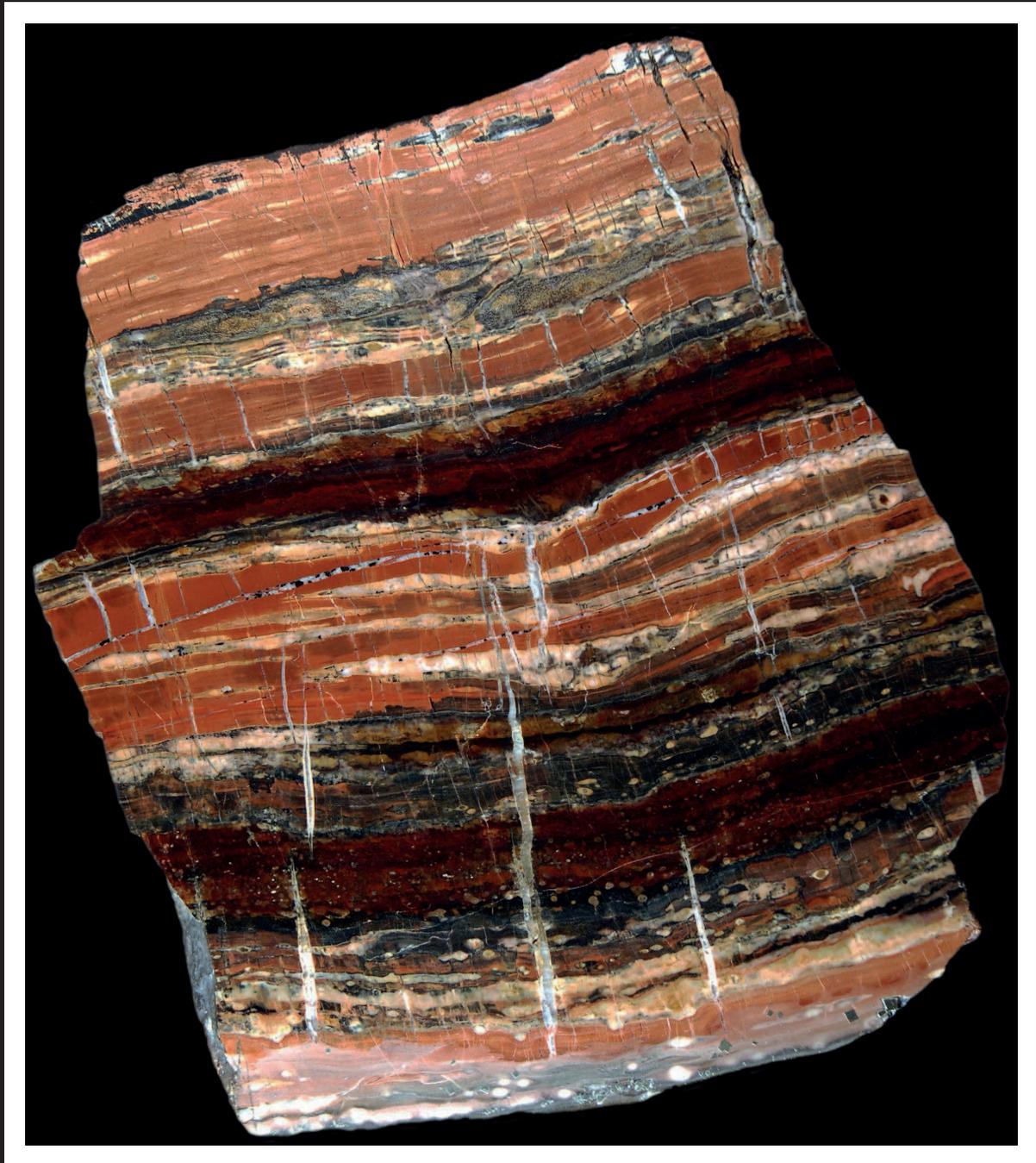


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Volume 16, 2013



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The journal of British Isles topographical mineralogy

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FRONT COVER:

Cut and polished section through the lowermost 16 cm of the manganese ore bed obtained from Llyn Du Bach Mine, Harlech, Merionethshire, Wales. National Museum of Wales Specimen No. NMW 2013.18G.M.1.

BACK COVER:

Bob King admiring a fine North Pennine fluorite at the British Mineral and Gem Show in Leicester (March 1981). Reprinted with the kind permission of the Leicester Mercury.

Journal of the Russell Society

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Editorial

Sadly we start this volume with an obituary to the founding father of the Russell Society, Dr Robert (Bob) King, who died on 25 September 2013. Bob was pivotal in establishing the Journal of the Russell Society as a vehicle to achieve the Society's aims of researching, conserving and recording British topographical mineralogy. Roy Starkey's obituary outlines Bob's career and achievements and is followed by a selected bibliography of Bob's extensive publications. Bob influenced the lives of many aspiring geologists and mineralogists, professional and amateur alike, especially in the areas around Leicester and Cardiff where he spent much of his working life.

It is therefore particularly appropriate that this volume includes a paper on Leicestershire mineralogy: in this case, occurrences of hydrocarbon-containing materials. Frank Ince's review makes extensive reference to Bob King's mineralogical research, much of which has remained somewhat hidden from view in Bob's unpublished PhD thesis.

Other papers in this volume also have long histories - in various ways. Trevor Bridges provides Part 2 of an article on phosgenite and matlockite in Derbyshire, Part 1 of which was published in Volume 1 in 1983. He explains in his introduction why Part 2 took a little longer than he anticipated. This is followed by several short contributions on aspects of the mineralogy of the North Pennine Orefield. Then, following Frank's review of 'black blobs' in Leicestershire, the focus shifts to North Wales with articles on the complex and intriguing mineralogy of the manganese ore bed, and the first report of the rare earth element bearing mineral chernovite-(Y) in Wales.

Volume 16 concludes with an excursion to the Lewisian gneiss terrain of the northwest Highlands of Scotland and a remarkable occurrence of coarsely crystalline zircon. Andy Moffat and Roy Starkey's paper has a painful 'sting in the tail': their locality has been stripped and destroyed by unscrupulous mineral collectors. Indeed for this reason the authors felt that publication of the occurrence would be unhindered by fears of exploitation, which is often the reason for keeping secret the exact locations of mineral occurrences. This setback is frustrating but we should turn our anger to positive use by pursuing with increased vigour the goals of the Russell Society to research, conserve and record the mineralogical treasure-house of the British Isles.

Following publication of this volume, I am passing the editorial baton to Malcolm Southwood who has agreed to take on the role, despite being domiciled in the antipodes! My thanks to all Council members, authors of Journal contributions and the team of reviewers for their support over the 10 year period during which I have been Editor. I am immensely grateful to Frank whose role as Journal Manager has broadened to one of Co-Editor, and similarly this year to Malcolm who has in effect been 'Deputy Editor'. I am delighted that editorship of the Journal is passing into such capable hands.

Norman Moles
Honorary Journal Editor

Malcolm will be pleased to receive any contributions to the Journal of the Russell Society Volume 17 (2014). Please send a copy of your manuscript, figures, etc. *via* e-mail to: mal.southwood@bigpond.com; or by post to: Dr Malcolm Southwood, 7 Campbell Court, Warrandyte, Victoria 3113, Australia.

Robert (Bob) Joseph King (1923-2013)

Roy E. Starkey

Bob King will be known to almost all current and past members of the Society, as its founder, and greatest advocate. He was a major figure in the fields of British mineralogy and mineral collecting, with a network of friends and colleagues that spanned the globe.

Robert Joseph King was born on the 18th March 1923 in Leicester, England. He attended the City Boys School, Leicester, and obtained a post as a student at Leicester (New Walk) Museum, until interrupted by World War II. Bob served in North Africa and Italy, returning with a large suite of minerals from Monte Somma (Mt. Vesuvius). After being demobbed from the armed forces in 1946, he worked for eight years on a farm in Newton Harcourt, Leicestershire. He became friends with the late John Harry McDonald (Mac) Whitaker who would send people bringing mineral specimens into the Leicester New Walk Museum to “go and speak with Mr. King at Newton Harcourt”.

Mac regularly visited Bob to discuss identifications and localities in Leicestershire, forming a friendship which later led to him recruiting Bob to a post as technician in the Geography Department of the University of Leicester in 1954, (together with Trevor Ford and Tony Evans). Mac formed the Geology with Geography Department in 1952 and by 1954 Geology had become an independent department that flourished under Mac’s team (and later with Peter Sylvester-Bradley). It became one of the UK’s leading teaching and research departments, of which Mac was a key member until his retirement in 1985.

Bob progressed to become Chief Technician and Curator, a role which suited his interests and skill set admirably. He studied for an external degree from Imperial College, London, gaining an MSc in geology in 1972, and went on to read for a PhD on “The Mineralogy of Leicestershire” (1973), in the Geology Department at Leicester, a subject which remained an abiding passion for much of his life.

Bob’s interest in minerals started when he was about 8 years old, encouraged by his father (Robert William King) who was a strong believer in getting out to look at the natural world, and also bought Bob his first mineral book. Being based in Leicester, he focused initially on collecting in the East Midlands, but from the late 1930s he diversified, going further afield (using public transport and a bicycle) in search of fine mineral specimens. The Cumbrian iron mines, the North Pennines, and the Caldbeck Fells in the northern Lake District were some of his most popular collecting areas.

Bob was a protégé of the late Sir Arthur Edward Ian Montagu Russell, 6th Baronet, MBE, FRS (1878-1964) perhaps the most famous British mineralogist of the 20th century. He corresponded and exchanged specimens with Sir Arthur, visiting him at his home in Swallowfield Park, near Reading.

Bob was married to his first wife, Iris in 1949, who sadly died, and with whom he had two children, Barry and Josephine. Later, in 1977, he married his present wife Sally, with whom he also had two children, Amy and Daniel, and enjoyed many happy years.

In his professional life Bob was a member of numerous organisations including the Mineralogical Society of Great Britain (since 1948; Elected Fellow in January 1998); Fellow of the Institute of Quarrying (since December 1981); Fellow of the Institute of Science and Technology (since March 1996); and Founder Member of Geological Curators Group in 1974 (and winner of its A.G. Brighton Medal in 1995).

Bob’s local geological and mining interests lead to him participating in the activities of the Peak District Mines Historical Society (with his great friend and colleague Trevor Ford); the Leicester Literary and Philosophical Society, where he became Life President of the Geology Section (C); and in his later years, following a move to rural Gloucestershire he became keenly involved with the Cotteswold Naturalists Field Club.

The Russell Society was born, out of an evening class, on the 27th October 1972 when approximately thirty people, all from the area in and around Leicester, met to inaugurate a mineralogical society. Bob sought the blessing of Lady Russell to adopt her late husband’s name, and the rest, as they say, is history. Bob provided early leadership and direction, and served as President from 1973-1975.

The early days of the Society saw many exciting initiatives, including the sinking of a shaft to gain access to a small lead deposit (Tickow Lane Mine), and extensive investigations and a feasibility study on reopening the famous Earl Ferrers’ Lead Mine at Staunton Harold.

Ten years after the founding of the Society, Bob proposed that a new publication be launched, The Journal of the Russell Society, the aim being to provide a vehicle for the publication and recording of papers relating to British Topographical Mineralogy. The Journal continues today as a respected peer-reviewed publication, regularly reporting significant new finds and research projects, both by members and third party researchers and mineralogists.

Bob’s very fine personal mineral collection was purchased in 1983 by The National Museum of Wales, Cardiff, where it now forms an important part of the collections. As part of this arrangement Bob took up an honorary post at the Museum, where he planned to conduct research on his collection and the many associated field notes and documents. He and Sally moved from Leicester to St. Athan, near Cardiff, and enjoyed five years living in South Wales, seeing through the establishment of the Russell Society’s Wales and West Branch, in which they both played an active role.

Things did not work out quite as Bob had hoped on the mineralogical front, and he and Sally decided to move to Tewkesbury in 1988 where Bob took up the post of Curator at the John Moore Countryside Museum, providing an opportunity for him to rekindle his fondness for the countryside, agriculture and the broader field of natural history. They later moved out of town to a plot near Longdon, where they built a house with a large garden and beautiful rural views.

In 1980 Bob had suffered a stroke whilst working at Leicester University, but from which he made an excellent recovery. Sadly, he suffered another stroke in 2008, from which he never fully recovered, and his health deteriorated steadily over a number of years. He was however invariably pleased to see me when I called-in every couple of months or so on my way home from work, eager to hear the latest mineralogical news and gossip, and wanting to know what everyone was up to in the mineral world.

With Bob's declining health he and Sally decided to move to Bishops Cleeve, just outside Cheltenham, to be nearer to their daughter Amy and also to shops and services. During this period Bob undertook extensive research on the minerals of Gloucestershire, a programme of work which led to a series of papers in the Proceedings of the Cotteswold Naturalists' Field Club from 2007-2012.

Bob's published works are predominantly in the fields of specimen and topographic mineralogy, but he also compiled a comprehensive series of articles under the title "The Care of Minerals" intended to be of use to both collectors and mineralogical curators. His article on "The Boltsburn mine, Weardale, County Durham, England" won the award for "best article of the year" in the Mineralogical Record for 1982. Even in retirement, Bob's written output was impressive, and he was engaged to write a regular column for the journal *Geology Today*, taking a different mineral or mineral group in each issue, and providing an introductory review aimed at the non-specialist reader. The series began in 1985 with "Minerals Explained 1: Fluorite" and concluded with "Minerals Explained 50: "Olivine Group" in 2009, comprising a total of fifty articles and a true *tour de force* of educational specimen mineralogy writing. Being a strong believer in the value of handling and studying specimens, Bob sought to acquire representative examples of the minerals he was to describe in each issue, and this gradually built up to become what was known as the "New King Collection", and which was eventually sold by auction to Society members and friends on 26th June 2011.

The Russell Society celebrated its 20th Anniversary in 1992 by establishing a new international award, the Russell Medal, to recognise "...outstanding contributions which lead to the education and promotion of topographical and specimen mineralogical studies, specimen and site documentation, preservation and conservation." There was unanimous agreement amongst the Society Council that the first recipient should be Dr R.J. King, and Bob was duly presented with the medal at the Society's Annual General Meeting in Leicester in May 1992.

Bob's contributions to earth science have been formally recognised, firstly in 2000 by the naming of *Offacolus kingi*, a chelicerate arthropod which he discovered in the concretions of the Silurian-aged Wenlock Formation in Herefordshire (Orr *et al.*, 2000); and in 2002 the new mineral bobkingite, $\text{Cu}^{2+}_5\text{Cl}_2(\text{OH})_8(\text{H}_2\text{O})_2$, was named for him. The mineral is a hydrous cupric chlorohydroxide that occurs as a secondary mineral with malachite and azurite on massive cuprite at the type locality, New Cliffe Hill Quarry, Stanton-under-Bardon, Leicestershire, first described from a specimen collected by Society member Neil Hubbard (Hawthorne *et al.*, 2002).

A man of many interests, Bob greatly enjoyed gardening and had a formidable knowledge of natural history. He was also an accomplished chorister, singing firstly at Leicester Cathedral and, following their move to Longdon, in the choir at Tewkesbury Abbey.

Bob passed away peacefully in his sleep on 25th September 2013. He is survived by his wife Sally, daughter Amy and son Daniel; son Barry and daughter Josephine from his earlier marriage, and grandchildren Michael, Lily and Emily, of whom he was extremely proud. Always interested and enthusiastic about anything to do with geology and mineralogy, he was keen to encourage newcomers and youngsters, and always took time to explain things to those less knowledgeable about the subject. Bob will be greatly missed, but also remembered for the many contributions which he made and for the lives he touched.

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Sally King, Bob King and Bob Symes at the presentation of the first Russell Medal at the Russell Society AGM on 17th May 1992. Photograph: Nigel Moreton.

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PHOSGENITE AND MATLOCKITE IN DERBYSHIRE (PART 2)

Trevor F. BRIDGES

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A computer-based stability field model has been used to investigate the conditions required for the formation of the matlockite, phosgenite and anglesite mineral assemblage that occurred in Bage Mine, Cromford, Matlock, Derbyshire. The deposit is limestone hosted but the orebody is dominated by baryte and the inert nature of this mineral has allowed the acidity resulting from the oxidation of pyrite to stabilise the deposit. It is shown that the solubility of fluorite should be sufficient to provide the concentration of fluoride ion, expressed as its activity (aF^-), required to allow matlockite to form. The main problems arise from the fact that oxidising conditions would have been needed over a long period of time, but since the Triassic the deposit has almost certainly been below the level of the water table, where conditions would usually be reducing. Depending on the activities of sulphate ion (aSO_4^{2-}) and, to a lesser extent, calcium ion (aCa^{2+}) in solution, a wide range of chloride ion activities (aCl^-), would be satisfactory for the formation of both phosgenite and matlockite. Possible sources of chloride ion are sea water from the Permo-Triassic Period, when the water table could have been much lower than at present, or a late stage hydrothermal spring. The latter appears to be the better option since it provides a wider range of suitable chloride and fluoride ion concentrations for the formation of the mineral assemblage, but leaves the problem with the water table unless the deposit formed from such a spring during the Permo-Triassic Period.

INTRODUCTION

Part 1 of this paper (Bridges and Smith, 1983) was mainly concerned with the history of the occurrence of phosgenite and matlockite at Bage Mine, Cromford, Derbyshire. At that time, work was in progress on a geochemical study of the occurrence, which it was anticipated would be published in 1984. However, it became apparent that the complexity of the system prevented the current author doing a proper study at that time and 'Part 2' was not produced (See Author's Note at the end of the paper). Having recently prepared a computer-based stability field model to carry out a geochemical study on the lead oxychloride mineral assemblage in the Mendip Hills (Bridges *et al.*, 2012), it was decided to see if the model could be extended to include fluoride ion as an additional variable, thus allowing investigation of the conditions required for the formation of matlockite. This proved to be possible and the result is that Part 2 of the original paper is finally presented.

Since publishing the original largely historical paper, major historical works on the mineralisation at Bage Mine have been published by Burr (1992 and 1994). The first of these includes a number of excellent photographs of specimens. In brief, the deposit was discovered in about 1785, specimens being acquired by Charles Greville. In 1851, further specimens came to light and William Lettsom despatched Bryce McMurdo Wright Snr. to obtain some. Wright followed up these specimens and their source and obtained over 100 specimens, which are now sought by collectors around the world.

The suite of minerals from Bage Mine under study are phosgenite, $Pb_2(CO_3)Cl_2$, matlockite, $PbFCl$, anglesite, $PbSO_4$ and cerussite, $PbCO_3$. They occur in excellent crystals associated with corroded galena, PbS , baryte, $BaSO_4$, and minor amounts of other minerals such as fluorite, CaF_2 . Both the chemistry of the minerals and the appearance of the specimens demonstrates that the deposit is supergene in origin and not primary.

In limestone hosted orebodies the stable supergene lead mineral is usually cerussite. Minerals requiring a relatively low pH, such as anglesite, normally only occur in limestone hosted orebodies if the main gangue minerals are carbonate free, e.g. baryte and fluorite, or in cavities completely enclosed by galena. The Bage Mine deposit meets these requirements and this is almost certainly why the rare assemblage in the mine has been able to form and remain preserved. However, while small amounts of anglesite are of fairly common occurrence in suitable Pennine orebodies, phosgenite and matlockite are not and clearly require special formational conditions. That is the subject of this study.

THE GEOCHEMISTRY

Five variables need to be considered in the formation of this assemblage of minerals, namely pH, concentrations of sulphate, chloride and fluoride ions expressed as activities (aSO_4^{2-} , aCl^- and aF^- , respectively) and the partial pressure of carbon dioxide (pCO_2) in equilibrium with the system, this in effect being a concentration. In addition, it is necessary to consider concentrations of calcium ion (aCa^{2+}) since high levels of this ion could reduce aF^- due to the fairly low solubility of fluorite. To investigate such a complex system properly requires a computer based model and, as stated above, this was adapted from the model used to investigate the Mendip Hills lead oxychloride assemblage (Bridges *et al.*, 2012). Preparing useful stability field diagrams for the system requires selecting two variables for the axes and then assigning realistic values to the remaining three variables. This in turn requires knowledge of the likely sources of the ions in the system and this is discussed in the section that follows.

Sources of the components of the system

The first essential requirement is that for these minerals to form the local environment must have remained oxidising over a long period of time. The second is that from the work on the lead oxychlorides (Bridges *et al.*, 2012), the absence

of leadhillite, $Pb_4(SO_4)(CO_3)(OH)_2$ and paralaurionite, $PbCl(OH)$ at Bage Mine means that pCO_2 must have been raised above atmospheric, since these two minerals are still stable at slightly more than atmospheric levels of CO_2 . Also, the presence of anglesite requires a relatively low pH. The most likely explanation for these geochemical conditions is that there was some pyrite (or marcasite), FeS_2 , present in the vein material or wall rock and that the sulphuric acid released by the oxidation of this lowered the pH while releasing CO_2 by reaction with carbonates. This is still happening at Bage Mine where thick gypsum crusts have formed on walls and clearly indicate the presence of pyrite, (John Jones, *personal communication*). The lead ions, Pb^{2+} , required for the formation of the supergene lead minerals, must have come from the oxidation of galena.

The most difficult ion to assign to a source is the chloride, there being two possible, but very different sources. One is a late stage hydrothermal brine, possibly similar to that intercepted deep in Cambokeels Mine, Weardale and reported by Manning and Strutt (1990). The second is seawater or partly evaporated seawater from the Permo-Triassic Period. There are problems with both of these sources, but they do provide two reasonable extremes for the purpose of the geochemical study. The problems are then discussed later.

Finally, the source of the fluoride ion needed for the formation of matlockite is most likely to have been the presence of fluorite in the orebody. Although fluorite is usually considered to be a very inert mineral, this study shows it is sufficiently soluble to give adequate concentrations of fluoride ion in solution, provided aCa^{2+} is not excessively high, which could be possible with a hydrothermal brine.

Values for the activities of the ions

Assigning activity values requires knowledge of thermochemical data for all the relevant ions and minerals in the system expressed as the Gibbs free energy of formation (ΔG_f°). Values have been obtained from standard compilations such as Robie *et al.* (1978) and Smith and Martell (1976), with the data of Näsänen *et al.* (1962)

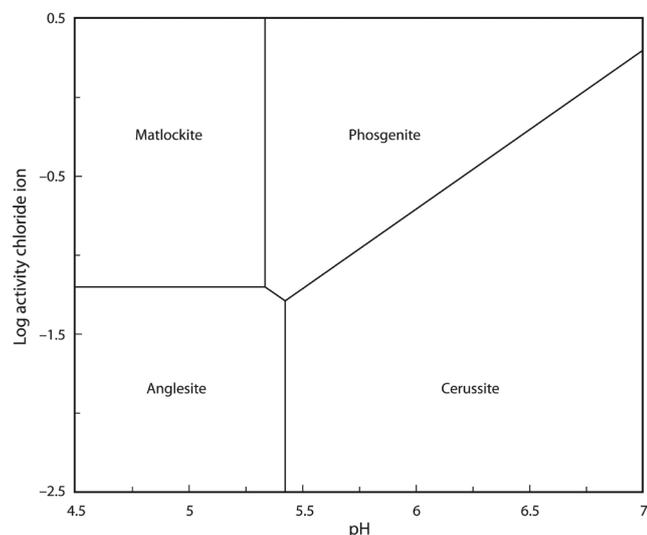


Figure 1. Stability field diagram at pCO_2 of 0.02, aSO_4^{2-} of $10^{-3.6}$ and aF^- of $10^{-4.4}$.

for phosgenite. The data for matlockite were provided by Peter Williams (*personal communication*).

Anglesite, formed by the oxidation of galena, needs a minimum aSO_4^{2-} of a little over $10^{-3.9}$, before it can crystallise out. If matlockite and phosgenite form instead of anglesite, this activity will be raised by the release of sulphate ions into solution from the oxidising galena. If sea-water or partly evaporated seawater was the main source of the sulphate, this value could rise to $10^{-2.7}$, (Garrels and Thompson, 1962). The system was, therefore, investigated at values between these two limits, the difference being approximately a factor of ten in concentration.

There is disagreement in the above standard compilations about the ΔG_f° of fluorite. However, if fluorite is dissolved in water then using an average of the data yields an aF^- of $10^{-3.4}$. For reasons that will be outlined later, it is most unlikely that the solutions would be as concentrated as this, so values less than this were investigated using the model.

Because of the difficulty in deciding the source of the chloride, this is used as the y-axis and covers a wide range of values. The x-axis is pH and brackets the boundary between anglesite and cerussite.

As stated above, the requirements of pH reduction and oxidising conditions will have raised pCO_2 . However, once the value is high enough to exclude the formation of leadhillite ($pCO_2 > 0.011$, 1.1% v/v) the actual value used is of little importance, since this parameter then only serves to move the stability fields to higher or lower pH without altering the geochemical relations of the minerals to each other. Since leadhillite does not occur at Bage Mine, a pCO_2 of 0.02 (2% v/v) was used for the diagrams. It could easily have been much higher than this, in which case the stability fields would move en bloc to lower pH.

The model and diagrams

As with the lead oxychlorides study (Bridges *et al.*, 2012), the model makes no assumptions about the source of the minerals and elements in the deposit and since all the thermochemical data are held in a common database, they

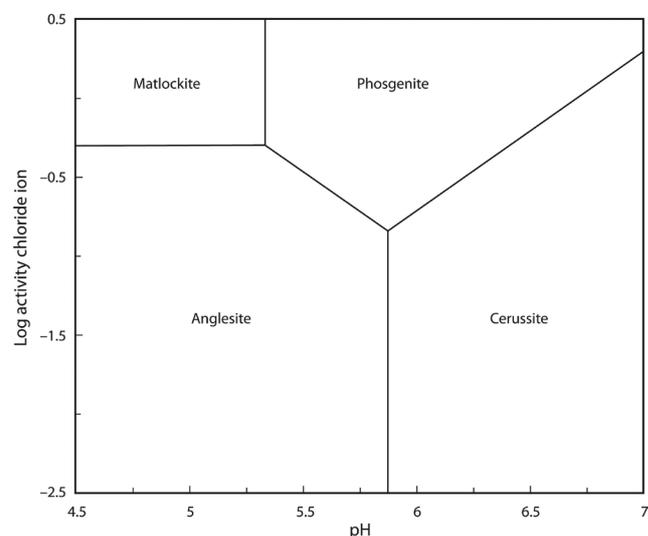


Figure 2. Stability field diagram at pCO_2 of 0.02, aSO_4^{2-} of $10^{-2.7}$ and aF^- of $10^{-4.4}$.

can be updated immediately if better data become available. The model includes ion balances to ensure impractical assumptions are not being made inadvertently. (The above paper gives more information on the construction of the model than is provided here).

Having constructed the model, it was used to investigate changes in the various parameters to see how the conditions of formation for the various minerals developed. The $a\text{SO}_4^{2-}$ values used are $10^{-3.6}$ for Figure 1 (see p. 7) and $10^{-2.7}$ for Figure 2 (see p. 7). The former is double the absolute minimum required for anglesite to be able to form and represents low concentrations of sulphate. The latter represents the saturation value for calcium sulphate in seawater (Garrell and Thomson, 1962). This value will not change significantly if the seawater is partially evaporated. It must be pointed out again that these two diagrams just represent likely extremes and that any value in between is possible. Some hydrothermal brines do contain sulphate (Edmunds, 1975) and seawater can always be diluted with rainwater or low sulphate groundwaters. The diagrams then just merge towards each other.

There is no means of knowing how concentrated the original solutions were with respect to fluoride ion, but an assumption had to be made in order to present the data. The high concentration of calcium sulphate in seawater generates a relatively high calcium ion activity which will reduce $a\text{F}^-$. Also, hydrothermal brines often have high concentrations of calcium chloride which would have the same effect. It was decided to use a value one tenth of the saturation level in pure water for both diagrams, which corresponds to an $a\text{F}^-$ of $10^{-4.4}$. This is quite low enough to take into consideration the calcium present in seawater, but might not be so for hydrothermal brines. This possibility is discussed later.

MINERAL ASSOCIATIONS

The two stability diagrams permit mineral associations to be predicted, which can be compared with specimen material to see if either of the diagrams provides a better fit with reality. To follow this up, a visit was made to the Natural History Museum (NHM) to carefully inspect the Bage Mine specimens in their collections. Some of the specimens of the key minerals were free of matrix and Figure 3 shows a typical example; a magnificent matlockite specimen in the Ludlam collection, which the author felt was worthy of a wider audience. When on matrix, the NHM specimens tended to be a large crystal of one of the key minerals, with mainly minor crystals of other minerals. Based on specimens from other collections, this probably just reflects collector/curator choice, rather than being a characteristic of the deposit. The matrix is usually galena, corroded to a variable extent and sometimes showing relict crystal faces. Baryte is commonly associated with the galena, both as fairly massive pieces in the galena, but also as tiny coxcomb crystals in some cavities. Small fluorite crystals are also common and interestingly are not obviously corroded, perhaps indicating the fluoride ion originated from outside the cavities in which the crystals grew or that the solutions were already saturated with respect to fluoride.

Small crystals of sphalerite are evident on some specimens and are not highly corroded. Since sphalerite is more easily oxidised than galena, this would also seem to suggest some of the cavities were mainly a repository for crystal growth rather than being the main centre of the oxidation reactions.

Moving on to the geochemical interpretation, the $a\text{Cl}^-$ of seawater is approximately $10^{-0.5}$ (-0.5 on the y-axis of the diagrams). The saline spring intercepted in Cambokeels Mine, Weardale at a depth of 100 m OD, had an $a\text{Cl}^-$ a little higher than this when first measured in 1988, but somewhat lower in 1989, probably due to dilution by meteoric water (Manning and Strutt, 1990). While considerable variation around $10^{-0.5}$ is obviously possible, this figure at least makes a plausible starting point for discussion.

Anglesite was a common feature of the deposit and Figure 4 shows an excellent specimen in the Russell Collection. Under all conditions, the stability diagrams show that anglesite formation is favoured by low $a\text{Cl}^-$ and high $a\text{SO}_4^{2-}$ values, but it has a substantial field on both diagrams. At slightly higher pH, cerussite could form with anglesite and Figure 5 shows a group of large anglesite crystals encrusted with small cerussite crystals. This does



Figure 3. A matlockite crystal group, 47 mm wide. Ludlam Collection.



Figure 4. An anglesite crystal, 30 mm long, on corroded galena and baryte. J. Tennant-Jones Collection, (BM. 1964, R11933).

not appear to be a replacement, indicating the cerussite formed at conditions very close to the anglesite-cerussite boundary.

From Figure 1 it can be seen that under a wide range of a_{Cl^-} with pH in the range 5 to 5.5, phosgenite and matlockite have extensive stability fields and both could readily form and also co-exist. They do occur together on NHM specimens, mostly as a large crystal of one with small crystals of the other. Figure 6 is of a specimen of matlockite with a small crystal of phosgenite and Figure 7 shows an enlarged area of the above with the phosgenite marked '>'. Figure 8 is an exception, in that it consists of a large broken blade of matlockite in large phosgenite crystals. The formation of both of these minerals is favoured by high a_{Cl^-} and a_{F^-} in solution. Geochemical investigation of the system

showed that the formation of matlockite tolerates significant changes upwards and downwards in a_{F^-} indicating that the assumption of one tenth saturation is not critical.

Figure 2 shows conditions which are distinctly less favourable for both matlockite and phosgenite formation, requiring a higher a_{Cl^-} than seawater or a higher a_{F^-} than $10^{-4.4}$ to enable matlockite to form. The concentration of calcium in the system would allow some increase in a_{F^-} , but some dilution by rain water is desirable. In addition, Figure 2 shows that phosgenite has a greatly reduced stability field. All in all, these conditions definitely favour anglesite formation over matlockite and phosgenite.

Figures 1 and 2 show that matlockite and anglesite can co-exist over a wide range of pH. It can be difficult to



Figure 5. A group of anglesite crystals encrusted with cerussite. The specimen is 90 mm high. Williams of Burncoose Collection. (BM. 1964, R11935).



Figure 6. Two large matlockite crystals with a small (2 mm) phosgenite crystal nearby. The field of view is 55 mm. Kendall Hazeldine Collection, NHM Accession No. 2004. (BM. 1964, R2004).



Figure 7. An enlargement of part of Figure 6 showing the 2 mm phosgenite crystal (arrowed). (BM. 1964, R2004).



Figure 8. A broken matlockite crystal embedded in phosgenite. The field of view is 30 mm. Ludlam Collection. (BM. 1985, Lud16062).

visually distinguish between small crystals of anglesite and cerussite unless the latter show signs of pseudo-hexagonal twinning. However, on some specimens it is possible to be reasonably confident of this association and Figure 9 shows a group of matlockite crystals with small anglesite and coxcomb baryte crystals in the same cavity.

Figure 1 and 2 both show phosgenite and cerussite can co-exist under appropriate conditions and this association is apparent on specimen material, but the cerussite always consists of very small crystals. Figure 10 shows a large phosgenite crystal, where corroded galena is encrusted with cerussite.

Figures 1 and 2 both show that phosgenite and anglesite can co-exist, but it is only possible to be confident of this association on one specimen, which is shown on Figure 11. On this a near vertical dark anglesite crystal is embedded in phosgenite. Elsewhere on the specimen is a small corroded anglesite crystal.

Neither Figures 1 nor 2 show a field where matlockite and cerussite could co-exist, but in the case of the conditions shown in Figure 1, this would be possible if the saturation level of fluorite was greater than the one tenth assumed. While it is not possible to be certain visually, this combination seems likely to have occurred on one specimen.

Prior to the study, it was hoped it would throw light on the likely source of the chloride. The above mineral associations definitely show that the low sulphate model based on a late stage hydrothermal brine is more favourable for the formation of the minerals and their associations than the Permo-Triassic seawater approach, but there are problems which are discussed below. There is no evidence to throw light on the age of the deposit, but the size of the crystals and their insolubility suggests it may have formed prior to the last glaciation.

DISCUSSION

It must be emphasised that the deposit is clearly supergene in origin and conditions must have remained oxidising for a long period of time. This basically means that the deposit must have formed above, at, or only slightly below the water table over a long period of time, since below the water table access to oxygen is rapidly terminated and conditions usually then become reducing.

In recent decades a large part of Bage Mine has been opened up and explored by the Wirksworth Mines Research Group, their findings being reported by Warriner (1982). Beyond a single crystal of phosgenite and some anglesite found in a kibble of galena 6 m above the 200 ft (60 m) level on the Bage Vein, no further phosgenite and matlockite have been found (Jones, 1982). Based on this research it is considered that the deposit lay somewhere between the 200 ft and 300 ft levels. In this part of the mine the Butler Vein branches off the Bage Vein and then both are cut by the Wallclose Vein. Bryce McMurdo Wright said the minerals came from an 'air shaft' and there is such a shaft in this area and there was galena encrusted by cerussite in this shaft, but none of the rarer minerals. If this was the site, then the deposit



Figure 9. A group of matlockite crystals, with small anglesite crystals and baryte in the cavity below the matlockite. The field of view is 25 mm. Ludlam Collection. (BM. 1985, Lud3374).



Figure 10. A large phosgenite crystal with small cerussite crystals encrusting corroded galena and baryte and fluorite in association. The specimen is 40 mm wide. Ludlam Collection. (BM. 1985, Lud16078).

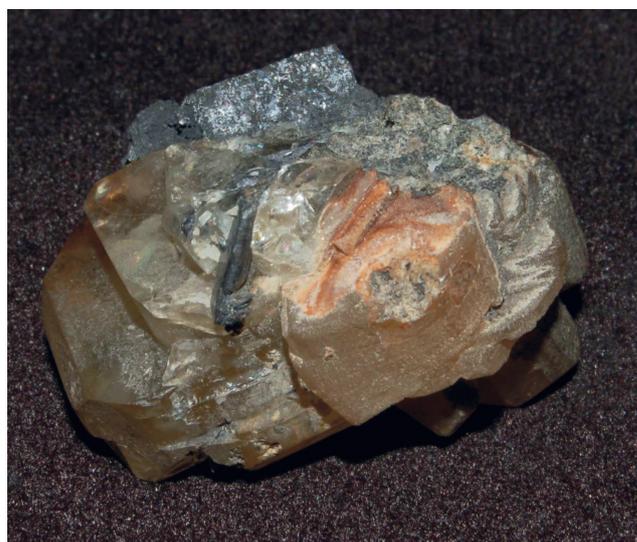


Figure 11. A blade of anglesite embedded in phosgenite. The specimen is 35 mm wide. Williams of Burncoose Collection. (BM. 1964, R7202).

was completely worked out; not impossible considering the great demand for the specimens. It must also be noted that on the Butler Vein at the 200 ft level there are phreatic cave features indicating a long period of time below the water table (John Jones, *personal communication*).

It is reasonable to postulate a very low water table in Permo-Triassic times and it is possible that Zechstein seawater could have percolated to the deposit while it was near or above the water table. However, if so the deposit must have formed very close to the primary mineralisation episode in Derbyshire which is considered to have taken place in late Carboniferous to Permian times. If such waters were the source of the chloride, then similar deposits might be expected in other places where the required elements occur in a deeply oxidised mineral vein e.g. Coldstones Quarry, Pateley Bridge, Yorkshire. The unique character of the Bage deposit and the large stability fields of matlockite and phosgenite in Figure 1 do indicate the hydrothermal brine approach to be the more likely. It does, however, leave the problem of how such a brine could have combined with oxidising conditions for a long period of time.

The spring intercepted in Cambokeels Mine was definitely reducing in nature (Manning and Strutt, 1990) since it had an odour of H₂S. It did have a very low concentration of sulphate, and a relatively high concentration of calcium, but not enough to affect the *aF* assumed above. There is no direct evidence of such a spring in Bage Mine. In 1970 the then Institute of Geological Sciences (now British Geological Survey) published a hydrogeochemical survey of ground waters in the Derbyshire Dome (Edmunds, 1971). In keeping with most of the samples analysed in the study, the chloride ion concentrations were low for the Meerbrook and Cromford soughs, which drain the whole Bage area, at a few 10s of mg.l⁻¹ (ppm). However, water flows from these soughs are enormous and would seriously dilute any saline spring. Elsewhere in Derbyshire higher concentrations of chloride do occur and in a spring at Bradwell it reached 420 mg.l⁻¹ and at Taddington High Well, it was 990 mg.l⁻¹. These concentrations are too low for matlockite and phosgenite formation, but could indicate the presence of more concentrated hydrothermal brines at depth in the Derbyshire orefield. The main problem with this source is that since the Triassic Period the water table has almost certainly been above the deposit for most of the time until drainage tunnels were constructed and the deposit certainly did not form during the working period.

There is a further possibility. After emplacement of the primary mineralisation, if the water table fell to near the level of the site of the deposit, then a late stage hydrothermal spring in the Permo-Triassic could have formed the minerals. In this case the minerals would have had to survive several glaciations and remain isolated from later rises in the water table. This is not impossible. Pristine specimens of minerals such as galena, sphalerite and fluorite are common in current mine workings and would not remain so if exposed to groundwaters. Geochemically this would seem to be the best option, but regrettably, there is at present no definite answer to the time and conditions prevailing when this rare mineral deposit formed.

Finally it is worth noting that a very low concentration of fluoride ion in solution will stabilise matlockite over cotunnite, PbCl₂. If a galena-fluorite-bearing vein outcrops on a sea shore, it is at least possible that matlockite could occur with phosgenite in cavities.

ACKNOWLEDGEMENTS

The author would like to thank Mike Rumsey for assembling the relevant specimens in the Natural History Museum and for helping with visual identification of minor species. Pete Williams is thanked for the thermochemical data for matlockite. John Jones is thanked for lengthy discussions and information on Bage Mine. Trevor Ford and Roy Starkey have also helped the author organise his thoughts on possible sources of the chloride. The late Julie Green made the stability diagrams suitable for publication.

AUTHOR'S NOTE

Part 1 of this paper was prepared at the suggestion of the late Michael E. Smith, who provided most of the information presented. At the time, I was working on the geochemistry, but this was before I had started preparing computer based models of such systems. With five variables to take into consideration, I realised I was out of my depth and unable to do a proper investigation at the time, so Part 2 never appeared as planned. The result is a gap of 30 years between Parts 1 and 2 for which I sincerely apologise. I would like to dedicate this paper to the memory of Mike Smith.

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UNUSUAL FLUORITE FROM OLD TOWNS QUARRY, NEWTON AYCLIFFE, CO. DURHAM

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Old Towns Quarry is one of a number of abandoned workings in the Permian rocks of south-east Co. Durham. The rocks are dolomitised limestones and contain numerous small cavities which hold a range of minerals including fluorite, baryte, calcite and minor sulphides. At Old Towns Quarry, in the early 1990s, cavities were found which were lined with a most unusual form of fluorite. The fluorite mainly takes the form of thin tablets which are highly orientated giving pronounced specular reflectance with a point light source. It is suggested that this requires the presence of an earlier mineral to orientate the fluorite as it crystallised out and that the most likely candidate for this role is gypsum, which while not found at Old Towns Quarry, is found at other quarries in the area.

INTRODUCTION AND GEOLOGY

While Carboniferous strata underlie most of the countryside of Co. Durham, in the east and particularly the south-east, the rocks of predominantly Late Carboniferous Westphalian (Coal Measures) Group are overlain unconformably by Permian rocks. These consist of an irregular sequence of thin breccias and thicker dunal sandstones deposited under arid desert conditions, followed by a succession of carbonates (the so called Magnesian Limestones) and interbedded evaporites deposited after the desert was abruptly flooded by the Late Permian Zechstein Sea. The magnesium-rich carbonates (dolostone) have long been extensively quarried as a flux for steel manufacture and as a source of ballast.

Old Towns Quarry [NZ 256 245] is a long abandoned operation that worked carbonates near the base of the Raisby formation, which is the first major deposit of the Zechstein succession. In common with similar exposures elsewhere in south-eastern Co. Durham, the formation contains numerous, generally small, cavities, probably resulting from the dolomitisation process as postulated by Lee (1994). The rocks vary considerably in hardness and are usually grey to buff in colour. Minor mineralisation is of common occurrence, but well below commercial quantities. Hirst and Smith (1974) and more recently Dunham (1990) provide a summary of such mineralisation and Dunham also specifically mentions the presence of amber fluorite, with

baryte and some galena and sphalerite at Chilton Quarry [NZ 3008 3137]. This fluorite has normal cubic morphology.

At Old Towns Quarry the surface of the cavities is usually lined with a thin microcrystalline crust of yellowish carbonate with rhombic morphology. The other minerals present are then deposited on this surface in a layer that rarely exceeds 10 mm and is often much less than this. While fluorite is by far the most interesting, for completeness, the other minerals present are described first. Note that the following descriptions are based on specimen material collected in the early 1990s.

THE MINERALS

BARYTE, BaSO₄

Baryte is fairly common as crusts of white coxcomb crystals forming thin linings in cavities. Individual crystals reach 5 mm across and amalgamate to form layers up to a similar thickness. The baryte formed later than the fluorite, which is sometimes encrusted with small coxcomb blades. The baryte is often iron stained.

CALCITE, CaCO₃

Calcite is common as small irregular trigonal crystals which reach up to 15 mm long, but are generally much smaller than this. It is the last mineral to form, with the possible exception of some of the pyrite, and rarely cements

fragments of fluorite that have broken off their base. (Note that flowstone calcite was found in places in the quarry, but not in the cavities).

GALENA, PbS; CERUSSITE, PbCO₃

Galena is not common in specimen material, but has been found, a good example being a mass of crystals, 35 mm across, in a cavity with baryte, calcite and fluorite. It formed later than the fluorite and baryte, but small crystals of calcite occur on the surface of the galena. The galena is heavily oxidised and encrusted with small cerussite crystals which reach 1 mm, but are mostly much smaller than this. The fluorite crystals under the galena are cubic, colourless and reach up to 1 mm on edge.

PYRITE, MARCASITE, FeS₂

Within some cavities there are small irregular crystals of brown stained pyrite which reach 2 mm across. Often associated with these are tiny groups of flaky crystals, also brown stained, which are probably marcasite. Some of the pyrite occurs on calcite, but it is not clear whether it formed later than the calcite or has detached and fallen on to it from earlier growth.

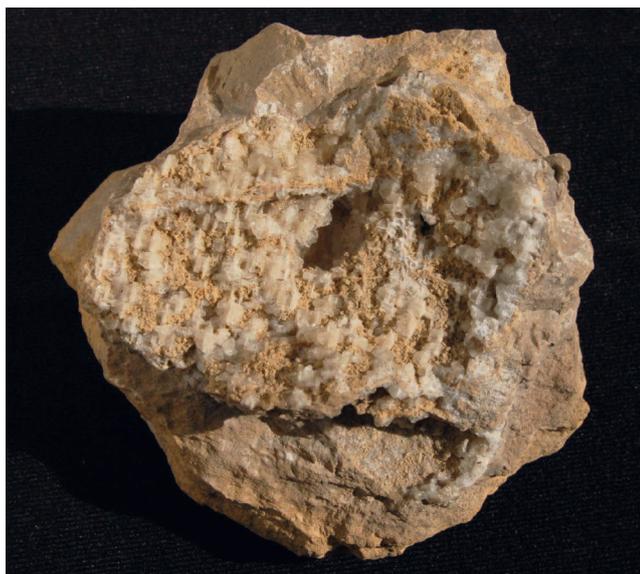


Figure 1. 'Reticulated fluorite' in a cavity from Old Towns Quarry. Specimen width 80 mm.



Figure 2. 'Reticulated fluorite', Old Towns Quarry. Specimen width 65 mm.

FLUORITE, CaF₂

Many of the cavities in the limestone are wholly or partly lined with a thin crust of fluorite crystals and Figures 1 and 2 show typical specimens. The crusts are often discontinuous, so individual crystals and groups of crystals frequently do not touch. Colour varies from colourless to pale yellow and rarely brown. Purple spots occur in some of the paler crystals. The fluorite fluoresces very pale yellow under short wave UV light and is phosphorescent. The fluorite is remarkable in two respects, which will be dealt with in turn.

1. While some of the fluorite occurs as small cubes, generally no more than 4 mm on edge (sometimes microcrystalline) and rarely as elongated prisms with a square cross-section, most occurs as relatively thin tablets. Figure 3 shows typical tablets associated with an elongated prism. The long edges of the tablet crystals range from 2 to 9 mm while the short edge is typically 0.5 to 1.5 mm wide. The long edges are sometimes stepped. When crystals intersect, they often do so at 45°, forming cellular octahedra. Most of the crystals are transparent, lustrous and have no signs of any internal zonation.
2. While the tabular nature of the fluorite is unusual, even more remarkable is the high degree of parallel orientation of the crystals. With appropriate orientation to a point light source (including sunlight), this results in a high level of simultaneous specula reflectance off numerous crystal faces (Figure 4, see p. 14). Rotating a specimen normally results in three planes of reflectance due to the 45° intersection of the individual crystals. This reflectance crosses gaps between individual crystals,



Figure 3. Fluorite blades with an elongated prism. Image width 5 mm. Photograph: David Green.

crystal groups and, as can be seen in Figure 4, can cross a relatively wide gap. It is this specula reflectance that gave rise to the term 'reticulated fluorite' used by local collectors.

DISCUSSION

The mineral assemblage in the cavities is not unusual for the area; only the fluorite is out of the ordinary and clearly requires an attempt at an explanation. The fact that the pronounced orientation of the crystals crosses gaps would seem to imply that some earlier phase has caused the crystal alignment. One possibility is fluorite itself, but this would have had to have filled the cavities, then dissolved away leaving numerous small residues to orientate later growth. This does happen to a small extent in the nearby Northern Pennine Orefield (Bridges and Wilkinson, 2003, 2005), but subsequent regrowth is always cubic and usually with random orientation. The original fluorite crystals would, in any case, have had to be far larger than any found anywhere else in the local quarries. All things considered, fluorite seems to be a most unlikely cause of the orientation.



Figure 4. Fluorite blades showing specula reflectance bridging a cavity. Image width 50 mm. Photograph: David Green



Figure 5. Gypsum in a cavity from Cornforth Quarry. Specimen width 50 mm.

Another possibility is halite, which would have the advantage of easy later removal. However, neither halite nor halite pseudomorphs have ever been found in the Raisby Formation at any of the local quarries, the nearest beds being much higher up the succession. It is also difficult to see why halite should cause the tabular nature of the crystals.

The most obvious contender for the role would seem to be gypsum. While gypsum has not been found at Old Towns Quarry to the best of the authors' knowledge, it does occur in other similar quarries in the area, usually as large single crystals filling cavities. Figure 5 is of a specimen of gypsum in a cavity in dolomite from Cornforth Quarry [NZ 320 344]. The edge of the gypsum crystal in the cavity shows signs of dissolution, leaving a crust of small calcite crystals on the limestone. If a mineralising fluid, rich or preferably saturated with dissolved fluorite, percolated to the junction between rock and gypsum in a cavity, the relatively high solubility of gypsum could raise calcium ion activity ($a_{Ca^{2+}}$), in the fluid, resulting in the displacement and crystallisation of some fluorite from the solution. Although gypsum is in the monoclinic crystal system as opposed to the cubic of fluorite it has the advantage of readily forming flat tabular crystals. It is, therefore, suggested that an original gypsum crystal exerted a physical or chemical control on fluorite growth, such that tabular crystals formed and also controlled the orientation. The two minerals do have the Ca^{2+} ion in common. Clearly this explanation is just an hypothesis, but it does seem to be plausible considering the geology and mineralogy of the area.

Specimens of the fluorite have been placed in the collections of the Natural History Museum, London, the Oxford Museum of Natural History and the Great North Museum (Hancock), Newcastle upon Tyne.

ACKNOWLEDGEMENT

David Green is thanked for the photographs in Figures 3 and 4.

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CORONADITE AND ROMANÈCHITE FROM THE NORTHERN PENNINE OREFIELD

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There are very few published accounts of manganese oxide minerals from the Northern Pennine Orefield of England. Of those, some lack sufficient analytical data to give confidence in the identifications made.

Dunham (1990, p. 91) recorded “psilomelane”, and possible pyrolusite, from Remington’s Vein, Great Dunn Fell but the former is no longer considered a distinct species, and the latter was unconfirmed. Young *et al.* (1996) identified the Great Dun Fell “psilomelane” as romanèchite and described coronadite from Sedling Vein, Weardale, both on the basis of XRD. XRD alone is insufficient to definitively identify coronadite, their published chemical formula is incorrect, and no chemical evidence was presented to support the identification.

Bridges and Young (1998) cite reports of pyrolusite from Great Dun Fell but do not state how it was identified. It has since been confirmed by XRD at Grasshill, Teesdale (Young *et al.*, 2005). In addition to Sedling Vein, Bridges and Young (1998) cite reports of undefined soft manganese oxides, and “psilomelane” from other North Pennines localities.

More recently Cotterell *et al.* (2012) identified cryptomelane, using XRD and EDS, as locally common at Grasshill mines in Upper Teesdale within black manganese-rich limonite. They also described coronadite as thin, glossy, black, crusts coating supergene lead mineralisation from the dumps at Grasshill, and matt, black, botryoidal coatings, *in-situ*, on cerussite within a deeply weathered galena vein. Their identification of coronadite was on the basis of XRD and its intimate association with other lead-bearing minerals, but was not supported by detailed chemical data.

Whilst romanèchite is distinguishable from other manganese oxides by XRD, coronadite is not. Coronadite is a member of the coronadite group within the hollandite super group of minerals (Biagioni *et al.*, 2013). In these MnO_6 octahedra are joined together by sharing of vertices and edges forming a framework structure containing tunnels of sufficient size to accommodate various cations. In the coronadite group, the tunnels are two MnO_6 units wide by two high (2 x 2). In romanèchite they are wider (2 x 3), and other permutations are possible, creating a variety of minerals (Post, 1999).

Members of the coronadite group are defined by the dominant cation in the tunnels (Biagioni *et al.*, 2013). The tunnel cations, and the corresponding minerals, are sodium (manjiroite), potassium (cryptomelane), barium (hollandite),

lead (coronadite) and strontium (strontiomelane). The ideal formula is $\text{M}(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$ where M is one of the cations above. Additionally, Fe^{3+} can substitute for Mn^{3+} and Biagioni *et al.* (2013) suggested the name ferrihollandite for the Fe end member. Romanèchite, despite being chemically similar to hollandite, is structurally distinct and is therefore not a member of the coronadite group. The composition of romanèchite is generally given as $(\text{Ba}, \text{H}_2\text{O})_2(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10}$ (Back and Mandarino, 2008; Klein and Dutrow, 2007). However, Post (1999) has shown that barium ions and water molecules, in a ratio of 1:2, reside within the manganese oxide tunnels, with the Ba^{2+} ions balanced by substitution of Mn^{3+} for some of the Mn^{4+} in the tunnel structure; on this basis he proposed an “ideal” formula for romanèchite of $\text{Ba}_{0.66}(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10} \cdot 1.34\text{H}_2\text{O}$. Although some authors, including Young *et al.* (1996) and Bridges and Young (1998), give Mn^{2+} , the reduced manganese oxidation state in all members of the hollandite supergroup is Mn^{3+} (Post, 1999; Biagioni *et al.*, 2013).

Being isostructural with other members of the coronadite group (Post and Bish, 1989) coronadite is not distinguishable by XRD alone. XRD will only indicate a mineral with the coronadite group structure. A quantitative chemical analysis is required to determine the dominant tunnel cation. This paper provides quantitative analyses of material collected from Sedling Vein, in Weardale, and from Skears Firestone Level, on the west side of Hudeshope Beck, near Middleton-in-Teesdale [NY 941 278]. Manganese oxides have not previously been reported from this latter locality. In each case samples were hand-picked to be as free as possible from visible contaminants, and were studied by XRD and XRF.

Samples of black material were collected from the vicinity of the grid reference [NY 869 407] given by Young *et al.* (1996) at Sedling Vein. These came from small tips beside a track, a fragment found on the track itself, and material from the gully below. Of these three proved to be iron oxide as shown by their brown streak, and XRD data, which matched goethite. One piece from a tip, and the fragment found on the track nearby, had black streaks. The piece from the tip gave an ill-defined XRD pattern with some broad peaks consistent with a coronadite group phase, but the only easily identifiable peaks were due to quartz and fluorite. The piece from the track was slightly better and gave a coronadite group pattern, free from quartz and fluorite, but was poorly crystalline.

Samples were taken from two points in Skears Firestone Level. The richest material came from a vein followed by a passage on the left. Some more material was found up a laddered rise. In each case it is present as black, friable material on crumbly fluorite. The material from the first spot is often mammillated, and sometimes has a steely-grey appearance on broken surfaces. XRD of the first gave a distinct mixed romanèchite and coronadite group pattern. That from up the rise was less well crystallised, but five weak peaks could be matched with the coronadite group.

Analyses of the samples, performed on a Bruker S8 Tiger XRF spectrometer, are shown in the table. With the exceptions of PbO and MnO₂, all the oxides listed were within the ranges to which the instrument was calibrated. When within range, their accuracy is normally to one decimal place, with a detection limit of around 0.1 %. PbO was calibrated up to 20.0 % and Mn₃O₄ up to 40.0 % (= 45.6 % MnO₂). For higher levels the measurements were found to deviate slightly. A lab made sample with 6.0 % Fe₂O₃, 40.0 % PbO and 54.0 % Mn₃O₄ (= 61.6 % MnO₂) gave, respectively, 6.4, 44.1 and 58.7 (= 66.9) %. In addition, readings of 1.0 % Na₂O, 0.1 % CaO, 0.1 % TiO₂, and 0.2 % SrO were obtained. These, and the extra 0.4 % Fe₂O₃, probably represent interferences. The other oxides were unaffected.

Accordingly, the PbO content of the Sedling Track sample is probably about 3 % lower than the stated value, and some of the other PbO and MnO₂ values may also be slightly lower than stated. This explains the high totals for the Sedling samples, in which the lead content exceeds the calibration limit. Although this makes some of the data semi-quantitative, it is adequate for the purposes of this paper as it proves the dominant tunnel cations.

In the table manganese is cited as MnO₂, but some is actually Mn₂O₃. It follows that there will be a slight

	Skears	Skears Rise	Sedling Tip	Sedling Track
Na ₂ O	0.7	0.9	1.0	1.0
MgO	0.2	0.1	0.0	0.0
Al ₂ O ₃	0.0	0.0	0.5	0.4
SiO ₂	0.3	0.0	9.9	0.5
K ₂ O	0.5	0.6	0.5	0.6
CaO	2.1	1.6	5.1	0.2
TiO ₂	0.1	0.0	0.1	0.1
MnO ₂	66.2	48.7	51.7	61.6
Fe ₂ O ₃	3.0	0.2	4.5	5.4
ZnO	0.4	2.0	0.4	0.6
SrO	0.2	0.2	0.2	0.2
BaO	8.7	0.5	0.2	0.3
PbO	15.5	19.2	31.7	40.1
Total	97.7	74.0	105.8	111.0

Table. XRF analyses expressed as weight % oxide.

excess of oxygen leading to slightly higher totals. For pure coronadite of ideal formula this would result in an excess weight of 1.8 %, and for romanèchite 3.3 %. These excesses are offset by substances not included in the analyses, e.g. fluorine (from fluorite) and water, which can be present in the tunnels of coronadite group minerals (Post and Bish, 1989), or water or carbonate associated with other elements (Ca, Fe and Zn). Romanèchite also contains 4.39 % water. Totals therefore will not be exactly 100 %.

The low total for the second Skears analysis is due to insufficient sample. The method requires fusion of 0.7000 g of sample with 7.0000 g of lithium tetraborate flux to make a “bead” that is placed in the instrument. Only 0.4537 g of sample was available, but 7.0000 g flux was still needed to ensure a large enough bead. But the instrument was calibrated on the basis of a 0.7/7 ratio of sample/flux. The data is still adequate to establish the dominant cations.

The analyses of the Skears material support the XRD data. The sample from the side passage was shown to be a mixture of romanèchite and a coronadite group phase, and this is confirmed by XRF. The barium can be accounted for by the romanèchite. Sodium and potassium are insignificant, but lead is high, indicating that the coronadite group mineral is coronadite. The sample from up the rise is low in barium, confirming the absence of romanèchite in the XRD data, and also eliminating hollandite. Sodium and potassium are likewise low, but lead is very high. Thus coronadite is the most likely phase.

Both Sedling Vein samples are very high in lead, confirming again the presence of coronadite. In fact the lead contents are well in excess of the theoretical value (27.4 % PbO). On the basis of chemical analyses and Rietveld refinement of X-ray powder diffraction data, Post and Bish (1989) concluded that coronadite was anomalous amongst coronadite group minerals. Typically coronadite group minerals with divalent tunnel cations have only half of the available sites filled. Coronadite can have up to two-thirds of the sites occupied. The formula of a coronadite with two-thirds of the tunnel sites filled is Pb_{1.33}Mn₈O₁₆, although Post and Bish (1989) report values as high as 1.4 for Pb which equates to 31.7 % PbO. Still higher values (up to 38.8 % PbO) have been reported for coronadite from Old Liganure Mine, Co. Wicklow, Ireland (Moreton *et al.*, 2006) and the value from the sample from the track at Sedling Vein is probably almost as high. Unless coronadite can accommodate even more Pb it may be that another Pb-bearing phase (e.g. cesàrolite) is present in intimate association with the manganese mineral although, as with the Irish examples, there was no evidence for this in the XRD data.

The presence of coronadite in the Northern Pennine Orefield has now been confirmed using a combination of structural and chemical analytical techniques and a new locality for the manganese oxides romanèchite and coronadite is documented. Doubtless more localities will be found for these, and other manganese oxide minerals, but the difficulty in characterising them means that they are likely to continue to be undetermined to species level.

Any future researchers wishing to identify manganese oxides, especially of the coronadite group, are advised to complement XRD with a full chemical analysis. Further investigation of coronadite is also merited to ascertain just how much lead it can accommodate in its structure.

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HEMIMORPHITE REPLACEMENTS OF RUGOSE CORALS FROM SWALEDALE, NORTH YORKSHIRE

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The numerous lead, zinc, fluorite, baryte bearing veins of the northern Pennine orefields, both in the Alston and Askrigg blocks of northern England, are commonly associated with intense and extensive replacement of limestone wall rocks (Dunham 1990; Dunham and Wilson, 1985). Within these 'flats', features of the original limestone, including bedding, stylolites and rarely fossils, are known to be preserved locally by the primary, or hypogene, minerals characteristic of these deposits.

Subsequent to their original emplacement, near-surface alteration has locally been intense, resulting in the widespread formation of a wide range of supergene species (e.g. Bridges and Young, 1998; Tindle, 2008; Young and Symes, 2008), though the timing of this alteration is not clear. Most widespread of this type of alteration has been the production, in the Alston block portion of the orefields, of economic concentrations of 'limonitic' ironstones from the supergene oxidation of hypogene siderite and ankerite. Significant, and locally workable, concentrations of smithsonite, derived from supergene alteration of primary sphalerite, are known from several places in both the Alston and Askrigg orefields. A feature of the vein and flat deposits of the Askrigg Block is the widespread occurrence of supergene hemimorphite, no doubt derived from alteration of abundant original sphalerite. So far as is known no attempts have ever been made to work hemimorphite from any of these deposits as a commercial ore.

Whereas good examples of many supergene pseudomorphs after hypogene species are known from deposits across the orefields, supergene alteration, when intense, typically destroys many of the primary features and textures of the original deposits.

LOCATION AND DESCRIPTION

Recent collecting by the writer has revealed the presence, at Grovebeck Mine, Swaledale [SE 0275 9675], of rare examples of crystalline hemimorphite clearly replacing original solitary corals. The dumps at Grovebeck contain an abundance of blocks of hemimorphite which, in common with its widespread presence elsewhere in the district, typically occurs here as cavernous masses up to 30 cm across composed of cellular crusts made up of spherules of colourless to pale buff hemimorphite crystals up to a few millimetres across. Young *et al.* (2012, p. 60) described hydrozincite as powdery masses partially filling some cavities within these hemimorphite masses.

Clear remnants of the structure of solitary rugose corals, entirely preserved in crystalline hemimorphite, have been recovered from a handful of these hemimorphite blocks (Figs. 1 and 2; see p. 18). Corallites up to 2 cm across were found, within which obvious remnants of internal septa were clearly preserved. Although the preservation is sufficient to identify these structures as replacements of corallites,



Figure 1. Two solitary rugose corals replaced by buff crystalline hemimorphite. The outer wall of the corallite is clearly visible on that on the left; remnants of internal septa may be seen in both. Grovebeck Mine, Swaledale. B. Young specimen (BY8987/A), width 6 cm. Photograph: P.E. Young.



Figure 2. Solitary rugose coral with internal septa clearly visible, seen in section, replaced by buff crystalline hemimorphite. Grovebeck Mine, Swaledale. B. Young specimen (BY8987/B), width 2 cm. Photograph: P.E. Young.

insufficient detail remains to indicate the identity of the corals even to a generic level. However, the features present are consistent with corals of the genera *Dibunohyllum* or *Aulophyllum*, both known to be present within the Main Limestone, the main wall-rock of the deposits worked at Grovebeck (Dunham and Wilson, 1985).

DISCUSSION

Whereas supergene pseudomorphs after primary species, for example smithsonite after sphalerite or goethite after marcasite (Young and Bridges, 2011) are known from numerous northern Pennine locations, so far as the writer is aware no replacements of fossils by hemimorphite have ever been reported. Although it is conceivable that such fossils in limestone may have been replaced by hypogene sphalerite during the original emplacement of the deposits, the few specimens of such replacements seen by the writer from the Alston area of the orefields preserve only very

crude remnants of the original palaeontological features. It is inconceivable that crystallisation of comparatively coarsely textured hemimorphite during supergene alteration of such hypogene sphalerite replacements would have preserved recognisable details such as the internal septa of rugose corals. The presence of hemimorphite replacing fossil textures in the specimens described here is interpreted as evidence of the availability, and mobility, of zinc-rich fluids during supergene alteration and their ability to replace fossils within limestone that had hitherto been unaltered, or only very weakly altered, by the primary mineralising fluids.

As none of the Grovebeck workings are known to be accessible to examination and no mineralisation is visible *in situ* at the surface, it is not possible to comment in detail on the relationships of this supergene alteration with the hypogene assemblages or the wall-rocks which host these deposits.

Dunham and Wilson's reference (1985, p. 174) to a natural cavern system within the Grovebeck workings is intriguing. Elsewhere in the orefield at Pikedaw, near Malham, supergene smithsonite was deposited in a karstic cavern system in economically workable quantities (Raistrick, 1954, 1983; Dunham and Wilson, 1985; Arthurton *et al.*, 1988; Bevins *et al.*, 2010). It is thus possible that here at Grovebeck supergene hemimorphite may be hosted in a karstic environment, the conditions of which may have influenced its formation. A search of the orefield may reveal occurrences of mineral assemblages which offer opportunities to examine such supergene mineralisation *in situ* in cavern systems. If so, useful evidence of the conditions and possible timing of such supergene alteration may be found.

Whilst considering the development of supergene hemimorphite in these deposits it is interesting to note that whereas both smithsonite and hemimorphite are common in the supergene assemblages of the Askrigg orefield, the latter mineral is perhaps the most widespread and abundant. In contrast, smithsonite is by far the dominant zinc supergene species in the Alston Block deposits. In this context, the most significant difference between the two portions of the Northern Pennine orefields is perhaps the restriction of widespread Namurian Chert wall-rocks to the Askrigg area: such wall-rocks are absent in the Alston portion of the field. The abundance of hemimorphite in the Askrigg area may result from a ready supply of silica-rich groundwaters in a chert-dominated setting during supergene alteration. Supergene groundwaters in the Alston area were commonly carbonate-rich and typically deficient in silica.

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‘CELLULAR’ QUARTZ FROM TEESDALE, NORTHERN PENNINES

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Distinctive cellular honeycomb-like aggregates of quartz, formed as the septa in septarian clay ironstone nodules, and now isolated by complete dissolution of the original ironstone matrix, are known in a number of old collections, though in many instances locality information is lost or unrecorded. Examples of these curious objects, together with all stages in their dissolution from the parent nodules, are described from two localities at two stratigraphical horizons within mudstones of the Upper Carboniferous (Namurian) Stainmore Formation of Teesdale, County Durham in the Northern Pennines. Comparisons are made with un-provenanced museum specimens, though no diagnostic characteristics have been found in the Teesdale examples which might assist in identifying the origins of these.

INTRODUCTION

Many old collections of British minerals include specimens of quartz which, from its curious morphology, has been referred to as ‘cellular’ quartz. The epithet is appropriate as the specimens closely resemble groups of cells within a honeycomb (Fig. 1). Unfortunately, as so often with old collections, the specimens commonly lack precise, or in many instances any, locality information. In addition, the few known published references to this distinctive form of quartz are vague with regard to provenance. Sowerby (1807-9; pp. 13-14 and Plate 207) described and figured a fine example but merely referred to it as:

...the production of Cumberland...

‘Cumberland’ was commonly quoted as a generalised location in many early descriptions of Northern Pennine mineral occurrences: it does not necessarily indicate that the specimens were derived from the former administrative county of Cumberland (now Cumbria). Rudler (1905) noted the presence of this form of quartz:

...in most mineral collections...

but referred to it simply as originating from Teesdale, County Durham. Although brief mention was made of such ‘cellular’ quartz aggregates, known locally as ‘beetle stones’, at Pike Law and Coldberry Gutter in Teesdale (Bridges and Young, 2007; Symes and Young,

2008), no detailed descriptions of the specimens or of their stratigraphical origins were given by these authors. This paper offers such descriptions.

Recent field work by the authors has revealed that this form of quartz is common at two locations, and from



Figure 1. Cellular quartz from Coldberry Gutter. In this example all traces of the original clay ironstone matrix have been weathered away. Specimen is 6 cm across. B. Young specimen (BY3977). Photograph: B. Young.

two separate stratigraphical horizons, in Teesdale, County Durham in the Northern Pennines. Their attention has also been drawn to a third Northern Pennine occurrence in Weardale, though as the few specimens known from this locality were recovered from glacial deposits, the precise origin of that material remains unknown.

Although the ‘cellular’ quartz, reported here from the Northern Pennines, appears to be a product of authigenic processes within the Carboniferous sediments, it seems to be limited in its distribution to a very restricted number of locations.

As the characteristics of the ‘cellular’ quartz, and its likely mode of origin, appear to be virtually identical in all specimens examined at the locations identified in this study, these characteristics will be discussed before describing the locations themselves.

Whereas no systematic search of museum collections has been undertaken in this study, it is hoped that the descriptions and interpretations of the Teesdale occurrences presented here may perhaps aid understanding of similar specimens which may exist in old collections where locality information may be incomplete, ambiguous or absent.

CHARACTERISTICS OF ‘CELLULAR’ QUARTZ

Specimens of this form of quartz from Teesdale comprise open honey comb-like aggregates of thin plates, or septa, composed of compact white to pale buff coloured crystalline quartz (Fig. 1). The plates typically vary between 1 and 4 mm in thickness and form polygonal ‘cells’ which most commonly exhibit irregular hexagonal, or more rarely pentagonal or square outlines. Whereas most of these cell boundaries are straight, curved examples are also common. In some specimens the ‘cells’ exhibit an inward tapering form (Fig. 2). Although in many specimens ‘cells’ are empty, more commonly remnants of a previous filling of siderite mudstone, in varying states of oxidation to ‘limonite’, are conspicuous and give a clear indication of the origin of these specimens as the dissolution products of ironstone septaria (Figs. 2, 3 and 4).

These distinctive quartz aggregates and the partially weathered septarian nodules, are known locally in Teesdale as ‘beetle stones’ (Bridges and Young, 2007; Symes and Young, 2008), doubtless owing to the somewhat fanciful resemblance of the partially weathered nodules to beetle carapaces. This term has long been applied to septarian nodules elsewhere in Great Britain. For example, Arkell and Tomkeieff (1953) record the use of this term for septarian nodules in the Millstone Grit of the South Wales Coalfield, though the authors are not aware of specimens exhibiting completely weathered-out cellular quartz septa from that area.

ORIGIN OF SEPTARIAN NODULES AND OF ‘CELLULAR’ QUARTZ

Septarian nodules, or septaria, are typically rounded or flattened nodules of limestone or siderite mudstone



Figure 2. Cellular quartz from Pike Law Hush. Remnants of the clay ironstone matrix remain in parts of this specimen. Note the inward tapering form of quartz septa in the lower part of the specimen. Specimen is 5 cm across. Photograph: R.E. Starkey.

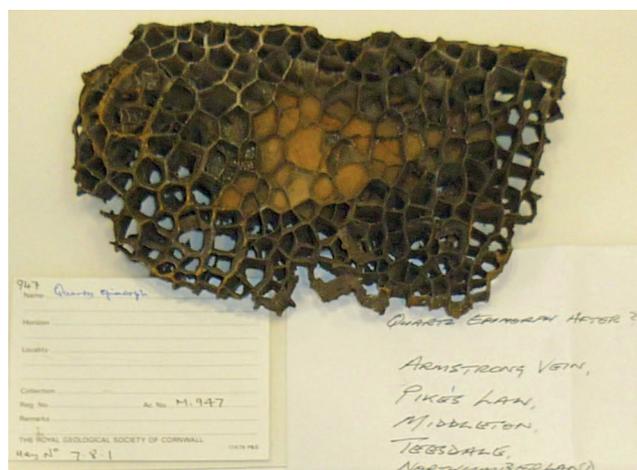


Figure 3. Cellular quartz labelled ‘Armstrong Vein, Pike Law Mines, Teesdale’. Residual clay ironstone remains in the centre of the specimen. Specimen is 18 cm across. British Geological Survey specimen, originally held by the Royal Geological Society of Cornwall (M947). Photograph: R.E. Starkey.



Figure 4. Quartz septa partially exposed from deeply weathered clay ironstone nodule. Note that in this example the quartz septa do not reach the outer surface of the nodule. Pike Law Hush. Specimen is 10 cm across. B. Young specimen (BY8932). Photograph: B. Young.

(clay ironstone) commonly found as discontinuous layers or bands within mudstone formations. They are distinguished internally by a network of intersecting, and commonly radiating, polygonal mineral-filled, or partially filled, cracks. The cracks are generally regarded as a result of shrinkage of the nodules as they developed during diagenesis within the enclosing mudstone. The 'syneresis' cracks so formed were then filled at a later stage in diagenesis by introduced minerals, most commonly calcite, though dolomite and siderite occur in some examples. The filling of such cracks with quartz appears to be unusual. A feature of many septaria is the radial pattern of the mineral-filled cracks which commonly widen towards the centre of the nodule and which tend to die out towards the periphery. Pettijohn (1957, Plate 9) illustrated a septarian nodule in which advanced weathering of the nodule matrix had produced a residual 'box-work' structure, known as a 'turtle back' or 'melikaria', similar in appearance to the cellular quartz specimens described here from the Northern Pennines.

At both locations examined in this investigation, flattened tabular disc-like siderite mudstone (clay ironstone) nodules, up to 200 mm across and 50 mm thick occur as discontinuous layers in mudstones within the Stainmore Group of Carboniferous (Namurian) age. Most of the Teesdale examples seen in this investigation exhibit an internal septarian structure, in which the septa typically display a vertical orientation at right angles to bedding; radiating septa are uncommon here.

Although some septa are composed of calcite and/or dolomite with local concentrations of dickite, quartz is by far the most abundant mineral forming the septa at both Teesdale locations described here. Quartz septa, which protrude from the nodule surfaces, reflect weathering of the nodules and the removal by mechanical disintegration or dissolution of the siderite mudstone matrix (Figs. 5 and 6). Complete removal of the siderite mudstone matrix by weathering has produced the distinctive honey comb-like masses of 'cellular' quartz.

Artificial leaching, by boiling in hydrochloric acid, of a typical clay iron stone nodule from Pike Law Hush yielded a honey comb-like aggregate of 'cellular' quartz identical to those found at both Pike Law and Coldberry Gutter (Fig. 7).

Brief comments follow on the two individual occurrences of 'cellular' quartz identified in Teesdale.

PIKE LAW MINES

This area of old workings, which comprises an extensive group of ancient opencast workings and hushes on a complex of lead-bearing veins, lies astride the hill road from Newbiggin in Teesdale to Westgate in Weardale. The veins are hosted within the Great Limestone and immediately overlying clastic sediments of the Stainmore Formation (Namurian) up to the horizon of the Firestone Sill sandstone (Dunham, 1990; Bevins *et al.*, 2010). The Great Limestone is well exposed in many of the old opencasts with, in places, intermittent exposures of the overlying mudstones and sandstones. In a recent description



Figure 5. Quartz septa standing proud of weathered surface of clay ironstone nodule. Pike Law Hush. Specimen is 17 cm across. Photograph: B. Young.



Figure 6. Quartz septa partially weathered from clay ironstone nodule. Hill End, Frosterley. Specimen is 5 cm across. Photograph: Claire Holloway.



Figure 7. Cellular quartz mass produced by leaching clay ironstone nodule in boiling hydrochloric acid. Pike Law Hush. Specimen is 10 cm across. Photograph: R.E. Starkey.

of the geology and mineralisation, Bridges and Young (2007) commented briefly on the presence here of ‘cellular’ quartz in debris from old workings, and illustrated an old specimen from the collections of the Great North Museum (Hancock), Newcastle upon Tyne, which they presumed to have originated here.

The present investigation has revealed that several discontinuous layers of these nodules occur within a vertical interval of a few metres within the dark grey mudstone which here overlies the Great Limestone, exposed in the upper reaches of Pike Law Hush [NY 9035 3145] on the east side of the road. Numerous weathered-out nodules litter the exposure and the slopes beneath it (Fig. 8). They are composed of extremely fine-grained siderite mudstone which exhibits a uniform mid-grey colour and sub-conchoidal fracture on fresh surfaces. Outer, weathered surfaces are typically dark brown to orange-brown and commonly reveal conspicuous protruding quartz septa, the prominence of which varies according to the degree of weathering (Fig. 5). Many more deeply weathered nodules exhibit concentric layers of ‘limonitic’ alteration, in places clearly revealing that in many examples the quartz septa do not extend to the outer layers of the nodules (Fig. 4). Completely weathered specimens, consisting solely of weathered-out quartz septa occur here, but are rare. The example illustrated in Figure 3, originally in the collection of the Royal Geological Society of Cornwall (Accession Number M947), now in the custody of the British Geological Survey at Keyworth, Nottingham, exhibits remnants of the original clay ironstone matrix. The specimen is unusual amongst early examples of this material by being accompanied by apparently detailed locality information. However, its attribution to the ‘Armstrong Vein’ is puzzling. No vein of this name is described from this site by Dunham (1990), Bridges and Young (2007) or Bevins *et al.* (2010) and no vein of this name is depicted on the British Geological Survey 1:10560 scale geological map of the site (Durham 31SW). From its extremely close resemblance to specimens collected recently by the authors (e.g. Figs. 1, 2 and 7) it is reasonable to suggest that it too may have originated from the exposures within Pike Law Hush.

Whereas most of the quartz septa consist of compact fine-grained quartz, in a few examples the filling of wider shrinkage cracks, up to 10 mm wide, has been incomplete. In these examples clear, colourless ‘rock crystal’ quartz occurs as prismatic crystals up to 2 cm long with sharp pyramidal terminations (Fig. 9).

In a few nodules the quartz septa include inner coatings of a white fine-grained crystalline clay mineral, provisionally identified as dickite.

COLDBERRY GUTTER

Coldberry Gutter is a very large opencast excavation on the Lodgesike-Manorgill Vein system which forms a conspicuous landscape feature which crosses the watershed between the Bow Lee and Hudeshope valleys on the north side of Teesdale. Rocks belonging to the Stainmore Formation (Namurian) are exposed in the sides of the ‘gutter’. The northern wall exposes beds from the Firestone

sandstone up to the Low Grit Sill sandstone (Dunham 1990). Beds up to the equivalent of the Grindstone Sill sandstone, including a thin limestone which may be the correlative of the Upper Felltop Limestone, are exposed in the southern wall. Young (2011) has described the occurrence here of millerite, together with quartz and calcite within septarian siderite mudstone nodules which occur as beds in the mudstone immediately beneath the Low Grit Sills sandstone exposed in the northern wall of the ‘gutter’.

During this investigation, the authors identified a small number of septarian siderite mudstone nodules, virtually identical to those seen at Pike Law, amongst the abundant talus within the gutter in the vicinity of Young’s (2011) millerite locality [NY 9300 2896]. Like those at Pike Law, these are composed of very fine-grained mid-grey siderite mudstone, the septarian shrinkage cracks of which are commonly filled with fine-grained quartz. Weathering has resulted in the quartz septa protruding from the dark brown oxidised surfaces and, in a very few instances, complete removal of the siderite mudstone matrix has produced honey comb-like aggregates of ‘cellular’ quartz (Fig. 1) identical to those found in greater abundance at Pike Law. Whereas these nodules were not located in situ, their occurrence lying loose on the deeply weathered mudstone exposures on the northern slopes of the ‘gutter’ strongly suggests that their origin lies within the mudstones immediately beneath the Low Grit Sill sandstone.



Figure 8. Clay ironstone septarian nodules (‘beetle stones’) on weathered exposure of mudstone, Pike Law Hush. Hammer shaft is 35 cm long. Photograph: B. Young.



Figure 9. Clear ‘rock crystal’ quartz crystals up to 2 cm long in centre of clay ironstone nodule. Pike Law Hush. Specimen is 8 cm across. Photograph: B. Young.

In addition to fine-grained quartz, as at Pike Law some of the nodules here include wider open septa up to 10 mm wide lined with 'rock crystal' quartz crystals with prism faces up to 4 mm long and pyramidal terminations. Several of these crystals are notable for exhibiting a distinctive sceptred form. A few larger crystals of 'rock crystal', up to 15 mm long, have also been seen. An off-white fine-grained crystalline clay mineral, also provisionally identified as dickite, locally coats some of the smaller quartz crystals.

Several nodules also include septa composed of brown-weathering siderite, which in cavities up to 5 mm across, locally exhibit euhedral curved rhombic forms.

CELLULAR QUARTZ FROM OTHER LOCATIONS

Within the Northern Pennines, the authors' attention has recently been drawn to the discovery of a handful of siderite mudstone nodules, up to 60 mm across, with out-weathered quartz septa of identical appearance of those described above from Teesdale, from the bank of the Bollihope Burn at Hill End, Frosterley [NZ 003 350] (Fig. 6) (Claire Holloway, *personal communication*, 2012). A close examination of this site revealed that the Carboniferous rocks overlying the Great Limestone are here concealed beneath a mantle of glacial till. There are no exposures of mudstones or other beds overlying the Great Limestone in the vicinity and, although the till exposed in the slipped stream banks includes a variety of locally-derived rock types, no clay ironstone nodules were seen by the authors during this investigation. It is therefore concluded that the few septarian nodules previously found here represent a fortuitous find of material derived from within the till. Their presence at this location suggests that such quartz-rich septarian nodules must be present within the Namurian rocks within the catchment of the ice sheet responsible for the formation of these till deposits, presumably higher in the Bollihope valley or surrounding areas of Weardale. Their source in situ is not known.



Figure 10. Cellular quartz septa weathered from a septarian nodule, the entire matrix of which has been dissolved away. The specimen is about 12 cm across. Hunterian Museum specimen (GLAHM 111595). Photograph: Hunterian Museum.

Although the authors have not undertaken a comprehensive search of major mineral collections, two specimens of 'cellular' quartz, one in the collections at the Hunterian Museum, University of Glasgow and the other at the Lapworth Museum, University of Birmingham, are noteworthy as examples of this distinctive and unusual form of the mineral. Although both specimens lack any locality information their very close similarity to the specimens described here from Teesdale merits brief comment here.

A specimen in the Hunterian Museum (Accession Number: GLAHM 111595) (Fig. 10) which lacks any original acquisition or locality information, bears a remarkable resemblance to some of the Teesdale specimens described above. The museum records include little information on the specimen, though suggest that it may be a candidate for a supposed 'fossil wasps' nest' known to have been acquired by William Hunter around 1780 from a friend of a collector by the name of Swediaur (or Schwediauer) (Durant and Rolfe, 1984). The museum notes comment that, as most of the material mentioned by Swediaur originated in Hungary or Austria, this specimen too may have come from eastern Europe, though the possibility of a Northern Pennines provenance cannot be discounted. A specimen in the Aston Hall Collection (Accession Number 32.23), now part of the Birmingham Museums and Art Gallery Collections at the Lapworth Museum of Geology, University of Birmingham, comprises a deeply weathered septarian nodule with thin quartz septa and remnants of the original clay ironstone matrix (Fig. 11). The specimen lacks any locality information, though is virtually identical in appearance to many of the specimens seen at Pike Law during the present investigation.

DISCUSSION

Septarian siderite mudstone nodules characterised by the presence of quartz septa, and which have locally undergone intense weathering or dissolution leading to



Figure 11. Cellular quartz showing thin quartz septa and residual clay ironstone in centre of specimen. The specimen in the Aston Hall Collection (now part of the Birmingham Museums and Art Gallery Collections at the Lapworth Museum, University of Birmingham) carries no locality information, though is typical of specimens described in this paper from Teesdale. Specimen is about 10 cm across. Photograph: R.E. Starkey.

the production of residual masses of 'cellular' quartz with a distinctive honey comb-like appearance, have been identified at two sites, and at two separate stratigraphical horizons, within mudstones of the Stainmore Formation in Teesdale. Closely similar specimens from a third site in Weardale appear to have been derived from glacial deposits and cannot therefore be assigned a precise geographical or stratigraphical provenance. However, in view of the generally local derivation of glacial deposits in this part of the Pennines, a primary source comparatively close to Hill End, and at a similar stratigraphical horizon to those from Teesdale seems extremely likely.

Although septarian nodules with carbonate septa are locally common in the Carboniferous mudstones of the Northern Pennine dales, despite many years of detailed field investigations of the rocks of the area, the authors are unaware of any other locations for such quartz-rich septaria. The authors have been unable to undertake a comprehensive search of major museum collections for similar examples of this unusual form of quartz as part of this study. However, in view of Rudler's (1905) comment that examples of this form of quartz from Teesdale were to be found "in most mineral collections", it is likely that many such specimens still exist, though perhaps with locality information, if any, restricted to 'Teesdale'.

No features have been observed in any of the specimens from either Pike Law or Coldberry Gutter which might reasonably be regarded as diagnostic of these locations. The origins of other un-provenanced specimens of such 'cellular' quartz, although identical in appearance to those described here from Pike Law and Coldberry Gutter, cannot therefore be suggested.

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A REVIEW OF THE OCCURRENCES OF HYDROCARBON-CONTAINING MATERIALS IN LEICESTERSHIRE

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This review describes the occurrences of hydrocarbon-containing materials in Leicestershire. It also highlights the role that the analytical work that has been carried out on some of this material has had on the former controversy related to the origin of naturally-occurring oil and bitumen. These, and other, analyses have also shown that some of the hydrocarbon-containing materials from Leicestershire are enriched with a number of transition metals: including copper, vanadium, uranium and rare earth metals.

INTRODUCTION

The substances commonly referred to as 'hydrocarbons' are mainly complex mixtures of hundreds, if not thousands, of hydrocarbons and their derivatives together with other compounds (an extensive review of the subject has been published by Gaines *et al.*, 2009). Bearing in mind this heterogeneity, these 'hydrocarbons' will be described generically as hydrocarbon-containing materials or mixtures (HCMs). The majority of the HCMs that form the world's gas, oil and bitumen reserves have been produced by biogenic mechanisms, i.e., they are biologically-derived; however, some HCMs may also be formed by abiogenic processes (Bath *et al.*, 1986; see also Gaines *et al.*, 2009). Given that some of the occurrences of HCMs from Leicestershire have played a significant part in the earlier controversy related to their biogenic or abiogenic origin, a number of analyses will be summarised below.

Whilst some biogenic HCMs are almost pure hydrocarbons *sensu stricto* (C_xH_y), others contain various proportions of chemically modified hydrocarbon derivatives that incorporate other elements, e.g., nitrogen and/or oxygen and/or sulphur ($C_xH_yR_z$ where $R = N/O/S$), together with some dissolved gases and/or liquids and small amounts of inorganic compounds: e.g., those containing calcium, iron, copper, nickel, vanadium, uranium, etc. (Parnell, 1988a). Given this heterogeneity, it is, perhaps, inevitable that the nomenclature of the HCMs is rather ill-defined; however, the plethora of names that have been given to various HCMs has been listed by several authors and will not be repeated here; see: Greg and Lettsom (1858, pp. 8-19), Dana and Ford (1932, pp. 775-779) and Read (1984, pp. 341-348).

Many of the HCMs that occur in Leicestershire have not been subjected to detailed chemical analysis; consequently, for the purposes of this review, they will be divided into the four broad classes: gas, oil and bitumen, together with coal and jet:

- Gas: Mixtures of chemicals that are gases at room temperature and atmospheric pressure. They are mainly hydrocarbons (C_xH_y , $x \leq 4$) mixed with other gaseous compounds: e.g., water vapour, nitrogen, hydrogen sulphide, carbon dioxide.
- Oil: (including the materials termed petroleum or naphtha): Mixtures of chemicals that are free-flowing liquids at room temperature and atmospheric pressure.

They are mainly hydrocarbons (C_xH_y), together with modified hydrocarbons ($C_xH_yR_z$), and they frequently contain other liquid compounds: e.g., water, brine, and various dissolved gases: e.g. hydrocarbons, nitrogen, hydrogen sulphide, carbon dioxide.

- Bitumen (including the materials termed pyrobitumen, asphalt, asphaltite, asphaltum or mineral pitch): These viscous to solid, tar- to pitch-like mixtures of chemicals will be referred to as bitumen (this appears to be the preferred term in the geosciences; other sciences sometimes use the term asphalt). Bitumen contains a greater proportion of higher molecular weight and modified hydrocarbons ($C_xH_yR_z$) and these are usually mixed with volatile components, non-bituminous organic matter and some inorganic compounds. Samples of bitumen can be highly viscous liquids; others vary in consistency from plastic to brittle solids. At room temperature and atmospheric pressure any dissolved volatile components contained in the more mobile samples of bitumen are gradually released. On exposure to air the more reactive compounds may be oxidised. Both of these processes result in harder, more solid bitumens.
- Coal and jet: Coal is the general name given to stratified accumulations of solid carbonaceous material derived from vegetation. A number of different types of coal have been described (in the order of decreasing carbon content): anthracite, bituminous coal, cannel coal and lignite (brown coal); although, cannel coals are derived from spores, algae and/or pollen rather than bulk vegetation. Jet is formed from isolated waterlogged timbers that have been buried in sediment. Coal and jet are not considered further in this review, apart from a brief summary of the extent of the Leicestershire coalfields and an occurrence of jet from Harston.

During the preparation of this article information on specimens in various collections was acquired: the King Collection (now at the National Museum of Wales, Cardiff); the Department of Geology, University of Leicester; the Leicester City Museum (New Walk Museum), Leicester; Calke Abbey (National Trust), Ticknall, Derbyshire; and the collections of Steve Critchley, Neil Hubbard and John Jones. A number of specimens from these collections are described below: those from the King Collection are identified as Kxxxx (NMW83.41G.Myyyy) and from the King Reserve

Collection Kxx-yyy, those from the Department of Geology at the University of Leicester identified as LEIUG xxxxx and those from New Walk Museum, Leicester are identified as LEICS Gxxx.yyyy.z.

LOCATIONS

The locations of the occurrences of HCMs in Leicestershire are shown in Figure 1.

Ashby Woulds, Ashby-de-la-Zouch

King (1973) described an occurrence of an oil impregnation in septarian siderite-mudstone nodules from the 'Pot A Mudstones' in the Pottery Clay Series of the Middle Coal Measures in the clay pit worked by Messers Ellistown Pipes Ltd. at Albert Village [SK 301 177]; there is now a water-filled pit, together with extensive worked ground and waste tips to the south, that occupy a large part of SK 30 17. The geology of this area has been described by Worssam and Old (1988), and Carney *et al.* (2001) noted that there had been intermittent opencast extraction of fireclay at the Donnington Extension [SK 3062 1760] with the resources being the seatearths occurring within the 150 m-thick 'Pottery Clays' formation. Mining was initially concentrated in the seatearths from P31 (Derby) coal down to P34 (Ell) coal but strata down to the P41 seam had also been worked.

King (1973) noted that:

the petroleum soaks the siderite mudstone to various shades of dark brown to almost black and is concentrated towards the centre of the nodules. The soaked siderite, when crushed and strongly heated, readily burns with a sooty-flame [see K69-121].

King (1983) also referred to an 'oily compound' in his description of the occurrence of galena in septarian nodules near Albert Village where:

the septa voids themselves are barren of sulphides, the only minerals being present being crystallised siderite, sometimes sphaerosiderite, and an oily compound...galena, sphalerite and sometimes calcite have then been developed in the cracks.

Breedon Hill Quarry, Breedon on the Hill

The occurrences of bitumen at Breedon Hill Quarry [SK 40 23] were found in the Milldale Limestone Formation (dolostones and mud-mound reef facies). These limestones and the younger Cloud Hill Dolostone Formation (mudstones and mud-mound dolostones) are of Carboniferous age and are separated by a marked unconformity (with fissure and cave development) from the overlying Triassic Breedon Breccia and the sandstones, siltstones and mudstones of the Sherwood Sandstone and the Mercia Mudstone groups (Ambrose, 2013).

Colman (1997) described a small nodule that was found on the margins of a cave void, in the lowest bench (Tim Colman, *personal communication*), of Breedon Hill Quarry; possibly the cave at SK 4070 2351 noted by Ambrose and Carney (1997a, Figure 2). The dark grey to black sub-spherical nodule (about 20 mm in diameter) resembled bitumen; however, some parts were very hard on crushing

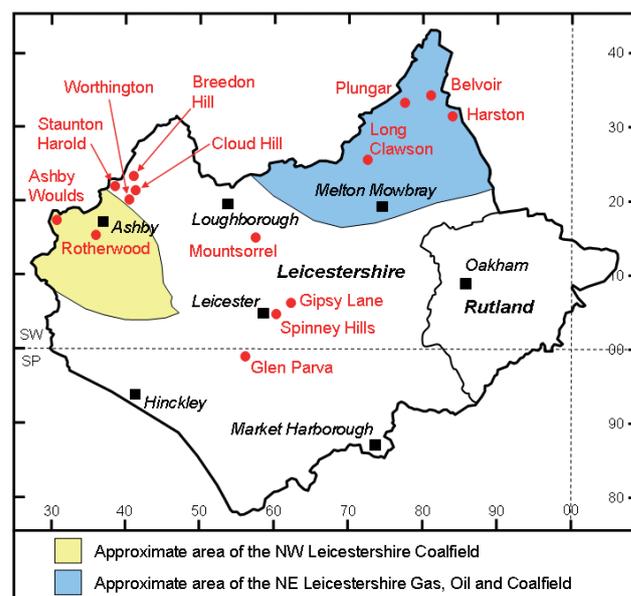


Figure 1. The locations of hydrocarbon-containing materials in Leicestershire.

(like a sulphide). It was poorly crystalline, with an 'earthy' texture; the surface had a 'knobbly' appearance as it consisted of abundant small spheroids that were highly reflective when freshly broken and was associated with calcite, a crystalline orange mineral (possibly baryte) and appeared to be coated by later clay. The nodule was found to be radioactive and an XRF scan showed that it probably contained more than 1% uranium. Autoradiography indicated that the uranium appeared to be distributed throughout the black earthy material, but not in a uniform fashion, as it was clearly composed of numerous very small (sub-mm) point sources (possibly uraninite). This occurrence was also summarised in Carney *et al.* (2001).

In their description of the copper mineralisation at Breedon Hill Quarry, Carney, *et al.* (2001) recorded the occurrence of thick calcite vein systems within bitumen-stained, brecciated dolostones to the northwest of a prominent northeast- to north-trending fault that traverses the quarry (Ambrose and Carney, 1997a); this occurrence would appear to be near SK 406 235. The bitumen-staining was found in cavities in the brecciated dolostones that were lined with scalenohedral calcite associated with chalcopyrite, minor sphalerite and spherules of malachite (Carney *et al.*, 2001).

Cloud Hill Quarry, Breedon on the Hill - Worthington

In the past the Cloud Hill Quarry [SK 41 21] has also been known as Breedon Cloud Quarry or just Breedon Cloud. The boundary between the parishes of Breedon on the Hill and Worthington passes through the quarry and, whilst the majority of the quarry is in the parish of Breedon on the Hill, the south west corner is in the parish of Worthington (both parish names have appeared on mineral labels). The general geology of the locality is similar to that of Breedon Hill Quarry (described above). From literature records, it is clear

that some of the bitumen that occurs at Cloud Hill Quarry is radioactive. The occurrences of bitumen and uraniferous bitumen will be considered in separate sections; however, the mineral associations described in both sections should be born in mind.

Bitumen

King (1973) recorded two rather poorly-defined localities for bitumen from the Cloud Hill Dolostone Formation on the west to northwest side of the quarry that were found during visits in 1939; although, the same mineral specimen (K39BC2) was referred to in the description of both occurrences:

- Early in 1939, millerite was found in cavities in dolomite where the only associate was bitumen which partially filled adjacent cavities (King, 1973, p. 149). Whilst the exact locality was not recorded, it was almost certainly on the western side of the quarry, immediately to the east of the site of the former lime kiln; from old maps of the quarry this would appear to be near SK 410 214.
- In July 1939, bitumen was found in cavities in the dolomite; also associated with millerite (King, 1973, p. 520). Whilst the exact locality was not recorded, it was at the northern extremity of the western face of the quarry; from old maps of the quarry this would appear to be near SK 411 218. The cavities in the dolomite had a maximum diameter 2.3 mm and the bitumen occupied no more than 50% of the available volume; it was soft and jet-black and resembled the bitumen found at Mountsorrel (see the Mountsorrel section, below).

In their description of the Milldale Limestone Formation at Cloud Hill Quarry, Carney *et al.* (2001) noted an exposure on the southern face of beds with undulating bounding surfaces comprising green and grey, commonly bituminous clay, shaly mudstone and siltstone. This location would appear to be near SK 414 209.

Uraniferous bitumen

The occurrence of uraniferous bitumen at Cloud Hill Quarry was found on the east side of the quarry (King and Ford, 1968) and the first record is that of Sylvester-Bradley and King (1963), who noted that:

radioactive bitumen occurs as small, globular masses... in decalcified dolomite in the Carboniferous Limestone of Breedon Cloud, Leicestershire, just below the Triassic unconformity; associated are chalcocite, galena, calcite, dolomite, marcasite and a molybdenum mineral, with (as oxidation features) malachite, azurite, cerussite, and goethite.

The molybdenum-containing mineral was later shown to be wulfenite (King, 1980). King and Ford (1968) also noted that lead-copper mineralisation, associated with baryte, calcite and uraniferous hydrocarbon, had formed on the east face of the quarry at the unconformity between the dolomitised Carboniferous Limestone and the Triassic rocks; they described the occurrence in more detail:

at Cloud Hill quarries this development is exposed to perfection...[and] takes the form of a series of gulls, extending to an average depth of 6 m from the [Triassic] marl and sandstone overburden. In these gulls the limestone has been almost completely de-calcified, the resultant residue being

a bright yellow sand composed of quartz grains, dolomite crystals and downwards percolating Triassic sand...at the extreme base of the gulls a hydrocarbon mineral appears. It takes the form of globules and small veins in the intensely dolomitised limestone. This mineral is quite brittle and resembles anthracite in appearance. As it is quite strongly radioactive it may be termed a thucholite, although its exact composition is as yet unknown.

Thucholite usually contains thorium, uranium and various HCMs (Dana and Ford, 1932, p. 778); however, subsequent analyses do not mention thorium (see below).

In his description of the same occurrence, King (1973) noted that:

there is but one locality where this [uraniferous bitumen] has been found, namely Cloud Hill Quarry (SK 413 214)... it occurred as roughly spherical masses, droplets, rough masses and veinlets of greenish-black compact brittle material, with a perfect conchoidal fracture, closely resembling anthracite. Droplets and spherules have been seen to attain a diameter of 18 mm, and a width of 4.6 mm. An average of 6 weighings has provided a specific gravity of 1.48 and a hardness of approximately 2.5. The mineral occupies the base of solution cavities in highly metasomatised limestone and is associated with yellow dolomite sand and a little limonite. These solution cavities, with a few exceptions, do not extend below the level of the first quarry bench, i.e., about 18 m... A lead-shielded Geiger-counter showed that the asphaltite is fairly radioactive...[and]...compares well with the hydrocarbon mineral which occurs in the [Ty Gwyn] copper mine on the Great Ormes Head at Llandudno...[and]... is slightly less radioactive than the material from the Great Laxey Mine on the Isle of Man.

K2433-63 (NMW83.41G.M.9320) is an example of the bitumen from Cloud Hill Quarry and it has been shown to be very weakly radioactive (Tom Cotterell, *personal communication*).

Bath *et al.* (1986) reported analytical data (neutron activation analysis) for the trace metal composition of the uraniferous bitumen from fourteen UK localities; these included Cloud Hill Quarry where globular masses of bitumen, together with Cu/Pb/Mo/Fe minerals, occurred in dolomitic Carboniferous Limestone just below an unconformity with Triassic rocks. The results for four of the fourteen localities are shown in Table 1 (see p. 28) and it can be seen that a number of metals are present in significant amounts. As it contains 1.94 wt% uranium, the bitumen from Cloud Hill Quarry is similar to that from Ty Gwyn, Great Orme (1.38 wt% uranium) but it contains less than the bitumen from both Southwick (4.57 wt% uranium) and Laxey (9.60 wt% uranium). A bulk analysis of the bitumen from Cloud Hill Quarry yielded 4600 ppm uranium; this occurred predominantly as uraninite (Bath *et al.*, 1986). In the context of the base metal mineralisation in the East Midlands, it is interesting to see that the Cloud Hill Quarry bitumen also contains significant amounts of copper (900 ppm) and vanadium (3930 ppm). The presence of several of the rare earth elements (REEs) is, perhaps, more surprising (see Table 1).

Parnell (1988b) also listed Cloud Hill Quarry as one of the ten occurrences of bitumen that were investigated for their uranium content; although, some of the results shown

	Cloud Hill ¹	Great Orme ²	Southwick ³	Laxey ⁴
U ⁵	1.94 wt%	1.38 wt%	4.57 wt%	9.6 wt%
U ⁶	0.46 wt%	1.30 wt%	4.57 wt%	18.75 wt%
La ⁵	80	<30	<200	500
Ce ⁵	<300	1070	700	<2000
Nd ⁵	<800	600	2600	<4000
Sm ⁵	2200	2100	6500	1.1 wt%
Eu ⁵	10	8	443	215
Tb ⁵	6.2	4.0	285	94
Yb ⁵	9	<5	440	160
Lu ⁵	2.2	2.1	22	22
Ni ⁵	n.a. ⁷	4000	n.a. ⁷	<30
V ⁵	3930	115	420	290
Cu ⁵	900	9700	6000	6000

1. Cloud Hill Quarry, Breedon on the Hill, Leicestershire.
2. Ty Gwyn, Great Orme, Conwy.
3. Southwick, Dumfries and Galloway.
4. Laxey, Isle of Man.
5. Bath, *et al.*, 1986; neutron activation analysis (Northern Universities Reactor Centre, Risley, Cheshire), values in ppm (metal), unless stated otherwise.
6. Parnell, 1988b; neutron activation analysis (Imperial College Reactor Centre, Silwood Park, Berkshire), values in wt % (metal).
7. n.a. = not analysed.

Table 1. Partial elemental composition of selected UK bitumen samples (taken from Bath *et al.*, 1986; Parnell, 1988b).

in Table 1, e.g. Cloud Hill Quarry 0.46 wt % uranium; Laxey 18.75 wt% uranium, differ from those recorded by Bath *et al.* (1986). Calcium (6-7 wt%) was also present but appeared to be distributed throughout the samples and was therefore within the bitumen rather than as a component of a uranium-containing mineral; inclusions of gangue minerals were found within the bitumen: isolated dolomite crystals and some baryte (Parnell, 1988b).

In his description of the occurrences of uraninite in the UK, Tindle (2008) noted that it occurred as microscopic inclusions in hydrocarbons within hydrothermal Pb-Zn veins cutting Carboniferous Limestone at Breedon Cloud, near Shepshed. It was noted earlier that Breedon Cloud (Cloud Hill Quarry) is between Breedon on the Hill and Worthington; not near Shepshed.

Earl Ferrers' Mine, Dimmingsdale, Staunton Harold

The bitumen from the Earl Ferrers' Mine [SK 37 21] occurred in the Carboniferous rocks exposed in the former lime workings and lead mines: the Brigantian Ticknall Limestone Formation (dolostones and limestones) and possibly the adjacent Pendelian Morridge Formation (mudstones, siltstones and limestone). These beds are overlain by sandstone of Kinderscoutian age. The

Thringstone Fault (a major northwest-southeast trending reverse fault that passes ~300 m to the southwest of Dimmingsdale) brings the Carboniferous rocks into contact with the later Wingfield Flags (sandstones) and the Pennine Lower Coal Measures. A marked unconformity separates the Carboniferous rocks from the overlying siltstones and sandstones of the Triassic Sherwood Sandstone Group (Ambrose and Carney, 1997b; Carney *et al.*, 2001).

Hull (1860) noted that:

at Ticknall and Dimmingsdale [*sic*], the limestone is worked in caverns, and at the latter the rock is highly metalliferous. In one of the veins, the following minerals were obtained; copper pyrites, galena, calcareous spar, sparry iron-ore, blende, and bitumen.

In his description of specimens in the Ludlam Collection, Rudler (1905) repeated most of Hull's comments and indicated that Specimen No. 1377 was a good example of the occurrence of bitumen (using the term 'asphalt') at Staunton Harold, near Ashby-de-la-Zouch; Ashby-de-la-Zouch is the town in Leicestershire that is nearest to Staunton Harold.

Sylvester-Bradley and King (1963) noted that:

specimens retrieved from the dumps from the old lead mines at Staunton Harold...show that the bitumen formed about 35 per cent of the gangue, and is intimately associated with dolomite, baryte, galena, blende, chalcopyrite and rare hemimorphite.

King and Ford (1968) summarised the occurrence of bitumen in the Earl Ferrers' Mine and indicated that:

the metallic minerals are galena...blende...and pyrite. The gangue of these veins is of great interest. Baryte is the most prolific mineral...The remaining gangue minerals, constituting perhaps 60% of the whole gangue, are an asphaltite-type hydrocarbon and calcite.

King (1973) referred to these reports and provided a more detailed description of the occurrence of bitumen noting that:

asphaltum is an important and striking member of the paragenesis...of the old lead mine at Staunton Harold (SK 377 217)...it is evident, from a study of many specimens, that the distribution of asphaltum was partially restricted in the mine area, though, where it occurred, it was in great quantity...local heresay states that when access was obtained in 1939, asphaltum hung down in one of the adits in the form of stalactites, almost blocking progress along it. Some of it was extracted and used as fire-lighting material by the Hall's gamekeeper [Staunton Harold Hall, the seat of the Ferrers family]...The six small shaft dumps in the mine area...have all yielded asphaltum [see Figures 2 and 3]. One, furthest from the site of the old laundry (west) and south of the road to the Hall...has yielded several hundred specimens, all showing an association of asphaltum and galena, etc. This remarkable association of asphaltum and galena is well shown in specimen K788-1947 [NMW83.41G.M.855; Figure 4, and also Plate 3 in King (1983, p. 36)]...which shows a thin vein running through dolomitised limestone, along which the specimen has been broken. The brilliant cleavage faces of the galena, associated with jet-black asphaltum and red baryte, makes a striking contrast...Like the Mountsorrel asphaltum, that from Staunton Harold, when newly exposed is relatively mobile, hence the stalactites, and will very slowly ooze out of the veins. It tends to harden in time, developing a conchoidal fracture, but never

becomes brittle...The baryte, which always precedes the asphaltum precipitation, is almost always present...see also K2399-1947 [NMW83.41G.M.451]...At times, spherulitic asphaltum develops at Staunton Harold. The spherules may be enclosed in the gangue, but most commonly, they occur as almost perfect spheres in cavities, or attached to the matrix by a very small point on their surface area...These spheres may attain the maximum observed diameter of 6 mm, and provide positive evidence of the paragenetic sequence. Being young in the sequence, they are frequently 'frosted' with minute crystals of chalcopryrite. The spherules are jet-black, highly lustrous, and show no surface features being perfectly smooth. Like the vein material, they are soft, but produce a conchoidal fracture like pitch, see K3269 [NMW83.41G.M.9307].

Recently about 40 specimens with mineral associations that are characteristic of material from Staunton Harold have been found in the collections of Calke Abbey (~1 km to the northwest of Dimmingsdale; the former home of the Harpur-Crewe family and now a National Trust property). Amongst these specimens is an outstanding example of the spherulitic habit of bitumen noted above: an almost spherical globule of smooth, black bitumen (17 mm) associated with chalcopryrite, pyrite, galena, sphalerite and baryte (Fig. 5). A specimen in the John Jones Collection (No. 76079)



Figure 2. Veins of black, pitch-like bitumen with galena and sphalerite on baryte from Earl Ferrers' Mine (105 mm x 65 mm); Specimen No. LEIUG 24176; Photograph: Frank Ince.



Figure 3. A vein of black, pitch-like bitumen (showing flow features) with galena and pyrite on baryte from Earl Ferrers' Mine (65 mm x 35 mm); Specimen No. LEIUG 23591; Photograph: Frank Ince.

confirms the relatively early formation of bitumen as it contains a black lustrous spheroid (5 mm) encased in a calcite-galena matrix. Another specimen in the John Jones Collection (No. 75034) contains a section of an oval void (8 mm x 6 mm) in black bitumen associated with calcite and galena in dolomitised limestone (Fig. 6, see p. 30); in the past this void probably contained water or brine.

Staunton Harold was one of the three occurrences of bitumen (together with Mountsorrel and Windy Knoll) that were investigated by Xuemin *et al.* (1987) in an attempt to resolve the, then current, controversy related to the biogenic or abiogenic origin of HCMs (see the Mountsorrel section for a more detailed description of these investigations). The results suggested that the bitumen from Staunton Harold is of biogenic origin. Parnell (1988b) also listed Staunton Harold as one of the ten occurrences of bitumen that were investigated for their uranium content; however, the material from Staunton Harold did not contain any uranium. Parnell (1988b) also noted that the bitumen occurred with galena; although there was no evidence that they were coeval.

In his description of the occurrences of uraninite in the UK, Tindle (2008) mentioned that it occurred as microscopic inclusions in HCMs within hydrothermal

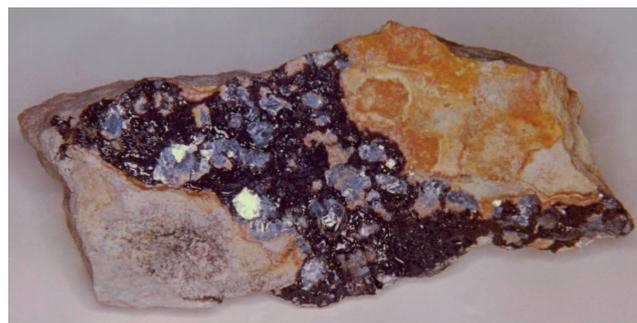


Figure 4. Black bitumen and lustrous galena on baryte from Earl Ferrers' Mine; Specimen No. K788-1947 (NMW83.41G.M.855); Photograph: Bob King.



Figure 5. A nearly spherical mass of black bitumen (17 mm) with chalcopryrite, pyrite, galena and sphalerite on pink baryte (155 mm x 90 mm), almost certainly from Earl Ferrers' Mine; Calke Abbey specimen; Photograph: Frank Ince (reproduced with the permission of Mariana Byng, National Trust Images).

Pb-Zn veins cutting Carboniferous Limestone at Staunton Harold, Ticknall, Leicestershire. It should be noted that the border between Leicestershire and Derbyshire follows the course of the Calke Brook that runs through Dimmingsdale; consequently, whilst Ticknall is a much larger village and close to Staunton Harold, Staunton Harold is in Leicestershire and Ticknall in Derbyshire (in the past this geographical quirk has caused some confusion with respect to the provenance of specimens from Staunton Harold).

Gipsy Lane Brick Pit, Leicester

The bitumen from the, now disused, Gipsy Lane Brick Pit [SK 61 06 - SK 61 07] occurred in the gypsum-rich horizons of the Cropwell Bishop Formation (Branscombe Mudstone Formation) of the Triassic Mercia Mudstone Group (Carney *et al.*, 2009; Manning, 2010a). These beds are overlain by mudstones of the Blue Anchor Formation and the later Penarth Group: the Westbury Formation and the Cotham Member of the Lilstock Formation (Carney *et al.*, 2009). Most of the area is now occupied by an



Figure 6. Part of a oval void (8 mm x 6 mm) in black bitumen associated with calcite and galena in dolomitised limestone from Earl Ferrers' Mine (45 mm x 40 mm); John Jones specimen (No. 75034); Photograph: Frank Ince..



Figure 7. Small black spheroids of bitumen (to 2 mm) on gypsum from Gipsy Lane Brick Pit (110 mm x 75 mm); Specimen (FI-0539) and photograph: Frank Ince..

industrial estate; however, a relatively small area at the north end of the former workings has been designated as an SSSI [SK 6190 0712].

Faithfull and Hubbard (1988) investigated the composition of the small black spheroids that were associated with the gypsum nodules (Fig. 7) that occur in the Gipsy Lane Brick Pit and demonstrated that they contained coffinite ($USiO_4 \cdot nH_2O$); they also noted that:

the spheroids undergo partial combustion when heated in air, thus appreciable quantities of organic material are probably present...[and] the coffinite/organic matrix seems to be homogeneous at magnifications at least up to 1000X.

In addition to the coffinite, Faithfull and Hubbard (1988) recorded that the bitumen-rich spheroids contained:

a grey copper sulphide, a pink nickel arsenide, and a cobalt-nickel-copper arsenide-sulphide...[that] may form 0% to 50% of the volume of the spheroids...mineralogical expressions of these elements are not clear from the diffraction patterns...[and] work on these phases is continuing.

The spheroids also contained small amounts of other elements, e.g. iron, phosphorus and yttrium (which led to an early, erroneous, identification of chernovite, $YAsO_4$, as a component of the spheroids); the Triassic marl also contained black, vanadium-rich areas. Oxidation of the various components of the spheroids has, in some cases, resulted in the formation of malachite, erythrite, lavendulan (Fig. 8), and rare azurite; however, Faithfull and Hubbard (1988) noted that, in general, only one of these minerals is present on any one spheroid. They also pointed out that the mineralogy at Gipsy Lane Brick Pit was similar to the U-Cu-Co-Ni-As mineralisation at Budleigh Salterton, Devon (see Bateson, 1987). The geology and mineralogy of Gipsy Lane Brick Pit has been summarised by Manning (2010a).

Glen Parva Brick Pit, Glen Parva

In the past the Glen Parva Brick Pit [SP 56 98] was also known as the Butterley and Blaby Brick Pit; the area has been landscaped and part of it is now occupied by a housing estate. It is worth noting that there is a disused brick pit in South Wigston [SP 587 985] that has also been known

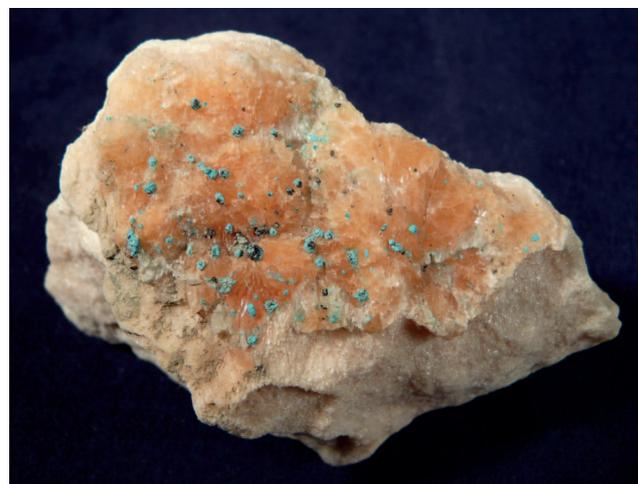


Figure 8. Bluish-green lavendulan with residual black bitumen on gypsum from Gipsy Lane Brick Pit (65 mm x 40 mm); Neil Hubbard specimen (No. 1231); Photograph: Frank Ince.

as the Glen Parva (or Wigston Junction) Brick Pit (Carney *et al.*, 2009, p. 20). The oil from the Glen Parva Brick Pit probably occurred in the Cotham Member of the Lilstock Formation of the Penarth Group (see below); this horizon was preceded by the Westbury Formation of the Penarth Group and the earlier Mercia Mudstone Group (Carney *et al.*, 2009). For a description of the geology of the brick pit and the first UK occurrence of tangeite and volborthite see King and Dixon (1971).

King (1973) described an oil-coated specimen of celestine from the Glen Parva Brick Pit, K2741 (NMW83.41G.M.8710), noting that it was:

given to the writer by the late Mr B.N. Wale of Loughborough in 1938, [and] is known to have originated from the Glen Parva Pit, but the exact horizon is unknown...celestine is present... of a pale bluish-white colour...[with] calcite...baryte and marcasite...[the specimen] reacts strikingly under short wave ultraviolet light, the calcite being a strong orange colour and the celestine a pale bluish-white...the activator which promotes the exotic orange colour under short wave ultraviolet light, is unknown, but occasionally oily films suggests that a hydrocarbon compound may be involved.

A search of the accessible parts of the former brick pit in 2013 did not reveal any similar material. In their description of the Cotham Member of the Lilstock Formation (see above), Carney *et al.* (2009) described some disc-shaped nodules up to 0.6 m across that were found in the Cotham Member in excavations that were carried out at Knighton, Leicester [SK 599 006]; the internal cavities of these nodules contained crystals of celestine partially replaced by baryte. It seems reasonable to suggest that the celestine from the Glen Parva Brick Pit occurred at the same horizon.

Harston No. 5 Ironstone Pit, Harston

The jet from the Harston No. 5 Pit [SK 84 31] was probably derived from the Lower Jurassic Whitby Mudstone Formation (Upper Lias). This mudstone overlies Marlstone Rock Formation (ferruginous sandstone and ironstone) and the earlier Dyrham Formation (siltstone and mudstone) and is succeeded by the Middle Jurassic Northampton Sand Formation (ooidal ironstone) (Carney *et al.*, 2004).

King (1973) described the occurrence of jet from the ironstone workings as being:

common throughout the local Lias...small masses, up to 360 mm in length and up to 114 mm thick, representing coniferous driftwood, are of frequent occurrence in the Upper Lias of Harston, northeast of Croxton Kerriel, especially in the Harston No. 5 Pit at SK 846 310. The Upper Lias beds exposed here do not extend higher than the upper beds of the [Harpoceras] falciferum zone, and the jet occurs most frequently...[in] the H. exeratum subzone. The jet is not of lapidary standard, the woody texture being pronounced, but there are areas which are dense and may lend themselves to cutting and polishing. The colour is typically jet-black.

Leicestershire coalfields

The Leicestershire coalfields are described in Worssam and Old (1988), Carney *et al.* (2001) and Carney *et al.* (2004); however, apart from a general description of the extent of the Leicestershire coalfields (see Figure 1), the

HCMs occurring in the Coal Measures are not considered further in this review.

Leicestershire gas and oilfield

The northeast of Leicestershire (see Figure 1) is part of the East Midlands Oil Province where a series of major rift basins in Carboniferous rocks contain oil: mainly in Namurian sandstones, with smaller amounts in the Coal Measures and fractured Dinantian limestones. This part of the East Midlands has been explored for oil (and gas) since before the Second World War and a number of small oilfields have been developed: the 33 oil wells of the Plungar oilfield [SK 76 31 - SK 77 35] produced 304,067 barrels of oil from 1954 until 1980; at Long Clawson [SK 7245 2565] oil production started in 1990; oil has also been discovered at a number of other localities in the Vale of Belvoir, e.g. Belvoir No. 1 [SK 8092 3397] (Harrison *et al.*, 2002; Carney *et al.*, 2004). The cores from a number of boreholes that have been drilled in various parts of northeast Leicestershire have also shown the presence of oil and/or bitumen in Carboniferous rocks (Carney *et al.*, 2004; Nigel Smith, *personal communication*); some of these occurrences are shown in Table 2 (see p. 32).

Bath *et al.* (1986) described an occurrence of bitumen in a borehole in the Vale of Belvoir; it was found in a vesicular basalt that was encountered in the Coal Measures. Despite some efforts to identify the site of this borehole, its location remains uncertain; it might be one of the Harlequin boreholes near Radcliffe on Trent, Nottinghamshire (Nigel Smith, *personal communication*) but could be the Bottesford 2 Borehole (see Table 2). The very viscous, black bitumen was found in vesicles in the basalt and it was noted that it hardened after collection. It contained various biomarkers and was thought to be a mixture of biodegraded and non-biodegraded bitumen of high maturity; there was no evidence for an abiogenic component (Bath *et al.*, 1986).

Mountsorrel quarries

There have been a number of distinct quarries in the parishes of Mountsorrel and Quorn (see Figure 11 in King and Ford, 1968, p. 49). Bitumen has only been recorded from two of these quarries and the occurrences will be described in separate sections.

Mountsorrel Main Quarry, Mountsorrel

In the past Mountsorrel Main Quarry [SK 57 14] has also been known as Castle Hill Quarry. The occurrences of oil and bitumen were associated with a basalt-microgabbro (dolerite) dyke, probably of Carboniferous age, that was intruded into the Ordovician Mountsorrel Granodiorite (Carney and Pharaoh, 1999; Carney *et al.*, 2009). These igneous rocks are separated by a marked unconformity from the overlying mudstones of the Triassic Mercia Mudstone Group (Gunthorpe Member and the later Edwalton Member). Mountsorrel Main Quarry has been designated as an SSSI for its diverse mineralogy and the importance of the occurrence of bitumen in the controversy related to the biogenic or abiogenic origin of hydrocarbon-containing materials (Manning, 2010b). Whilst the majority of the

Borehole	Grid Reference	Rock ¹	Depth (m)	Oil
Long Clawson No. 1	SK 7350 2841	MG	1142-1143 1147	Sweet oily smell Sweet oily smell
Long Clawson No. 2	SK 7245 2506	MG	824-833 846-859	0.8 barrels per day 76 barrels per day
Great Framlands	SK 7257 2229	MG	755-765 796-798	Oil show Oil show
Bottesford No. 2	SK 8043 3740	CM, V, MG, CL	612-965	Intermittent traces of heavy oil
Redmile No. 1	SK 8086 3440	CM, MG CL	588-893 927-936	Intermittent oil/tar stains Patchy oil stains
Belvoir No. 1	SK 8092 3398	MG	887	27 barrels per day
Croxton Abbey	SK 8284 2719	CM MG	668 705-711	Slight oil stains Slight oil stains/impregnations
Croxton Banks	SK 8298 3004	CM	223	Bitumen

1. Rock: MG Millstone Grit; CM Coal Measures; V Volcanic; CL Carboniferous Limestone.

Table 2. Boreholes containing oil/bitumen from northeast Leicestershire (Carney *et al.*, 2004; Nigel Smith, *personal communication*).

quarry has been back-filled and landscaped, exposures of the granodiorite and the dyke have been preserved in a small area at SK 5759 1496 (Carney *et al.*, 2009).

Oil

King (1973) described an occurrence of oil as:

a minor occurrence...in the now abandoned main quarry at Mountsorrel [SK 579 149]. The western limits of the quarry are bounded by a large plane surface, which represents the faulted footwall of a dolerite dyke, striking 309°, with an average dip of 60° to the southwest. The dyke, to the southwest of this wall, remains only as thoroughly smashed and metasomatised gouge, up to 1.3 m wide. Strong tectonic movement along it subsequent to its deposition is obvious. Running through the highly chloritised gouge are multiple-vein assemblages of calcite with minor dolomite and pyrite. These thin strings frequently aggregate to form veins up to 124 mm in width. These are highly cavernous and usually completely soaked in oil. The cavities are usually lined with well crystallised calcite...and frequently filled, almost to capacity, with highly mobile soot-brown coloured petroleum, which literally pours out of the cavities...in time this mobility is lost, the liquid becomes more viscous and eventually drips from the cavities to form small stalactites. Some of these cavities are relatively large, attaining a diameter of 94 mm. The petroleum fluoresces a strong olive-green colour under short wave ultraviolet light, though this may be modified by the underlying calcite which fluoresces yellowish-orange. There is little or no reaction under long wave ultraviolet light.

King (1973) based part of this description on two specimens in his own collection: K258-1947 (NMW83.41G.M.9284) and K2362 (NMW83.41G.M.9285) and he also referred to two specimens in the collections at New Walk Museum, Leicester: LEICS G223.1924.136.0: massive light brown calcite with traces of dark brown oily material in some of the crevices; LEICS G645.1965.0: a thin cavernous carbonate vein (to 15 mm wide) containing dark brown to black, now pitch-like, bitumen (Fig. 9).

Bitumen.

In his description of Specimen No. 1378 in the Ludlam Collection, Rudler (1905, p. 179) noted that bitumen was associated with calcite, which has crystallised in the joints of the Mountsorrel granodiorite. King (1959) placed the occurrence of bitumen from Mountsorrel Main Quarry in his 'Hydrothermal Stage 3 (Dolerite)' component of the paragenesis and he noted that:

the great dolerite dyke, which is so imposing in the main Mountsorrel quarry, is accompanied by a complex development of veins, influencing both the dolerite and the granodiorite... These veins may be in single or composite form, and are made up of calcite, dolomite, pyrite, goethite and an asphaltic compound in a wide range of associations".

King (1959) described the bitumen as an:

asphaltic compound: The exact nature of this mineral has not yet been determined. It seems probable from preliminary tests that more than one asphaltic compound is present,



Figure 9. Dark brown to black, pitch-like bitumen in a carbonate vein from Mountsorrel Main Quarry (70 mm x 25 mm); Specimen No. LEICS G645.1965.0; Photograph: Frank Ince.

and that the substance is more likely to be a mixture. It is a very common member of this suite and may be collected from every metasomatic vein where exposed. It is most frequently associated with calcite and dolomite, particularly in geodes when it commonly obscures its associates. Very often on the breaking open of a cavity it will pour out as a mobile oily liquid...and ignites readily with a flame...but more usually it is viscous and drains from the cavity much more slowly. This process is never completed as due to either volatilisation or to oxidation, it gradually hardens on exposure to a black pitch-like substance and stalactitic growths may be observed where the liquid has drained from some large cavity [Figure 10]. When liquid it possesses an oily and not disagreeable smell, but when in solid form it is odourless. In the latter state it melts at 92°C, this being the average of six samples. Above this temperature it burns with a bright but sooty flame and leaves much ash.

King (1959) also recorded the minerals that were associated with the bitumen: calcite, dolomite, magnesite?, pyrite, marcasite, goethite, clay mineral, chlorite, epidote and quartz.

King (1973) provided a more detailed description of the occurrence of bitumen (usually referred to as “asphaltum”) and indicated that:

the old main quarry at Mountsorrel has produced a great variety of habits and exotic specimens of asphaltum. Individual habits are dependant upon the associated minerals. Whatever the association, the asphaltum is always jet-black in colour and, when completely enclosed by its associates (most commonly dolomite), is soft and plastic. Under its own weight it becomes mobile and slowly oozes out of the cavities in which it occurs [see Figures 11 and 12]. Due to oxidation or loss of volatiles, the material slowly hardens. Though it develops a conchoidal fracture, it never becomes brittle or splinters like anthracite under pressure. A needle will always produce an indentation. The principle gangue mineral is a highly cavitated dolomite, the cavities of which are commonly occupied by asphaltum, though never to complete capacity...There is always a bubble-shaped void in the asphaltum, indicating the former presence of brine. The size of the cavities [in the dolomite] varies greatly, but the maximum diameter observed is 38 mm. Most cavities are unconnected one with another, indicating the contemporaneous origin of the asphaltum and the dolomite. Occasionally pyrite and calcite are associated, lining cavities in the dolomite, but they are never very obvious, often being buried beneath the younger asphaltum. Asphaltum may also form well-developed veins, associated with the same gangue. These are usually quite thin and occupy open joints, forming a stockwork in both doleritic and granitic wallrocks. Exceptionally, wide veins do occur from time to time, one of which measured 87 mm in width. Some, due to their isolation from the atmosphere, are very soft and tacky and collapse under their own weight. Others, presumably previously subjected to weathering conditions, are quite competent and may be extracted ex situ as runner-like blocks. The Mountsorrel asphaltum is intimately connected with the hydrothermal activity which followed the intrusion of the dolerite dykes, the Hydrothermal Stage 3 of King (1959). Metasomatism has more or less affected the dolerite and its flanking granodiorite to varying depths on either side of the dykes, but the best asphaltic development has always been on the footwall side, extending out into the granodiorite for a distance of 1.8 m...Under shortwave ultraviolet light the asphaltum-dolomite specimens show a striking colour contrast. The asphaltum fluoresces dull yellowish-green,

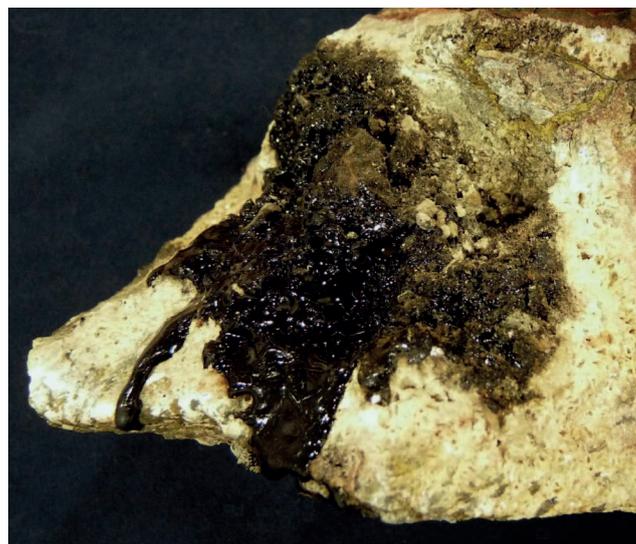


Figure 10. Dark brown to black, pitch-like bitumen (showing flow features) with pyrite and goethite in a brecciated dolomite vein from Mountsorrel Main Quarry (95 x 75 mm); Specimen No. LEIUG 69429; Photograph: Frank Ince.



Figure 11. Black, pitch-like bitumen (with flow features) oozing through a cavity lined with pyrite and dolomite, from the footwall of a dolerite dyke on the bottom level of the NW face (November 1957), Mountsorrel Main Quarry (320 mm x 150 mm); John Jones specimen (No. 81206); Photograph: Frank Ince.



Figure 12. A close-up of Figure 11: black, pitch-like bitumen (with flow features) oozing through a cavity lined with pyrite and dolomite, from Mountsorrel Main Quarry (150 mm x 110 mm); John Jones specimen (No. 81206); Photograph: Frank Ince.

while the dolomite transmits [emits?] a dull red light. Under longwave ultraviolet light the dolomite retains its red colour, but the asphaltum does not react.

In his description of dolomite from Mountsorrel Main Quarry King (1973) noted that in one situation:

it takes the form of complete replacement of the calcite by dolomite, forming large rough crystals pseudomorphous after scalenohedral calcite...The dolomite is usually pure white, but on occasions is stained by its associates, especially asphaltum and goethite,...[and] is highly cavernous [see Figure 13], producing a froth-like appearance. This is partly a primary structure, but pseudomorphism plays a part in its development. The cavities are very varied in dimension, the largest observed being 38 mm in diameter, but the average diameter is 9.1 mm. They are usually empty, but may contain asphaltum (up to $\frac{3}{4}$ capacity, the remaining $\frac{1}{4}$ sometimes consisting of sodium chloride brine), magnesite, marcasite, and sometimes small rhombic calcite.

King (1973) also noted that the bitumen was associated with: calcite, dolomite, pyrite, marcasite, goethite, magnesite, jarosite; see K1037-1952 (NMW83.41G.M.9305) and K2363-1961 (NMW83.41G.M.9306).

Whilst describing the occurrence of bitumen at Earl Ferrers' Mine, Staunton Harold (see above), it was mentioned that the analysis of bitumen from the East Midlands played an important part in the investigation of the biogenic or abiogenic origin of HCMs and samples of the oil and bitumen from Mountsorrel Main Quarry have been the subject of a number of investigations. King (1959) and Ford (1968) suggested that the oil and bitumen migrated from overlying Namurian shales during a stage of hydrothermal mineralisation. Sylvester-Bradley and King (1963) and Ponnampereuma and Pering (1966) thought that they might be of abiogenic origin; however, its carbon isotope ratio was shown to be similar to that of biogenic petroleum samples (Pering and Ponnampereuma, 1969).



Figure 13. Black pitch-like bitumen in cavernous dolomite with minor calcite and pyrite from Mountsorrel Main Quarry (70 mm x 70 mm); Specimen No. LEICS G33.1964.7 (one of seven similar specimens); Photograph: Frank Ince.

Aucott and Clarke (1966) described the chemical and amino acid analysis of the bitumen from Mountsorrel Main Quarry that was obtained from freshly broken-open cavities in the calcite-dolomite veins within altered granodiorite and also from cavities in the calcite-dolomite veins within a crush breccia containing angular fragments of intensely altered green granodiorite. Bearing in mind the results of the analyses of bitumen from Cloud Hill Quarry (see Table 1), it is interesting to note that an XRF analysis of the ash from partially purified bitumen from Mountsorrel Main Quarry contained chromium and two REEs: cerium (200-400 ppm) and lanthanum (75-100 ppm); although, uranium was not detected. Aucott and Clarke (1966) also reported the presence of a variety of amino acids in the material from Mountsorrel Main Quarry in amounts similar to those found in recent muddy sand and they suggested that these amino acids indicated a biogenic origin for the bitumen. Xuemin *et al.* (1987) investigated the bitumen from Mountsorrel Main Quarry (together with material from Staunton Harold and Windy Knoll, Castleton, Derbyshire) and their studies were designed to resolve the controversy related to the biogenic or abiogenic origin of these HCMs. Their analyses indicated that a range of biomarkers were present in the soluble fraction and also in samples that had been subjected to hydrous pyrolysis at 330°C; these biomarkers included n-alkanes, acyclic isoprenoids, tricyclic terpanes and tetracyclic steranes and hopanes. The results of these studies suggested that the oil and bitumen are of biogenic origin and have been subjected to varying degrees of biodegradation and thermal maturation.

Parnell (1988c) reviewed the work in this area and concluded that:

the Mountsorrel Granodiorite...contains fracture-bound hydrocarbon shows...[that] occur particularly in calcite/dolomite veins at the margin of cross-cutting Hercynian dolerite dykes, and as vein-like masses within the dolerite. The simplest explanation for this origin is that they were derived from Carboniferous rocks which once covered the pluton...the scenarios discussed in this review show that the mere association of hydrocarbons with granites is not evidence for an abiogenic origin. In most cases, including those from Britain, a means of migration from sedimentary sources rocks can be envisaged. Organic geochemical studies of soluble hydrocarbons from within three British granites have all yielded biomarkers.

Mountsorrel Quarry, Quorn (Quorndon)

Mountsorrel Quarry, more commonly known as Buddon Wood Quarry, [SK 56 14 - SK 56 15] is in the parish of Quorn and exploits the Ordovician Mountsorrel Granodiorite. A marked unconformity separates the igneous rocks from the overlying Triassic Mercia Mudstone Group (Gunthorpe Member and the later Edwalton Member).

Carney and Pharaoh (1999) described a sub-vertical dolerite dyke (2-3 m wide) that crosses the quarry, following an approximately east-west course that is related to the trend of the principle fracture systems in the Ordovician granodiorite; the geological map of the area indicates that this dyke is probably the same dyke that was exposed in Mountsorrel Main Quarry. It was noted that joints parallel



Figure 14. Black bitumen in dolomitic Triassic breccia from Mountsorrel (Buddon Wood) Quarry (100 mm x 85 mm). Specimen (FI-1250) and photograph: Frank Ince.

to the dolerite had been filled during a later mineralising event (after the emplacement of the dyke but still probably of Carboniferous age) with cavernous veinlets of dolomite associated with calcite, bitumen, pyrite and a clay mineral.

In 2004 a newly-cleared area on the top bench in the northeast corner of the quarry, near SK 565 154, was investigated and some cavities (up to 50 mm x 45 mm) in a large block of dolomite-rich Triassic breccia were found to contain a very dark brown to black viscous bitumen with a highly reflective surface. The bitumen was mobile enough to flow very slowly into voids in the matrix and a light covering of grains of dolomite on its surface (produced during collection) became partly enveloped (Fig. 14); since being collected, the bitumen has lost its mobility.

Rotherwood Borehole

In their section on the occurrences of Carboniferous rocks in the Coalville area, Worssam and Old (1988) described the sequence in the Rotherwood Borehole [SK 3458 1559], south of Ashby-de-la-Zouch, noting that:

an unusual feature of the Dinantian of the Rotherwood Borehole is the abundance of bitumen. Near the top of the succession [60-65 m], it forms casts of *Latiproductus* sp., and it also occurs in veins with quartz and pyrite, cutting lithologies down to 111 m, and filling many of the cavities in the dolomite.

See also Plate 7a in Worssam and Old (1988, p. 23) where the figure caption describes bitumen veins that occur near the base of the borehole (108.5 m) in nodular, dolomitic limestone.

Spinney Hills, Leicester

Harrison (1876) described an occurrence of bitumen from Spinney Hills, Leicester from the, now obscured, brick pits (near SK 602 046) to the west of Spinney Hill Park (Carney *et al.*, 2009). These pits are shown on the 1888 Ordnance Survey maps; however, they are now covered by a housing estate that was built between 1888 and 1904. The brick pits exploited the mudstones of the Mercia

Mudstone Group: the Cropwell Bishop Formation (Branscombe Mudstone Formation) and Blue Anchor Formation (Carney *et al.*, 2009). From a comparison of the report published by Harrison (1876) with the current geological map of the area, the bitumen appears to have been found in the shales (and mudstones) of the Westbury Formation of the Penarth Group.

In his description of an occurrence of the 'Rhaetic' beds near Leicester, Harrison (1876) noted that they:

are to be seen in three brick-pits situated at the northern extremity of the Spinney Hills, a low range forming the eastern boundary of the town of Leicester and the Soar valley...the next stratum (No. 7)...consists of rather dark shales with sandy partings...1 ft thick...there are, too, some curious oval markings, with fine striae radiating from the centre; but these may be inorganic...a white amorphous mineral, kaolinite, with a little bitumen, fills many fissures in the beds of shale; and the cavities left by radiating selenite crystals cover the surface in great abundance. Flakes of mica spangle many of the sandy partings with occur in the upper part.

This occurrence of bitumen was also noted by King (1973) in his description of the occurrences of kaolinite in Leicestershire.

Worthington Borehole

In their section on the occurrences of Carboniferous rocks in the Breedon on the Hill area, Ambrose and Carney (1997a) described the sequence in the Worthington Borehole [SK 4047 2104] and they indicated that there were various oil shows in the Ticknall Limestone Formation between 137-176 m. Carney *et al.* (2001) recorded the same occurrences in their summary of the hydrocarbon exploration in the Loughborough area; although, they give the location of the borehole as SK 4045 2101.

DISCUSSION

Geological formation and occurrences of hydrocarbon-containing materials

Relatively simple HCMs can be formed by abiogenic reactions; however, all of the occurrences of gas, oil and bitumen in Leicestershire described in this review are of biological origin (Bath *et al.*, 1986; Parnell, 1988c). The complex series of processes involved in the production of gas, oil and bitumen from decaying biomass has been extensively reviewed by Gaines *et al.* (2009) and they also describe the analytical advances that have led to our current understanding of these important processes and the timescales over which these processes take place. It is worth noting that the formation and/or remobilisation of HCMs requires heat, which can be the result of simple burial, or be related to hydrothermal activity and/or the heating effect produced by the intrusion of igneous rocks.

There are several distinct geological settings for the occurrences of HCMs in Leicestershire:

- HCMs have been found in four different settings within the Carboniferous sedimentary sequence and it is likely that all of these occurrences were formed by the later remobilisation of carbon-rich material in the

Carboniferous rocks, e.g. the Namurian shales (King, 1959; Parnell, 1988c) and Coal Measures: 1. in a series of rift basins in Carboniferous rocks in the Vale of Belvoir: mainly in Namurian sandstones, with smaller amounts in the Coal Measures and fractured Dinantian limestones; 2. associated with the dolomitised limestone of Breedon Hill and Cloud Hill quarries. It is probable that the occurrences in the boreholes at Rotherwood and Worthington are also in this group; 3. at the Earl Ferrers' Mine associated with Pb/Cu/Zn-rich mineral veins in dolomitised limestones near the junction between the Carboniferous Limestone and the Millstone Grit and only ~300 m from the Coal Measures (to the southwest of the Thringstone Fault); 4. in siderite-rich nodules in Coal Measures found in the Ashby Wolds.

- HCMs are associated with basic igneous intrusive rocks, probably of late-Carboniferous age, and have been found with the dolerite intrusions at Mountsorrel and a basalt intrusion in the Coal Measures that was found in a borehole in the Vale of Belvoir. These occurrences were probably produced by the hydrothermal remobilisation of carbon-rich material derived from adjacent Carboniferous rocks, e.g. the Namurian shales (King, 1959; Parnell, 1988c) and Coal Measures; at Mountsorrel these Carboniferous rocks have been removed by erosion. Although some of the bitumen found at Mountsorrel Quarry is associated with a Triassic breccia, it may be related to the other occurrences in the quarry.
- Small amounts of HCMs occur in the Triassic mudstones at Glen Parva Brick Pit and Gypsy Lane Brick Pit, and also in the early Jurassic rocks at Spinney Hills Brick Pit. It seems likely that these occurrences were diagenetic or derived from the late Triassic and/or early Jurassic shales that are rich in organic material.

Metal enrichment in bitumen

Given the hydrophilic (water-loving) properties of most metallic cations, the occurrence of metal enrichment in some samples of, largely, hydrophobic (water-hating) HCMs might seem surprising. Having said this, there are a number of processes by which HCMs could be associated with metals (particularly those from the transition metal

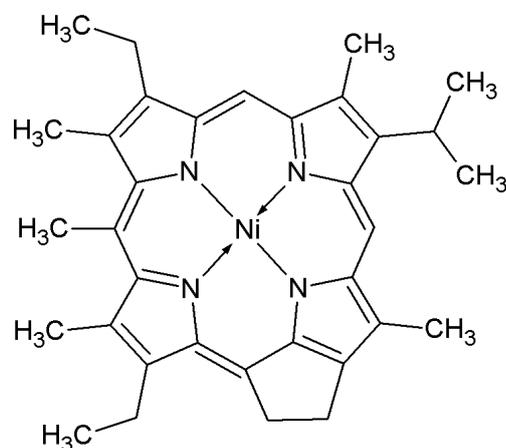


Figure 15. The structure of abelsonite; a nickel-containing metalloporphyrin.

groups). Parnell (1988a) described a variety of ways in which the association of metals with HCMs could have occurred and he includes a discussion of three processes related to metal-organic associations, five modes of metal-organic interaction and six processes by which ore mineral inclusions could have formed. Only a few of the occurrences of HCMs in Leicestershire have been investigated for their metal content; however, some of the processes that could be more important in the formation of metal-enriched bitumen in Leicestershire are noted below (together with the localities at which those processes might have been particularly relevant):

- Mineral inclusions could be present in the bitumen with the minerals having been entrained during hydrocarbon migration or precipitated in the bitumen from hydrothermal metal-containing brine-bitumen fluids (Breedon Hill Quarry, Breedon Cloud Quarry, Earl Ferrers' Mine, Mountsorrel Main Quarry).
- Organic matter could have scavenged and reduced metals from oxidised groundwaters, with the products being subsequently incorporated into the bitumen. In their description of the coffinite that occurred as a constituent of the bitumen-rich spheroids from Gypsy Lane Brick Pit, Faithfull and Hubbard (1988) suggested that broken-up algal mats could scavenge metallic cations under reducing conditions before the products, e.g. cobalt-nickel-copper arsenide-sulphides, were enclosed by the growing gypsum nodules (Gypsy Lane Brick Pit). Uranium-rich bitumen might represent a special case: oxidised hexavalent uranium is readily soluble in groundwaters, e.g. as carbonate complexes such as $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, but given local oxygen-poor environments, e.g. if these groundwaters were mixed with hydrocarbons or organic matter, U^{6+} could be reduced to U^{4+} (Parnell and Eakin, 1987) and precipitated as uraninite (Min *et al.*, 2005) (Breedon Hill Quarry, Breedon Cloud Quarry, Earl Ferrers' Mine). If sufficient silicate ions were available coffinite could be formed (Gypsy Lane Brick Pit).
- The forms in which many of the metals that occur in bitumen from Leicestershire have not been recorded. In addition to metal oxide and sulphide inclusions, organometallic complexes could also be present: 1. oil and bitumen contain a number of alkanolic acids and decomposing organic matter contains humic acids (see Gaines *et al.*, 2009), these acids could form complexes with some of the metallic cations; 2. given that abelsonite (Fig. 15) is a well-characterised nickel porphyrin complex (Anthony *et al.*, 2003, p. 1), vanadyl porphyrin complexes occur in various shales (Millson *et al.*, 1966; Sundararaman and Boreham, 1993) and the porphyrin complexes of iron (haemoglobin) and cobalt (vitamin B_{12}) are well-known, it is tempting to suggest that some of the metallic cations might be present as metalloporphyrin complexes (all occurrences).
- Parnell (1988b) and Eakin (1989) suggested that bitumen associated with uraninite might have been formed by an alternative mechanism: the condensation and polymerisation of radiolysis products from the irradiation of lower molecular weight HCMs by

pre-existing uranium-rich phases, e.g. uraninite (Breedon Hill Quarry, Cloud Hill Quarry, Gipsy Lane Brick Pit).

CONCLUSIONS

It seems most probable that most of the bitumen, and many of the metals, were derived from the metal- and HCM-rich fluids expelled from the Carboniferous rocks that were (and still are) present in the East Midlands (King, 1959; King and Ford, 1968; Parnell, 1988b). In the context of the copper and vanadium mineralisation in Leicestershire, the high level of copper (900 ppm) and vanadium (3930 ppm) in the Cloud Hill Quarry bitumen (Bath *et al.*, 1986; Parnell, 1988b) could be significant and it is interesting to speculate whether such occurrences have any relationship to the base metal mineralisation found at the sub-Triassic unconformity in Leicestershire (Pearson and Jeffery, 1997; Hubbard *et al.*, 2005; Ince, 2005). Analysis of a range of oil and bitumen samples from Leicestershire (and the rest of the East Midlands) could help determine if such a relationship is important; studies of this type are being considered.

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A NEW ASSEMBLAGE OF MANGANESE SILICATES IN THE LOWER CAMBRIAN MANGANESE ORE BED, HARLECH, MERIONETHSHIRE, WALES

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An analytical study, using XRD, of individual coloured bands within the lower half of the Lower Cambrian manganese ore bed at Llyn Du Bach Mine in the northern part of the Harlech Dome, North Wales, has revealed a suite of unusual manganese silicates within distinct, darker, chocolate-brown to black bands. Sonolite and tephroite occur within the lowest band in association with calcian rhodochrosite and traces of kellyite. A second chocolate-brown band slightly higher up in the ore bed contains a similar assemblage containing sonolite, tephroite and minor kellyite, in association with calcian rhodochrosite, minor spessartine and possible jacobsite. A noticeable depletion in spessartine content occurs within these bands. The suite of manganese silicates, and additionally alleghanyite, reported here has also been identified in the equivalent lowest band at a second locality in the northern part of the Harlech Dome and in the manganese ore bed in the southern part of the Harlech Dome supporting the view that the mineralogy of the ore bed was influenced by regional metamorphism. Given the persistent nature of the ore bed across the Harlech Dome it is expected that a similar assemblage occurs throughout the region. Several mineralogical errors have been discovered, relating to previous identifications of certain manganese silicates within the ore bed, caused by an over reliance on chemical data: previous reports of rhodonite appear erroneous, although chemically correct, being a misidentification of the polymorph pyroxmangite; manganese humite group minerals are confirmed, but the original analytical data are questioned.

INTRODUCTION

Manganese mineralization has been known in the Harlech area of North Wales (Fig. 1) from the early part of the nineteenth century. Lewis (1833) described, in Vol. 1, a trade in manganese from Barmouth and, in Vol. 2, the parish of Llanbedr (Ardudwy) was said to contain manganese, ‘the procuring of which also affords employment to a portion of the inhabitants’. A more specific reference was made under the parish of Llanenddwyn (Ardudwy) where, ‘the village is pleasantly situated, and the inhabitants are partly engaged in the manufacture of webs, partly in the working of mines of manganese, which metal is found in the parish, and the rest in agriculture’.

During that early period of mining it was black oxide of manganese that was sought, from outcrop, and according to Halse (1887) from about 1835 to 1840 it was sent to Glasgow for use in the production of bleaching powder.

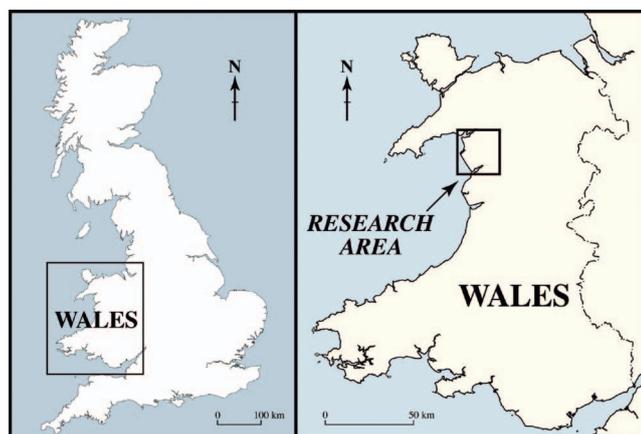


Figure 1. Location map of the research area in North Wales.

The black oxide forms a superficial oxidation product above the primary manganese ore bed and as a consequence the mines were soon exhausted. The black oxidized ore shows no trace of the primary form and therefore during the earliest phase of mining the geology was not understood. It was believed that the ore occurred in veins or lodes and that was how the Geological Survey of Great Britain recorded the deposits on their one-inch-to-the-mile maps from as early as 1855 (Sheet numbers 59 N.E. [Machynlleth] and 75 S.E. [Harlech]). Ramsay (1866) made no reference to the occurrence of manganese within the Cambrian rocks in Merionethshire, but later referred to the manganese deposits as, ‘merely parts of softer strata impregnated with oxide of manganese in the line of the strike’ (Ramsay, 1881) although he still allowed them to be mapped as lodes. Le Neve Foster (1887) reiterated the fact that Ramsay was of the opinion that the deposits were not true lodes.

The development, in 1883, of a practical method of adding manganese to steel to increase its hardness and durability saw renewed interest in the deposits (Down, 1980). The interest lay not in the black oxide, but in the underlying primary manganese in the form of mixed silicates and carbonates. During late 1884 and early 1885 development took place at many mines, with production commencing in 1886. By autumn 1886 the Dyffryn Mining Company was producing 400 tons of ore per week from four mines (Halse, 1887). The number of mines operating in the Harlech area reached its peak of 21 in 1891, but declined steadily thereafter due to the low grade of the ore. Production continued into the early twentieth century with a second peak during the First World War, but output fell once again after the war and the last mine closed in 1928. In 1942 the threat to the maintenance of exports of manganese ore from India, due to the advance of the Japanese into

Burma, led to an assessment of the Merionethshire deposits by the Ministry of Supply (Groves, 1952). Despite the identification of significant reserves of ore the decision was taken to reopen the Benallt Mine on Pen Llŷn instead, in view of the better ore grade and quicker development time (Groves, 1952). The reserves at Benallt Mine were entirely exhausted by the time the mine closed at the end of the Second World War leading Groves (1952) to recommend the Merionethshire deposits as the most suitable supply of manganese ore should imports into Britain be threatened again. During the 1950s a mining company took out leases on several mines, but no developments were made (Down, 1980).

The total quantity of ore produced by the Merionethshire mines has often been quoted as around 44,000 tons (see for example: Groves, 1938; 1952; Thomas, 1961; North, 1962; Allen and Jackson, 1985). However, this is not the true

amount as it is for the period 1892 to 1928 and therefore does not include the most productive phase of mining between 1886 and 1891, when 57,000 tons of ore were sold (Phillips and Louis, 1896). Re-examination of all of the production statistics shows that the total amount of ore extracted from the Merionethshire mines exceeded 101,000 tons.

Bennett (1987b), who erroneously stated that production was at its peak during the First World War and mistakenly reported that the ore mined was the black oxide used for steel manufacture and later the primary ore as a glass colourant, estimated that a resource of 102 Mt of ore averaging 40.32 wt% MnO (equating to 41 Mt of MnO, or 32 Mt of Mn) remains, making this the largest deposit of manganese in the British Isles. Groves (1952) suggested a slightly lower grade of ore, averaging approximately 28 % Mn, but it is undoubtedly still a significant deposit. The probability of manganese being mined in the future is

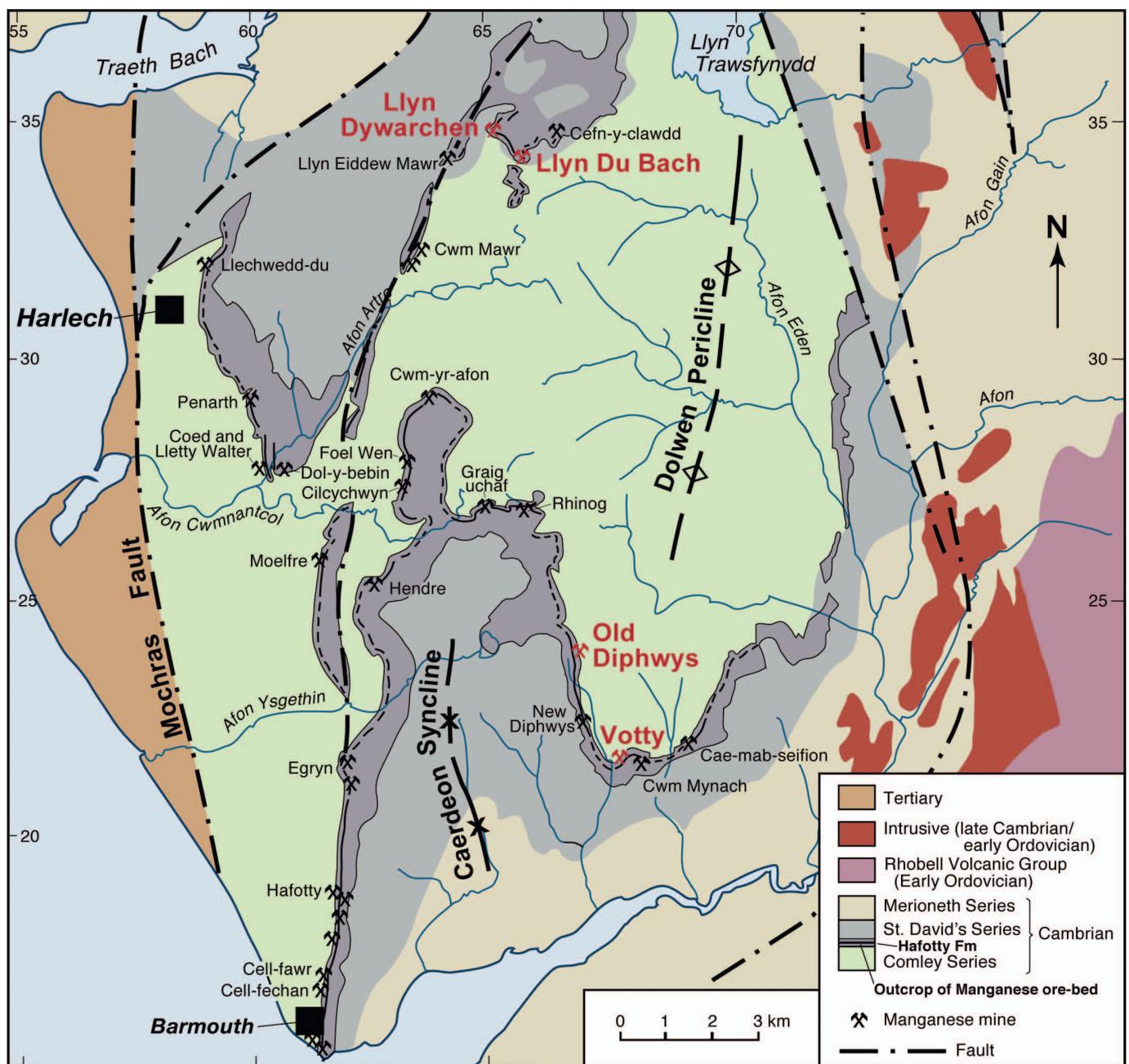


Figure 2. Geological location map of the Harlech Dome. The mines mentioned in this article are highlighted in red.

negligible as the whole outcrop lies within the Snowdonia National Park established in 1951.

GEOLOGY

The rugged mountainous area inland of Harlech, in North Wales is geologically known as the Harlech Dome and is the historical type area for the Cambrian (Rushton, 1999; Rushton and Prigmore, 1999). A thick sequence of marine clastic sedimentary rocks of Lower to Middle Cambrian age crop out over a wide, broadly elliptical area roughly centred upon the lofty rocky summits of the Rhinog range of mountains. The succession is known as the Harlech Grits Group and is divided on the basis of lithology into six formations dominated by thick sequences of alternating greywacke and pelite with features characteristic of deposition by turbidity currents (Bennett, 1987b). Many of the pelites, particularly within the Hafotty and Gamlan Formations, contain a marked enrichment in manganese (Bennett, 1987b). The Lower Palaeozoic sequences, formed in and on the margins of a major tectonic depression commonly termed the 'Welsh Basin', have suffered low-grade burial-related regional metamorphism (Bevins and Rowbotham, 1983). Studies of illite crystallinity and metamorphic mineral assemblages in basic igneous rocks by Bevins *et al.* (1981) indicate metamorphic grades reached greenschist facies within the Harlech Dome.

A significant concentration of manganese occurs in the form of a complex mixture of silicates and carbonates within a hard, cherty, sedimentary bed near to the base of the Hafotty Formation, within the Harlech Grits Group, and has been termed the Lower Shales or Manganese Shales. The manganese ore bed, which is typically between 30 and 40 cm thick, is laterally persistent throughout most of the Harlech Dome (Fig. 2), but thins to the north and east. The ore bed has been studied extensively by Woodland (1939), Mohr (1956; 1964; 1966), Mohr and Allen (1965), Glasby (1974), Binstock (1977) and Bennett (1987a,b), but with differing interpretations.

The earliest detailed studies of the ore bed, by Woodland (1939) and Mohr (1964), proposed a mechanism of manganese enrichment involving manganese derived by intensive weathering of a spilitic/keratophyric terrain. During the 1970s (De Béthune, 1972; Glasby, 1974; Binstock, 1977) the concept of early diagenetic precipitation of $MnCO_3$ was favoured, but Bennett (1987a) questioned all of these earlier interpretations, instead proposing a hydrothermal source for the manganese, from metal-bearing brine, possibly exhaled onto the sea floor. Bennett (1987a) cited the enrichment of manganese relative to iron within the ore bed as evidence of distal facies of a submarine exhalative system.

Bevins and Mason (2010) provide a geological review of the manganese ore bed based upon the interpretations of Bennett (1987a). In the model proposed by Bennett (1987a) hydrothermal brines exhaled onto the sea floor would precipitate base metals, and iron, close to source while more soluble manganese would precipitate, later, further away from source. However, in a slightly regressive step, Bennett (1987b) provided three alternative models for the source of

manganese, but concluded that because none of them can be adequately tested due to the limited outcrop and subsurface data on the Cambrian rocks of the Welsh Basin, the ultimate source of the manganese remains unresolved. Following the initial deposition of manganiferous sediments the mineralogy of the ore bed has been significantly modified by diagenesis and lower greenschist facies metamorphic recrystallization (Bennett, 1987a).

It is widely documented that Professor Charles Lapworth, who during an excursion to Barmouth with T. Stacey Wilson in 1896, realised that the manganese occurred not in veins but in a single bed and that it, if mapped through the country inland, would unravel the geological complexities of the district (Matley and Wilson, 1946; Bennett, 1987a). Lapworth did indeed realise the stratigraphic importance of the ore bed as a marker horizon but Le Neve Foster (1887) had already pointed out that the deposits are not true lodes but stratified beds. Lapworth died before completing his work, but part of it was published by Andrew (1910) and then Matley was given the opportunity to complete the mapping.

In 1915, Dewey and Bromehead described one ore bed, and the mines that had worked it, in the Geological Survey memoir on tungsten and manganese ores. However, in an apparent backwards step, the third edition of the same memoir (by Dewey and Dines, 1923) grouped the mines on the basis of earlier, unpublished, mapping by J.G. Goodchild in 1893 which showed two ore beds: a Lower and an Upper Manganese Bed. Goodchild mapped the two beds of ore (MS. six-inch Geological Maps, Merioneth, 26 N.W., S.E.; 31 S.E.; 32 N.E.; and 36 N.W.) separated by at least 260 m (850 ft.) of rock/grits (Groves, 1952). It is now accepted that there is only one ore bed (Matley, 1932; Woodland, 1939; Groves, 1952) which occurs in the Lower Shales near to the base of the Hafotty Formation in the Harlech Grits Group. Goodchild's Upper Manganese Bed is probably a thin bed of spessartine-quartz rock within the Gamlan Formation (Allen and Jackson, 1985).

MINERALOGY

The mineralogical composition of the manganese ore bed has been much studied but, ironically, the detailed research of Woodland (1939) and Bennett (1987b) was carried out long after mining had ceased. During the latter part of the 19th century, while the mines were active, the primary ore was rather simplistically described as consisting of mixed carbonates and silicates of manganese.

The first, albeit brief, account of the ores was provided by Le Neve Foster (1887) who described the primary ore as, 'manganese in the form of carbonate, with a small proportion of silicate; but at outcrop it is changed into a hydrated black oxide.' Shortly afterwards Halse (1887) concluded that the ore is a mechanical mixture of carbonates, silicates and oxides of manganese, with oxide, carbonate and sulphide of iron, magnesium carbonate, free silica and appreciable clay. Dewey and Dines (1923) considered the mixture to consist of dialogite (rhodochrosite) and rhodonite, but other than chemical analyses of ore it is not known how they

came to their identification. Cox and Wells (1927) repeated this identification, describing the ore bed as consisting of alternations of dialogite and rhodonite.

Woodland (1935) made the important discovery that manganese garnet, spessartite (hereafter referred to as spessartine), is the dominant silicate within the ore. Woodland (1939) distinguished between the different coloured components of the ore and produced detailed descriptions of each. Woodland (1939) also demonstrated that rhodonite is subordinate and that spessartine and dialogite (hereafter referred to as rhodochrosite) dominate in the red and yellow bands in broadly similar proportions (slightly above 50 % rhodochrosite in the yellow bands and slightly below 50 % in the red) with a little silica (quartz) in the red bands. The reason for the marked difference in colour between the bands was shown to be the presence of small quantities, 1 to 1.5 %, of hematite in the red material incorporated, as inclusions, within the spessartine crystals. Woodland (1939) recorded that occasionally the yellow material is replaced by cream material containing significantly more carbonate up to two-thirds of the rock. Woodland (1939) described bluish black material as in the main a modification of the red type (intergrowths of rhodochrosite and spessartine) but coloured by small, indefinitely shaped grains of a black opaque mineral, shown by chemical analysis to be manganese dioxide. The MnO content of the material increases progressively from red through yellow and cream, to the bluish black material (Woodland, 1939).

De Béthune (1972), who studied the mineralogy of the bluestone overlying the manganese ore bed, suggested that the research presented by Woodland (1939) was so thorough that little else was left to be discovered. Bennett (1987b) produced a detailed study of the petrology and origin of the manganese ore bed and reached similar mineralogical conclusions to Woodland (1939). Bennett (1987b) described the red laminated ore as dominantly spessartine, with quartz, calcium manganese carbonates (kutnohorite and rhodochrosite) and minor chlorite, magnetite and hematite. The yellow material, described by Bennett (1987b) as concretionary ore, could be composed entirely of manganese-rich carbonate. The majority of Bennett's (1987b) analyses of carbonate in the yellow concretionary ore plot as calcian rhodochrosite with a maximum of 85.72 % MnCO₃ recorded. This explains the relative absence of the characteristic bright pink colour normally associated with pure, end-member, rhodochrosite. Bennett (1987b), like Woodland (1939), made no clear distinction between the dark chocolate brown, black or purplish red material and the red laminated ore but noted briefly, under 'other ore types', distinctive thin (<1 cm) pale brown units interbedded with the red laminated ore, at several localities, as comprising intergrown microcrystalline quartz, spessartine and chlorite.

Supergene oxidation of the primary ore bed occurs rapidly on exposure to air and moisture resulting in the development of crusts of black manganese oxide. De Béthune (1972) reported that the dominant phase within the black material is actually residual spessartine and that the manganese oxides formed through meteoric alteration are subordinate. Glasby (1974), however, identified todorokite

as the principal phase in the secondary manganese oxide layer rather than pyrolusite as suggested by Woodland (1938).

Previous studies have relied heavily on chemistry-based techniques in the determination of the mineralogical constituents of the individual bands within the ore bed. Woodland (1939) used wet chemistry and optical methods to determine the mineralogy. De Béthune (1972), who studied the bluestone overlying the ore bed, applied microprobe methods while Bennett (1987b) employed multiple techniques including whole rock XRF analysis, mass spectrometry, EPMA and XRD. Glasby (1974) used XRD to determine the mineralogical constituents of a small number of samples in support of a geochemical study but, until now, no attempt has been made to thoroughly investigate the mineralogy of the individual coloured bands within the ore bed using detailed XRD analysis. Modern X-ray diffraction equipment and software allow rapid identification of complex, mixed phase samples to be undertaken. Furthermore, this method allows distinction to be made between chemically similar mineral species and can provide semi-quantitative estimates of the relative proportions of individual phases within discrete bands in the ore bed.

ANALYTICAL METHOD

A systematic study of individual bands within an 18 cm thick section through the lower part of the ore bed (the full thickness of the ore bed at Llyn Du Bach Mine is approximately 28 cm, but obtaining a complete section is extremely difficult) was carried out using XRD at Amgueddfa Cymru – National Museum Wales. Several samples of the ore bed, collected from an ore pile at the



Figure 3. Cut and polished section through the lowermost 16 cm of the manganese ore bed obtained from Llyn Du Bach Mine. Specimen No. NMW 2013.18G.M.1.

north end of Llyn Du Bach Mine [SH 658 341], were cut, lapped, and polished to display the banded texture (Fig. 3). In order to characterize the complex mineralogical assemblage within each individual coloured layer a set of three smaller sections (Specimen Numbers NMW 2013.18G.M.2a-c) suitable for mounting for analysis within an X-ray diffractometer, was produced from another sample. Each band was analysed, non-destructively, using a PANalytical X'PertPRO diffractometer fitted with a multipurpose sample stage (MPSS) and equipped with an X'Celerator solid state detector using Cu K α radiation and operating at 40 kV 30 mA. Analyses were performed across a pre-set surface area, on each cut specimen, adjusted to fit the available surface area of each individual layer within the ore bed. The area analysed ranged from 5 mm x 1 mm to 20 mm x 10 mm with each analysis typically taking about 30 minutes.

Further analyses were performed on a similar, but much smaller, cut specimen (NMW 24.247.GR.32), from the nearby Llyn Dywarchen Mine. The Llyn Dywarchen specimen (Fig. 4) had previously been analysed by EMPA by Bennett (1987b) who recorded the presence of manganese humite group phases together with baryte in a microconcretion and in adjacent carbonate-rich red laminated ore as fine-grained aggregates.



Figure 4. Sample 65 mm tall, collected in the 1920s from Llyn Dywarchen Mine, displaying the lowermost 38 mm of ore bed and 27 mm of the underlying pyritic mudstone. The lowest chocolate-brown band is displayed at the top of this specimen and consists of alleghanyite and rhodochrosite with minor kellyite and possible galaxite (see Figure 10 for analytical details). Specimen No. NMW 24.479.GR.32

Additionally, specimens of ore bed from Llyn Du Bach, Llyn Dywarchen and Old Diphwys mines (Fig. 5) were sampled for analysis using X-ray powder diffraction (XRPD). Using this method, small, fragments of material from the lowest, darker, chocolate-brown coloured band were removed and ground to a fine powder, by hand, using a small agate pestle and mortar. The powder was placed onto a zero background silicon disc and held in place using a drop of acetone. The sample disc was then mounted inside the diffractometer and analysed during rotation. A similar method was employed to analyse discrete, pinkish, lenses (Fig. 6, see p. 45) within the ore bed at Votty Mine on the west side of Mynydd Cwm-mynach.

Spectra obtained from all of the samples analysed contain diffraction peaks which represent multiple phases consistent with the complex nature of the ore bed as described by Woodland (1939) and Bennett (1987b). Using X'Pert HighScore software the diffraction patterns were resolved into their individual mineralogical constituents. The diffraction peaks of constituent phases were matched to those in the Powder Diffraction File (PDF) database. The relative proportions of each phase were calculated semi-quantitatively by the software where both scale factor and reference intensity ratio (RIR) ratings are available in the PDF data for each constituent phase.



Figure 5. The lowest chocolate-brown band is displayed across the middle of this 9 cm tall specimen collected from alongside the loading bay at Old Diphwys Mine [SH 680 232]. The pale grey mudstone at the base of the specimen is the pyritic mudstone which marks the base of the ore bed. The chocolate-brown band contains sonolite, alleghanyite and rhodochrosite. Specimen No. NMW 2013.30G.M.3. See Figure 11 for analytical details.

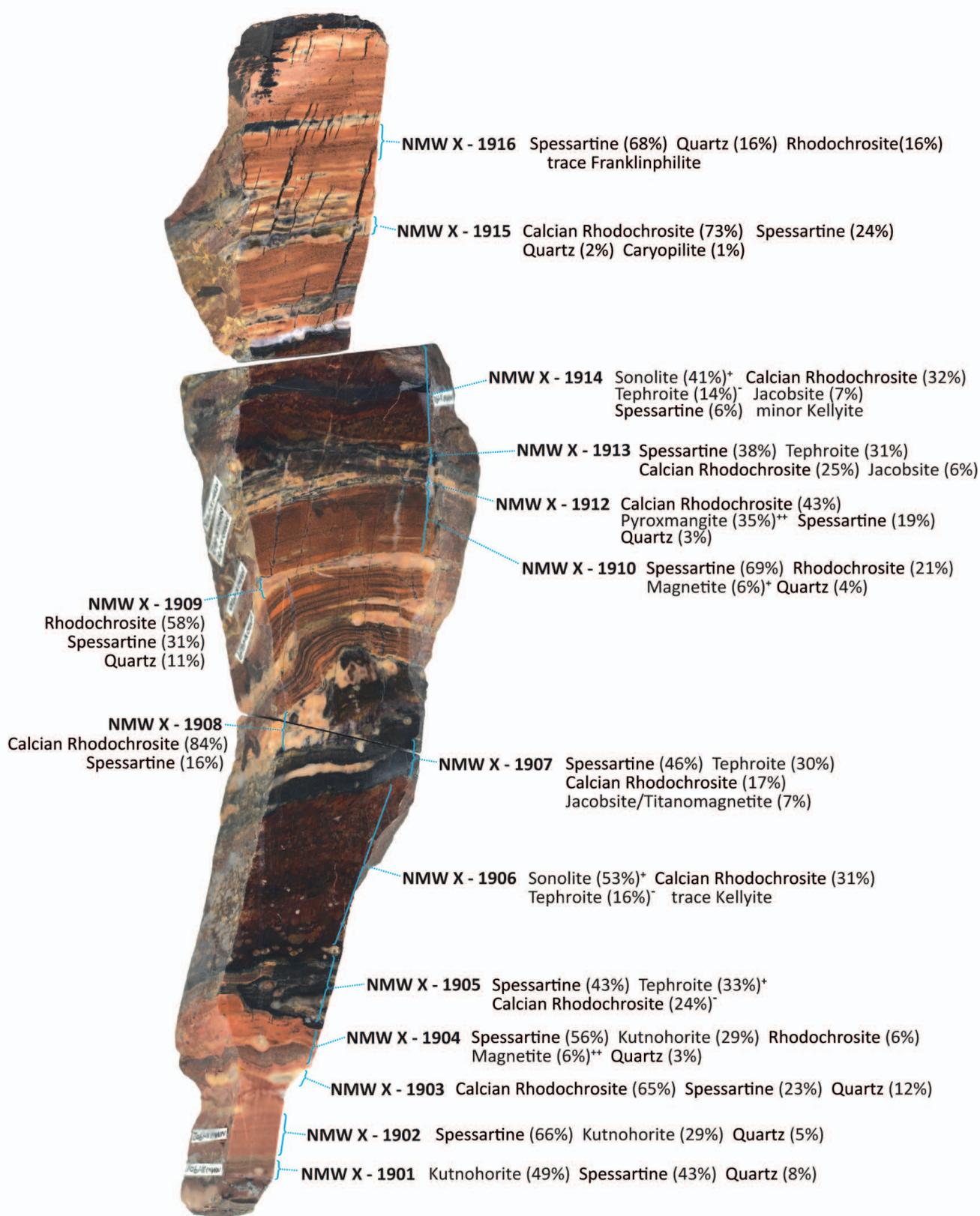


Figure 7. Annotated section through the lowermost part of the ore bed at Llyn Du Bach Mine consisting of three small blocks (Specimen Nos. NMW 2013.18G.M.2a-c) cut and polished to allow analysis using XRD. The relative proportions of each mineral are calculated by X'Pert HighScore software using semi-quantitative analysis where both the scale factor and reference intensity ratio (RIR) rating are available in the PDF data for each phase.

- ++ = an apparent significant overestimation
- + = an apparent slight overestimation
- = an apparent slight underestimation
- = an apparent significant underestimation.

RESULTS

Analytical data are presented in a number of forms. These include: a cross-section through the lowermost 18 cm of the ore bed (Fig. 7, see p. 44), from Llyn Du Bach Mine, annotated to show the mineralogical constituents of each coloured band; XRD/XRPD spectra selected to highlight the identification of specific phases within the complex mineralogical mixtures present within individual coloured bands at Llyn Du Bach Mine (Figs. 8 and 9), within the lowermost chocolate-brown band at Llyn Dywarchen Mine (Fig. 10) and Old Diphwys Mine (Fig. 11, see p. 46), and within a pink lens at Votty Mine (Fig. 12, see p. 46); combined XRD spectra to demonstrate the mineralogical similarities between the two chocolate-brown bands at Llyn Du Bach Mine (Fig. 13, see p. 46) and their contrast with the brick-red and cream bands.

Analytical data confirm the findings of Woodland (1939) and Bennett (1987b) that the individual coloured bands consist of complex mixtures of manganese-bearing silicates and carbonates (see Fig. 8 for example) but additionally a suite of unusual manganese silicates not before recorded in the ore bed has been identified. The presence of spessartine, rhodochrosite, kutnohorite, quartz and magnetite is verified and sonolite, tephroite, alleghanyite, pyroxmangite and kellyite are recorded for the first time along with probable jacobite and possible galaxite. Rhodonite, described by Dewey and Bromhead (1915) as one of the main ore



Figure 6. A layer (at the top of this specimen) of pink pyroxmangite collected by the author from an ore stockpile at Votty Mine [SH 676 214]. The dark brown horizon at the base of the specimen is interpreted as the lowest chocolate-brown band. The specimen is 7 cm tall. Specimen No. NMW 2013.31G.M.1.

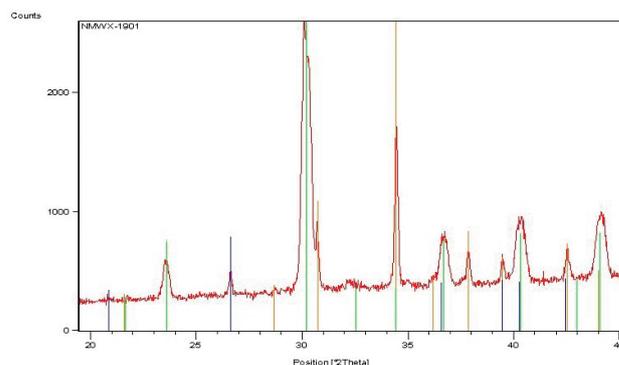


Figure 8. XRD Spectrum No. NMW X-1901 showing the presence of kutnohorite (PDF No. 01-084-1291) (green) in association with spessartine (PDF No. 01-070-8533) (orange) and quartz (PDF No. 01-085-0504) (dark blue). The position of this layer within the ore bed is shown in Figure 7. Specimen No. NMW 2013.18G.M.2a from Llyn Du Bach Mine.

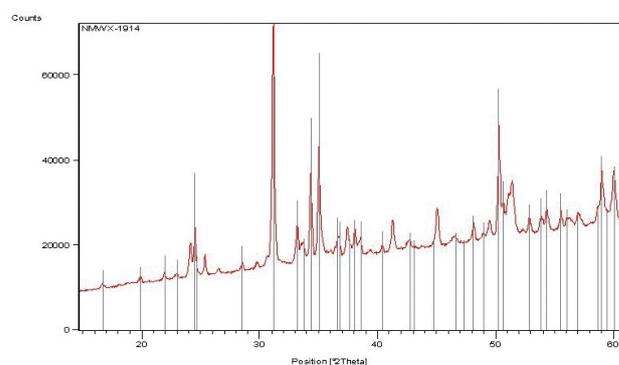


Figure 9. XRD Spectrum No. NMW X-1914. Peak positions for tephroite (PDF No. 00-035-0748) are marked in grey. The unmarked peaks represent sonolite, calcian rhodochrosite, spessartine, jacobite and kellyite. The position of this layer within the ore bed is shown in Figure 7. Specimen No. NMW 2013.18G.M.2b from Llyn Du Bach Mine.

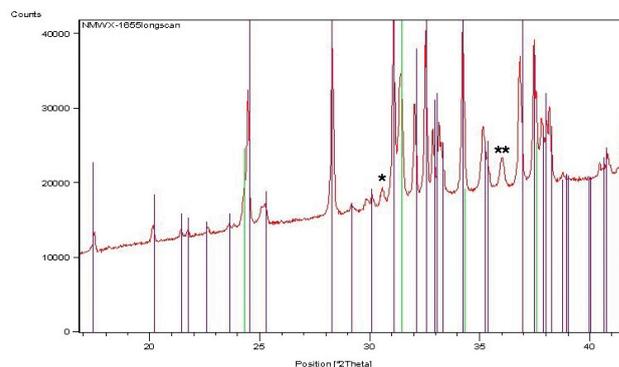


Figure 10. XRPD Spectrum No. NMW X-1655. Peak positions for alleghanyite (PDF No. 01-071-2076) are shown in purple and rhodochrosite (PDF No. 00-044-1472) in green. From the lowermost chocolate-brown band at Llyn Dywarchen Mine, in Specimen No. NMW 24.479.GR.32, displayed in Figure 4. Unmarked peaks at 30.5542 (*) and 35.9776 (**) $^{\circ}$ 2Theta are very close to the two strongest peaks for the spinel group mineral galaxite, but further analytical work is required to provide a definitive identification.

minerals but later shown by Woodland (1939) to be a minor phase, was not identified but the discovery of pyroxmangite suggests that the identification of rhodonite was erroneous.

Spessartine is virtually ubiquitous, occurring in all but one of the analyses presented in Figure 7. The proportion of spessartine is always much higher in the brick-red bands, typically between 56 to 69 % (in semi-quantitative analyses), but still appreciable within the, paler, cream bands (between 16 and 31 %) confirming the findings of Woodland (1939). The only band within which spessartine is apparently absent is the lowermost mottled, chocolate-

brown layer which contains the manganese silicates sonolite and tephroite, along with calcian rhodochrosite. Even so, spessartine is probably still present, but in such small quantities that its diffraction peaks are too small to discern it from the surrounding phases.

No hematite was detected whatsoever, even within the brick-red bands where Woodland (1939) identified it as inclusions within spessartine. However the 1 to 1.5 % recorded by Woodland (1939) is probably below the limit of detection, using XRD, and the non-detection issue would be exacerbated if the hematite was poorly crystallized.

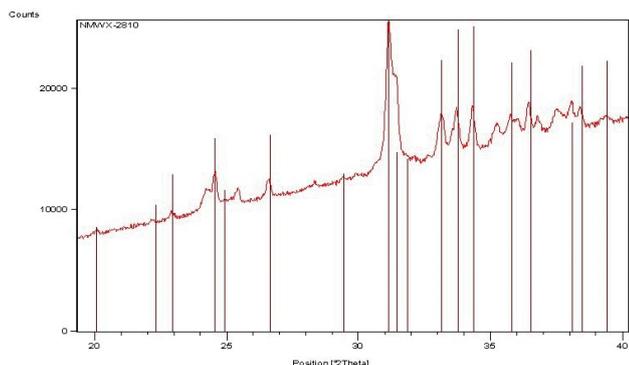


Figure 11. XRPD Spectrum No. NMW X-2810. Sonolite (PDF No. 00-022-0725) peaks are shown in dark brown. The unmarked peaks represent alleghanyite and rhodochrosite. From the lowermost chocolate-brown band at Old Diphwys Mine in Specimen No. NMW 2013.30G.M.2a. The same band is displayed in Figure 5.

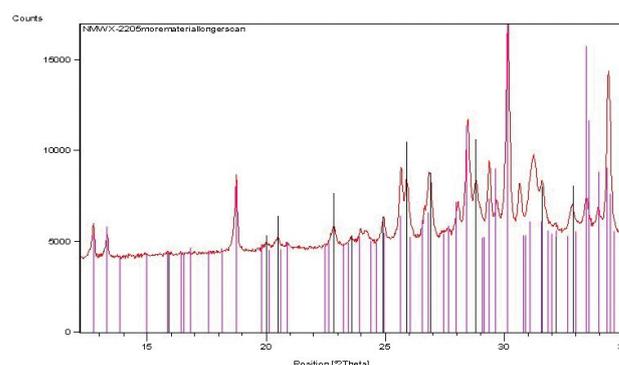


Figure 12. XRPD Spectrum No. NMW X-2205. Pyroxmangite (PDF No. 01-070-4424) peaks are shown in pink and baryte (PDF No. 01-080-0512) peaks in black. Specimen No. NMW 37.676.GR.18 from Votty Mine. Unmatched peaks at 30.651 and 31.233 $^{\circ}$ 2Theta represent spessartine and calcian rhodochrosite respectively.

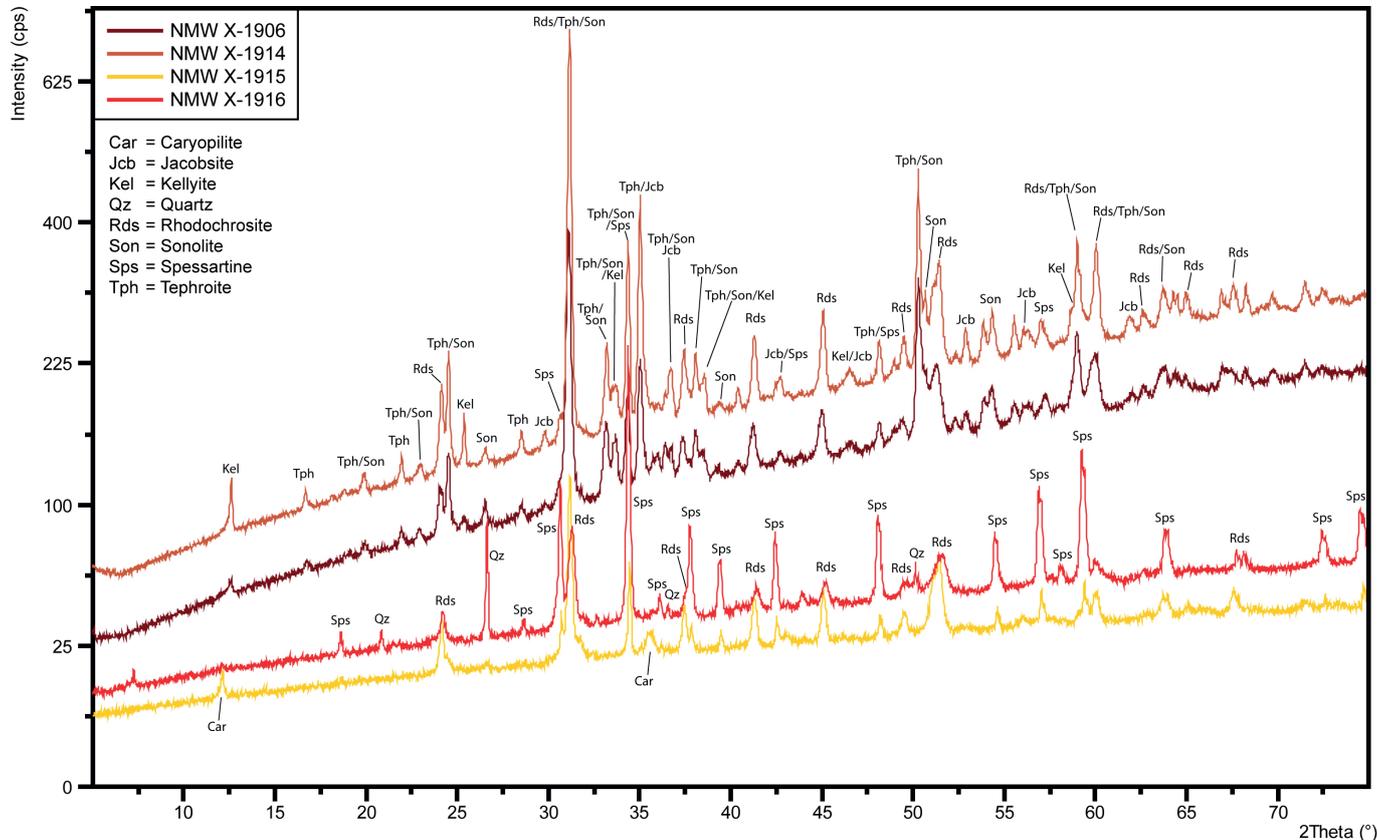


Figure 13. Combined XRD spectra showing the similarity between the two chocolate-brown bands (NMW X-1906 and NMW X-1914) and the clear differences between the red (NMW X-1916) and cream (NMW X-1915) bands relative to each other and compared with the chocolate-brown bands at Llyn Du Bach Mine. Individual peaks are labelled to show which mineral species they represent. Intensity is displayed as counts per second.

Of the carbonates kutnohorite, identified by Bennett (1987b) using EPMA, is confirmed (Fig. 8) but is restricted to the lowest brick-red and beige horizons whilst rhodochrosite occurs as the main carbonate higher up in the ore bed sequence (Fig. 7). A noticeable shift in the XRD peak positions for some of the carbonates from rhodochrosite towards those for dolomite, within a number of horizons (Fig. 7), is attributed to the increased proportion of calcium within the rhodochrosite structure, as reported by Bennett (1987b), rather than the presence of dolomite. This is supported by Bennett's (1987b) comprehensive analytical data on carbonates within the ore bed which show that the magnesium content of carbonates is typically low (an average of 4.25 mol % MgCO_3 in the yellow concretionary ore and an average of 7.85 mol % MgCO_3 in the red laminated ore) and that, chemically, the majority of carbonates plot as calcian rhodochrosite. Carbonates are noticeably dominant within the cream material with up to 84 % recorded.

In this study, the material of most interest is the chocolate-brown bands, the detailed mineralogy of which remained largely elusive to previous researchers. Woodland (1939) described chocolate-purple bands as a modification of chocolate-red bands and less frequent, darker, bluish-black material as essentially still intergrown rhodochrosite and spessartine, but with small, indefinitely shaped, grains of black, opaque, manganese dioxide. No manganese dioxides have been identified during this study but, like hematite, if the grains represent less than one or two percent of the total volume then it may not be detected using XRD.

Bennett (1987b), like Woodland (1939), made no distinction between the dark chocolate brown, black or purplish red material and the red laminated ore but noted briefly, under 'other ore types', distinctive thin (<1 cm) pale brown units interbedded with the red laminated ore, at several localities, as comprising intergrown microcrystalline quartz, spessartine and chlorite. It is not clear how Bennett (1987b) identified chlorite and the presence of minor pennantite within the ore bed, noted by Bennett (1987a), is unsubstantiated. Pennantite has not been identified, by XRD or XRPD, during this study and inspection of Bennett's (1987b) chlorite analyses reveals that all of the compositions fall far short of the manganese content required for pennantite.

XRD and XRPD of two distinct chocolate-brown bands occurring in the lower part of the ore bed across the Harlech Dome (Fig. 3) have revealed a diverse range of unusual manganese silicates including sonolite, tephroite, alleghanyite and kellyite.

Sonolite, $\text{Mn}^{2+}_9(\text{SiO}_4)_4(\text{OH},\text{F})_2$, a humite group mineral typical of manganese deposits metamorphosed to low-grades, was tentatively identified by Bennett (1987b) as a constituent of rare, orange-yellow, manganese silicates associated with baryte in a micro-concretion, in adjacent carbonate-rich red laminated ore, and as fine-grained aggregates in a single sample (NMW 24.479.GR.32) of manganese ore bed from Llyn Dywarchen, near Moel Ysgyfarnogod. Bennett (1987b) suggested that one EMPA

(Sample No. 12459) resembled sonolite and that another sample (Sample No. 12457) resembled relatively pure manganhumite. Bennett's (1987b) identifications were subsequently reported as the first British occurrences of both species by Bevins (1994) and were listed as the only known examples of these species in Britain and Ireland by Tindle (2008). Bennett (1987b) reported that his EPMA totals were low and variable and inspection of his data (Table 8.2 in Bennett, 1987b) shows that neither analysis bears any resemblance to manganhumite or sonolite. A third analysis (Sample No. 12458), presented by Bennett (1987b), was not ascribed to any specific mineral but has important connotations here.

Re-examination of the specimen (Fig. 4) studied by Bennett (1987b) using XRD (Analytical Numbers NMW X-1652 and X-1655) shows that the chocolate-brown band containing orange-brown micro-concretions consists of dominant alleghanyite in association with rhodochrosite and what appears to be a spinel group phase, possibly galaxite (Fig. 10). Alleghanyite, $\text{Mn}^{2+}_5(\text{SiO}_4)_2(\text{OH})_2$, like sonolite, is a humite group mineral but has a composition broadly consistent with that presented by Bennett (1987b) for Sample No. 12458. The specimen analysed measures only 4 cm across and therefore does not represent the full ore bed succession. However, the presence of coarse cubic pyrite crystals in the lower bands and in the accompanying host rock demonstrates that the specimen is from the base of the ore bed. The alleghanyite-bearing band commences at a height of 3 cm above the base of the ore bed.

The 18 cm thick cut section from Llyn Du Bach Mine (Fig. 7) displays two chocolate-brown bands. One commences at 4 cm and the other at 11.5 cm above the base of the ore bed, each surrounded by darker, almost black material. Sonolite has been identified, during this study, as a major constituent in both bands. In the lowermost chocolate-brown band (NMW X-1906), in specimen NMW 2013.18G.M.2a, spessartine is absent with sonolite dominant, associated with calcian rhodochrosite, tephroite and traces of kellyite. This band corresponds with the alleghanyite-bearing layer in specimen NMW 24.479.GR.32. In the upper chocolate-brown band, in specimen NMW 2013.18G.M.2b, sonolite again appears dominant, but tephroite is a significant constituent (Fig. 9) with calcian rhodochrosite and minor spessartine, jacobsite/titanomagnetite and kellyite.

In order to determine whether the composition of the lowermost chocolate-brown band is uniform throughout the ore bed, several specimens from Old Diphwys Mine, some 12 km distant from Llyn Du Bach Mine, were analysed to determine whether the corresponding chocolate-brown band, at 2 cm above the base of the ore bed (Fig. 5), contains the same assemblage. Samples were collected from alongside a loading bay, at SH 680 232, at the base of the tramway half a mile away from the mine workings. XRPD data from two separate areas of the same band demonstrate compositional variation with rhodochrosite dominant with minor tephroite, alleghanyite, sonolite and kellyite in specimen NMW 2013.30G.M.1 (Analysis No. NMW X-2808) and sonolite dominant with minor

rhodochrosite and alleghanyite in specimen NMW 2013.30G.M.2a (Fig. 11).

Tephroite, $Mn^{2+}_2SiO_4$, an olivine group mineral typical of metamorphosed, manganese-rich sediments (Anthony *et al.*, 1995), is more widespread than sonolite and alleghanyite, in the ore bed. In the specimen from Llyn Du Bach Mine, tephroite is identified in five distinct bands (Fig. 7). The quality of the peaks for tephroite is excellent (Fig. 9), but in the semi-quantitative analyses its proportions are always under represented (Fig. 7). Tephroite occurs within all of the, darker, chocolate-brown to black bands where it is consistently indicated to be between 14 and 33 % of the total composition, but it is probably much more important. Tephroite has not been detected within the cream, beige or brick-red bands.

Kellyite, $(Mn^{2+}, Mg, Al)_3(Si, Al)_2O_5(OH)_4$, a rare serpentine group mineral known from metamorphic manganese deposits, is present within both chocolate-brown bands at Llyn Du Bach Mine (Figs. 9 and 13) and within the lowermost chocolate-brown band at Llyn Dywarchen Mine (Fig. 10). Unfortunately, only one PDF (No. 00-029-0885) is registered for kellyite and it does not contain the necessary data to allow semi-quantitative determinations to be made. It is, however, a minor phase and probably represents only a few percent of the chocolate-brown bands. Kellyite was first described (Peacor *et al.*, 1974) from Bald Knob, North Carolina, U.S.A., where it occurs in an assemblage very similar to that described here in the manganese ore bed. Traces of the rare stilpnomelane group mineral, franklinphilite, reported elsewhere in this issue (Cotterell and Hubbard, 2013) occur in one of the upper brick-red bands (Fig. 7).

A small number of analyses record the presence of magnetite and other spinel group phases. Magnetite is widely distributed throughout the ore bed (Mohr, 1963) in small, sub 0.15 mm, euhedral, crystals. XRD data indicate the presence of magnetite in a number of brick-red bands (Fig. 7). A similar magnetite series phase occurs within the upper chocolate-brown band and in a couple of black layers, but a systematic shift in the peak positions suggests a variation in chemistry, perhaps to jacobsite or titanian magnetite. The presence of jacobsite in the ore bed was mooted by (Mohr, 1963) on the basis of a relatively high Mn content in magnetite from Nantcol. Mohr (1963) suggested that the high Mn content was probably due to diadochic replacement of Mn^{2+} for Fe^{2+} within the structure of magnetite. Mohr's (1963) data suggested that 8 % jacobsite is present in the magnetite at Nantcol. Bennett (1987b) described Ti-Mn-Fe oxides consistent with ferropyrophanite occurring as small opaque grains sparsely scattered throughout the manganese ore. The possible presence of galaxite, a spinel series phase, in the lower chocolate-brown band at Llyn Dywarchen Mine is tentatively indicated by two peaks (Fig. 10). A detailed analytical study of the chemistry of spinel group phases within the ore bed is required in order to identify the presence of jacobsite and galaxite with certainty.

The presence of rhodonite has not been confirmed by this study. However, the discovery (Fig. 12.) of its polymorph,

pyroxmangite, in pink concretions (to 12 mm x 9 mm) within cream bands of baryte in dark reddish-brown horizons in manganese ore (specimen NMW 37.676.GR.18) collected, by Dr Woodland, from Votty Mine on the west side of Mynydd Cwm-mynach suggests that an error was made in his identification. Woodland (1939) described rhodonite as, 'formed in certain rare instances (for example, in a few of the yellow bands)' and reported anhedral plates of rhodonite in some of the yellow bands. This error is understandable when one considers that Woodland was reliant on chemical data. Mohr (1964) reported that 'large euhedral crystals of rhodonite are abundant in Ore specimens from two localities in the Harlech Dome' but that 'otherwise this mineral is absent'. Mohr's (1964) localities are not disclosed but it is reasonable to assume that it is also pyroxmangite. Further analyses (NMW X-2856 and NMW X-2860) of recently collected material (Fig. 6), have shown that pyroxmangite is widespread at Votty Mine and probably occurs at a number of horizons in the lower portion of the manganese ore bed at this location. Pyroxmangite also occurs as a constituent of a thin cream horizon at Llyn Du Bach Mine (Fig. 7).

Comparison of the XRD spectra for the chocolate-brown, brick-red and cream coloured bands (Fig. 13) demonstrates the obvious differences in mineralogical composition between individual layers.

DISCUSSION

Groves (1952) highlighted the somewhat remarkable fact that the mineralogical nature of an ore of which many tens of thousands of tons had been mined over a period of about 40 years should have remained imperfectly known for so long. Detailed mineralogical, petrological and geochemical studies by Woodland (1939), Mohr (1956; 1964), Mohr and Allen (1965), De Béthune (1972) and Bennett (1987b) produced much useful data and seemed at the time to have thoroughly explained the mineralogical complexities of the ore bed. Indeed De Béthune (1972) suggested that there was little left to discover after Woodland's (1939) thorough descriptive work.

It is now apparent that the mineralogy of the ore bed is far more complex. The earlier studies are all underpinned by chemical data for mineralogical identifications. The fine-grained nature of the mineralogical constituents has also hampered identification using optical means. Analytical methods and techniques have improved significantly over time and access to analytical facilities, in particular XRD, has improved too. Bennett (1987b) came close to identifying some of the manganese humite group species, but his methodology appears questionable when his analytical data are thoroughly inspected.

Using data obtained by XRD, this study has revealed the presence of sonolite, tephroite and kellyite within both of the dark chocolate-brown bands at Llyn Du Bach Mine and tephroite within all of the other darker (black) bands within lower half of the manganese ore bed. XRPD has identified slight mineralogical variations within individual bands between locations, with the presence of alleghanyite in the lowest chocolate-brown band at Llyn Dywarchen and

Old Diphwys mines. These two distinct horizons appear to have been overlooked in the past, perhaps due to limitations in analytical technology, but the importance of investigating every layer systematically is well demonstrated here.

The absence of rhodonite in any of the analyses reported here, combined with the presence of its polymorph pyroxmangite within one of the cream coloured layers at Llyn Du Bach Mine and in small pink lenses at Votty Mine, suggest that previous identifications of rhodonite were made in error based on chemical rather than structural data. Rhodonite and pyroxmangite can coexist, but evidence presented here suggests that only pyroxmangite occurs within the manganese ore bed. This is supported by the investigations of De Béthune (1972), who was unable to recognise rhodonite with certainty, and Bennett (1987b), who did not mention rhodonite at all.

Published analyses (Groves, 1952) of the manganese content of the ore bed within the Harlech Dome show a range from 25.51 to 32.76 % Mn which is low for an 'ore'. Woodland (1939) noted that in the ore bed the MnO content increases progressively from red through yellow and cream, to the bluish black material. Allen and Jackson (1985) also recorded that 'the less common bluish black bands are substantially richer in Mn with values up to 39 per cent' but claimed that, in addition to minor finely divided todorokite, they contain rhodochrosite and spessartine in the ratio of about 3:1. The present study concurs that the chocolate-brown bands are enriched in manganese, but has shown that this enrichment is due to the presence of the manganese silicates sonolite, alleghanyite, and tephroite, all of which typically contain above 50 % Mn, rather than a dominance of manganese carbonate.

The suite of manganese silicates reported here is typical of manganese deposits metamorphosed to low grades. This supports the assertion of Bevins *et al.* (1981) and Bevins and Rowbotham (1983) that the Cambrian succession in the Harlech Dome has undergone regional metamorphism to greenschist facies.

It is also worth mentioning here the mineralogical similarities between the Harlech Dome manganese ore bed and the enigmatic manganese deposit at Bald Knob, North Carolina, U.S.A. The Bald Knob deposit contains a diverse range of manganese silicates and is the type locality for three species: alleghanyite, galaxite and kellyite (Ross and Kerr, 1932; Peacor *et al.* 1974). No natural exposures of the ore deposit exist - the underground exposures were last accessible during the early twentieth century (Ross and Kerr, 1932) - but material derived from the small dumps has been investigated thoroughly revealing two distinct assemblages: manganese-carbonate-rich rocks; and silica-rich rocks (Simmons, *et al.*, 1981). Original sedimentary layering in the form of banding in the ore was noted by Simmons, *et al.* (*op cit.*) and Winter *et al.* (1981). Flohr (1992) interpreted the Bald Knob deposit as manganiferous sediments of submarine hydrothermal origin, hosted within the late Proterozoic Ashe Formation comprising metagreywacke gneiss, quartz-mica schist and phyllite with interlayered amphibolite, garnet-amphibolite and actinolite-chlorite

rocks. Despite the older, late Neoproterozoic, age of the Bald Knob deposit the conditions of deposition proposed by Flohr (1992) are similar to those proposed for the Lower Cambrian ore bed in the Harlech Dome by Bennett (1987a) and supported by Bevins and Mason (2010). The similarities in mineralogy between the two deposits suggest that the chemistry of the protolith at Bald Knob was very close to that which formed the manganese ore bed in the Harlech Dome.

At Bald Knob, metamorphism to mid-amphibolite facies (Winter *et al.*, 1981; 1983) has significantly modified the original sediments, producing a suite of unusual manganese silicates including manganhumite. Winter *et al.* (1983) interpreted manganhumite to be a high pressure phase. If this is indeed the case, and the proto-ore at Bald Knob and the Harlech Dome was similar, then the absence of manganhumite in the ore bed in the Harlech Dome supports the findings of Bevins *et al.* (1981) and Bevins and Rowbotham (1983) that the Cambrian succession in the Harlech dome has undergone regional metamorphism to greenschist facies, but no greater. It is hoped that the broad range of manganese silicates reported here will allow data on metamorphic conditions within the Harlech Dome to be refined further, but this will form the basis of a separate study.

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FRANKLINPHILITE IN VEINLETS IN THE LOWER CAMBRIAN MANGANESE ORE BED, HARLECH, MERIONETHSHIRE, WALES

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An unusual assemblage of manganese-, iron- and rare earth-bearing silicates has been discovered within narrow, bedding perpendicular, veinlets within the Lower Cambrian manganese ore bed at Llyn Du Bach Mine, near Moel Ysgyfarnogod, Merionethshire, North Wales. Previous authors have interpreted the veinlets as syneresis cracks, syn-sedimentary or tectonic deformation features but their form and geological setting indicate that they are extension veins possibly related to a period of tectonic inversion from extension to compression during the onset of Acadian deformation. Mineralization within the veinlets is directly related to the chemistry of the surrounding manganese ore bed, indicating a process of lateral secretion, while the presence of franklinphilite and caryopilite suggest formation under metamorphic conditions. Franklinphilite is reported for the first time in the British Isles.

INTRODUCTION

The mountainous area inland from Harlech, in North Wales, is geologically known as the Harlech Dome; for a detailed map, see Cotterell (2013, this issue p. 40). Although not technically a dome the name was applied by Matley and Wilson (1946) because a thick sequence of Cambrian age sediments are exposed in a roughly circular area. Folding, faulting and regional low-grade (lower greenschist facies) metamorphism have affected the whole Cambrian succession resulting in a structure more complicated than a simple dome (Allen and Jackson, 1985). The Harlech Grits Group, which forms most of the central part of the Harlech Dome, consists of thick sequences of alternating greywacke- and pelite-dominated formations (Bennett, 1987). The prominent rugged crags so typical of this part of Wales are formed by the thick sandstone units (Fig. 1, see p. 52).

A concentration of manganese (typically about 28%; Groves, 1952) occurs in what is known as the Lower Shales, or Manganese Shales, near to the base of the Hafotty Formation in the Harlech Grits Group. The manganese bearing horizon is known as the manganese ore bed, on account of it having been mined at more than 30 different sites (Down, 1980). The ore bed is quite persistent and has proved a useful stratigraphic marker across the region. The ore bed has an average thickness of 30 cm (12 inches), but typically varies from 25 to 51 cm (10 to 20 inches) with an exceptional localized thickness of 1.5 m (5 feet) reported at Cwm Bychan (Halse, 1887) and Egryn Mine, near Llanaber (Dewey and Dines, 1923).

The manganese ore bed is a hard, cherty, rock comprising layers of massive red, cream and brown material. The mineralogical composition of the ore bed is complex and has formed the basis of detailed studies by Woodland (1939)

and Bennett (1987). Essentially the ore bed consists of fine-grained mixtures of manganese silicates and carbonates, but with traces of hematite and magnetite imparting a strong influence on the colour of each layer. Recent research, by Cotterell (2013), has revealed that the mineralogy of the ore bed is far more complex than had previously been reported.

Despite being a very competent rock (a fact noticeable if you try to hammer a fresh sample from it), the ore bed weathers rapidly on exposure to air and water through oxidation of the carbonate component to form a soft, black, rock composed of todorokite (Glasby, 1974) and residual spessartine (De Béthune, 1972). Consequently, fresh outcrops are very difficult to find. This is compounded by the fact that any easily accessible outcrops were mined out. It is now easier to obtain samples of the ore bed from stockpiles left behind at some of the mines than to try and sample the ore bed *in-situ*.

VEINLETS

At Llyn Du Bach Mine the manganese ore bed frequently contains thin (mm scale) veinlets and, less common, larger (cm scale) veins. The presence of veinlets within the Lower Cambrian manganese ore bed was noted by Woodland (1939) and Bennett (1987) who produced differing interpretations. Woodland (1939) noted several different types of veins, but focused on describing the common narrow veinlets which traverse the red and yellow bands approximately at right angles to the bedding which he concluded to be contraction (syneresis) cracks resulting from dehydration of a colloidal gel. Woodland (1939) reported a noticeable thinning of veinlets passing from the yellow into the red bands and described the infill as dialogite (rhodochrosite) and chalcedonic silica (quartz). Woodland (1939) also recorded 'ordinary' quartz veining and quartz infilling irregular rectangular jointing. Bennett (1987) suggested that



Figure 1. Typical scenery in the northern Rhinogs. Prominent, thick, shallow dipping sandstone horizons weather to form a 'stepped' profile. The slabs in the foreground are the Manganese Grit lying above the manganese ore bed and bluestone within the Hafotty Formation near Llyn Du Bach Mine. The view is looking due south to Craig Ddrwg which is dominated by thick greywacke units in the Rhinog Formation. The summit of Craig Ddrwg (top right) exposes the lowest beds of the Hafotty Formation with the manganese ore bed exposed on a ledge just below the summit; the apparent jump in the position of the ore bed is caused by a west-north-west to east-south-east trending fault running across the centre of the photograph at the base of the hillside in the middle distance.

two types of veinlet exist, both normal to bedding: discrete, continuous fracture-filling; and indistinct discontinuous replacive veins. Bennett (1987) disagreed with an origin related to syneresis, instead proposing formation as a result of directional syn-sedimentary or tectonic deformation, but preferring a tectonic origin.

Specimens from Llyn Du Bach Mine reveal multiple generations of veining, all of which are interpreted here to be pre-tectonic in age. The focus of this article is to describe the mineralogy of some of the earliest veinlets which typically, but not exclusively, cross-cut the laminated cream and red sections of the manganese ore bed perpendicular to bedding. The mineralogy of the veins is more complicated than the simple carbonate and quartz assemblage described by Woodland (1939). Wider, quartz-dominated, veins of a later generation are also commonplace and have, elsewhere in the ore bed, been shown to contain the rare manganese tungstate, hübnerite (Cotterell *et al.*, 2010).

MINERALOGY

Near Llyn Du Bach south of Moel Ysgyfarnogod a small ore pile (Fig. 2), at grid reference SH 658 341, marks the end of the miners track and the northern end of one particular outcrop of the ore bed. Samples collected from the ore pile display the typical banded nature of the ore and, also, frequently contain small (mm scale) veinlets which crosscut the individual bands, usually, perpendicular to bedding. In one sample, Amgueddfa Cymru Collection Number NMW 2012.2G.M.1, thin (1 to 2 mm) dark brown veinlets were observed crosscutting the cream and red bands (Fig. 3) in a section between two darker chocolate-brown horizons at a height of 6 to 10 cm above the base of the ore bed. It is these veinlets that are discussed here.

Visual identification of the constituent phases within the veinlets, other than quartz, was impossible and so a small quantity of material was removed and powdered for testing by X-ray powder diffraction (XRPD) using



Figure 2. The northern end of the outcrop of the manganese ore bed at Llyn Du Bach Mine at SH 658 341. The manganese ore bed, which is not visible, has been removed from the base of the outcrop (centre left in the photograph) leaving the overlying bluestone (distinctly laminated beds) and Manganese Grit (upper half of photograph) as an overhang. Note the shallow dip of the beds. The miners track ends at this point with a grass covered stockpile of manganese ore (lower centre of photograph).

the method described by Cotterell (2013). The resultant diffraction pattern (NMW X-1838) represented a mixture of minerals but with modern 'search and match' software it is possible to identify multiple phases within a single spectra. One set of peaks showed similarities to several stilpnomelane group minerals including, stilpnomelane, lennilenapeite and franklinphilite; the remaining peaks matched those of caryopilite.

The presence of a stilpnomelane group phase was not unexpected: stilpnomelane had already been identified by XRD (Natural History Museum, London: X-ray

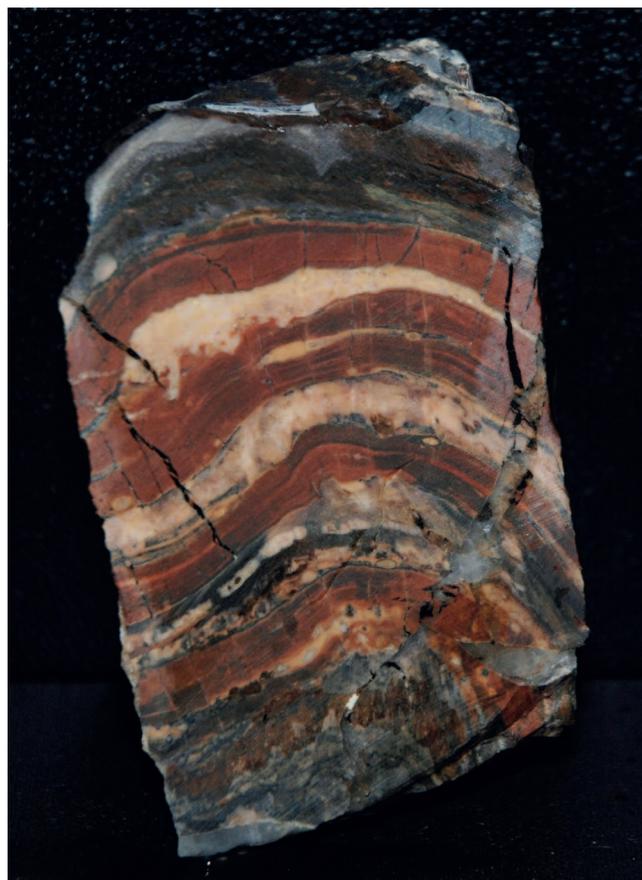


Figure 3. Thin, dark brown, franklinphilite-caryopilite veinlets cross-cutting an 8 cm thick section of bedded manganese ore from Llyn Du Bach Mine. Specimen No. NMW 2012.2G.M.1.

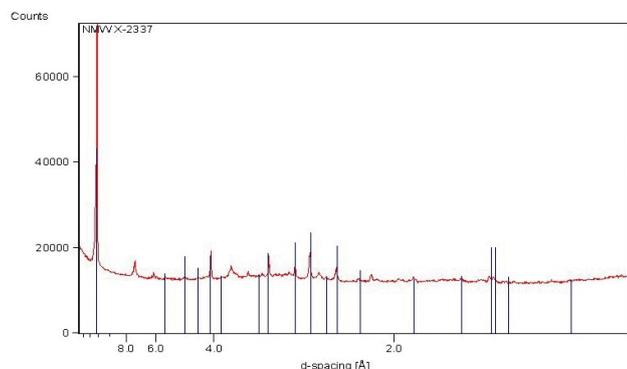


Figure 4. X-ray powder diffractogram for XRD No. NMW X-2337 (red line) of Llyn Du Bach Mine material overlain by the powder diffraction pattern (PDF reference code 00-046-1455) for franklinphilite (dark blue). The unmatched peaks represent caryopilite.

No. x19863) at 'Moelfre' (Bevins, 1994) and specimens of black, bladed, stilpnomelane in the G.J. Williams Collection at Amgueddfa Cymru are from Moelfre Mine (NMW 27.111.GR.430) and Cwm Mawr No. 2 Mine (NMW 27.111.GR.526) - mines which also worked the manganese ore bed in the Harlech dome. Stilpnomelane is also widespread in oolitic ironstone, of Ordovician age, elsewhere in North Wales (Hallimond, 1924; Hallimond, 1925; Pulfrey, 1933; Matthews and Scoon, 1964; Bevins, 1994) and Bloxam and Price (1961) described stilpnomelane in a variety of rocks associated with the, Lower Llanvirn age, Cregennen granophyre sheet south of the Harlech Dome.

A second, much longer, XRPD analysis was performed in order to accurately identify the stilpnomelane group phase. The diffraction pattern (NMW X-2337) showed clear similarities to the rare Mn-analogue of stilpnomelane - franklinphilite (Fig. 4). Caryopilite was again recorded as an accessory mineral. The peak positions (d-spacings) and intensities correlate with the published data for franklinphilite (Table 1).

Franklinphilite, ideally $(K,Na)_4(Mn^{2+},Mg,Zn)_{48}(Si,Al)_{72}(O,OH)_{216}\cdot 6H_2O$, is a modulated layer silicate which forms a solid solution series with both stilpnomelane and lennilenapeite (Dunn *et al.*, 1984; Dunn *et al.*, 1992). Despite the abundance of stilpnomelane group

New Jersey ¹		Llyn Du Bach Mine ²	
d (Å)	Intensity	d (Å)	Intensity
12.3	100	12.21	100
5.54	5	5.52	1
4.79	20	4.79	1
4.40	10	4.41	1
4.08	20	4.07	11
3.83	2	3.82	1
3.18	2		
3.06	20	3.05	8
2.737	30	2.743	4
2.583	40	2.594	10
2.449	2	2.453	1
2.362	30	2.372	5
2.201	10	2.211	1
1.897	2	1.900	1
1.694	5	1.697	1
1.594	30	1.601	2
1.580	30	1.588	2
1.541	5	1.548	1
1.376	2	1.382	1

1. After Dunn *et al.* (1992).

2. This study: NMW 2012.2G.M.1b, NMW X-2337.

Table 1. Comparative X-ray powder diffraction data for franklinphilite.

minerals worldwide franklinphilite has only been recorded from a small number of localities worldwide (see: <http://www.mindat.org/min-1599.html>).

Due to the apparent rarity of franklinphilite, and the fact that it forms a solid solution series, it was deemed necessary to obtain accurate chemical data in order to verify its existence at Llyn Du Bach Mine. To allow accurate chemical analysis to be made using SEM-EDS a resin mounted polished block was produced (NMW 2011.2G.M.1f). The sample was cut to display a cross-section through the bedded manganese ore cut by one of the veinlets.

High magnification SEM imagery (Fig. 5) obtained during EDS analysis confirmed, as shown by XRPD, that two distinct phases make up the majority of the veinlet, along with inclusions of other phases. Detailed

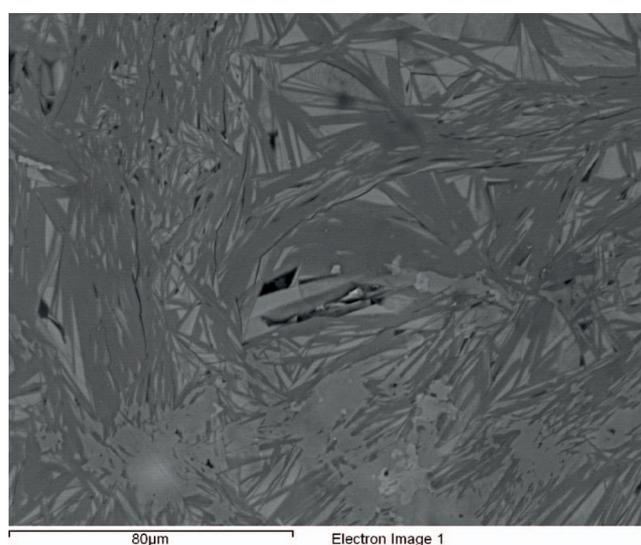


Figure 5. Scanning electron micrograph backscatter electron image of franklinphilite (dark grey needles) and caryopilite (medium grey). Specimen No. NMW 2011.2G.M.1f. Scale bar 80 μm .

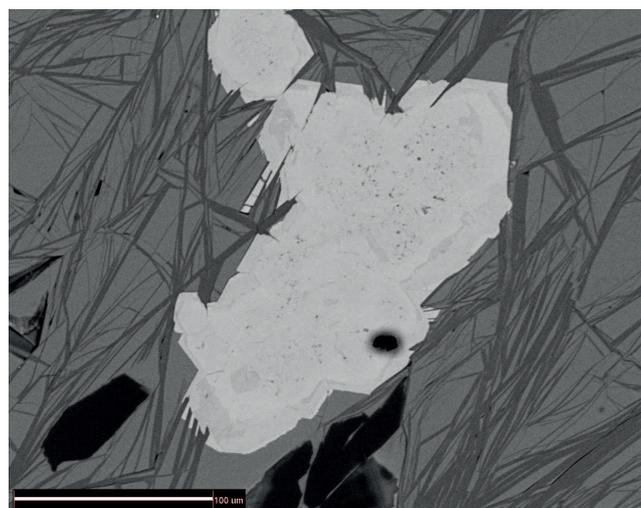


Figure 6. Scanning electron micrograph backscatter electron image of franklinphilite (dark grey needles) and caryopilite (medium grey, massive) enclosing a zoned euhedral allanite-(Ce)-ferriallanite crystal (bright, centre). Specimen No. NMW 2011.2G.M.1f. Scale bar 100 μm .

EDS analyses revealed that franklinphilite (Table 2) occurs as platy crystals enclosed by iron-rich caryopilite (Table 3). Backscatter electron images (Figs. 5 and 6) showed that the specific gravity of caryopilite is slightly greater (mid grey) than that of franklinphilite (dark grey).

The composition of franklinphilite recorded differs slightly from the type specimen of Dunn *et al.* (1992). Firstly type franklinphilite contains an appreciable, but non-essential, quantity of Zn. Thus, Dunn *et al.* (1992) quote the ideal formula for franklinphilite as, $\text{K}_4\text{Mn}_{48}(\text{Si},\text{Al})_{72}(\text{O},\text{OH})_{216}\cdot n\text{H}_2\text{O}$.

Secondly, the proportion of K is considerably higher in the Llyn Du Bach Mine material than would normally be expected for a stilpnomelane group mineral. Dunn *et al.* (1984) recorded an inhomogeneity in K within lennilenapeite and Mn-dominant stilpnomelane and suggested volatilization of K during microprobe analysis as a possible cause. Lennilenapeite does itself contain significantly more K

	Franklin ¹	Llyn Du Bach ²	Llyn Du Bach ³
MgO	6.4	4.19	3.65
ZnO	5.9	n.d. ⁴	n.d.
Na ₂ O	0.4	n.d.	0.07
Al ₂ O ₃	3.6	5.10	5.47
SiO ₂	44.0	43.30	42.47
K ₂ O	1.5	2.95	6.17
CaO	n.d.	0.45	0.07
TiO ₂	n.d.	0.26	0.32
MnO	22.3	22.75	23.32
Fe ₂ O ₃	7.8	9.98	9.53
CuO	n.d.	0.39	0.26
BaO	n.d.	n.d.	0.10
F	n.d.	n.d.	0.53 ⁵
H ₂ O	[8.1]		[8.04]
Totals	100.00	89.37	100.00

- Franklin, New Jersey, USA; from Dunn *et al.* (1992); by electron microprobe, H₂O by difference.
- Llyn Du Bach Mine (this study); NMW 2011.2G.M.1f; by EDS, single spot analysis.
- Llyn Du Bach Mine (this study); NMW 2011.2G.M.1f; average of five EDS analyses in a line across a single crystal. H₂O by difference.
- n.d. = not determined.
- F detected in three of the five analyses.

Franklin franklinphilite equates to: $(\text{K}_{2.64}\text{Na}_{1.07})_{\Sigma 3.71}(\text{Mn}_{26.08}\text{Mg}_{13.18}\text{Zn}_{6.02}\text{Fe}^{3+}_{2.72})_{\Sigma 48}(\text{Si}_{60.77}\text{Al}_{5.86}\text{Fe}^{3+}_{5.38})_{\Sigma 72}(\text{O}_{163.23}(\text{OH})_{52.77})_{\Sigma 216}\cdot n\text{H}_2\text{O}$.

Llyn Du Bach Mine franklinphilite (average of five analyses) equates to: $(\text{K}_{11.58}\text{Na}_{0.20}\text{Ca}_{0.10}\text{Ba}_{0.05})_{\Sigma 11.93}(\text{Mn}_{28.95}\text{Fe}_{10.57}\text{Mg}_{8.06}\text{Ti}_{0.35}\text{Cu}_{0.30})_{\Sigma 47.96}(\text{Si}_{62.43}\text{Al}_{9.57})_{\Sigma 72}[(\text{O}(\text{OH}))_{198}^{2.52}]_{\Sigma 201.4}\cdot n\text{H}_2\text{O}$.

Table 2. Comparative chemical composition data for franklinphilite.

than both stilpnomelane and franklinphilite and this is reflected in the formula proposed by Dunn *et al.* (1984): $K_{6-7}(Mg,Mn,Fe^{2+},Fe^{3+},Zn)_{48}(Si,Al)_{72}(O,OH)_{216} \cdot 16H_2O$. The reason for high K levels in the Llyn Du Bach Mine material is unexplained. However, there is no reason to doubt the accuracy of the EDS K reading, as a subsequent analysis of a stilpnomelane specimen produced a lower total consistent with stilpnomelane. One explanation could involve the substitution of K for Zn, but this is unlikely given that Zn should be present in a different structural site. Dunn *et al.* (1984) emphasised that the imprecision of K_2O and H_2O values does not affect the species status of the stilpnomelane group minerals, because status is wholly dependent upon the ratios of octahedrally co-ordinated cations Fe, Mg, Mn and Zn.

Caryopilite, intimately associated with franklinphilite in the veinlets, is an iron-rich variety. Published compositions of caryopilite are highly variable, as seen in Table 3, but a combination of XRPD (Fig. 4) and EDS data (Table 3) for Llyn Du Bach Mine material confirm that it is caryopilite.

	Sterling Hill ¹	Bald Knob ²	Llyn Du Bach ³	Llyn Du Bach ⁴
SiO ₂	32.1	36.35	35.53	37.32
Al ₂ O ₃	n.d. ⁵	0.21	0.61	n.d.
As ₂ O ₃	6.5	n.d.	n.d.	n.d.
FeO	1.7	1.09	n.d.	n.d.
Fe ₂ O ₃	n.d.	n.d.	11.53	13.54
MnO	48.8	42.39	37.03	38.76
ZnO	0.9	<0.03	n.d.	n.d.
MgO	1.9	8.01	2.26	2.25
CaO	n.d.	0.03	n.d.	n.d.
CuO	n.d.	n.d.	n.d.	0.21
F	n.d.	<0.05	n.d.	0.88
Cl	n.d.	0.14	n.d.	n.d.
H ₂ O	[8.1]	[9.22]	[13.04]	[9.22]
-O = (F,Cl) ₂		[0.08]		[0.34]
Totals	[100.00]	97.44	[100.00]	101.84

1. Sterling Hill, New Jersey, U.S.A, from Anthony *et al.* (1995); by electron microprobe, H₂O by difference.
2. Bald Knob, North Carolina, U.S.A from Anthony *et al.* (1995); by electron microprobe, H₂O calculated from stoichiometry.
3. Llyn Du Bach Mine (this study). NMW 2011.2G.M.1f; single spot analysis by EDS, H₂O by difference.
4. Llyn Du Bach Mine (this study). NMW 2011.2G.M.1f; single spot analysis by EDS, H₂O calculated from stoichiometry.
5. n.d. = not determined.

Table 3. Comparative chemical composition data for caryopilite.

Sub 200 micron wide, high density, euhedral inclusions observed within franklinphilite-caryopilite veinlets during SEM-EDS analysis contain significant rare-earth content and fit compositionally with allanite-(Ce), but with an unusual enrichment in Mn (Table 4). Zonation is apparent in backscatter electron images (Fig. 6) and a single analysis (Table 4) produced a composition within the field of ferriallanite-(Ce), but once again with significant Mn. Minute (40 µm x 5 µm), high density, elongate inclusions between platy franklinphilite crystals are shown by SEM-EDS to be pyrophanite.

	Allanite -(Ce) ¹	Ferriallanite -(Ce) ²	Manganoan ferriallanite -(Ce) ³	Manganoan allanite -(Ce) ⁴
SiO ₂	29.79	28.72	29.47	29.30
TiO ₂	0.02	1.85	n.d.	n.d.
Al ₂ O ₃	12.75	6.07	8.20	12.15
Y ₂ O ₃	0.04	n.d. ⁵	n.d.	n.d.
La ₂ O ₃	7.2	5.12	5.21	4.66
Ce ₂ O ₃	12.8	10.86	12.56	15.09
Pr ₂ O ₃	1.0	1.63	n.d.	n.d.
Nd ₂ O ₃	3.10	5.29	3.13	1.02
Sm ₂ O ₃	0.60	n.d.	n.d.	n.d.
Gd ₂ O ₃	0.06	n.d.	n.d.	n.d.
Er ₂ O ₃	0.02	n.d.	n.d.	n.d.
Fe ₂ O ₃	10.64	n.d. ⁶	21.42 ⁷	17.38 ⁷
FeO	9.02	25.30 ⁶	n.d. ⁷	n.d. ⁷
MnO	0.85	0.82	7.34	5.79
MgO	0.64	n.d.	n.d.	0.35
CaO	10.10	10.85	8.12	7.67
H ₂ O				
H ₂ O ⁺	1.64			
H ₂ O ⁻	0.10			
Totals	100.37	96.51	95.43	93.41

1. Allanite-(Ce) from Luangwe Bridge area, Zambia, from Anthony *et al.* (1995); wet chemical and spectrographic analysis.
2. Ferriallanite-(Ce) from Mount Ulyn Khuren, Altai Range, Mongolian People's Republic, from Kartashov *et al.* (2002); average of four WDS electron microprobe analyses.
3. Manganoan ferriallanite-(Ce) from Llyn Du Bach Mine (this study). NMW 2011.2G.M.1f; single spot analysis by EDS.
4. Manganoan allanite-(Ce) from Llyn Du Bach Mine (this study). NMW 2011.2G.M.1f; average of two spot analyses by EDS.
5. n.d. = not determined.
6. Fe calculated as FeO only.
7. Fe calculated as Fe₂O₃ only.

Table 4. Comparative chemical composition data for allanite group phases.

Dark reddish-brown, bladed to prismatic crystals of hübnerite occur commonly as inclusions in rhodochrosite-quartz veinlets in the manganese ore bed as previously described by Cotterell *et al.* (2010; XRPD NMW X-2684). XRPD analysis (NMW X-2684) of a dark reddish-brown, bladed to prismatic, crystal (NMW 2013.35G.M.3a) from Llyn Du Bach Mine has shown that hübnerite inclusions are common within rhodochrosite-quartz veinlets in the manganese ore bed as previously described by Cotterell *et al.* (2010). Paragenetically, franklinphilite appears to be one of the earliest phases within veinlets predating carbonates and quartz. Occasionally platy, orange-brown, franklinphilite crystals occur along the edges of carbonate-quartz veinlets enclosed in quartz.

DISCUSSION

At the type locality of Franklin Mine, New Jersey, franklinphilite was reported (Dunn *et al.*, 1992) from two assemblages. In the holotype specimen, found on the Buckwheat Dump, franklinphilite occurs as dark brown radiating clusters of platy crystals both intimately intergrown with medium brown friedelite in the central 1 cm of a vein cutting through a complex breccia and as darker brown, more coarsely crystallized, material at the margins of the vein. The associated breccia contains calcite, fragmentary franklinite, fine-grained friedelite, chamosite, aegirine, dense fine-grained interlayered 7-Å and 14-Å phyllosilicates of the mixture formerly known as baumite and fragments of willemite. In the second assemblage, franklinphilite is black, nearly opaque, and associated with nelenite, rhodonite and tirodite.

Texturally the material from Llyn Du Bach Mine is similar to that described and figured by Dunn *et al.* (1992). The backscatter electron image of franklinphilite used as Figure 2 in Dunn *et al.* (1992) shows striking similarities to Figure 5 in this paper; however, while the franklinphilite from Franklin occurs intergrown with friedelite, $\text{Mn}^{2+}_8\text{Si}_6\text{O}_{15}(\text{OH},\text{Cl})_{10}$, at Llyn Du Bach Mine franklinphilite is intergrown with caryopilite, $(\text{Mn}^{2+},\text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$, itself a friedelite group mineral (Peacor and Essene, 1980). This is where the similarities end as the unique mineral deposit at Franklin (Dunn, 1995) is different in almost every respect to the Harlech manganese ore bed.

Franklinphilite from Llyn Du Bach Mine is dark chocolate-brown to orange-brown in colour, differing subtly in appearance to stilpnomelane which is usually dark brown to black in hand specimen. Visual distinction between the two species is impossible but our investigations indicate that franklinphilite is very common at Llyn Du Bach Mine, is probably a minor component of the ore bed itself (Cotterell, 2013), and may also be present in veinlets at the adjacent Llyn Dywarchen Mine (NMW 24.279.GR.29).

Elsewhere in the Harlech Dome stilpnomelane was reported by Bevins (1994) at 'Moelfre' and Cwm Mawr Mine. The 'Moelfre' occurrence was identified by XRD at the Natural History Museum, London while, specimens from Moelfre Mine and Cwm Mawr No. 2 Mine are represented in the G.J. Williams Mineral Collection at Amgueddfa

Cymru and consist of coarse, platy, black stilpnomelane crystals in veins. For verification, several small fragments of platy, black, stilpnomelane crystals collected recently from Moelfre Mine (NMW 2012.12G.M.2) were analysed by SEM-EDS. These are stilpnomelane, but with significant substitution of manganese for iron up to a ratio of Fe:Mn of 1:0.64. It is unclear why this material is not identical to the phase identified at Llyn Du Bach Mine, but it is possible that because the stilpnomelane vein at Moelfre Mine is quite wide (over 1 cm) a dilution of manganese over iron has occurred. There is also evidence to suggest that the vein, at Moelfre Mine, does not cut through the ore bed and therefore the host rock is depleted in manganese relative to iron.

Further afield in North Wales, stilpnomelane is of widespread occurrence in Ordovician age, bedded oolitic and pisolitic ironstones where it is typically found as veinlets. Good examples are known from Tyllau Mwn, Pen-yr-allt, Bryn-y-castell and Betws Garmon iron mines (Bevins, 1994). Hallimond (1925) interpreted the veinlets in certain Welsh oolitic ironstones, including Pen-yr-allt, as having developed as a result of contact metamorphism with greenstones and other igneous intrusions. However, the widespread presence of veinlets within ironstones with no obvious local igneous heat source precludes this theory. Matthews and Scoon (1964) interpreted the stilpnomelane veinlets at Tyllau Mwn as post-metamorphic features, although it was noted that no precise data was available regarding the conditions under which they had formed. In a recent review of the mineralization at Tyllau Mwn, Bevins and Mason (2010) proposed that stilpnomelane-bearing veins formed during regional, burial-related, metamorphism in a similar way to the 'Alpine-type' veins of the Ffestiniog-Porthmadog area in Snowdonia with localized migration of fluids into fractures with minerals reflecting the geochemistry of their source rock.

At Llyn Du Bach Mine, and throughout the Cambrian succession in the Harlech Dome, regional, burial related, low-grade metamorphism to lower greenschist facies (Bevins *et al.*, 1981; Bevins and Robinson, 1988) has altered the mineralogical composition of the sediments. The affect is most pronounced in the manganese ore bed where a complex assemblage of silicates and carbonates of manganese has developed (Woodland, 1939; Bennett, 1987; Cotterell, 2013). Peak metamorphism is interpreted to have occurred prior to tectonic deformation and cleavage development (Bevins and Robinson, 1988) in an extensional setting with high heat flow. Sedimentary cover was thickest during early- to mid-Silurian times and it is likely that peak, burial-related, metamorphism was reached during this period.

Veinlets within the manganese ore bed have received only minor attention from previous researchers and are, perhaps, deserving of a thorough study. Narrow veinlets traversing the bands approximately at right angles to bedding have been variously described as contraction (syneresis) cracks resulting from dehydration of a colloidal gel (Woodland, 1939) and directional syn-sedimentary or tectonic deformation features (Bennett, 1987). Woodland

(1939) also recorded fairly common irregular quartz veinlets traversing the ore vertically and quartz infilling irregular rectangular jointing. Bennett (1987) suggested that two types of veinlet exist: discrete, continuous fracture-filling; and indistinct discontinuous replacive veins. Both types occur normal to bedding. It is evident, from studying specimens collected at Llyn Du Bach Mine, that multiple episodes of vein formation exist but, as noted by Bennett (1987), the vast majority of veinlets occur in a sub-parallel orientation indicating some form of structural control.

The geological structure known as the Harlech Dome formed during the final, Acadian, phase of the Caledonian orogeny (McKerrow *et al.*, 2000) in late Silurian to early Devonian times when tectonic movement uplifted the Lower Palaeozoic Welsh Basin (Howells *et al.*, 1981). The thick Lower Cambrian succession known as the Harlech Grits Group was folded with the formation of the Dolwen Pericline at its core. Extensive faulting on the western side of the dome resulted in the repeated outcrops of the manganese ore bed seen today. Llyn Du Bach Mine is situated within a small faulted block on the north-west side of the Harlech Dome, but the manganese ore bed and the overlying bluestone and Manganese Grit dip uniformly at a shallow angle with little evidence of deformation discernible in outcrop (Fig. 2). Despite this, the distinctive coloured bands within, the ore bed at Llyn Du Bach Mine frequently displays folding and small-scale faulting (Fig. 7). Bennett (1987) attributed folds and thrusts in the ore bed to syn-sedimentary slumping. Both ductile and brittle syn-sedimentary deformation features are displayed and it is possible that some of the earliest veining is related to this phase of deformation.

Franklinphilite occurs in many of the veins/veinlets observed at Llyn Du Bach Mine. The commonest franklinphilite-bearing veinlets occur in brick-red bands in the upper section of the ore bed as bedding perpendicular fracture fillings ranging in scale from microscopic to several mm in width. Veinlets infill fractures related to brittle, syn-sedimentary, deformation with small scale faulting common (Fig. 7). The narrowest fractures are filled with dark brown, platy, franklinphilite and golden-brown, fibrous, caryopilite, but wider (mm scale) veinlets are infilled with quartz. All three minerals show evidence of fibrous growth textures developed perpendicular to vein walls. Where faulting occurs fibrous growth textures indicate that vein opening postdates faulting.

Thin (mm scale) franklinphilite-bearing veinlets of short strike-length (typically in the order of 2 to 4 cm) crosscut many sections of the ore bed, but with a marked thinning of all veins within the darker chocolate-brown bands (Fig. 3). Franklinphilite is not present in every sample from the ore bed, but where it does occur a concentration of franklinphilite-bearing veinlets tends to occur within a 4 cm thick, section of interlayered brick red and cream bands between two darker chocolate-brown bands (the mineralogy of these chocolate-brown bands is described in detail by Cotterell, 2013) at a height of between 6 and 10 cm from the base of the ore bed. These veinlets are, again, perpendicular to bedding and show a lensoid

form (Fig. 8). Veinlets are particularly common in the lowermost bands in the ore bed, but these are predominantly infilled with carbonate and quartz (Fig. 8) and rarely franklinphilite.

Rarer shallow angle veinlets contain rhodochrosite or quartz, or both, but generally not franklinphilite. Their relationship with the vertical veins has not been determined although there is some evidence to suggest that, irrespective of orientation, wider veins cross-cut thinner veinlets. Thick, centimetre scale, milky quartz dominated veins which cut through almost the entire ore bed sequence, perpendicular to bedding, rarely contain franklinphilite, but where they do franklinphilite shows signs of having been brecciated from an earlier, reactivated, veinlet.



Figure 7. Syn-sedimentary faulting within the upper section of the manganese ore bed. Parallel, bedding perpendicular, faults are mineralized with dark brown franklinphilite and white quartz. Specimen No. NMW 2013.35G.M.1 Llyn Du Bach Mine. Specimen 5 cm tall.



Figure 8. Lensoid veinlets, perpendicular to the bedding, containing carbonate-quartz and minor franklinphilite cutting through the lowest horizons in the manganese ore bed at Llyn Du Bach Mine. Specimen No. NMW 2013.35G.M.2. Specimen 10 cm across.

The common, lensoid, veinlets show similarities to the bedding normal quartz veins of the, younger, High-Ardenne slate belt interpreted, by Van Noten *et al.* (2011), as extension veins related to the compressional tectonic inversion of a sedimentary basin under low grade metamorphic conditions. Van Noten *et al.* (2011) suggested that tectonic inversion from extension to compression from the latest stages of basin development to the earliest onset of an orogenic event results in a rapid increase in fluid pressure which, concomitant with decreasing differential stress, can create bedding normal extension fractures. Subsequent successive hydraulic fracturing and sealing at low differential stress results in fracture infill, vein formation, vein thickening and vein extension.

In the manganese ore bed, bedding-perpendicular veins frequently show fibrous quartz developed perpendicular to vein walls, a growth texture indicative of extension (Van Noten *et al.*, 2011). Platy franklinphillite crystals also occasionally show stretching away from the vein walls. Slivers of host rock incorporated within wider veins, and lying parallel to the vein walls, are interpreted as evidence of a crack-seal mechanism of vein formation. Repeated fracturing, reactivation, and extension of veinlets is likely to have led to the formation of some of the longer, carbonate-quartz-dominated, veins in the ore bed.

Sedimentation in the Lower Palaeozoic Welsh Basin ceased during the mid Silurian with a shift from an extensional, depositional, environment to a compressional, mountain-building, episode with the onset of Acadian deformation in late Silurian times. Bevins and Robinson (1988) argued that low grade metamorphism in the Lower Palaeozoic successions resulted from an extensional setting, pre-deformation, in the Welsh Basin. The geological evolution of the Lower Palaeozoic Welsh Basin shares similarities with the younger, Ardenne-Eifel sedimentary basin in Germany and it therefore seems plausible that bedding normal vein formation in the manganese ore bed could have occurred through a process similar to that described by Van Noten *et al.* (2011).

The geochemistry of the veinlets shows a clear affinity to the mineralogy of the host rock - the manganese ore bed - indicating a process of intraformational redistribution or lateral secretion. Bevins and Mason (2010) proposed a similar mechanism for the formation of stilpnomelane-bearing veins within oolitic ironstone at Tyllau Mwn. Inclusions within the franklinphillite-caryopilite bearing veinlets support this contention. Manganean allanite-(Ce), reported here, requires elevated levels of rare earth elements and data provided by Bennett (1987) shows that the ore bed, and in particular the red laminated ore, is enriched in cerium. Tiny inclusions of pyrophanite within the veinlets can be explained by the presence of ferropyrophanite, described by Bennett (1987), as small (sub 0.01 mm) anhedral grains within the red laminated ore. On the rare occasion that veins extend beyond the ore bed into the overlying bluestone, at Llyn Du Bach Mine, green chlorite occurs in preference to franklinphillite reflecting a change in chemistry of the host rock. Franklinphillite and caryopilite are both metamorphic minerals indicating that the veinlets

developed during metamorphism of the manganese ore bed which also supports a mid to late Silurian age.

Due to the vast extent of the manganese ore bed across the Harlech dome, there is significant potential for further discoveries of franklinphillite.

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CHERNOVITE-(Y) IN REDUCTION SPOTS IN WELSH SLATE

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Chernovite-(Y) occurs with quartz, calcite, epidote, dravite, and synchysite-(Ce) in green reduction spots in lower Cambrian slates from Alexandra Quarry, Gwynedd, Wales. This is the first definite record of the mineral from Britain and the first report of an arsenic-bearing mineral in this type of geological environment.

INTRODUCTION

Chernovite-(Y), ideally $YAsO_4$, is a rare mineral which is known from relatively few localities worldwide. The name honours Professor Aleksandr Aleksandrovich Chernov (1877-1963), a Russian geologist and explorer. Chernovite-(Y) is a member of the xenotime group of minerals. It forms a solid solution series with xenotime-(Y), ideally YPO_4 , and wakefieldite-(Y), ideally YVO_4 . The type locality is on the Nyarta-Sya-Yu River in the Polar Urals, Russia, where chernovite-(Y) occurs in piemontite veinlets in a liparite (rhyolite) porphyry (Fleischer, 1968). Other localities in rhyolitic host rocks include Paramount Canyon, New Mexico, USA (Anthony *et al.*, 2000); Rejkovo, Tisovec, Banská Bystrica Region, Slovakia (Ondrejka *et al.*, 1995); and in altered rhyolites at Fuchs Quarry, Sailauf, Bavaria, Germany (Anthony *et al.*, 2000). Chernovite-(Y) has also been reported from Alpine-type veins on the west flank of Cherbadung, Binntal, Switzerland where it is associated with niobian rutile, magnetite, asbecasite and cafarsite (Anthony *et al.*, 2000). It occurs in the arsenic-rich Tennvatn pegmatite, Sørfold, Norway (Ellingsen *et al.*, 1995) and at the Jaguaraçu pegmatite, Minas Gerais, Brazil in association with milarite, albite, euxenite, monazite, muscovite and zircon (Anthony *et al.*, 2000).

Chernovite-(Y) crystallises in the tetragonal system. The crystals from the type locality in the Urals are prismatic, less than 1 mm in length, and colourless to pale yellow (Fleischer, 1968): those from alpine-type fissures in gneisses at Pizzo Cervandone, Italy reach up to

5 mm in length, and are found as lemon yellow to green pseudo-octahedral crystals (Graeser and Roggiani, 1976).

Up until the present study, chernovite-(Y) was an unconfirmed British mineral: the single and tentative record being by Embrey (1978) who reported the possible occurrence of chernovite-(Y) in black globules from Gipsy Lane Brick Pit, Leicestershire. Enquiries about this specimen (which is held at the Natural History Museum, London) have found a reference to identification of some djurleite on gypsum but no mention of any chernovite (Mike Rumsey, *personal communication*). Analytical work by Faithfull and Hubbard (1988) on Gipsy Lane specimens had shown that the black spheres contain the uranium-bearing silicate coffinite.

LOCATION

The purple slate with green reduction spots described herein is from Alexandra Quarry [SH 518 561], near Rhosgadfan, Gwynedd, Wales (Fig. 1). The slate at this locality is a purple, cleaved siltstone of Cambrian age which is part of the Llanberis Slates Formation. A complex faulted anticline runs approximately NE-SW through the middle of the quarry producing exposures of the younger, green sandstones of the Bronllwyd Grits Formation in the southwest walls. Near the summit of Moel Tryfan, to the west, underlying sandstones and conglomerates of the Arfonian Fachwen Formation are exposed. A large dolerite dyke runs through the quarry and is exposed in the north-west corner. The majority of the specimens were collected from loose material near the quarry entrance (at about SH 515 559). In particular, samples were selected in which the central areas of the green spots were raised, black, and vuggy.

LITHOLOGY

The mineralogy of both the purple and green areas of the slate is dominated by muscovite, quartz, epidote and chlorite with accessory minerals including monazite. The petrography of the purple slate was not examined in detail in this study but the analyses corroborate the descriptions of Borradaile *et al.* (1991) who examined similar slates from Penrhyn Quarry near Bethesda. Fine-grained hematite is present in the purple areas but absent in the green areas and there is a corresponding reduction in the iron content of the green areas. Borradaile *et al.* (1991) found no significant differences in the chemical composition of the iron-bearing minerals chlorite and epidote in the green and purple slates,

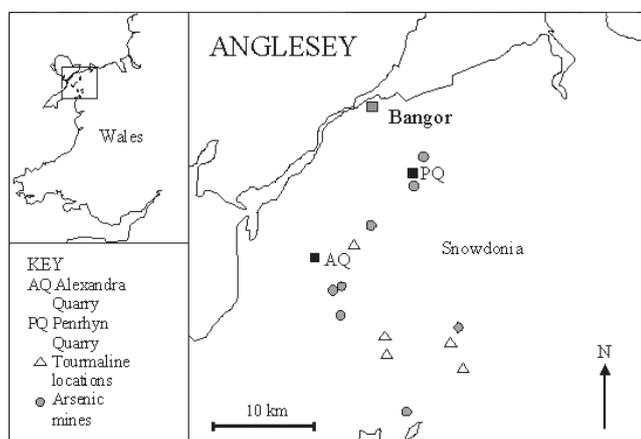


Figure 1. Map showing the location of Alexandra Quarry in North Wales and other related mineral deposits discussed in the text.

but noted that about twice as much chlorite was present in the green areas.

Examination by scanning electron microscopy revealed that some of the black central spots were vuggy, whereas others had been infilled. A typical infilled cavity in the centre of a green spot is shown in Figure 2. Euhedral dravite crystals appear to have grown into a cavity and have subsequently been enclosed by epidote and synchysite-Ce.

MINERALS

The minerals in the reduction spots are described in detail below. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to identify the species present. Some samples were prepared as polished blocks; others were examined as chips without preparation. All were carbon coated for analysis by energy dispersive spectrometry (EDS) and wavelength dispersive spectrometry (WDS). Some of the samples for XRD were powdered.

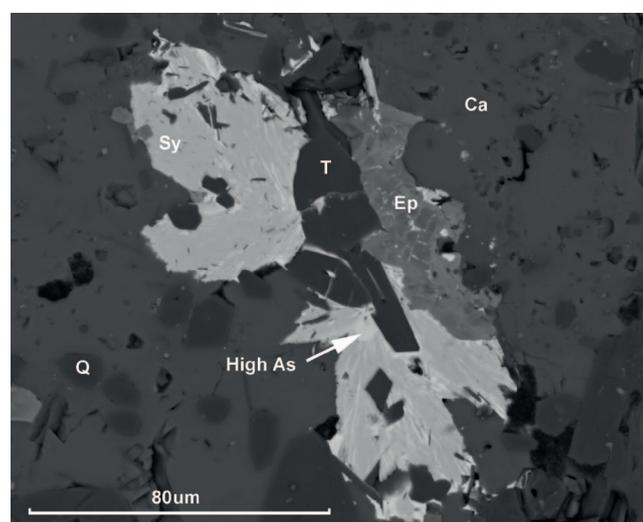


Figure 2. Typical infilled vug in green spot in slate. Key: T = euhedral dravite; Sy = synchysite-(Ce) which has infilled the void with bright stripes of possible parisite-(Ce); As = an area rich in arsenic but too small for analysis; Ep = epidote. The surrounding material (Ca) is calcite with subhedral quartz crystals (Q). Scale bar 80 μm..

CHERNOVITE-(Y), $YAsO_4$

Energy dispersive analyses showed that bright patches in some grains of synchysite-(Ce) contained high levels of arsenic. These arsenic-rich areas were typically too small for accurate quantitative analysis, but one sample with a large number of small subhedral crystals (Fig. 3) was found. The spot analyses listed in Table 1 show the arsenic-bearing phase to be chernovite-(Y). The analyses have the following similarities: the specimens have ~10 wt% P_2O_5 substituting for As_2O_3 ; the REEs are from the middle lanthanides with gadolinium and dysprosium being the most abundant elements present; light REEs are virtually absent; there is very little vanadium, though up to a few wt% V_2O_5 was determined in some of the spots (not shown here due to poor totals); there are trace amounts of Pb in all the analyses.

DRAVITE, $NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$

Euhedral tourmaline crystals grow outwards from the walls of cavities in many of the reduction spots, in some cases they are enclosed by later calcite and synchysite-(Ce) (Fig. 2). Analyses by EDS and XRD (reference number

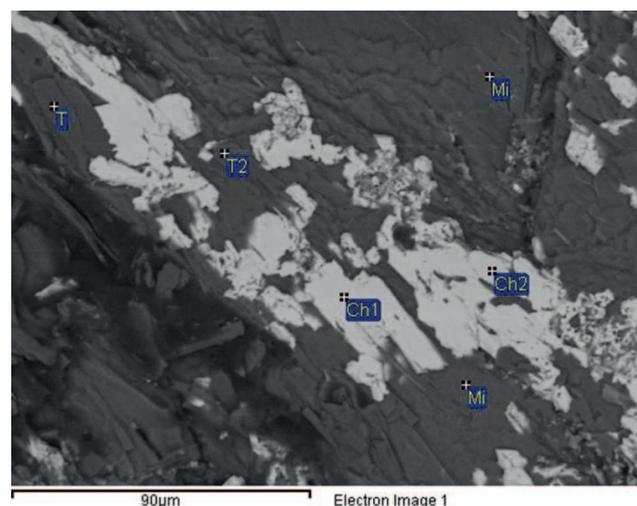


Figure 3. Large cluster of chernovite-(Y) crystals (Ch1, Ch2) in a matrix of the silicate minerals including dravite (T, T2), quartz and muscovite (Mi). Scale bar 90 μm.

	P_2O_5	V_2O_5	As_2O_3	Y_2O_3	La_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Er_2O_3	Yb_2O_3	PbO	Totals
AQ1	9.67	0.45	32.89	35.59	-	1.22	1.59	5.23	6.11	2.51	1.09	0.16	96.51
AQ2	9.33	0.37	33.68	36.80	-	1.28	1.35	4.86	5.95	2.76	1.76	0.60	98.74
AQ3	7.74	0.64	34.81	37.60	-	1.10	1.35	5.23	6.78	2.95	2.01	0.42	100.63
AQ4	9.75	0.45	32.86	35.55	-	1.22	1.59	5.22	6.10	2.51	1.09	0.16	96.50
AQ5	9.33	0.37	33.69	36.81	-	1.28	1.35	4.86	5.95	2.76	1.76	0.60	98.76
AQ6	7.74	0.64	34.82	37.60	-	1.10	1.35	5.23	6.78	2.95	2.01	0.42	100.64
SZ	5.5	-	40.3	36.9	15.1	-	-	-	-	-	-	-	97.8

AQ = samples from Alexandra Quarry, North Wales.

SZ = a sample from Binntal, Switzerland from Graeser *et al.* (1973) for comparison.

Table 1. Analyses of chernovite-(Y) in wt%.

NMW X-2506) show that the tourmaline is dravite. Several spot analyses revealed a fairly consistent composition with a Na₂O content varying from 1.69 wt% to 2.12 wt% and a MgO content from 6.71 wt% to 7.80 wt%. No evidence of zoning was observed within the grains.

EPIDOTE, Ca₂(Fe³⁺,Al)Al₂O.OH.Si₂O₇.SiO₄

An epidote-group mineral, which typically contains 11 wt% total REEs, is common in the reduction spots. Using the nomenclature recommended by Armbruster *et al.* (2006) the calculations of Table 2 show that, although the epidote-group mineral has a composition which tends towards a member of the allanite series (Ca,Ce,La,Y)₂(Mn²⁺,Fe²⁺,Fe³⁺,Al)₃O.OH.Si₂O₇.SiO₄, it is best described as a REE-rich epidote as the predominant cation in the A2 site is Ca.

SYNCHYSITE-(Ce), Ca(Ce,La)(CO₃)₂F

The bright central area in Figure 2 contains a mineral with a composition that alternates between high Ca, low Ce and low Ca, high Ce. Synchysite-(Ce) was identified as the more abundant phase by SEM and XRD (Reference Number NMW X-2488). The areas of lower Ca, high Ce were too small for accurate analysis; they are thought to be parisite-(Ce). Other spot analyses suggest the presence of bastnäsite-(Ce) but this could not be confirmed.

DISCUSSION

The green spots that are common in sedimentary rocks typically form in reducing conditions which develop around organic remains during diagenesis. In this process the Fe³⁺, which is present as fine-grained red hematite, is reduced to more soluble Fe²⁺, which is removed, revealing the underlying colour of the rock.

Interestingly, studies of the magnetic signatures of the purple and green zones at Penrhyn Quarry by Nakamura and Borradaile (2001) found that the formation of the green spots may post-date the development of the slaty cleavage. If slate formation had deformed the green spots the magnetic fabric of the purple and green areas ought

to be identical, however Nakamura and Borradaile (2001) found the magnetic signatures of the two were different. This suggested that the green spots had formed after the development of the slaty cleavage and that deviations from a spherical shape were due to preferential rates of chemical alteration in an anisotropic medium. No information is available about the magnetic signatures of the reduction spots at Alexandra Quarry and Nakamura and Borradaile (2001) do not suggest that all reduction spots post-date the development of cleavage; it is therefore not entirely clear when the green spots formed.

Tourmaline is well known in Snowdonia: it occurs as detrital grains and as tourmalinised grits at Cwm Dwythwc (Fearnside, 1908); at Bwlch Gwyn (Williams, 1927); Aberglaslyn and Beddgelert (Beavon, 1963); and in the contact aureole of the Tan-y-Grisiau microgranite (Bromley, 1969). The tourmaline-group species dravite requires chemical analysis and XRD data for identification to species level; unpublished data on samples of Caradocian sandstone from Cwm Bychan, Beddgelert studied by Beavon (1963) have identified schorl and foitite, with outer rims of dravite; however this is the first report of dravite crystals from Welsh slate. Dravite is widespread in metamorphic and metasomatic assemblages. More detailed analysis would be required for it to be valuable as petrogenetic indicator mineral in the current context.

The mineral assemblage in the spots at Alexandra Quarry, which includes carbonates, chlorite, epidote and quartz, is typical of low-temperature metamorphic alteration. It may be that some of the minerals developed as a result of regional processes, but the presence of a large dolerite dyke in the corner of the quarry may have provided the hydrothermal circulation and some of the chemical input required for the minerals to develop.

Synchysite-(Ce) is a hydrothermal mineral that appears to develop as a result of the alteration of calcite. It is commonly associated with the other structurally similar fluorocarbonates parisite and bastnäsite; both of which are probably present at Alexandra Quarry. It has been recorded by Graeser and Schwander (1987) that synchysite can be

Oxide	Wt%	Mole Units	O units	O (norm = 12.5)	Cation Units (norm = 8)	Z	M	A
SiO ₂	34.61	0.57603	1.15205	5.71977	2.88765	Si	2.88765	
TiO ₂	0.49	0.00614	0.01227	0.06092	0.03076	Ti		0.03076
Al ₂ O ₃	24.11	0.23646	0.70939	3.52201	2.37080	Al	0.11235	2.25845
Fe ₂ O ₃	11.04	0.06913	0.20740	1.02973	0.69315	Fe ³⁺		0.69315
MnO	1.36	0.01917	0.01917	0.09519	0.09611	Mn		0.01765 0.07846
CaO	17.67	0.31510	0.31510	1.56444	1.57962	Ca		1.57962
La ₂ O ₃	2.93	0.00899	0.02698	0.13395	0.09017	La		0.09017
Ce ₂ O ₃	5.89	0.01795	0.05384	0.26730	0.17993	Ce		0.17993
Nd ₂ O ₃	2.41	0.00716	0.02149	0.10669	0.07182	Nd		0.07182
Totals	100.51	1.25614	2.51770	12.5	8		3	3 2

Table 2. Composition of epidote from Alexandra Quarry, North Wales. Ca²⁺ is the dominant cation at the A2 site; the REE atoms are subordinate totalling 0.090 + 0.180 + 0.072 = 0.342; minor Mn²⁺ is also present at this site. The M sites are dominated by Al³⁺.

altered to the arsenate gasparite-(Ce) at Pizzo Cervandone in Italy. A similar alteration towards a REE arsenate may explain the presence of high levels of arsenic in some of the synchysites in this study. Rare-earth minerals are relatively common in north Wales but their presence in cavities in reduction spots has not been recorded previously.

There has been considerable interest in the geochemistry of arsenic in recent years due to its relatively high toxicity. In North Wales, arsenopyrite has been extracted from mines in Cambrian metasediments. The nearest mines to Alexandra Quarry are shown in Figure 1. The speciation of the arsenic at Alexandra Quarry, where it occurs as a primary arsenate, is intriguing. No other arsenic-bearing minerals have been reported from the quarry or from geologically similar localities in the area; indeed this is the first definite record of chernovite-(Y) from the United Kingdom. This may be an artefact of selection as the reduction spots are little studied. It would be interesting to study other reduction spots, and to investigate the area more fully, to determine whether the mineralogical relationships can be better defined and the timings and origins of the spots and their associated mineralisation better understood.

ACKNOWLEDGEMENTS

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ZIRCON PYROXENITE FROM UPPER BADCALL, SUTHERLAND, NORTH-WEST SCOTLAND

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Coarse euhedral crystals of greyish-pink zircon up to 16 mm in length were collected in early 2012 from an Archean zirconiferous pyroxenite south of Scourie in the Loch an Daimh Mor area near Upper Badcall, Sutherland in NW Scotland. This occurrence is considered to be unique in the UK both for the size and colour of the zircon crystals and their occurrence in ultrabasic rocks. Previous research suggests that the zircons are of magmatic origin and that they partially recrystallized during subsequent metamorphic events.

INTRODUCTION

The occurrence of zircon in the Lewisian Archean metamorphic basement complex has been reported by several workers e.g. Corfu (1994, 1998), Friend *et al.* (2007), Kelly *et al.* (2008), Kinny and Friend (1994, 1997), Love *et al.* (2004), Timms (2006), and Upton (1999). These occurrences are currently (2013) the subject of a PhD research program on the Lewisian terrane accretion of NW Scotland by David MacDonald at Liverpool University. Lewisian zircons are typically small and colourless, often visible only in thin sections. For research purposes, they are extracted by crushing the host rock, or analysed in the rock sample using laser techniques.

Zircon is generally found in the more siliceous magmas, occurring as an accessory mineral in granites, diorites, syenites and pegmatites. The durability of zircon enables it to survive as an accessory mineral in high grade

metamorphic rocks such as gneisses and granulites, and as a heavy mineral in detrital sedimentary rocks. The Lewisian gneiss in this area is derived mainly from trondhjemitic plutonic igneous rocks (a variety of tonalite) that were intruded by layered igneous intrusions (Bowes *et al.*, 1964).

Zircon is rare in mafic igneous rocks, and very rare within ultrabasic rocks (apart from potassium bearing ultramafic rocks such as carbonatites, kimberlites, and lamprophyres); hence the significance of this particular occurrence where the zircon is hosted within a pyroxenite.

GEOLOGICAL BACKGROUND

The zirconiferous pyroxenite occurs as pods and lenses within a highly fractured, heterogeneous, layered ultrabasic serpentinite and calc-chlorite rock complex. The pyroxenite is largely unaltered, outcropping as a low crag (Fig. 2) on the margin of the complex.

This particular complex is one of a series of similar layered basic to ultrabasic bodies in the area, and all are considered to have been intruded close to the peak Badcallian granulite-grade metamorphism and associated magmatism in the Archaean, dated at 2.48–2.49 Ga (billion years). Zircon grain analysis (Timms *et al.*, 2006) shows radioactive trace elements of 16–50 ppm U and 165–110 ppm Th. The zircons were dated using lead isotope ratios producing a $^{207}\text{Pb}/^{206}\text{Pb}$ mean age of 2.47 Ga \pm 30 Ma (million years).

Dating of zircon grains is important in unraveling the geological history of metamorphic complexes such as the Lewisian, but interpretation is difficult and results have often been ambiguous. Corfu *et al.* (1994) collected zircons from a deformed sheet of trondhjemitic gneiss at Badcall Bay and interpreted the derived age of 2.72 Ga as that of magmatic crystallization. However, they found that the outer shells of the grains yielded older dates than the cores, an interpretation that has subsequently been disputed (Love *et al.*, 2004, Friend *et al.*, 2007).

Friend *et al.* (2007) consider that the Lewisian of the area represents a series of accreted terranes of differing ages and early history. Zircon evidence from the gneisses

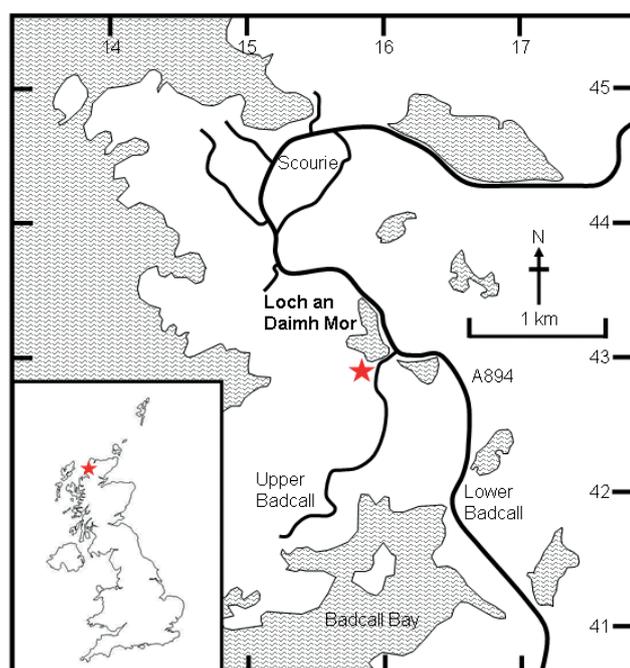


Figure 1. Location map.

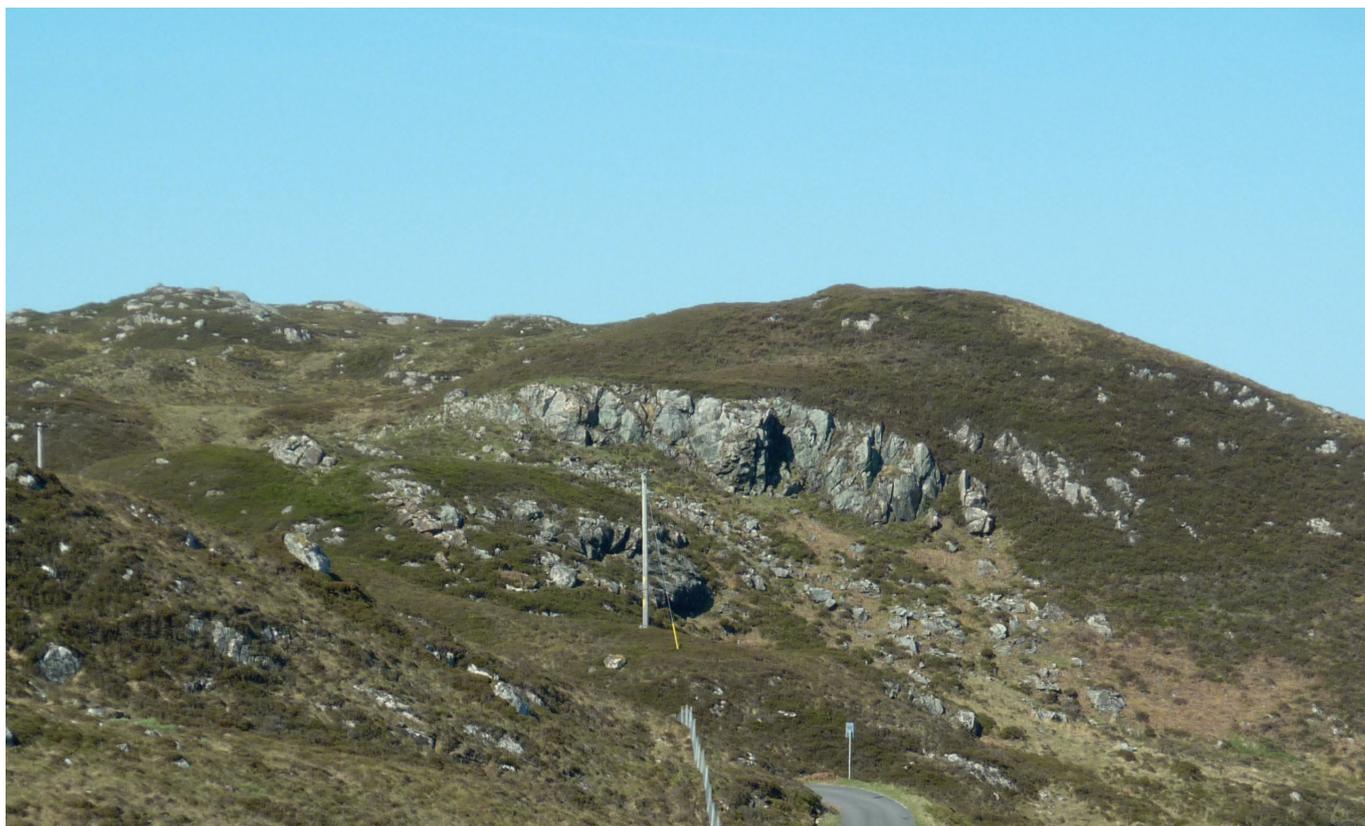


Figure 2. View of the outcrop. Photo: R.E. Starkey.

is increasingly supporting this conclusion (D. MacDonald, *personal communication*). Friend *et al.* (2007) state that trondhjemite magmatism originally took place at 2.9 Ga, and subsequently the rocks were subjected to a localized partial melting event at 2.72 Ga followed by the 2.49 Ga Badcallian granulite facies event. However, Kinny and Friend (1997) report xenocrystic samples of zircon from gneiss at Scouriemore as yielding dates of 3.115 Ga \pm 18 Ma. If correct, these dates may represent the age of the trondhjemitic protolith.

Lewisian rocks in the area have been partially retrogressed and overprinted by Proterozoic Laxfordian amphibolite facies metamorphism at c. \pm 1.6 Ga. This retrogressive metamorphism does not appear to have affected either the zirconiferous pyroxenite or granulite facies gneisses, but has affected the more mafic gneisses and peridotite layered intrusions.

FIELD OCCURRENCE

The field descriptions presented here are based on examinations undertaken by the authors mainly during 2012, although with a number of earlier visits during the previous 40 years. The terrain is a fairly typical Lewisian Gneiss landscape of low, rough rocky outcrops with areas of bog and poor quality grazing vegetation. The nearest settlement is at Upper Badcall to the south west.

The zircon occurs in a fairly accessible low crag in pods and lenses of pyroxenite with associated metaperidotites. The outcrop at [NC 1589 4289] is a short distance from the minor single track road leading from the A894 to

Upper Badcall. The distinctive pink zircon crystals, rarely up to 16 mm but averaging 2.5 mm, contrast with the black to very dark greenish-black pyroxenite matrix (see Figures 3-5; for Figures 4 and 5, see p. 66). Weathered crystals are light brownish-pink. The zircon is distributed heterogeneously throughout the rock forming clusters and clots and also as dispersed but aligned crystals, or on boundary surfaces of the layered intrusion.

The loose weathered material with a very high density of zircon probably originated from higher up the crag where

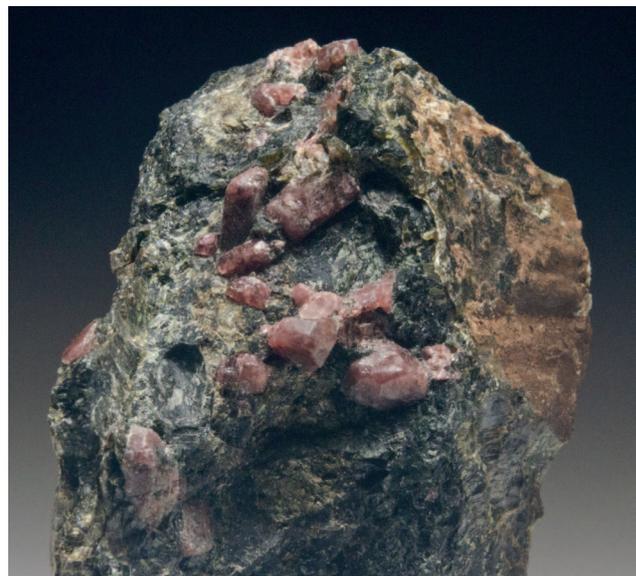


Figure 3. Euhedral crystals of pinkish zircon in pyroxenite - 40 mm x 50 mm (largest crystal is 8 mm long). Photo: R.E. Starkey.

a significant amount of weathered material was observed in-situ. A visit by one of the authors (RS) in May 2012 noted that the zircon had almost all been removed, as had a large (16 mm) fractured euhedral zircon crystal.

COLLECTING HISTORY

Zircon-bearing ultrabasic rocks from the area have only recently been reported (Kinny and Friend 1994, 1997 and Timms *et al.* 2006) although they have been known to collectors for a number of years and referred to as 'Badcall zircon'. Kinny and Friend (1997) describe a 12.5 mm pink zircon hosted by pyroxenite collected from one of a series of ultrabasic / mafic bodies south of Loch an Daimh Mor at [NC 158 428]. This is probably the same locality as that described here. Timms *et al.* (2006) reported the collection of a 12.5 mm pink zircon from north of Loch an Daimh Mor. Interestingly, despite the extensive field work by Bowes *et al.* (1964) there is no reference to zircon in their paper and only a limited mention of pyroxenite. Heddle (1901) notes the occurrence of zircon at a number of Scottish localities but makes no reference to this area.



Figure 4. Prismatic zircon crystal (10 mm long) embedded in pyroxenite. Photo: R.E. Starkey.



Figure 5. Euhedral crystals of pinkish zircon (largest crystal is 11 mm long). Photo: R.E. Starkey.

The occurrence of zircon in the area was known to the late Gordon Sutherland. One of the authors (AM) catalogued Mr Sutherland's collection and noted several small specimens of zircon pyroxenite, and also some weathered out, loose but fresh zircon crystals. These specimens are very similar to the material found in 2012. There were no specific locality details with those specimens, other than a reference to 'Upper Badcall'. It is probable that this locality was the source of the zircon in Gordon Sutherland's collection, and also material collected by Kemp Meikle in 1969, since there is an entry in the BMS (British Micromount Society) reference collection catalogue "There are several, glassy pink zircon pieces with a few crystal faces. These were identified by optical properties and confirmed by RMS (Royal Museum Scotland). These occurred in an ultrabasic dyke".

ZIRCON MINERALOGY

The zircon occurs as distinctive coarse greyish-pink, stubby, euhedral prismatic crystals with flat or pyramidal terminations. Crystal size is rarely up to 16 mm, more commonly 1 to 3mm. As the distribution of the zircon in the pyroxenite is highly variable, concentrations vary considerably from less than 1% to as high as 85% along defined planes and rare clusters up to 100% (visual estimates). The mean is probably around 5 to 10%.

The zircon fluoresces a strong pale yellow under short-wave (254 nm) ultraviolet light. The yellowish fluorescence common in zircon is generally attributed to the presence of uranium. Interestingly, rare earth elements which are generally enriched in zircons are linked to particular fluorescence colours (Foster, 1948), e.g. samarium and terbium stimulate red fluorescence and dysprosium green. Hafnium is commonly present in zircons, usually around 2% HfO₂ (A.G. Tindle, *personal communication*) and this element is possibly an activator of the fluorescence.

ORIGIN OF THE ZIRCON

The zircon occurs in unaltered pyroxenite rock within the largely altered layered ultrabasic intrusion. It seems probable that the rim of the crystals is related to the pyroxenite magmatic event, with the crystal core being much older and hence "inherited". Overprinted garnet amphibolite, garnet pyroxenite, and garnet pyroclastite occur within the gneiss country rock close to the outcrop. Similarly aged picrite dykes with large (10-20 mm) olivine crystals occur in a Laxfordian overprinted basement terrane near Clachtoll to the south, and indicate the general resistance of these ultrabasic rocks to subsequent regional metamorphic events.

Timms *et al.* (2006) studied a 12.5 mm crystal of zircon to determine the age of crystallization of the pyroxenite, therefore interpreting the zircon as a primary crystallization product.

Kinny and Friend (1994) describe work done by Pidgeon and Bowes (1972) on clear, rounded zircons collected from localities at Upper Badcall Bay and Kylestromie and considered them to be of metamorphic origin. However,

specimens of zircon collected from these localities and examined by Kinny and Friend (1994) found colourless prismatic grains with pyramidal terminations in addition to the rounded, multifaceted grains. Many were found to have complex internal structures resembling igneous oscillatory zoning and are considered to be remnants of zircons that crystallized in the tonalitic protoliths of the granulites. Other grains contain features characteristic of metamorphic alteration, with remnants of the internal oscillatory structures overprinted with (or by) homogeneous overgrowth rims due to metamorphic recrystallization. The zircons are generally depleted in U and Th but the overgrowth rims are particularly depleted in these two elements suggesting association with the Badcallian partial melting event.

CURATION AND CONSERVATION

Representative examples of material from the occurrence have been deposited with the National Museum of Wales (Cardiff); Natural History Museum (London); National Museums Scotland (Edinburgh); Oxford University Museum of Natural History; and the Hunterian Museum (Glasgow).

Sadly it has come to the authors' attention that commercial collectors have stripped the exposure between February and May 2012 with material being offered for sale in late 2012. This behaviour is deeply regrettable.

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NOTES FOR CONTRIBUTORS

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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.

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

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

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

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.

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