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The journal of British Isles topographical mineralogy

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FRONT COVER:

Barytocalcite crystals, from the upper flat, Admiralty Concession Flat, Nentsberry Haggs Mine, Nenthead, Cumbria. Specimen width 60 mm. Trevor Bridges specimen and photograph.

BACK COVER:

Professor Matthew Forster Heddle in academic dress, taken shortly before he retired in 1883.
© Private Collection.

Journal of the Russell Society

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EDITORIAL

When I agreed to take over the role of Journal Editor from Norman Moles I was a little concerned as to whether, even in these days of instantaneous electronic communication, the tyranny of distance would somehow impede the process of editing a British journal from the other side of the world. Without the able and generous assistance of a number of people it may, indeed, have been an issue and I would therefore like to express sincere personal thanks to the authors who have contributed articles to Volume 17 and to the referees who reviewed them. Our Journal Manager, Frank Ince, has provided me with a great deal of help and guidance (over and above his managerial duties), as has “retired” editor Norman Moles.

Volume 17 begins in Scotland with a paper that is a little different to most of the material published by the Russell Society hitherto. Matthew Forster Heddle and his *magnum opus*, *The Mineralogy of Scotland*, are names familiar to all students of British minerals, but most of us know little about the man himself. Hamish Johnston has been researching the life and times of his great-great-grandfather and will shortly publish a full-length biography of Scotland’s pre-eminent mineralogist. I am delighted that Hamish offered us a slimmed-down version for publication in the Journal, and I very much hope that other biographical articles might follow. We stay north of the border for a note on the occurrence of gonnardite from Assynt, where relatively large masses of unusually pure gonnardite occur, not in the familiar Tertiary basalt host-rocks, but in a silica-poor alkaline igneous intrusive complex.

Moving to Wales, three papers continue the story of manganese mineralisation in the northern part of the Principality. Supergene processes account for concentrations of manganese minerals near Caernarfon, in Gwynedd, while ganophyllite-group minerals are described from the Lleyn Peninsula, including first British occurrences of eggletonite and tamaite. Staying on Lleyn, a third contribution describes the first British occurrence of the brittle mica kinoshitalite, from the Bennalt Manganese Mine at Rhiw. Heading south to Central Wales, fragments of mineralised breccia containing the rare mineral elyite have been recovered from a site near Llancynfelyn, where recent archeological studies have unearthed evidence of an ancient smelting hearth.

Across the border in Shropshire, a study of material from the Pim Hill Mine provides evidence to support the view that Pim Hill, rather than Mottram St Andrew, might be the type locality for mottramite. Two papers follow on the Northern Pennines Orefield (NPO). The Admiralty Concession Flat at the Nentsberry Haggs Mine affords a unique opportunity to study barium mineralisation *in situ* which, in turn, provides observational evidence for how the observed sequence of minerals developed. ‘Ankeritisation’ is a part of that process, and ‘ankerite’ is a commonly-encountered mineral in the NPO; yet as the second paper demonstrates, under IMA rules of nomenclature, much of this ankerite is in fact iron-bearing, or iron-rich dolomite. A little further west, in the Caldbeck Fells, the first British occurrence of stibioclaudetite is described from Wet Swine Gill.

Finally we return to Scotland with a review of Roy Starkey’s long-awaited book “Crystal Mountains Minerals of the Cairngorms”; a work that I suspect will appeal equally to mineralogists, gemologists and historians.

Malcolm Southwood

Honorary Journal Editor

ERRATA

Cotterell, T.F. and Hubbard, N. (2013). Franklinphilite in veinlets in the Lower Cambrian Manganese Ore Bed, Harlech, Merionethshire, Wales. *Journal of the Russell Society*, **16**, 51–59. Throughout the paper a specimen was incorrectly identified by the accession number NMW 2011.2G.M.1f; the corrected accession number is NMW 2012.2G.M.1f.

Ince, F. (2013). A review of the occurrences of hydrocarbon-containing materials in Leicestershire. *Journal of the Russell Society*, **16**, 25–38. In Figure 1 the upper sheet letters were incorrectly identified as SW; the corrected sheet letters are SK.

MATTHEW FORSTER HEDDLE (1828–1897), SCOTTISH MINERALOGIST: HIS LIFE STORY

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INTRODUCTION

For all his fame as a mineralogist, Matthew Forster Heddle (1828–1897), author of *The Mineralogy of Scotland* (Heddle, 1901) is not well-known as a man. Almost every scientific paper written about him relies for its biographical content on the obituaries of Goodchild (1898, 1899) and Collins (1897) and the memoir by Alexander Thoms at the beginning of Heddle's (1901) two-volume work. From these has emerged the image of a man of great endurance who strode over the Scottish hills extracting minerals with a 28 lb¹ hammer and explosives. This does not do justice to someone who overcame many difficulties in pursuit of his goal of writing the definitive encyclopaedia of the minerals of Scotland. This paper presents a fuller, if brief, story of Heddle's life and achievements.

FAMILY

Heddle, always known as Forster, was born in Orkney on 28th April 1828. The obituaries relate that his physical feats were explained by his distant Scandinavian origins, but more relevant to his character were his parents, Robert Heddle (1780–1842) and Henrietta Moodie (c.1793–1833). Robert Heddle worked first for his brother-in-law W.H. Fotheringhame, a Kirkwall lawyer. His older brother John Heddle (1776–1812) studied medicine in Edinburgh and joined the army as a surgeon's assistant. These were the days of the Napoleonic Wars and John, promoted to surgeon, was sent to the island outpost of Gorée off French-occupied Senegal in West Africa. Here, in November 1805, he was the recipient of the last letter from the Scottish explorer Mungo Park (1771–1806) who earlier that year was on Gorée preparing for what was to be his final, fatal journey to explore the upper River Niger.

Robert soon followed his brother into the army. He was a paymaster, serving first in the West Indies before transferring to Gorée where he was re-united with his brother. After Britain captured Senegal in 1809 Robert became Assistant Commissary, a post in which he was responsible for the army's supplies and the government's customs functions. This brought him into contact with agents of the African princes, many of them slave traders, and British merchants. Seeing the money to be made, Robert resigned and became a merchant. He also formed a relationship with Adelaide Laferrrière, a mixed-race woman from a commercial family, with whom he had four daughters.

Ironically the defeat of Napoleon was bad for British merchants in Senegal. The Treaty of Paris (1815) handed back to France her former West African possessions and British merchants were harassed from the moment the

French returned in 1817. Robert left for Britain in August 1818 bringing back a fortune of £90,000² and his daughters, placing them in a school at Hackney, London. Their mother died in Africa three months later.

Having inherited the family's Orkney properties when John died, Robert immediately began to buy more estates. One of these was Melsetter on the island of Hoy, which Robert bought for £26,000 from the trustees of the bankrupt Major James Moodie. He was the last of many generations of Moodies to own Melsetter: his sons left to make a new life in South Africa, and he died soon afterwards in Edinburgh. Robert Heddle courted Moodie's daughter Henrietta and married her in November 1818. He was 38, a hard-nosed businessman, and she was 25, a romantic idealist in thrall to her family home, the wild Pentland Firth and the secret valleys of Hoy.

Robert and Henrietta had eight children, of whom Forster was the youngest to survive into adulthood. He was named after Robert's friend Matthew Forster, head of Forster and Smith, the largest British company trading to West Africa. Later the compliment was reciprocated when Matthew Forster named one of his ships *Robert Heddle*. Apart from pursuing his African and other business interests Robert continued to buy properties in Orkney. "I have boxes of titles...they are so numerous," wrote Robert's Edinburgh lawyer Thomas Innes (Innes, 1842) after his death. Robert was also active in politics and constantly involved in legal disputes over property, one case even reaching the House of Lords. Tragedy struck in 1833 when Henrietta died. Robert remarried in 1835 but his second wife Elizabeth was distant from the children. It is unsurprising that the young Forster, growing up in a world of conflict and emotional deprivation, sought solace in the natural world around him. In 1841 his sister Eliza eloped, to the outrage of her controlling father.

CHILDHOOD AND EDUCATION

When Robert died in 1842 Forster and three siblings became the responsibility of curators led by Fotheringhame. Another was Matthew Forster who by now was M.P. for Berwick, and fighting to preserve his reputation in a Parliamentary enquiry into the alleged participation of British merchants in the illegal slave trade. Robert sent all his sons to the Edinburgh Academy, Forster entering in 1837, but in late-1842 Fotheringhame transferred Robert junior (1826–1860) and Forster to Merchiston Castle Academy.

² The National Archives Currency Converter calculates old sums of money at 2005 values, but is no longer being updated. £1,000 in 1818 was worth £41,920 in 2005. This converts to £53,020 at 2014 values using <http://www.thisismoney.co.uk/money/bills/article-1633409/Historic-inflation-calculator-value-money-changed-1900.html>.

¹ 12.7 kilograms.

Here the headmaster was Charles Chalmers (1792–1864), brother of Thomas Chalmers (1780–1847) who in 1843 led the split of the Free Church from the Church of Scotland.

The boys did very well at school and both won many prizes. Their elder brother, John George Heddle (1819–1869), inherited the family estates but neither Robert nor Forster showed any interest in following their father into business. Forster was destined to become a farmer until his last year at school when he announced that he would become a doctor. In October 1844 he entered Edinburgh University. He lodged at 51 Albany Street with Dr John Brown (1810–1882), a respected doctor with artistic and literary interests who in 1859 published *Rab and his Friends*, regarded as the best animal story of the 19th century. In those days Edinburgh was the centre of British medical education and Forster was taught by eminent professors, among them James Young Simpson (1811–1870), pioneer of the use of chloroform as an anaesthetic. In Kirkwall, Fotheringhame received regular reports on Forster's performance and issued instructions to Brown. Although Forster's application to his studies was good, Fotheringhame constantly exhorted him to further effort and encouraged extra classes in French and Latin. He strongly criticised Forster's attendance at shooting salons, purchase of fishing equipment and any expenditure unconnected with his studies.

EARLY MINERALOGICAL ACTIVITIES

Forster Heddle (hereafter referred to as Heddle) was much influenced by Professor of Chemistry, William Gregory (1803–1858), and Professor of Natural History, Robert Jameson (1774–1854). Their subjects connected with Heddle's enthusiasm for collecting rocks and minerals, an interest he developed after his plant collection was accidentally damaged by a school-friend. As early as 1846 Heddle (aged 18) presented a mineral collection to a new museum in Orkney. By 1850, well-connected with collectors and dealers, Heddle had amassed a large collection of specimens from all over the world (Heddle, 1850). That summer³ he went to Germany to study chemistry and mineralogy at Clausthal and Freiberg, both important mining and mineral centres with associated colleges. In 1851 Heddle's good exam results and thesis *The Ores of the Metals* (Heddle, 1851) secured his M.D. degree. Heddle now entered medical practice in the Grassmarket area, then one of the poorest and most disease-ridden parts of Edinburgh where people lived in cramped, subdivided buildings lacking sanitation and water supplies. Heddle was not employed as a Poor Law doctor and probably acted as assistant to a general practitioner. He lived at 8 Clarence Street in Stockbridge. Not suited to medical practice, Heddle persisted for some six years, no

³ Note that Goodchild said that Heddle went to Germany on concluding his studies, *i.e.* in 1851. The author's research of extant letters shows that Heddle was in Germany in 1850, and was in Shetland in 1851 at the time when, according to Goodchild, he would have been in Germany. Goodchild would have recorded what Heddle told him when they were working together at the Edinburgh Museum of Science and the Art in the 1890s, by which time Heddle acknowledged that his memory was deteriorating.

doubt because of his need for income, but by 1854 he was applying for academic posts in mineralogy.

Enthused by his German experience, Heddle joined the Edinburgh Geological Society in late 1850 and made an immediate contribution. Founded in 1834 by the Edinburgh mineral dealer and teacher Alexander Rose (1781–1860) and a group of his students, the Society was now somewhat moribund. In December 1851 Heddle was elected President in the hope that he could rejuvenate it, but although he frequently contributed papers he was not a committee man and his presidency failed to achieve the hoped-for improvement in membership and reputation. Perhaps his mind was elsewhere; in 1851 Heddle also became a Fellow of the Royal Physical Society of Edinburgh when Hugh Miller (1802–1856), the famous self-taught geologist and writer, was President. Heddle was particularly active: he contributed eight papers between 1854 and 1856 in which year he became a member of the Society's Council. While at Edinburgh University, Heddle met an older student, Robert Philips Greg (1826–1906). Greg was the son of a wealthy Manchester cotton mill owner, but his business skills being poor, he soon withdrew to concentrate on mineralogy. He asked Heddle to edit his book, *Manual of the Mineralogy of Great Britain and Ireland* (Greg and Lettsom, 1858), co-written with William G. Lettsom (1805–1887), a diplomat. Heddle did so, adding his chemical analyses and information on Scottish mineral sites to the book. A Heddle heulandite specimen is shown in Figure 1.

ST ANDREWS

Between 1855 and 1856 Heddle contributed seven papers to the *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* edited by Sir David Brewster (1781–1868) and others. Brewster was Principal of St Andrews University when, in 1856, the Professor of Chemistry, Arthur Connell (1794–1863) fell ill and became unable to teach his classes. Heddle was asked to deputise and did so on his return from several months' mineral collecting in the Faroes on a chartered ship, the *Cock of the North*, planned with his friend Patrick Dudgeon of Cargen (1817–1895). Dudgeon had returned to Scotland after a successful business career in the Far East and no doubt footed the bill. They were to become lifelong friends, Heddle later naming one of his daughters after Dudgeon's wife Cecilia and dedicating to him a private publication of his *Geognosy and Mineralogy of Scotland* and other papers⁴. At first Heddle lived between Edinburgh and St Andrews, all the while exploring, collecting, and lecturing in geology at Grange House School, Edinburgh. He then moved to St Andrews where he continued to take Connell's classes until 1862 when, on Connell's resignation, he secured the professorial chair in his own right. In the meantime, in 1858, Heddle married Mary Mackechnie (1830–1891), daughter of an army surgeon who had retired to St Andrews. Over the next

⁴ Heddle arranged for off-prints of his *Geognosy and Mineralogy of Scotland* and miscellaneous other published papers to be bound together in a book. A small number of copies were made, with some variation in the contents, the latest paper dating from 1892. National Library of Scotland, shelfmark: ABS.2.204.030.

sixteen years they were to have ten children of whom seven survived into adulthood. They lived at West Port House, 172 South Street before moving in 1874 to St Leonards House, former dwelling of George Buchanan (1506–1582), tutor to Scottish King James VI, and of Sir David Brewster who was responsible for its current gothic appearance. By 1859 Heddle had published six more papers in the *Philosophical Magazine*.

The chair of chemistry at St Andrews University freed Heddle from medicine but was something of a poisoned chalice. Its income came from a modest private endowment supplemented by a government grant that was smaller than it should have been because of inaccurate information given to the 1858 Universities' Commission. Unlike the other chairs it was excluded from a share of the University's income from farm rentals. Furthermore, at a time when the compulsory M.A. curriculum was under pressure (there were no science degrees in those days) some of Heddle's colleagues, led by the Professor of Natural History, William Swan (1818–1894), engineered the exclusion of chemistry. This meant that Heddle lost class fees when, inevitably, his student numbers dropped. To cap it all, chemistry was an expensive subject and inadequate financial provision meant that Heddle had to pay for equipment and materials from his own pocket. Personal financial problems were to trouble Heddle until the end of his life.



Figure 1. Heulandite. Crystals to 1 cm, with chlorite, on basalt, Kilmacolm, Renfrewshire. Heddle Collection G.438.23. © National Museums Scotland.

Heddle was popular as a teacher who rebuilt his class numbers by attracting students with experiments often regarded as conjuring tricks. The independent-minded Heddle sometimes found himself in conflict with the University. At a time when all students were male, one of Heddle's first acts in 1862 was to give a class ticket to a female would-be medical student, Elizabeth Garrett (1836–1917). This was overturned by the University, but Garrett remained in St Andrews for some months and took private lessons with Heddle. As Elizabeth Garrett Anderson she went on to become famous as Britain's first woman doctor. In 1865 Heddle angered Principal James Forbes (1809–1868) with his "strange and perverse conduct" when, as a member and elder of St Leonard's parish, he sided with the congregation against the University in a public dispute over the use of the United College church (Forbes, 1865, pp. 634–638). A photograph of Heddle from this period is shown in Figure 2.

Soon after his arrival in St Andrews, in 1856, Heddle was elected a member of the St Andrews Literary and Philosophical Society, founded in 1838 by Brewster and others with the aim of promoting literary and philosophical research, and establishing a museum. Membership was a useful way for Heddle to meet influential local people, and in 1861 he led a dig at Dura Den near Cupar to collect fossil fish for the museum. One of the species discovered was



Figure 2. Studio portrait of Matthew Forster Heddle, probably dating from his early years in St Andrews, c.1865. © Private Collection.

later named after him: *Gyroptychius heddlei*. Heddle also joined the Royal and Ancient Golf Club. He participated regularly in the Spring Medal competitions, but was not a very good golfer; in 1861 he went round in 135 strokes. Heddle always got on well with the students. He acted as organiser and chief judge when the Scottish inter-university games were held at St Andrews, and was popular at a time when relations between the professors and students were not good. Principal Forbes, backed up by Heddle's *bête noire* Swan, tried to suppress the students' annual Kate Kennedy pageant which had become a symbol of student freedoms. Touring the streets the students shouted out three groans outside the homes of Forbes and Swan, but three cheers at those of Heddle and others.

Heddle did not confine himself to University affairs. The Dundee Police Commissioners used him as an expert witness in cases against factory owners over smoke nuisance. Two other issues in which he was involved, and which attracted huge public interest, were the quality and price of gas supplied by the two Dundee gas companies and the safety of the Cupar water supply. Heddle often lectured on chemistry and geology as part of public educational programmes organised by civic authorities for their citizens. On one occasion Heddle announced the result of his analyses of the calorific value of coal dug from the different Fife pits, and afterwards an enterprising Dunfermline coal merchant used it to promote coal from the Halbeath colliery.

HEDDLE'S FIELD WORK

Heddle published only one short scientific paper (Heddle, 1866) between 1860 and 1875 and so was all but invisible to the wider mineralogical world. During these years, and beyond, he was busy exploring Scotland and the Islands to observe the geology, search for minerals and record his findings. The University session ran from early November to late April so every year Heddle had the six summer months for field work. He used his spare time during the winter months to carry out the chemical and optical analysis of his minerals. A Heddle julgoldite specimen is shown in Figure 3.

It is evident from Heddle's writings that much of his exploration was done alone, but he was often accompanied by friends, themselves accomplished naturalists, most with valuable local knowledge. The most important of these was Patrick Dudgeon, himself a distinguished mineralogist. The two men explored Dudgeon's home area of Dumfries and Galloway, and over a number of years used a yacht for transport and accommodation on visits to many localities on the coast of the Scottish mainland and in the Western and Northern Isles. Although not specifically stated, it is probable that it was with Dudgeon that Heddle visited the famous, and inaccessible, locality of Sgur nam Boc on Skye. A Heddle Collection label of stilbite from this locality is shown in Figure 4.

Another frequent companion in these years was James Nicol (1810–1879), Professor of Natural History at Aberdeen University. Nicol had been engaged in a bitter dispute with Sir Rodrick Murchison (1792–1871), Director-General of the British Geological Survey, over

the structure of north-west Scotland. Murchison proposed that the observed geology could be explained simply in terms of a stratigraphic sequence, while Nicol believed that the succession resulted, in part, from faulting. Nicol did not change his mind but in 1866 withdrew from public debate on the issue which, once finally resolved in 1884, showed that he had been largely correct. Heddle and Nicol explored and collected minerals together, mainly in the Aberdeenshire area, and Nicol was in the habit of sending Heddle interesting specimens for analysis.

Church ministers were prominent among Heddle's companions. Always highly educated, and usually with time on their hands, ministers were numerous among Scotland's scientists and natural historians. Heddle relied on Rev. Charles Clouston (1800–1884), minister of Sandwick, for some of his work on Orkney, Clouston having written the geology section in the *New Statistical Account of Scotland* (Clouston, 1845, pp. 46–51). Rev. James Maxwell Joass (1830–1914), minister of Golspie, was an antiquarian and keen mineralogist who had a wide knowledge of Caithness and Sutherland and good local contacts, including the Duke of Sutherland who gave permission for their mineral explorations. Joass was on the spot during the Kildonan gold

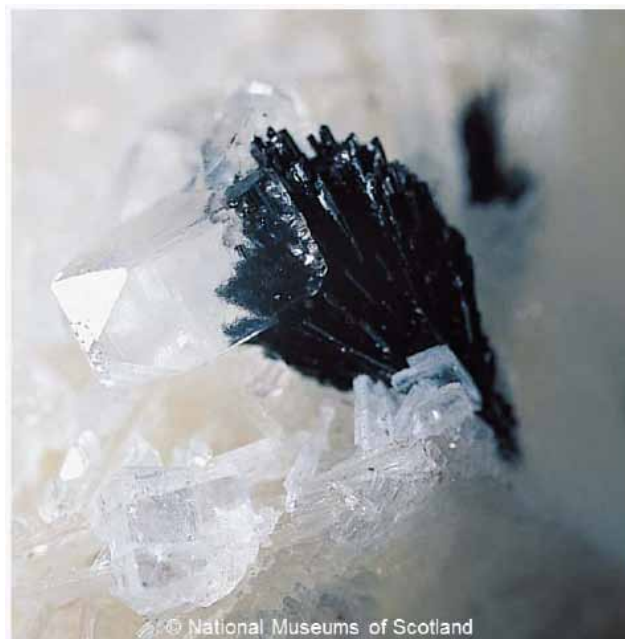


Figure 3. Radiating spray of thin blades, 3.5 mm long, of julgoldite on pectolite, Auchinstarry Quarry, Kilsyth. G.435.27. © National Museums Scotland.



Figure 4. Early museum label for Heddle specimen of stilbite. He specified in his will that every specimen was to have "Heddle Collection" on its ticket. © National Museums Scotland.

rush of 1868–1869 and provided Heddle with notes of his own surveys, the two men later visiting the terrain together. It was Joass and Nicol who in 1875 brought to Heddle's attention a mineral-bearing boulder on the flank of Beinn Bhreac near Tongue, Sutherland. Estimated at 100 tons, its origin was Ben Loyal, some five miles away (Heddle, 1883a):

I regard this as mineralogically the most wonderful and interesting stone in Scotland...a perfect mineral casket, containing in its small bulk as many minerals as do some counties.

A vein two feet wide ran through the boulder from which Heddle extracted seventeen different minerals (Heddle, 1883b):

These, arranged in order of their occurrence from the substance of the stone to the centre of the vein, were:- Babingtonite. Ilmenite. Fluor. Amazonstone. Sphene. Oligoclase? Allanite. Quartz. Orangite and Thorite. Specular Iron. Magnetite. Strontianite. Lepidomelane. Bhreckite. Radiated Cleavelandite. And a substance of a somewhat doubtful nature.

Portsoy, Banffshire, was one of Heddle's favoured mineral areas, and here he met Rev. William Peyton (1832–1894), a Free Church minister. They undertook many collecting trips together, especially after Peyton moved to Broughty Ferry, Angus in 1878. Like other of Heddle's contacts, Peyton often sent him mineral specimens.

Rev. George Gordon (1801–1893), minister of Birnie near Elgin, was an eminent natural historian who corresponded with Darwin and Huxley. He facilitated visits to his area by Heddle, Dudgeon and Nicol in 1877. In 1878 Gordon collected, at Heddle's request, specimens that he lacked from localities in Shetland.

Like ministers, medical practitioners were often interested in mineralogical pursuits. Two with whom Heddle collected were Dr John Wilson (1838–1905) of Wanlockhead, Lanarkshire and Dr Thomas Aitken (c.1835–1892), the Superintendent of the Inverness District Lunatic Asylum and founding Secretary of the Inverness Scientific Society and Field Club, for which Heddle led excursions in 1878 and 1879. Of Heddle's other companions perhaps the most important was Archibald Geikie (1835–1924) who he had known since his Edinburgh days. Heddle and Geikie discussed mineralogical problems in their letters, and Geikie was also a confidant with whom Heddle shared his personal problems. In the 1870s Geikie was Director of the Geological Survey of Scotland and associated with the opinions of his late mentor Murchison. Geikie and Heddle visited Sutherland together during 1877 (Heddle, 1877a) and again in 1880–1881 (Heddle, 1881b) by which time the debate about the geology of north-west Scotland had been re-activated. An extract of a letter from Heddle to Geikie in 1878 is shown in Figure 5.

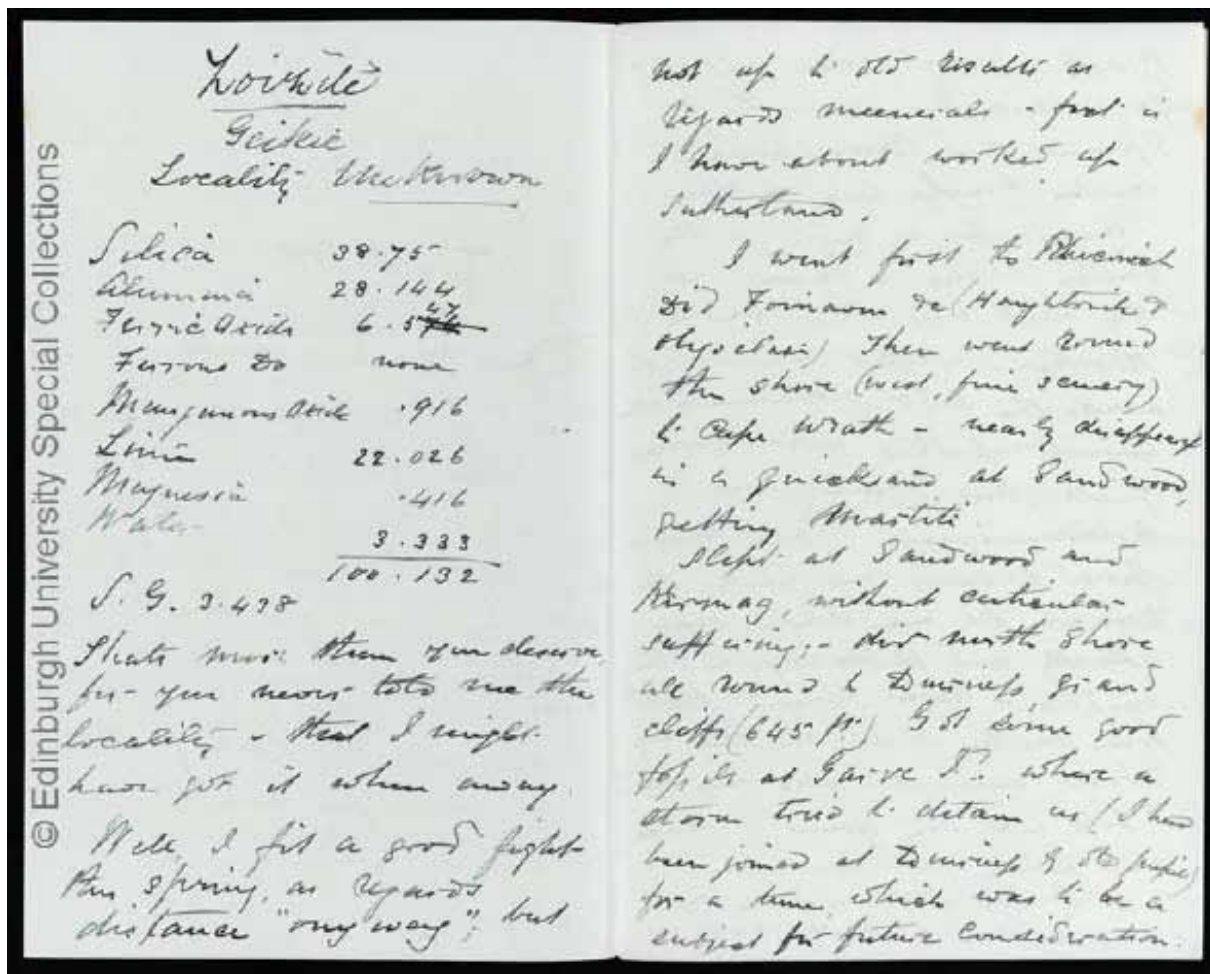


Figure 5. Part of a letter from Heddle to Archibald Geikie, 5th July 1878, in response to an enquiry about his activities. Heddle provides an analysis of a mineral sent earlier by Geikie and describes his recent visit to Sutherland. GB0237 Gen525/2. © Edinburgh University Special Collections.

1876: HEDDLE IN THE LIMELIGHT

The extent of Heddle's explorations is evident from the explosion of publications that appeared from 1876, the year when Heddle re-emerged onto the national mineralogical stage at the age of 48. In February he and others (including Nicol and Geikie) founded the Mineralogical Society of Great Britain and Ireland, Heddle becoming a vice-president, and the second president 1879–1881. Peyton soon became the Secretary for central Scotland, organising in 1880 an excursion to Talisker Bay in Skye led by Heddle. A modern photograph of Talisker is shown in Figure 6. From the start the *Mineralogical Magazine* was dominated by Heddle papers, principally his *Geognosy and Mineralogy of Scotland* which was published in thirteen parts between 1878 and 1884 and geological maps of Shetland and Sutherland in 1879 and 1882 respectively. In these papers Heddle described the topography, geology and mineralogy of each county, starting with Shetland, then Orkney, Caithness and ending with Sutherland. For Heddle "there is no county in Scotland which presents us with so many varieties of rock as Shetland" (Heddle 1878). Orkney was less interesting, but greatly superior to Caithness which was "pre-eminent in dearth of minerals" (Heddle, 1880). Some two-thirds of Heddle's *Geognosy and Mineralogy of Scotland* was devoted to Sutherland, reflecting the scale of his struggle with the problems of its geology. These were resolved by Charles Callaway (1838–1915) and Charles Lapworth (1842–1920) and confirmed in 1884 by detailed mapping undertaken for the Geological Survey by Benjamin Peach (1842–1926) and John Horne (1848–1928). Heddle met Callaway several times in the field during 1881–1882 (Oldroyd, 1990, p. 207) and provided Lapworth with thin section slides (Heddle, 1884). A Heddle thin-section from Sutherland is shown in Figure 7.

In 1876 the Royal Society of Edinburgh began publishing Heddle's *Chapters on the Mineralogy of Scotland* and immediately elected him a Fellow. The Society published seven chapters up to 1883, with an eighth published after his death. In these Heddle structured his material around mineral families drawing on minerals found all over Scotland. The Society recognised the importance of Heddle's original work and in 1879 awarded him its prestigious Keith Prize for *The Rhombohedral Carbonates* (Heddle, 1876) and *The Felspars* (Heddle, 1879). Heddle was now in the illustrious company of other prize-winners such as David Brewster, George Boole (1815–1864) and James Clerk Maxwell (1831–1879).

If all this were not enough, Heddle wrote an 87-page article on *Mineralogy* for the ninth edition of *Encyclopaedia Britannica* (Heddle, 1883c, pp. 346–431). His relations with the Mineralogical Society were deteriorating, however. The Society acknowledged that his work had been the mainstay of the *Mineralogical Magazine* but there were some who thought that "portions of his papers are not mineralogical, scarcely indeed scientific" (Hudleston, 1884). The Society decided to restrict its publishing to specifically mineralogical papers and did not publish Heddle's next *Geognosy* paper on the islands of Ross and Cromarty read at The Society in 1884.



Figure 6. Mineral-bearing cliffs on the north side of Talisker Bay, Skye. Heddle first came here in the 1850s, and in 1880 led a Mineralogical Society field trip to the locality. © Roy Starkey.



Figure 7. Thin-section (76 x 5 mm) of schist from Ben Loyal, Sutherland. One of a large collection of Heddle microscope slides held by the Hunterian Museum, University of Glasgow. © University of Glasgow.

For his part Heddle recognised that he did not have the geological knowledge to complete the *Geognosy* as originally conceived and from now on his omnibus work would follow the structure of his chapters for the Royal Society of Edinburgh. Apart from the *Geognosy* papers Heddle had by now published fourteen technical papers in the *Mineralogical Magazine*, and from 1887 a further thirteen appeared in which he announced significant findings. Heddle also published occasionally in *Nature*, and latterly in the *Transactions of the Geological Society of Glasgow* and the *Transactions of the Edinburgh Geological Society*, as well as occasional popular pieces.

PROBLEMS AT ST ANDREWS

Given Heddle's success in life it comes as a surprise that he was deeply unhappy in the 1870s. Pressure on his finances grew as his family got larger and, although Principal Shairp (1819–1885) acknowledged that Heddle was badly paid, the University did nothing to help. It was itself impoverished, and some colleagues, who were much better paid than Heddle, looked to their own self-interest by continuing to try to keep chemistry out of the M.A. curriculum. Heddle was driven to applying for chairs elsewhere but was not successful. His greatest hope in 1873 was, with the help of Geikie, to secure work with the Geological Survey, then expanding its work in Scotland. Dudgeon also lobbied for the creation of a post for which Heddle would be the pre-eminent candidate. This did not materialise so Heddle explored paying work in the summer months even though to do this would be at the expense of his scientific work, to which he attached the highest importance. In 1877 he hoped that a mineralogy lecturer post in Glasgow might be elevated to a chair that would “set me free from this dead hole”, as he described St Andrews (Heddle, 1877b). All this affected Heddle's health: he was showing the first signs of heart disease and suffering from lumbago and anxiety.

St Andrews University itself was also in a bad way. In 1876 student numbers, at 130, had fallen to their lowest, while Edinburgh had 2,351, Glasgow 1,773 and Aberdeen 667. That same year a Royal Commission was established to look into the Scottish Universities, but its report in 1878 provided little comfort. St Andrews was too small to develop, so the Commission recommended only enough support to keep it going. Heddle knew that St Andrews was vulnerable, even describing it in his evidence to the Commission as a “sinking ship” (Inglis, 1878). He was one of the few professors who recognised that salvation lay in setting up science and medical faculties in the neighbouring industrial city of Dundee where there was unmet demand for higher education. In 1875 Heddle backed his judgement by delivering, with three other professors, a programme of public lectures there. Heddle was right, and in due course a University College was created in Dundee, although linked to London. Only during 1897, after years of wrangling, did it become part of St Andrews University.

HEDDLE THE MOUNTAINEER

In 1880 Heddle became involved with the work of the Royal Society of Edinburgh's Boulder Committee, formed

in 1871 to collect information about erratic boulders, identify their source and develop a theory of how they had come to be moved. Every year until 1883 Heddle spent a month or more traversing different parts of Scotland day after day. Heddle was not simply a mineral collector; he loved the mountains for themselves. This is evident from lyrical passages in his papers on Sutherland. Of Ben Loyal, the source of the Beinn Bhreac boulder, Heddle (1881a) wrote:

Thinking of Scotland's Hills, we ever return to *this* as the Queen of All. For gracefulness, chasteness, versatility, and nobility of form, it stands pre-eminent.

Heddle revelled in the sense of well-being that the mountains gave him, and when his lumbago was severe he walked the hills to drive away the pain.

Heddle was present at the opening of the Ben Nevis observatory in October 1883 and proposed one of the toasts at the celebratory dinner in the Alexandra Hotel, Fort William. Hugh Munro used some of Heddle's altitude measurements in his *Tables of the 3000-Foot Mountains of Scotland* published in the *Scottish Mountaineering Club Journal* in September 1891. Munro found 538 summits of which he regarded 283 as separate mountains and 255 as tops. Earlier, in February 1891, Heddle (1891) told the St Andrews Literary and Philosophical Society that:

...there were 409 hills in Scotland above 3,000 feet high of which he had been at the top of 350, the total height of which was 1,183,000 feet.

Heddle was competitive; in 1891 he proudly told Geikie “Peyton 270 – Phillip⁵ 260, others nowhere” (Heddle, 1891). Writing after Heddle's death, Munro (1898) said:

There can be little doubt that Professor Heddle had climbed far more Scottish mountains than any man who has yet lived...No district was unknown to him, and scarcely any high mountain unclimbed by him...in 1893...it was decided to admit a limited number of Honorary Members to the Club mainly because we desired to do honour to Professor Heddle.

RETIREMENT: A NEW START

In 1883 the solution to Heddle's problems at St Andrews appeared in the unlikely person of Baron Albert Grant (1831–1899), a charismatic company promoter and financier. At this time the newspapers were full of reports of gold strikes in the Transvaal in South Africa. Grant teamed up with a Mr Gwynne Owen who had secured the rights to two farms reputedly rich in gold. They formed the Lisbon-Berlyn (Transvaal) Goldfields Company Ltd. and in Heddle found someone happy to take leave from his University post for a five-year contract as the Company's mineralogist, geologist and assayer. For this he was to receive a huge salary, shares and an annuity. Heddle had not yet visited the site but his name and qualifications featured in Company advertisements to give confidence to investors (Classified advertisement, 1883, p. 1). Heddle left for South Africa in January 1884 with his elder son Robert (1861–1902) employed as his assistant. When he arrived Heddle found gold, but not in the quantities expected, nor was it easy to extract. Heddle left in June 1884: he was now a threat

⁵ Colin Phillip (1855–1932) was a landscape painter and founder member of the Scottish Mountaineering Club.

to the Company which had already spent huge sums on Californian mining equipment. It publicly belittled Heddle's abilities, then sued him for breach of contract and for repayment of the annuity. Heddle riposted by threatening to petition for a winding-up order on the Company on grounds of insolvency. When the case reached court in London the Company secured an injunction against Heddle's petition but Heddle kept all the money paid and due to him. Both the Lisbon-Berlyn Company and Grant were soon bankrupt.

The St Andrews University Court agreed that Heddle, now 56, could retire on 15th November 1884 "on the ground of infirmity," thus giving him access to his pension. They also awarded him Emeritus status. A photograph of Heddle from his last years as Professor of Chemistry is shown in Figure 8. Heddle's successor as Professor of Chemistry was Thomas Purdie (1843–1916), one of Heddle's former students, who had taken his classes while he was abroad. In retirement from teaching Heddle resumed his explorations, recording, analysing and writing. A new collecting companion was James Currie (1863–1930) born into a wealthy family whose large shipping company was based at Leith. Twenty-five years younger than Heddle, Currie learned much from his mentor, and later contributed a chapter to *The Mineralogy of Scotland* (Heddle, 1901). A Heddle thin-section of greenockite is shown in Figure 9.



Figure 8. Professor Matthew Forster Heddle in academic dress, taken shortly before he retired in 1883. © Private Collection.

Heddle also became close to Alexander Thoms (1837–1925), the eldest son of a successful Dundee manufacturer who had retired to St Andrews and was a member of the Literary and Philosophical Society when it elected Heddle a member in 1856. Around 1860 Thoms went to Bengal to work for his maternal uncle Josiah P. Wise (1803–1879), a prominent indigo planter. When the

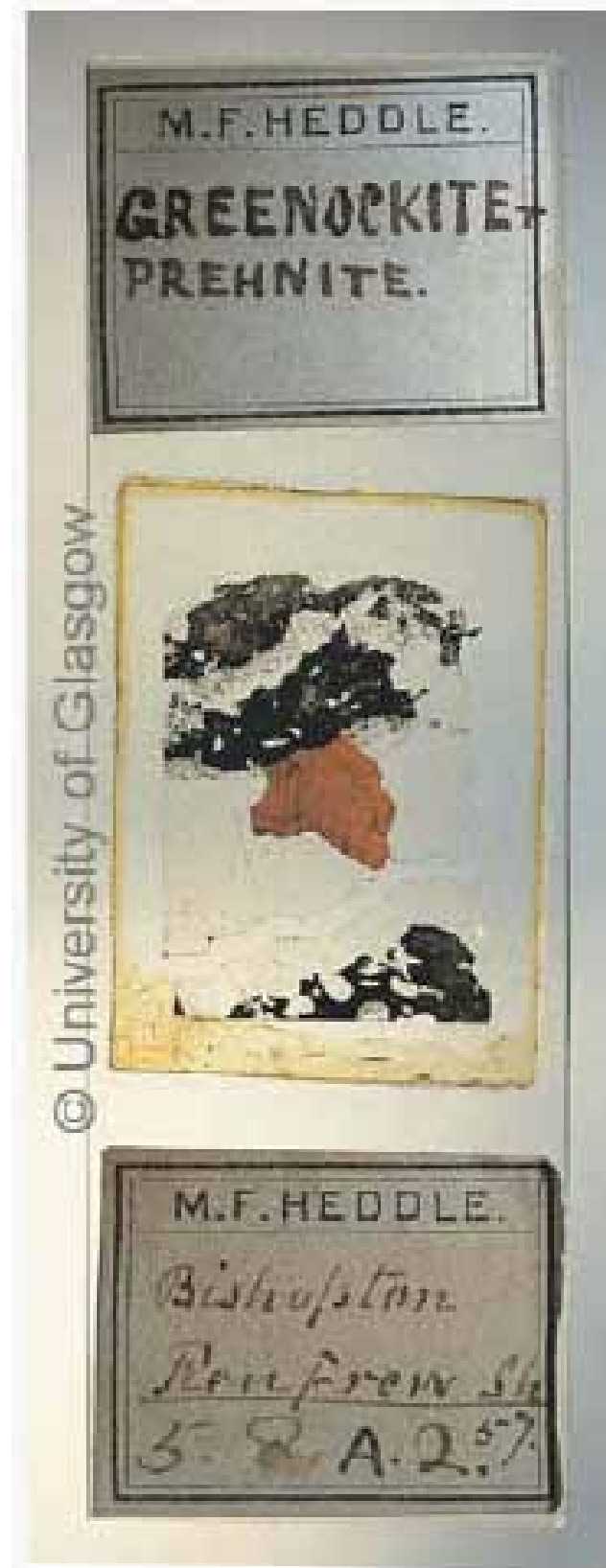


Figure 9. A Heddle thin-section (76 x 25 mm) of greenockite in prehnite. Bishopston, Renfrewshire. © University of Glasgow.



Figure 10. Agate brooch made for Cecilia Heddle. 9 cm. across. The source of the stones is not documented, but Brian Jackson (*personal communication*) suggests: thorax: bloodstone from Rhum; abdomen: agate from Burn Anne, Galston, Ayrshire; forewings: uncertain, but perhaps from Kinnoul Hill or Path of Condie; hindwings: probably from the ‘Blue Hole’ at Usan or North Fife. © Private Collection.

indigo business declined they moved into the emerging tea planting industry in Assam. In 1878 Thoms, now a wealthy man, retired to St Andrews and soon married, only for his wife to die a year later in 1880. Thoms remarried in 1884 but became a widower again in 1890, this time with a five-year-old son to care for. Heddle taught Thoms mineralogy, and the two men went exploring and collecting together, especially for agates in Angus and Fife, Thoms building up a large collection of his own. An agate brooch made for Heddle’s daughter Cecilia is shown in Figure 10.

In 1887 Heddle resumed his friendship with John Harvie-Brown of Dunipace (1844–1916), a distinguished ornithologist and naturalist blessed with a large family fortune. They had first met by chance on a visit to St Kilda in 1879, and in 1881 Heddle joined him on a cruise on *Crusader*, a chartered vessel. In 1887 Harvie-Brown’s own yacht, the *Shiantelle* (Figure 11), was launched in Fraserburgh and for six weeks every summer until 1891, Heddle, Harvie-Brown and William Norrie, a photographer, cruised the Scottish islands gathering material for their respective books. They visited Shetland, Orkney, all the Inner Hebrides, and almost every island and islet in the Outer Hebrides from North Rona and the Flannans down to Mingulay and Barra Head in the south. These included places Heddle had visited before with Dudgeon, but where there was unfinished business. Harvie-Brown’s diaries (Harvie-Brown, 1879–1894) describe their exploits. On 11th May 1888 at the marble quarry on Iona, off Mull, they:

...hammered away...with ‘Little Billy’, Heddle’s 28-lber and chisels and a’ [*sic*] to get at a vein of steatite.

Heddle and Dudgeon had found moonstone on the tiny islet of Stroma in the Sound of Harris, (Figure 12, see p. 12), and now, on 8th July 1887:

...a heap of it was quarried out but the best block defied us, and hammer handles were all broken. But the Dr. is determined not to give it up.

The next day, the handles repaired, Heddle went back: Besides getting out the moonstone block of 18lbs. and a



Figure 11. John Harvie-Brown’s yacht *Shiantelle*. She carried a paid crew of five and a steward who looked after the owner and his guests. Photograph (Harvie-Brown, 1888) © National Museums Scotland.

mountain or two of graphic granite...a block they got out but could not bring is pretty carefully calculated at 7 cwt⁶. Being very fine, we decided to go again with full force of men, planks and tackles, and we lowered it successfully and brought it off in the boat...it was a pretty piece of quarrying and work.

The block was “2 feet by 2 by 1 foot thick” and was destined for Aberdeen where it would be cut into three tabletops:

We decided to hoist it off the boat direct onto the deck of the *Dunara*⁷ on Monday morning.

Heddle contributed geological chapters to Harvie-Brown’s books on the Outer Hebrides and Inner Hebrides (Harvie-Brown and Buckley, 1888, pp. 227–246; 1892, pp. 244–254). The voyages were also great fun: Harvie-Brown’s diaries (Harvie-Brown, 1879–1894) reveal Heddle as good company, a practical joker, and story-teller. The 1887 cruise ended at Fairlie, Ayrshire on 4th August when:

By 1 a.m. my brains nearly became chrystalised [*sic*] with Heddleite and Blackwoodite and mixture of tobacco reek and whisky.

When becalmed in the Faroes on 1st July 1894 they spent time reading novels, smoking, chatting, snoozing and “listening enraptured to the Doctor’s ‘littel tails’ [*sic*].” Heddle was also an admirer of pretty girls. In the Faroes on 26th June 1894:

‘Young Heddle’ distinguished himself as usual with the fair sex, making many juvenile jokes, etc. !!

⁶ 356 kilograms.

⁷ The *Dunara Castle*, the steamer serving the Western Isles and St Kilda.

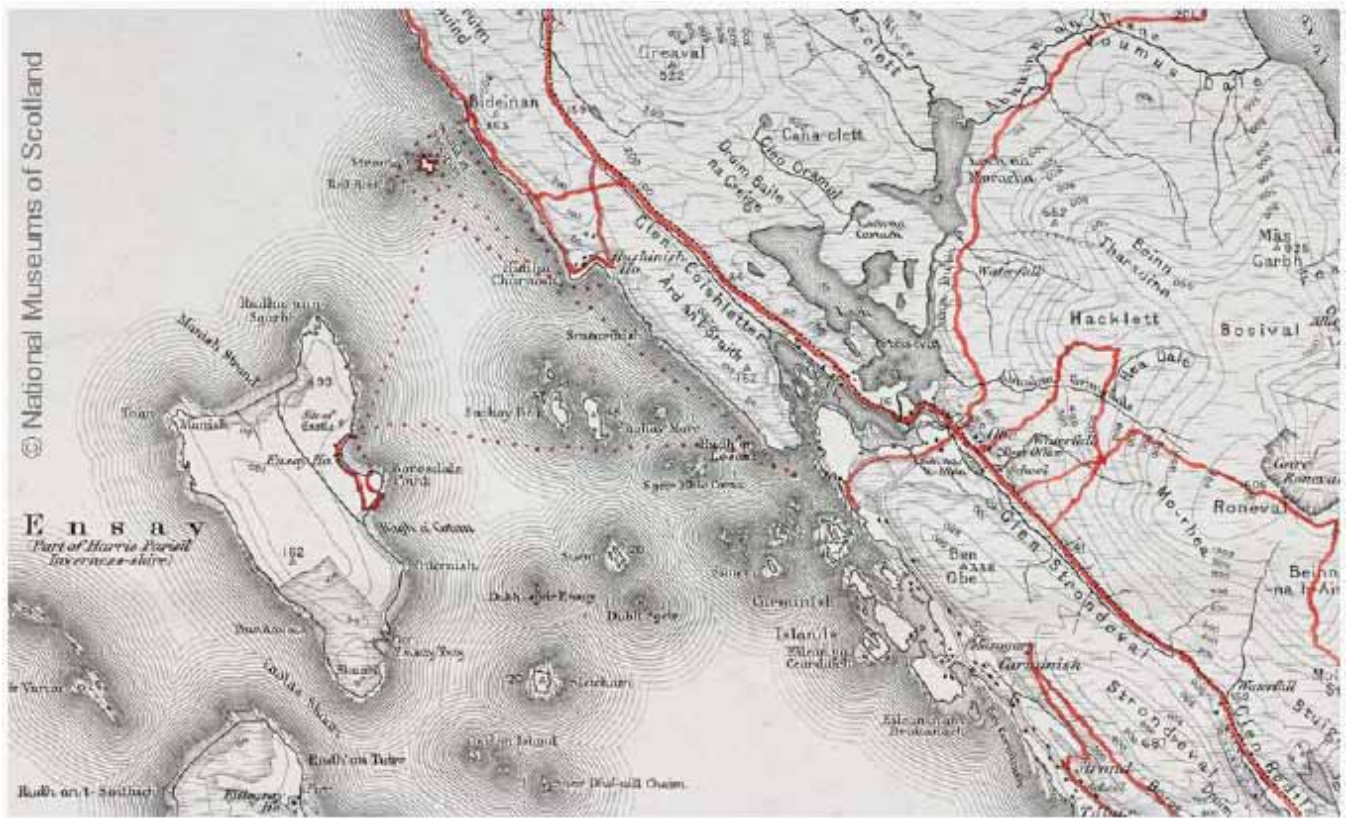


Figure 12. Heddle-marked 1" Ordnance Survey map of part of the Sound of Harris. The dotted red line shows the route of the *Shiantelle* and the solid red line that of Heddle's pedestrian explorations. Stroma (Sromaigh), [NF 987 886] lies NNE of Ensay close to the coast of Harris. © National Museums Scotland.



Figure 13. The complete Heddle family in c.1880. Standing (L to R): Ethel (who became a prolific novelist), Clementina (who married Alexander Thoms), and Robert (who accompanied his father to Transvaal in 1884). Sitting (L to R) Cecilia (great-grandmother of the author), Heddle, Catherine, Mary, Matilda and Stuart (who emigrated to America in 1892). © Private Collection.

HEDDLE'S LAST YEARS

By 1890 Heddle's health was deteriorating further; he endured pain from his heart disease and chronic lumbago, the latter doubtless the result of years of poor lifting techniques as he quarried for minerals. His loyal, patient wife Mary was also unwell, and she died on 13th November 1891. Heddle's eldest daughter Clementina (1860–1942) now looked after the household. Robert had already left home to work in London, and Cecilia (1867–1911) had married in 1888 and gone with her husband William Westgarth Thomson (1853–1902) to the Philippines. In April 1892 Heddle's younger son Stuart (1871–1931) emigrated to America. "Son going to America to learn farming – worry and cost heavy," Heddle told Harvie-Brown (Heddle, 1892). For the time being Heddle's three other daughters Ethel (1862–1842), Matilda (1869–1942) and Catherine (1874–1946) were still at home. A Heddle family gathering is shown in Figure 13.

Heddle was now thinking seriously about his legacy: the mineral collection and his book *The Mineralogy of Scotland* (Heddle, 1901). As early as 1878 Heddle contemplated selling his general collection in order to raise funds. Now in late 1890 Patrick Dudgeon fronted negotiations on the sale of Heddle's Scottish collection with Lazarus Fletcher (1854–1921), Keeper of the Department of Mineralogy at the British Museum (Natural History) in London. Much as he needed money, and could easily sell pieces for large sums to collectors in Germany and America, Heddle was determined that his collection should remain intact. Negotiations fell through over Heddle's refusal to allow the British Museum to cherry pick his best specimens.

A second proposal was to sell part and donate the remainder of his collection to the museum in St Andrews run jointly by the Literary and Philosophical Society and the University. This time Heddle's advocate was Thoms, whose administrative skills had revived the Society when he became Secretary in 1889. The proposal would require a museum extension to be built, but failure to raise the necessary funds caused the plan to fall through in April 1894. In the meantime, in 1892 and 1893, Heddle was working at the invitation of Ramsay Traquair (1840–1912), Keeper of the Natural History Section of the Edinburgh Museum of Science and Art, to integrate its general mineral collection with that of Patrick Dudgeon, donated by him in 1878. Discussions about Heddle's Scottish collection followed and when the St Andrews scheme collapsed the Edinburgh Museum was ready to pay £1000 for 1000 specimens and receive Heddle's donation of the remaining 6000 specimens. Heddle now worked hard for nine months setting up the display of the collection, working with J.G. Goodchild, (1844–1906), Curator of the Geological Survey Collections.

With the mineral collection's future assured, Heddle was left with the task of completing *The Mineralogy of Scotland* (Heddle, 1901). He had written most of the book and was occupied with the many drawings of crystals. The detailed work of editing must have been difficult. Quite apart from his physical ill-health, Heddle's memory was becoming unreliable: he commented on this to both Geikie

and Gordon as early as 1891. In June 1894 Heddle went on a final cruise with Harvie-Brown, this time to the Faroe Islands aboard the *Daydream*. This was not a success, the expedition having to be curtailed when Heddle became ill. There was no question of Harvie-Brown taking Heddle on his expedition to Rockall in 1896, but he later sent Heddle a rock specimen gathered from the seabed below it.

Heddle was working on the display of his collection in the Edinburgh Museum when his closest friend Patrick Dudgeon died in February 1895. In the obituary he wrote for the *Mineralogical Magazine* (Heddle, 1895) Heddle said he gained solace for his grief from:

...the thought that each day's labour brings him nearer the completion of that which is to stand as an abiding monument to the *originator of the collection of Scottish minerals*.

The collection opened to the public in September 1895, the *Scotsman* newspaper (Anon., 1895, p. 4) declaring that:

...the Heddle-Dudgeon Collection is not only the most representative gathering of Scottish minerals, but it is also, it is safe to say, the finest national collection of the minerals of any one country in the world.

In St Andrews Heddle involved himself with the Literary and Philosophical Society, regularly taking the chair at meetings and giving talks. By now he was the oldest vice-president and had contributed more papers than any other individual member. He supported other local natural history organisations and participated in University Court meetings, never afraid to put forward his opinions at election times. In 1895 Heddle was a member of a committee set up to organise the creation of two new chairs in medicine. He was by now something of a local celebrity, sought out by journalists for his memories of old St Andrews, and by eminent visitors like Lord Avebury (1834–1913) who in 1896 was entertained by Heddle at his home and taken on local geological excursions along the coast. That year Heddle's determination also enabled him to go on the occasional collecting excursion with Currie.

In the meantime Heddle, who missed his wife and the emotional support she gave him, and who had always enjoyed female company, had formed a relationship with a younger woman whom he hoped to marry. He was deeply unhappy when, in October 1896, she decided not to accept his proposal (Heddle, 1896):

I am just unmarried and miserable. Life is of no use to me or others now, and I cannot one bit get over my affection for her. I am utterly mystified, but she says it would make her 'unhappy.' That of course is a settler.

There now seemed little to live for, but with *The Mineralogy of Scotland* unfinished, Heddle continued with his work as best he could.

HEDDLE'S DEATH AND LEGACY

As a doctor Heddle knew his life was nearing its end, and on 25th April 1897 a family gathering took place on the occasion of his sixty-ninth birthday. All his seven children were present except for Cecilia who was in the Philippines with her husband and daughter Mary. In August 1897 Heddle revised his will, and distributed all his equipment and residual mineral and agate collections to his friends, Thoms

being the principal beneficiary. On 12th September 1897 he wrote a valedictory letter to his son Stuart in America (Heddle, 1897):

I have been suffering so fearfully lately that I hope God will have mercy on me and take me away out of such misery.

By now Heddle was employing a nurse. He died at St Leonards House at 6.30 am on 19th November 1897 of the heart disease from which he had been suffering for many years. He was buried in the old part of St Andrews Cathedral burying ground, near St Rule's Tower, on 22nd November 1897. The funeral was conducted as a University ceremonial occasion attended by the Principals, Professors and students. Heddle's death was widely reported in newspapers across the United Kingdom.

In his will Heddle appointed a committee to complete and oversee the publication of *The Mineralogy of Scotland*. Thoms told the St Andrews Literary and Philosophical Society (1897) that:

...the manuscript is in a forward state, while there are nearly 900 beautifully drawn figures of crystals, and over 600 of his own analysis of minerals. It is hoped that this very valuable work may be published 'ere long.

The committee consisted of Heddle's daughters, Thoms, Goodchild and Currie. Goodchild took on the role of editor and his son Wilbert Goodchild (1877–1944)⁸ completed Heddle's drawings. Currie provided a chapter on pseudomorphs, while Thoms wrote a memoir of Heddle's life and created a list of the minerals to be found in each county. Thoms and Clementina had more in common than membership of the publication committee. Over the last few years of Heddle's life they had been the two people closest to him and, now free of her responsibilities to her father, Clementina married Thoms in April 1898.

After three years' work *The Mineralogy of Scotland* (Heddle, 1901) was published in two volumes by David Douglas of Edinburgh. A review in the *Mineralogical Magazine* (Anon., 1902) said it was:

...a fitting memorial to Professor Heddle, so well known for the enthusiasm and energy with which he studied the minerals of his native country. No one was better acquainted with the mineral localities of Scotland.

When the list of British minerals in Greg and Lettsom's *Manual of the Mineralogy of Great Britain and Ireland* (1858) was updated in 1898 and 1931, 287 minerals were recorded, of which 121 came from Scotland. Heddle was responsible for 80 of these (Macpherson, 1983). His enduring recognition was demonstrated in 1987 when a newly discovered mineral was named after him: mattheddleite. (Livingstone *et al.*, 1987). Heddle's status today is described in the Foreword to Alec Livingstone's masterful *Minerals of Scotland Past and Present* (Livingstone, 2002, p. vii):

No account of Scottish mineralogy would be complete without a tribute to Professor Matthew Heddle...whose 1901 treatise on *The Mineralogy of Scotland* is a fitting memorial to that most famous of Scotland's mineralogists.

⁸ Wilbert Goodchild was a medical student in Edinburgh at the time. He later became the first medical superintendent of the Blencathra Sanatorium in Cumbria when it opened in 1904, and published *Precious Stones* in 1908.

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GONNARDITE FROM AN ALKALINE SYENITE PEGMATITE AT ALLT A' MHUILLIN QUARRY, ASSYNT, SUTHERLAND, SCOTLAND

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Since its original description in 1896, gonnardite has had a difficult history. Its tendency to be intergrown with other zeolites, particularly the closely related natrolite and thomsonite, has hampered detailed characterisation. Further confusion has arisen from the use of the names ranite and tetranatrolite to describe material now regarded as gonnardite. Artioli and Galli (1999) clarified matters considerably with a review of the literature, and a re-examination of type material. They concluded that gonnardite has a disordered natrolite structure, its variable composition is intermediate

between natrolite and thomsonite, and the names ranite and tetranatrolite were discarded, in preference to the name gonnardite, which had priority.

Tindle (2008) summarised a scattering of localities for gonnardite in Scotland and Northern Ireland. These are all hosted by Tertiary basalt lavas and, as is typical of the mineral, yielded small samples often intimately associated with other zeolites. Large pure masses of gonnardite have not been reported from the British Isles, and are not the norm for this mineral.

Relatively pure gonnardite, up to several centimetres across, has now been found to occur in a pegmatite in the disused Allt a' Mhuillin Quarry, near Loch Borraran, Assynt, Sutherland [NC 2869 0953]. In the north-east corner of the quarry were found boulders and, immediately next to them an *in situ* vein up to 30 cm wide, of pegmatite. The pegmatite consists of grey subhedral to anhedral orthoclase crystals (to up *c.* 8 cm across) in a matrix of white, fine-grained massive gonnardite and light blue vishnevite (Fig. 1). The gonnardite is often cut by veinlets, a few millimetres wide, of a light grey material which, on analysis, proved to be an intimate mixture of gonnardite and sericite mica. Occasional plates of black mica, up to a few centimetres across, complete the assemblage.

Identification of these was by a combination of XRD and quantitative XRF, except the black mica, which was visual only. The XRD match between the white mineral and a simulated pattern for gonnardite (Treacy and Higgins, 2001) was excellent (Fig. 2). However all samples were found to have very small additional peaks which could not be entirely eliminated from the samples. Some could be attributed to sericite mica, and their intensities were proportional to K content; a few could not be assigned. The XRF analysis for the gonnardite is summarised in the Table and is for a nearly pure composite sample, with the smallest content of impurities as indicated by XRD. "Balance" is



Figure 1. Polished 13 x 7 cm section of pegmatite showing pale blue vishnevite (top left), dark grey orthoclase, lighter grey gonnardite/sericite mixture and white gonnardite.

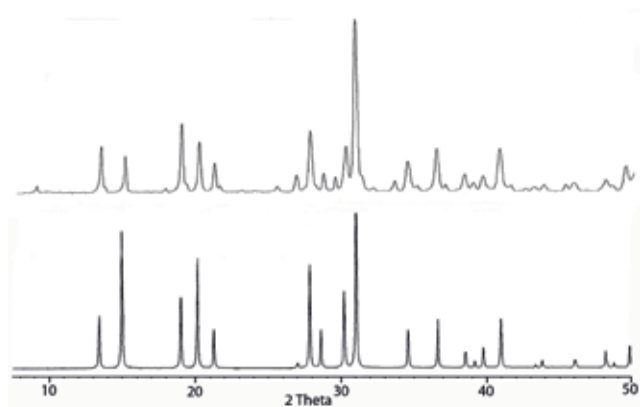


Figure 2. XRD pattern for gonnardite from Assynt (top) compared to simulated pattern (bottom).

assumed to be water. Treating K as Na, and Sr as Ca, this approximates to the formula $\text{Na}_{3.4}\text{Ca}_{2.2}\text{Al}_{9.7}\text{Si}_{10.2}\text{O}_{40} \cdot 10.7\text{H}_2\text{O}$. If all the K is assumed to be derived from sericite (ideally $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, if K-end member) then deducting the corresponding amounts of Al_2O_3 , SiO_2 and H_2O (1.9, 2.3 and 0.2 % respectively) leaves $\text{Na}_{3.5}\text{Ca}_{2.3}\text{Al}_{9.6}\text{Si}_{10.2}\text{O}_{40} \cdot 11.1\text{H}_2\text{O}$. However, K could reasonably be a minor constituent of gonnardite, and levels up to 1.61 % are reported by Nawaz (1988). In that case the amounts of Al_2O_3 , SiO_2 and H_2O accounted for by sericite may be much less, and the first formula the more accurate.

Either formula is close to the ideal tetranatrolite (i.e. gonnardite) of Ross *et al.* (1992), $\text{Na}_6\text{Ca}_2\text{Al}_{10}\text{Si}_{10}\text{O}_{40} \cdot n\text{H}_2\text{O}$, and is within the compositional variations of Artioli and Galli (1999) who report Ca contents ranging from almost nil to 2.85 Ca per formula unit. The presence of a little strontium is unusual, but not without precedent. Nawaz (1988) found 1.77 % SrO in a single electron probe analysis of a gonnardite from Hill's Port, Co. Antrim, but few published analyses indicate more than 0.1 % SrO. The vishnevite and orthoclase accompanying the gonnardite also had traces of SrO (0.5 and 0.3 % respectively) and the orthoclase 0.5 % BaO. This is probably a reflection of the unusual chemistry of the host rocks.

The geology of the Loch Borraran area is complex, and unique in the U.K. It consists of silica-poor, nepheline-bearing, and very alkali rich, intrusive rocks. They include some of the most potassium-rich igneous rocks known, and the only known U.K. example of a carbonatite. An important intrusion, exposed in the Allt a' Mhuillin Quarry, is a pyroxene-melanite, nepheline-syenite, often referred to in older literature as 'borolanite'. For a detailed description see Parsons (1999).

The pegmatites cutting the 'borolanite' have long been known to contain a mineral assemblage unique in the U.K., and including zeolitic minerals. Stewart (1941) listed sulphatic cancrinite, analcime, calcite, titanite, zircon, melanite garnet, allanite (which he called "orthite") and orthoclase. Earlier, Shand (1909) noted either natrolite or mesolite from a nearby stream exposure (in the Allt a' Mhuillin). This has recently been identified as natrolite by XRD and DTA (Alan Dyer, *personal communication*). Livingstone (1993) renamed the sulphatic cancrinite 'vishnevite' in accordance with modern nomenclature. That gonnardite has not previously been reported is surprising, given the richness and purity of the material.

This is the first time gonnardite has been reported in the U.K. from a non-basaltic host rock. This, and the unusual chemistry of the host rock, may account for its exceptional development and purity. Although unusual for the British Isles, the occurrence is not unique globally. Gonnardite

Oxide	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	SrO	Balance
Wt %	30.9	38.5	10.1	0.6	7.2	0.7	12.0

Table. XRF analysis of gonnardite from Allt a' Mhuillin Quarry, expressed as weight %.

crystals of sufficient purity and quality for the single crystal X-ray work that determined its structural similarity to natrolite were found in a syenite pegmatite in Norway (Mazzi *et al.*, 1986). This environment may be favourable for the formation of pure examples of gonnardite and should be considered by future workers.

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SUPERGENE MANGANESE MINERALISATION AT GYRN DDU AND BWLCH MAWR, CLYNNOG-FAWR, CAERNARFON, GWYNEDD, WALES

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Nineteenth century trial workings for manganese occur in Ordovician sediments at Gyrn Ddu and Bwlch Mawr in the parishes of Llanaelhaearn and Clynnog-Fawr respectively. Scant historical information relating to these workings exists, but what little there is suggests that manganite and psilomelane are the main manganese phases. Recent fieldwork and analyses have shown the earlier reports to be erroneous with the mineralisation consisting of cryptomelane, pyrolusite and lithiophorite. The manganese assemblage occurs in joints and fractures, rather than true veins, and has formed through supergene processes. The source of the manganese is uncertain, but we postulate that weathering of the granodiorite porphyry, significant intrusions of which form the summits of Gyrn Ddu and Bwlch Mawr, may have played a part in the mobilisation of manganese and in the formation of these deposits.

INTRODUCTION

The Gyrn Ddu – Gyrn Goch – Bwlch Mawr range of hills rises up like an island from the low-lying northern Lleyn Peninsula. The summits expose several intrusions of granodiorite porphyry and microgranite, flanked on the lower slopes by mudstones of Ordovician age (Fig. 1, see p. 18). Small scale trial workings for manganese are widespread within the sedimentary rocks, but re-vegetation since these workings were last active means that most of them are invisible to the casual observer. The history and

mineralogy of these trials has generally been overlooked in favour of much larger manganese mines at Rhiw, to the south, and the more extensive Middle Cambrian bedded manganese deposits in the Harlech Dome.

According to Lewis (1833) copper ore and manganese were known to exist in the mountains “Gyrn Gôch and Gyrn ddŷ” in the parish of Clynnog, but “no spirited efforts had yet been made for working the mines”. Interest in the manganese deposits developed between 1839 and 1842 with letters sent to Lord Newborough requesting permission

to prospect for manganese on his land in Clynnog parish (Gwynedd Archives No. XD2/18890 and No. XD2/19913). Further evidence of mineral exploration in this area was presented in the form of the word “manganese” in two locations on Ordnance maps dated 1841, but it is likely that any operations were still exploratory. In 1844 the situation in the parish of Clynnog was unchanged (Lewis, 1844) but a year later Lewis (1845) recorded that in the parish of “Llanelhairn”, between the mountains “Gyrn-ddû and Mynydd Bronmiod” is a wide pass, “Bwlch-mawr”, where:

...a manganese mine has been opened, and within the last two years, a great quantity of the ore has been forwarded to Port Llanaelhaiarn, and shipped to Liverpool.

No other details of these earlier workings have been found, but Groves (1952) recounted under the heading “Gyrn-ddu, Llanaelhaiarn” the recollections of Mr. Harry Thomas of Rhiw:

...who remembered manganese ore being brought down by pack horses from the foot-slopes of the mountain some 60 to 70 years ago.

This might correlate with operations at the “Llanaelhaiarn mines” during 1872-1876 when John Cowper was the owner (Down, 1980). The only record of production is 50 tons of ore in 1872 (Down, 1980). He implied, incorrectly, that it must have been a very high quality ore because its value of £250 (i.e. £5/ton) was about five times that of other manganese ores at that time. However, manganese ore from the

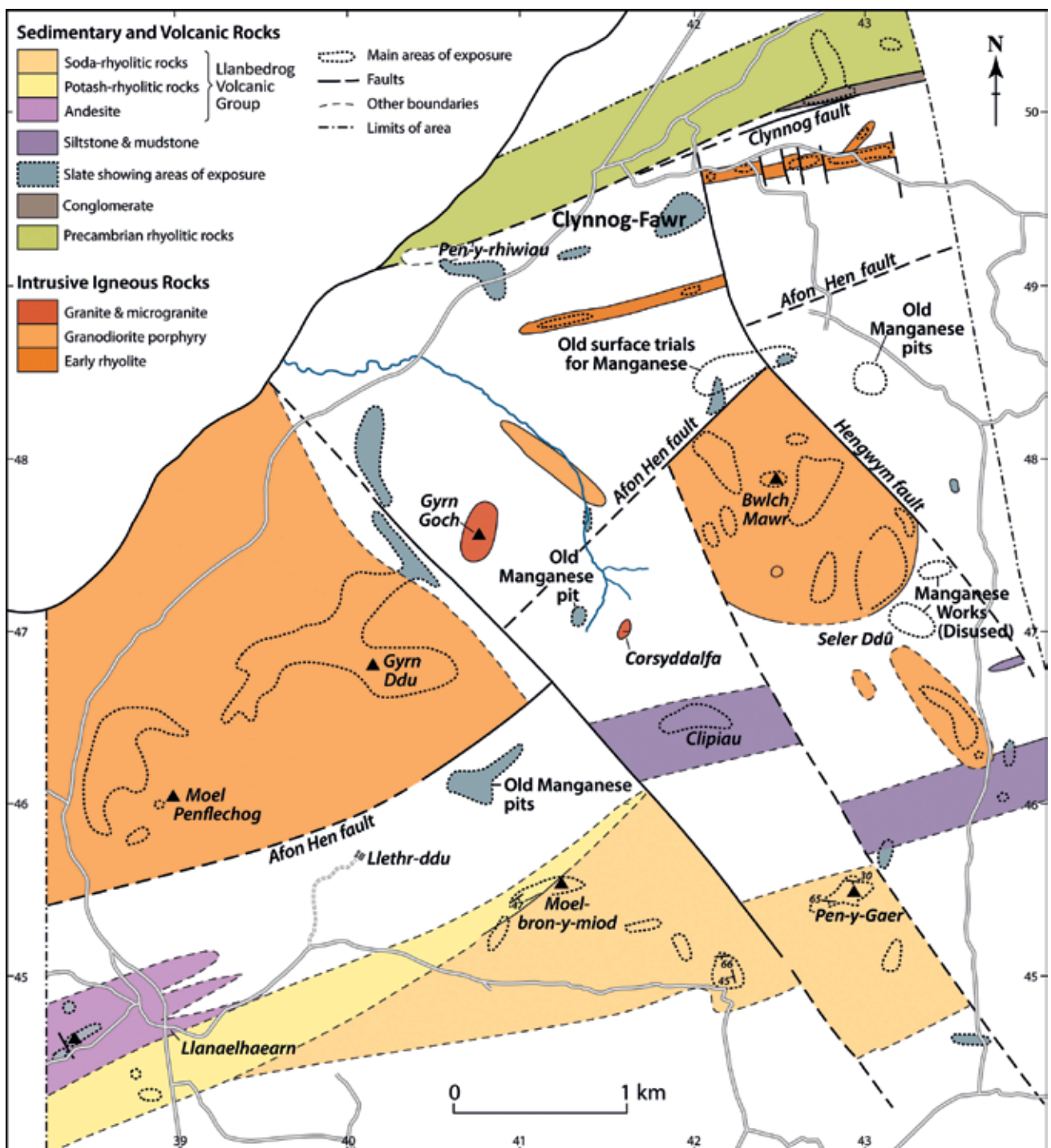


Figure 1. Geological map. Modified after Tremlett (1964).

Arenig mines, in Merionethshire, was selling at £11 a ton during the 1870s (Halse, 1891–1892) which suggests that the Llanaelhaearn ore was actually rather poor. Part of the confusion here probably lies with the different uses of manganese: the black manganese oxide ores used in the glass making industry were far more valuable than the manganese silicate ores required for steel making and it appears that Down (1980) has compared the price of the “Llanaelhaearn mines” oxide ore with the world price for manganese silicate ore.

GEOLOGY

The detailed geology of the Clynnog-Fawr district is presented by Tremlett (1964) but, unfortunately, no mention is made of the presence of manganese or manganese mines. The only geological account of the manganese workings at Gyrn Ddu is that produced by Groves (1952) as part of an assessment of iron and manganese ore resources in Great Britain and Northern Ireland. Groves was one of very few geologists to visit the manganese trial workings and therefore his observations are invaluable. Groves reported that the manganese ore occurs in joints or fissures, rather than true veins, in manganese-stained shale. The numerous adits were already blocked when Groves inspected the site, but he judged them to all be short on the basis of the very limited size of the associated dumps. In some cases the cuttings leading to the entrances to some of the adits provided good exposures of shale, the surface of which was invariably well coated with manganese oxides (Groves, 1952). Samples of manganese ore obtained from the waste heaps were always “in thin pieces ¼ to 2 inches thick”, leading Groves to conclude that they were obviously derived from joints or fissures. Mammillary and botryoidal structures in the ore provided him with evidence of deposition from solution (Groves, 1952).

Down (1980), despite drawing on information from Groves (1952), described three beds of ore without explanation. During a minesite survey across Wales, Bevins and Mason (1998) described the deposits as bedded manganese.

Fieldwork carried out by one of us (TFC) supports the assertions of Groves (1952) that there is no evidence whatsoever of a bedded deposit. Manganese mineralisation in the form of dark grey to black manganese oxides is hosted by Ordovician sediments of Arenig–Llanvirn age (Nant Ffrancon Subgroup). The sediments are overlain, unconformably, by Caradoc ash flow tuff (Llanbedrog Volcanic Group). The summits of the main hills expose intrusions which are also believed to be Caradoc in age. Gyrn Ddu and Bwlch Mawr are granodiorite porphyry, while Gyrn Goch is microgranite.

The manganese deposits at Gyrn Ddu have been little studied mineralogically. Smyth *et al.* (1864) listed a specimen (No. 588) of psilomelane and manganite from “Gyrn du, near Clynog, Caernarvon, North Wales” in the collections of the Museum of Practical Geology in London. The collection was transferred to the British Museum (Natural History) in 1985 and that specimen is now registered as BM 1985,MI13085 in the Natural History

Museum, London. This is the specimen of manganite from “Gyrndu” recorded by Bevins (1994) as “preserved in the Mineral Collection of the Natural History Museum.” Recent powder XRD (PXRD) analysis (NHM XRD No. G8062) of the specimen has shown that it is not manganite, but a member of the coronadite group. Hall (1868) also listed manganite and psilomelane as occurring in Silurian rocks from Clynnog, Caernarvon, Caernarvonshire, Wales. Groves (1952) described the manganese ore as “oxide ore: psilomelane and/or pyrolusite” although no analyses were made.

THE MANGANESE TRIAL WORKINGS

A study of the 1950s and 1960s 1:25 000 and 6” to the mile scale Ordnance Survey maps of the Gyrn Goch – Bwlch Mawr area reveals surface excavations at several locations. These include the workings recorded by Bevins and Mason (1998) at “Llanaelhaearn” [SH 407 461] and “Seler Du” [SH 431 469]. In addition there are surface excavations at Corsyddalfa [SH 416 472], a disused pit at Pen-y-Gaer [SH 431 456], and an old level on the northeast slopes of Bwlch Mawr at SH 433 478.

Aerial photography reveals that trial workings are far more widespread, in particular around the flanks of the Bwlch Mawr intrusion, but always within sediments of the Nant Ffrancon Subgroup. A noticeable concentration of surface trenches is apparent on the north slopes of Bwlch Mawr at SH 421 483 and SH 430 484, but also at SH 434 474 a little to the north of Seler Ddû. Bevins and Mason (1998) listed a manganese mine site at Bwlch Mawr [SH 421 479], but recorded it as “not located” during their site survey. It is likely that it correlates with one of these trial workings.

EXPERIMENTAL

In order to obtain a representative suite of the manganese ore minerals which were absent from the Mineral Collection at Amgueddfa Cymru one of us (TFC) carried out fieldwork to the sites described above. The majority of the sites identified show clear evidence of surface excavations but are completely overgrown, thus preventing a full assessment of the mineralogical constituents. The layout and positioning of most of the excavations (trenches and small pits typically well away from any noticeable forms of civilisation) indicate that they are all related to mineral exploration rather than production. Two of the sites are more extensive and have produced examples of what could be termed ‘manganese ore’: Gyrn Ddu (Llanaelhaearn) and Seler Ddû.

The detailed mineralogy of these two localities was investigated by PXRD using a PANalytical X’PertPRO diffractometer, equipped with an X’Celerator solid state detector using Cu K α radiation and operating at 40 kV 30 mA, at Amgueddfa Cymru. In the proceeding descriptions we provide the accession numbers of the specimens analysed, but not the individual analytical numbers which can be traced through the Amgueddfa Cymru database. In most cases PXRD is sufficient to enable a confident identification of manganese oxide minerals, but



Figure 2. Aerial photograph of the manganese workings at Gyrn Ddu showing numerous small trial adits and associated tips. View looking slightly west of due north. Photograph by David Roberts, Pixaerial.

for coronadite-group minerals (coronadite, cryptomelane, hollandite, manjiroite and strontiomelane) it is only reliable to series-level and chemical data is required to establish with certainty the individual species. For the purpose of this study a small quantity of the residual PXRD powder from a coronadite-group phase from Gyrn Ddu was mounted on an SEM stub and analysed by SEM-EDS, using a CamScan Maxim 2040 variable pressure scanning electron microscope fitted with an Oxford Instruments energy dispersive X-ray spectrometer at Amgueddfa Cymru. The resultant analysis showed the elements Al, Si, P, K, Mn, Fe, and O, indicating a mixture of phases but, importantly, K is the only cation attributable to a coronadite-group phase and, in this case, indicates cryptomelane.

Gyrn Ddu [SH 405 461 to SH 409 463]

This is the manganese mine described by Lewis (1845) and investigated by Groves (1952). Its name translates into English as “Black Horns” and a short distance downhill from the mine is a building called Llethr-ddu or “Black Slope”. Perhaps both of these names are a reference to the presence of black manganese oxides. The site was marked on the 1841 Ordnance map with the word “manganese” with what appears to be a substantial road linking the workings to the coast. Bevins and Mason (1998) listed this site under the name “Llanaelhaiarn” noting numerous small overgrown adits. The site is actually quite extensive, but the vast majority of workings are grass-covered (Fig. 2). A study of ‘ore’ specimens collected from the one remaining and accessible

dump reveals that the manganese mineralisation does not form true veins, but cements fragmented bleached mudstone (Fig. 3). Hard, grey, botryoidal cryptomelane (NMW 2007.16G.M.2; identification supported by SEM EDS) is the dominant manganese mineral (Fig. 4) with soft black crusts composed of lithiophorite (NMW 2007.16G.M.4). Dark grey metallic prismatic microcrystals of pyrolusite (Fig. 5) occur in some cavities (NMW 2007.16G.M.1 and NMW 2007.16G.M.3), but are not common.

Seler Ddû [SH 432 471]

This site is quite extensive and has the appearance of a series of quarry-like excavations and associated grass-covered tips (Fig. 6, see p. 22), but underground workings accessed by adits are also evident. The name translates as “Black Cellar” perhaps in reference to the underground workings. The first reference to manganese here appears in a letter (Gwynedd Archives No. XD2/18890) to Lord Newborough, in 1839, within which H. Cooper of Aberglaslyn, Beddgelert, indicates that manganese was being raised on a farm called Cai hir, Clynnog, near a farm called Cors y wlad. Cae-hir is a ruin some 600 m east-north-east of these workings. In 1841, “manganese” was marked at this site on the first edition Ordnance map with a track linking it with the workings at Gyrn Ddu and beyond to the coast. Bevins and Mason (1998) reported that “Seler Du” was grass-covered, but with abundant limonite on the tips. The ore was described as “oolitic Fe/Mn”. Material collected (by TFC) in 2013 is identical

to that from Gyrn Ddu. Dark grey, layered, botryoidal manganese oxides (NMW 2014.11G.M.3) comprising silvery-grey, metallic, pyrolusite microcrystals and a hard, dark grey to black, coronadite-group phase (no chemical data has been obtained), cement small fragments of bleached mudstone.

A short distance to the north of Seler Ddû, at SH 434 474, a few small overgrown workings in the form of short adit levels and overgrown tips can be seen. Manganese staining is common on the few areas of the tips where vegetation is absent, but manganese ore is uncommon. One slightly richer specimen (NMW 2014.11G.M.1) of manganese mineralisation in the form of a rather porous black and



Figure 3. Grey to black, botryoidal manganese oxides (probably cryptomelane), cementing brecciated bleached mudstone. Manganese trials at Gyrn Ddu. Specimen 6 cm tall. National Museum of Wales Collection No. NMW 2014.11G.M.11.



Figure 4. Botryoidal cryptomelane. Manganese trials at Gyrn Ddu. Field of view 4 cm tall. National Museum of Wales Collection No. NMW 2007.16G.M.2.

orange vein, cutting through bleached mudstone, contains small, grey, metallic microcrystals of pyrolusite with a coronadite-group phase and goethite.

Trial workings at Corsyddalfa [SH 416 472], trenches along the northern slopes of Bwlch Mawr [SH 420 483 to SH 422 483] and a disused pit at Pen-y-Gaer [SH 431 456] are all too overgrown to allow a detailed study of the mineralogy. The workings at Pen-y-Gaer are of some historical interest, as they correlate with prospecting activity at Tyddynhir in 1842 (Gwynedd Archives No. XD2/19913). However, despite being referred to as “Tyddynhir manganese mine” later that year, the operations were insolvent (Gwynedd Archives No. XD2/20095).

DISCUSSION

The manganese workings in the Gyrn Ddu – Gyrn Goch – Bwlch Mawr range of hills are nothing more than trials but their mineralogy and, in particular, their geological setting is of interest because they present a style of mineralisation that is unique among Welsh manganese deposits.



Figure 5. Grey, metallic, pyrolusite with dull black coronadite-group phase (probably cryptomelane) cementing brecciated bleached mudstone. Manganese trials at Gyrn Ddu. Specimen 8 cm tall. National Museum of Wales Collection No. NMW 2007.16G.M.1.



Figure 6. Aerial photograph of the manganese workings at Seler Ddû (just below centre) viewed from the southeast with the prominent hill of Bwlch Mawr. Photograph by David Roberts, Pixairial.

Groves (1952) recognised that the manganese oxides occur in joints or fissures in manganese-stained shale rather than in true veins. He also noted that much of the shale exposed in cuttings leading to the underground workings is stained black with manganese. Mammillary and botryoidal structures observed in the ore suggested to him that deposition was from solution. Manganese is a very mobile element and is supplied to a terrestrial rock–water cycle from igneous rock (Petrie, 1999). Once igneous source rocks are exposed, manganese is mobilised primarily by oxidation–reduction, acid dissolution, and organic chelators (Petrie, 1999). From solution, manganese is re-deposited into fresh or saline waters as oxides, carbonates, silicates and sorbed phases. In some of the streams draining the Gyrn Ddu – Gyrn Goch – Bwlch Mawr range of hills manganese oxides can be seen precipitating as black coatings on the surface of pebbles. We postulate that the granodiorite porphyry intrusions which form the summits of Gyrn Ddu and Bwlch Mawr, are a source of manganese which, once mobile, enters the sedimentary shales and mudstones which form the flanks of this range of hills, through every available joint and fracture. Compositional data provided by Tremlett (1964) shows that granodiorite porphyry from Gyrn Ddu contains 0.19 wt% MnO which is quite high, for an igneous rock.

The chemistry of the manganese oxides, with no base metals but with elevated potassium, aluminium and phosphorous, supports an igneous source, rather than

oxidation of an underlying manganese-rich base-metal vein deposit (Cotterell, 2009). Precipitation of manganese from meteoric waters is ongoing, having commenced as soon as the intrusions became exposed at surface. Glacial activity has, undoubtedly, removed sections of the softer sedimentary rocks within which manganese oxides have concentrated along joints and fractures, but it has also uncovered more of the intrusions which weather to provide additional manganese. In some instances manganese oxides coat quartz crystals within pre-existing quartz–chlorite veins, but these are unrelated to any base-metal mineralisation.

Very little of what can be considered to be ore is found on the dumps indicating that either the miners were very thorough in their extraction and separation of ore, or that the mineralisation is poorly developed and low grade. Groves (1952) reported that the ore was “apparently good stuff – probably containing 40–50 per cent Mn,” but that no analysis had been made. The record of the price obtained when these mines were active in the 1870s (Down, 1980) suggests otherwise. It is possible that the richest manganese oxide ore was of very good quality, but that the style of mineralisation inhibited the extraction of pure manganese oxide with much dilution caused by manganese-stained shales. Groves (1952) concluded that the mines could not be worked profitably and our interpretation of the geology suggests that these deposits are unlikely to extend much below the surface.

It is evident that the manganese mineralisation occurs in joints and fractures and not in a bedded deposit as described by Down (1980) and, subsequently, by Bevins and Mason (1998). The presence of manganite has not been confirmed by our analyses and the identification of pyrolusite as small, discrete, prismatic crystals suggests strongly that the original report of manganite was a misidentification.

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GANOPHYLLITE-GROUP MINERALS FROM THE MANGANESE MINES AT RHIW, PEN LLŶN, GWYNEDD, WALES: INCLUDING THE FIRST BRITISH OCCURRENCES OF EGGLETONITE AND TAMAITE, AND EVIDENCE FOR A BARIUM ANALOGUE

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A study of historically, and recently, collected ganophyllite-group minerals from the disused manganese mines at Rhiw, northwest Wales, has revealed a wide range of compositions spanning several species, some of which are new to the British Isles. Material from Nant Mine contains significant barium with one analysis suggesting the possibility of a new, barium-dominant, member of the ganophyllite-group.

INTRODUCTION

The lead author (TFC) has been involved in studying the complex mineralogy of the Rhiw manganese mines for many years. Between 2006 and 2007 a detailed study of ganophyllite-group minerals from the Rhiw mines was undertaken and some of the results were published, albeit briefly, in *Minerals of Britain and Ireland* by Tindle (2008). The considerable data accumulated during the study is crucial to supporting the identifications presented in Tindle (2008) and is of value to researchers interested in the mineralogy of this important group of mines and those studying ganophyllite-group minerals. The current paper presents the new data and reviews the relevant published analytical data.

GANOPHYLLITE GROUP

The ganophyllite group of minerals, with the general formula $(K,Na,Ca)_xMn^{2+}_6(Si,Al)_{10}O_{24}(OH)_4 \cdot nH_2O$ where $x = 1-2$ and $n = 7-11$ (IMA website: [http://pubsites.uws.edu.au/ima-cnmc/IMA_Master_List_\(2014-03\).pdf](http://pubsites.uws.edu.au/ima-cnmc/IMA_Master_List_(2014-03).pdf)), are complex modulated layer silicates that contain 2:1 trioctahedral layers of $Mn^{2+}-O_6$ octahedra and silicate tetrahedra (Hughes *et al.*, 2003). The dominant cation dictates the individual species with K = ganophyllite; Na = eggletonite; Ca = tamaite. Barium frequently substitutes for these cations, but rarely does it become dominant. Ganophyllite-group minerals typically, but not exclusively, occur in metamorphosed manganese deposits.

Ganophyllite, the K-dominant member after which the group is named, was described by Hamberg (1890) as a new mineral from the Harstig Mine, near Pajsberg, Wermland, Sweden but Peacor *et al.* (1984) drew attention to the fact that the original analysis indicates sodium as the dominant alkali metal. However, new chemical data provided by Kato (1980) and Dunn *et al.* (1983) demonstrated that samples from Pajsberg have $K > Na$. Peacor *et al.* (1984) suggested

that the likely source of excess sodium in Hamberg's analysis is acmite which forms abundant inclusions within massive material and which would have been incorporated in the original ganophyllite sample used for wet chemical analysis. Modern microprobe analyses overcome this problem. Dunn *et al.* (1983) recalculated the formula of Pajsberg ganophyllite as $(K_{1.03}Na_{0.66}Ca_{0.28}Ba_{0.03})_{\Sigma 2.00}(Mn_{7.27}Fe_{0.09}Mg_{0.19}Zn_{0.04}Al_{0.41})_{\Sigma 8.00}(Si_{10.10}Al_{1.93})_{\Sigma 12.03}[O_{28.96}(OH)_{3.04}]_{\Sigma 32.00}(OH)_{4.00} \cdot 8.39H_2O$.

A true Na-analogue of ganophyllite was described from Big Rock Quarry, Little Rock, Arkansas, U.S.A., by Peacor *et al.* (1984) and named eggletonite in honour of Dr Richard A. Eggleton who published widely on the crystal chemistry and structure of the stilpnomelane group, to which eggletonite and ganophyllite are related. Type eggletonite has a composition of $(Na_{0.82}K_{0.40}Ca_{0.39}\square_{0.39})_{\Sigma 2.00}(Mn_{6.61}Zn_{0.08}Mg_{0.16}Fe_{0.61}Al_{0.56})_{\Sigma 8.02}(Si_{10.33}Al_{1.67})_{\Sigma 12.00}[O_{28.92}(OH)_{3.08}]_{\Sigma 32.00}(OH)_{4.00} \cdot 10.66H_2O$ and occurs as prismatic microcrystals in small pegmatite or miarolitic pockets within altered nepheline syenite (Peacor *et al.*, 1984).

A Ca-analogue of ganophyllite, tamaite, was described by Matsubara *et al.* (2000) from the Shiromaru Mine, Okutama, Tama District, Tokyo, Japan where it was found in an outcrop of weakly metamorphosed manganese ore. The ore deposit occurs within a block of Triassic chert enclosed by middle to upper Jurassic sandstone. Tamaite was first identified as a micaceous mineral forming a minor component of brick-red gangue near a banalsite veinlet. Subsequently two much richer discoveries were made:

1. Veinlets up to 1.5 mm wide containing micaceous platy crystals up to 0.5 mm in diameter in association with celsian, barian orthoclase, aegirine and manganooan grossular;
2. Spotted subhedral crystals to 0.1 mm across in celsian–barian orthoclase veinlets in association with native copper and strontio Piemontite.

Matsubara *et al.* (2000) proposed the ideal formula $(Ca,K,Ba,Na)_{3-4}Mn_{24}(Si,Al)_{40}(O,OH)_{112} \cdot 21H_2O$. It is worth noting here that there is great variation in the published formulae for ganophyllite-group minerals but for the samples analysed during this study we have used the standard format employed by the IMA.

The possibility of a Ba-analogue of ganophyllite was raised by Matsubara *et al.* (2000) due to the substitution of barium and calcium for potassium and sodium cations observed in tamaite. All ganophyllite-group minerals from the Shiromaru Mine are characterized by BaO contents higher than those previously reported by Hamberg (1890), Kato (1980), Dunn *et al.* (1983), Peacor *et al.* (1984) and Mottana *et al.* (1990). However the highest BaO content of 2.59 wt% recorded by Matsubara *et al.* (2000) is still far short of being barium-dominant. Indeed the atomic proportions (based on the IMA formula) of the cations equate to Ca 0.41; K 0.23; Na 0.21; Ba 0.20; Σ 1.04 whereby barium is the minor constituent. Analytical data reported in the current paper reveal much higher contents of BaO, up to 4.53 wt.%, in ganophyllite-group minerals from Nant Mine, near Rhiw, Pen Llŷn, Wales. One analysis equates to Ba 0.39; K 0.38; Ca 0.17; Na 0.10; Σ 1.04 suggesting that the Ba-analogue of ganophyllite does exist.

RHIW MANGANESE MINES

Manganese was first exploited in the neighbourhood of Rhiw (Fig. 1) at the southern end of Pen Llŷn (Lleyn Peninsula), in north Wales, in the 1820s (Lewis, 1833). The material sought was black manganese oxide required for the manufacturing of bleach in glass making; much of which, according to Lewis (1833), was sent to Liverpool. There was widespread exploration for manganese oxides in north Wales at that time and this broadly correlates with the exhaustion of the once famous mine at Upton Pyne, near Exeter (Berger, 1811).

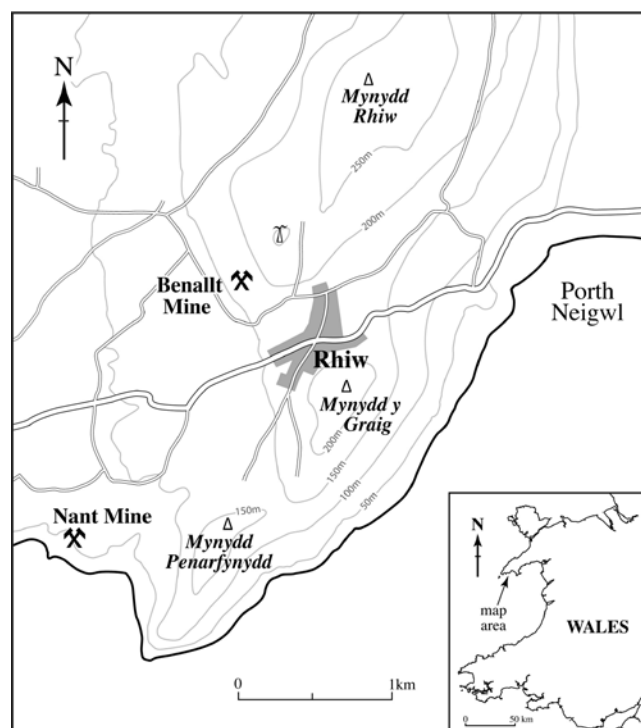


Figure 1. Location map.

The deposits of manganese oxides at Rhiw were superficial and rapidly became exhausted leading to the closure of the mines. Beneath the worked out manganese oxide deposits at Rhiw lay a hard compact form of manganese combined with silica and a small proportion of carbonate. This material proved ideal for the manufacturing of steel and so began a second phase of mining that resulted in the largest production of manganese ore in the British Isles.

The geology and mineralogy of the Rhiw manganese deposits is extremely complex but both its interest to mineralogists (Russell, 1911) and strategic importance during the Second World War led to detailed studies (Groves, 1947a, b and c; 1952). Mining operations during the Second World War provided an opportunity to rediscover some of the rare barium feldspars described by Russell (1911) but, instead, uncovered many rare manganese and barium silicates including several species new to science (Campbell Smith *et al.* 1944; 1946; 1949). A review of the type species was provided by Cotterell (2012), whilst an excellent summary of the geological setting of the Rhiw mines is given by Bevins and Mason (2010, pp. 208–222).

EXPERIMENTAL

Russell (1946) produced the first, albeit brief, record of ganophyllite in the British Isles noting that he had collected rhodonite in association with ganophyllite at Nant Mine, Llanfaelrhys, near Rhiw, Pen Llŷn, in 1911. Subsequently, in 1945, ganophyllite was found at the nearby Benallt Mine during operations by the Ministry of Supply and a more detailed account was provided by Campbell Smith (1948). Campbell Smith's identification was based, largely, on X-ray photography (Laue photographs) with no quantitative chemical analyses performed due to a lack of available material.

The earliest specimens of Welsh 'ganophyllite' in the mineral collection at Amgueddfa Cymru are samples from Nant Mine which form part of the Griffith John Williams Collection (NMW 27.111.GR.433 and NMW 27.111.GR.434). The specimens, one of which bears the date 1917, were originally labelled as muscovite, then manganophyllite, and at some later date amended to ganophyllite. The ganophyllite occurs as sub mm golden, micaceous, crystals within a veinlet exposed on the surface of the specimens (Fig. 2, see p. 26). The host matrix consists of finely intergrown celsian, tephroite, jacobsonite and pennantite with caryopilite veinlets in association (Cotterell, 2006). It is known that G. J. Williams and Arthur Russell were good friends and that, being H.M. Assistant Mine Inspector for the North Wales and Ireland Division, Williams had access to all of the mines in north Wales working at that time.

Analysis of one of G.J. Williams' 'ganophyllite' specimens (NMW 27.111.GR.433) by powder X-ray diffraction (PXRD) (NMW X-1535 and NMW X-1630), using a PANalytical X'PertPRO diffractometer equipped with an X'Celerator solid state detector using Cu K α radiation and operating at 40 kV 30 mA, in 2006, confirmed that it is indeed a member of the ganophyllite group. However,



Figure 2. Micaceous ganophyllite-group phase in a veinlet cutting manganese ore containing finely intergrown celsian, tephroite, jacobsonite and pennantite. Nant Mine. Specimen 9 cm tall. NMW 27.111.GR.433 (from the G.J. Williams Collection).

the similarity in peak positions between all members of the ganophyllite-group minerals prevented a confident identification to species level. In order to fully characterise this material chemical data were obtained by SEM-EDS, using a CamScan Maxim 2040 variable pressure scanning electron microscope fitted with an Oxford Instruments energy dispersive X-ray spectrometer at Amgueddfa Cymru. Initial results, using the residual powder from the PXRD analysis, supported the ganophyllite-group identification but produced a range of compositions from $\text{Na} > \text{Ba} > \text{K} > \text{Ca}$ to $\text{Ba} > \text{K} > \text{Na} > \text{Ca}$. These results were unexpected and a more detailed set of analyses was desirable. A polished block containing several fragments of ganophyllite crystals was produced in order to provide a perfectly flat surface for more accurate SEM-EDS analysis. The resultant data (Table 1) showed that the composition is less variable and less rich in sodium, but that barium concentrations are significant, suggesting a barium-rich ganophyllite. In one analysis a slight dominance of barium over potassium suggests that there may exist a fourth, yet to be described, member of the ganophyllite group.

During 2006 specimens were collected from a small dump, at SH 2213 2814, at Benallt Mine (by RT). They displayed a dark orange-brown, micaceous, phase associated with calcite in thin veinlets cutting compact, dense, low-grade manganese ore comprising finely intergrown celsian, tephroite and caryopilite/bementite (NMW X-1487). Several samples were submitted to

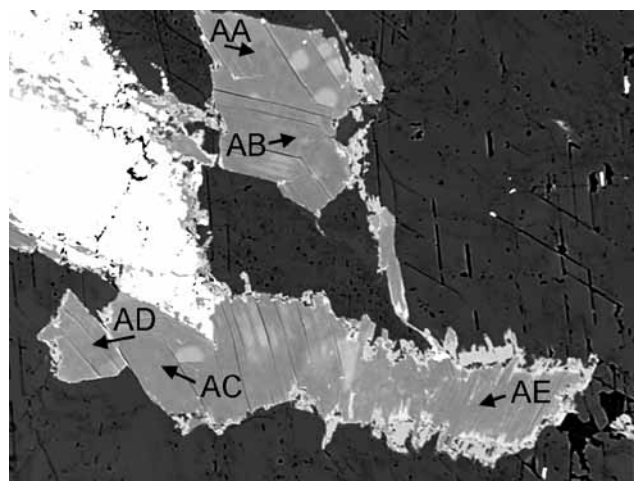


Figure 3. Backscatter electron scanning electron micrograph showing intergrown ganophyllite group phases (mid-grey), celsian (white) and calcite (dark grey). Field of view 525 μm . Benallt Mine. NMW 2006.4G.M.2b.

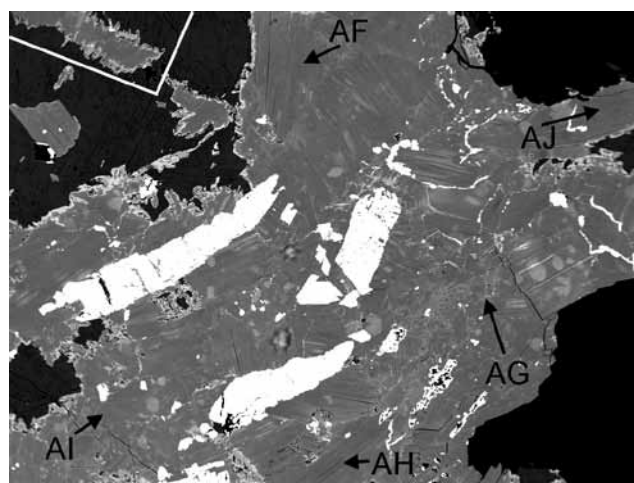


Figure 4. Backscatter electron scanning electron micrograph showing intergrown ganophyllite-group phases (mid-grey), celsian (white) and calcite (dark grey to black). Field of view 1500 μm . The area marked in the top left corner is shown in Figure 3. Benallt Mine. NMW 2006.4G.M.2b.

Amgueddfa Cymru for identification. The micaceous mineral is visually similar to ganophyllite from Nant Mine and so a detailed investigation was begun. PXRD showed the mineral to be a ganophyllite-group phase. A cross-section through part of the veinlet was prepared into a polished block (NMW 2006.4G.M.2b) and analysed using SEM-EDS at Amgueddfa Cymru and EPMA at the Open University (Figs. 3 and 4). The analytical data (Tables 1, 2 and 3; Table 2, see p. 28; Table 3, see p.29) reveal that three ganophyllite-group phases are present with a range of compositions between ganophyllite, tamaite and eggletonite.

Two further discoveries of ganophyllite-group minerals were made in July 2006 (by TFC) from tips at Nant Mine. Samples collected from a tip near to the incline at the cliff edge, at SH 2001 2647, contain an orange, micaceous, ganophyllite-group mineral (NMW X-1602) intergrown with cream coloured fibrous caryopilite (NMW X-1601), rhodochrosite, celsian and pyroxmangite (NMW X-1603) in veinlets cutting through dense,

	Harstig ¹	Franklin ²	Harstig ³	Nant ⁴	Nant ⁵	Benallt ⁶
SiO ₂	40.00	40.40	39.67	37.28	36.54	44.03
TiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	0.01
Al ₂ O ₃	7.90	7.90	7.95	7.94	7.96	7.91
FeO	0.40	0.30	n.d.	n.d.	n.d.	0.71
Fe ₂ O ₃	n.d.	n.d.	0.90	n.d.	n.d.	n.d.
MnO	34.0	34.1	35.15	33.74	33.74	35.40
MgO	0.50	0.20	0.20	n.d.	n.d.	0.05
CaO	1.00	1.50	1.11	0.88	0.73	1.67
Na ₂ O	1.30	1.10	2.18	0.41	0.24	0.68
K ₂ O	3.20	2.60	2.70	1.36	1.35	2.84
BaO	0.60	0.30	n.d.	4.02	4.53	1.46
ZnO	0.20	0.60	n.d.	n.d.	n.d.	0.01
Li ₂ O	n.d.	n.d.	trace	n.d.	n.d.	n.d.
PbO	n.d.	n.d.	0.20	n.d.	n.d.	n.d.
CuO	n.d.	n.d.	n.d.	0.85	0.74	n.d.
H ₂ O ⁷	[10.9]	[11.0]	9.79	[13.52]	[14.17]	[5.22]
Total	100.0	100.0	99.85	100.00	100.00	100.00

1. Ganophyllite from Harstig Mine, Pajsberg, Wermland, Sweden, from Dunn *et al.* (1983); by electron microprobe. Smithsonian Institution No. B17240. Formula calculated as (K_{1.06}Na_{0.66}Ca_{0.28}Ba_{0.06})_{Σ2.06}(Mn_{7.51}Fe_{0.09}Mg_{0.19}Zn_{0.04}Al_{0.86})_{Σ8.69}(Si_{10.43}Al_{1.57})_{Σ12.00}O_{31.56}(OH)₄·7.05H₂O.
2. Ganophyllite from Franklin, New Jersey, U.S.A, from Dunn *et al.* (1983); by electron microprobe, average of 10 analyses, H₂O by difference. Formula equates to (K_{0.87}Na_{0.56}Ca_{0.42}Ba_{0.03})_{Σ1.88}(Mn_{7.54}Al_{0.98}Zn_{0.12}Mg_{0.08}Fe_{0.07})_{Σ8.79}(Si_{10.55}Al_{1.45})_{Σ12.00}O_{31.72}(OH)₄·7.58H₂O.
3. ‘Ganophyllite’ from Harstig Mine near Pajsberg, Wermland, Sweden, from Hamberg (1890). Composition equates to eggletonite, but Peacor *et al.* (1984) interpreted this analysis as ganophyllite with acmite contamination.
4. Ganophyllite from Nant Mine, Wales (this study). NMW 27.111.GR.433; average of six SEM-EDS spot analyses. Equates to (K_{0.37}Ba_{0.34}Ca_{0.20}Na_{0.17})_{Σ1.08}(Mn_{6.13}Cu_{0.14})_{Σ6.27}(Si_{7.99}Al_{2.01})_{Σ10.00}O₂₄(OH)₄·8.69H₂O.
5. Ba-dominant ganophyllite from Nant Mine, Wales (this study). NMW 27.111.GR.433; single SEM-EDS spot analysis. Equates to (Ba_{0.39}K_{0.38}Ca_{0.17}Na_{0.10})_{Σ1.04}(Mn_{6.23}Cu_{0.12})_{Σ6.34}(Si_{7.96}Al_{2.04})_{Σ10.00}O₂₄(OH)₄·9.98H₂O.
6. Ganophyllite from Benallt Mine (this study). NMW 2006.4G.M.2b; average of five EPMA (AC, AE, AF, AG and AH; see Figures 3 and 4). Equates to (K_{0.69}Ca_{0.34}Na_{0.25}Ba_{0.11})_{Σ1.39}(Mn_{5.71}Al_{0.16}Fe_{0.11}Mg_{0.01})_{Σ5.99}(Si_{8.38}Al_{1.62})_{Σ10.00}O_{24.04} (Note that due to a low oxygen total in this analysis, OH and H₂O have not been calculated).
7. [H₂O by difference].

Table 1. Comparative compositional data for ganophyllite. Analyses are expressed as weight % oxides. n.d. = not determined. (Note that trace element contents are shown in order to optimise totals.)

massive manganese ore consisting of jacobsonite–celsian–tephroite (NMW X-1604). A second, small, tip on the north side of Nant-y-Gadwen [SH 2003 2658] produced small specimens (for example NMW 2007.20G.M.14) of white calcite containing orange veinlets of a micaceous ganophyllite-group phase (NMW X-1619). Specimens from neither of these two ganophyllite occurrences have been characterized chemically.

DISCUSSION

Using a combination of X-ray photography (Laue photographs) and optical data Campbell Smith (1948) identified two distinct types of ‘ganophyllite’ at Benallt Mine, one of which was in agreement with the optical measurements of the original ganophyllite described by Hamberg (1890). Lindberg Smith and Frondel (1968)

showed that the same two closely related minerals occur at Franklin, New Jersey and proposed that the name ganophyllite be restricted to the phase which was first recorded at Harstig Mine. The second type of ‘ganophyllite’ was presented as a new mineral by Lindberg Smith and Frondel (1968) and given the name bannisterite to honour Dr Frederick Allan Bannister whose X-ray data helped Campbell Smith (1948) to establish its presence at Benallt Mine. Neither Campbell Smith (1948) nor Lindberg Smith and Frondel (1968) produced quantitative chemical data for Benallt Mine ganophyllite.

Dunn *et al.* (1983) published the first chemical data for ganophyllite from Benallt Mine using a specimen (BM 1949,164) from the Natural History Museum, London. Re-examination of Dunn *et al.*'s (1983) data (Table 3) shows the Benallt Mine material to have a composition

	Shiromaru ¹	Benallt ²	Benallt ³	Benallt ⁴	Benallt ⁵	Benallt ⁶
SiO ₂	41.23	39.49	43.01	44.36	43.69	38.82
Al ₂ O ₃	7.79	9.30	7.74	8.07	7.91	7.74
FeO	0.16	0.20	0.61	0.62	0.62	0.55
MgO	0.23	0.02	0.03	0.05	0.04	n.d.
MnO	35.17	36.27	35.85	35.52	35.69	34.30
CaO	1.94	2.67	1.76	1.89	1.83	2.31
Na ₂ O	0.34	0.13	0.50	0.48	0.49	0.48
K ₂ O	0.82	0.55	1.43	1.51	1.47	0.68
BaO	2.03	n.d.	1.08	1.43	1.26	1.93
H ₂ O ⁷	11.07	[11.37]	[7.98]	[6.08]	[7.00]	[13.19]
Total	100.78	100.00	100.00	100.00	100.00	100.00

1. Shiromaru Mine, Okutama, Tokyo, Japan, from Matsubara *et al.* (2000); average of four electron microprobe analyses and a single H₂O determination. Equates to (Ca_{1.65}K_{0.83}Ba_{0.63}Na_{0.52})_{Σ3.63}(Mn_{23.70}Mg_{0.05}Al_{0.50}Fe_{0.11})_{Σ24.13}(Si_{33.52}Al_{6.65})_{Σ40.00}[O_{95.26}(OH)_{16.74}]_{Σ112.00}·21H₂O.
2. Benallt Mine, Wales, from Kato (1980); X-ray microprobe analysis performed by Dr Haga. NHM No. BM 1944,36. Equates to (Ca_{0.57}K_{0.14}Na_{0.05})_{Σ0.76}(Mn_{6.09}Fe_{0.03}Mg_{0.01})_{Σ6.13}(Si_{7.83}Al_{2.17})_{Σ10.00}O₂₄(OH)₄·3.92H₂O.
3. Benallt Mine, Wales (this study). NMW 2006.4G.M.2b; EPMA spot AB.
4. Benallt Mine, Wales (this study). NMW 2006.4G.M.2b; EPMA spot AD.
5. Benallt Mine, Wales (this study). NMW 2006.4G.M.2b; average of two EPMA spots AB and AD. Equates to (Ca_{0.37}K_{0.36}Na_{0.18}Ba_{0.09})_{Σ1.00}(Mn_{5.77}Al_{0.12}Fe_{0.10}Mg_{0.01})_{Σ6.00}(Si_{8.35}Al_{1.66})_{Σ10.01}O₂₄(OH)₄·2.46H₂O.
6. Benallt Mine, Wales (this study). NMW 2006.4G.M.2b; average of three SEM EDS analyses taken from near spot AD that was analysed in 4. Equates to (Ca_{0.52}Na_{0.19}K_{0.18}Ba_{0.16})_{Σ1.05}(Mn_{6.06}Fe_{0.10})_{Σ6.16}(Si_{8.10}Al_{1.90})_{Σ10.00}O₂₄(OH)₄·7.24H₂O.
7. [H₂O by difference].

Table 2. Comparative compositional data for tarnaite. Analyses are expressed as weight % oxides. n.d. = not determined.

equating to the atomic proportions Na 0.39; Ca 0.37; K 0.36; Ba 0.13; Σ1.25 therefore marginally within the compositional field for eggletonite which had not, at that point, been described as a new member of the ganophyllite group (Peacor *et al.*, 1984). Matsubara *et al.* (2000) highlighted an apparent Ca-dominant ganophyllite, at Benallt Mine, with 2.67 wt% CaO, using analytical data obtained by Dr Haga at the University of Tokyo, from Natural History Museum Specimen No. BM 1944,36, presented in Kato (1980). Re-examination of Haga's data reveals that this is the most calcium-rich tarnaite yet recorded, equating to the atomic proportions Ca 0.57; K 0.14; Na 0.05; Σ0.76.

Data presented here, in Tables 1, 2 and 3, show that all three ganophyllite-group phases are present at Benallt Mine in veinlets cutting manganese ore. Compositional zonation between end-members in the ganophyllite group is well-known and occurs on all scales from ore-body right down to individual crystals on the microscale. Matsubara (2000) reported all three ganophyllite-group members at Shiromaru Mine, Okutama, Tokyo, Japan and Noe and Veblen (1999) produced highly variable compositions from ganophyllite from Franklin Furnace, New Jersey, USA.

Such small-scale zonation makes accurate identification of ganophyllite-group minerals very complex. Visual identification is impossible. PXRD is useful in establishing

the presence of ganophyllite-group phases, but compositional variations in the alkali component results in some overlap between the X-ray patterns for these minerals. Furthermore some published XRD spectra are based on ganophyllite-group minerals whose chemistry has not been adequately determined. Detailed chemical data is therefore essential to any accurate identification to species level.

At Nant Mine, similar, veinlets cutting manganese ore collected in 1917 contain a much paler, golden coloured, ganophyllite with consistently high levels of barium. The barium content is unprecedented with one analysis consistent with what would be expected for a Ba-analogue of ganophyllite (Table 1). The evidence, presented here, for a fourth member of the ganophyllite group – a barium dominant phase – is compelling and worthy of a further analytical study.

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	Big Rock ¹	Benallt ²	Shiromaru ³	Benallt ⁴
SiO ₂	41.5	40.3	40.34	38.87
Al ₂ O ₃	7.6	8.2	7.61	7.70
FeO	3.0	0.2	0.00	0.57
MgO	0.4	0.1	0.40	n.d.
ZnO	0.2	0.2	n.d.	n.d.
MnO	31.4	34.6	34.23	34.35
CaO	1.5	1.70	2.28	1.85
Na ₂ O	1.7	1.0	2.01	1.69
K ₂ O	1.3	1.4	0.54	1.60
BaO	n.d.	1.6	1.95	1.79
H ₂ O ⁵	[11.4]	[10.7]	[10.64]	[11.58]
Total	100.00	100.00	100.00	100.00

1. Big Rock Quarry, Little Rock, Arkansas, U.S.A. from Peacor *et al.* (1984); by EPMA. Equates to (Na_{0.82}K_{0.40}Ca_{0.39}□_{0.39})_{Σ2.00}(Mn_{6.61}Zn_{0.08}Mg_{0.16}Fe_{0.61}Al_{0.56})_{Σ8.02}(Si_{10.33}Al_{1.67})_{Σ12.00}[O_{28.92}(OH)_{3.08}]_{Σ32.00}(OH)_{4.00}·10.66H₂O.
2. Benallt Mine, Wales, from Dunn *et al.* (1983); by electron microprobe. NHM No. BM 1949,164. Equates to (Na_{0.39}Ca_{0.37}K_{0.36}Ba_{0.13})_{Σ1.25}(Mn_{5.88}Al_{0.03}Fe_{0.03}Mg_{0.03}Zn_{0.03})_{Σ6.00}(Si_{8.09}Al_{1.91})_{Σ10.00}O₂₄(OH)₄·5.09H₂O.
3. Shiromaru Mine, Okutama, Tama district, Tokyo, Japan, from Matsubara *et al.* (2000); by SEM EDS. Equates to (Na_{0.79}Ca_{0.50}Ba_{0.16}K_{0.14})_{Σ1.59}(Mn_{5.88}Mg_{0.12})_{Σ6.00}(Si_{8.18}Al_{1.82})_{Σ10.00}O₂₄(OH)₄·3.98H₂O.
4. Benallt Mine, Wales (this study). NMW 2006.4G.M.2b; single SEM EDS spot analysis from near spot AD (analysed in 4 in Table 2). Equates to (Na_{0.68}K_{0.43}Ca_{0.41}Ba_{0.15})_{Σ1.67}(Mn_{6.07}Fe_{0.10})_{Σ6.17}(Si_{8.11}Al_{1.89})_{Σ10.00}O₂₄(OH)₄·5.95H₂O.
5. [H₂O by difference].

Table 3. Comparative data for eggletonite. Analyses are expressed as weight % oxides. n.d. = not determined.

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KINOSHITALITE FROM THE BENALLT MANGANESE MINE, RHIW, PEN LLŶN, GWYNEDD, WALES: A FIRST BRITISH OCCURRENCE

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Kinoshitalite: ideally $(\text{Ba},\text{K})(\text{Mg},\text{Mn},\text{Al})_3\text{Si}_2\text{Al}_2\text{O}_{10}(\text{OH})_2$, is a rare tri-octahedral brittle mica. It was described from the Noda-Tamagawa Mine, Noda, Iwate Prefecture, Tokaku Region, Honshu Island, Japan, where it occurs in a hausmannite and tephroite-bearing assemblage (Yoshii *et al.*, 1973). The name honours Dr Kameki Kinoshita (1896–1974), an investigator of Japanese ore deposits.

Here we report the first British occurrence of kinoshitalite as small (*c.*0.5 mm), black flakes on the surface of unusually violet-coloured natrolite from the dumps from the Benallt Manganese Mine, near Rhiw, in North Wales. The flakes (Fig. 1) are dispersed over areas of approximately 1 cm² (Fig. 2) and resemble those from the type locality illustrated on the Mindat website (<http://www.mindat.org>).

Kinoshitalite was identified by powder X-ray diffractometry at the University of Wolverhampton using a Phillips PW 1710 instrument. The principal d-spacings and relative intensities are listed in the Table, together with those for kinoshitalite from the type locality. The differences in I/I₀ are attributable to possible variations in cation sites

in the layered structures, coupled with the presence of the barium which is known to cause reduction in intensities in zeolite powder patterns due to its high absorption coefficient for Cu K_α radiation (Dyer *et al.*, 1968). Similar variations have been noted in other kinoshitalite powder patterns (see for example Gnos and Armbruster, 2000).

DISCUSSION

The Benallt Mine is one of the most important mineralogical localities in Wales. It was the subject of a recent review by Cotterell (2012) which provides a comprehensive account of the history of the mine, its geology and type minerals.

The Mindat website lists 35 recognised minerals from Benallt Mine, but this considerably underestimates the true mineralogical diversity of this site (Tom Cotterell, *personal communication*). The recent discoveries of epidote-(Sr) and piemontite-(Sr) (Cotterell and Tayler, 2012a) and gorceixite, a barium aluminium phosphate hydroxide (Cotterell and Tayler, 2012b), shows the potential for further discoveries at the site.

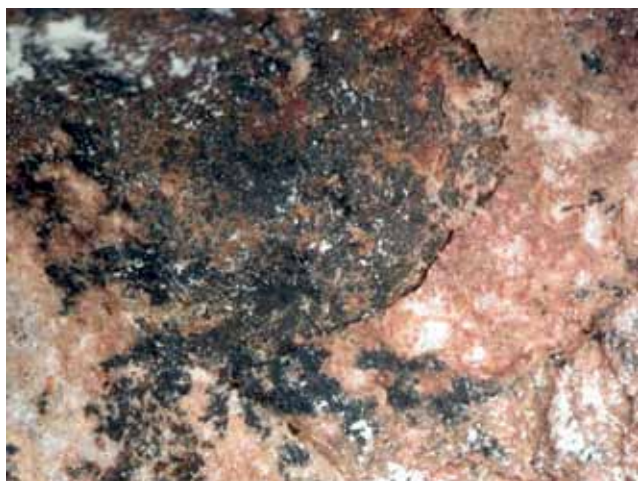


Figure 1. Kinoshitalite (and pennantite?) on the surface of natrolite. Field of view approximately 10 mm. David Green photograph.



Figure 2. Natrolite from the dumps of the Benallt Mine. Specimen size 7.5 cm. David Green photograph.

Pennantite $(\text{Mn}_3, \text{Al})(\text{Si}_3, \text{Al})\text{O}_{10}(\text{OH})_8$, a manganese-bearing phyllosilicate of the chlorite group is described by Cotterell (2012) as a common, orange-brown, constituent of the orebody. It is probable that it is the brownish mineral distinguishable in Figures 1 and 2. Pennantite can also occur in much darker colours, as a result of weathering and oxidation, and identification can be difficult (Cotterell, 2012) but, unlike kinoshitalite, it has a major d-spacing at 7.1 Å in its powder pattern (Campbell Smith *et al.*, 1946).

Kinoshitalite has been reported in association with natrolite, harmotome, laumontite and thomsonite at Långban in Sweden (Nysten *et al.*, 1989, pp. 89–183); with analcime, bellbergite, erionite, flörkeite, gismondine, levyne, offretite, phillipsite, stellerite, thomsonite, tschörtnerite, and willhendersonite, at Caspar Quarry, Bellerberg, in the Eifel district, Germany (<http://www.mindat.org>); with edingtonite and harmotome, at the Brunswick No. 12 Mine, New Brunswick, Canada (McClenaghan *et al.*, 2009) and with harmotome and laumontite in the Rožná Deposit, Moravia, Czech Republic (Doležalová *et al.*, 2005).

A recent publication (Choi *et al.*, 2009) described the synthesis of a manganese mica in aqueous media at 200°C

Benallt		Noda-Tamagawa Mine	
d Å	I/I ₀	d Å	I/I ₀
10.0	45	10.0	3
5.0	50	5.0	3
		<i>4.61</i>	6
		<i>4.41</i>	6
		<i>4.20</i>	32
3.92	5	3.92	15
3.66	6	3.66	22
3.39	100	3.39	34
		<i>3.33</i>	4
3.14	10	3.14	29
2.91	10	2.91	34
2.69	10	2.69	18
2.65	8	2.65	20
2.63	10	2.63	100
2.53	52	2.51	12
		<i>2.31</i>	10
		<i>2.25</i>	10
2.17	8	2.17	25
		<i>2.10</i>	13
2.02	50	1.99	31

Table. The d-spacings and relative intensities for kinoshitalite from the Benallt Mine and the type locality, Noda-Tamagawa Mine, Japan (data taken from Bailey, 1984). The figures in *italics* refer to lines coincident with the standard natrolite pattern.

and at high pH. These conditions may be similar to those produced by the low-grade metamorphism at Benallt when the kinoshitalite formed with the elevated pH provided by the zeolite surface (e.g., Wark *et al.*, 1993).

Dyer and White (1989) reported that studies of clinoptilolite from Death Valley Junction, Inyo County, California, USA, showed it to contain “mini-nodules” of manganese minerals and they suggested that the high pH associated with the zeolite surface may have aided the formation of these as well as manganese nodules found on the ocean bed.

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ELYITE FROM A ROMAN LEAD SMELTER NEAR LLANCYNFELYN, CENTRAL WALES

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Published occurrences of elyite ($\text{Pb}_4\text{Cu}(\text{SO}_4)_2\text{O}_2(\text{OH})_4 \cdot \text{H}_2\text{O}$) in Wales currently number four: Esgairhir Mine, Llechweddhelyg Mine, Frongoch Mine and Dolyhir Quarry. Here, a fifth is reported, from a rather unusual locality.

INTRODUCTION

The area between Talybont, Tre'rddol and Llancynfelyn, in northern Ceredigion, is of special interest to the mining historian and the mineralogist alike. Extraction of lead and copper ores from narrow but high-grade veins, often with a complex primary mineralogy, has had a long history that is only slowly coming to light. The key mines of the area are Llancynfelyn, whose Bronze Age origins have been demonstrated (Timblerlake, 1995), the Brynyrarian – Erglodd – Penpompren group of workings, east of the A487 main road and the Tanyrallt and Alltycrib mines on the hill to the west of Talybont. Detailed archaeological surveys have yet to be undertaken at most of the latter sites but the presence of stone hammers, recorded close to old surface workings at Erglodd and Alltycrib (Hughes, 1981), is usually regarded as a sign of considerable antiquity. A recent series of discoveries beneath agricultural land adjacent to these mines (1000 m S of Llancynfelyn, 600 m WNW from Erglodd and 500 m NW from Tanyrallt) has added evidence for Roman mining activity in this area and has in addition provided a fifth Welsh locality for the extremely rare supergene lead-copper mineral, elyite.

ARCHAEOLOGICAL SUMMARY

During June 2004, Dyfed Archaeological Trust undertook the partial excavation of a medieval timber trackway situated between Talybont and Llancynfelyn (Fig. 1). The work, a detailed account of which is provided by Page *et al.* (2012), involved students from the Institute of Archaeology and Antiquity at the University of Birmingham. Two areas of the trackway were examined and dendrochronological dates suggest that three of the timbers were from trees that were felled between 1080 AD and 1120 AD.

One of the excavation trenches, located at the southern end of the site [SN 649 906], resulted in the discovery of extensive deposits of burnt stony debris, slag and charcoal underlying the trackway. Samples of the charcoal were submitted for radiocarbon dating and dates of 60 BC to 90 AD and 20 AD to 220 AD were obtained, indicative of substantial industrial activity in late Iron Age – Roman times, in an area with an established Roman association: the Erglodd fortlet, discovered in 1976 and occupied from 72 AD to 140 AD, lies only 500m SE from the site.

A further programme of excavation was commenced in 2005, resulting in the discovery in trench T21 of a smelting hearth, lined with blocks of coarse sandstone (with a fused surface, containing small globules of metallic lead), with associated fragments of slag and mineralised breccia. During a site visit in June 2005, the author collected samples of mineralised breccia from T21, with a view to attempting to provenance them. The excavations were subsequently backfilled and the site returned to farmland.

PRIMARY MINERALISATION FROM T21: DESCRIPTION

Small fragments of quartz-veined, brecciated, Lower Silurian mudstone were common amongst the stony debris encountered in several of the excavations, although sulphide-rich material was relatively scarce. Such breccias are abundant on the waste-tips of all of the mines mentioned in the introduction, although the primary sulphide mineralogy exhibits subtle variations from mine



Figure 1. Location map. Location within Wales and larger-scale images of the area of investigation. Pale blue crosses mark the locations of the mines mentioned in the text. Aerial images © Google Earth.

to mine. To see if it was possible to further characterise the ore, five polished sections were prepared from sulphide-rich samples at the National Museum, Cardiff. The sections all revealed abundant, slightly deformed galena (with curvilinear cleavage traces), carrying microscopic (5–250 µm) inclusions of ullmannite, bournonite and chalcopyrite. This inclusion-rich galena association is quite characteristic of the polymetallic A1-c primary assemblage that occurs widely in the Central Wales Orefield (Mason, 1997). Its position within the older (A1) phase of regional primary mineralisation is shown in the Table.

Late pyrite and marcasite, belonging to a much younger phase of regional mineralisation, formed a crosscutting veinlet in one of the polished sections from T21. The younger mineralisation of the Central Wales Orefield was subdivided into six assemblages (A2-a through to A2-f) by Mason (1997), and quartz + pyrite/marcasite ± sphalerite ± calcite was the youngest primary assemblage described in that paper.

PRIMARY MINERALISATION FROM T21: PROVENANCE

The A1-c assemblage occurs at all of the mines in the Talybont area, although the low quantities of chalcopyrite and apparent absence of siegenite in the samples collected from T21 suggests that the ore may not have been from the nearby Erglodd or Brynyrarian mines, where these minerals are unusually common (Mason, 1998). At Llancynfelyn Mine, sphalerite is relatively common whilst late-stage pyrite and marcasite appear to be absent. A more likely source, and indeed the nearest mine to the smelter, is Tanyrallt, at the northern end of the Alltycrib hill, together with the immediately adjacent Alltycrib Mine. Little now remains of Tanyrallt Mine, although a suite of ore samples was obtained in the late 1980s from the tips. These showed a four-stage paragenesis:

1. Brecciation; cementation by quartz (with traces of pyrite), ferroan dolomite and sphalerite (A1-b).

Assemblage	Characteristics	Sulphides	Gangue
A1-a	Minor Cu	<i>Chalcopyrite</i>	Quartz, ferroan dolomite, <i>chlorite</i>
A1-b	Moderate Zn	<i>Pyrite</i> + sphalerite	Quartz , ferroan dolomite, <i>chlorite</i>
A1-c	Major Pb–Ag polymetallic	<i>Pyrite</i> + siegenite + <i>cobalt pentlandite</i> + millerite + chalcopyrite + <i>pyrrhotite</i> + <i>tueckite</i> + ullmannite + <i>gersdorffite</i> + <i>electrum</i> + tetrahedrite + bournonite + <i>boulangierite</i> + galena	Quartz
A1-d	Minor Cu–Pb–Zn	Chalcopyrite + galena + “honey-blende” sphalerite	
A1-e	Major ferroan dolomite		Quartz, ferroan dolomite
A1-f	Minor cavity-fill/cross-veining	Siegenite + cobalt pentlandite + millerite + chalcopyrite + galena	Quartz

Table. The early or A1 assemblages from the primary mineralisation of the Central Wales Orefield, listed in chronological order. Minerals are listed in their order of deposition and in terms of abundance: **bold** = abundant phase; regular font = minor phase; *italic* = trace phase.



Figure 2 Cavity in cerussite-rich veinstone, lined with hydrocerussite (white) and a sheaf of distinctive, purple acicular elyite crystals (length 1.5 mm). Specimen: J.S. Mason Collection.

2. Re-brecciation; cementation by galena (with ullmannite and bournonite inclusions) and minor chalcopyrite (A1-c).
3. Rare “honey-blende” sphalerite in cavities (A1-d).
4. Minor net-veining by pyrite and marcasite with localised overgrowth by reddish-brown sphalerite and vuggy calcite (A2-f).

Samples collected at the same time from the more extensive remains at Alltycrib revealed a similar paragenesis, with the addition of tetrahedrite and boulangerite present as small inclusions in the A1-c galena and less A2-f marcasite and pyrite than at Tanyrallt. However, given that these adjacent mines worked parts of one lode system, these differences are just as likely to have been down to the fortunes of sample selection and sectioning rather than to represent anything meaningful in terms of mineral distribution.

The relatively small suite of samples from T21 has a good match to the A1-c mineralisation at the Tanyrallt and Alltycrib mines, suggesting that one or both of them were being worked in Roman times. However, the Llancynfelyn and Brynyrarian – Erglodd – Penpompren groups of mineworkings still remain as additional candidate sources. Llancynfelyn was worked during the Bronze Age and the surface workings at Erglodd, where numerous stone hammers have been recorded, are thought likely to be similarly ancient. If Tanyrallt and/or Alltycrib were worked by the Romans, it is extremely unlikely that any other existing – and closely adjacent – workings would have been ignored by them. Furthermore, the small number of samples examined from T21, which was a single small pit within a large area of industrial activity, may not be representative of the entire site but just of one small part of it. Additional excavation work would be required in order to explore these issues further.

SUPERGENE MINERALISATION FROM T21: DESCRIPTION

Supergene mineralisation associated with samples recovered from the excavations was typically limited to superficial weak copper-staining. However, a single small

(<3 cm) fragment of gossanous iron oxide impregnated with massive cerussite was collected. When split in two, it revealed cerussite associated with bladed to platy reddish microcrystalline litharge (confirmed by XRD: NMW X-2049), with the outer parts of the sample being the most litharge-rich. Traces of malachite were also noted. A single small central cavity was lined with a thin white crust of hydrocerussite (confirmed by XRD: NMW X-2072) and contained a sheaf of characteristically purple laths of elyite to 1.5 mm in length (Fig. 2), visually identified by its diagnostic colour. This is only the fifth occurrence of elyite in Wales, and with the two specimens obtained from this one sample, there are still less than a dozen known Welsh specimens in existence.

DISCUSSION

Elyite is one of many uncommon supergene sulphate minerals that characteristically occur within localised geochemical micro-environments, sometimes of part-anthropogenic origin. The mineral can occur in unmodified natural environments, for example at the type locality (Williams, 1972), and in the UK at Dolyhir Quarry (Cotterell *et al.*, 2011) and Greystones Quarry (de Nul, 2005), but such occurrences are in a clear minority, with many more occurrences noted from weathered mine-waste and smelter-slugs. The spatial association of elyite with cerussite, litharge and hydrocerussite has also been recorded at another Central Wales site, Frongoch Mine, where Green *et al.* (1996) commented on its occurrence within a localised, part-anthropogenic alkaline environment.

The specimen in question is clearly original veinstone which has been subjected to heat but not the intense heating that one would expect within a smelting-hearth. In this instance, the formation of litharge as a microcrystalline phase associated with cerussite may have been brought about by fire-setting as a method of shattering the lodestuff *in situ*, a known Roman mining technique. The method, widely employed in antiquity, involved building a roaring brushwood fire against the rock and once the rock was sufficiently hot, quenching it suddenly with cold water. The consequential rapid contraction led to cracking of the rock which could then be hewn away with picks and hammers.

Massive cerussite occurs in scattered locations across Central Wales (Mason, 2004), in all cases at near-surface locations, which would be the most likely sites for early working of the lead-bearing lodes. Although not recorded in quantity at Tanyrallt or Alltycrib, the older opencast workings at these mines are either part-buried and/or densely overgrown, thereby precluding detailed mineralogical assessment without significant excavations.

As de Nul (2005) notes, lead oxide minerals such as litharge and minium are typically associated with elyite where fire-setting has taken place. The lead oxides form as a consequence of the alteration of lead minerals such as cerussite; subsequent interaction of the oxides with water produces highly alkaline solutions from which basic lead oxysalts such as elyite, hydrocerussite and lanarkite crystallize.

Given that this find came from an excavation of just a small part of the smelter-site, the potential for more examples of this assemblage is doubtless, should any further excavations be made.

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THE MINERALOGY OF PIM HILL MINE, SHROPSHIRE, WITH A STUDY OF MOTTRAMITES

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Underground exploration of Pim Hill Mine, the probable type locality of mottramite, has revealed the distribution of mottramite in the workings, including material similar in appearance to co-type material. Other minerals have also been found, including wroewolfeite. Infrared spectroscopic studies of mottramites from a number of localities have shown that two types exist, their spectra differing mainly in the relative intensities of their O-H deformation vibrations.

INTRODUCTION

Opening of the entrance level of Pim Hill Mine has afforded an opportunity to explore the workings and to study its mineralogy; in particular, to follow up the preliminary results of Braithwaite (1994) which reinforced the conclusions of Russell and of Kingsbury (1956) that Pim Hill Mine, rather than Mottram St Andrew, is the true type locality of mottramite. Braithwaite (1994) also noted differences between the infrared (IR) spectra of mottramites from Pim Hill and from Mottram, which we have now studied in more detail.

Pim Hill Mine is centred near SJ 487 213 near Harmerhill (Harmer Hill) village, but lies in the parish of Preston Gubbals, Shropshire. According to Dewey and Eastwood (1925, p. 19) the mine worked ores of copper and cobalt from a “bed of productive rock” at the base of the Keuper sandstones, some vanadium also being recovered. Warrington (1980) and Carlon (1981) cite evidence from the Shropshire Record Office (SRO: Bridgwater 212/Box 105) that in 1710 “Harmear Hill or Middle Hill” was the subject of a 14-year mining lease. This may be the earliest record of mining activity involving Pim Hill. The mine was worked on a small scale between about 1870

and 1875 for copper, with traces of cobalt and vanadium, from a mineralised N-S fault, the workings consisting of three shafts at 100 yard intervals, a small level, some surface excavations and a quarry (Pocock and Wray, 1925, pp. 89–90). Carlon (1981) states that the fault is mineralised with baryte, malachite, asbolite and “vanadium” where it brings the Mottled Sandstone in contact with the Keuper Sandstone and Waterstones (Carlon, 1981). The mine was also worked for vanadium in about 1878 (Warrington, 1980) and tried for cobalt in the early 1900’s with little success (Carlon, 1981). Warrington (1980) quotes a report in the

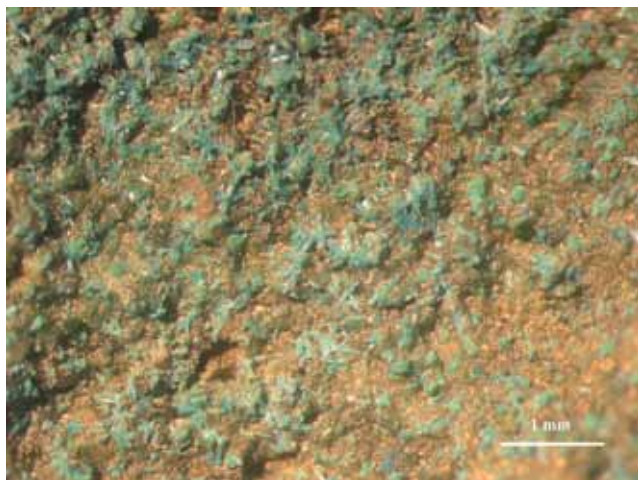


Figure 1. Wroewolfeite crystals on sandstone, Pim Hill. RSWB 95-4. Richard Braithwaite photomicrograph.

Mining Journal for 1878 (Vol. 48, p. 623) that platinum was found, and suggests that this is likely to be an error for vanadium. Kingsbury (1956) reported that the ore was sent to the plant at Mottram St Andrew, Cheshire, for leaching. Roscoe (1876), the discoverer of mottramite, collected his type material from the heaps at this plant.

The copper ore is described as “green copper ore” coating boulders in the quarry by Pocock and Wray (1925, pp. 89–90), and presumed to be malachite by later authors. The cobalt ore is ‘asbolite’ or cobaltan ‘wad’, and the vanadium ore is mottramite. Mottramite was collected by Arthur Russell in 1930 from Pim Hill, and investigated by Bannister and Hey (1933). They described thin crusts of minute black crystals on sandstone and noted that the crystals yielded an olive-green powder on grinding. However, it is not recorded from which part of the workings the mottramite was collected. Russell, and also Kingsbury (1956), described the sandstone matrix of Roscoe’s mottramite as being more like that of Pim Hill than of the Mottram sandstone, and concluded that Pim Hill was therefore likely to be the type locality of mottramite. This conclusion was reinforced by IR spectra and analyses comparing Roscoe’s material with samples from Mottram and Pim Hill and revealing differences between them (Braithwaite, 1994).

INVESTIGATION OF THE SITE

One of us (RSWB) briefly investigated the site in the summer of 1961, finding a small vein gash filled with

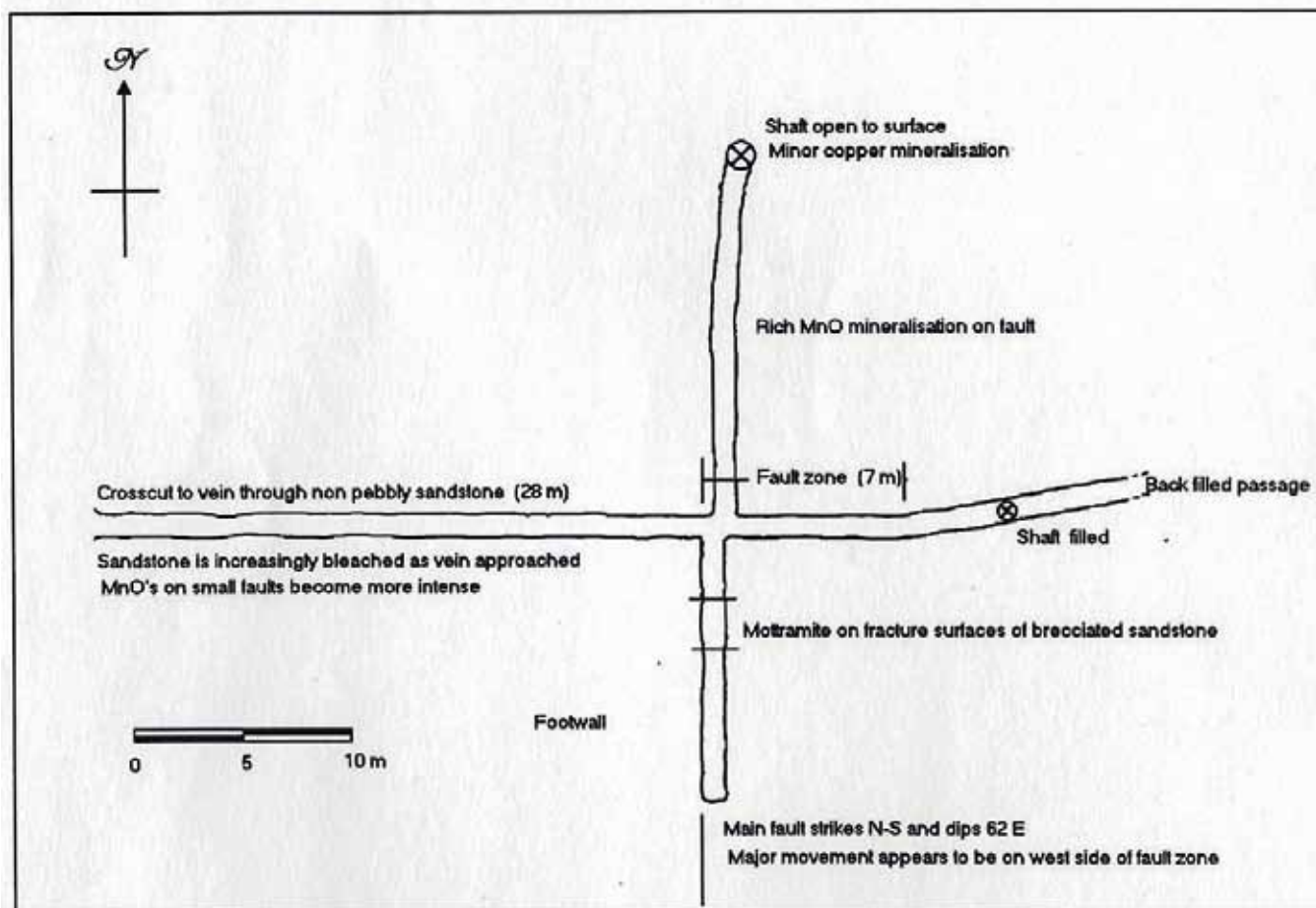


Figure 2. Plan of level workings, Pim Hill Mine. Al Burgess and David Green survey.

rubbish, noting an open shaft, and finding the quarry at SJ 4875 2135 grossly overgrown, with no mineralisation visible. On a further visit in 1995 (with JIW) a shaft north of the vein gash at SJ 4875 2144 was descended and found to be blocked with rubbish about 6 metres down. Patches of green mineralization penetrating into the sandstone on the shaft walls were sampled and found to be composed of ‘chrysocolla’, containing malachite needles within cavities and tiny green blades of wroewolfeite up to about 0.3 mm long on the surfaces (Fig. 1). Deep green samples of the “chrysocolla” gave a broad-banded IR spectrum typical of this material. The malachite was also checked by IR spectroscopy and by microchemistry. It effervesced in dilute hydrochloric acid, and treatment of this solution with ammonium tetrathiocyanatomercurate(II) showed no zinc to be present. The wroewolfeite was also checked by IR spectroscopy, three samples giving spectra similar to those of wroewolfeites from Nantycagal Mine in central Wales, as reported by Braithwaite (1982). No trace of mottramite was found in this shaft.

The level was dug open and explored by Shropshire Caving and Mining Club in 1989–1990. One of us (DIG) explored the shaft and level, and surveyed the level in 1993–1994 (Fig. 2), which was also explored and described by Roy Starkey in 1995 (Roy Starkey, *personal communication*), and by one of us (JIW) later in the same year. From 1990 to 1993 the shaft was partly open



Figure 3. The crosscut entrance level, Pim Hill Mine, looking east. Roy Starkey photograph.

to the level, but by 1995 the junction was blocked by rubbish. We warn potential visitors that the shaft and level have been used to dump unpleasant agricultural waste, including toxic chemicals. The entrance to the level (Fig. 3) is at SJ 4873 2152, which is driven in woodland as a crosscut extending eastwards from the scarp side of a north–south sandstone ridge into the cross-shaped workings (Fig. 2). The sandstone in the crosscut is not pebbly, and is stained with hematite. This staining lessens after 28 metres as the mineralised fault zone is approached. The fault zone, about 7 metres wide, strikes almost exactly north–south and dips steeply (62°) to the east. A north–south passage follows the fault zone, and the crosscut continues to the east past a blocked shaft to a back-filled blockage. The northern passage, mineralised with manganese oxide, links with the shaft. The southern passage, with a mineralised fracture zone, ends after about 12 metres.



Figure 4. Patch of olive green mottramite in southern passage, Pim Hill Mine, similar to Roscoe’s material (Roscoe, 1876). Field 25 cm across. Roy Starkey photograph.

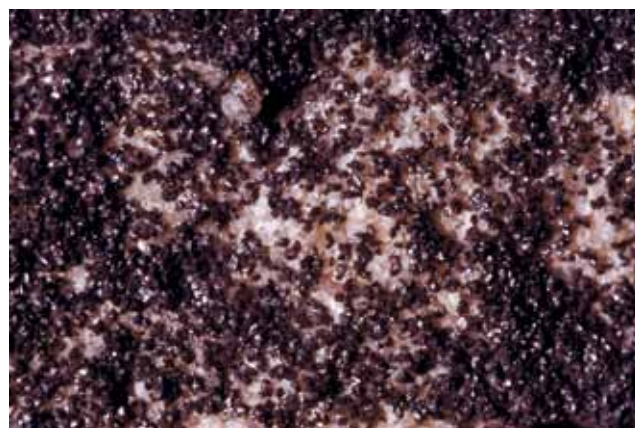


Figure 5. Mottramite crystals on sandstone, Pim Hill. Field 5 mm across. David Green photomicrograph.

Mottramite was found on fracture surfaces of pale coloured sandstone in the southern passage as thin olive-green (Fig. 4, see p. 37) and yellowish crusts and mostly as dark brown crystals. They occur as scattered crystals to intergrown crusts on the sandstone. Most of the mottramite crystals are equant and about 0.1 mm across,

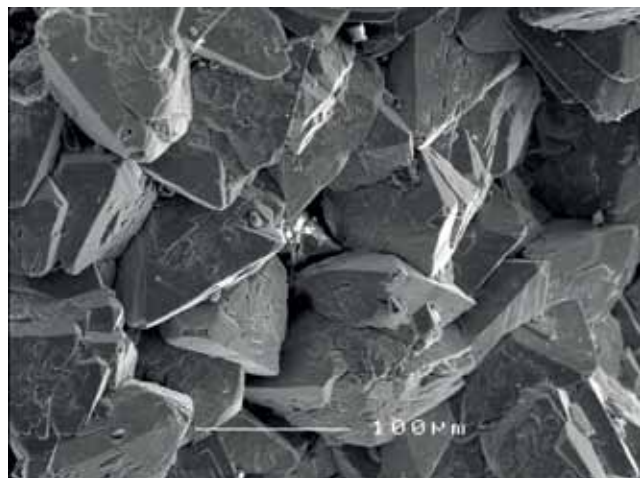


Figure 6. Mottramite crystals, Pim Hill. (SEM photograph; scale bar 100 μm).

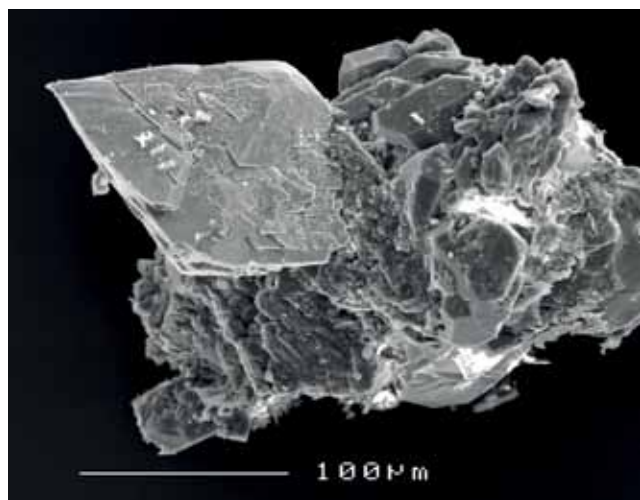


Figure 7. Mottramite crystals, Pim Hill. Note the small idiomorphic recrystallised quartz crystal beside the bottom right-hand corner of the large mottramite crystal. (SEM photograph; scale bar 100 μm).



Figure 8. Olive green mottramite from Roscoe's laboratory (Roscoe, 1876). Richard Braithwaite photograph.

but are very rarely up to about 0.6 mm across (Figs. 5, 6 and 7; Fig. 5 see p. 37). Analyses and IR spectra of the mottramite are reported in Braithwaite (1994) and further microprobe analyses are presented in the Table. The patch of olive-green crust shown in Fig. 4 is of particular interest in that it is identical in appearance to Roscoe's original material studied in Braithwaite (1994) (Fig. 8). No other green minerals were found in the level. Spots and patches of soft black amorphous manganese oxide 'wad' or 'asbolite' are common, and are sometimes associated with the mottramite. IR spectra of this 'wad' show one strong Mn-O absorption with shoulders in the 1000–400 cm⁻¹ region, with maximum varying from 546 to 510 cm⁻¹. Many black manganese oxide minerals have multiple separate absorptions in this region, romanèchite or 'psilomelane' having the nearest reported spectrum (Potter and Rossman, 1979), the variation in absorption maximum reflecting compositional change or structural disorder.

INFRARED SPECTRA INDICATING TWO TYPES OF MOTTRAMITE

The IR spectra of 15 samples of mottramite from various localities have been studied, including those reported in Braithwaite (1994). They fall into two classes, differing mainly in the relative intensities of the strong absorption near 820 cm⁻¹ and of the weaker ones near 970 and 940 cm⁻¹. These absorptions are almost certainly O-H deformations, as are those at similar wavenumbers in the structurally similar

	1	2	3	4
CuO	17.90	6.53	14.66	19.75
PbO	50.66	51.49	48.46	55.42
ZnO	0.99	1.78	3.59	
CaO	0.81	0.72	0.09	
SrO	0.07	0.17	0.12	
Na ₂ O	0.08	0.06	0.17	
V ₂ O ₅	19.15	19.90	19.37	22.58
As ₂ O ₃	1.91	2.00	0.45	
P ₂ O ₅	0.46	0.12	0.01	
(V+As+P) ₂ O ₅	21.52	22.02	19.83	
SiO ₂	0.27	0.11	0.17	
SO ₃	0.06	0.02	0.08	
Cl	0.02	0.03	0.03	
O=Cl	0.01	0.01	0.01	
Total	92.39	92.94	87.21	97.75

Column headings:

1. Sample P298. Average of 5 spot analyses.
2. Sample P299. Average of 5 spot analyses.
3. Sample P300. Average of 4 spot analyses. One analysis contaminated with quartz was ignored.
4. Theoretical for PbCu(VO₄)OH.

Table. Microprobe analyses of mottramites from Pim Hill Mine, expressed as wt% oxides. The theoretical composition of "ideal" mottramite is provided for comparison.



Figure 9. Mottramite crystals, from Mottram St Andrew, Cheshire. The acicular crystals are malachite. (SEM photo; scale bar 100 μm).

olivenite-group arsenates and revealed by their shifts on deuteration (Braithwaite, 1983). Another O-H deformation near 490 cm^{-1} follows their changes in relative intensity. In those mottramites studied from Pim Hill (6 samples), from Tsumeb, Namibia (3 samples) and from Taouz in Morocco (1 sample) these O-H deformation absorptions are fairly strong, but are less strong in some yellowish powdery material from Pim Hill.

In samples from Mottram St Andrew in Cheshire (2 samples), Wanlockhead in Scotland (2 samples), and Mammoth St Anthony Mine in Arizona (1 sample) these absorptions are not visible, probably being buried in the tail of the strong $\text{VO}_4\text{ v}_3$ absorption near 721 cm^{-1} . The other strong $\text{VO}_4\text{ v}_3$ absorption is near 850 cm^{-1} . The O-H stretching absorption complex in the Pim Hill group of mottramites near $3100\text{ to }3140\text{ cm}^{-1}$ shifts to $3155\text{--}3175\text{ cm}^{-1}$ in those studied from the Mottram St Andrew group.

This shift to higher wavenumbers suggests a decrease in the strength of hydrogen bonding in the mottramite from Mottram St Andrew, compared with that from Pim Hill. Frost *et al.* (2014) have recently published a detailed study of the Raman and IR spectra of the O-H stretching and vanadate absorption regions of a sample of arsenian mottramite from Tsumeb. In their study the absorption profiles in these regions were resolved into their complex component absorptions. Some of these components were identified, others must have included arsenate and metal O-H deformations, but the presence of arsenate absorptions confuses distinction between the two types we have discussed. SEM photographs of mottramites from Pim Hill and from Mottram St Andrew are shown for visual comparison of the two types (Figs. 6, 7 and 9).

ACKNOWLEDGEMENTS

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THE MINERALOGY OF THE ADMIRALTY CONCESSION FLAT, NENTSBERRY HAGGS MINE, NENTHEAD, CUMBRIA

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The Admiralty Concession Flat is situated at the west end of the Second Sun Vein in Nentsberry Haggs Mine, Nenthead, Cumbria. Based on recent research, the first stage in the development of the flat was probably dolomitisation followed by major ‘ankeritisation’, which resulted in porosity and cavity formation in the rock adjacent to the vein.

Flat formation was aided by brecciation and dissolution of limestone, these effects being clearly visible in the flat.

The main sulphides are sphalerite and galena and minor pyrite is also present. These minerals, with ‘ankerite’ and quartz are common constituents of cavities. The main mineralogical interest lies in the relatively minor, but complex barium mineralisation in the cavities, which can be examined *in situ*. The flat has two principal levels. In the lower level of the flat, baryte was deposited, often in large crystals, followed by extensive baryte dissolution leaving numerous corroded crystals and epimorphic shapes, particularly in barytocalcite. It is suggested the dissolution was the result of bacteriogenic sulphate reduction producing barium sulphide, which reacted with carbonate and calcium in the hydrothermal brine to form barytocalcite with some witherite and alstonite. In the upper level, witherite is the main mineral with some barytocalcite. It is not clear whether this is a separate phase of mineralisation or whether it formed from barium sulphide in solution moving into the upper level from the lower. Finally, there was some alteration of the barium carbonates to form a surface crust consisting of microscopic crystals of baryte and calcite.

INTRODUCTION

Nentsberry Haggs Mine lies in a district of the Alston Block of the Northern Pennine Orefield (NPO) known as Alston Moor. The names of the mine and the flat (strictly a strata-bound deposit) in the title are those in common use at the present time, but there is confusion on names in the literature, possibly in part due to the mine workings bridging the county boundary between Cumbria (Cumberland in pre-1974 literature) and Northumberland.

On the north-east side of the Nenthead to Alston road, just below Nentsberry Bridge, a number of veins were worked, but according to Wallace (1861) the only one producing much ore was the “Nentsberry Haggs sun vein”. The main access to the whole mine was driven on this vein and is called the Nentsberry Haggs Horse Level. On older plans the mine is referred to as “Nentsberry Haggs Mine”, presumably derived from the name of the horse level. However, on some later plans it is “Nentsbury Mine” and at times it has been called “Haggs Mine”. Dunham (1948; 1990) calls the mine “Nentsberry Mine”.

The workings in Cumbria were part of a lease known as the Admiralty Concession, the lease being held by the Vieille Montagne Zinc Co. in the early 20th Century. The flat, which is the subject of this paper, is within the Concession and it is probably this which has given rise to the name in current use. There is further confusion on the name of the vein that gave rise to the flat. Dunham (1990, p. 140) describes it as the Sun Vein in Cumbria and the

Second Sun Vein in Northumberland. However, it is labelled as the Second Sun Vein on the mine abandonment plan and Figure 1, taken from the plan, shows this part of the mine.

The flat is unique in the NPO in that it is the only accessible site (albeit with considerable difficulty) where complex barium mineralisation can be examined *in situ*. It is best known for spectacular crusts of large curved barytocalcite crystals, specimens of which have found their way into museum collections around the world. The flat also exhibits the dissolution of baryte, normally considered to be a very insoluble mineral, and the resultant formation of minerals based on barium carbonate. Bridges and Green (2006) noted this occurrence as one of four localities exhibiting this phenomenon in the Northern Pennines.

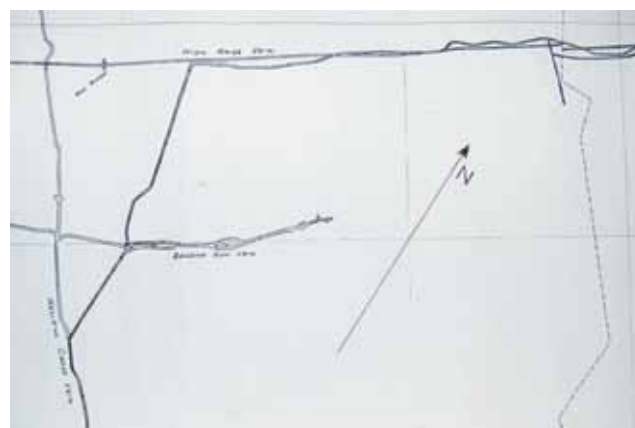


Figure 1. Plan of the Second Sun Vein, showing its relationship to the Wellgill Cross Vein and the High Raise Vein.

A significant amount of research has been carried out on the flat in recent years and this paper is intended to summarise this work.

THE SITE AND ITS GEOLOGY

The horse level was begun from the side of the Alston to Nenthead road, with the portal at NY 7661 4503. At first it follows an approximately northeast course on the Nentsberry Haggs Vein in the shales below the Four Fathom Limestone. This vein terminates against Carrs Vein, a major fault which throws the strata down to the northwest by about 60 m. The horse level continues through this fault on the same course until it reaches the Wellgill Cross Vein, which is also accessible *via* a level from Brownley Hill Mine. After the two levels meet, the workings, still driven in shales below the limestone, follow the Wellgill Cross Vein southwest for a short distance, before branching off north towards the High Raise Vein. This branch intersects



Figure 2. Slickensided surface in the northeast wall of the flat.

the Second Sun Vein at which point the level is in shales directly below the Great Limestone (Namurian). The High Raise Vein runs to the northeast until it reaches a major group of veins discovered in about 1925 by the Vieille Montagne Zinc Co. The whole of the vein system is illustrated by Dunham (1990, p. 136) although this does not show the southwest end of the Second Sun Vein.

On reaching the Second Sun Vein, which is exposed as a shatter belt about 3 m wide, the old miners put in two rises to reach the flat above, which is now called the Admiralty Concession Flat. Figure 2 shows a slickensided face in the flat, with horizontal striations indicating strike slip movement. Most of the flat workings are to the southwest of this fault line. One of the rises is just behind the figure.

Figure 3 shows a side elevation of the flat, which has been worked on two levels. The whole flat is in the Great Limestone and the smaller upper working is at the High Flat Horizon, directly under the Tumbler Beds, which in places are in a serious state of collapse with large suspended, loose slabs of rock in the roof. The much longer lower working is almost certainly at the Middle Flat Horizon.

The limestone has been extensively altered to a hard calcium–iron–carbonate rock and there are numerous cavities which can reach several metres across. There may have been much larger cavities before the flat was worked for sphalerite and galena. The cavities are often lined with combinations of drusy quartz, ‘ankerite’ crystals and sulphides. The barium mineralisation formed late in the paragenesis and is restricted to three areas, one in the upper and two in the lower workings. These are marked ‘Ba’ on Figure 3.

The barium mineralisation in the upper and lower workings is significantly different. Barytocalcite and baryte are the dominant barium minerals in the lower working, while witherite is dominant in the upper. Other minerals such as sphalerite, ‘ankerite’ and galena occur at both levels. Very little oxidation of the primary minerals has taken place and that which is present is almost certainly post-mining.

THE MINERALS

Most of the barium carbonate based minerals are coated with, or wholly or partially replaced by, a white micro-crystalline crust of baryte and calcite. This crust can vary from nearly pure baryte to nearly pure calcite.

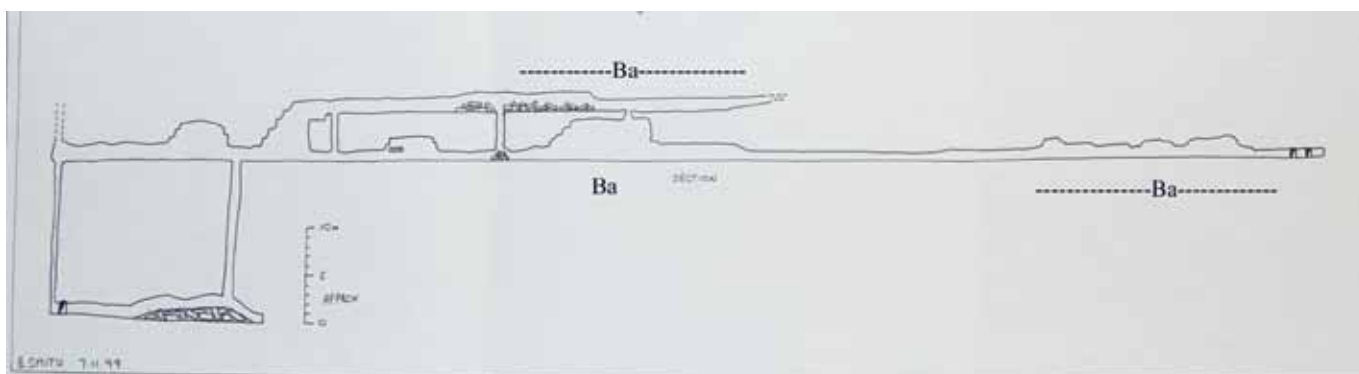


Figure 3. Sketch showing a side elevation of the workings, with areas of barium mineralisation marked ‘Ba’.

Its composition has been confirmed by X-ray diffraction. This alteration occurred during the hydrothermal phase of the mineralisation; it is not the result of oxidation processes.

Minerals where the identity is considered not to be confirmed, or the mineral is no longer present, are shown in italics.

ALSTONITE, $\text{BaCa}(\text{CO}_3)_2$

Young (1985) lists four localities where alstonite has been found in the Alston Block of the NPO. Included in this report is a note that Sir Arthur Russell found alstonite in 1931 in Cox's Vein in "Nentsberry Mine". Later, Young *et al.* (1990) report alstonite *in situ* in Brownley Hill Mine, Nenthead, and a note of the occurrence of alstonite in the Admiralty Concession Flat is included in Green and Young (2006). In the current study an *in situ* occurrence has been found. It takes the form of several small clear pseudo-hexagonal pyramidal crystals in a small isolated occurrence in the lower flat. Crystals reach 8 mm in length and have distinct striations parallel to the pyramids. Figure 4 shows a cavity with such crystals, with a small



Figure 4. Alstonite crystals up to 8 mm long in a small cavity. Field of view 50 mm.



Figure 5. Alstonite crystal, 7 mm long encrusted with baryte-calcite.

area coated with the calcite-baryte crust. Crystals partly or completely altered to the crust described above are far more common. These are often doubly terminated and occur on sphalerite, quartz, baryte and broken surfaces of wall rock (Fig. 5). The altered alstonite is most common in cavities in the northeast end of the lower flat.

ANKERITE, $\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$

There is now doubt about the status of ankerite in the NPO and for this reason 'ankerite' and 'ankeritisation' are placed in inverted commas throughout this paper. A discussion of the problem is included in this Journal (Bridges *et al.*, 2014).

Thin crusts of saddle shaped crystals of 'ankerite', nearly colourless when unoxidised, but often oxidised to pale shades of brown, occur throughout the working but are more abundant at the northeast end of the lower flat. The crusts are frequently associated with sphalerite and less often with quartz. 'Ankerite' deposition continued into the barium mineralisation phase as evidenced by epimorphic gaps after baryte in 'ankerite' specimens (Fig. 6).

ARAGONITE, CaCO_3

Minute clusters of radiating needles of aragonite up to 1 mm long occur on specimens of sulphides and calcite. They are comparatively rare.

BARYTE, BaSO_4

Baryte is common in the lower flat, particularly in the north-east end (Fig. 3). It is rare in the upper flat, mainly occurring as the alteration crust mentioned above. In the lower flat, it normally forms in quartz/sulphide/'ankerite'-lined cavities as terminated blades which can reach 15 cm



Figure 6. 'Ankerite' from the roof of the northeast end of the lower flat, showing epimorphic gaps after baryte. Specimen width 80 mm.

on edge and exceed 20 to 30 mm thick. While crystals are usually translucent (Fig. 7) remarkably clear crystals have been found (Fig. 8). Many of the crystals have fractured and broken off their original matrix and some have been cemented together by witherite and less commonly by alstonite (Figs. 7 and 9). The crystals are commonly etched and often partly dissolved. However, there are complete cavities in barytocalcite with the morphology of baryte, where none of this mineral remains. These phenomena are well illustrated by Bridges and Green (2006). Excluding the minute crusts described above, crusts of spear shaped secondary baryte occur rarely in the upper flat.

In one area of the deposit, baryte crystals are embedded in a rock which appears to be silt, which is silicified in places. This silt has the appearance of the debris left behind after the dissolution of limestone (Fig. 10). There are epimorphic cavities with baryte morphology in this rock



Figure 7. Baryte crystal 15 cm wide, fractured and re-cemented with witherite and alstonite.



Figure 8. Transparent baryte crystal, 10 cm wide.

and there are small 'ankerite', galena and sphalerite crystals on the silicified material (Fig. 11, see p. 44).

BARYTOCALCITE, $BaCa(CO_3)_2$

Barytocalcite is widely distributed in the Alston Block of the Northern Pennine Orefield, Young (1985) listing 19 definite localities and four further doubtful sites. Young (1993) recorded three more sites and added notes on the well known occurrence of barytocalcite at Blagill Mine, Nenthead, Cumbria. Nearly all of these localities were the result of examining dump material.



Figure 9. Baryte crystals, partly coated with witherite, the latter was then coated with a baryte-calcite crust. The specimen is 50 mm wide.



Figure 10. Baryte crystals embedded in a silt-like rock. Field of view approx. 0.5 m.

Barytocalcite is still available for examination *in situ* in the Admiralty Concession Flat. It is very abundant towards the northeast end of the lower flat and is common near the northeast end of the upper flat (Fig. 3), where it is usually associated with witherite. Most barytocalcite crystals in the lower flat have the characteristic curved surface described in the introduction, with surfaces altered to white or a pale brown colour by alteration crusts. Figure 12 shows a typical example. Small lustrous, colourless, monoclinic prismatic crystals up to 5 mm in length occur in some cavities, but are rare (Fig. 13). Tabular crystals of partly dissolved baryte occur embedded in masses of barytocalcite in the lower flat, but these are rare (Fig. 14). In the upper flat, the barytocalcite is usually pale brown and associated with witherite, sometimes forming crystals as shown in Figures 15 and 16.

CALCITE, CaCO_3

Calcite is common as coatings of very small (up to 2 mm) scalenohedral and nailhead crystals on other



Figure 11. Silicified 'silt', epimorphic after baryte, showing small crystals of 'ankerite', galena and sphalerite. Specimen width 45 mm.



Figure 12. Typical specimen of the classic barytocalcite from the lower flat. Specimen width 10 cm.

minerals. Occasionally it forms small, lustrous, colourless, near-mamillary hemispherical crusts, with a minute three sided pyramidal surface visible when magnified. Larger nailhead crystals have been found, but are very rare.

EPSOMITE, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Long needles of epsomite hang down from the roof of the working and are clearly post-mining in origin. These needles are more common in the upper flat than the lower.

FLUORITE, CaF_2

No fluorite has been found in the working. However, small cubic epimorphs in quartz have been found in the lower flat, which strongly suggests that it was present at some point in the hydrothermal mineralisation process, but was subsequently dissolved by the mineralising fluids (Fig. 17). Similar epimorphs from other localities are reported by Bridges and Wilkinson (2003; 2005) and these provide justification for believing the original mineral was fluorite.



Figure 13. Monoclinic barytocalcite crystals on a specimen 30 mm wide, from the lower flat.



Figure 14. Partly dissolved baryte crystal in barytocalcite, with a witherite crystal in the cavity. Field of view 10 cm.



Figure 15. Barytocalcite embedded in witherite, from the upper flat. Specimen width 9 cm.



Figure 16. Barytocalcite crystals, from the upper flat. Specimen width 60 mm.



Figure 17. Epimorphs of quartz after fluorite from the lower flat. Specimen width 35 mm.

GALENA, PbS

Cubo-octahedral crystals of galena, usually associated with sphalerite, are common throughout the working. The crystals are generally fairly small and rarely exceed 15 mm across. Slight surface oxidation has taken place, but the crystals typically retain a silvery metallic lustre (Fig. 18).

GOETHITE, Fe³⁺O(OH)

Pyrite, which is fairly rare in the flat, is usually partly oxidised to brown goethite (Fig. 19). Much of the ‘ankerite’ is stained brown by what are probably limonitic ochres of this mineral. Patches of brown to yellow limonitic ochre, similar to those in other workings in the Nenthead area, are fairly common in the area between the two rises at the southwest end of the working, where there is dripping water. However, most of the working is quite dry and goethite is relatively rare (see melanterite below).

GYPSUM, CaSO₄·2H₂O

Minor post-mining encrustations of gypsum crystals occur rarely on the roof of the upper flat. Gypsum also occurs as small crystals and encrustations on sulphide mineral specimens as the result of post-mining oxidation.



Figure 18. Cubo-octahedral galena crystals with sphalerite and minor goethite and quartz. Specimen width 14 cm.



Figure 19. Goethite encrusting pyrite with yellow jarosite. Field of view 35 mm.

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

Harmotome is rare in the Northern Pennine Orefield. Four localities were noted by Young and Bridges (1984), and a fifth in the Brownley Hill Mine by Green and Nudds (1998). In 1931 Sir Arthur Russell found harmotome *in situ* in Settlingstones Mine, from which locality it remained fairly common until the mine's closure in 1969 (Young and Bridges, 1984). Another of the localities reported is the Wellhope Shaft of 'Nentsberry Mine' where several small crystals have now been found on the dumps.

Harmotome occurs *in situ* in the Admiralty Concession Flat. It is rare but has been found as small elongated prismatic crystals, usually less than 1 mm in length, with a typical cruciform cross-section, in association with sphalerite, mainly in the upper flat. Only one specimen has been found in the lower flat. The terminations are usually poor, but occasionally show the typical 'roof top' sections of harmotome from the Northern Pennines.

HYDROMAGNESITE, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$

Small white hemispherical aggregates of an unidentified basic magnesium carbonate occur very rarely on sphalerite, calcite and baryte pseudomorphs after alstonite (Green and Young, 2006). Analysis by EDS shows that the only element with an atomic number greater than 10 in these aggregates is magnesium; they dissolve in dilute hydrochloric acid with effervescence and therefore contain carbonate. Analyses by X-ray diffraction were complicated by the small amount of material available and strong preferred orientation effects produced by the minute platy crystals. The powder diffraction pattern and crystal morphology indicate structural similarities with hydromagnesite, but the pattern match is not good enough to provide a confident identification.

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

Post-mining alteration has resulted in minor brilliant white botryoidal coatings of hydrozincite on sphalerite in some cavities.



Figure 20. Cubes of pyrite with minor oxidation coating in places. Field of view 35 mm.

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

Oxidation of pyrite has given rise to small areas, up to 5 mm across, of an earthy yellow mineral which is very similar to material positively identified as jarosite at other sites in the orefield. Figure 19 (see p. 45) shows a typical example with goethite on pyrite and on this specimen there is a slight development of crystal structure in places, which is also typical of the mineral.

MELANTERITE, $FeSO_4 \cdot 7H_2O$

Melanterite occurs rarely in the lower flat, in the form of blue crystals intimately mixed with limonitic ochres, in a cavity about 0.5 m wide.

PYRITE, FeS_2

Small golden yellow cubes of pyrite up to 2 mm on edge occur mainly along joints in the roof of the upper flat and occasionally in a joint in the wall (Fig. 20). Most of the limonite is the result of pyrite oxidation, almost certainly post-mining.

QUARTZ, SiO_2

Crusts of small pyramidal quartz crystals, lining cavities in the wall rock, are common throughout the whole working. The mineral is commonly associated with sphalerite and galena. Crystals rarely exceed 10 mm across and are usually very much smaller than this.

On the floor of a single cavity on the lower level, thin blades of quartz were cemented endwise on to fragments of rock scattered on the base of the cavity (Fig. 21). Often one side of these blades is more smooth than the other and occasionally sulphides have formed on one side only. It is likely that this quartz crystallised on baryte, which subsequently dissolved, allowing the quartz to fall.

SPHALERITE, ZnS

Sphalerite is abundant throughout the whole working and museum quality specimens have been found during this



Figure 21. Fragments of quartz on a specimen from the base of a cavity. Specimen width 6 cm.

study. Lustrous black crystals line numerous cavities in the wall rock. Individual crystals up to 10 mm across occur, but are mostly significantly smaller than this. Sphalerite also occurs as a component of metasomatic alteration of the limestone wall rock. Figure 22 shows a typical sphalerite specimen.

SULPHUR, S

Minute pale yellow crystals (<1 mm) of sulphur occur associated with gypsum on sphalerite. The sulphur formed as the result of post-mining oxidation of sulphides at relatively low pH.

WITHERITE, BaCO₃

Witherite occurs in the upper and lower flats, mostly with different morphologies. The sites are marked 'Ba' on Figure 3. It becomes abundant towards the north-east end of the upper flat, where it mainly occurs as radiating masses, often with a rudimentary pseudo-hexagonal morphology (Figs. 23 and 24). The surfaces of these masses are usually white as the result of the alteration described above, but glassy crystals do occur (Fig. 25).



Figure 22. Specimen of sphalerite with minor galena. Specimen width 16 cm.



Figure 23. Radiating witherite from the upper flat. Specimen width 15 cm.



Figure 24. Pseudo-hexagonal crystals of witherite from the upper flat. Specimen width 6 cm.



Figure 25. Glassy crystals of witherite from the upper flat. Specimen width 8 cm.



Figure 26. Pseudo-hexagonal prismatic crystal of witherite on corroded baryte. Specimen width 6 cm.



Figure 27. Broken and corroded baryte crystals cemented with mamillary witherite. Specimen width 12 cm.

In the lower flat, the witherite is often associated with baryte. Figure 26 (see p. 47) shows a pseudo-hexagonal prism on corroded baryte and Figure 27 shows baryte crystals embedded in witherite with a mamillary surface; this mamillary form can become nearly hemispherical. Prismatic crystals with pyramidal terminations (sometimes doubly terminated) also occur and occasionally, the prism faces are missing and the crystals take the form of complex pyramids. Nearly all these forms are encrusted with calcite/baryte as described above. Finally, crusts of small, flat, hexagonal plates cement broken crystals of baryte, sometimes associated with altered alstonite. These smaller crystals almost always have white surfaces, due to late stage alteration. Figure 7 is a typical example of a fractured baryte crystal cemented with altered witherite and alstonite.

DISCUSSION

The mineralisation of the Alston Block of the Northern Pennine Orefield (NPO) is remarkable for its zoning. In an area roughly centred on Weardale, the main gangue mineral is fluorite, with very little barium mineralisation. This zone is then surrounded by a zone in which barium minerals, particularly baryte, dominate and there is very little fluorite. The boundary between the two zones is quite sharp, with only minor overlap. The definitive map of the zoning was prepared by Sir Kingsley Dunham as part of his PhD research and has been reproduced and used on many occasions since (e.g. Dunham, 1990, p. 80–81). Recently, using gravity, seismic and magnetic data, the British Geological Survey have prepared a three-dimensional model of the hidden batholith under the orefield (Kimbell, *et al.*, 2010). This shows the batholith consists of five steep sided plutons, contiguous at depth, with the fluorite zone centred on the Weardale Granite Pluton and also over the top of the Tynehead Pluton. The baryte zone tends to be over the flanks of the plutons and it is suggested that fluorite-rich brines were channelled through the Weardale and Tynehead Plutons, while the barium and sulphate-rich brines were channelled up the flanks of the plutons. Dunham noted that in an area of ground in the vicinity of Nenthead, there

was very little of either of the two main gangue minerals, this area being particularly rich in sphalerite and galena. This area lies over the northern flank of the Tynehead Pluton and extends across a broad embayment towards the Weardale Pluton. Nentsberry Higgs Mine lies in this area, closer to the barium mineral boundary than that of fluorite. Although the main mineralogical interest of the flat lies in its barium mineralisation, it must be made clear that the amount present is well below commercial quantities.

Prior to being worked by the old miners, it is probable that the flat consisted of a large number of cavities, varying from quite small to minor caverns. The relicts of this are still visible in the walls. The flow of mineralising fluids in the flat, and possibly also along the fault, would have been discontinuous, but movement of the fault could easily change fluid movement pathways in the flat itself. That movement of faults happened quite frequently in the mineralisation period of the NPO is evidenced by common examples of brecciation and slickensiding in primary sulphides such as galena and sphalerite. Changes in fluid chemistry combined with different pathways through the flat is the best explanation for the different mineralogical content of many of the cavities. It also probably explains the restricted placement of the barium minerals in the flat and the changes that took place after deposition of the baryte.

Based on the work of Bouch *et al.* (2006) on a number of sites in the Alston Block of the NPO, including the nearby Smallcleugh Mine [NY 788 430], the first stage of the mineralisation was probably dolomitisation, followed by iron-rich dolomitic metasomatism in the process commonly (and conveniently) called ‘ankeritisation’, of the limestone adjacent to the vein. This resulted in the significant development of cavities and porosity in the rock, a process aided by brecciation and dissolution of the limestone. The brecciation is very obvious in the workings. The dolomitisation–‘ankeritisation’ phase was followed by the deposition of sulphides, mainly sphalerite and galena in the cavities, with quartz and ‘ankerite’. All these minerals are still present in the workings, although it has to be presumed there was much more galena before the flat was worked. The sulphide mineralisation stage did not completely fill many of the cavities leaving space for the final phase; the deposition of the barium minerals, although this phase overlapped somewhat with ‘ankerite’ (Fig. 6) and silicification (Fig. 11). The sulphide phase included probable minor deposition of fluorite, which was coated with quartz before finally dissolving (Fig. 17).

By far the most interesting aspect of the mineralogy of the workings is the barium mineralisation. It is the only flat in the orefield where the complex relations between baryte and the barium carbonate minerals can be seen *in situ*. The first stage was the deposition, in open cavities in the lower flat, of baryte crystals, which as shown above can be relatively large. It is now generally accepted that this deposition is the result of the mixing of a brine rich in barium chloride with one rich in sulphate. The process could actually be seen happening in the coal mines of eastern Co. Durham (Edmunds, 1975), where the sulphate was derived from Permian evaporites under the North Sea.

However, in the case of baryte from the northern part of the NPO, based on the isotopic signature of the sulphur ($\delta^{34}\text{S}$), the sulphate was derived from Lower Carboniferous evaporite deposits at depth in the Solway Basin (Crowley *et al.*, 1997).

In one area of the lower flat, the baryte crystals are embedded in rock which appears to have formed from a fine silt (Fig. 10). It is not clear whether the baryte crystals grew into a soft sediment or were later engulfed by it. Later some of the silt was silicified into a hard rock with the appearance of a fine-grained sandstone. Some of this silicified material has very small crystals of galena and sphalerite on surfaces. Figure 11 shows a typical example, with slots where baryte has dissolved out. Minute crystals of galena and sphalerite protrude from surfaces.

Eventually the baryte deposition ceased and some of the baryte crystals became fractured. Corrosion and dissolution of much of the baryte then ensued, this being accompanied by formation of significant amounts of barytocalcite and smaller amounts of witherite and alstonite in the lower flat. There is clear evidence that the deposition of the barytocalcite overlapped with the corrosion and dissolution of the baryte in the form of numerous epimorphs of barytocalcite after baryte and partly dissolved crystals of the latter in the former. Figure 14 is a typical example of this and another very good example is shown in Bridges and Green, (2006, Figure 5). Figure 26 shows a crystal of witherite on corroded baryte, demonstrating that the formation of witherite in the lower flat also accompanied the corrosion. Clearly there was a major change in solution chemistry after the end of the baryte deposition period. The most likely explanation for this is movement on the fault altering fluid pathways in the flat. This could also account for the fracturing of the baryte crystals

Bridges and Green (2006) argue that the corrosion and dissolution of the baryte is the result of bacteriogenic reduction of sulphate in the baryte to produce barium sulphide (BaS), which is readily soluble in aqueous media. This process could have resulted in brines with a higher concentration of barium ($a\text{Ba}^{2+}$) than those observed in the coal field by Edmunds (1975) and this would have aided formation of barium carbonate based minerals, particularly witherite. It must be pointed out that there is nothing in this more detailed study of this locality to refute the bacteriogenic hypothesis, which remains the best explanation for baryte dissolution and the subsequent formation of barium carbonates. Bridges and Green (2006) also point out that formation of barium carbonate based minerals is favoured by brines with a low concentration of calcium chloride since this then allows higher concentrations of carbonate ion in solution ($a\text{CO}_3^{2-}$). That such brines existed is evidenced by the work of Cann and Banks (2001) and Bouch *et al.* (2006). It is likely that all these factors came together to produce the barium based mineralisation seen in the lower flat. It is also worth noting that the formation of barium sulphide would increase the concentration of sulphide ion in solution ($a\text{S}^{2-}$) which in turn would have aided the formation of sphalerite and galena crystals on the 'silicified epimorphic silt' (Fig. 11).

The above offers a reasonable explanation for the two stages of the barium mineralisation in the lower flat, but it does not account for that in the upper flat, where the baryte stage seems to be missing and the dominant mineral is witherite. This could have formed from brines rich in barium chloride, but this definitely requires low calcic brines as explained by Bridges and Green (2006). There is, however, an alternative explanation. It is possible that some of the barium sulphide solution, formed in the lower flat, followed a pathway into the upper flat, where a hydrothermal brine with slightly different chemistry favoured witherite formation more than barytocalcite.

Finally, the brines appear to have become more sulphate and carbonate-rich again, resulting in the alteration of the surface of much of the barium carbonate mineralisation to form the white crust described above.

Since the flat was first opened, damp conditions and exposure to the atmosphere have resulted in relatively minor oxidation of some of the sulphides, particularly pyrite. The sulphuric acid resulting from oxidation of the latter has resulted in the formation of minor amounts of epsomite, gypsum, melanterite and probable jarosite observed in the working.

Specimens illustrating the mineralisation described above have been placed in the collections of the Great North Museum – Hancock.

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ANKERITE: ITS COMPOSITION AND FORMULAE, AND ITS STATUS IN THE NORTHERN PENNINE OREFIELD

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The composition field of the dolomite-group mineral ankerite is defined inconsistently in the geological literature. Guidelines introduced by the International Mineralogical Association (IMA) use the dominant element at a particular structural site to define species boundaries. The dolomite-group minerals have a general formula $\text{Ca}M^{2+}(\text{CO}_3)_2$, where the M^{2+} cations are commonly Mg^{2+} , Fe^{2+} and Mn^{2+} in various combinations. IMA guidelines define ankerite as the dolomite-group species with Fe^{2+} as the dominant cation in the M^{2+} position. This definition is at variance with many of those used in the older geological literature. In recent years, most mineralogical journals have adopted IMA-approved species boundaries as standard and the differing historical definitions have the potential to introduce errors.

The solid solution between dolomite, ideally $\text{CaMg}(\text{CO}_3)_2$, and ankerite is unusual in that it only extends to about 80 mol% substitution of Fe^{2+} for Mg. The hypothetical Fe^{2+} -dominant end-member, $\text{CaFe}^{2+}(\text{CO}_3)_2$, has never been synthesised or identified in nature. Although there is good reason to use $\text{CaFe}^{2+}(\text{CO}_3)_2$ as the ideal formula for ‘ankerite’ for some purposes, it is more appropriate that a formula such as $\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn}^{2+})(\text{CO}_3)_2$ is used in general discussions as it recognises the necessity of another divalent cation being present in the structure. A system of descriptors that facilitates the semi-quantitative identification of the composition of dolomite-group minerals in terms of the various metallic ions that might be present is suggested. Both the formula and the descriptors noted above are useful in discussions of the mineralisation in the Northern Pennines and other areas. In the Northern Pennine Orefield, quantitative analyses dating from the 1940s onwards show that much of the material that is described as ankerite should be described as Fe^{2+} -bearing or Fe^{2+} -rich dolomite.

INTRODUCTION

A common understanding of terminology is essential in any scientific subject. In the biological sciences, the introduction of a binomial system of species names in the mid-eighteenth century (and its subsequent development) provided a unifying framework that allowed taxonomists to categorise the natural world. The evolution of the species concept in mineralogy was less well regulated. A consistent system of guidelines which govern the nomenclature of minerals has only been developed by the International Mineralogical Association (IMA) in the last half century (Nickel and Grice, 1998).

The way in which geological sub-disciplines developed during the twentieth century has had the result that some species names are used in different ways in different areas of study. This can be a source of confusion and has the potential to introduce unintentional (syntactic) errors if the literature from disparate fields is cited in an uncritical fashion. A relevant example is furnished by the dolomite-group mineral ankerite (see Bridges *et al.*, 2014).

A brief review of the nomenclature of solid solutions, the relationship between the dolomite group and the closely-related calcite group, and their structures, is useful.

In a simple binary solid solution, the compositional divide between two minerals is defined by the IMA at

50 mol% (Nickel, 1992). A familiar example is provided by the solid solution between baryte (BaSO_4) and celestine (SrSO_4) in which the species divide is at a 50:50 molar ratio of Ba:Sr. This is a **simple** solid solution as the end-members (baryte and celestine) and all the chemical compositions in between have the **same** crystal structure. There are no intermediate compositions with different crystal structures, and therefore, no valid intermediate species (*N.B.* ‘barytocelestine’ is not a valid species).

The minerals of the calcite group are rhombohedral carbonates with a general formula $M^{2+}\text{CO}_3$, in which M is a divalent metal¹ with an ionic radius of about 100 pm (1 Å). The structure of the calcite-group minerals consists of layers of planar carbonate (CO_3^{2-}) ions which lie between layers of divalent metal cations in octahedral coordination [MO_6] (Chang *et al.*, 1996). Common calcite-group minerals include: calcite (CaCO_3), magnesite (MgCO_3), siderite ($\text{Fe}^{2+}\text{CO}_3$) and rhodochrosite ($\text{Mn}^{2+}\text{CO}_3$).

¹ The letter M is commonly used in general formulae to represent a number of different metallic elements. It is important to note that M is a **variable** and it must be defined with respect to the formula to which it refers; it is italicised to indicate that it is a variable and to differentiate it from the symbols for specific chemical elements. The M used in the general formula for the calcite group does not represent the same selection of elements as the M in the general formula for the dolomite group; each is defined with respect to the formula to which it refers.

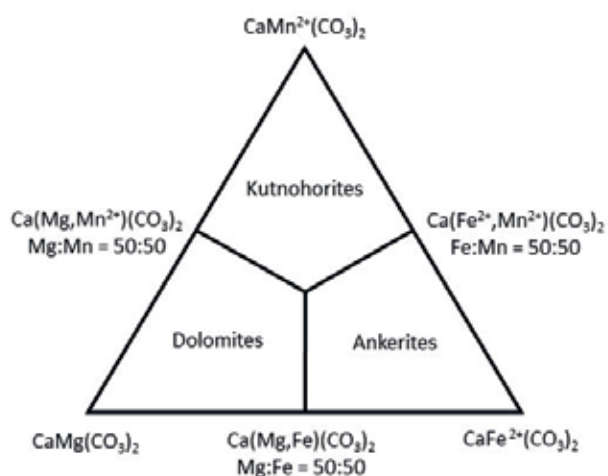


Figure 1. Ternary diagram illustrating the composition fields of dolomite, ankerite and kutnohorite.

Unlike the solid solution between baryte and celestine, solid solutions among the rhombohedral carbonates have the added complexity that structural order can develop in certain compositional ranges. In the solid solution between CaCO_3 and MgCO_3 , for example, the ordering of equal numbers of Ca and Mg ions into alternating layers produces a crystal structure that is **different** from the crystal structure of calcite and magnesite. This distinctive crystal structure is sufficient to define a new species, with an ideal formula $\text{CaMg}(\text{CO}_3)_2$, the mineral dolomite². Similar structurally-distinct intermediate species, ankerite and kutnohorite, are present in the solid solutions between calcite and siderite, and calcite and rhodochrosite, respectively (Chang *et al.*, 1996). The composition fields of dolomite, ankerite and kutnohorite are plotted on the ternary, triangular diagram shown in Figure 1.

ANKERITE: IMA-APPROVED DEFINITION

The dolomite group of minerals comprises five species (Back, 2014). The general formula of the four calcium-bearing members can be written $\text{CaM}^{2+}(\text{CO}_3)_2$; three of these are of particular interest here, namely: dolomite ($M = \text{Mg}$), ‘ankerite’ ($M = \text{Fe}$) and kutnohorite ($M = \text{Mn}$). In ternary or higher order substitutions, IMA guidelines use the dominant element³ at a particular structural site to determine the species name (Nickel, 1992; Hatert and Burke, 2008). The name ankerite can only be applied to a mineral in which iron is the dominant element in the $\text{Fe}^{2+}/\text{Mg}/\text{Mn}^{2+}$ -containing $[\text{MO}_6]$ layer (*N.B.* the word dominant in this

context has a particular meaning: it indicates that there must be **more** Fe atoms in the $[\text{MO}_6]$ layer than atoms of any other **single** element⁴). In the dolomite group, if Mg^{2+} is the dominant M^{2+} the mineral is dolomite, if Fe^{2+} is dominant the mineral is ankerite and if Mn^{2+} is dominant the mineral is kutnohorite. This can lead to the counterintuitive situation in which an element with less than 50 mol% occupancy of a particular site can still be dominant. To take an example, a dolomite-group mineral with 42 mol% Fe^{2+} , 29 mol% Mg, 29 mol% Mn^{2+} is an Mn^{2+} - and Mg-rich ankerite because iron, although it is present at only 42 mol% is the dominant M^{2+} element with the largest number of atoms in the $\text{Fe}^{2+}/\text{Mg}/\text{Mn}^{2+}$ -containing $[\text{MO}_6]$ layer.

ANKERITE: OTHER NAMING CONVENTIONS

The development of analytical techniques that allowed rapid determinations of the composition of minerals generated large datasets and encouraged the development of *ad hoc* systems of nomenclature for some of the common rock-forming minerals. An example is furnished by the series between the olivine-group minerals forsterite (Mg_2SiO_4) and fayalite ($\text{Fe}^{2+}_2\text{SiO}_4$). The compositional divide between these species is at a 50:50 molar ratio of Mg:Fe; however, petrologists found it useful to introduce additional ‘species’ which ran from forsterite through chrysolite, hyalosiderite, hortonolite and ferrohortonolite to fayalite (*e.g.* Deer *et al.*, 1992). Of these, only the end-members, forsterite and fayalite, are currently recognised by the IMA; the intermediate names are obsolete and gradually falling into disuse.

The publications of W.A. Deer, R.A. Howie and J. Zussman (‘DHZ’), are key volumes in mineralogical petrology. They were begun well before the IMA had developed a consistent approach to mineral nomenclature and commonly adopted compositional schemes that were found useful by petrologists. Dolomite and ankerite are important rock-forming minerals, and in these works, the composition field of dolomite is considered to extend to Mg/Fe = 4, (*i.e.* 20 mol% Fe^{2+}) (*e.g.* Deer *et al.*, 1965, 1992, 2013). Compositions with more Fe are described as ankerite. This scheme found approval among carbonate sedimentologists and petrologists, and has also been adopted by some ore mineralogists (*e.g.* Bak, 1993). It is important to determine which description is being used in any particular publication as many compositions described as ankerite correspond to Fe^{2+} -rich dolomite in the IMA-approved scheme or Fe^{2+} -bearing dolomite (see below).

ANKERITE FORMULAE

A chemical formula expresses information about the composition of a mineral in a concise manner. Different sorts of formulae are appropriate for different purposes and a brief review is useful. The most familiar mineral

² An intermediate in the CaCO_3 – MgCO_3 solid solution with a composition Ca:Mg of 50:50 is not necessarily dolomite. To be dolomite it must also have an ordered structure in which the Ca and Mg atoms are arranged in alternating layers. Disordered intermediate compositions (including 50:50) are well-known (*e.g.* Bathurst, 1975); however, they cannot be described as dolomite as they do not have the dolomite structure. They are Mg-rich calcite or Ca-rich magnesite.

³ Strictly, the dominant element rule only applies to substitutions among elements of the same valency; the guidelines for heterovalent substitutions are more complex (Hatert and Burke, 2008).

⁴ The meaning of iron-dominant is different from adjectival modifiers such as iron-bearing or iron-rich, which are used to indicate significant substitution (but not dominance) of a particular element at a site in a mineral structure (Bayliss *et al.*, 2005).

formulae are those for end-member compositions; these are described as ideal formulae. Simplified formulae, which indicate important substitutions are more flexible and also in common use. Formulae which contain information about structural sites are becoming more popular in some quarters, especially in descriptions of complex silicate mineral groups. Detailed compositional studies use empirical formulae, which list minor constituents.

The guidelines adopted by the IMA make ideal end-member formulae easy to write. The diopside–hedenbergite solid solution series can be taken as an example (Hatert and Burke, 2008). The ideal formula for diopside is $\text{CaMgSi}_2\text{O}_6$ and for hedenbergite is $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$. More complex substitutions may require subtle modifications, but can be accommodated; they are comprehensively discussed in Hatert and Burke (2008). Simplified formulae differ from ideal formulae in that they include information about common substitutions: diopside, for example, can be written $\text{Ca}(\text{Mg},\text{Fe}^{2+})\text{Si}_2\text{O}_6$, showing that Fe^{2+} may substitute for Mg. Simplified formulae take up more space on the page, but communicate more information and unlike ideal formulae they can be tailored to suit a particular purpose.

Empirical formulae, which include all of the chemical constituents determined in a particular analysis or group of analyses, provide detailed information at the expense of generality. They are specific to a particular set of data, and can be unwieldy.

The solid solution from dolomite, ideally $\text{CaMg}(\text{CO}_3)_2$, to ankerite only extends to about 80 mol% substitution of Fe^{2+} for Mg (*i.e.* it is a partial solid solution). The ideal end-member ‘ankerite’ composition, $\text{CaFe}^{2+}(\text{CO}_3)_2$, has never been synthesised or identified in natural material and there is reason to believe that it does not exist; see Rosenberg (1968), Essene (1983), Chang *et al.* (1996, pp. 219–222) and Chai and Navrotsky (1996). One of the most Fe^{2+} -rich ankerite compositions known, containing almost 75 mol% ‘ferrodolomite’ (an obsolete name given by some authors to the hypothetical Fe^{2+} -dominant end-member, $\text{CaFe}^{2+}(\text{CO}_3)_2$), is listed by Smythe and Dunham (1947) from Carricks Mine in Weardale and is discussed below. Very few ankerite specimens containing more than 80 mol% Fe have been reported; see Figure 3 in Essene (1983) for a compilation of over 250 analytical results. The Fe^{2+} -rich limit of the solid solution appears to lie at a point where three quarters of the *M* atoms in the layer are Fe, and this apparently simple ratio may reflect an underlying structural restriction; see Reeder and Dollase (1989) and Chang *et al.* (1996, pp. 219–222). However, a detailed study of the energetics of the dolomite–ankerite solid solution by Chai and Navrotsky (1996) concluded that there was insufficient energy gain on ordering to stabilise end-member $\text{CaFe}^{2+}(\text{CO}_3)_2$ with respect to siderite plus calcite.

The ideal ‘ankerite’ formula, $\text{CaFe}^{2+}(\text{CO}_3)_2$, (*e.g.* Back, 2014), disguises the fact that no substance with this composition has ever been identified. A significant amount of another divalent cation, commonly Mg, but possibly also Mn^{2+} , appears to be required for ankerite to form. In a discussion of ankerite from the Northern Pennine Orefield,

the simplified formula $\text{Ca}(\text{Fe}^{2+},\text{Mg},\text{Mn}^{2+})(\text{CO}_3)_2$ (as adopted by Anthony *et al.*, 2003) is more appropriate than the ideal formula. The use of comma-delimited symbols in the order they are given in the bracket ($\text{Fe}^{2+},\text{Mg},\text{Mn}$) indicates (in the standard convention) that Fe^{2+} is dominant (as it is listed first), and shows that Mg and/or Mn^{2+} are invariably present. The same is not true of dolomite, for which $\text{CaMg}(\text{CO}_3)_2$ can be adequate; although even in this case many Fe^{2+} -bearing or Fe^{2+} -rich specimens from the Northern Pennine Orefield would be better represented by $\text{Ca}(\text{Mg},\text{Fe}^{2+},\text{Mn}^{2+})(\text{CO}_3)_2$.

If the terminology of Dunham (1990) or Deer *et al.* (1992) is adopted, no unambiguous simplified or end-member formula can be applied to ankerite, as a range of compositions that vary from Mg- to Fe^{2+} -dominant must be specified. This problem was one of the reasons for the introduction of the 50:50 rule in mineral nomenclature and its more complex derivatives (Nickel, 1992).

It would be useful to be able to identify smaller areas of the $\text{CaM}^{2+}(\text{CO}_3)_2$ ternary composition diagram (Fig. 1) in a semi-quantitative manner with a description that can include Mg and Fe^{2+} and Mn^{2+} . To this end, the system shown in Figure 2 (see p. 54) is suggested: the red lines define 20 mol% Mn^{2+} , Fe^{2+} and Mg and the small green lines 95 mol% Mn^{2+} , Fe^{2+} and Mg. This division of the three kite-shaped areas in Figure 1 results in three groups of five distinct areas that should facilitate the semi-quantitative description of the composition of kutnohorite, ankerite and dolomite. Areas 1 and 11 define the compositions that are essentially pure kutnohorite and dolomite (see below for a discussion of area 6). The remaining areas may be defined by using combinations of M^{2+} -bearing ($M^{2+} < 20$ mol%) and/or M^{2+} -rich ($M^{2+} > 20$ mol%) descriptors; taking area 14 in the dolomite composition field as an example: $\text{Mn}^{2+} > 20$ mol% and $\text{Fe}^{2+} < 20$ mol% and the composition would be described as an Mn-rich and Fe-bearing dolomite.

The majority of the fifteen areas shown in Figure 2 can be populated by data from analyses of samples of dolomite, ankerite and kutnohorite; see Figure 3 in Essene (1983) and also Figure 3 (see p. 54). Areas 6 and 7a (the red dotted line in Figure 2 defines 80 mol% Fe^{2+}) identify compositions with high Fe^{2+} (> 80 mol% Fe^{2+}) and low Mn^{2+} and Mg (< 20 mol% Mn^{2+} and Mg). As noted above, ankerite containing more than about 80 mol% Fe^{2+} has never been synthesised or identified in nature, and appears to be unstable with respect to the formation of siderite and calcite; see Rosenberg (1968), Reeder and Dollase (1989), Chang *et al.* (1996, pp. 219–222) and Chai and Navrotsky (1996).

ANKERITE IN THE NORTHERN PENNINE OREFIELD

This paper is written with particular reference to ankerite and dolomite from the Alston Block of the Northern Pennine Orefield where descriptions of the mineralogy commonly use the term ‘ankerite’ to describe any dolomite-group mineral containing more than about 5 mol% Fe. The classic descriptions of the mineralisation of the Alston Block are provided by Sir Kingsley Dunham (Dunham, 1948; 1990). In these works the term ankerite is

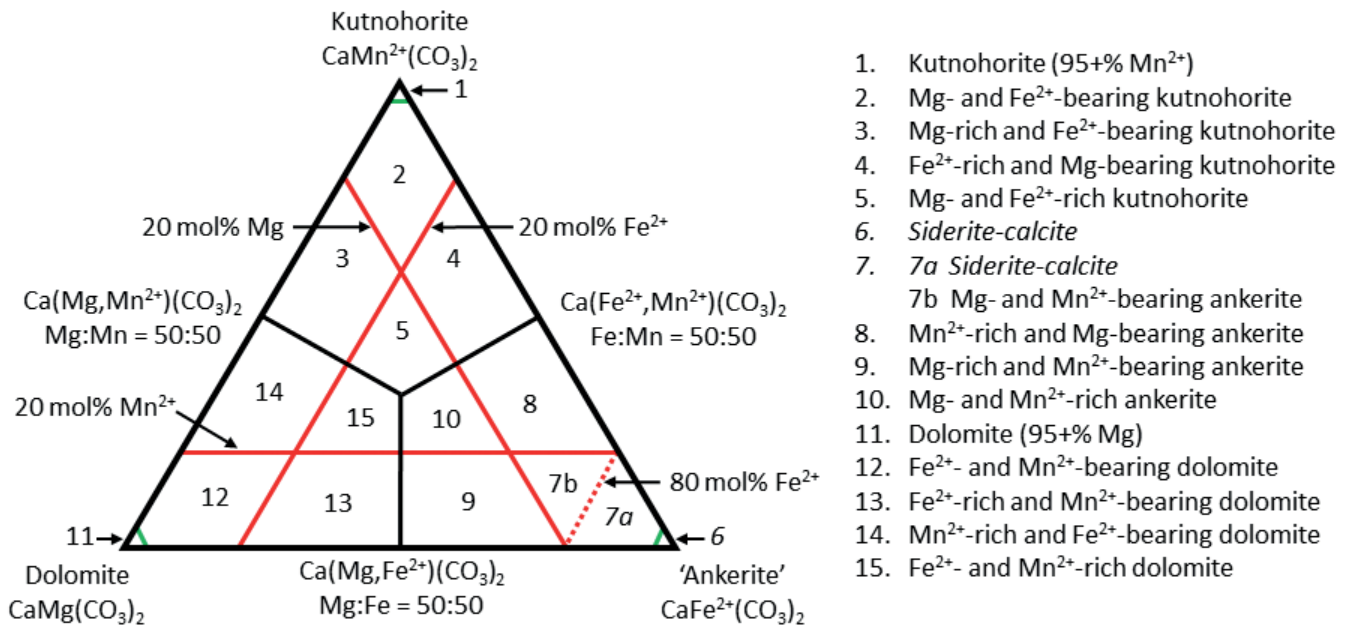


Figure 2. A ternary diagram showing the suggested nomenclature for the dolomite-group minerals.

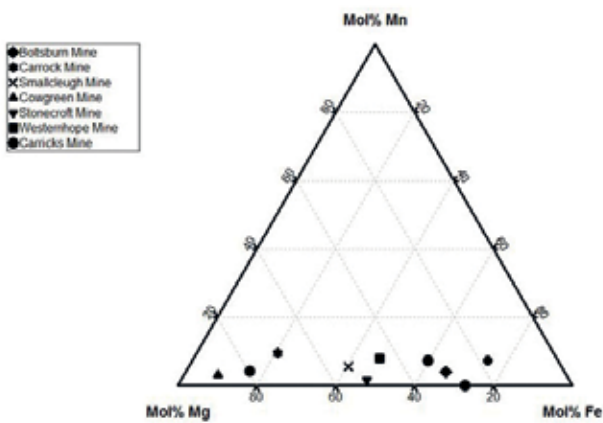


Figure 3. A ternary plot of the analytical data from Smythe and Dunham (1947) for ankerite from the Northern Pennine Orefield (with an additional point for Carrock Mine in the Caldbeck Fells). The data in Smythe and Dunham (1947) and Dunham (1990) are listed as weight percent carbonates. In this plot, they are converted to mol% carbonates as this is the way in which composition fields are defined. Note that there are very few compositions with more than 75 mol% Fe. Excess calcium of between 0 and 10 mol% is likely to be present as calcite nanodomains in the dolomite-group mineral structure. It is this calcite excess that is thought to cause the curvature of crystals of the dolomite-group minerals (Barber *et al.*, 1985).

used in a traditional sense to include any member of the dolomite group that contains even a modest amount of iron. For example, Dunham (1990, p. 75) notes:

Previous investigators have generally considered dolomite to be among the commonest of the carbonates here [the Alston Block of the Northern Pennine Orefield], but the present investigation has shown that most of the minerals formerly classified as dolomite are in fact ankerites.

The terms dolomite and ankerite are not used in the modern sense in this quotation; Dunham reserves dolomite to describe compositions very close to the end-member formula, CaMg(CO₃)₂.

Dunham's early publications shed some light on his use of terminology. The composition of dolomite and ankerite can be estimated using refractive index measurements (*e.g.* Deer *et al.*, 1962) and some of the first determinations by this technique were on specimens from the Northern Pennines (Dunham, 1941). The first detailed chemical analyses of ankerite from the orefield were reported in a collaboration with J.A. Smythe, working at the then Kings College, Newcastle (Smythe and Dunham, 1947). Widely ranging compositions are listed; however, even the least iron-rich specimen, from Cowgreen Mine in Teesdale, which contains less than 10 mol% iron at M²⁺, is described as ankerite.

In Dunham's early papers and the later works in which they are cited (*e.g.* Dunham, 1990), the term ankerite is consistently used to describe dolomite-group minerals containing more than 10 mol% Fe at M²⁺, and occasionally used for compositions with just a few mol% Fe. This terminology is not criticised herein as it was developed before modern species boundaries were defined; nevertheless, it must be borne in mind when citing the results of these earlier studies in any publication that uses or assumes IMA-approved species names.

Only one full chemical analysis of a specimen from the Nenthead area is provided by Smythe and Dunham (1947); however, a range of compositions is inferred for dolomite-group minerals from Nentsberry Hags Mine, Brownley Hill Mine and Smallcleugh Mine using refractive index determinations (Smythe and Dunham, 1947; Dunham 1990). Even those specimens with the lowest refractive indices, corresponding to approximately 5 mol% Fe or less, are described as "dolomitic ankerite". A re-interpretation of the refractive index measurements (tabulated in Dunham, 1990, p. 76) shows that both dolomite and ankerite (using modern definitions) occur at Nenthead; both species occur at Nentsberry Hags Mine and they are discussed in Bridges *et al.* (2014).

A detailed study of flat (strictly strata-bound) deposits in the North Pennines was carried out by Bouch *et al.* (2006), who conducted more than 100 EPMA analyses of dolomite-group minerals. The samples were taken from host rock and veins from Smallcleugh Mine, Rogerley Mine and Wellheads Hush. There is considerable variation in the *M*-site iron content of the dolomite-group minerals in these data, ranging from virtually zero to *ca* 70 mol% Fe; under IMA guidelines, the majority of the compositions fall within the dolomite composition field.

The analyses reported by Smythe and Dunham (1947) are by classical wet chemistry; they are superior to modern microprobe determinations in some ways as they include direct determinations of carbonate content. The compositions of samples of 'ankerite' from six mines in the Northern Pennine Orefield are listed as % w/w oxides. These compositions are also listed as wt% carbonates and tabulated as such in Dunham (1990, p. 75). In the context of this discussion a recalculation to molar ratios is useful.

Carricks Mine, Weardale.

There are three analyses from this mine:

1. **Far Vein West, Boring No. 8:** 71.9 m; replacement of Great Limestone. This sample recalculates to an Fe:Mg molar ratio of 16.7:83.3 with 1.1% w/w Mn. This lies within the dolomite composition field and it is best described as an Fe²⁺- and Mn²⁺-bearing dolomite.
2. **No.4 Cross Vein, Boring No. 4:** 2.7 m; replacement of Great Limestone. This recalculates to a molar Fe:Mg ratio of 64.4:35.6 and is clearly ankerite. The Mn content is relatively low at 1.9% w/w and it is best described as an Mg-rich and Mn²⁺-bearing ankerite.
3. **Lowe's Vein West, Boring No. 1:** 57.9 m; replacement of Great Limestone. For this sample the molar Fe:Mg ratio is 80.8:19.2 with 1.8% w/w Mn. This is clearly ankerite, it has 75.3 mol% Fe, 17.7 mol% Mg and 7.0 mol% Mn which represents one of the highest iron contents that has been recorded in the ankerite–dolomite solid solution (see Figure 3 in Essene (1983) for an extensive compilation of over 250 analytical results). It is best described as an Mg- and Mn²⁺-bearing ankerite.

Cowgreen Mine, Teesdale

A single analysis of suitably-prepared coarse mill tailings yielded a molar Fe:Mg ratio of 9.1:90.9 with 1.9% w/w Mn. This specimen is clearly dolomite; the relatively low iron content does not justify the description Fe²⁺-rich and would be best described as an Fe²⁺- and Mn²⁺-bearing dolomite.

Stonecroft Mine, Tynedale

A sample of coarse rock from the dump recalculates to a molar Fe:Mg ratio of 47.7:52.3 with 0.4% w/w Mn. This would be best described as an Fe²⁺-rich and Mn²⁺-bearing dolomite.

Westernhope Mine, Weardale

This sample is from the Great Limestone adjacent to the Great Vein. It recalculates to a molar Fe:Mg ratio of

51.1:48.9 with 2.0% w/w Mn. This falls just within the ankerite composition field using modern terminology and is best described as an Mg-rich and Mn²⁺-bearing ankerite.

Smallcleugh Mine, Nenthead

This sample was taken from streaks parallel to bedding planes in the Hansome Mea Flats. Plate 3 in Dunham (1990, p. 149) matches this description perfectly. The analysis recalculates to a molar Fe:Mg ratio of 42.7:57.3 with 1.5% w/w Mn and, therefore, lies just within the dolomite composition field and is best described as an Fe²⁺-rich and Mn²⁺-bearing dolomite.

The compositions described in the foregoing text are plotted on a ternary diagram in Figure 3, together with data for samples from Boltsburn Mine in Weardale and Carrock Mine in the Caldbeck Fells, Cumbria. The Carrock Mine data indicate that the 'ankerite' from the Harding Vein contains only 7.5% FeO: it was described as a "ferroan dolomite" in Cooper and Stanley (1990), a term that is no longer approved (see Bayliss *et al.*, 2005); it would be best described as an Fe²⁺- and Mn²⁺-bearing dolomite. There is a wide variation in compositions in Figure 3 ranging up to about 75 mol% Fe²⁺, which is one of the most Fe²⁺-rich ankerites from anywhere in the world. All of these compositions are described as ankerite in Dunham (1990); in modern terminology half of them are Fe²⁺-rich or Fe²⁺-bearing dolomite.

In the absence of analytical data there is no easy way to determine whether an unknown dolomite-group mineral is dolomite or ankerite. A close association with siderite (as at Boltsburn and Carricks mines) might raise the suspicion of a composition in the ankerite field, but does not provide a guarantee.

Of the characterisation techniques available to amateur mineralogists, refractive index determinations are complex and prone to error. Wet chemistry requires bulk samples with uniform compositions, access to reagents and a reliable chemical balance. Sink-float density determinations on small fragments may be the best simple guide as the density of the dolomite–ankerite series varies considerably with composition (from ~2.87 to 3.11 g cm⁻³).

CONCLUSIONS

Much material from the Northern Pennine Orefield that was described as ankerite falls within the dolomite composition field. This terminological problem is endemic in the wider geological literature and should be considered in any research on this mineral group. In discussions of ankerite from the Northern Pennine Orefield and many other localities, the simplified formula Ca(Fe²⁺,Mg,Mn²⁺)(CO₃)₂ is more appropriate than the ideal formula CaFe²⁺(CO₃)₂. A system has been suggested that facilitates the semi-quantitative description of the composition of the dolomite-groups minerals in terms of the various metallic ions that might be present. In the absence of compositional data there is no easy way to separate an Fe²⁺- and Mn²⁺-bearing dolomite from ankerite; both minerals can weather to form a dark brown iron-rich crust. A close

association with siderite might provide a useful indication of an ankerite composition, but provides no guarantee.

ACKNOWLEDGEMENTS

Thanks are due to Neil Hubbard who drew our attention to the change in the ideal formulae of ankerite in *Fleischer's Glossary of Mineral Species* (Back, 2014) which began this investigation. Thanks also go to Peter Williams for a discussion of ideal and simplified formulae, Richard Braithwaite and Malcolm Southwood for their valuable input and to Mike Styles and Paul Carter (British Geological Survey, Keyworth) for their assistance in locating several of the references cited.

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STIBIOCLAUDETITE, A FIRST BRITISH OCCURRENCE, FROM WET SWINE GILL, CALDBECK FELLS, CUMBRIA

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The recent description of stibioclaudeite (AsSbO_3), a mineral which is differentiated from claudeite (As_2O_3) by a site-specific substitution of Sb for As, prompted a re-examination of ‘antimony-rich claudeite’ from Wet Swine Gill in the Caldbeck Fells, Cumbria. The acceptance of stibioclaudeite as a new species places a constraint on the composition field of claudeite that was not present when the ‘antimony-rich claudeite’ was originally reported. The boundary between the two minerals is at $\text{As}_{1.5}\text{Sb}_{0.5}\text{O}_3$: compositions that are more Sb-rich are stibioclaudeite, those that are less Sb-rich are claudeite. The empirical formula determined in 1998 for ‘antimony-rich claudeite’ from Wet Swine Gill was $\text{As}_{1.2}\text{Sb}_{0.8}\text{O}_3$. Nine further analyses by wavelength-dispersive X-ray spectrometry, reported herein, produced $\text{As}_{1.05}\text{Sb}_{0.95}\text{O}_3$. Both are close to end-member stibioclaudeite. Qualitative analyses by energy-dispersive X-ray spectrometry indicated the presence of substantial amounts of Sb in every specimen that was examined. No Sb-poor compositions were found. These data suggest that claudeite should be removed from the species list from Wet Swine Gill and the first British occurrence of stibioclaudeite added. Stibioclaudeite occurs in quartz veinstone which is rich in primary antimony minerals. It is restricted to cavities and fractures near the base of the oxidation zone where it occurs as colourless, transparent, monoclinic crystals with a resinous lustre and perfect cleavage. It overgrows antimony-bearing sulphides and sulphosalts, is overgrown by sénarmonite and sulphur, and rarely contains bright red metastibnite inclusions. It is suggested that stibioclaudeite forms under low-temperature supergene conditions at a relatively low oxidation potential from solutions that are rich in As and Sb in their intermediate As(III) and Sb(III) oxidation states.

INTRODUCTION

In the early 1980s, a vein containing primary lead, iron, arsenic and antimony mineralisation was discovered in fine-grained sedimentary rocks of the Ordovician Skiddaw Group at Wet Swine Gill in the Caldbeck Fells, Cumbria. The vein crosses the stream halfway up the flank of Coombe Height [NY 3140 3220¹]. It is about 0.3 m wide, trends approximately 060°, dips steeply, and is exposed over a strike length of a few metres. Shortly after its discovery, vein material was collected from an exposure in the northeast bank, leaving a near-vertical slit up to about 1 m deep.

The primary mineralisation was described by Fortey *et al.* (1984), who reported an early Sb–As–Fe assemblage (mainly stibnite and berthierite, with lesser arsenopyrite, sphalerite, jamesonite and antimony) and a later Sb–Pb assemblage (zinkenite with lesser fülöppite and semseyite). Fortey *et al.* (1984) also briefly described a handful of supergene minerals. Subsequent research has extended this list to include anglesite, bariopharmacosiderite, beudantite, ‘bindheimite’², cerussite, goethite, pharmacosiderite, scorodite, sénarmonite, ‘stibiconite’², sulphur, valentinite and the first British occurrences of parasymplectite and metastibnite (Cooper and Stanley, 1990; Neall and Green,

¹ There is a small positional error in the grid references quoted by Fortey *et al.* (1984) and subsequent authors.

² The status of the lead- and antimony-bearing members of the pyrochlore supergroup, bindheimite and stibiconite, has been the subject of considerable recent research and is worthy of a short review. In a standardisation of pyrochlore-supergroup nomenclature Atencio *et al.* (2010) discredited the poorly defined ‘grandfathered’ species bindheimite and stibiconite and renamed them using a site-specific chemical scheme. Bindheimite became oxyplumboroméite, and stibiconite either oxycalcioroméite (Leverett *et al.*, 2012) or ‘stibioroméite’ (a name which falls outside the strict rules of the proposed scheme and reflects the fact that careful quantification of the oxidation state of Sb and of the water and vacancies in the structure is required for proper characterisation). It proved impossible to find the original type specimens of bindheimite or stibiconite, and in a clarification, Christy and Atencio (2013) noted that the status of bindheimite and stibiconite should be changed from ‘discredited’ to ‘questionable’ pending further research. Until these issues are resolved it seems prudent to retain the old but questionable species names.

2001; Tindle, 2008). In addition to these, 'claudeite' was recorded by Leppington and Green (1998) as follows:

Claudeite occurs as colourless to white thin-tabular crystals up to 3 mm long...and as foliated masses up to 5 mm across in cavities in vein-quartz. The crystals resemble gypsum in appearance, with a well developed cleavage on (010) and a similar monoclinic habit, but can be distinguished by their resinous lustre. They are early in the supergene paragenesis and are commonly associated with transparent octahedral s enarmontite and, rarely, with sulphur, both of which appear to be later than the claudeite.

Quantitative chemical analyses indicated an antimony-rich composition with a formula $As_{1.2}Sb_{0.8}O_3$. There is considerable substitution of antimony for arsenic, but the formula fell within the claudeite composition field as it was defined in 1998. The mineral, therefore, was described as "antimonian claudeite". A shift in peak positions in the powder diffraction pattern to slightly lower 2θ values compared to end-member claudeite was attributed to the increase in unit-cell size produced by the substitution of Sb for As in the structure.

STIBIOCLAUDEITE

Stibioclaudeite was described from the famous Tsumeb Mine in Namibia by Origlieri *et al.* (2009). Its crystal structure is similar to claudeite and is best understood by comparison with that species. Claudeite is made up of corrugated sheets of corner-linked AsO_3 units. There are two distinct sites for As atoms in the structure: $As(1)$ and $As(2)$. Antimony, which has a larger ionic radius than arsenic, can only substitute in the $As(2)$ site. Under the rules of the International Mineralogical Association, a greater than 50% occupancy at such a structural site is sufficient to define a new species. Stibioclaudeite has the ideal formula $AsSbO_3$, and a slightly larger unit cell than claudeite. The boundary between the two species, using the 50:50 site-substitution rule, is at $As_{1.5}Sb_{0.5}O_3$. Although a complete solid solution between claudeite and stibioclaudeite exists, compositions that contain **more** Sb than $AsSbO_3$ are unlikely to occur as Sb is too large to occupy the $As(1)$ site (Origlieri *et al.*, 2009); therefore, the composition field of stibioclaudeite ranges from $As_{1.5}Sb_{0.5}O_3$ to $AsSbO_3$.

A re-examination of 'claudeite' from Wet Swine Gill seemed appropriate in the light of these data. The original powder diffraction pattern was found to be a good match for stibioclaudeite. The original analyses indicated a composition of approximately $As_{1.2}Sb_{0.8}O_3$, which is within the stibioclaudeite composition field. As these analyses were obtained by energy-dispersive spectrometry (EDS) on a relatively old instrument, further data were sought. A small fragment was detached from a specimen in the CML Collection and prepared for analysis by wavelength-dispersive spectrometry on an electron microprobe. A mean of nine spot analyses, normalised to a formula with three oxygen atoms (ignoring small quantities (<1% wt% SrO) of an element determined as strontium, which is an artefact due to a line overlap), produced the empirical formula $As_{1.05}Sb_{0.95}O_3$. On the basis of these analyses and a number of additional qualitative analyses on different specimens by

EDS, all of which indicated major Sb substitution for As, it was concluded that 'claudeite' specimens from Wet Swine Gill should be re-labelled 'stibioclaudeite'. The original "antimonian claudeite" from Wet Swine Gill (Leppington and Green, 1998), and all of the specimens examined in this research are stibioclaudeite. To date, no specimens of claudeite (*i.e.* no specimens with a molar ratio of $As/Sb > 3$) have been found.

At Wet Swine Gill, stibioclaudeite occurs as colourless, translucent to transparent, monoclinic crystals with a resinous lustre and perfect cleavage on (010). It is restricted to cavities in antimony-rich vein quartz collected from the base of the oxidised vein, several tens of centimetres below the original exposed surface. It is commonly associated with stibnite, antimony-bearing sulphosalts and s enarmontite and rarely with valentinite and sulphur, a few crystals are stained deep red by minute inclusions of metastibnite. The tabular to prismatic crystals, which resemble gypsum (Fig. 1) may reach 5 mm in length, but are more commonly 1 to 2 mm long. Fish-tail twinning (Fig. 2) is well developed in some cases.

In addition to its occurrence as euhedral crystals in cavities in antimony-rich quartz veinstone, polycrystalline patches of stibioclaudeite up to about 10 mm across span hairline cracks (almost certainly produced by recent weathering) in quartz blocks at the base of the oxidation zone. These cracks are not wide enough to allow well formed crystals to develop.

DISCUSSION

Stibioclaudeite is restricted to fractures and cavities in blocks collected from near the base of the oxidation zone at Wet Swine Gill. It is not found in unoxidised veinstone or the highly oxidised near-surface vein assemblage. Its occurrence as euhedral crystals in cavities and fractures, and close association with s enarmontite, sulphur and valentinite, indicate that stibioclaudeite formed by supergene oxidation. Its localised distribution near the base of the oxidation zone and paragenesis in the fractures and cavities in which it occurs, directly overgrowing vein quartz, antimony sulphides and sulphosalts and overgrown by s enarmontite and sulphur, suggest that stibioclaudeite is an early (and perhaps relatively unstable) supergene phase. The arsenic- and antimony-bearing supergene assemblage at the base of the oxidation zone, which includes metastibnite, parasymplectite, stibioclaudeite, s enarmontite, sulphur and valentinite, is replaced by bindheimite, stibiconite, an as yet uncharacterised iron antimony oxide (possibly tripuhyite), beudantite, scorodite and pharmacosiderite-group minerals, in the more oxidised environment nearer to surface. The occurrence of rich patches of stibioclaudeite in hairline fractures surrounding unoxidised veinstone at the base of the oxidation zone suggests crystallisation from solutions at a relatively low oxidation potential. A low activity of reduced sulphur is probably also required to prevent the formation of sulphides such as metastibnite, which is locally common as a supergene encrustation in cavities and fractures near the base of the oxidation zone. Note that the term 'oxidation zone' used herein does not imply a simple vertically zoned

structure, as diagrams in textbooks occasionally suggest, but a more heterogeneous structure in which oxidising fluids penetrate hairline cracks and cavities, altering the surrounding sulphides and sulphosalts, but leaving resistant veinstone blocks, which lack fractures, relatively unaltered.



Figure 1. Prismatic colourless monoclinic stibioclaudeite, 2.5 mm in length, on stibnite from Wet Swine Gill, Caldbeck Fells, Cumbria. Mike Leppington Collection.



Figure 2. A tabular stibioclaudeite crystal, 1.1 mm in length, on quartz, with a typical resinous lustre and characteristic fish-tail twinning from Wet Swine Gill, Caldbeck Fells, Cumbria. Mike Leppington Collection.

A mean of nine analyses by wavelength-dispersive spectrometry on an electron microprobe produced the empirical formula $As_{1.05}Sb_{0.95}O_3$, with relatively little variation and no compositions containing more than 50 mol% Sb. These data are similar to those reported by Origlieri *et al.* (2009) for type material from Tsumeb, Namibia, which has a comparable empirical formula: $As_{1.088}Sb_{0.912}O_3$. This suggests that the solutions at both localities contained sufficient concentrations of Sb to fully populate the *As*(2) site (an observation which is not surprising at Wet Swine Gill, where primary antimony minerals are extremely abundant). The absence of any compositions containing more than 50 mol% Sb supports the contention that the *As*(1) site in claudeite/stibioclaudeite is unable to accept antimony (Origlieri *et al.*, 2009).

Solution conditions in the hairline fractures and cavities near the base of the oxidation zone clearly favour the formation of stibioclaudeite. Studies of the solution speciation of arsenic and the Eh–pH conditions in which different arsenic-bearing supergene minerals precipitate (*e.g.* Vink, 1996) show that claudeite (which is closely related to stibioclaudeite) forms in relatively reducing conditions from solutions with very high *As*(III) activities. The solution speciation and supergene chemical behaviour of antimony is less well understood and has been the subject of considerable debate in recent years (*e.g.* Vink, 1996; Diemar *et al.*, 2009; Leverett *et al.*, 2012). Relatively reducing conditions are likely to be required to avoid the formation of highly stable *Sb*(V) minerals, such as ‘stibiconite’ (Leverett *et al.*, 2012).

Detailed chemical modelling of the conditions required for stibioclaudeite to form is beyond the scope of this discussion. It is nonetheless satisfying that the field observation that minerals containing *As* and *Sb* in intermediate oxidation states (such as stibioclaudeite) are restricted to the deeper parts of the ‘oxidation zone’ is supported by modelling. As the weathered surface of the vein is approached, the oxidation potential increases and the solution speciation of *As*, *Sb* (and *Fe*) changes, stabilising minerals such as beudantite, bindheimite, goethite, pharmacosiderite, stibiconite and scorodite, which contain the redox-sensitive elements antimony, arsenic and iron in their higher *Sb*(V), *As*(V) and *Fe*(III) oxidation states, respectively.

Recent research by Leverett *et al.* (2012) shows that the iron antimony oxide tripuhyite ($FeSbO_4$) should also be stable in highly oxidising near-surface conditions. In this context it is interesting to note that a survey of ‘yellow ochres’ from Wet Swine Gill by energy-dispersive X-ray spectrometry revealed several specimens of an iron antimony oxide. Analyses by XRD are required to identify this phase.

Stibioclaudeite has been reported from relatively few localities worldwide and a discussion of their mineralogical and geochemical similarities and differences is worthwhile. The type locality is the famous Tsumeb Mine in Namibia where a complex and diverse range of minerals occur in a pipe-like dolostone-hosted *Cu–Pb–Zn* orebody

(e.g. Gebhard, 1999). Stibioclaudeite is very rare at Tsumeb; it occurs with quartz, leiteite, ludlockite and smithsonite in cavities in primary tennantite. Using data for synthetic AsSbO_3 , Origlieri *et al.* (2009) suggest that stibioclaudeite requires a temperature of between 300 and 400°C to form. However, its occurrence as euhedral crystals in cavities in primary tennantite, and association with supergene minerals, strongly suggest a much lower temperature. The maximum temperature determined by fluid inclusion studies for the primary hypogene copper mineralisation at Tsumeb of 210 to 280°C (Haynes, 1985), which is significantly lower than the proposed 300 to 400°C; and stibioclaudeite is closely associated with leiteite, which is thought to form from arsenic-rich supergene fluids at about 40°C (Cesbron *et al.*, 1977). In this context it is worthwhile noting that minerals commonly crystallise from aqueous solutions at temperatures well outside their thermal stability fields. It is likely that stibioclaudeite is an early component of the supergene assemblage at Tsumeb, a situation which is paragenetically similar to Wet Swine Gill. The occurrence with leiteite and ludlockite is noteworthy: leiteite, ideally $\text{ZnAs}^{3+}_2\text{O}_4$, and ludlockite³, ideally $\text{PbFe}^{3+}_4\text{As}^{3+}_{10}\text{O}_{22}$, both contain arsenic in its intermediate As(III) oxidation state and provide an indication of relatively reducing conditions.

Stibioclaudeite has been reported with arsenolite, picropharmacolite, parasymplectite and villyaellenite at the Borgofranco mines in Piedmont, Italy (Campostrini *et al.*, 2012), where it appears to have formed by the recent supergene oxidation of primary arsenic and antimony minerals. Parasymplectite, ideally $\text{Fe}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, contains iron as Fe(II). Its occurrence at the Borgofranco mines and at the base of the oxidation zone in arsenopyrite-rich veinstone at Wet Swine Gill (Neall and Green, 2001) provides a further indication of relatively reducing conditions.

The artificial analogue of stibioclaudeite occurs in assemblages formed by the weathering of smelter slag in the Freisach-Hüttenberg area of Carinthia, Austria (Kolitsch *et al.*, 2013). Although this occurrence does not fall within the strict definition of a mineral, its mode of formation, as a precipitate from low-temperature aqueous fluids, has geochemical similarities with Wet Swine Gill.

Stibioclaudeite has been identified as a minor component of polyphase inclusions in spodumene from Greenbushes Mine, Western Australia. The Greenbushes Pegmatite, which lies within the Balingup Metamorphic Belt of the Yilgarn Craton, is the world's largest lithium and tantalum deposit. It is classified as a lithium–caesium–tantalum (LCT) type rare-element pegmatite and is highly enriched in spodumene. Stibioclaudeite occurs as minute crystals, typically <6 µm in length, with other arsenic and antimony minerals in inclusions in the spodumene (Anderson and McCarron, 2011). These inclusions are thought to have formed in a strongly reducing

carbonate-rich magmatic fluid which exsolved from the pegmatite melt. This geological setting is fundamentally different from those described in the foregoing discussion; it shows that stibioclaudeite is not restricted to low-temperature supergene environments, but the requirement for reducing conditions remains.

The specimens described herein were collected before the current collecting restrictions came into force in the Caldbeck Fells. Due to its small size and vulnerable nature, Wet Swine Gill is now a 'red zone' locality and collecting is highly restricted. In this context, it may be of interest for readers with a research interest in the locality to know that duplicate specimens of vein material collected by Norman Thomson (Green *et al.*, 2012) are preserved in the collections of the Oxford University Museum of Natural History and one of the authors (TN).

The foregoing discussion strongly suggests that claudeite should be removed from the list of minerals from Wet Swine Gill. The only other locality in the British Isles where claudeite has been reported is Huel [Wheal] Sparnon near Redruth, Cornwall (Hintze, 1904; Macpherson, 1983; Golley and Williams, 1995). No determinative data were provided, and no specimen could be located, and Leppington and Green (1998) concluded that this record was in need of confirmation. Following publication of that article, characteristic monoclinic bladed crystals of what may well be claudeite were reported to one of us (CML) on a specimen from Wheal Sparnon in a private collection of Cornish minerals (Martin Vincent, *personal communication*). If this were to be confirmed analytically it would represent the only known claudeite from the British Isles.

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³ The chemical formula of ludlockite was originally given as $(\text{Fe}^{2+},\text{Pb})\text{As}^{5+}_2\text{O}_6$, but was shown by Cooper and Hawthorne (1996) to be $\text{PbFe}^{3+}_4\text{As}^{3+}_{10}\text{O}_{22}$, which has As in its intermediate As(III) oxidation state and Fe as Fe(III).

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“CRYSTAL MOUNTAINS MINERALS OF THE CAIRNGORMS”

by Roy E. Starkey

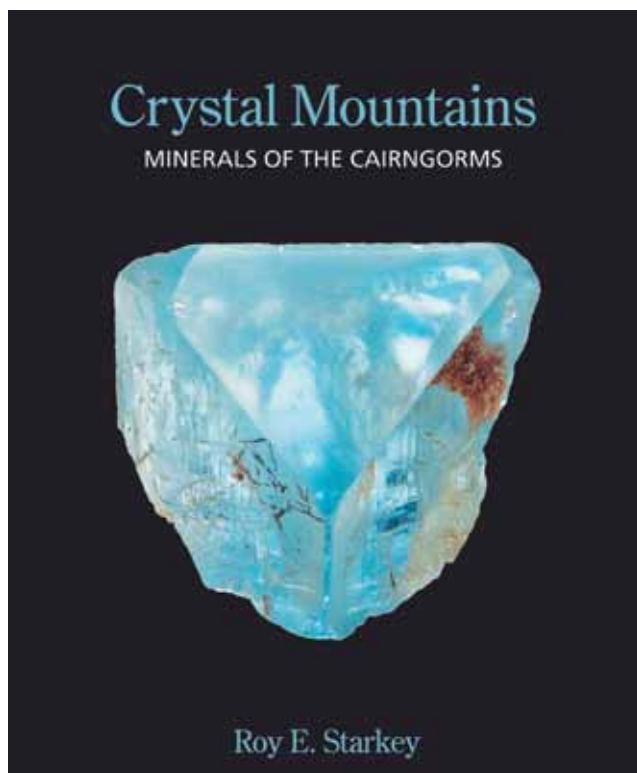
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With five of the six highest peaks in Scotland, the Cairngorms are the most extensive area of mountain terrain in the British Isles. Snow falls are common, even in the height of summer, and the high plateau is mantled in white for much of the year. The area is famous for the eponymous crystals of dark smoky quartz which have been used in traditional Scottish jewellery for centuries. Local interest in ‘Cairngorm stones’ probably peaked in the nineteenth century following the purchase of the Balmoral Estate by Prince Albert and Queen Victoria. Crystal hunting remained popular for a time and there was considerable demand for cutting rough from lapidaries and jewellers. Specimens of quartz, beryl and topaz that escaped the lapidaries’ clutches gradually found their way to collectors and museums and

by the end of the nineteenth century, Matthew Forster Heddle was able to devote a significant amount of text in *The Mineralogy of Scotland* to localities in the area. The resurgence in interest in British minerals and gemstones in the second half of the twentieth century extended as far as the Cairngorms, but few finds were recorded in detail. The specimens and data that survive now lie scattered in collections, public and private, throughout Scotland and beyond.

Many society members will be familiar with Roy Starkey’s fascination with the Cairngorms. Taking inspiration from Matthew Forster Heddle, he has studied the area and its minerals for almost thirty years. *Crystal Mountains Minerals of the Cairngorms*, (abbreviated



hereafter to *Crystal Mountains*) is the culmination of this effort. The book comes in two versions, a hardback edition with a print run of 100, which will appeal to the bibliophile and dedicated collector, and a less expensive softcover edition with a longer print run aimed at the general reader.

The size and design of *Crystal Mountains* is similar to the well known volumes on the minerals of Cornwall and Devon (Embrey and Symes, 1987); the Caldbeck Fells (Cooper and Stanley, 1990) and Northern England (Symes and Young, 2008). Its cover illustration is a beautiful blue topaz found in 1975 on the slopes of Cairn Gorm by the late Ken Attwood. A thoughtful foreword by Dr Alec Livingstone, formerly the Keeper of Minerals at National Museums Scotland, sets the scene. It sits opposite a frontispiece showing Loch Avon, the Shelter Stone Crag and Fèith Buidhe, where a cairngorm crystal weighing 50 lb was discovered in 1851. The author's preface provides a personal perspective on the book; it is followed by three pages of acknowledgements which stand as testimony to the extent of the research. It is clear from the outset that few stones have been left unturned.

The introductory chapter sets the Cairngorm mountains in context, describing the area of study, its situation, topography, landscape, climate, natural history, culture and development. Two maps in the old Bartholomew style provide an impression of the mountains and surrounding settlements and will be particularly valuable to anyone getting to grips with the local topography. Long 'asides' which fall outside the thread of the main text are set in pale blue boxes. The first chapter has two such missives, one on the perennial problem of terminology (Cairngorms, Cairngorm, cairngorm and Cairn Gorm have different meanings) and the other on mountain safety.

Convention dictates that a historical account follows the introduction, and *Crystal Mountains* devotes 21 pages to this. The historical account is supported by extensive quotations from the adventurers, explorers and writers who roamed the hills in search of 'Cairngorm stones'. It covers the eighteenth and nineteenth centuries in detail and includes a significant and important account of collecting in the latter part of the twentieth century, a period which is neglected in many works of a topographic nature. The writer and naturalist Seton Gordon, who devoted a chapter of his classic work *The Cairngorm Hills of Scotland* (1925) to 'Cairngorm stones' is figured. Another photo shows a group of students on a lapidary and gem hunting course organised by Glenmore Lodge, camping out in the hills. There are descriptions of fine specimens found by the gem hunters in the 1960s, including a 9 lb cairngorm from Beinn a' Chaorainn and a beautiful citrine from Cairn Gorm, but sadly, few of these specimens can now be traced.

A geological overview is an essential part of any topographic work, and especially important if a particular rock type is used to define the area of study. Introductory paragraphs outline the big picture, showing how the landmass that would become Scotland was trapped in a complex continental collision in the mid Palaeozoic. The Cairngorm Granite was intruded into the resulting metasedimentary sequence during Caledonian mountain building, about 425 million years ago. Simplified geological maps show the extent and internal structure of the granite. The Cairngorm gem minerals that are of particular historic and collector interest occur in miarolitic cavities and the central zones of pegmatites. Modern studies suggest that these crystals form relatively rapidly in remnant fluids rich in volatile and incompatible elements. For most of its geological history the Cairngorm Granite lay buried, deep within the crust. It was gradually exposed by uplift and erosion in the Tertiary. The distinctive geomorphology of the area is the result of geologically recent processes, notably glaciation. In more recent times the landscape has been shaped by catastrophic weather events, such as the Muckle Spate of 1829.

The longest chapter in *Crystal Mountains*, occupying pages 44 to 100, provides a detailed, meticulous and copiously illustrated description of the minerals from the granite. The author briefly notes a range of species associated with deposits in the surrounding metasediments, but has chosen to exclude these from the text. In most works of a topographic nature, species are listed in alphabetical order, but in this case the 'big three', quartz, beryl and topaz, are given precedence.

The Cairngorm mountains lend their name to cairngorm, a term which is used in a general sense to describe any yellow-brown to dark brown quartz. Cairngorm quartz is common in the area. It ranges from pale transparent yellow-brown to almost black; crystals are commonly zoned and often overgrown by a late-stage milky white coating. The cause of the colouration is discussed and the use of heat treatment to improve the desirability of worked stones described. A gallery of images includes many famous specimens, which are presented in approximate order of size and weight. Many of the specimens are of historic interest. Their stories

are included in long figure captions which may occupy a paragraph or more. The Invercauld cairngorm, for example, which was formerly displayed at Braemar Castle, weighs in at almost 50 lbs and is 46 cm in height. It was found in the late eighteenth century and is the largest fine specimen to survive intact. The largest crystal in the Royal Collection at Balmoral is only marginally smaller; it was found by James Grant of Ryvoan in 1851 in a 'pot' on the Fèith Buidhe and purchased by Queen Victoria. Large and fine specimens, now at the Natural History Museum (NHM), London, were once the property of the Countess of Seafield. Two of the finest collector specimens, in the National Museums Scotland, Edinburgh and the NHM, are illustrated side by side on pages 62 and 63. The NHM specimen is superb, and has a marvellous pedigree; it was in the collection of the collector-dealer John Henry Heuland (1778–1850) and sold at the Heuland sale in 1832 to Isaac Walker (1793–1853). Walker's collection was subsequently acquired by the dealer Samuel Henson, and the specimen purchased by the British Museum (Natural History) in 1912. The specimen is almost completely undamaged and roughly the size of a bottle of fine wine! In modern times, quartz crystals up to about 8 kg in weight have been collected; a pale translucent crystal 25 cm long found in 1947 on Ben Macdui is particularly notable. The 25 pages devoted to quartz are rounded off by two photos showing unusual amethystine banding in prismatic and sceptre crystals.

The Cairngorms are one of the few places in the British Isles where gem quality beryl can be found. The crystals are usually 'etched' and, as noted as early as the eighteenth century, commonly "foul and cracked". Nonetheless, gem quality crystals up to about 10 cm in length, typically of a pale green to yellow colour, and occasionally grading towards aquamarine blue, have been found. Remarkable historic specimens from the collections of the NHM and the Royal Collection at Balmoral are figured together with fine contemporary specimens from the author's personal collection.

Topaz is the most elusive of the 'big three' gem species in the Cairngorms. Contemporary specimens are few, a notable exception being the lovely pale blue crystal found in 1975 by Ken Attwood at an old digging on Cairn Gorm (Figure 195 and Cover). Most nineteenth century specimens are water worn 'pebbles', though many give a good indication of their original crystal shape. The largest surviving crystal, now in the collection of the NHM weighs 712 g and measures 90 × 65 × 80 mm. Topaz from the Cairngorms commonly contains multiphase fluid inclusions; these were the subject of an early paper by the renowned nineteenth century physicist David Brewster. The story of a remarkable 8 oz topaz crystal (Figure 117), now in the collection of Aberdeen University, illustrates how a careful analysis of data can piece together the history of an important specimen. This specimen appears to have been found at the foot of Ben Avon in 1808 or 1809, and was described several times in the nineteenth century as it passed between different collectors and dealers.

The mineral chapter of *Crystal Mountains* rounds off with an alphabetical listing of less significant species. One

is of particular interest. Many areas have their mysteries; metaphorical Lasseter's reefs or Lost Dutchman mines. In the Cairngorms this function is appropriated by the rare mineral genthelvite which was found somewhere in Coire an Lochain in the 1960s. Figure 151 shows crude but attractive tetrahedral crystals, which were presented to the NMH by W.C. Morgan in 1966. The discovery was of sufficient note to merit an article in *Mineralogical Magazine*, but subsequent fieldtrips by Morgan himself (who did not realise the significance of what he had found at the time) and later collectors have failed to locate a single further specimen.

The final 60 pages of *Crystal Mountains* are largely people-centred. They describe the diggers who searched the hills for gems in the eighteenth and nineteenth centuries; royal interest, particularly in the Victorian period; collectors and collections; mineral dealers; lapidaries, jewellers and their creations; and end with the curious tale of the contribution Cairngorm quartz almost made to the British need for electronic components in the Second World War.

The specimens that grace the cabinets of country houses, museums and wealthy collectors and the rough stones cut by lapidaries and jewellers in the nineteenth century were supplied, for the most part, by itinerant diggers seeking their fortune in the hills. The sites of some of the old diggings can be seen to this day; Figure 159 shows an old working driven through a buttress on Beinn a' Bhuid (which, by a strange morphic coincidence, is shaped like a huge cairngorm). Nineteenth century accounts describe dozens of men scraping a living from the high plateau; large areas were certainly trenched to a considerable depth. By the beginning of the twentieth century crystal hunting had all but ceased, but a nostalgic interest in the activity remained and articles appeared periodically in newspapers and books.

Royal interest in 'Cairngorm stones' began a little before the purchase of the Balmoral Estate by Prince Albert and Queen Victoria. The young queen made an ascent of Ben a' Bhuid in 1850, and collected some very pretty cairngorms. A stone found by Prince Albert on an excursion two years earlier had been cut to produce a brooch. A significant number of specimens from the Cairngorms are preserved in the Royal Collections at Balmoral and Osborne House. They include some of the finest quartz and beryl from the area. Although precise location data is generally lacking, the Royal Collections contain many important specimens. They are not on public display and the large number of specimens figured in *Crystal Mountains* is, therefore, particularly welcome.

Historic collectors who had (or have) significant specimens from the Cairngorms include Thomas Allan (1777–1833), Robert Ferguson (1767–1840), Matthew Forster Heddle (1828–1897), Caroline Stuart, Countess of Seafield (1830–1911) and the Farquharson family of Invercauld (this last collection, which is now housed at Braemar Castle, was recently organised and curated by the author). Three modern collectors, Ken Attwood (1923–2010), Gordon Sutherland (1918–2005) and Basil Dunlop (1936–) are also selected for special mention as

each amassed specimens comparable to the nineteenth century classics. The collectors and their collections are described and many important specimens figured. There is a sense of frustration that the Gordon Sutherland Collection is poorly documented and relatively inaccessible. It is hoped it will find a safe home, perhaps at a publically accessible site. Good specimens from private collections commonly find their way into public, university or society collections and the author provides a particularly complete survey of these.

Two chapters on lapidaries, jewellers and their creations are copiously illustrated with wonderful and occasionally bizarre items which include 'Cairngorm stones' in their make up. They range from attractive silver brooches set with large faceted cairngorms to ceremonial daggers with cut cairngorm pommels and include two grotesque ram's head snuff mulls which wouldn't be out of place on the set of a gothic horror movie. Scottish jewellery is popular and widely collected and the chapters illustrate the remarkable variety of objects made using 'Cairngorm stones'. The authenticity of some objects is difficult to verify as many Scottish makers used smoky quartz from foreign localities in the creations. The lapidary tradition continues to this day. Stones cut by the late Ken Attwood and Doug Morgan are figured in *Crystal Mountains*. Figure 227 shows a 75 ct cairngorm found by the late Gordon Sutherland, cut by Ian Combe, set in a silver and gilt casket and presented to Mikhail Gorbachev on a visit to Aberdeen in 1993.

A final chapter relates the story of two Cambridge academics, Peter and Nora Wooster, and their attempts to source suitable quartz crystals for use in the electronics industry during the Second World War. Natural crystals were in short supply and the Woosters made excursions to several areas of the British Isles in search of specimens. They visited the Cairngorms in 1942 and drew up plans to dig in the hills (a lack of manpower meant their scheme came to naught). Back in Cambridge, the Woosters made significant contributions to the development of a process for making synthetic quartz crystals, mostly in a laboratory set up in the family home!

An epilogue, glossary, reference list and index round off *Crystal Mountains*. The book ends with an uncaptioned photo of snow-covered mountains in which a single adventurer is walking into the middle distance.

And so to the recommendation. Should this be on your bookshelf? And is it good value for money? Don't panic! If you read this far, there's not much further to go... It will be obvious to the knowledgeable reader that no other book which is comparable in scope or content to *Crystal Mountains* exists. It is thoroughly researched, clearly written, and draws

a vast amount of previously unpublished data together in a well illustrated, well designed format. The cover price (£25 for the softback edition) represents excellent value for a specialist book with a small print run. *Minerals of Cornwall and Devon*, the first comparable 'modern' work on the mineralogy of the British Isles was heavily subsidised and retailed for £9.95 when it was published in 1987. In today's money that equates to almost exactly £25! More recent topographic works, such as *Minerals of Scotland Past and Present* (2002: £35) and *Minerals of Northern England* (2008: £30) cost more. Similar comparisons can be used to demonstrate that *Crystal Mountains* is well illustrated, indexed and referenced. The design is clean and uncluttered, with clear differentiation of the quotations and footnotes and good use of white space around figures. Reproduction, particularly of difficult subjects such as dark smoky quartz, is excellent.

A question that must have occurred to anyone with a deep and abiding passion for a particular subject is what to do with the years of accumulated knowledge? In a sense *Crystal Mountains* provides an answer. Roy is to be congratulated for a remarkable achievement. I can wholeheartedly recommend the book to anyone with an interest in the minerals of the British Isles (the likely readers of this review); it will sit comfortably on the bookshelf beside *Cornwall and Devon*, the *Caldbeck Fells* and *Northern England*. It will also have an appeal to those with an interest in the natural and social history of the Cairngorms and surrounding area, collectors of Scottish jewellery and *objets d'art*, walkers and climbers, and those with an interest in the Royal family.

Copies of *Crystal Mountains* can be obtained from the publisher at the address above or online at www.britishmineralogy.com. The website provides full details of the cost (including postage and packing) and purchases can be made online *via* PayPal. The book will be shipped protected in plastic and enclosed in a thick cardboard book-pack.

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David Green

NOTES FOR CONTRIBUTORS

TYPESCRIPTS

Authors are encouraged to prepare papers in electronic format using Microsoft Word and to send the file(s) as e-mail attachment(s) to the Editor. Templates for the format of articles and notes are available from the Editor and the Journal Manager. Do not embed figures and tables within the text, but indicate where they should be inserted. At the end of the manuscript provide figure captions and any tables with their captions. All pages should be numbered in the footer. Each paper will normally be reviewed by two referees. Submission of a paper to the Journal is taken to imply that it has not been considered for publication elsewhere and that all necessary permissions have been obtained and, where appropriate, acknowledged by the authors. Material accepted for publication can not be published elsewhere in the same form without the consent of the Editor. The submitted material should normally contain original observations or experimental results relating to mineral occurrences in the British Isles, although other suitable topics may be considered. Full articles should include an abstract of up to 250 words summarising the significant points of the paper; notes (up to 1500 words) do not require an abstract. Review articles are welcomed.

FORMAT AND PRESENTATION

Papers should be submitted in the style and format of the Journal, and divided into appropriate sections and subsections. A recent issue of the Journal should be consulted for examples. Titles of papers should be adequately informative. Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. 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]). Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, microchemical analyses, etc.). It may not be necessary to reproduce such data in full in the text, but they should be supplied to the Editor if required by the referees in the course of their assessment. For mineral occurrences of particular note (e.g. new occurrences in the British Isles or at a particular locality) authors are strongly encouraged to record the specimen number and the institution or collection where the specimen is lodged.

FIGURES

All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Figure 1, etc., or (Fig. 1), etc. Figures must have descriptive captions, and the scale must be indicated either on the photograph or by specifying, e.g., width of view or crystal size in the caption.

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

TABLES

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

TERMINOLOGY

Authors should adhere to the nomenclature and terminology of the International Mineralogical Association. The most recent *Fleischer's Glossary of Mineral Species* (at present the 11th edition, by Back, 2014) can be used as a guide to mineral nomenclature, but where this conflicts with *Hey's Mineral Index* (1993) or *Mineralogical Magazine* and *Mineralogical Abstracts* usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (*Acta Crystallographica*, (1967), **22**, 45).

ABBREVIATIONS

Except for common non-scientific abbreviations and those for standard units of measurement, abbreviations should be spelt out in full at their first mention in the article, e.g. platinum group mineral (PGM). If used, 'n.d.' in tables must be defined (as 'not determined' or 'not detected'). The following abbreviations may be used without explanation: XRD = X-ray diffraction analysis; XRF = X-ray fluorescence analysis; EPMA = electron probe microanalysis (electron microscopy analysis); EDX = energy dispersive analysis (same as EDA, EDAX, EDS); SEM = scanning electron microscope or microscopy; TEM = transmission electron microscope or microscopy; IR = infrared; UV = ultraviolet.

REFERENCES

References should be indicated in the text thus: (Brown, 1967) or 'as stated by Brown (1967)'; (Green and Brown, 1985) for two authors; (Green *et al.*, 1986) for three or more authors. If two or more references would give rise to identical citations in the text, they may be distinguished by appending 'a', 'b', etc. to the publication year.

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

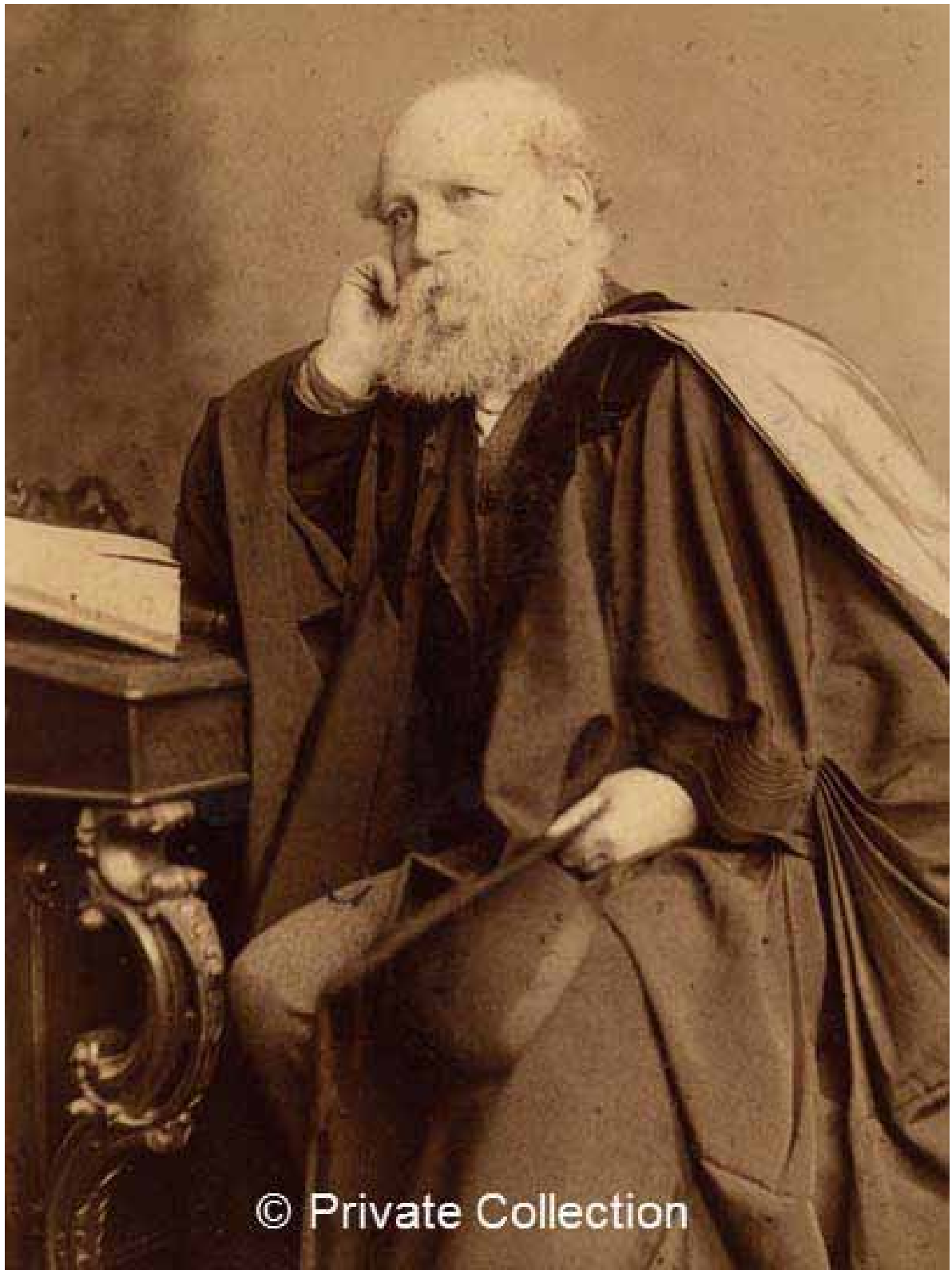
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