and smithsonite are reported by Gill (1974), and the first and last of these are briefly noted by Dunham and Wilson (1985). Zinc-bearing supergene minerals are locally common. Smithsonite occurs as buff to brown lenticular crystals on baryte and is rarely found as thick botryoidal crusts which may be stained bright yellow by cadmium sulphide inclusions. Fan-like groups of transparent hemimorphite line cavities in compact limonitic ochre. Hydrozincite occurs as white crusts.

The specimens which initiated this study were obtained from a house clearance company which acquired part of Keith Snell's collection following his death. Labels glued onto two boxes record 'fraipontite from Buckden Gavel Mine'; one is catalogue number SB 582 and the other LB 3890. In the absence of a catalogue it has not proved possible to trace details of precisely where, when or by whom they were collected, but Russell Society members are known to have organised occasional field visits to the site in the twentieth century (Mike Smith, *personal communication*, 1995).

A white crust on specimen SB 582 was identified as hydrozincite[1]. White porcellaneous material in brown baryte-rich matrix on specimen LB 3890 (Fig. 1) was identified by XRD as fraipontite with minor admixed gibbsite. Fraipontite fills irregular pockets and replaces fossils (possibly crinoid ossicles) in the limestone, and has a minutely mammillated surface in cavities, where it commonly overgrows tabular baryte. Close examination shows that some brown patches are iron-stained fraipontite whereas others are limonite-stained dolomitic limestone.

A semi-quantitative analysis by EDS revealed aluminium, silicon and zinc as the major elements with an atomic number greater than nine. Minor (<2 at%) sodium, phosphorus, sulphur and iron are also present.

As no further contextual data is associated with the specimen, an appeal was made to mineralogists who had known Keith in the hope that further material would be located. A second specimen was identified in the David McCallum Collection (catalogue number E215). This nondescript block contains white powdery to porcellaneous fraipontite surrounding angular clasts of dark brown limonite-baryte veinstone and pale clasts of sparry limestone (Fig. 2). The fraipontite (identified by EDS) is associated with colourless and transparent to opaque and white glassy opaline silica with a distinctive conchoidal fracture (also identified by EDS). Deposition of the silica began earlier than fraipontite but there is a paragenetic overlap between the two phases.

An associated field slip records that this specimen is from a limonitic collapse breccia in the Main Limestone at the north end of the Main Pipe at Buckden Gavel Mine.

Copperthwaite Vein

The first British fraipontite was identified in 1967 on specimens collected at Copperthwaite Vein in Swaledale by George Ryback[2] (Ryback and Tandy, 1992). The original description records soft white botryoidal crusts with smithsonite and hemimorphite but no further contextual information.

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[1] A bright white crust of lath-like crystals up to 3 mm thick overgrows hemimorphite and is in places overgrown by a later generation of that mineral on specimen SB 582. Wet chemistry and EDS show that this is hydrozincite. It is recorded here as an illustration of the difficulties in identifying fraipontite and also as the first published record of hydrozincite from Buckden Gavel Mine.

[2] George Ryback (1936–2003), a research chemist, honorary member of staff at the Natural History Museum in London, and former editor of the *Journal of the Russell Society* (Braithwaite, 2003).

Figure 2. White fraipontite, some areas intimately intergrown with opaline silica, 90 × 65 mm, enclosing clasts of altered limestone from Buckden Gavel Mine, Wharfedale, North Yorkshire. Specimen E215 in the David McCallum Collection. Photo David Green.

The workings at Copperthwaite are ancient and extensive. They extend along a roughly east–west course for about 2 km across Fremington Edge northeast of the village of Reeth. To the west the workings were part of the Fremington or Grinton liberties and to the east, on Marrick Moor, they were part of the Hurst mines (Gill, 2001).

The vein is exposed as a mineralised shatter belt up to about 50 m wide where it cuts through the Underset and the Main limestones below Fremington Edge. It extends to the east across Marrick Moor as a curviform fissure in the Main Chert and Richmond Chert. The workings on Marrick Moor are mostly via shallow shafts sunk directly on the vein. The principal primary gangue minerals are baryte and calcite and there is a little local fluorite. Galena is the major ore and Dunham and Wilson (1985) record minor primary sphalerite.

Supergene oxidation is extensive. Hemimorphite was identified as fan-like crystal groups in cavities with siderite in early analyses by the British Geological Survey (Dunham and Wilson, 1985). Smithsonite occurs locally, mostly as grey lenticular crystals, but occasionally as white to yellow-green botryoidal crusts. Cerussite is the most abundant lead-bearing supergene mineral and pyromorphite occurs as yellow to green crusts in a few areas where the vein is entirely within siliceous wall-rock.

The precise locality and geological context of the fraipontite reported by Ryback and Tandy (1992) is not recorded and further specimens were sought. A specimen identified in this study is from "shallow workings in the Richmond Chert at NZ 0595 0023" (Peter Briscoe, *personal communication*, 2022). White powdery to minutely botryoidal material partly fills cavities lined with crustose smithsonite, brick-red cinnabar, and supergene fluorite in massive laminar baryte. X-ray diffractometry shows that the powdery material is an intimate mixture of fraipontite and the rare calcium aluminofluoride prosopite. A broad peak near 10 Å probably represents a poorly crystallised residual mica-group mineral (rather than halloysite-10 Å). The co-crystallising prosopite and fraipontite are visually indistinguishable. They are the subject of a short complementary article (Briscoe *et al.*, 2022) and are not discussed further here.

Providence Mine

Providence Mine [SD 887 966] worked the north–south trending Sargill–Providence vein system above the village of Muker on the southern side of Swaledale (Dunham and Wilson, 1985). Most of the mineralisation is in replacement flats in the Main Limestone. Aragonite, baryte, calcite and galena are common on the spoil heaps. The supergene assemblage is dominated by limonitic goethite. Hydrozincite is common as bright white spherulitic masses and crusts with partly oxidised pale brown sphalerite, iron and manganese oxides, minor smithsonite and hemimorphite.

Fraipontite occurs as white porcellaneous masses with conspicuous syneresis cracks (Fig. 3). It fills cavities or fractures lined with poorly formed colourless hemimorphite, grey smithsonite and minor cerussite in limonitic galena-bearing matrix. The X-ray powder pattern is a perfect match for fraipontite and also includes a very broad peak centred at about 15 Å which is characteristic of smectite-group minerals.

A semi-quantitative analysis by X-ray fluorescence spectrometry revealed that zinc, aluminium and silicon are the only major elements with an atomic number greater than ten. There is also minor (<1 at%) calcium, magnesium, nickel and lead.

Figure 3. White porcellaneous fraipontite in limonitic matrix, 65 × 45 mm, from Providence Mine, Muker, Swaledale, North Yorkshire. A small label glued onto the matrix records an eight-figure grid reference [SD 8875 9660] which confirms that it is from Providence Mine in Swaledale and not one of the other Yorkshire lead mines of the same name. David Green collection and photo.

Virgin Moss Mine

Virgin Moss (or Virgin) Mine lies within the Bolton Royalty on the high ground between Wensleydale and Swaledale. The productive workings were mostly between the Main Limestone and the Richmond Chert (Dunham and Wilson, 1985). The mine extends from the horse level entrance at SE 0022 9335 across gently rising ground for about 1.5 km to the NNW. Shallow dumps mark the course of the vein over half that length.

Baryte is the most abundant primary gangue mineral, and the carbonates calcite and witherite are locally common. Galena was the principal primary ore. Witherite was worked in a small way from 1843 (Spensley, 2014: p. 161) and eight tons were returned in 1887 (Carruthers *et al*., 1915: p. 42). Sharp goethite pseudomorphs after marcasite are present on most of the spoil heaps. Sphalerite is rare, but its former presence is indicated by an abundance of cellular hemimorphite. Matrixless cerussite groups up to about 50 mm across, stained black by finely divided galena, were found when the dumps from the horse level were dug to provide aggregate to surface local tracks in the early 1990s (Norman Thomson, *personal communication*, 2006). A substantial amount of fraipontite was uncovered at the time and Young *et al*. (1992) provide a detailed description:

> "In the field the fraipontite is relatively conspicuous because of its dull, pale apple-green to whitish green colour. It is typically present as pockets and discontinuous bands up to 5 cm across within ochreous brown, and in some instances rather cellular, 'limonite'".
>
> "Most specimens of the mineral exhibit a compact, rather enamel-like texture with a dull waxy lustre on smooth or subconchoidal fracture surfaces. Many specimens display prominent colloform banding in slightly different shades of green ... In several instances an open cellular texture is present within the fraipontite, with cavities up to 2 cm across lined by crudely mammillated surfaces of the mineral. Some of these specimens bear a superficial resemblance to green smithsonite. A few specimens have been found in which a fibrous radiating crystalline texture occurs within the banded green mineral".
>
> "The pale apple-green, enamel-like material gave an x-ray powder pattern of fraipontite with variable amounts of gibbsite. Back-scattered electron imaging revealed gibbsite patchily disseminated throughout the fraipontite. No evidence of replacement of fraipontite by gibbsite or *vice versa* was seen".

Little can be added to this excellent description of the material from the horse level on the basis of the material available to this study.

In 2006, one of the authors (DG) was given a field-box from the Norman Thomson Collection (see Green *et al*., 2012) containing specimens from the original find. They include white to pale green and brown porcellaneous

Figure 4. A thin translucent resinous gel-like sodium-rich layer coating white to yellow-brown fraipontite in a cavity in baryte-goethite matrix from a spoil heap [SD 9973 9459] about 250 m NNW of Hill Top Shaft, Virgin Moss Mine, Wensleydale, North Yorkshire. The field of view is 1 mm across. David Green Collection. Photo John Chapman.

masses to large hand size from the spoil heaps near the horse level [SE 0023 9331] as described in the foregoing text. There are also a few specimens of weathered waxy green to yellow-brown fraipontite in limonitic matrix from a spoil heap about 250 m NNW of Hill Top Shaft [SD 9973 9459] and a single specimen from one of the intermediate spoil heaps. These appear to have been collected at a later date and show that fraipontite is present along the whole length of the vein. They are different in appearance to the specimens from the horse level. Cavities in baryte and limonitic goethite contain green, yellow-brown and white spherulitic masses of fraipontite coated in a thin transparent gel-like layer (Figs 4 and 5). On some specimens the fraipontite encloses rounded granules of pale grey cerussite up to about a millimetre across (identified by EDS).

Syneresis cracks are sometimes present (Fig. 6) and it appears that the mineral has dried out and lost water (as also seems likely in the specimen from Providence Mine shown in Figure 3), or some osmotic process has resulted in shrinkage.

Semi-quantitative analyses by EDS show that the thin gel-like layer which coats the surface of specimens from Hill Top Shaft is sodium-rich fraipontite. The outer layer contains up to 5 at% Na, but the value rapidly reduces on broken surfaces to <2 at%. A wide variety of elements are present at less than 1 at%. These include calcium, iron, magnesium, nickel, phosphorus, lead and sulphur, which have been detected in samples from the other localities described in this study, and barium, copper and potassium, which have not. As well as these relatively common elements, one analysis included a little less than 1 at% thallium.

DISCUSSION

This account, which is based on a survey of a few small north-of-England collections, shows that fraipontite is more widespread in the Askrigg Block than previous records suggests. It occurs as hand-sized blocks at several localities and it is surprising that it is not

Figure 5. A thin translucent sodium-rich layer coating yellow-brown fraipontite in a cavity in baryte-goethite matrix from a spoil heap [SD 9973 9459] about 250 m NNW of Hill Top Shaft, Virgin Moss Mine, Wensleydale, North Yorkshire. The field of view is 1 mm across. David Green Collection. Photo John Chapman.

Figure 6. Syneresis cracks in pale green to brown fraipontite from a spoil heap [SD 9973 9459] about 250 m NNW of Hill Top Shaft, Virgin Moss Mine, Wensleydale, North Yorkshire. The field of view is 6.5 mm across. David Green Collection. Photo John Chapman.

recorded by Dunham and Wilson (1985). This may be 'collector bias', as massive white to brown minerals are commonly overlooked, or a reflection of the fact that fraipontite is easily confused with other minerals, as the misidentification of hydrozincite from Buckden Gavel Mine illustrates.

The localities described in the foregoing text have some commonalities. All are in highly oxidised zinc-rich deposits with an abundance of limonitic goethite in either the Main Limestone or the overlying chert. It has not been possible to examine any of the mineralisation *in situ*, but it seems probable that it formed when primary marcasite destabilised, producing acidic solutions which leached zinc and aluminium from nearby veinstone. Reaction with surrounding carbonates deposited iron oxyhydroxides, fraipontite and gibbsite as the pH increased toward neutral. A more detailed investigation of the associated species, particularly opaline silica and prosopite (Briscoe *et al.*, 2022), might help to constrain the conditions of formation.

Analyses show that fraipontite contains a wide range of minor and trace elements. It is possible that the sodium-enriched surface layers reported on the specimens from Virgin Moss Mine are the result of ion exchange produced by soaking in a sodium-rich dispersant such as Calgon®[3], a process that was popular at the time the specimens were collected. Nickel is present in samples from several localities and seems likely to have been released by the decomposition of iron sulphides. Barium, iron, lead and sulphur may be contaminant particles of baryte, goethite and cerussite, all of which are common in fraipontite-bearing assemblages. Of the other minor elements, the presence of thallium in a single analysis from Virgin Moss Mine is the most intriguing. Thallium is of concern as an environmental pollutant. Studies by more sensitive analytical techniques seem worthwhile as a single determination at a concentration of <1 at% might be an artefact. The authors would be happy to provide well provenanced samples if such research was considered worthwhile.

Problems associated with calculations of the empirical formula of fraipontite from electron microprobe data are discussed in Young *et al*. (1992). They are compounded by the fact that fraipontite is intimately intergrown with gibbsite in many specimens. They pose an interesting challenge and are discussed in more detail in the Appendix.

CONCLUSION

Fraipontite is more abundant in the Pennine orefields than the few previous reports suggest. It typically occurs as white powdery aggregates and white to pale green and yellow-brown porcellaneous masses which infill cavities in zinc-rich limonitic matrix in highly oxidised replacement deposits. White to pale green and brown masses are intimately intergrown with gibbsite and opaline silica at Buckden Gavel Mine in Wharfedale. White porcellaneous masses occur with smithsonite and hemimorphite at the isolated workings at Providence Mine near Muker in Swaledale. Colourful specimens to large hand size occur along an extensive length of vein at Virgin Moss Mine on the high ground between Wensleydale and Swaledale. Intimate intergrowths of fraipontite and the rare calcium aluminofluoride prosopite occur at Copperthwaite Vein near Reeth in Swaledale.

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APPENDIX – EMPIRICAL FORMULAE

Fraipontite is a member of the kaolinite-serpentine group of minerals, which are made up of negatively charged tetrahedrally coordinated aluminosilicate sheets (*T*-sheets) in a regular 1:1 interstratification with positively charged octahedrally coordinated sheets containing balancing divalent and trivalent metal cations (*M*-sheets).

Idealised *M*-sheets can have two distinct stoichiometries. In trioctahedral minerals all the octahedrally coordinated voids contain a divalent cation, in dioctahedral minerals two out of three of the voids contain a trivalent cation and the other is empty. Fraipontite is a member of the serpentine subgroup, which is trioctahedral, because divalent zinc ions dominate the *M*-sheet, but the presence of some trivalent *M*-sheet aluminium provides a complication.

Complexities in calculating the empirical formula of fraipontite arise because of the difficulty of unambiguously assigning aluminium to a particular structural site. Fraipontite has a structural formula that can be written:

$$(X)_3[(Y)_2O_5](OH)_4$$

where X represents octahedrally coordinated Zn^{2+}, other suitable M^{2+}, Al^{3+} and possibly other suitable M^{3+}, or a vacancy; and Y represents tetrahedrally coordinated Si or Al. The ideal formula is a rather unhelpful $(Zn,Al)_3[(Si,Al)_2O_5](OH)_4$. In view of the nature of the *M*-sheet it is better written $(Zn,Al,\square)_3[(Si,Al)_2O_5](OH)_4$ to explicitly record the presence of *M*-sheet vacancies, which are indicated by the open square, $\square$.

Calculations of empirical formulae are complicated by the intimate admixture of fraipontite with the aluminium hydroxide gibbsite and poorly crystallised iron oxyhydroxides. The analyses listed in Young *et al*. (1992) provide an opportunity to examine the procedure. At the start it seems reasonable to exclude any analyses with a large excess of aluminium (possibly due to admixed gibbsite) or iron (possibly due to iron oxyhydroxides). This leaves the data listed in Table 1.

	SiO_2	Al_2O_3	FeO	MgO	CaO	CuO	NiO	ZnO	Total
1	27.47	14.29	1.35	0.65	0.37	0.4	0.23	46.26	91.02
2	27.61	13.97	1.46	0.73	0.4	0.4	0.26	45.79	90.62
6	27.35	13.99	1.69	0.94	0.34	0.29	0.32	44.98	89.9
7	27.33	13.67	1.29	1.1	0.38	0.32	0.33	45.27	89.69
8	27.42	13.87	1.33	0.74	0.33	0.37	0.27	45.76	90.09

Table 1. Quantitative analyses of fraipontite from Virgin Moss Mine with anomalously high aluminium or iron values removed, from Young *et al*. (1992).

Calculations are then based on an idealised anionic group with five oxygens and four hydroxyls per formula unit (effectively 14 negative charges). Aluminium is added into the *T*-sheet so that Si+Al=2 and the remainder is assigned to the *M*-sheet. Any deficiency in the *M*-sheet sum, which should be 3.00, is assigned as a vacancy, and an iterative adjustment to the coefficients is made as necessary. This produces a mean empirical formula from the data listed in Table 1 of:

$$(Zn_{2.02}M^{2+}_{0.20}Al_{0.64}\square_{0.14})[(Si_{1.65}Al_{0.35})O_5](OH)_4,$$

which is charge balanced with *M*- and *T*-sheet sums of 3.0 and 2.0, respectively. There is more aluminium in the *T*-sheet than in the formula reported in the original study because full occupancy is assumed and vacancies are assigned to the *M*-sheet. Borrowing nomenclature from the zeolite group the *T*-sheet has an *R*-value:

$$R = Si/(Si+Al) = 0.825,$$

which is relatively silica rich and may be useful as a way to characterise the Si:Al ratio in the mineralising solution.

WATER SPAR:
A SEMANTIC PUZZLE

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Three uses of the term 'water spar' are examined. An early twentieth century definition which regards water spar as an intergrowth of strontianite and witherite from Victoria Level in Swaledale has gained acceptance in the mineralogical literature, but analyses show that this material is strontium-bearing aragonite, with an empirical formula $Ca_{0.95}Sr_{0.05}CO_3$. A claim that water spar is an unusual variety of celestine from the north Pennines is entirely unsupported. The earliest use of the term, in reference to the calcium carbonate flowstone encountered in caves and fissures in lead mines, is the only defensible definition.

INTRODUCTION

The changes in the meaning of words as languages develop are well known to lexicographers and language historians. Extreme cases, including words that have evolved into the opposite of their original meanings, are catalogued in Steinmetz (2008). Science is not immune to such semantic drift. Firm agreement on species names is a comparatively recent innovation and their precise definitions are still being refined. Occasional disagreements in the meaning of mineralogical terms will come as no surprise to readers. 'Water spar' furnishes one such example.

MODERN DEFINITION

Water spar is described by Tindle (2008: p. 529) as "a local (Yorkshire) name for an intergrowth of witherite and strontianite". Both of these minerals are found in lead veins in the Yorkshire Pennines (Dunham and Wilson, 1985; Young, 1987; Wood, 1993) but there are no credible reports of intergrowths (Dunham, 1990; Dunham and Wilson, 1985). Tindle (2008) cites the third edition of *Gypsum and Anhydrite, Celestite and Strontianite*, one of the *Special Reports on the Mineral Resources of Great Britain*, as the source of the definition. In that volume, Sherlock and Hollingworth (1938: p. 89) record:

> "on the waste heaps at the mouth of Victoria Level, there are quantities of a translucent white or very pale yellowish-green mineral, with mammillated surfaces and a finely-radiate internal structure; on further examination this 'water spar' (as it is known locally) proved to be a mixture of witherite and strontianite. The exact source of this peculiar mineral is not at all certain, because the Victoria Level cut two veins, the Watersikes[1] and the Watersikes Sun; but the latter was more distant from the level mouth and was probably the last to be worked so that debris from it would figure largely on the surface of the waste-heaps".

This exact paragraph also appears in the first and second editions of the same volume, with an additional note that the original identifications were made by R. G. Carruthers[2] (Sherlock and Smith, 1915; 1918). Carruthers is first author of a companion volume which deals with economic deposits of barytes and witherite and the paragraph also appears in that volume (Carruthers *et al*., 1915: p. 44).

SEMANTIC HISTORY

The claim that water spar is an intergrowth of strontianite and witherite [*vide supra*] dates from the early twentieth century, but the name has a much longer history. It is used in Woodward (1729: p. 148) in an introduction to a catalogue of 'sparry minerals'. Several of these are from lead mines in the Yorkshire Dales and in one entry (Woodward, 1729: p. 154), water spar is described as:

> "A ramose Efflorescence, of a fine white Spar, found hanging from a Crust of like Spar, at the top of an old wrought Cavern in one of Mr. Bathurst's Lead-Mines on Molderside-Hill, in Arkendale, Yorkshire. There was Water, trickling down thence, by means where of this was form'd. Its Formation must have been recent, and since that Cavern was made".

This description is consistent with calcium carbonate flowstone, possibly post-mining in origin, but more probably the lining of a mineral-bearing cave or fissure that was encountered by the miners. The term appears in other early accounts of Pennine mineral deposits, the most useful of which is Bradley (1862: p. 31) which describes water spar as:

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[1] Two different spellings are used: Dunham and Wilson (1985) prefer Watersykes whereas Carruthers *et al*. (1915) prefer Watersikes and Gill (2001: p. 73 and p. 81) uses both Watersykes and Watersikes.

[2] Robert George Carruthers (d. 1965) worked for the British Geological Survey in the first half of the twentieth century. He specialised in palaeontology and structural geology and is best known for his theories of glacial geology (L. F. P., 1966).

> "[a] chiefly calcareous Spar the result of water percolation through the Limestones and its action on the carbonate of lime".

The semantic history is further complicated by Smythe (1922: p. 114), who, at about the same time as Carruthers, offered an entirely different definition:

> "... the strontium analogue of barytes, known as celestine, has been found at Daddry Shield, near St. John's Chapel, Weardale, and also in Swaledale, at the Old Gang mine. In each case the mineral (the Water Spar of Swaledale) occurs in a vein carrying galena and is colourless, whereas the typical celestine, as the name indicates, is blue".

This is easy to discredit. Celestine has never been confirmed at any Pennine lead mine (Young, 1985; Dunham, 1990) and detailed topographic studies show that strontium substitution in baryte from Swaledale is never more than a few wt% (Small, 1977). In a comprehensive review of the mineralisation in the Askrigg Block, Dunham and Wilson (1985) note that "no free celestine occurs". As Sir Kingsley Dunham worked with J. A. Smythe, it is unlikely he would have made such a statement without reasonable evidence. The suggestion that water spar is celestine can be dismissed.

Two potential definitions remain: the older and more general reference to calcium carbonate flowstone from the lead mines of Yorkshire Dales; and the later and more specific reference to intergrowths of strontianite and witherite from Victoria Level. As the later reference is to distinctive material from a particular locality it can be investigated in more detail.

VICTORIA LEVEL

The Watersykes veins occupy substantial north-west–southeast trending faults which diverge from the east–west trending Old Rake – Reformer vein system to the east of Gunnerside Gill (Dunham and Wilson, 1985: p. 130; Gill, 2001: p. 73). The southwestern end of Watersykes Vein was tried via Jock's Crosscut from Bunton Level in Gunnerside Gill in the mid-nineteenth century. The results were encouraging and Victoria Level [NY 9659 0064] was begun in the late 1850s[3] to test the southeastern extension in the Main Limestone. It was driven WSW from Ashpot Gutter, and intersects Watersykes Vein about 567 m from the portal.

Rich lead ore was found in a baryte-calcite gangue along a strike length of 610 m, providing excellent returns for the Old Gang Company (Raistrick, 1975; Gill, 2001). The workings eventually linked up with Jock's Crosscut, which was driven a further 180 m to the southwest, cutting Watersykes Sun Vein. The intersection was sufficiently encouraging to merit a second cross-cut to explore the southeastern extension beneath Ash Pot Holes. This produced ore in the final period of working and Carruthers *et al*. (1915) suggest that it may have been the source of the water spar.

Dunham and Wilson (1985) note the occurrence of dirty white baryte, aragonite and minor strontianite on the extensive spoil heaps at Victoria Level (Fig. 1), but make no mention of water spar. Ineson and Young (2006: p. 55) record calcite, baryte and galena, and note that although water spar had been reported, specimens "are very difficult to find today".

A 'finger dump' outside Victoria Level extends for about 125 m ENE along the north bank of Ash Pot Gutter. Most of the spoil is dark shale. Sandstone, limestone, rare chert and ironstone nodules are also present and there is iron-stained carbonate veinstone near to the level mouth. The sandstone and limestone contain calcite veins which rarely develop crude crystals along a central parting. Baryte forms cellular intergrowths of chisel-shaped crystals which are typical of the area. Galena is commonly overgrown by calcite in limonitic vein breccia, and occasionally occurs as isolated matrixless masses.

The original specimen or specimens of water spar do not appear to have survived, but the description is detailed and specific (Carruthers *et al*., 1915: p. 44):

> "a translucent white or very pale yellowish-green mineral, with mammillated [*sic*] surfaces and a finely-radiate internal structure".

Similar material remains on spoil heaps near the level entrance (Fig. 2), and an old specimen in the David McCallum Collection (Fig. 3) is an excellent match.

Analysis by X-ray powder diffraction indicates the white mineral illustrated in Figure 3 is aragonite. Tiny spots of matrix suggest it was originally enclosed in brown limestone and the morphology strongly suggests that it was deposited in an open void. There is no way to

Figure 1. The spoil heap outside Victoria Level reaches about 10 m high and consists of dark shale with sandstone and limestone blocks up to about 30 cm across. Mineralised material is concentrated near to the level entrance. Photo David Green.

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[3] There is some uncertainty in the date: Gill (2001) gives 1858; Raistrick (1975) gives 1859; and Dunham and Wilson (1985) give 1860.

Figure 2. The best example of 'water spar' observed on the Victoria Level dumps in April 2021. Almost certainly aragonite flowstone, the specimen is white to pale green on the side shown in the image and pale blue-green on the reverse. It matches Carruthers' description very well with rounded "mammillated [*sic*] surfaces and a finely-radiate internal structure" on broken edges. Such material is recorded as rare by Ineson and Young (2006); this example appears to have washed out of ore-bearing material dumped near the mine entrance in the floods of June 2019. Photo David Green.

determine whether this was in a mineralised fracture or cave-like fissure, but the latter seems more likely.

The composition was determined by X-ray fluorescence spectrometry. Hand-picked material as free as possible from contamination was ground to a fine powder, sieved, and 1.00 g weighed for analysis. Fused discs were made by mixing the powder with a lithium borate flux (type 66:34 supplied by XRF Scientific, Perth, Australia) and heating in a platinum crucible. The analyses were made on a Bruker Tiger S8 XRF spectrometer. The instrument was calibrated to a nominal accuracy of 0.1 wt% in the range 0.1 to 25 wt% for aluminium, barium, calcium, iron, lead, magnesium, manganese, potassium, silicon, strontium, sodium, titanium and zinc. The accuracy was checked against prepared standards for barium and strontium, which are of particular interest in this study.

The analyses revealed that calcium is the dominant element, but it is present at such a high concentration that the measured values are beyond the calibration range. Measured values of 5.6 wt% SrO and 0.1 wt% BaO are reliable. These data correspond to aragonite with a mean empirical formula $Ca_{0.95}Sr_{0.05}CO_3$. It is almost certain, therefore, that the material described as water spar by Carruthers is strontium-bearing aragonite.

Figure 3. A broken 90 × 60 mm block of a white to very pale green silky translucent 'water spar' aragonite (identified by XRD) with rounded slightly iron-stained surfaces in the central cavity from Victoria Level, Old Gang Mines, Swaledale, North Yorkshire. Specimen E346 in the David McCallum Collection. Photo David Green.

CONCLUSION

Three contradictory definitions of ‘water spar’ are outlined in the foregoing text. The suggestion that it is celestine can be dismissed with confidence. The claim that water spar is an intergrowth of strontianite and witherite from Victoria Level in Swaledale has gained a degree of acceptance in the mineralogical literature, but analyses show that this material is strontium-bearing aragonite. The early use of water spar to describe calcium carbonate flowstone encountered in the lead mines of the Yorkshire Dales is not open to doubt. Calcium carbonate flowstone (aragonite and calcite) is common on mine dumps in Swaledale and Dunham and Wilson (1985) note that caves which post-date the primary mineralisation were found in many of the mines in the Yorkshire Dales. The origin of the term appears to be wrapped up in its association with dripping water.

POSTSCRIPT

After the article had been typeset the authors discovered an additional use of the term water spar. In a description of witherite from Snailbeach in Shropshire, Aikin (1817) noted “The veinstones are calcareous spar, often approaching to schiefer spar, and foliated heavy-spar (called here *water spar*, because from the looseness of its aggregation most of the water drains through it into the mine)”. This confirms an association with flowing water.

ACKNOWLEDGEMENTS

Thanks go to Stephen Moreton for analysis of the specimen from Victoria Level, to Tom Cotterell, Neil Hubbard, Roy Starkey and Brian Young for information about water spar, and the referees for their valuable comments.

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ANTIMONY MINERALISATION IN THE ENGLISH LAKE DISTRICT: A REVIEW

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Veins in which antimony minerals are the main or sole ore minerals have long been known at several localities across the Lake District though, apart from a vein described from Wet Swine Gill in the Caldbeck Fells, these have hitherto attracted comparatively little research interest. A small number of recently discovered and hitherto unreported occurrences, which are recorded here, await detailed mineralogical investigation. Although conclusive evidence cannot be established, it is likely that these antimony-dominated deposits pre-date the district's widespread suite of lead-zinc veins and that remobilisation of antimony contributed to the widespread occurrences of antimony-rich minerals as inclusions within galena in these later veins. At least one occurrence of stibnite-rich veinstone in drift suggests that further antimony-rich veins lie undiscovered beneath superficial deposits.

INTRODUCTION

The Lower Palaeozoic rocks of the English Lake District host a diverse suite of metalliferous veins with various ages of emplacement. Most abundant and widespread are veins dominated by copper minerals and veins in which the main ore minerals are those of lead and zinc. Smaller, but significant amounts of iron and tungsten ores, together very modest tonnages of antimony, arsenic, cobalt, manganese and nickel ores have also been worked and substantial tonnages of baryte, a common gangue mineral in many of the lead-zinc veins, have also been produced.

Lake District mining can be traced back to Elizabethan or perhaps even earlier times, and although some small scale working for zinc and tungsten ores continued into the 1980s, all mining has ceased and is unlikely ever to resume, in what is today both a National Park and UNESCO World Heritage Site. Whereas the area's main suites of metalliferous mineralisation have long been the subject of mineralogical and historical research, recorded in a voluminous literature, many aspects of the nature and working of some of the 'minor' minerals have been largely overlooked. In this paper we review the area's hitherto little understood and as yet poorly documented antimony mineralisation, drawing both upon the rather meagre published accounts and the authors' as yet unpublished observations.

GEOLOGICAL BACKGROUND

The Lower Palaeozoic rocks of the Lake District, which comprise a thick succession of sedimentary and volcanic rocks ranging in age from late Cambrian to Silurian, have long attracted research, most recently during the comprehensive re-survey of the area by the British Geological Survey (BGS) and its academic partners during the 1980s and 1990s. Excellent modern summaries of the area's geology, all of which contain references to earlier and more detailed studies, include British Geological Survey (1992), Akhurst *et al*. (1997), Eastwood *et al*. (1968), Firman and Lee (1986), Millward *et al*. (2000, 2004, 2010), Woodhall *et al*. (2000) and Stone *et al*. (2010). Whereas details of this complex geology are out of place here, the following brief overview offers the necessary context in which to view the mineralisation discussed in this paper.

The oldest of these rocks, the Skiddaw Group of late Cambrian (Tremadoc) to early Ordovician (Llanvirn) age, which comprises a succession of over 5 km of mudstones, siltstones and greywackes, occupy a wide outcrop extending from the Loweswater fells and the Skiddaw massif, eastwards to Eycott Hill near Troutbeck. These rocks also crop out in an inlier at Black Coombe, near Millom in the south of the district.

In the Caldbeck Fells, on the northern flank of the Skiddaw Group outcrop, these rocks are overlain unconformably by the varied succession of lavas and volcanic sediments, at least 3 km thick, known as the Eycott Volcanic Group of Llandeilo to Caradoc age.

On the southern flank and forming the main mountainous country of the Lake District, Skiddaw Group rocks are overlain unconformably by the Borrowdale Volcanic Group, also of Llandeilo to Caradoc age, which comprises a complex succession of in excess of 6 km of lavas, volcanic sediments and contemporaneous intrusions.

Basic intrusion complexes at Carrock Fell and Haweswater are associated with the later phases of igneous activity in the Eycott and Borrowdale groups respectively.

The gentler fell country of the southern Lake District corresponds with the outcrop of the very thick succession of mudstones, siltstones and sandstones, collectively known as the Windermere Supergroup, of late Ordovician to early Silurian age.

The modern stratigraphical classification of all of these rocks resulting from the recent BGS mapping is depicted on BGS 1:50 000 scale sheets 23 (Cockermouth) (British Geological Survey, 1997), 38 (Ambleside) (British Geological Survey, 1998) and 29 (Keswick) (British Geological Survey, 1999).

Underlying much of the Lake District is an extensive Upper Ordovician to Lower Devonian composite granitic batholith of which the exposed Eskdale, Ennerdale, Skiddaw, Threlkeld and Shap granites are part (Lee, 1986) together with a concealed granitic body which lies beneath a wide thermal aureole in the Loweswater area (Cooper *et al*., 1988).

LAKE DISTRICT MINERALISATION

In common with its geology, the Lake District's mineral deposits have also long been the subject of research resulting in a voluminous technical literature. Whereas a detailed description of the area's mineral deposits is unnecessary, the following brief summary will help to view the antimony occurrences described here in their regional geological context. In addition to the works previously cited, key works relating specifically to the mineral deposits include those by Kendall (1884), Postlethwaite (1913), Eastwood (1921), Rastall (1942), Dunham (1952), Ineson and Mitchell (1974), Dagger (1977), Firman (1978), Stanley (1979), Stanley and Vaughan (1980, 1982), Fortey *et al*. (1984), Young (1987), Cooper and Stanley (1990), Lowry *et al*. (1991), Millward *et al*. (1999) and Bevins *et al*. (2010). References to other more detailed texts are listed in these. Other works relevant to particular aspects of individual occurrences are cited in the text that follows.

Metalliferous veins are common and widespread within the varied lithologies of the Skiddaw, Eycott and Borrowdale Volcanic groups and in many of the major intrusions but are rare within rocks of the Windermere Supergroup. They may be grouped into distinct suites according to their mineralogy and likely ages of emplacement. Most abundant and widespread are suites of veins dominated by copper minerals and those in which lead and zinc ores predominate, but veins characterised by concentrations of other mineral assemblages, such as the tungsten veins at Carrock Fell and Buckbarrow Beck, the apatite-rich veins in the Ennerdale area, widespread hematite veins, and veins in which antimony sulphides are the main or sole ore minerals, and which are the subject of this paper, can also be distinguished. A notable feature of Lake District mineralisation is the apparent concentration of veins above, or close to, ridges in the roof of the concealed batholith or above its north and south walls, a close correlation which is consistent with the almost complete absence of significant mineralisation within rocks of the Windermere Supergroup (Dagger, 1977; Firman, 1978; Stanley and Vaughan, 1982).

In their review of Lake District mineralisation Stanley and Vaughan (1982) offered a genetic classification in which they proposed several mineralising episodes, in some instances within the same vein. They suggested an early Devonian age for copper and tungsten veins and, whilst acknowledging numerous close similarities between the area's lead-zinc veins and those hosted within the Carboniferous rocks of the nearby Northern Pennine orefields for which a late Carboniferous to early Permian age had been advocated by Dunham (1948) and Vaughan and Ixer (1980), proposed an early Carboniferous age for these. The widespread hematite veins were interpreted as a distal expression of the major post-Triassic hematite mineralisation of the west and south Cumbrian iron orefields. Extensive supergene alteration, perhaps as early as the Jurassic was tentatively proposed for the supergene assemblages, most notably in the Caldbeck Fells. More recently, Millward *et al*. (1999) have presented evidence for much of the area's copper mineralisation pre-dating the early Devonian cleavage-forming event. In view of the many similarities between the Lake District lead-zinc veins and those hosted within the Carboniferous rocks of the Northern Pennines, Young (in Stone *et al*., 2010) has suggested a late Carboniferous to early Permian age for the Lake District lead-zinc veins and that these may be viewed as counterparts of the North Pennine mineralisation exposed at deeper structural and stratigraphical levels in the Ordovician rocks of the Lake District.

Whilst recognising the small number of antimony veins as the products of a discrete mineralising episode Stanley and Vaughan (1982) were uncertain of the likely age of their emplacement, though Fortey *et al*. (1984) inferred that the Wet Swine Gill Vein could be contemporaneous with the early Devonian Carrock Fell tungsten mineralisation.

ANTIMONY MINERALISATION

Stanley and Vaughan (1981) described the widespread occurrence of antimony-bearing minerals as microscopic inclusions in the galena of the Lake District's main lead-zinc veins, and the presence of macroscopic tetrahedrite has been noted at Paddy End Mine, Coniston (Russell, 1925), Driggith and Roughton Gill mines on Caldbeck Fells (Hartley, 1984), Goldscope Mine, Newlands Valley (Young, 1987), and Eagle Crag Mine, Patterdale (Young, in Bevins *et al*., 2010). However, at all of these locations these antimony minerals are clearly minor constituents of those lead-zinc veins.

Those locations (Fig. 1) at which antimony minerals are the dominant, or sole, ore minerals are reviewed here. With the exception of the Wet Swine Gill Vein, published references are very brief and give little

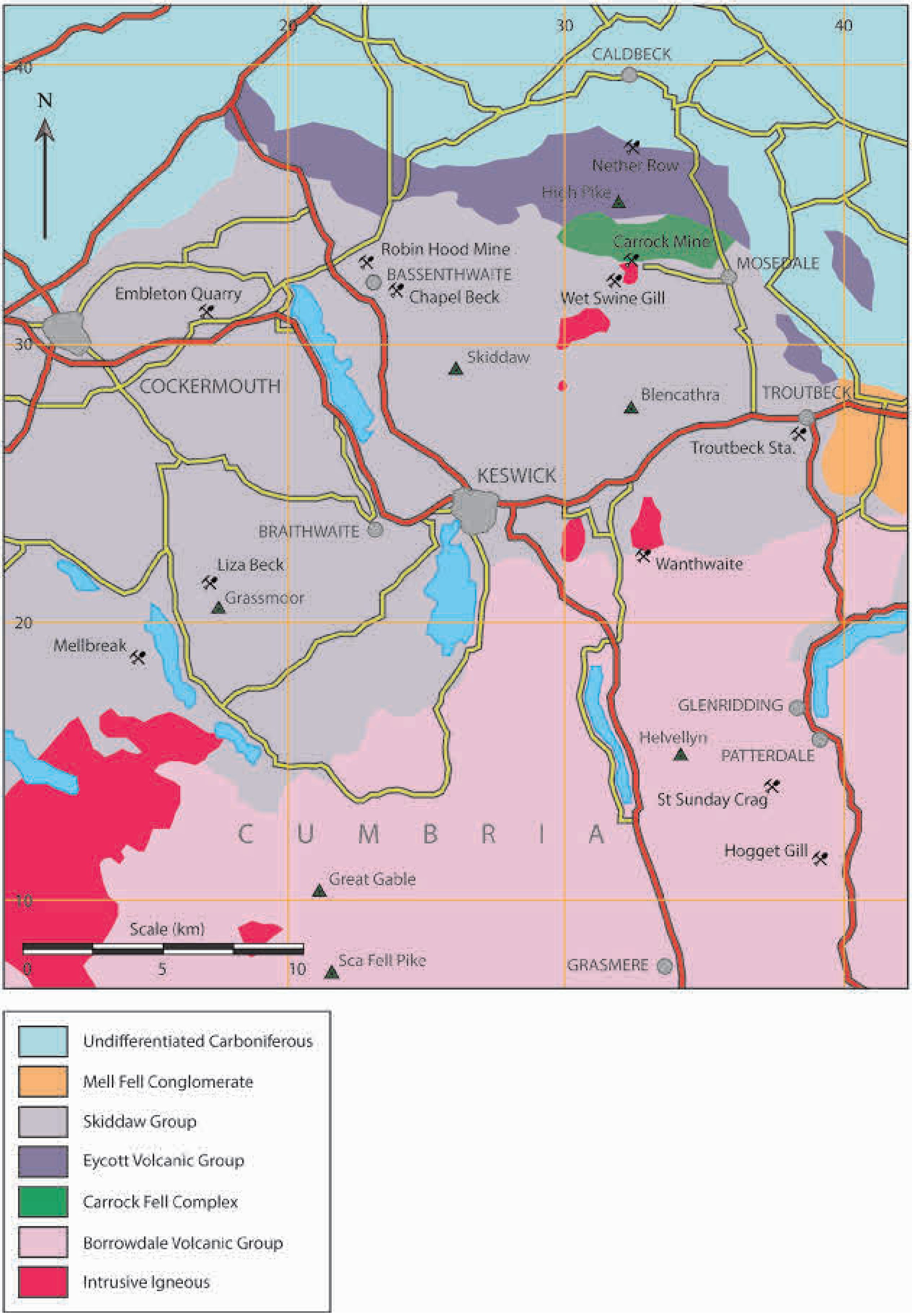

Figure 1. Simplified geological sketch map showing the locations of the principal localities described in this paper.

detail: a few are described here for the first time and several, mentioned by Kingsbury and Hartley (1956; 1958), are of dubious reliability. The possible relationship of these veins with the widespread occurrence of antimony mineral inclusions within the lead-zinc veins is examined in the discussion section.

Robin Hood Mine

Robin Hood Mine near Bassenthwaite [NY 228 330] is the only locality within the Lake District known to have been mined as a commercial source of antimony ore (stibnite) (Greg and Lettsom, 1858; Bristow, 1861; Hall, 1868; Dewey *et al*., 1920). Postlethwaite (1889–90) recorded "…20 tons … of antimony oxide [*sic*]…" obtained here, though without any indication of the date of working or any further description. Whereas no published description of the form or nature of the deposit is known and, although the site of an adit level to the northeast is depicted here within the outcrop of the Bitter Beck Formation of the Skiddaw Group on BGS 1:50 000 scale sheet 23 Cockermouth (British Geological Survey, 1997), no indication of a vein or any other information on the site or its mineralisation is depicted. Little remains today to mark the site of these workings but, although when visited by one of the authors (BY) in 1981, no mineralisation was exposed at the surface, meagre remnants of mine spoil were located from which specimens of stibnite and associated minerals were recovered. At that time, an adit driven northeast from the roadside remained open and was entered but found to be blocked only a few tens of metres inbye. Only grey Bitter Beck Formation slate wall-rock, without any sign of mineralisation, was seen.

It is assumed that the deposit comprised one or more veins of unknown width and strike length hosted within the Bitter Beck Formation of the Skiddaw Group.

Davidson and Thomson (1948) noted that stibnite occurred "... in massive form in quartz and in confused aggregates of tiny crystals ... sometimes associated with traces of stibiconite ...". Young (1987) records a specimen in the Natural History Museum collection which comprises "... radiating bladed crystals on mudstone associated with valentinite ...". Cervantite, chalcopyrite, dickite, dolomite, gold, pyrite, sphalerite, stibiconite, stibnite and valentinite are listed by Mindat (2022) but without any indication of the authentication of some of the species. A specimen of gold in the Kingsbury collection held by the Natural History Museum, is claimed to have been collected here but in view of the widespread falsification of locality details claimed by Kingsbury (Ryback *et al*., 1998, 2001), its authenticity is open to challenge: no other gold specimens are known or reported from this locality.

Specimens collected from the spoil by one of us (BY) in 1981 included stibnite in the form of randomly orientated bright grey metallic bladed crystals mainly $\leqslant 10$ mm long, and rarely up to 15 mm, within massive white quartz (Fig. 2), in places accompanied by compact white dickite and creamish white dolomite. Rare examples of clusters of acicular stibnite crystals <1 mm long filled cavities up to 10 mm across within quartz (Fig. 3). In several specimens masses of quartz-stibnite veinstone up to 30 mm across were seen to be attached to pale cream or pale brown medium grained sandstone including one in which a 25 mm wide quartz-stibnite vein with stibnite blades are orientated at right angles to the vein's walls (Fig. 4). Whereas the stibnite specimen in the Natural History Museum collection noted above is associated with mudstone wall-rock, the only wall-rock lithology seen attached to stibnite during the author's examination of the site was sandstone, a lithology present as laminae in rocks of the Bitter Beck Formation. A few examples of scattered crystals of brown sphalerite up to around 1 mm across were found associated with stibnite, quartz and dickite. No gold was found in any of these specimens. In a few veinstone blocks, yellow earth coatings and masses up to a few millimetres across were tentatively identified as stibiconite, in places pseudomorphing stibnite blades. Irregular thin crusts and pockets of yellowish-brown stibiconite up to a few millimetres across were locally common (Fig. 5) and rare white to colourless radiating crystals <1mm across were provisionally identified as valentinite.

Chapel Beck Mine (or High Mill Trial)

According to Tyler (2003) a small trial was made at Chapel Beck, Bassenthwaite [NY 238 319] in 1845, apparently following the supposed discovery of a nearby vein exposure, in which an assay of a sample, undertaken in Hamburg, confirmed the presence of antimony and reported the ore to be of very high quality, presumably for its antimony content, though this is not clear from

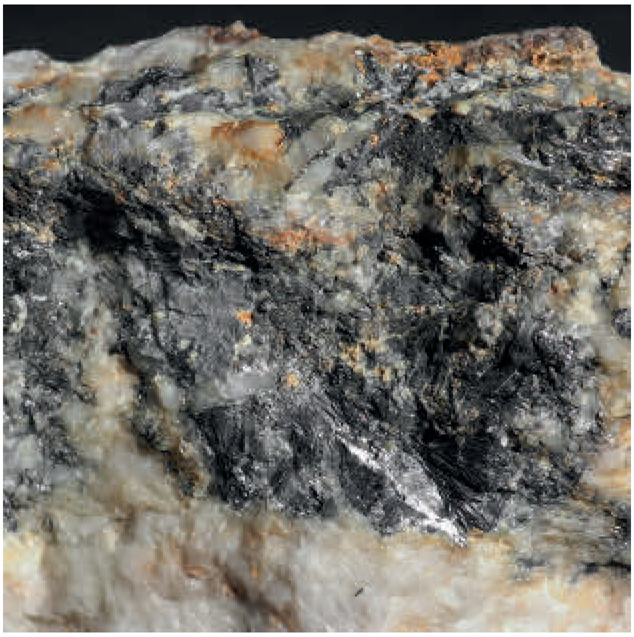

Figure 2. Bright metallic bladed stibnite crystals in quartz. Robin Hood Mine, Bassenthwaite, Cumbria. Specimen No. 2042 in the Brian Young Collection. The field of view is 25 mm across. Photo Andy Hopkirk.

Figure 3. Acicular stibnite crystals in cavity in quartz. Robin Hood Mine, Bassenthwaite, Cumbria. Specimen No. 2041 in the Brian Young Collection. The cavity is 10 mm across. Photo Andy Hopkirk.

Tyler's description. Although this vein was not recorded during the BGS re-survey of sheet 23 (Cockermouth) (British Geological Survey, 1997) a visit to the site by one of the authors (PKT) in 2000 revealed a narrow roughly east–west quartz and pyrite vein within silty mudstone wall-rocks of the Kirk Stile Formation of the Skiddaw Group in the beck. No evidence of antimony mineralisation was found and no specimens of stibnite from here are known to the authors. The original ore sample may have been derived from the nearby Robin Hood Mine, which was being worked at about this time.

Figure 4. Bladed stibnite crystals in a quartz vein in sandstone wall-rock. Robin Hood Mine, Bassenthwaite, Cumbria. Specimen No. 2040 in the Brian Young Collection. The field of view is 50 mm across. Photo Andy Hopkirk.

Figure 5. Pale yellowish brown earthy stibiconite with grey stibnite on quartz. Robin Hood Mine, Bassenthwaite, Cumbria. Specimen No. 2187 in the Brian Young Collection. The field of view is 70 mm across. Photo Andy Hopkirk.

Troutbeck Station

Two historic records from Troutbeck Station [NY 390 270] constitute the most intriguing report of Lake District antimony mineralisation.

Ward (1876) noted:

> "... in the construction of the Keswick and Penrith Railway there was discovered in blue drift-clay at Troutbeck Station, a solid block of antimony sulphide [stibnite] weighing 1 cwt [50.8 kg], and unenclosed in any matrix. Mr J. Wood tested and proved its nature as it was at first thought to be galena ...".

Postlethwaite (1913) subsequently reported:

> "... in 1895, when the line between Threlkeld and Troutbeck stations was doubled, a smaller piece of the same mineral was found in the boulder clay about 5 or 6 lbs [2.3 to 2.1 kg] weight ...".

A portion of this block, given by Postlethwaite to Sir Arthur Russell in 1912, held in the Russell Collection at the Natural History Museum (Registration No. BM 1964, R180) (Starkey, 2022), comprises a dense mass of bladed stibnite crystals up to about 15 mm long in crudely parallel alignment and similar in appearance to the few richest known stibnite specimens from Robin Hood Mine. We are unaware of any other specimens retained from these finds, and the fate of what would be extremely interesting ore samples is unknown.

Both were substantial specimens, apparently of some purity, but clearly were glacial erratics. The finding of two large samples within the wide assortment of glacially transported erratics invites speculation on the presence of a significant stibnite-bearing vein in the catchment of the till (boulder clay) here. Whereas many aspects of the Quaternary history of the Lake District remain elusive (Evans, 2015), a southerly or south-easterly derivation appears most likely for the till deposits preserved today around Troutbeck. Thus, it seems most probable that the source of the stibnite boulders here lay in those directions. Thus, although Russell's stibnite-rich specimen bears some resemblance to the Robin Hood material, it is difficult to envisage a mechanism whereby this, or any other occurrence near Robin Hood, could have contributed to the till at Troutbeck.

Caldbeck or Carrock Fells

Although Greg and Lettsom (1858) and Hall (1868) made reference to stibnite, or 'antimonite' from this rather vague location they gave no descriptions of the mineral and offered no more precise locality information. Kingsbury and Hartley (1956) suggested that in view of their claims of other antimony species at Carrock Fell Mine, these imprecise earlier reports may have been misidentifications. However, it is perhaps just possible that these earlier authors might have been aware of the Wet Swine Gill occurrence, or of specimens derived from it, or from other Caldbeck Fell locations, e.g. Netherrow.

Wet Swine Gill

Notwithstanding the possibility that specimens from here may have been known to Greg and Lettsom (1858) and Hall (1868) (see above), the vein at Wet Swine Gill on Coombe Height [NY 3144 3215] appears to have been unknown, or at least forgotten, until discovered by the late John Ingham in the early 1980s. Unusually for a then relatively well exposed Lake District vein, no evidence of any trial excavations on it were found. The vein has been the subject of the most detailed investigation of any Lake District antimony-bearing vein. Fortey *et al.* (1984) gave details of its mineralogy and interpretations of its likely origins and significance in furthering understanding of the origins and evolution of Lake District metalliferous mineralisation and only a brief summary of the main aspects of the occurrence will be given here. The site is today notified as a Site of Special Scientific Interest (SSSI) and has been further described and interpreted in the Geological Conservation Review volume (Young in Bevins *et al.*, 2010). However, the vein exposure is today concealed beneath landslipped debris from the stream banks.

The vein cuts hornfelsed silty mudstones of the Kirk Stile Formation of the Skiddaw Group in the aureole of the Skiddaw Granite. When examined by Fortey *et al.* (1984) it was seen to be up to 0.5 m wide, striking northeast–southwest and dipping steeply to the southeast. It consists of fine- to medium-grained quartz, commonly with a spherulitic texture, in which occur scattered irregular patches of a wide range of fine-grained antimony ore minerals, listed in approximate order of abundance by Fortey *et al.* (1984) as: stibnite, zinckenite, berthierite, jamesonite and very minor amounts of native antimony, semseyite and fülöppite, sphalerite and arsenopyrite (Fig. 6). Due to their fine-grained and intergrown nature few of these minerals can be reliably identified in hand specimen: their identities were determined by XRD, polished thin sections and microprobe analyses. Although the distribution of metallic minerals is uneven within the vein, X-ray fluorescence examination of small ore-rich fragments revealed maximum antimony values of over 15% (D. J. Bland, *personal communication* in Fortey *et al.*, 1984).

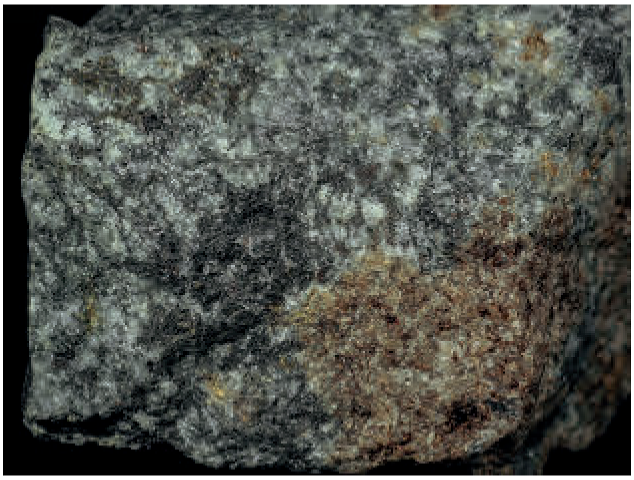

Figure 6. Typical specimen of rich Wet Swine Gill veinstone. Wet Swine Gill, Caldbeck Fells, Cumbria. Specimen No. 4801 in the Brian Young Collection. The field of view is 45 mm across. Photo Andy Hopkirk.

Stibnite occurs as needle-like crystals up to 4 mm long, commonly forming tufts extending into intergranular vugs within quartz. Zinckenite forms patches up to 15 mm across which locally enclose small bundles of stibnite crystals. Berthierite is present as stout prisms up to 2 mm long. Jamesonite occurs as straight or curved capillary crystals between 60 and 250 μm long with diamond cross sections 2 to 20 μm in width. Fülöppite occurs as dark grey patches of metallic fibrous crystals associated with stibnite; semseyite as thin coatings or as rare minute ($\leqslant$20 μm diameter) inclusions in zinckenite; and native antimony as $\leqslant$20 μm diameter granules in quartz. Sphalerite is present as rare orange-red grains <50 μm wide and arsenopyrite was noted as clusters of euhedral crystals up to 60 μm across. Supergene minerals reported by Fortey *et al.* (1984) include buff-coloured earthy stibiconite, commonly replacing bladed antimony sulphide and sulpho-salt minerals (Fig. 7) and pale yellow bindheimite forming thin earthy crusts on joint surfaces of veinstone (Fig. 8). Thin films of a red mineral were suggested to be kermesite, though insufficient material was available to confirm this. Subsequent authors have added stibioclaudetite (Leppington and Green, 1998; Green *et al.*, 2014), parasymplesite (Neall and Green, 2001), metastibnite and valentinite (Tindle, 2008) to the supergene assemblage.

Fortey *et al.* (1984) also described a second vein, carrying small amounts of jamesonite and tourmaline with light grey supergene patches tentatively identified as stibiconite, also hosted in hornfelsed mudstones of the Kirk Stile Formation, exposed in the trackside approximately 500 m east of the Wet Swine Gill vein [NY 3212 3224].

Figure 7. Pale buff stibiconite replacing bladed antimony sulphides. Wet Swine Gill, Caldbeck Fells, Cumbria. Specimen No. 3033 in the Brian Young Collection. The field of view is 10 mm across. Photo Andy Hopkirk.

Nether Row Farm Level

At Nether Row Farm Level on the northern edge of the Caldbeck Fells [NY 3230 3704] a small and very much overgrown spoil heap contains veinstone from a trial level driven into one or more veins within the andesitic tuffs and breccias of the Potts Ghyll Formation of the Eycott Volcanic Group. Excavations in the heap during the BGS investigation of the Caldbeck Fells in 1986, revealed a small number of blocks of fine-grained colourless to white quartz in which cavities up to around 1 mm across were lined with tiny lustrous small dark grey acicular crystals and fibrous masses of boulangerite and jamesonite, together with small grains up to 2 mm across of massive bournonite and arsenopyrite, all confirmed by XRD. This veinstone differed markedly from other mineralised material in the dump in which lead and arsenic supergene species predominated. The occurrence is intriguing as it suggests that a small antimony-rich vein may have been cut in these trail workings.

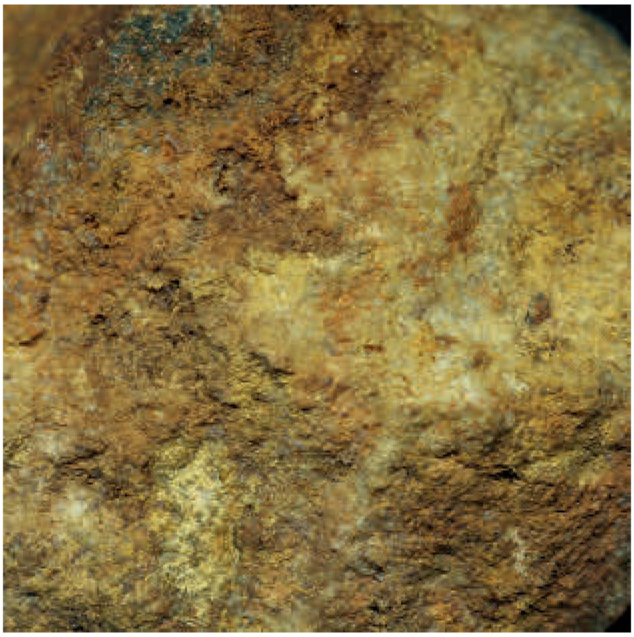

Figure 8. Earthy coatings of yellow to brown bindheimite on quartz. Wet Swine Gill, Caldbeck Fells, Cumbria. Specimen No. 5868 in the Brian Young Collection. The field of view is 35 mm across. Photo Andy Hopkirk.

A few fragments of similar antimony-rich veinstone, also without lead and arsenic species, have been found both by one of the authors (PKT) and separately by C. M. Leppington (*personal communication*) from the Endeavour Level dump at Potts Gill Mine [NY 319 365], though it has not been possible to positively identify the antimony minerals present in this material. No other occurrences of obvious antimony mineralisation are known from the numerous spoil heaps on the adjacent fells.

Saint Sunday Crag

Kendal (1884) referred briefly to the presence of stibnite at Saint Sunday Crag in the Helvellyn Range [NY 36 13] though without any description or more precise location details. Davidson and Thomson (1948) also claimed the mineral from here as "... small needle-thick veinlets ... in quartz strings ...", also without location or more detailed descriptive details. No sign of veins matching this description were seen within the varied lithologies of the Helvellyn and Deepdale formations of the Borrowdale Volcanic Group exposed on Saint Sunday Crag during the detailed BGS re-survey of the area in the 1980s, and we are unaware of the whereabouts of any specimens collected here. Although the reports thus remain unsubstantiated, it is interesting to note that macroscopic specimens of tetrahedrite, some exhibiting good euhedral crystals, are comparatively common on the spoil heaps from workings on lead-zinc veins at Eagle Crag and Nethermost Cove at the head of Grisedale.

Hogget Gill

The presence of rich concentrations of berthierite within blocks of quartz built into the walls of an older smelt mill at Hogget Gill, Patterdale [NY 3888 1132], was reported as a personal communication from C. J. Stanley by Fortey *et al*. (1984). This material was still visible in the old walls when visited by one of the present authors (BY) in 1983 and the identity of the abundant berthierite was confirmed by XRD from small samples taken from loose blocks. In the richest specimens berthierite occurs as compact masses up to >45 mm across composed of crudely parallel, slightly curved, narrow bladed, bright grey metallic crystals up to >10 mm long and around 1 mm wide within massive white and locally brown iron-stained quartz (Fig. 9). A few loose quartz veinstone boulders found here contained abundant berthierite as 3 mm thick crusts up to >30 mm across, accompanied by minute arsenopyrite

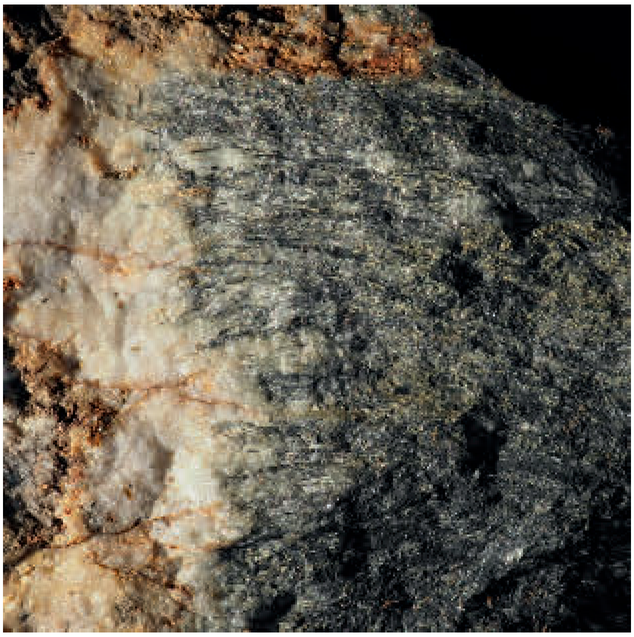

Figure 9. Rich mass of bladed berthierite crystals in quartz. Hogget Gill smelter site, Patterdale, Cumbria. Specimen No. 2629 in the Brian Young Collection. The field of view is 25 mm across. Photo Andy Hopkirk.

crystals. Within the 0.9 to 1.5 m wide plexus of quartz veins exposed here within volcaniclastic sediments of the Deepdale Formation of the Borrowdale Volcanic Group, the only antimony sulphide identified by XRD was jamesonite in the form of narrow bladed crystals up to 15 mm long (Fig. 10), together with tiny >0.5 mm long acicular crystals within small cavities in quartz (Fig. 11), accompanied locally by small (mainly >1 mm) euhedral pyrrhotite crystals and a few supergene coatings of pale yellow bindheinite. Whereas Stanley (*personal communication*) suggested that the berthierite-rich blocks within the smelter are likely to have been derived from an east–west trending vein exposed within the adjoining bed of Hogget Gill they are not a close match to the veinstone exposed here today and it is not clear whether these exposed veins were the source of the berthierite-rich blocks present at the smelter site. If not, at least one other antimony-rich vein may remain undiscovered in the vicinity, though no such vein was identified during the recent detailed BGS mapping of the area.

Figure 10. Bladed crystals of jamesonite in quartz. Vein exposure in bed of Hogget Gill, Patterdale, Cumbria. Specimen No. 3506 in the Brian Young Collection. The field of view is 15 mm across. Photo Andy Hopkirk.

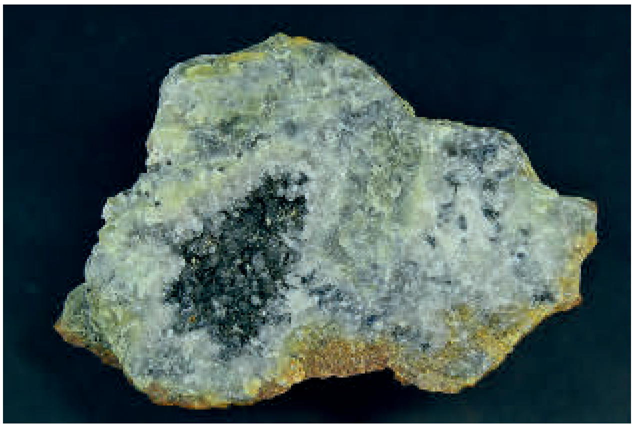

Figure 11. Acicular crystals of jamesonite in cavity in quartz. Vein exposure in bed of Hogget Gill, Patterdale, Cumbria. The field of view is 50 mm across. Photo Peter Todhunter.

Carrock Mine

At Carrock Mine [NY 323 329] tungsten-bearing veins cut metamorphosed Kirkstile Formation (Skiddaw Group) mudstones, greisenised Skiddaw Granite and members of the Carrock Fell intrusive complex. Kingsbury and Hartley (1956) recorded small amounts of boulangerite, jamesonite and zinkenite. It is noteworthy that there are no subsequent reliable reports of these minerals from these much studied veins. However, it is conceivable that some specimens of cosalite and bismuthinite, both of which have been reliably recorded from these veins in more recent years and which commonly exhibit a closely similar habit to the species noted by Kingsbury and Hartley, may have been misidentified. In discussing the origins and affiliations of the Wet Swine Gill Vein Fortey *et al.* (1984) speculated that Kingsbury and Hartley's record of antimony minerals in the Carrock Fell veins might indicate a genetic connection and that the early quartz- and antimony-iron-arsenic mineralisation at Wet Swine Gill may be coeval with the early sulphide mineralisation at Carrock Fell.

Embleton Quarry

Specimens of stibnite associated with gold, arsenopyrite, tetrahedrite, dickite and scorodite said to have been collected from quartz veins cutting the diorite intrusion at Embleton Quarry [NY 175 308] by Arthur Kingsbury are held in the Kingsbury Collection at the Natural History Museum. The only mineralisation visible in this quarry in recent decades is an east–west trending 0.3 m wide vein composed of quartz, dolomite, dickite and minor chalcopyrite. It carries no stibnite or other obvious antimony minerals and bears no resemblance to any other stibnite bearing veins in the area. The Kingsbury specimens do not resemble the veinstone seen by the authors at this location. Whereas it is, of course, possible that an antimony-bearing vein may have been exposed at the time of Kingsbury's visit, it is noteworthy that no other specimens of antimony minerals, or indeed gold, from here are known in other collections. Therefore, in view of Kingsbury's widespread falsification of locality details (Ryback *et al.*, 1998, 2001) together with the present authors' observations at this location the presence of stibnite here must be viewed as at best unconfirmed and probably unlikely.

Wanthwaite Crags

Lead- and arsenic-bearing veins locally occupy the complex faulted contact of the Buttermere Formation of the Skiddaw Group with the Birker Fell Formation of the Borrowdale Volcanic Group on Wanthwaite Crags, St John's in the Vale [NY 325 226].

Postlethwaite (1913) refers to stibnite from here though without any further description and we are unaware of any specimens from this location. Kingsbury and Hartley (1958) also list stibnite associated with arsenopyrite, pyrite, sphalerite and unspecified "sulpho-salts" in a quartz-carbonate gangue, and Young (1987) notes a specimen of stibnite in the Kingsbury Collection in the Natural History Museum as:

> "... radiating aggregates in quartz in places associated with kermesite and senarmontite from the dumps of No. 3 Level on the South Vein ...".

A specimen of jamesonite, claimed to have been collected here by Kingsbury is also in the Kingsbury Collection in the Natural History Museum. Despite repeated careful searches at this location none of the mineralisation seen by the present authors or described by others at Wanthwaite Crags bears any resemblance to the Kingsbury specimens or indeed to any other Lake District stibnite occurrences. In view of its Kingsbury associations, the presence here of stibnite or other antimony mineralisation is thus doubtful.

Gasgale Gill and Force Crag

The deeply incised valley of the Liza Beck, known as Gasgale Gill, coincides approximately with a belt of roughly east–west thrusting and faulting within the mudstones and greywacke sandstones of the Kirkstile and Loweswater formations of the Skiddaw Group along the northern margin of the belt of thermal metamorphism and metasomatism known as the Crummock Water aureole (Cooper *et al.*, 1988).

Loose blocks of white quartz within the stream beneath Gasgale Crags [NY 174 215] have been found to contain local concentrations of bright grey metallic bladed crystals of stibnite up to around 10 mm long (David Green, *personal communication*). This veinstone, which resembles that of Robin Hood Mine, has not been found *in situ* here, though a belt of ENE–WSW trending parallel white to pale grey quartz veins up to around 2 m wide forms a conspicuous rib on the southern flank of Whin Ben on the north side of the beck [NY 1645 2110]. Much of the quartz comprises radiating crystalline spherulitic aggregates up to 25 mm across in which local concentrations of widely scattered bright mostly subhedral arsenopyrite crystals up to 1 mm across are accompanied by similarly sized rare grains of dark brown sphalerite and locally galena. In addition, a few specimens contain scattered aggregates of sub-parallel acicular lustrous crystals of an as yet unidentified grey metallic mineral. Its appearance is consistent with that of stibnite and it is conceivable that this vein, or an eastwards extension of it, could be the source of the stibnite-bearing quartz noted previously.

Further east, blocks of stibnite-bearing quartz, similar to the loose blocks already described from Gasgale Gill have been found on dumps from the uppermost workings of Force Crag Mine [NY 192 215] (Fig. 12). The main Force Crag Vein exhibits a very similar ENE–WSW trend to that exposed on Whin Ben which may be a westerly extension of it. It is therefore possible that these stibnite-bearing blocks may be derived from the Force Crag Vein or a branch of it, though no *in situ* exposures of stibnite-bearing veinstone has been found here.

These occurrences merit detailed investigation.

Mellbreak

On the col between the two summits of Mellbreak above Crummock Water [NY 144 189] a hitherto unrecorded east–west striking quartz vein up to 0.5 m wide is exposed cutting mudstones and greywacke

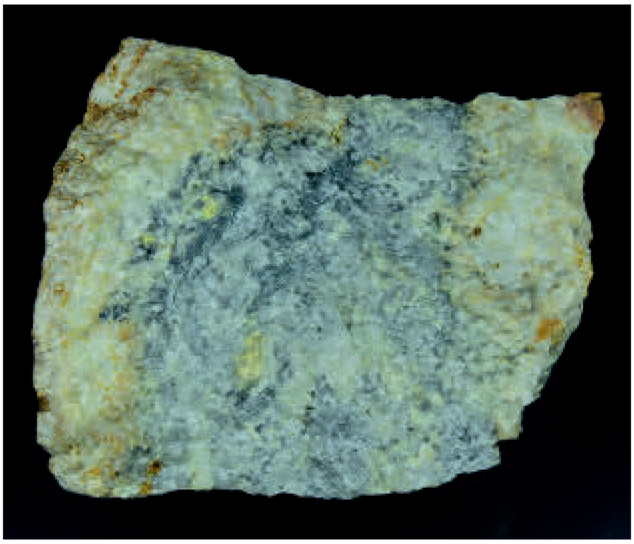

Figure 12. Small bladed stibnite crystals in quartz. Old dump above the upper workings of Force Crag Mine, Braithwaite, Cumbria. The field of view is 70 mm across. Photo Peter Todhunter.

sandstones of the Kirkstile Formation of the Skiddaw Group which here lie within the broad zone of metamorphism and metasomatism of the Crummock Water aureole (Cooper *et al*., 1988) (Fig. 13). It consists predominantly of fine-grained quartz in which rich pockets of finely crystalline bright grey metallic sulphides up to 5 cm across are common (Fig. 14). Small crystals of arsenopyrite, pyrite and rare sphalerite up to 1 mm across are accompanied by conspicuous concentrations of a silvery grey metallic mineral forming bladed crystals up to 1 mm long, in places forming feather-like aggregates (Fig. 15). Much of this veinstone bears a remarkably close resemblance to that of the Wet Swine Gill Vein, described above and, although no conclusive determinations of the included minerals has been possible, the bladed mineral is here tentatively suggested to be stibnite or a similar antimony mineral. Surrounding these concentrations of grey sulphides the fine-grained quartz exhibits a pale brown cellular appearance apparently resulting from supergene alteration of the sulphides, a feature also commonly seen in the Wet Swine Gill Vein.

The vein was not identified during the re-mapping of BGS sheet 29 (Keswick) (British Geological Survey, 1999) though a number of minor faults were identified on the hill top. It can be traced eastwards towards the steep crags on the eastern side of the hill and further exposures of what may be the same vein can be traced on the lower slopes of the hill above the eastern side of Crummock Water.

This occurrence also merits further investigation.

Figure 13. Stibnite-bearing vein exposure on the summit of Mellbreak, Crummock Water, Cumbria. Photo Peter Todhunter.

Figure 14. Typical specimen of stibnite-rich veinstone. Mellbreak, Crummock Water, Cumbria. The field of view is 100 mm across. Photo Peter Todhunter.

DISCUSSION

Antimony-bearing minerals occur within two principal parageneses in the Lake District. They are the dominant or sole ore minerals in quartz veins at the localities discussed here and are also present as inclusions within galena, or as macroscopic accessory amounts, in the much more widespread suite of lead-zinc veins.

Apart from the Wet Swine Gill occurrence very little research has been undertaken on the Lake District's antimony-dominated veins, save for confirming the identity of species found within some of them.

For most locations the antimony mineralisation discussed here is known only from mine spoil or, in the case of Troutbeck Station, glacial erratic blocks. *In situ* exposures of confirmed antimony minerals are known only from Wet Swine Gill and Hoggett Gill, together

Figure 15. Small plume-like aggregates of stibnite in quartz. Mellbreak, Crummock Water, Cumbria. The field of view is 30 mm across. Photo Peter Todhunter.

with the as yet unconfirmed occurrences, reported here from Mellbreak and Gasgale Gill. Even in these locations exposure is very limited. The Wet Swine Gill Vein is today concealed by material slipped from the stream banks and is no longer available for study *in situ*. The stibnite occurrence at Saint Sunday Crag relies on unsubstantiated reports by Kendall (1884) and Davidson and Thomson (1948) and is not supported by any known specimens and no signs of antimony mineralisation were found here during the detailed BGS mapping of the area during the 1980s. Doubts remain over the authenticity of the locations known only from descriptions by Kingsbury and Hartley (1956; 1958). Despite Robin Hood Mine being the only known Lake District site from which antimony ores are known to have been worked almost nothing is known of the nature of the deposit or of its likely origins or affinities. As noted above, the small deposit is assumed to comprise one or more veins of unknown orientation, width and extent hosted within the Bitter Beck Formation of the Skiddaw Group. Apart from the rather inconclusive suggestion of antimony mineralisation at Chapel Beck, Robin Hood is isolated by several kilometres from the nearest centres of metalliferous mineralisation of any type.

At Wet Swine Gill, Fortey *et al*. (1984) demonstrated that an early phase of antimony-arsenic-iron mineralisation comprising stibnite, berthierite, jamesonite, native antimony, antimony-rich arsenopyrite and sphalerite was followed by a later phase of antimony-lead mineralisation characterised by zinckenite, fülöppite and semseyite. Based upon Kingsbury and Hartley's (1956) reports of stibnite, boulangerite, jamesonite and zinckenite from the nearby Carrock Fell tungsten veins they suggested that the early phase of antimony mineralisation may be related to, and perhaps synchronous with, those veins of Devonian age. They further proposed that the zinckenite, fülöppite and semseyite assemblage reflected a later, perhaps Carboniferous, mineralising event in which antimony was remobilised by the lead-rich fluids responsible for the widespread lead-zinc veins of the Lake District. Since the presence of stibnite, boulangerite, jamesonite and zinckenite within the Carrock Fell veins has not been supported by subsequent studies, and in view of the serious doubts over the veracity of many of Kingsbury and Hartley's reports, unknown to Fortey *et al*. (1984) at the time of their investigation, the linking of the genesis of the Wet Swine Gill and Carrock Fell Mine veins is now rather less secure. However, fluid inclusion studies of the Wet Swine Gill and Carrock Fell veins, which reveal significant similarities with data obtained from studies of antimony deposits in the Massif Central of France (Bril, 1982) in which a genetic relationship can be demonstrated between antimony and tungsten and arsenic-bearing veins, lend support to the suggestion by Fortey *et al*. (1984) of a genetic link with the Devonian age tungsten mineralisation at Carrock Fell Mine.

As noted above, the stibnite occurrences at Gasgale Gill, and perhaps that at Force Crag, are closely similar both in appearance and apparent mineralogy to the Robin Hood deposit and the provisionally identified stibnite occurrence on Mellbreak appears to bear a remarkably close similarity to that seen at Wet Swine Gill. The discovery of stibnite from the Force Crag Vein suggests that stibnite may form part of a limited local development of an early phase of pyrite, marcasite, arsenopyrite mineralisation here consistent with the widespread Lake District Cu-Fe-As mineralisation. However, without further investigation, reliable comparisons between any of these occurrences, and speculations on their origins, would be premature.

It is worth noting that the Mellbreak mineralisation is hosted in bleached Kirk Stile Formation (Skiddaw Group) mudstones, today recognised as the Crummock Water aureole (Cooper *et al.*, 1988). The Gasgale Gill and Force Crag mineralisation is hosted in the same stratigraphical units within a kilometre north of the margin of this aureole. This zone of intense thermal metamorphism and metasomatism overlies a postulated concealed granitic intrusion (Ixer *et al*., 1979; Cooper *et al*., 1988). The metasomatism has been dated by Cooper *et al*. (1988) at 401±3 Ma. These authors noted that rocks within the aureole exhibit significant depletion in elements including Cl, Ni, S, Ni, Zn, Cu, Fe, Li, and Mn, together with net additions of As, B, K, Rb, Ca, F and Si. Quartz-tourmaline veins are abundant (Fortey and Cooper, 1986) and quartz-chlorite-apatite veins at Scar Crag and elsewhere in the area (Clark, 1963; Ixer *et al*., 1979; Young, 1987; Young, in Bevins *et al*., 2010; British Geological Survey, 1992) have also been attributed to a mineralising event associated with the formation of the aureole. In addition to the minerals listed, the Scar Crag Vein is notable for carrying small amounts of cobalt and arsenic minerals. Stanley and Vaughan (1982) assigned a Lower Devonian age to the Scar Crag Vein. Whereas Cooper *et al*. (1988) made no specific reference to antimony within the aureole, it is conceivable that mobility of that element within the aureole may account for the stibnite vein on Mellbreak. However, it is difficult to suggest any genetic connection between this metasomatism and the more distant Lake District centres of antimony mineralisation.

The occurrence of glacial erratic blocks of stibnite at Troutbeck is intriguing. These plainly indicate the presence of a deposit with at least locally rich concentrations of this mineral somewhere within the catchment for the till at Troutbeck. As discussed, a southerly or south-easterly derivation seems most likely for this and thus also the two stibnite-rich erratic boulders. No occurrences of antimony-rich material resembling these erratics are known within the likely source area of this till and, although these bear some resemblance to the ore mined at Robin Hood, the known ice-flow directions are inconsistent with the Bassenthwaite area as a possible source for these stibnite-rich erratics. It is therefore reasonable to suppose that an as yet undiscovered stibnite-rich vein, or veins, probably concealed beneath glacial or post-glacial deposits must lie somewhere within the source area of the Troutbeck till. The finding of this material on two occasions may be either serendipitous or could conceivably reflect a comparative abundance of such material. A careful watch for further stibnite-bearing erratics should be kept on further groundwork in the till of this area.

From this review it is clear that antimony-dominated mineralisation is more widespread across the Lake District than previously supposed, though insufficient data exist to propose any relationship between these veins and structural or igneous features, including the form of the underlying Lake District batholith.

The common occurrence of antimony-bearing minerals as inclusions within galena in the lead-zinc veins of the Lake District (e.g. Stanley, 1979; Stanley and Vaughan, 1981, 1982), and local abundance of tetrahedrite and other antimony-lead sulpho-salts within veins such as those at Paddy End Mine, Coniston (Russell, 1925), Driggith and Roughton Gill mines on Caldbeck Fells (Hartley, 1984), Goldscope Mine, Newlands Valley (Young, 1987), Eagle Crag Mine, Patterdale (Young, in Bevins *et al*., 2010), is consistent with the suggestion of Fortey *et al.* (1984) that a second phase of mineralisation which at Wet Swine Gill deposited zinckenite, fülöppite and semseyite, resulted from the remobilisation of antimony during a later phase of mineralisation which emplaced the Lake District's widespread lead-zinc veins.

CONCLUSIONS

Lake District veins in which a variety of antimony minerals are the main or sole metallic ores are more widespread than previously recorded.

These veins may be the product of a single early mineralising event, though the available evidence of its age of emplacement remains inconclusive.

Remobilisation of antimony during emplacement of widespread lead-zinc mineralisation of Carboniferous age may have resulted in the formation of abundant micro-inclusions of antimony sulphosalts in galena together with local macroscopic concentrations of tetrahedrite group minerals in some lead-zinc veins.

Newly discovered occurrences of antimony-dominated mineralisation merit further investigation.

An apparently rich and unknown stibnite-bearing vein must lie concealed somewhere within the source area of the till deposits at Troutbeck Station.

Some previous reports of antimony mineral locations appear unreliable.

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FERRISURITE FROM WANLOCKHEAD, DUMFRIES AND GALLOWAY: THE FIRST BRITISH OCCURRENCE

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The first British occurrence of ferrisurite, a structurally complex mineral in which smectite-like layers are intergrown with lead carbonate layers, is reported from Whyte's Cleuch, Wanlockhead, Dumfries and Galloway. Ferrisurite is the fifth lead-bearing silicate mineral recorded from Leadhills–Wanlockhead. A comparison with similar worldwide localities suggests other unusual lead silicates remain to be discovered in the area.

INTRODUCTION

Ferrisurite was originally described on dump-collected specimens from the Shirley Ann Mining Claim west of Death Valley, Inyo County, California, USA (Kampf *et al*., 1992). It has also been reported at Rivet Quarry, Réalmont, Occitanie, France; Monte Avanza Mine, Forni Avoltri, Udine, Italy; and the Blue Bell Mine, San Bernardino County, California, USA (Mindat, 2022a). At the type locality, lead-bearing supergene minerals occur with galena in metamorphosed micritic limestones (McAllister, 1955). Ferrisurite is thought to have formed in the early stages oxidation when supergene fluids attacked silicates in close proximity to galena.

As the name suggests, ferrisurite is related to surite, a rare supergene mineral first noted from the Cruz del Sur Mine, Comicó, Rio Negro, Argentina (Hayase *et al*. 1978). Surite has also been identified at Su Elzu, Ozieri, Sardinia, Italy; Can Rovira Quarry, Barcelona, Spain; Mammoth-Saint Anthony Mine, Pinal County, Arizona, USA; and Tsumeb Mine, Oshikoto, Namibia (Mindat, 2022b).

Although surite and ferrisurite are classed as clay minerals, they are not typical of the group as a whole. Their structure is an intercalation of smectite-like $(Fe,Al)_2(Si,Al)_4O_{10}(OH)_2{\cdot}nH_2O$ layers and lead-carbonate layers. The carbonate layers are described in Kampf *et al*. (1992) as varying in composition between cerussite and hydrocerussite. This has given rise to relatively complex formulae. The International Mineralogical Association currently approves $(Pb,Ca)_3Al_2(Si,Al)_4O_{10}(CO_3)_2(OH)_3{\cdot}0.3H_2O$ for surite and $Pb_{2.4}Fe^{3+}_2Si_4O_{10}(CO_3)_{1.7}(OH)_3{\cdot}nH_2O$ for ferrisurite (CNMNC, 2022). These can be interpreted as smectite-like layers, with Al^{3+} or Fe^{3+} at the octahedral site, intergrown with lead carbonate layers. The formula:

$$(Pb,Ca)_{2.5-3}(Fe,Al)_2(Si,Al)_4O_{10}(CO_3)_{1.5-2}(OH)_{2.5-3}{\cdot}nH_2O,$$

based on an $[O_{10}(CO_3)_{1.5-2}(OH)_{2.5-3}]$ anion group with between 25.5 and 27 charges per formula unit, is probably a more realistic reflection of the chemistry and structure. It allows some variability in the Si:Al ratio in the tetrahedral sheets, a feature which is typical of phyllosilicates.

LOCATION

Whyte's Cleuch is a small northeast–southwest trending valley about 1 km northwest of the village of Wanlockhead, Dumfries and Galloway. It lies within the Leadhills–Wanlockhead Site of Special Scientific Interest (SSSI), which was notified in 1990 for its mineralogical interest (Scottish Natural Heritage, 2019). A number of broadly north–south striking lead-copper veins hosted by sandstones and siltstones of the Ordovician Portpatrick Formation cut the valley sides (British Geological Survey, 1987). Numerous small spoil heaps contain a broad range of primary and supergene minerals.

The geology of the area is described in Floyd *et al*. (2002), with a summary in Floyd (2003). A detailed survey of the minerals is provided in Temple (1954) with a summary in Temple (1956). The species for which the district is famous are described in Gillanders (1991), Livingstone (2002) and Tindle (2008).

SPECIMEN DESCRIPTION

This study is based on a specimen, registered as BM 2019,3, in the mineral collection of the Department of Earth Sciences at the Natural History Museum (NHM), London. A dull greenish phase covers an area about 5 × 10 mm in a 20 × 16 × 14 mm fragment of iron-stained quartz (Fig. 1).

Examination using stereomicroscope reveals masses of intergrown fibres up to about 0.4 mm across, ranging from greenish white through khaki-green to deep olive-green (Fig. 2). Cavities in the surrounding quartz contain skeletal iron oxyhydroxides, the three-dimensional shape of which suggests the former presence of galena. Some cavities contain tiny prismatic white to very pale green crystals, assumed to be phosphohedyphane, which are later in the supergene paragenesis.

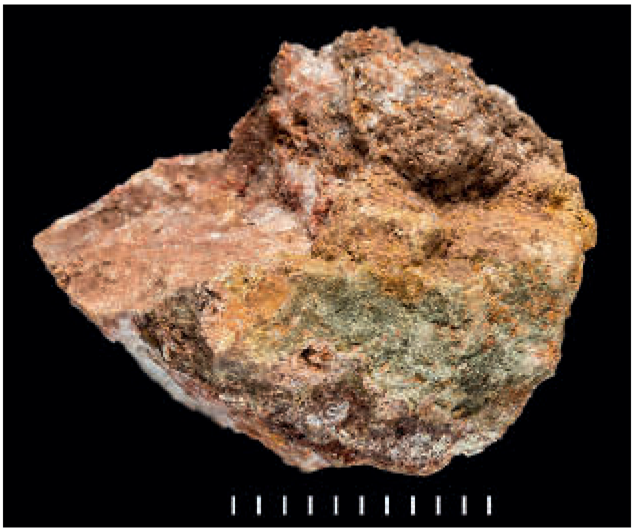

Figure 1. A whole-specimen photo of specimen BM2019,3, showing greenish ferrisurite on iron-stained quartz. Scale bar intervals are 1 mm. Photo © Trustees of the Natural History Museum.

ANALYSIS

Initial investigations were made by energy-dispersive X-ray spectrometry (EDS) on a Zeiss EVO scanning electron microscope. A small fragment of the fibrous mineral was removed and mounted on a carbon-coated stub. Analyses revealed the presence of aluminium, iron, lead and silicon. Ferrisurite is one of very few mineral species which contain all of these elements and comparisons with a specimen from the type locality (BM 1993,450) and online photos (Mindat, 2022a) revealed strong visual similarities.

The identification was confirmed by powder X-ray diffraction. A tiny fragment was removed and crushed *in situ* on a corundum substrate. The powder pattern was collected by an Inel curved position sensitive detector (PDS120) for 3300 seconds using CoKα radiation to minimise fluorescence. The pattern has broad peaks and conspicuous preferred orientation but the trace is sufficiently good to show that the mineral belongs to the 'surite–ferrisurite series'. As the EDS results showed Fe>Al, the mineral can be identified as ferrisurite.

Figure 2. The ferrisurite-rich area of BM2019,3 showing the feathery to lath-like habit of the pale to olive-green crystals. The field of view is about 10 mm across. Photo © Trustees of the Natural History Museum.

The variation in colour across some crystal aggregates (Fig. 3) suggests that the Fe:Al ratio may vary (ferrisurite is typically green whereas surite is white). Quantitative analysis would be required to fully explore the changes in composition, but it is extremely difficult to prepare appropriately flat polished surfaces of soft lath-like crystals. The possibility that some compositions are within the surite composition field cannot be discounted.

DISCUSSION

The ferrisurite from Whyte's Cleuch is easily visible to the naked eye. It may have escaped previous notice because of its predominantly green colour and feathery morphology, which is similar to moss or algal growths (Fig. 4). Specimens also lack the obvious specular reflections produced by drusy crusts of more conspicuous green supergene minerals such as phosphohedyphane and pyromorphite.

Minerals that contain both lead and silicon are absent at almost all of the thousands of potential localities that have undergone systematic scientific investigation. Although surite and ferrisurite are inconspicuous, their rarity is probably a genuine reflection of their unusual chemistry and structure. The fact that ferrisurite is the fifth lead-bearing silicate to be identified at Leadhills–Wanlockhead suggests that unusual geochemical conditions developed during supergene oxidation and invites comparison with similar localities worldwide.

More than one lead silicate is reported at five of the nine surite or ferrisurite localities listed on Mindat

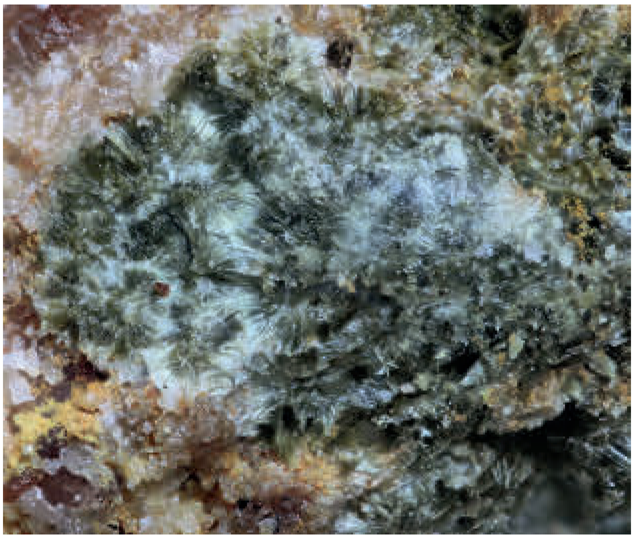

Figure 3. Radiating ferrisurite aggregates with conspicuous olive-green to white colour banding (note that the effect may be emphasised by the increase in light scattering produced as crystals in the radial aggregates separate). The field of view is approximately 1 mm across. Steve Rust specimen and photo.

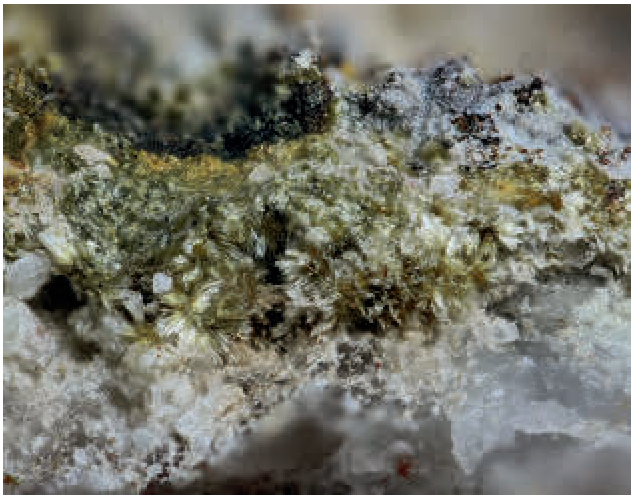

Figure 4. Acicular to lath-like olive-green ferrisurite infilling cavities in vein quartz. The field of view is approximately 1 mm across. Steve Rust specimen and photo.

(2022a,b). Unfortunately, identification techniques are not always stated and there are selection biases. Three of the localities have been studied in obsessive detail by specialists whereas one is so poorly described that its precise location is not recorded. The species are listed with formulae in Table 1.

The comparison with worldwide localities in Table 1 suggests a directed search for minerals such alamosite, melanotekite and plumbotsumite might be productive at Leadhills−Wanlockhead. Melanotekite, in particular, is easily overlooked. Of the other reported associates, kasolite (which contains uranium) can be excluded on geochemical grounds and kentrolite is unlikely as it does not normally occur in supergene assemblages.

The hypothesis that supergene lead silicates occur in geographical clusters is borne out by an examination of the mineralisation at Leadhills−Wanlockhead. Whyte's Cleuch is the only British kegelite locality (Neall and Green, 2005). Kegelite has strong structural similarities to ferrisurite. It contains smectite-like layers intergrown with leadhillite-like lead carbonate layers. In a solution with a high silicate activity, it may be [by analogy with leadhillite and cerussite (Bridges, 2015)] that $p(CO_2)$ exerts a control on formation, low values favouring kegelite, and higher values either surite or ferrisurite. An Fe^{3+} analogue of kegelite is yet to be described and the occurrence of ferrisurite (and pale green kegelite) at Whyte's Cleuch makes this a tantalising prospect.

The lead copper iron silicate creaseyite occurs as apple-green sprays on phosphohedyphane in mine spoil from the south side of Whyte's Cleuch (Rust and Green, 2009) and it is associated with:

> "white, pale blue, pale brown and even pale green lead silicates with a superficial ... resemblance to creaseyite which are not that mineral".

Creaseyite has an unusual and complex nanoporous structure (Malcherek *et al*., 2013). The uncharacterised phases with which it is associated deserve further study.

Mineral	Chemical Formula	No.	Comment
Creaseyite	$Pb_2Cu_2Fe_2^{3+}(Si_{4.67}Al_{0.33})O_{15.33}(OH)_3{\cdot}H_2O$	3	Widespread supergene lead-iron silicate. Reported at Whyte's Cleuch in Rust and Green (2009)
Melanotekite	$Pb_2Fe_2^{3+}(Si_2O_7)O_2$	3	Black and inconspicuous, easily overlooked in supergene associations
Plumbotsumite	$Pb_{13}(CO_3)_6(Si_{10}O_{27}){\cdot}3H_2O$	3	Rare supergene phase, could be mistaken for leadhillite-group minerals
Alamosite	$PbSiO_3$	2	Inconspicuous, easily mistaken for other white lead minerals
Queitite	$Pb_4Zn_2(SO_4)(SiO_4)(Si_2O_7)$	2	Has been reported at Horner's Vein, Leadhills (Jackson, 1990)
Plumbophyllite	$Pb_2Si_4O_{10}{\cdot}H_2O$	1	Very rare; easily confused with prismatic anglesite
Bobmeyerite	$Pb_4(Al_3Cu)(Si_4O_{12})(S_{0.5}Si_{0.5}O_4)(OH)_7Cl(H_2O)_3$	1	Known from a single location, inconspicuous, easily overlooked
Iranite	$Pb_{10}Cu(CrO_4)_6(SiO_4)_2(OH)_2$	1	Requires significant chromium in addition to lead and copper
Wherryite	$Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$	1	Very rare, green crystals might be confused with caledonite
Macquartite	$Cu_2Pb_7(CrO_4)_4(SiO_4)_2(OH)_2$	1	Very rare, requires significant chromium in addition to lead and copper
Kasolite	$Pb(UO_2)[SiO_4]{\cdot}H_2O$	1	Requires significant uranium as well as lead, unlikely at Leadhills−Wanlockhead
Larsenite	$PbZnSiO_4$	1	Lath like crystals might be confused with other lead silicates
Mathewrogersite	$Pb_7FeAl_3GeSi_{12}O_{36}(OH,H_2O)_6$	1	Very rare germanium-bearing phase; unlikely at Leadhills−Wanlockhead
Kentrolite	$Pb_2Mn_2^{3+}(Si_2O_7)O_2$	1	Not typically reported in supergene assemblages

Table 1. A summary of the lead silicate species reported from the eight surite or ferrisurite localities listed in Mindat (2019a,b). The third column lists the number of surite or ferrisurite locations at which the minerals have been identified. No data for the Leadhills−Wanlockhead district is included.

Two further lead silicates are known from the wider Leadhills–Wanlockhead mining district. Mattheddleite is widespread and has been identified at several dumps in Whyte's Cleuch (Tindle, 2008; Mindat, 2022c). Queitite occur as radiating millimetre-size spherules at Horner's Vein near Leadhills (Jackson, 1990).

Ferrisurite appears to have formed when oxidising solutions altered silicates in close proximity to galena in the early stages of supergene oxidation at Whyte's Cleuch. In the specimens examined in this study, ferrisurite is earlier than phosphohedyphane. Further investigations are required to properly assess how ferrisurite and the other lead silicates fit into the supergene paragenesis. Creaseyite and the as yet uncharacterised phases described by Rust and Green (2009) overgrow phosphohedyphane, which shows that the silicate ion activity was sufficiently high for lead silicates to crystallise late in the supergene sequence in places.

The nature of the lead carbonate layer in surite and ferrisurite is not completely understood. Recent research on the structural chemistry of layered lead carbonate minerals (Siidra *et al.*, 2018) makes this a topical field for research. Further study may help to constrain the nature of the lead carbonate layer and the existence (or not) of any long-range structural ordering. Although such investigations are beyond the scope of this note, they would necessarily be based on well characterised specimens from known localities such as the specimens described here.

ACKNOWLEDGEMENTS

MSR would like to thank Jon Evans of the Wanlockhead mining museum for hosting his visit and taking him to the dumps in Whyte's Cleuch, John Faithfull of the Hunterian Museum, Glasgow for discussions pertaining to mattheddleite, and Mark Welch of the NHM for crystallographic discussions. The authors would like to thank referees Peter Davidson and David Green for their constructive comments. Readers should note that the extensive dumps at Whyte's Cleuch lie within the Leadhills–Wanlockhead SSSI and appropriate permission must be obtained to collect geological material.

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KÖTTIGITE FROM STRONTIAN MINE, STRONTIAN, ARGYLL: A FIRST SCOTTISH OCCURRENCE

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Nickel- and cobalt-bearing köttigite occurs as pale pink spherulites and radiating colourless to pink lath-like, tabular and prismatic crystals in brecciated metabasite at Strontian Mine, Strontian, Argyll, Scotland. It is part of a widespread but inconspicuous supergene assemblage produced by recent (post-mining) oxidation. Köttigite appears to have formed in a reaction between zinc ions generated by oxidising sphalerite and arsenate, cobalt and nickel ions generated by oxidising pyrite. It is easily confused with the cobalt-dominated vivianite-group mineral erythrite, which has been claimed from the Strontian mines but remains to be confirmed. This is the first record of köttigite at any Scottish locality.

INTRODUCTION

Köttigite, ideally $Zn_3(AsO_4)_2{\cdot}8H_2O$, is an uncommon member of the vivianite group of minerals, monoclinic arsenates and phosphates with a general formula:

$$M(1)_1M(2)_2(TO_4)_2{\cdot}8H_2O.$$

The name honours Otto Friedrich Köttig (1824–1892) who investigated the chemistry of köttigite from the type locality, Daniel Mine near Schneeberg in Saxony (Köttig, 1849; Dana, 1850).

In the vivianite group, species-defining cations are mostly drawn from the transition elements. They include cobalt, copper, iron, magnesium, manganese, nickel and zinc. Arsenate and phosphate are the only species-defining anions. The M-site cation to T-site anion ratio is always 3:2. The molar abundances of the M-site cations distinguish köttigite (zinc dominant) from the more commonly reported erythrite (cobalt dominant) and annabergite (nickel dominant).

Köttigite is known from two English localities: colourless, transparent crystals up to 1 mm in length occur at Hilton Mine, Scordale, Cumbria (Bridges and Green, 2006); and drusy pale pink crusts at Sandbed Mine, Caldbeck Fells, Cumbria (Green *et al.*, 2006). An Irish occurrence, at Hayes's Adit, Moll Doyle Mine, Co. Wicklow, is briefly noted by Moreton and Green (2007; 2009). This is the first record at any locality in Scotland.

LOCATION

The village of Strontian is situated on the north shore of Loch Sunart in the historic county of Argyll. The mines in the hills above the village need no introduction to mineralogists. The principal workings, from west to east, are Corrantee, Whitesmith, Middleshop, Bellsgrove and Fee Donald. The central triptych, on the southern flank of Beinn Ruighe Raonuill, include the type localities for brewsterite-(Sr) and strontianite and have produced remarkable specimens of the barium zeolite harmotome.

The history of mining is described by Moreton and Green (2018). The veins were worked for lead ore, almost entirely at a loss, from the first quarter of the eighteenth century until the third quarter of the nineteenth century. Twentieth-century attempts at revival met with little success until the mid-1980s when the Strontian Mine was opened to work the Main Vein across the former Whitesmith, Middleshop and Bellsgrove sites for baryte. The operation was abandoned in the early 1990s and the site was subsequently acquired by a company which supplies aggregate for local use. Opportunities to collect fresh material occasionally arise when spoil is moved around.

GEOLOGY

Köttigite occurs in fractures in brecciated metabasite, a distinctive rock which formed when basic dykes parallel to the mineral veins were attacked by carbonating fluids. Calcite veins up to about 5 cm in width form complex networks around angular blocks of pale grey-green metabasite. They are typically symmetrical fissure fills which consist of dark well crystallised sphalerite overgrown and enveloped by coarse grey-white calcite.

Scalenohedral calcite crystals often line cavities where the veins widen. They are commonly modified or overgrown by crystals with different habits and fluorescence colours. Within the vein assemblage harmotome, marcasite, pyrite and quartz are widespread and common; ancylite-(Ce), brewsterite and millerite localised and rare; and the 'economic' primary minerals, baryte and galena, sporadic and uncommon.

It has not been possible to establish a fully consistent paragenetic sequence: sphalerite and millerite are usually early; calcite is always the principal primary vein fill; marcasite, pyrite and quartz are episodic; baryte is usually later than calcite; and harmotome, ancylite-(Ce) and brewsterite overgrow all of the other minerals and represent the final stage of primary mineralisation.

The discovery of millerite (which is very rare at Strontian) in a few cavities in the metabasite prompted a wider study of the minerals in this lithology. Minute pale pink spherulites were occasionally found in hairline fractures when blocks were broken up. They coat small hand specimens of grey-green metabasite on the richest specimens (Fig. 1). Examination using a stereomicroscope revealed radiating groups of prismatic (Fig. 2) to lath-like crystals (Fig. 3) where spherulites had grown across fractures and a few isolated groups of blocky to bladed crystals in cavities in calcite veins.

ANALYSIS

Fragments from three separate specimens were detached and mounted for analysis by energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM). Standardless analyses on unpolished surfaces are not quantitative, but they are sufficient to provide an indication of the molar ratios of the elements with an atomic number greater than ten.

Figure 1. Rich pale pink köttigite spherules in a fracture in pale grey-green metabasite from Strontian Mine, Strontian, Argyll. David McCallum Collection. The field of view is 1.5 mm across. Photo John Chapman.

Figure 2. A radiating group of relatively coarse colourless to pink prismatic köttigite crystals from Strontian Mine, Strontian, Argyll. David McCallum Collection. The field of view is 0.8 mm across. Photo John Chapman.

The chosen fragments consisted of an unusual blocky crystal with a somewhat orange tint from a calcite vein, and a colourless to pale pink tabular crystallite and several small masses of spherulites from the surrounding metabasite.

Figure 3. Radiating groups of lath-like pale pink prismatic köttigite crystals from Strontian Mine, Strontian, Argyll. David McCallum Collection. The field of view is 1.4 mm across. Photo John Chapman.

Arsenic and zinc were detected in the blocky crystal, but in proportions [Zn:As ~1:5] that are inconsistent with köttigite or any other natural zinc arsenate. Additional cations are required to balance the charge if the arsenic is present as arsenate, but no trace of cobalt, nickel or any other heavy element was detected. The analytical data may have been compromised by unusual interactions with the electron beam (Newbury and Ritchie, 2013) or alternatively undetected light elements may be present. No similar crystals remain on the original specimen. The results are recorded in the hope that additional specimens will come to light.

Arsenic and zinc with minor cobalt and nickel [Zn:Ni:Co = 7:2:1] were detected in the tabular crystallite in the correct molar ratios for a vivianite-group mineral [(Zn+Ni+Co):As = 14.7:10.3, which is ~3:2].

Arsenic and zinc with cobalt and nickel [typically Zn:Ni:Co = 3:2:1] were detected in several analyses of pale pink spherulites in the appropriate molar ratios for a vivianite-group mineral [(Zn+Ni+Co):As ~3:2]. Secondary electron images reveal that the surfaces of the spherulites are partially covered in monoclinic blades between about 5 and 10 µm in length. The proportions of nickel and cobalt are higher than in the tabular crystallite, but zinc is the dominant metal cation in every case.

The reconnaissance EDS study was sufficient to justify confirmatory analyses by X-ray diffractometry (XRD). Material was hand-picked and sent to Mineralanalytik in Germany. The powder patterns for the tabular crystallites and spherulites are characteristic of vivianite-group minerals (Joy Desor, *personal communication*, 2021). Together with the EDS analyses they confirm the pink material in fractures in the metabasite is köttigite[1].

DISCUSSION

Erythrite has been claimed in pink flowstone crusts collected at an unspecified underground locality at Strontian by Kemp Meikle and analysed using spot tests (positive for arsenate, cobalt and nickel) by his friend and collecting companion Norman Thomson (*personal communication*, 2006). The specimens described in this study provided an opportunity to investigate similar material using modern analytical techniques. Although the studied specimens are distinctly pink, cobalt (the dominant *M*-site element in erythrite) is present in smaller quantities than zinc and nickel in every analysis. Spot tests on their own are insufficient to differentiate annabergite, erythrite and köttigite. In the light of this study, the claim that erythrite has been identified at Strontian must be considered unproven.

The primary assemblage at Strontian is relatively unaffected by oxidation. Scouring by ice removed any major pre-Pleistocene oxidation zone. Recent fieldwork has identified two inconspicuous supergene assemblages, one the result of natural oxidation and the other post-mining in origin.

The natural assemblage is sporadically present in fractures and cavities near the top of vein exposures that have not been entirely blanketed by peat. Anglesite, cadmium sulphides, cerussite, hemimorphite, hydrozincite, malachite, smithsonite, sulphur and wulfenite (with iron and manganese oxides and oxyhydroxides) have been identified. No trace of the green to yellow pyromorphite reported by Greg and Lettsom (1858), and repeated by Heddle (1901), has been found.

The post-mining assemblage is sporadically present on the walls of mine levels and in fractures produced by mineral extraction. It includes brianyoungite, cadmium sulphides, gypsum, hydrozincite, jarosite and natrojarosite. Köttigite, which occurs *in situ* in metabasite deep within the opencuts, is part of this suite.

Köttigite is the only arsenate mineral that has been confirmed at any of the Strontian mines and the origin of the constituent ions invites speculation. Sphalerite, which is abundant in the veined metabasite, is the only realistic source of zinc. The presence of thin films of hydrozincite on sphalerite crystal surfaces and in the surrounding rock provides evidence of post-mining oxidation. Such films are characteristic of recent supergene oxidation at atmospheric $p(CO_2)$ values (Williams, 1990).

The source of the arsenic, cobalt and nickel is unclear. Iron sulphides and rare millerite occur in the metabasite, but no arsenic-bearing sulphosalts have been identified to date. The association between köttigite and pyrite (Fig. 4) suggests a possible source of the arsenic, cobalt and nickel. Nickel and cobalt commonly partition into iron sulphides (Schachner-Korn, 1982) and arsenic is not uncommon at levels of a few wt% in primary pyrite (Rickard *et al.*, 2017). Indeed, arsenic-bearing pyrite is the principal source of supergene arsenate in some mineral deposits (Savage *et al.*, 2000). Unfortunately, it has not been possible to determine the concentrations of these minor elements in the iron sulphides at Strontian in this study. Further analysis is desirable.

Köttigite is abundant where hairline fractures cross small porous sphalerite-rich metabasite clasts in the walls of calcite veins, but much less common where the fractures cross the calcite veins themselves (Fig. 5). This may be a reflection of the local availability of zinc ions, but seems more likely to reflect differences in nucleation potential on the reactive calcite surfaces. Surface reactivity may also account for the absence of köttigite as direct overgrowths on either pyrite or sphalerite. Any surface which is being altered by oxidation (pyrite and sphalerite) or attacked by the resultant acidic fluids (calcite) is unlikely retain a coating of köttigite.

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[1] It is worthwhile recording that XRD alone cannot reliably differentiate annabergite, erythrite and köttigite. The unit-cell parameters of erythrite and köttigite differ by a fraction of one percent and their powder patterns are essentially indistinguishable. Supplementary chemical data are required for reliable determinations.

Figure 4. Pink drusy köttigite surrounding slightly oxidised subhedral pyrite in a thin fracture in pale green metabasite. The pink patch has an unexplained hexagonal outline. David McCallum Collection. The field of view is 3 mm across. Photo John Chapman.

CONCLUSION

Köttigite occurs as pale pink spherulites and radiating clusters of lath-like, tabular and prismatic crystals in fractures in brecciated metabasite at Strontian Mine, north of the village of the same name, in the Lochaber District of Argyll. It is thought to have formed in a recent (post-mining) reaction between zinc from oxidising sphalerite and arsenate, cobalt and nickel from oxidising iron sulphides. It is the first supergene arsenate to be confirmed at any of the Strontian mines and the first köttigite from any Scottish locality.

Figure 5. Köttigite spherulites in a fracture in brecciated metabasite. The spherulites are concentrated where the fracture cuts the grey-green metabasite and sparse on the white vein calcite. David McCallum Collection. The field of view is 10 mm across. Photo John Chapman.

Careful analyses are required to distinguish köttigite from the better known members of the vivianite group. The end-member composition is colourless to white, but transition metal cations in solid-solution commonly colour natural crystals pink, red, orange, brown, blue or green. In such specimens köttigite is commonly mistaken for annabergite (green), erythrite (pink) or parasymplesite (blue-grey). More detailed examination of material from other British localities would probably reveal further occurrences.

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THE FIRST BRITISH OCCURRENCE OF A BETPAKDALITE-SUPERGROUP MINERAL AT CARROCK MINE, CALDBECK FELLS, CUMBRIA

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The heteropolymolybdate mineral betpakdalite-CaMg has been identified as an alteration product of molybdenite on a specimen in the collection at the Natural History Museum, London from Carrock Mine, Caldbeck Fells, Cumbria. The initial identification was made 1997, before the betpakdalite-supergroup was approved, and has been updated to reflect current nomenclature. The presence of a betpakdalite-supergroup mineral extends the variety of geochemical environments that are known to have developed during supergene alteration at Carrock Mine and increases the probability of further unusual discoveries.

INTRODUCTION

The minerals of the betpakdalite supergroup are relatively widespread but easily confused with other species and commonly overlooked by collectors and researchers. They typically form yellow, orange and green smears and microcrystalline crusts in molybdenum-rich orebodies which have been exposed to acidic supergene alteration.

The supergroup, as defined by Kampf *et al.* (2012), consists of three separate mineral groups with similar crystal structures, each of which takes its name from the first mineral that was identified (betpakdalite, mendozavilite, obradovicite). The first of these 'parent species' to be formally described, 'betpakdalite' from the Kara-Oba tungsten deposit in the Betpakdala Desert, Kazakhstan (Ermilova and Senderova, 1961), gives its name to the supergroup.

There are five species in the betpakdalite group, four in the mendozavilite group and three in the obradovicite group. All twelve have been approved by the International Mineralogical Association, but one, betpakdalite-FeFe, awaits formal publication. The minerals have a framework with gaps and channels that contain water and other loosely bound chemical components. Differences in the framework define each of the groups whilst the chemical contents of the gaps and channels define the individual species. Variations in reported compositions of 'betpakdalite', 'mendozavilite' or 'obradovicite' prior to the work of Kampf *et al.* (2012) are considerable.

The betpakdalite supergroup has a general structural formula:

$$[A_2(\mathrm{H_2O})_nB(\mathrm{H_2O})_6][\mathrm{Mo}_8T_2\mathrm{Fe}_3^{3+}\mathrm{O}_{30+x}(\mathrm{OH})_{7-x}],$$

where A and B are the loosely bonded components, T is either tetrahedrally coordinated phosphate or arsenate, n is a variable and x varies to maintain charge balance. Currently recognised supergroup members are listed in Table 1.

The new nomenclature is an example of what many systematic collectors describe as 'splitting'. To avoid a proliferation of mineral names individual mineral species are named by taking the 'root-name' of the parent species and adding a suffix. As there are two distinct sites in the structure, a two-part suffix which represents the contents of the gaps and channels is used. The only exception is the mineral melkovite, which

Betpakdalite Group	**Framework**	**Channels**	**Published**
Betpakdalite-CaCa	Mo-Fe-As	Ca & Ca	1961
Betpakdalite-NaNa	Mo-Fe-As	Na & Na	2012
Betpakdalite-FeFe	Mo-Fe-As	Fe & Fe	Named 2017, not yet published
Betpakdalite-NaCa	Mo-Fe-As	Na & Ca	1971, renamed 2012
Betpakdalite-CaMg	Mo-Fe-As	Ca & Mg	Informally 1999, named 2012
Mendozavilite Group			
Melkovite	Mo-Fe-P	Ca & Ca	1969
Mendozavilite-KCa	Mo-Fe-P	K & Ca	2012
Mendozavilite-NaCu	Mo-Fe-P	Na & Cu	2012
Mendozavilite-NaFe	Mo-Fe-P	Na & Fe	1986, renamed 2012
Obradovicite Group			
Obradovicite-KCu	Mo-Fe-As	K & Cu	1986
Obradovicite-NaCu	Mo-Fe-As	Na & Cu	2012
Obradovicite-NaNa	Mo-Fe-As	Na & Na	2012

Table 1. Current members of the betpakdalite supergroup.

corresponds to 'mendozavilite-CaCa', but has retained its original name as it was identified as a separate species prior to the definition of the supergroup.

The unusual compositions of betpakdalite supergroup minerals aid group-level identifications. Betpakdalites are rich in arsenic, iron and molybdenum whereas mendozavilites are rich in iron, molybdenum and phosphorus. Obradovicites have a different framework topology to betpakdalites, but also contain arsenic, iron and molybdenum.

Across all the groups, the chemical components in the gaps and channels in the structure include calcium, copper, iron, potassium and sodium ions and water molecules. The full range of chemical components (and therefore the potential species within the supergroup) has not been fully explored. Current analyses include compositions that are close to 'mendozavilite-NaCa'. Strontium is present in the channel sites in some specimens but not in species-defining quantities.

LOCATION

Carrock Mine in the Caldbeck Fells, Cumbria has the best exposures of high-temperature mineralisation in northern England. The north–south trending tungsten-rich quartz veins are genetically related to the Caledonian Skiddaw Granite. The mine and its environs have been popular with geologists and mineralogists for many years and feature in most field guides to the Lake District. The Carrock Mine – Brandy Gill GCR site is one of very few British localities where more than 100 mineral species have been recorded. A detailed description of the history, geology and mineralogy is beyond the scope of this article. The interested reader is referred to Cooper and Stanley (1990).

At the height of its popularity in the late 1970s and early 1980s, the mine was still being worked in a small way and field parties frequently arrived to learn about the mineralogy and igneous geology. Landscaping works in the 1990s covered the more interesting areas of the dumps and removed what remained of the modern processing works and the old stone-built mine office. The remainder of the site had become depleted by the end of the century. Collecting is now tightly controlled: it requires permission from both the landowner and Natural England.

Mineralogical discoveries up to the late 1980s are summarised by Young (1987) and Cooper and Stanley (1990) and collections based research continues to uncover new and interesting species (e.g. Rumsey 2007a,b; Rumsey, 2020). Although the operations were principally for tungsten, there is also significant arsenic, bismuth, copper, lead, molybdenum, tellurium and zinc mineralisation. Molybdenum is the focus of this research. Primary molybdenum mineralisation typically consists of aggregates of molybdenite laminae, 10–15 mm across, in vein quartz. Well formed crystals are rare, but occasionally occur in cavities. On some specimens there is evidence of minor supergene alteration, but it is not usually extensive, in most cases manifesting as a thin surface alteration of secondary minerals on top of largely unaltered primary molybdenite.

ANALYSIS

As part of an assessment the Natural History Museum's collection from Carrock Mine, a group of fragments labelled 'grunlingite and yellow powder', which had arrived for identification in about 1975, and were accessioned in 1993, was investigated. The samples are registered as BM 1993,327. They include more than ten fragments of vein quartz. Although the original label does not state that they are from Carrock Mine it was common for locality information to be given verbally to the curator or scientific officer who dealt with the enquiry at that time.

The fragments include different metallic minerals of varying sizes, shapes, textures and forms and it seems from the associated labels, which note the now discredited mineral 'grunlingite', and the NHM database entry which records tetradymite, that interest in the fragments was primarily in their ore minerals rather than supergene phases. The largest fragment has a molybdenite aggregate about 12 mm across with significant alteration. Unlike the majority of molybdenite from Carrock Mine, which is coated in either cream to pale yellow powellite (Rumsey, 2020) or darker dirty yellow ferrimolybdite (Cooper and Stanley, 1990), the alteration product on this specimen is bright lemon to canary yellow (Fig. 1). This feature, which was noted on the original label, ultimately led to an additional analysis in 1997, four years after the specimen was registered in the collection.

The identification process at the NHM followed a set pattern for many years: a sample went from the curation team to the labs with a pink/red label (or 'slip'), with a note of what was to be investigated. The specimen was returned with a green label (or 'slip') with a reference number for the identification, the method and the result. If the result was uncontroversial the catalogue was updated, the label corrected and the specimen replaced in the collection. If there was reason for further investigation, the specimen was set aside until a decision was made on how to proceed. The most common reasons for a stalled process were that the identification did not match what was thought to be present or that there was no sign of the supposed mineral species on the sample at all.

In amongst the 'green slips' with the specimen detailing ore minerals for investigation are the interpreted results of XRD film reference number 10903F, which indicate that the yellow earthy material is a mixture of betpakdalite and scorodite. This is of significance because betpakdalite has not been recorded in the British Isles, but the researchers at the time were more focused on the ore mineralogy and did nothing further with the data. Chemical analyses were performed on a probe block prepared from the sample in 1998 but this investigation was unrelated to the betpakdalite alteration. The fragments were then put aside, pending a curatorial decision as to the best way to renumber and

Figure 1. Canary to lemon yellow powdery betpakdalite on malleable flakes of molybdenite, alongside lustrous and well crystallised grey-beige scorodite (not well distinguished in this image) in a white vein-quartz with minor veinlets and aggregates of iron-stained mica. The field of view is about 20 mm across. Photo Mike Rumsey.

rename them. They fell below the radar until 2020, when they were rediscovered.

The original powder pattern (film no. 10309F) was re-examined and carefully compared with both the betpakdalite-group and obradovicite-group patterns. The two patterns are similar (Kampf *et al*., 2012) so a new pattern was collected, to avoid any ambiguity. Two <100 µm fragments were removed from the sample and mounted using ‘araldite’ on a non-diffracting amorphous-carbon fibre (10 µm diameter) glued to a glass support rod. The sample was mounted on a Rigaku Rapid II micro-diffractometer and a dataset collected using CuKα radiation (40 kV and 36 mA). Diffraction data were collected at ambient temperature using a 300 µm beam collimator, a primary graphite monochromator and a 2D curved image plate detector for two hours. A Gandolfi-type randomised sample movement was achieved by rotations on the φ and ω axes. The resulting pattern was a good match for betpakdalite-CaMg as listed on the ICSD database, and sourced from Cooper and Hawthorne (1999). Ruling out the possibility of an obradovicite-group mineral was important because had the pattern been that of orthorhombic obradovicite, the chemical composition (see below) would have indicated a potential new species.

X-ray diffractometry on its own is insufficient to provide a definite species determination in the betpakdalite supergroup (Kampf *et al*., 2012). The loosely bonded chemical species in the gaps and channels do not affect the framework structure sufficiently. Microprobe analyses of flat polished surfaces are ideally required for quantitative identification. The project was not sufficiently important to merit time on the NHM microprobe, but semi-quantitative energy-dispersive X-ray analyses were undertaken on a Jeol IT500 scanning electron microscope in low-vacuum mode, using default calibration settings.

The SEM revealed that the mineral is composed of minute six-sided plates with smooth surfaces free from significant imperfection or contamination. Analyses of suitably oriented flat surfaces reduces the errors associated with standardless analyses of unpolished samples. Several ‘area analyses’ on aggregates containing hundreds of plates in variable orientations were also gathered. No charging, an effect that can compromise results, was observed. The calculated atomic percentages of the chemical elements present were consistently Mo>Fe>As$\geqslant$Ca>Mg>Na with the exception of one of the area scans, which had Ca>As. The predominance of Mo and Fe and approximate equivalence of As and Ca is consistent with the betpakdalite group. In the analyses of flat crystals, the ratio of Fe/Mo and As/Mo varies from 0.4–0.3 and 0.25–0.2, respectively, which is consistent with the ideal betpakdalite framework[1] which has Fe/Mo = 0.375 and As/Mo = 0.25.

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[1] Kampf *et al*. (2012) note that if the Fe/Mo ratio is significantly different from the ideal framework value, a determination of the species is inappropriate as iron may be present in the gap and channel sites in the structure. This is exemplified by the unpublished species betpakdalite-FeFe where site occupancies have to be determined.

In betpakdalite-group minerals without iron in the gap and channel sites, the ratio of Fe/(Ca,Na,Mg,K,Cu) is 1.0. The range of values measured on the studied specimen is 0.89–1.15. This is within reasonable margins of error and therefore the proportions of calcium, magnesium and sodium (the only other elements identified in the study) are sufficient to confirm speciation. In all of the analyses Ca>Mg>Na. The analyses do not indicate which structural sites these elements occupy and, in some instances, this could result in an ambiguous identification. In this case the relative percentages are such that, regardless of the way in which the sites are populated, the species is betpakdalite-CaMg.

DISCUSSION

Betpakdalite-CaMg was first recognised as a distinct species by Kampf *et al*. (2012), but this specific composition had been the focus of earlier analyses in a structural study by Cooper and Hawthorne (1999). Betpakdalite-CaMg is currently known from five worldwide locations. The type locality is the famous Tsumeb Mine in Namibia and the millimetre-size blocky pseudo-orthorhombic crystals from this site are probably the largest and best of any locality. The specimen from Carrock Mine has a platy pseudo-hexagonal habit unlike those from Tsumeb.

No member of the betpakdalite supergroup has been previously reported from Britain. A recent study (Rumsey, 2020) showed that powellite is the most widespread alteration product of molybdenite during sub-aerial weathering in the British Isles, and is present at Carrock Mine. Minerals of the betpakdalite supergroup require acidic conditions with very high concentrations of molybdenum for the complex polymolybdate anions to form. It is likely that oxidising iron sulphides and arsenopyrite were the source of the iron and arsenate, and the acidic solutions leached the remaining elements from the surrounding veinstone. Arsenopyrite and iron sulphides decompose rapidly in oxidising near-surface environments but primary molybdenite is relatively stable and commonly remains fresh.

The diverse primary mineralisation at Carrock Mine provides considerable scope for further rare secondary minerals. The extreme conditions generated by relatively closed alteration have the potential to produce tellurium oxysalts and exotic secondary bismuth, tungsten or molybdenum minerals. The nature of the veinstone allows for different closed micro-environments to form in close proximity. This is exemplified by the specimen at the centre of this study. A different molybdenite grain embedded within the veinstone is associated with a darker yellow less well developed alteration product. This was also studied by EDS and is likely to be a member of the betpakdalite group but with a different channel composition, dominated by Fe and Ca, unfortunately this material was not of an appropriate quality to take the identification any further. Yet another area of interest on the same sample, shows a completely different molybdenum-rich alteration assemblage. A void created by the complete removal of a molybdenite crystal is filled with a fine-grained, poorly consolidated cream coloured mass of material that fluoresces under ultraviolet light. Analysis revealed this infill is a fine-grained mixture including powellite, a clear indicator of a different pH and lower activity of molybdenum.

Unfortunately, with the exception of the potential presence of copper in the gap and channel sites, which results in a green colouration, all of the betpakdalite-supergroup species are likely to be similar in appearance: lemon-yellow to orange-yellow in colour and easily mistaken for beyerite, bismite, bismoclite, ferrimolybdite, kettnerite, koechlinite, petitjeanite, powellite, preisingerite, russellite, rooseveltite and tungstite. Yellowish powdery material, especially samples labelled as ferrimolybdite, are worthy of investigation in searches for further betpakdalite-supergroup minerals from Carrock Mine and similar British localities.

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DIABOLEITE FROM PENBERTHY CROFT MINE, ST HILARY, CORNWALL

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Diaboleite occurs as dark blue blocky crystals with anglesite, cerussite and phosgenite in cavities in quartz from the late-stage low-temperature lead-zinc vein assemblage at Penberthy Croft Mine, St Hilary, Cornwall. Phosgenite was deposited in an acidic saline solution (pH <6) with low $p(CO_2)$ and subsequently etched and locally overgrown by diaboleite which crystallised as the copper ion activity increased and the fluid evolved towards a neutral pH.

INTRODUCTION

Diaboleite, ideally $Pb_2CuCl_2(OH)_4$, is a rare mineral which was first described from Higher Pitts near Priddy in the Mendip Hills (Spencer and Mountain, 1923). It typically occurs as small platy to prismatic crystals with a distinctive deep blue colour. The asymmetric crystal habit is a reflection of the coordination geometry of the lead atoms which have a large lone pair of electrons projecting toward four chloride ions on one side and four short bonds to hydroxyl groups on the other (Cooper and Hawthorne, 1995).

About forty natural occurrences (plus a number of locations where diaboleite has crystallised in smelter slag) are listed on Mindat (2022). Specimens with well formed tabular crystals to more than 20 mm on edge from Mammoth St Anthony Mine, Arizona, USA, are widely regarded as the benchmark for the species (Bideaux, 1980).

LOCALITY

Penberthy Croft Mine northeast of the village of Goldsithney in the parish of St Hilary, Cornwall [SW 555 324] worked a complex lode system in Devonian metasediments between the Land's End and Godolphin granites (Dines, 1956). The Main Lode is associated with an elvan dyke, and there are five other named lodes and numerous cross-courses and stringers. Mineralisation includes early burial-related quartz-albite-anatase-monazite veins, high-temperature arsenic-copper-tin-tungsten lodes (the major economic mineralisation), later low-temperature lead-zinc sulphide veins (the cross-courses), and late, low-temperature, iron-manganese mineralisation (Betterton, 2000).

With more than a hundred confirmed species, Penberthy Croft is one of Britain's most diverse mineral localities. Deep and extensive oxidation has produced the suite of secondary arsenates, arsenate-sulphates and phosphates for which the locality is famous. Post-mining alteration has added to the diversity, notably in the recent description of the closely related hydrated aluminium arsenates bettertonite and penberthycroftite (Grey *et al*., 2016, 2017) .

The specimen which is the subject of this article was found in a small cavity in a rather nondescript block of quartz veinstone which had been collected in the 1980s and stored with other samples until it could be properly investigated. The block, which was originally about 100 mm across, contained centimetre-sized clots of sphalerite, minor galena and patches of brochantite, cerussite and linarite. These minerals are typical of the low-temperature lead-zinc vein assemblage. A small cavity, which was exposed when the block was broken down, contained minute blue crystals associated with well formed anglesite, cerussite and colourless to white prismatic phosgenite up to 4 mm on edge (Figs 1–3).

The close association with phosgenite, distinctive blue colour and unusual asymmetric habit suggested the crystals might be diaboleite and a fragment was submitted to the Natural History Museum for identification. Energy-dispersive X-ray analysis on a scanning electron microscope revealed a molar lead:copper:chloride ratio of 2:1:2. No other mineral contains these elements in this atomic ratio; the nearest, cumengeite (with which diaboleite is readily confused), has a lead:copper:chloride ratio of 1:1:2. It is safe, therefore, to conclude that the blue crystals are diaboleite.

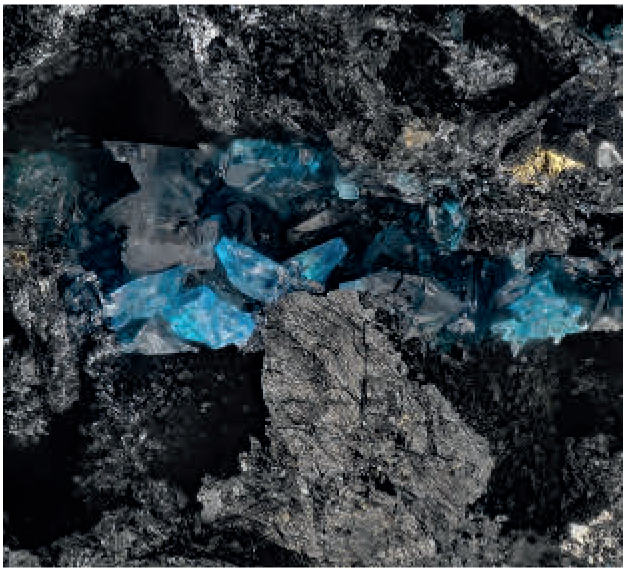

Figure 1. Sky-blue tabular diaboleite crystals with cerussite in dark corroded sphalerite. Specimen PBCM SR3a in the Steve Rust Collection from Penberthy Croft Mine, St Hilary, Cornwall. The field of view is 1.2 mm across. Photo Steve Rust.

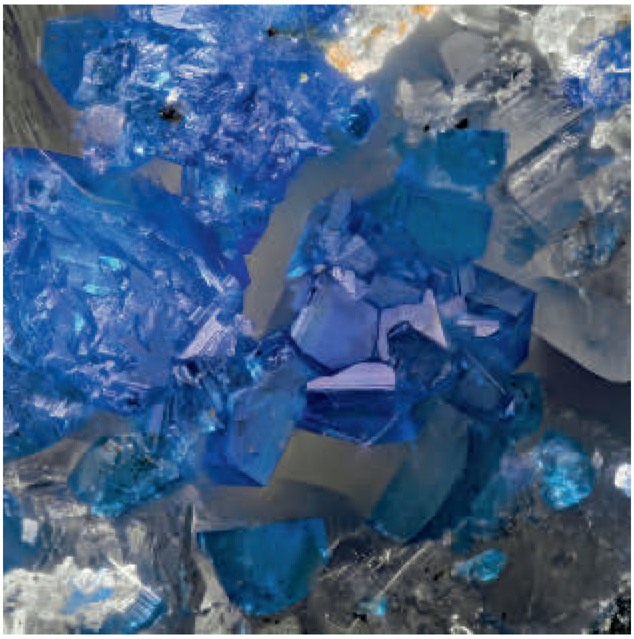

Figure 2. Deep blue diaboleite crystals overgrowing colourless phosgenite and minor anglesite. The crystals are hemimorphic with large basal pedion and small positive pedion. Specimen PBCM SR1a in the Steve Rust Collection from Penberthy Croft Mine, St Hilary, Cornwall. The field of view is 1.2 mm across. Photo Steve Rust.

DISCUSSION

Diaboleite has been recorded in two distinct geological environments in the British Isles. It is a rare late-stage mineral in the unusual manganese-oxide hosted lead deposits of the Mendip Hills and has been identified at a small number of localities where lead-copper veins have oxidised in the presence of seawater (Tindle, 2008: p. 197).

The mineralogy of the Mendip deposits is described by Turner and Rumsey (2010) and their geochemistry is explored by Bridges *et al.* (2012). On the majority of Mendip specimens diaboleite occurs as blue patches associated with dark green chloroxiphite in massive mendipite. Poorly formed prismatic crystals up to 9 mm in length are known from Merehead Quarry (Torr Works) near Shepton Mallet.

Diaboleite has been identified at several localities where lead-copper veins crop out on the north coast of Cornwall. It is a minor supergene phase in a quartz vein containing galena and minor chalcopyrite which is exposed in the intertidal zone at Daymer Bay near Polzeath (Starkey, 1987: p. 15) and occurs in a similar situation at Gunver Head[1] near Padstow (Braithwaite and Merry, 1996). Tiny crystals have been identified on chalcopyrite in a galena-bearing quartz vein which crops out in low cliffs at Trerubies Cove near Delabole (Neil Hubbard, *personal communication*, 2022). Diaboleite is also present in cavities in lead- and copper-rich smelter slag washed into The Gannel near Newquay (Harper, 2010).

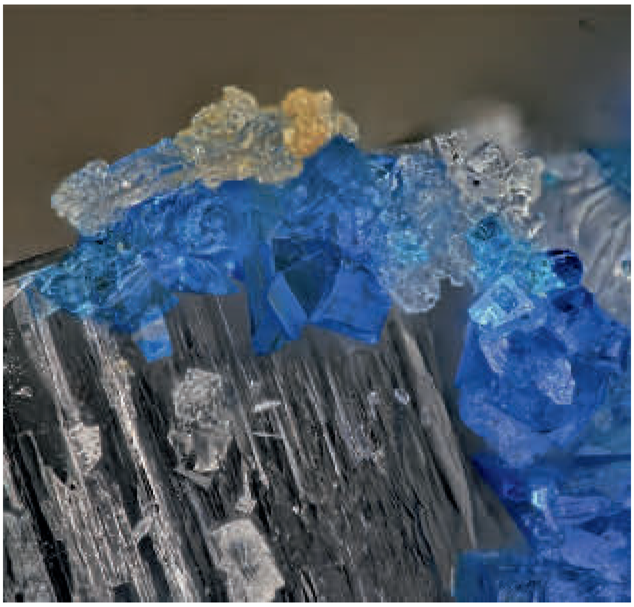

Figure 3. Tiny intergrown diaboleite crystals on a large deeply striated transparent phosgenite prism. Specimen PBCM SR2a in the Steve Rust Collection from Penberthy Croft Mine, St Hilary, Cornwall. The field of view is 1.2 mm across. Photo Steve Rust.

The geological environment at Penberthy Croft Mine is not directly comparable with any of the Mendip occurrences, but the geochemical models developed during investigations of these assemblages are useful. Early geochemical studies of the Mendip suite focused on the relationships between the unusual oxychloride minerals and the high chloride ion activity and low $p(CO_2)$ meant that carbonate minerals did not appear in the calculations (e.g. Humphreys *et al.*, 1980). More recent studies (e.g. Bridges *et al.*, 2012: p. 23) only mention diaboleite in passing. The Mendip models were extended to systems with higher $p(CO_2)$ in a study of the mineralisation at Mammoth St Anthony Mine (Abdul-Samad *et al.*, 1982), which noted:

> "over normal ranges of pH, an $a_{Cl^-} = ca.\ 10^{-2}$ will give rise to diaboleite in preference to either cumengeite or chloroxiphite, under which circumstances $a_{Cu^{2+}} = ca.\ 10^{-8}$".

The stability of diaboleite with respect to hydrocerussite, and of paralaurionite with respect to phosgenite, were used to constrain $p(CO_2)$ values, and a stability field diagram with $a_{Cu^{2+}} = 10^{-8}$, $a_{H_2CO_3} = 10^{-6.38}$, and $a_{Cl^-} = 10^{-2}$, in which the diaboleite stability field is bordered by phosgenite, cumengeite and wherryite, was constructed.

These calculations provide insights into the conditions in which the mineralisation at Penberthy Croft Mine developed. Wherryite can be ignored as Cooper and Hawthorne (1994) showed that it is a silicate-sulphate rather than a sulphate-carbonate as had been assumed. Its position in composition space is occupied by the surrounding phases, anglesite, caledonite, diaboleite and phosgenite, if the silicate ion activity is set to zero. The close association between diaboleite and

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[1] Also known as Cuddrabridge or Guddrabridge Mine, Padstow Consols, Trevone Consols and Wheal Galway.

phosgenite at Penberthy Croft limits $p(CO_2)$ values to between 10^{-5} (below which paralaurionite would replace phosgenite) and $10^{-3.4}$ (above which lead carbonates would replace diaboleite). A relatively dilute copper-bearing solution ($a_{Cu^{2+}} = 10^{-8}$), with a low sulphate ion activity (otherwise anglesite would be stable) and relatively high salinity are also required.

The conditions in which diaboleite might form were subsequently discussed by Williams (1990) using a slightly different stability constant for paralaurionite. This favours a slightly lower chloride ion activity (a_{Cl-} ~$10^{-2.5}$ or a little lower) if diaboleite is to form in the absence of cumengeite and paralaurionite. In these conditions, the field boundary between diaboleite and phosgenite is at a pH of about 6. These parameters provide the best geochemical model of the conditions in which the assemblage developed at Penberthy Croft.

Penberthy Croft Mine is several kilometres from the coast and the presence of chloride-rich supergene minerals is not the result of a direct interaction between lead- and copper-rich vein mineralisation and undiluted seawater. The calculations outlined above show that phosgenite and diaboleite remain stable at lower chloride ion activities (the molal mean activity of NaCl in seawater is about 0.667, whilst William's model suggests a_{Cl-} ~$10^{-2.5}$).

The most likely source of chloride ions is atmospheric precipitation, which has a variable but sporadically high chloride content in coastal areas. A study by Eriksson (1952) suggests the average chloride ion activity in rainwater at Penberthy Croft, which is about 4 km northeast of Mounts Bay, should be about $10^{-3.7}$, with substantial variation depending on the sea conditions and wind direction. This is an order of magnitude less than the chloride ion activity suggested by Williams (1990) and probably accounts for the rare and local occurrence of phosgenite and diaboleite at the site.

There is certainly no evidence of any interactions with late-stage hydrothermal chloride-rich brines, which have been proposed at other localities where diaboleite has been identified.

Phosgenite and diaboleite are rare at Penberthy Croft Mine. Both minerals require supergene environments with chloride ion concentrations that are greater than the values that are typical at inland sites. It seems likely that phosgenite formed in relatively acidic conditions (pH <6) generated when unusually chloride-rich rain-water reacted with pyrite and galena. It was etched and locally overgrown by diaboleite as chalcopyrite oxidised, the copper ion activity increased, and the supergene solutions evolved toward a neutral pH.

CONCLUSION

An isolated occurrence of the rare copper lead chloride diaboleite is reported from Penberthy Croft Mine, St Hilary, Cornwall. Minute crystals of a characteristic dark blue colour and hemimorphic habit occur in a small cavity with anglesite, cerussite and phosgenite. The mineralisation is thought to have developed in a local interaction between chloride-rich rainwater and chalcopyrite, galena and pyrite from the low-temperature lead-zinc vein assemblage.

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Thanks are due to staff at the Natural History Museum (London) for confirmation of the diaboleite by SEM-EDS and to the referees for suggestions which improved the manuscript. Readers should note that Penberthy Croft Mine was notified as an SSSI by English Nature for its mineralisation in 1993. The land is owned by the St Aubyn Estate. Permission for visits must be obtained through the agent for the St Aubyn Estate.

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MAKING IT MINE
SIR ARTHUR RUSSELL AND HIS MINERAL COLLECTION

By Roy E. Starkey
in association with the Natural History Museum, London.
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Available from the author at https://britishmineralogy.com, priced at £40 plus postage and packing.

Sir Arthur Edward Ian Montague Russell, 6th Baronet, dedicated the majority of his life to building what is regarded as the finest ever collection of British and Irish minerals. It is preserved at the Natural History Museum (NHM), formerly the British Museum (Natural History), London. Roy Starkey's latest book provides a detailed and lavishly illustrated account of Russell, his family, and the collection.

It is a monumental piece of work, showcasing superb examples of specimens from localities both famous and obscure. It describes a man of great humanity and compassion, someone with the common touch and, despite the grandeur of his title and collection, a person we as mineral collectors can readily relate to.

Always alert to a forthcoming anniversary, in 2014 Roy Starkey produced a web-based tribute: *An Appreciation of Sir Arthur Russell on the Occasion of the Fiftieth Anniversary of his Death - 24 February 1964*. In the same year Roy's first book, *Crystal Mountains Minerals of the Cairngorms* was published. It was followed, four years later, by *Minerals of the English Midlands*. Both volumes feature specimens from the Russell Collection.

Many authors would have been content after shedding so much light on Sir Arthur and his collection. But Roy is not one to rest on his laurels! His research had revealed that a much bigger story remained to be told and what could be better than to produce a book about Sir Arthur's life, his family and his collection, to coincide with the fiftieth anniversary of the formation of The Russell Society. This gave four years in which to execute an ambitious project and so a plan was drawn up.

The one component which could not be accounted for was not even in our vocabulary in 2018: coronavirus. With almost two years of disruption to travel, closure of museums and research facilities and extended periods of lock-down, one would have expected the publication to be delayed. But Roy is not one to allow a global pandemic to get in the way! And so, *Making it Mine Sir Arthur Russell and his Mineral Collection* was launched according to plan at the Oxford Mineral and Fossil Show on 8 May 2022.

This review considers the chapters sequentially. The book begins with a Foreword by Mike Rumsey, Principal Curator, Earth Sciences Department, NHM, London, there follows the Preface, Acknowledgements and a two-page Introduction. This describes how the author's became interested in Sir Arthur in 1982 after joining The Russell Society and the subsequent influence of Peter Embrey and Bob Symes of the NHM [formerly the British Museum (Natural History)], both of whom had met Sir Arthur and worked on his collection, and Bob King who had been a close friend of both Sir Arthur and Roy.

Making it Mine can be broadly split into three sections: Chapters two to eight provide a detailed background to the Russell family and Sir Arthur's life; Chapters nine to thirteen describe the mineral collection and how it was assembled; and Chapters fourteen to twenty-one examine particular facets of the collection.

Chapter Two, The Russells of Swallowfield, details the family history, beginning with Thomas Russell, Town Clerk of Dover, who died in 1688. It was his grandson, Henry, a highly respected lawyer working in India, who became the 1st Baronet (Bt.) in December 1812. A baronet is the lowest hereditary titled British order, with the status of a commoner but the right to use the prefix 'Sir.' A fascinating story of the social ascent and financial decline of the Russell family ensues. We become privy to the lives and loves of Sir Henry Russell (II), 2nd Bt., Sir Charles Russell (II), 3rd Bt., Sir George Russell (I), 4th Bt. and Sir George Arthur Charles Russell (II), 5th Bt., the protagonist's elder brother. Almost six pages are dedicated to Sir Arthur's mother, Constance Charlotte Elizabeth (nÕe Lennox), Lady Russell (1839−1925), affectionately known as 'Mano', whose lineage can be traced back to King Charles II.

The illustrations throughout the second chapter set the tone for the book. Wherever possible, the author has included an image of the person under discussion, be it a photograph or a painting. A fine likeness of every key figure in the Russell family is provided as far back as Thomas Russell's son, Michael Russell (II) (1711−1793). In later chapters this approach is maintained (wherever possible) for every mineral collector mentioned. This unstinting dedication provides a superb illustrated who's who of important British mineral collectors as far back as the eighteenth century; a delightful resource in its own right.

Chapter Three describes Swallowfield Park – The House, which is situated 60 km west of London and about 8 km south of Reading. Construction began between 1689 and 1691, replacing a Tudor mansion that had been the residence to four of Henry VIII's wives. Past and present photos illustrate its beautiful grounds together with shots of the house both inside and out. Swallowfield was purchased by Sir Henry Russell in 1820 and remained in the family until 1965 when Sir Arthur's widow Marjorie decided to downsize. One delicious gem is that in 1972, some five years after being sold to a private company, Swallowfield featured in the BBC science fiction series Doctor Who. Roy includes a great photo of actor Jon Pertwee in his iconic car 'Bessie' outside Swallowfield House while filming a storyline entitled The Time Monster. Look at this if you dare!

Chapters four to eight guide us through Sir Arthur's life, from his birth in Folkstone on 30 November 1878 to his death at Swallowfield on 24 February 1964. We learn of his childhood and upbringing, of his three marriages, four children and career, including his military service in World War I. After being invalided home following serving in the Red Cross as a military ambulance driver in France, he was recruited by the Ministry of Munitions to examine and report on metalliferous mines around the British Isles. Such resources were essential for the war effort and what more perfect wartime role could there have been for such an enthusiastic collector of minerals! The text describes the gentle, caring and genial personality of a man who loved all things associated with the natural world including birds, animals, trees and astronomy, not forgetting his beloved pets. Many modern mineral collectors share these passions and values.

The brief and cerebral Chapter Five, Goniometry and Crystal Drawing, is an unexpected diversion which explains the fundamentals of this almost forgotten skill. Sir Arthur was highly accomplished in the use of the optical goniometer and the necessary mathematics required to interpret the measurements and hence produce accurate three-dimensional crystal drawings. This, the only technical chapter, reveals Sir Arthur's deep understanding of crystallography.

The background to Sir Arthur's life concludes in Chapter Eight with his participation in the attempted revival of New Consols Mine at Luckett in East Cornwall. This project began in 1946, with Sir Arthur becoming gradually more involved and finally being appointed as joint Technical Director. The venture was unsuccessful and the mine eventually ceased working, with equipment being removed by September 1954.

Chapter Nine, Building the Collection, begins on page 98 and describes how Sir Arthur's interest was kindled and encouraged by his mother, Lady Constance, who from an early age herself had been captivated by minerals. Sir Arthur was collecting by the age of seven and some self-collected pieces, found when he was fourteen, remain in his collection.

A captivating diversion describes the mineral room at Swallowfield, a place we probably all wish we could travel back in time to explore. The next best thing would be a photograph or two, but sadly none is known to exist. Not daunted, Roy has included a reconstruction based on its dimensions, the cabinets now in the NHM, furniture and objects known to have been present and Christopher Russell's remarkably clear memory. The result of this exercise is a stunning ink drawing by artist Pippa Sweeney, an illustration you can pour over for considerable time delighting in the minutiae only a collector can. During the many iterations of the picture Christopher's recurring comment was "make it more-untidy!"

Chapter Ten describes Sir Arthur's lifelong passion for Field Collecting, conveying his unbounded enthusiasm and finely honed tactical approach. His collection contained around 6,100 self-collected specimens of which 3,500 were well labelled. Field trips were meticulously planned. Sir Arthur would research the literature, published and unpublished, and study specimens if these could be traced in private collections, universities or museums. Two of his favourite localities, Millclose Mine in Darley Dale, Derbyshire and Greenside Mine in Patterdale, Cumbria are described together with his lifelong love of collecting in Ireland, a country he visited about twenty-five times.

Chapter Eleven, the longest in the book, describes Old Collections. If I were forced to choose one as my favourite it would have to be this. Sir Arthur amassed his collection through the integration of self-collected material with purchased specimens or, in his case, entire collections. This account describes 38 collections in chronological order of acquisition. It begins with 160 specimens from the collection of John Hawkins (1761–1841) in 1905 and ends in 1958 with specimens from the Philip Rashleigh (1729–1811) and Alan Penrose Coode (1872–1958) collections. We discover more of these collectors and their collections and how Sir Arthur went about tracing them and of his negotiations to purchase them. Not all his missions ended in success, the collection of Sir Walter Synnot (1742?–1821) being one of the few that got away.

The variety of specimens showcased is breathtaking. Roy photographed every specimen on location in the Russell Room using a somewhat Heath Robinson portable studio. Call it what you may, it has delivered high quality images. The choice of specimens is careful, avoiding those which already feature in the literature. There is for example a quartz amethyst sceptre from Copper Hill Mine, Okehampton; two stunning Carn Brea Mine fluorites from John Ruskin's collection and a spectacular galena after pyromorphite from Wheal Hope. To this is added a remarkable calcite pseudomorphing ikaite from the River Clyde; a rather brooding yet gorgeous pyromorphite from Belton Grain Vein, Wanlockhead and a ridiculously fine chalcocite from St Ives Consols Mine, originally in the Williams Collection. Then there are two spectacular inky-blue fluorites from the Donald Bain Collection, one from

Wheal Mary Anne, the other from Holmbush Mine and finally, an exquisite, concentrically banded goethite from Restormel Royal Iron Mine, Lostwithiel.

Chapter Twelve, Mineral Dealing, is just five pages. A natural consequence of regular field collecting and the acquisition of so many old collections was a surplus of specimens. Every penny counted (towards buying further collections), so Sir Arthur put time and effort into selling the spare material. This chapter profiles some of his most distinguished customers, giving an insight into what they bought and how much they spent. Like many dealers he was adept at buying at the minimum price and selling for the maximum, but compared with today's prices (allowing for inflation) Sir Arthur now appears quite reasonable!

Chapter Thirteen, Colleagues and Contacts paints a fascinating picture of Sir Arthur's network of contacts, from the rich and famous through to dealers, miners and what we might term more ordinary collectors. Sir Arthur's intellect as well as his kind and affable personality naturally endeared him to all levels of society, enabling him to connect with and sincerely befriend anyone. The modern idiom is networking and it was through his web of contacts that he was able to keep a finger on the mineralogical pulse. On the first whisper of a secreted old collection or a newly discovered find, word would rapidly wend its way. Many of his important contacts were at the BM(NH) and the Mineralogical Society, both within easy reach because of Swallowfield's close proximity to London. He also had extensive connections in the mining industry and many additional museum and university contacts including his great friend Arthur Kingsbury. Brief biographies of his key contacts together with the typical range of specimen material each supplied are provided. There are several splendid group photographs, for example, the BM(NH) Department of Mineralogy in 1961; a group including some famous names having lunch above Virtuous Lady Mine in 1955; and a charming colour photo of Sir Arthur and Lady Russell in the grounds of Swallowfield Park with Department of Mineralogy staff on the occasion of the retirement of Jesse Sweet in 1961. Sadly, Jessie does not appear in the photograph as she is thought to have been the photographer.

Chapter Fourteen, The Bequest, explains in five succinct pages Sir Arthur's long-term ambition to pass the collection to the BM(NH) after his death. He first expressed this wish in March 1936, at the age of 57 and through successive correspondence and meetings over the ensuing years agreement was reached between both parties. However, the story is not without a strange twist, for unbeknown to the BM(NH) who now rightly assumed the collection was to be theirs, Sir Arthur opened discussions with the University of Oxford. The ensuing confusion is a real eye-opener, leaving us to wonder why Sir Arthur even contemplated muddying the waters in this way. The eventual bequest was, of course, to the BM(NH), but this left Oxford disappointed and more than a little bewildered.

Chapter Fifteen, The Collection, describes the transfer to the BM(NH) and subsequent curatorial input. In April 1964, W. A. Ferguson, Secretary of the British Museum, wrote to Christopher Russell stating that the Trustees of the BM(NH) had agreed Sir Arthur's terms for accepting the collection. A very young John Fuller and Bob Symes were despatched to Swallowfield and over many weeks carefully wrapped every specimen. The mineral cabinets and paper archive including journals, notebooks and every loose bit of paper containing jottings were also packed.

The stand-out name in this chapter is Arthur Henry Luckett, who joined the Department of Mineralogy in December 1969 and dedicated the best part of eight years to sorting and cataloguing the Russell Collection. The chapter ends with some interesting analyses. The statistics provide a useful appreciation of the collection's contents and shed light on how it evolved. One histogram tallies the total number of self-collected specimens for each year between 1897 and 1961, with a colour-coded breakdown of those collected in each of the four British nations and Ireland. Another chart reveals the top twenty species represented which, rather surprisingly, account for a little more than 50% of the total. At number one is fluorite (the collection's most common species) followed by calcite, baryte, cassiterite, quartz, galena, sphalerite, witherite, pyromorphite and, in tenth place, apatite. Another histogram plots the number of self-collected and purchased specimens which were accessioned into the collection each year. Acquisitions from collections certainly represent the lion's share. It is interesting to note that it grew steadily through both World Wars. As a self-confessed mineral geek, these statistics have got me thinking about my own collection: I am itching to perform similar analyses.

By the end of Chapter Fifteen, the main narrative is essentially complete, with every aspect of Sir Arthur's family history, life and legacy exquisitely covered. However, having built what Paul Desautels described as "probably the finest regional collection ever made", many outstanding specimens remained to be included. These are the subject of two major chapters: Specimen Gallery and Featured Locations. The selection criteria for inclusion in the Specimen Gallery are those of scientific and historic interest, visual impact, unusual associations or localities, and personal choice. Forty-five breath-taking pages ensue, featuring 136 specimens arranged in an anionic classification sequence, as they are in the Russell Collection. Choosing a few to highlight is like being asked to pick a favourite child, but here goes: chalcocite, Levant Mine (425); chalcopyrite, Tincroft Mine (429); sphalerite, Rampgill Mine (432); greenockite, Bishopton Railway Tunnel (435); galena, Wheal Hope (436); millerite, Cow Green Mine (439); fluorite, Wheal Mary Ann (444); fluorite, Glengowla East Mine (457); cuprite var. chalcotrichite, Old Gunnislake Mine (458); brookite, Twll-maen-grisial, Prenteg (471); calcite, Fucheslas Mine (483); apatite, Maen Quarry (497); topaz, Diamond Rocks (525);

kyanite, Banffshire (528) and connellite, Poldice Mine (556). Heartfelt apologies to the 121 that have been omitted!

Most of us have favourite localities and Sir Arthur was no different. During his research, Roy identified sixteen localities throughout Great Britain and Ireland which were high on his list, judging by the number of specimens he had and the frequency with which he visited. Locations range from Wheal Gorland and Virtuous Lady Mine in southwest England to Wanlockhead and Leadhills in southern Scotland, Benallt Mine in north Wales and Laharran Quarry in Ireland. There are six famous mines in Northern England and it is at this point we get to see some of the Russell Collection's iconic green fluorites from St Peter's Mine at Sparty Lea, Northumberland. Two specimens which sum up these sumptuous descriptions for me are the Philip Rashleigh clinoclase with olivenite (Fig. 724) and cubic fluorite crystals of rich inky blue with bevelled edges (Fig. 729) from Wheal Gorland.

Chapter Eighteen, Unpublished Work, succinctly describes some of Sir Arthur's uncompleted research. An early ambition had been to produce an updated revision of Greg and Lettsom's *Mineralogy of Great Britain and Ireland* which had been published in 1858. Sadly, the project never gained the required momentum and as time went on it must have become increasingly clear that it would never come to fruition. Sir Arthur had an interest in antimony mines and minerals and produced a monograph describing 52 localities in Great Britain and Ireland. He also had a great interest in gold from the British Isles and we are treated to two photographs of wonderful specimens, one from Hope's Nose, Torquay (self-collected in 1923) and one from Clogau (St Davids) Mine, Bont-ddu.

The Russell Archive is regularly referred to and Chapter Nineteen summarises its contents. The Russell Archive is an unofficial term which embraces three separate sources of information, each held in the NHM and all originating from Swallowfield. The information provided will be useful to future researchers and includes links for on-line searches. A selection of documents provides the reader an indication of the contents. The eclectic mix includes an invoice from W.J. Bennetts & Sons of Camborne for the photography of a grotto at Pendarves and the supply of prints; a coloured sketch showing the location of blue fluorite in the Ullcoats-Florence mine and, my favourite, an old postcard of the inclined tramway at the Alderley Edge copper mines in Cheshire.

Mike Rumsey (Principal Curator, Earth Sciences Department, NHM) has written the penultimate chapter, An Enduring Legacy. In just four pages he eloquently conveys the importance of the Russell Collection, providing a thought-provoking insight into its past, present and future curation and describes how it is made use of every day in a myriad of ways we could never imagine. Mike's text provides much food for thought. Referring to the tragic loss of the Wheal Gorland mine dumps and subsequent building over of this famous Cornish locality, he writes "Many mineralogical finds are 'one-offs', once they have been mined or quarried away this may be all the Earth has to offer." This chapter gives the reader an appreciation of the importance of mineral collections.

Making it Mine ends with a one-page Epilogue, reflecting on the unanticipated joys Roy experienced while working on the project. This addresses current policy towards UK museum funding, declining in-house expertise and the role of knowledgeable volunteers. Finally, and on an optimistic note, the potential revival in British mining is considered: polyhalite in North Yorkshire, Scottish gold, lithium, tin and tungsten in Cornwall and Devon and even copper, lead and zinc at Parys Mountain. *Making it Mine* ends with 18 pages of references, four useful appendices and a detailed 17 page index.

So there you have it. A lengthy review, but anything less would have been an injustice. I hope it conveys a feel for the depth and diversity of information in the book. Yes, it's all about Sir Arthur Russell, his family, his life and his celebrated collection, yet it is so much more.

I too would like to include some statistics. *Making it Mine* is beautifully illustrated, featuring 754 figures plus a full-page frontispiece, the well known black and white image of Sir Arthur armed with trilby, pipe and shovel on Bulmer's vein at Leadhills, Lanarkshire. No other photograph could be more fitting. There are 452 new, high quality mineral photographs representing some of the best specimens Britain and Ireland have produced (that's less than ten pence per photo). Of the remaining 302 figures, 95 are of people, 41 feature mineral localities, and 38 are of historic buildings. Various scenes comprise 24 figures and examples of documents from the Russell Archive account for a further 28. The remainder are of maps, charts and 68 miscellaneous photos which add richness and colour to the story.

Making it Mine is packed full of salient historic, technical and mineralogical information; yet it also includes countless delightful anecdotes and fascinating facts. The reader ends up armed with a wealth of absorbing information, at first seemingly unrelated to Sir Arthur and the mineral world, but every bit an essential part of the story. Such facts are often added as footnotes, some quite detailed. For example, I now know exactly what a Grade II listed building is, the basics of how an Atmos clock works, and that 90% of flying bombs were destroyed while still airborne using a radio proximity fuse, invented and manufactured in Salford. Don't even think about skipping a single footnote, every-one is a gem!

For anyone with a passion for minerals and/or mineralogical and mining history, *Making it Mine* is an absolute must. Priced at just £40 it is exceptionally good value; £40 will never be so well spent or bring so much pleasure. *Making it Mine* may reflect on the past, those halcyon days when Britain and Ireland were awash with metalliferous mines, when your underground safety gear was a tweed jacket and suitably doffed trilby, and when out collecting brookite and anatase at Prenteg, a little light blasting was not amiss! Yet it is also a book which constantly stimulates new ideas for future research projects.

In the very final paragraph, Roy generously gives the last word to Sir Arthur. I in turn feel it only appropriate to return the compliment to Roy. In the Epilogue's penultimate paragraph he signs-off "In drawing this book to a close and reflecting on all that I have learned about Sir Arthur Russell during its preparation, it is my sincere hope that you have enjoyed reading it and looking at the beautiful specimens as much as I have enjoyed the background research and pulling the story together".

We have indeed Roy and more than you could ever have hoped for.

Philip Taylor

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: https://russellsoc.org/publications/the-journal/. 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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