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EDITORIAL

Volume 18 of the Journal of the Russell Society is dedicated to the memory of Trevor Bridges who, as most members will know, passed away earlier this year.

Trevor's contribution to the Society – and to British mineralogy in general – has been immense, and Roy Starkey has kindly provided us with a tribute that summarises Trevor's many achievements. In terms of this Journal, Trevor's input has been quite extraordinary; over the past ten years, no less than one-third of the notes and papers contained in the Journal have been authored (or co-authored) by T.F. Bridges!

Two more of his papers are published in this volume. Trevor held a passionate interest in the chemistry of supergene alteration and several of his papers, over the years, have dealt with this subject on a locality by locality basis. For some time Trevor had planned an explanatory paper, pitched at an introductory level, to explain this chemistry and, in particular, the construction and use of stability field diagrams as an aid to understanding supergene mineral assemblages. I am pleased that his manuscript was almost completed before he passed away and that we are now able to publish it.

The second paper (Bridges and Starkey, 2015) is “vintage Trevor”, in that it combines field observations, literature research, and the thorough scrutiny of a suite of specimens, to draw pertinent conclusions about the development of a mineralised cavity at the Smalleugh Mine in the North Pennine Orefield, where Trevor focused much of his research effort.

We then move south, to Derbyshire, where Roy Starkey and John Faithful have been busy researching the occurrence of ‘Buxton Diamonds’. Their comprehensive account will be of interest to mineralogists and historians alike; although, sadly, specimens are much harder to come by than they appear to have been 200 years ago.

A short note follows on an interesting occurrence of amethyst at Screel Hill, Castle Douglas, in Scotland, by Stephen Moreton and his co-authors.

Britain's first confirmed thallium mineral was collected some 14 years ago from nodules in the Permian red beds at Budleigh Salterton, in Devon. However, analytical confirmation would, until recently, have required the destruction of virtually the entire specimen. Mike Rumsey and co-workers have now confirmed this mineral as crookesite, and their account demonstrates how advances in analytical techniques can provide a significant reward for patience when dealing with such a tiny quantity of an unidentified mineral.

Finally, many readers will recall the abridged biography of Matthew Forster Heddle, published in JRS 17, and authored by Hamish Johnston, Heddle's great-great-grandson. The full story of this doyen of Scottish mineralogy was published in 2015, and is reviewed here by Roy Starkey.

My sincere thanks to all of the contributors to JRS 18 – to the authors and, very specifically, to the referees who have donated their time to reading manuscripts and making constructive comments and suggestions. Last but by no means least, I would like to say a special thank-you to Frank Ince, who is retiring from the position of Journal Manager at the end of this year.

Malcolm Southwood

Honorary Journal Editor

ERRATUM

Hamish H. Johnston. (2014). Matthew Forster Heddle (1828-1897), Scottish Mineralogist: His life story. *Journal of the Russell Society*, **17**, 3-15. The correct caption for Figure 5 should be: Part of a letter from Heddle to Archibald Geikie, 5th July 1878, in response to an enquiry about his activities. Heddle provides an analysis of a mineral sent earlier by Geikie and describes his recent visit to Sutherland. GB0237 Gen525/2. © Edinburgh University Special Collections.

TREVOR F. BRIDGES (1935–2015)

I first met Trevor Bridges on 22nd June 1980 as we were walking down from Copa Hill at Cwmystwyth Mine in Mid-Wales. We had both been participants on one of the very early Welsh Mines Society field meetings, and as we chatted I realised that my companion was none other than THE Trevor Bridges whom I had recently invited to be a guest speaker at the South Staffordshire Mineral and Gemstone Society in Wolverhampton, of which I was then Secretary. Shortly after this, my wife Mary and I paid a visit to Trevor and Shelagh at their home in Derby, and thus began a long-term friendship which saw us watch each other's children grow up, and share a number of holidays together, most notably an annual pilgrimage to the Fort William area at Easter in search of snow-covered peaks.

Trevor was born in London and grew up in Yorkshire. He trained as a chemist and chemical engineer, gaining his degree from the University of Birmingham, a specialism of which he was justly proud, and a subject for which he had a great affection. He met his future wife Shelagh through the Coventry Mountaineering Club, and they were married in 1963.

A long-term employee of the Courtaulds Group, Trevor was faced with a mid-career crisis as that organisation struggled to cope with market conditions and major reorganisation. An opportunity arose on Tyneside at International Paint, a member of the Group, and in 1981 Trevor and family moved to the pleasant surroundings of a northern village, Ovington, near Prudhoe. Here, Trevor was in his element. He took a special interest in the mineralisation of the Northern Pennine Orefield, and he was one of a group of members who came together to form the Society's first branch outside of Leicester – the Northern Branch, in 1984.

Trevor's professional life saw him grappling with improving the production efficiency of a complex paint polymer manufacturing plant at Felling, near Gateshead, and latterly in a key role as the site's Health and Safety Consultant, making a real impact on people's lives and well-being, something which gave him immense personal satisfaction. As an ambassador of "science for the citizen" there are few who could surpass Trevor's tenacity and enthusiasm, and he relished the prospect of educating non-chemists in the ways of the elements.

Although not a "founder member", Trevor has certainly been a prominent and highly popular member of the Society for some 40 years. His contributions have been many and varied. Trevor's involvement with the Society goes back to 1975 and he appears in the list of members for that year, published in Newsletter No. 3, and that issue also carries what I believe to be Trevor's very first article on the chemistry of secondary (supergene) mineral formation. He followed this up in Newsletter No. 4 with a look at the importance of solubility in mineralising processes.

In 1976 Trevor gained 2nd place in the "Best single specimen collected on a society field meeting" category of the Russell Society Annual Competition, with a group of clear quartz crystals from Brownley Hill Mine, and

1st place in the "Micromount" category, with a baryte from Tear Breeches Mine, Matlock Bath. At this time, the Society was also working on a project to try and gain access to the fabled Earl Ferrers Lead Mine at Staunton Harold, and Trevor became involved as one of the diggers. He can be seen at the far left in the photo of "The Hard Gang" on page 45 of Newsletter No. 4. In Newsletter No. 5 Trevor described an occurrence of nickel minerals at Hilton Mine, and several specimens from this discovery were included amongst the lots at the auction of his collection in August of this year.

Trevor served as Vice-President from 1977-78, and as President in 1979. Trevor became Newsletter Editor for Nos. 14-19, and after the major make-over of the Society Constitution and establishment of the present Council and Branch structure, took the lead role as General Secretary of the Society in 1998. There is not space here to include a full account of all Trevor's various contributions, but I felt that some of the "early years" might be of most interest, and rekindle happy memories for those who knew him at that time.

Minerals, and the chemistry of minerals, occupied a huge part of Trevor's life, and his family shared in this interest as a matter of course. There was, however, much more to Trevor than simply collecting minerals, he was an accomplished climber and mountaineer, a Munroist (Compleator number 1953) in the Scottish Mountaineering Club Register in 1998, and a passionate and knowledgeable birdwatcher.

Never seeking the limelight, Trevor worked quietly on the subjects that interested him, and was always happy to explain, often complex, chemical matters to those less informed than himself, and using terminology that helped the listener to grasp the fundamentals of what was being discussed.

He published a considerable number of scientific papers, many of them in the *Journal of the Russell Society*, and often commented to me that he had not had time to write up as much as he would have liked. Even in his final weeks he was working to complete a paper on geochemistry, which appears elsewhere in this volume (Bridges, 2015). Many of his publications focused on supergene mineralogy, particularly in relation to northern England, the field in which Trevor carved a niche for himself. He had a particular fascination with barium mineralisation, and also brought his expertise in stability field diagrams to bear on helping to interpret the complex geochemistry of the lead oxychloride assemblages in the Mendips. A selection of his papers is referenced at the end of this tribute.

Trevor will be remembered by many as an educator and teacher. He was a popular speaker at the annual British Micromount Symposium, where he also assumed the role of auctioneer, and at meetings of the Russell Society and other organisations. In 1993 Trevor was only the second recipient of the Russell Medal, something which pleased him greatly, and which he wore with pride at each Society Annual Dinner.

Trevor's mineral collection numbering some 6000 specimens has been dispersed in a number of different directions – to the Hunterian Museum, the Oxford Museum of Natural History, the National Museum of Wales, the Hancock Museum (Newcastle Upon Tyne) and the Natural History Museum. The bulk of his more aesthetic display specimens were sold by auction in August of this year.

Although many readers will remember Trevor as a scientist, chemist and mineralogist, he was at heart a great family man, and enormously proud of his two sons Paul and David, and their respective families, which extend to six grandchildren.

Trevor passed away peacefully in his sleep on Thursday 23rd April after battling prostate cancer for some time. He has truly left a significant mark on the world in the field of mineralogy and he will long be remembered for his generosity, his enthusiasm and fair minded approach to life.

Roy Starkey

SELECTED PUBLICATIONS

- Bridges, T.F. (1982). An occurrence of nickel minerals in the Hilton Mine, Scordale, Cumbria. *Journal of the Russell Society*, **1**:1, 33–39.
- Bridges, T.F. (1983). An occurrence of annabergite in Smallcleugh Mine, Nenthead, Cumbria. *Journal of the Russell Society*, **1**:2, 18.
- Bridges, T.F. (1983). An occurrence of wulfenite, anglesite and native sulphur in the opencast above Ball Eye Quarry, Cromford, Derbyshire. *Journal of the Russell Society*, **1**:2, 48–51.
- Young, B., Bridges, T.F. and Hyslop, E.K. (1983). Leadhillite from the Northern Pennine Orefield. *Journal of the Russell Society*, **5**, 121–123.
- Livingstone, A, Bridges, T.F. and Bevins, R.E. (1990). Schulenbergite and namuwite from Smallcleugh Mine, Nenthead, Cumbria. *Journal of the Russell Society*, **3**, 23–24.
- Bridges, T.F. (1994). Book review - A Mineralogy of Wales. R.E. Bevins, 1994. *Journal of the Russell Society*, **5**, 128–129.
- Bridges, T.F. and Young, B. (1998). Supergene minerals of the Northern Pennine Orefield - A review. *Journal of the Russell Society*, **7**, 3–14.
- Young, B., Hyslop, E.K., Bridges, T.F. and Hubbard, N. (1998). Thauasite from High Sedling Mine, Weardale, County Durham, and from Shap, Cumbria, England. *Journal of the Russell Society*, **7**, 40.
- Bridges, T.F. and Green, D.I. (2005). Gearsutite, a second British occurrence, from the Ball Eye Opencast, Cromford, Derbyshire. *Journal of the Russell Society*, **8**, 75–77.
- Bridges, T.F. and Green, D.I. (2005). An update of the supergene mineralogy of Hilton Mine, Scordale, Cumbria. *Journal of the Russell Society*, **8**, 108–110.
- Bridges, T.F. and Wilkinson, H. (2005). Epimorphs of quartz after fluorite from Rampgill, Coalcleugh and Barneycraig mine system, Nenthead, Cumbria, England - an update. *Journal of the Russell Society*, **8**, 112
- Bridges, T.F., Green, D.I. and Rumsey, M.S. (2005). A review of the occurrence of antlerite in the British Isles. *Journal of the Russell Society*, **8**, 81–84.
- Bridges, T.F., Green, D.I., Cooper, M.P. and Thomson, N. (2005). A review of the supergene mineralisation at Silver Gill, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **8**, 85–97.
- Green, D.I., Bridges, T.F. and Neall, T. (2005). The occurrence and formation of galena in supergene environments. *Journal of the Russell Society*, **8**, 66–70.
- Bridges, T.F. and Green, D.I. (2006). The first British occurrence of köttigite, from Hilton Mine, Scordale, Cumbria. *Journal of the Russell Society*, **9**, 3.
- Bridges, T.F., Green, D.I. and Rumsey, M.S. (2006). A review of the mineralogy of Brae Fell Mine, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **9**, 39–44.
- Bridges, T.F. and Green, D.I. (2006). Baryte replacement by barium carbonate minerals. *Journal of the Russell Society*, **9**, 73–82.
- Green, D.I., Rumsey, M.S., Bridges, T.F., Tindle, A.G. and Ixer, R.A. (2006). A review of the mineralisation at Driggith and Sandbed Mines, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **9**, 4–38.
- Green, D.I., Tindle, A.G., Bridges, T.F. and Neall, T. (2006). Supergene mineralisation at Arm O'Grain, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **9**, 44–53.
- Neall, T., Green, D.I. and Bridges, T.F. (2006). Scotlandite in the British Isles: Its occurrence, morphology and paragenesis. *Journal of the Russell Society*, **9**, 83–89.
- Tindle, A.G., Bridges, T.F. and Green, D.I. (2006). The composition of tsumebite from Roughton Gill Mine, Caldbeck Fells, Cumbria. *UK Journal of Mines & Minerals*, **27**, 48–50.
- Bridges, T.F. and Green, D.I. (2007). Zoned oxidation deposits in Tynebottom Mine, Garrigill, Cumbria. *Journal of the Russell Society*, **10**, 3–9.
- Bridges, T.F. and Young, B. (2007). Geology and mineralogy of Pike Law Mines, Newbiggin, Teesdale, Co. Durham. *Journal of the Russell Society*, **10**, 18–26.
- Bridges, T.F., Green, D.I., Rumsey, M.S. and Leppington, C.M. (2008). A review of the mineralisation at Red Gill Mine, Caldbeck Fells, Cumbria, England. *Journal of the Russell Society*, **11**, 29–47.
- Bridges, T.F. and Green, D.I. (2008). Baryte formation in supergene environments in the Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **11**, 48–50.
- Green, D.I., Bridges, T.F., Rumsey, M.S., Leppington, C.M. and Tindle, A.G. (2008). A review of the mineralogy of the Roughton Gill Mines, Caldbeck Fells, Cumbria: Part 2, The Roughton Gill South Vein on Balliway Rigg. *Journal of the Russell Society*, **11**, 3–28.
- Bridges, T.F. (2009.) Mineralogical fraud - an appraisal of an unpublished manuscript by A.W.G. Kingsbury. *Journal of the Russell Society*, **12**, 27–32.
- Bridges, T.F. (2009). 'Lady's slippers' and a specimen of pyrite collected by Sir Kingsley Dunham from 'Nentsbury Mine', Nenthead, Cumbria. *Journal of the Russell Society*, **12**, 61–64.
- Green, D.I., Rumsey, M.S., Bridges, T. F. and Thomson, N. (2009). A review of the mineralisation at Ingray Gill, Caldbeck Fells, Cumbria. *Journal of the Russell Society* **12**, 33–45.

- Bridges, T.F. (2010). The mineralogy of a small flat deposit at Killhope, Weardale, with the first record of dundasite from the Northern Pennine Orefield. *Journal of the Russell Society*, **13**, 61–65.
- Bridges, T.F. (2010). A report on Westernhope Old Mine, Weardale, Co. Durham. *Journal of the Russell Society*, **13**, 66–70.
- Bridges, T.F., Green, D.I., Rumsey M.S. and Leppington, C.M. (2011). A review of the mineralisation of the Roughton Gill mines, Caldbeck Fells, Cumbria: Part 3 Roughton Gill Mine. *Journal of the Russell Society*, **14**, 3–23.
- Bridges, T.F., Rumsey, M.S. and Leppington, C.M. (2011). A report on Hay Gill Mine, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **14**, 62–68.
- Young, B. and Bridges, T.F. (2011). Goethite pseudomorphs after marcasite from the Northern Pennine Orefield. *Journal of the Russell Society*, **14**, 69–76.
- Bridges, T.F., Turner, R. and Rumsey, M.S. (2012). A geochemical study of the lead oxychloride mineral assemblage of the Mendip Hills, Somerset, UK using a stability field model. *Journal of the Russell Society*, **15**, 18–28.
- Green, D.I., Bridges, T.F. and Price, M.T. (2012). The Norman Thomson Collection. *UK Journal of Mines & Minerals*, **33**, 21–34.
- Young, B. and Bridges, T.F. (2012). Hydrozincite from Swaledale, Northern Pennines. *Journal of the Russell Society*, **15**, 58–62.
- Young, B., Bridges, T.F. and Tandy, P. (2012). Copper and barium mineralisation at Forcett Quarry, East Layton, North Yorkshire. *Journal of the Russell Society*, **15**, 62–72.
- Bridges, T.F. (2013). Phosgenite and matlockite in Derbyshire (Part 2). *Journal of the Russell Society*, **16**, 6–12.
- Bridges, T.F. and Pettigrew, T.H. (2013). Unusual fluorite from Old Towns Quarry, Newton Aycliffe, Co. Durham. *Journal of the Russell Society*, **16**, 12–14.
- Bridges, T.F., Green, D.I. and Ince, F. (2014). Ankerite: its composition and formulae, and its status in the Northern Pennine Orefield. *Journal of the Russell Society*, **17**, 51–56.
- Bridges, T.F. (2015). An introduction to supergene mineral formation in an oxidising lead-copper-and zinc-bearing ore deposit. *Journal of the Russell Society*, **18**, 5–16.
- Bridges, T.F. and Starkey, R.E. (2015). Mineral deposition in a cavity in Smallcleugh Mine, Nenthead, Cumbria. *Journal of the Russell Society*, **18**, 17–24.

AN INTRODUCTION TO SUPERGENE MINERAL FORMATION IN AN OXIDISING LEAD-, COPPER- AND ZINC-BEARING ORE DEPOSIT

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Groundwater, trickling into a sulphide-based lead, copper and zinc deposit sets in progress a series of reaction pathways that give rise to a wide range of supergene minerals such as cerussite, malachite and smithsonite. Oxygen dissolved in the groundwater reacts with sulphide minerals in the ores converting sulphur into sulphate and releasing metal ions into solution in a process known as oxidation. This process is very complex, with numerous intermediate stages, a summary of which is provided in this paper. Following the oxidation reactions, numerous further reaction pathways can be followed depending on factors such as the pH of the solution, the concentration of dissolved sulphate ions (often expressed as its activity, $a_{\text{SO}_4^{2-}}$), and the amount of free carbon dioxide gas present expressed as its partial pressure, p_{CO_2} (or its solution equivalent expressed as carbonate molecule concentration or alkalinity) and, finally, the reduction-oxidation (REDOX) potential of the solution, denoted as Eh. This introductory text explains what these factors are and how they are measured with, in most cases, an explanation of the chemical processes from which they arise. The best way to visualise the relationships of the minerals that form from these processes is by the use of stability field diagrams. The methods used to prepare these diagrams are explained and they are used to demonstrate the conditions under which the more common lead and copper supergene minerals form.

The zinc supergene system is also discussed briefly.

INTRODUCTION

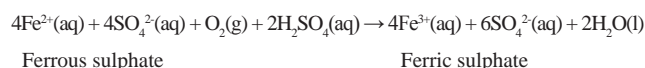
The most important sulphide minerals of lead (galena, PbS), copper (chalcopyrite, CuFeS_2) and zinc (sphalerite, ZnS), and also iron (pyrite and marcasite, FeS_2), are extremely insoluble in aqueous media and resist attack by all but the strongest of acids. They do, however, have an Achilles' heel in that they can be attacked, albeit very slowly, by oxygen dissolved in groundwater. This process,

which is called oxidation, almost inevitably results, initially, in the formation of sulphate and metal ions dissolved in the groundwater. These dissolved species can then go on to react with wall rocks and other minerals in the deposit to form the wide range of supergene minerals, such as cerussite, PbCO_3 , malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and smithsonite, ZnCO_3 , that is common in oxidised deposits.

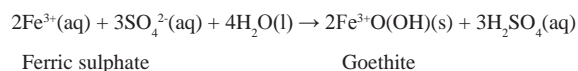
Oxygen dissolved in water in equilibrium with the atmosphere is a relatively powerful oxidising agent; however, as groundwater percolates into a deposit, the oxygen is gradually depleted and the potential for carrying

¹ Deceased. Correspondence relating to this paper should be addressed to the Editor.

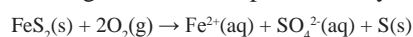
Given even a modest concentration of dissolved oxygen, this is usually followed by second and third reactions which oxidise the ferrous sulphate to ferric sulphate, $\text{Fe}^{3+}(\text{SO}_4)_3$, which, at any pH above approximately 2, reacts to form goethite, $\text{Fe}^{3+}\text{O}(\text{OH})$, and more sulphuric acid:



followed by



In arid conditions the iron sulphates can crystallise out as minerals such as melanterite, $\text{Fe}^{2+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$, and coquimbite $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. More importantly, however, the result of these reactions is usually the release of significant amounts of sulphuric acid which can lower the pH to 1, although it normally remains somewhat higher than this. There is another possible reaction, when access to oxygen is limited, which gives rise to sulphur, namely:



This reaction is particularly common in oxidising pyritiferous shales, but it can also result in small crystals of sulphur on supergene minerals in an oxidising sulphide deposit. Another fairly common mineral in oxidising pyrite deposits is jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, which also only forms at low pH.

A pH above neutral ($\text{pH} > 7$) is mostly due to the action of carbonates, particularly calcium carbonate, CaCO_3 , in the form of calcite or limestone. Calcium carbonate dissolved in pure water with no access to air results in a pH of about 10. When open to air, the solution absorbs carbon dioxide and the pH falls to about 8.3. This pH is not very high, but is sufficiently alkaline to stabilise carbonate ions in solution, which in turn can react with metals to form a wide range of carbonate supergene minerals. Higher pH waters can occur, but usually require the weathering of silicate rocks, particularly those of mafic composition. At higher pH even silica is soluble in water and this can lead to the form of supergene silicate minerals such as diopside and hemimorphite.

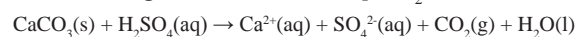
The prevailing pH in an oxidising mineral deposit usually depends on the balance between the availability of sulphuric acid and calcium carbonate. In limestone regions such as the Pennines, higher pH tends to predominate resulting in the dominance of supergene carbonate minerals such as cerussite and smithsonite. In carbonate deficient areas, sulphates can be more common, but carbonates still tend to be quite abundant. As an example, Redgill Mine in the Caldbeck Fells, Cumbria, England, is well known for interesting sulphate minerals (Bridges *et al.*, 2008), but carbonates such as cerussite and malachite are still common and, at the nearby Roughton Gill Mine, carbonates (and pyromorphite) predominate (Bridges *et al.*, 2011), with sulphates being relatively rare.

Carbon Dioxide, CO_2

The atmosphere contains a relatively low concentration of CO_2 . A value of 300 ppm is commonly assumed for

modelling supergene mineral formation (Garrels and Christ, 1965; Williams, 1990) and this value will be used here. It is noted, however, that the current CO_2 concentration is about 400 ppm, almost certainly due to burning fossil fuels (Oelkers and Cole, 2008). For the calculations necessary to study supergene reactions it is necessary to turn this into a partial pressure. Partial pressure can be considered as the % v/v divided by 100: 300 ppm equates to 0.03 % v/v and a $p\text{CO}_2$ of 0.0003 which can be expressed as a logarithm, i.e. $10^{-3.52}$. It is easier to write $10^{-3.52}$ than 0.0003 and it simplifies the ensuing arithmetic since multiplication and division become addition and subtraction respectively. It is worth noting that, ignoring industrial pollution, rain water passing through the atmosphere has a pH of 5.7, because the CO_2 dissolved partly forms carbonic acid, H_2CO_3 . Carbonic acid is very weak, but this small decrease in pH greatly facilitates the weathering of silicate and carbonate rocks.

In an oxidising mineral deposit the reaction between sulphuric acid and carbonates generates CO_2 which can result in a significant increase in $p\text{CO}_2$. The reaction is:

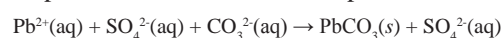


Depending on the availability of primary carbonates and sulphuric acid, the $p\text{CO}_2$ can vary between atmospheric and almost 1. Under unusual conditions, $p\text{CO}_2$ can fall below atmospheric and this will be considered later.

Under dry conditions the Ca^{2+} and SO_4^{2-} can combine to form gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This is of common occurrence on the walls of old mines, but in an oxidising deposit normally the Ca^{2+} and SO_4^{2-} stay in solution, which leads to the third important factor: sulphate ion concentration.

Sulphate Ion Concentration, $a\text{SO}_4^{2-}$

The sulphate ion, mostly generated by the oxidation of iron-bearing sulphides, usually stays in solution and can build up to relatively high concentrations. Furthermore, if carbonate supergene minerals form, the sulphate ions tend to remain in solution. Using the formation of solid cerussite, $\text{PbCO}_3(\text{s})$, from the reaction of carbonate ions with lead sulphate in solution as an example, the reaction is:



Thus sulphate ion concentrations can build up, and act as a controlling factor on supergene mineral formation. These concentrations are normally expressed as 'activities', a concept that is best explained by using an example. The molecular weight of common salt, NaCl, is 58.5 g (that is 1 mole of NaCl weighs 58.5 g based on the molecular weight of 1 atom of Na and 1 atom of Cl). Dissolve this amount of salt in enough water to make 1 litre of solution, then the true concentration, called molarity, is 1 g.mol.l⁻¹. However, if chemical reactions are carried out with the solution, it will behave as though there is less salt present than the true molar value due to ions and molecules in the solution interfering with each other. It is this smaller value which is important in most geochemical processes and which is called the activity of the ion or molecule, the symbol being '*a*' (in italics). Activity is a dimensionless quantity, but can be regarded as being equivalent to g.mol.l⁻¹; for convenience activities are also usually quoted as logarithms.

Supergene minerals can form at extremely low $a\text{SO}_4^{2-}$; a value of 10^{-8} is not unusual. There is usually an upper limit at about 10^{-2} , since above this value, except at very low pH, in the presence of Ca^{2+} ions gypsum would crystallise out removing some sulphate ion from solution.

STABILITY FIELD DIAGRAMS

Stability field diagrams (sometimes called simply stability diagrams) are the standard way of showing graphically the relationship of various minerals to each other and to the conditions under which they form. Understanding these diagrams requires knowledge of how they are prepared, and of the data needed to do this; the key explanations now follow.

Solubility Product

All chemical compounds, which include all minerals, have a thermochemical property called the Gibbs free energy of formation, ΔG_f^0 (see Robie *et al.*, 1978; by definition the ΔG_f^0 for native elements is zero). From this, a temperature dependant constant for the mineral, called its solubility product (here denoted K_{sp}), can be calculated. For geochemical purposes, K_{sp} is usually calculated at 25°C , which is an accepted approximation for the temperature likely to prevail in oxidising ore deposits. Tables of values of ΔG_f^0 and, in some cases, K_{sp} data are available for many of the more common minerals in the literature, a useful example being the compilation of Robie *et al.* (1978); however, individual research papers may have to be consulted for data related to the less common minerals, and there are numerous mineral species for which reliable constants have yet to be established.

The use of solubility products is best demonstrated with an example, in this case anglesite, PbSO_4 . If solid anglesite, $\text{PbSO}_4(\text{s})$, is left in water for several days, a very small amount dissolves to form a saturated solution containing both Pb^{2+} and SO_4^{2-} ions (this is a slight simplification but is adequate for the current purpose) and the equilibrium is:

$$\text{PbSO}_4(\text{s}) \leftrightarrow \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$

The K_{sp} for anglesite is $10^{-7.8}$ (Robie *et al.*, 1978), which gives the equilibrium equation:

$$a\text{Pb}^{2+} \times a\text{SO}_4^{2-} = 10^{-7.8}$$

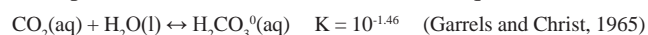
If the solution is allowed to partly evaporate, then some anglesite will crystallise out of the solution to maintain the above equilibrium. If water is added, more anglesite will dissolve. Adding a soluble sulphate, such as sodium sulphate, Na_2SO_4 , increases the $a\text{SO}_4^{2-}$ and would also cause some anglesite to crystallise out to maintain the above equilibrium. Any disturbance to the system results in the solution chemistry trying to correct the disturbance. This reaction to disturbance is known as *Le Chatelier's Principle*, since it was first recognised by the French chemist, Henry le Chatelier (1850–1936).

Carbonate Equilibria

Sulphuric acid in water completely dissociates into H^+ and SO_4^{2-} ions and it is the H^+ ions that make the solution acid. Similarly, caustic soda, NaOH , dissolved in water

completely dissociates into OH^- and Na^+ ions and it is the OH^- ions that make the solution alkaline. Sulphuric acid and caustic soda are strong acids and alkalis respectively (the latter often called bases) and are completely dissociated in water.

When CO_2 dissolves in water it forms carbonic acid, but this is a weak acid and it does not completely dissociate, so some of it remains in solution in an undissociated form and is denoted as H_2CO_3^0 . This process is controlled by a temperature related constant so that the equilibrium is:



This means that the equilibrium equation is:

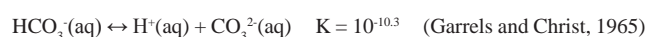
$$a\text{H}_2\text{CO}_3^0 = \log(p\text{CO}_2) \times 10^{-1.46} \quad (\text{Equation 1})$$

As an example, with the atmospheric concentration of CO_2 of 300 ppm, $p\text{CO}_2$ is 0.0003 which gives a $\log(p\text{CO}_2)$ of $10^{-3.52}$. Substituting into Equation 1 gives an $a\text{H}_2\text{CO}_3^0$ of $10^{-4.98}$, which is usually simplified to 10^{-5} .

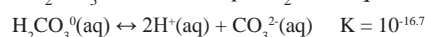
Some of the carbonic acid dissociates to form H^+ and HCO_3^- (bicarbonate) ions and again this equilibrium is controlled by a constant:



Finally a small part of the bicarbonate further dissociates to H^+ and CO_3^{2-} ions. This equilibrium is again controlled by a constant:



It is the H^+ ions from these two equilibria that make the solution slightly acid as mentioned under 'Carbon Dioxide' above. From the point of view of supergene carbonate mineral formation it is the carbonate ion concentration expressed as $a\text{CO}_3^{2-}$ which is important, bicarbonate being of no consequence. The above reactions can be combined into a single equation, although it is customary to use $a\text{H}_2\text{CO}_3^0$ rather than $p\text{CO}_2$; the equilibrium is:

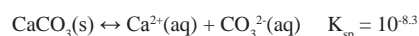


and the equilibrium equation is:

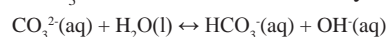
$$a\text{CO}_3^{2-} = 10^{-16.7} \times a\text{H}_2\text{CO}_3^0 / (a\text{H}^+)^2 \text{ or } 10^{-16.7} \times a\text{H}_2\text{CO}_3^0 \times (a\text{H}^+)^{-2} \quad (\text{Equation 2})$$

To use Equation 2, choose a value for $p\text{CO}_2$ and calculate $a\text{H}_2\text{CO}_3^0$ using Equation 1. Then choose a pH and calculate $a\text{H}^+$ and the result is the $a\text{CO}_3^{2-}$ of the carbonate ions in solution and this controls the formation of carbonate supergene minerals, permitting their relationship to other minerals to be calculated under the chosen conditions, as will be demonstrated later.

When solid calcite, $\text{CaCO}_3(\text{s})$, dissolves in water, it initially forms Ca^{2+} and CO_3^{2-} ions, controlled by the following equilibrium and the associated K_{sp} for calcite, which is $10^{-8.3}$ (Garrels and Christ, 1965).



However, in a reverse of the processes described above, some of the CO_3^{2-} ions are hydrolysed by water to form HCO_3^- and OH^- ions as shown by the equilibrium below.



This means a little more calcite has to dissolve to maintain the requirement of the solubility product; subsequently some of the HCO_3^- reacts with water to form a small amount of H_2CO_3^0 in the reverse of one of the previously-described

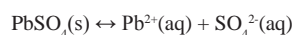
equilibria. The equilibrium constants for these reactions are essentially the same as for CO_2 in water corrected for pH. It is the OH^- ions that make the solution alkaline. As stated above, in pure water the pH can reach 10, but when exposed to air this falls to 8.3. It is also worth noting that as the pH falls, more calcite dissolves to maintain the equilibrium. When groundwater passes through a layer of vegetation, the $p\text{CO}_2$ is increased. If this groundwater passes through limestone, more calcite will dissolve. If this solution then emerges into a ventilated cave, CO_2 is lost to the atmosphere and to maintain the equilibrium some calcite is precipitated from the solution. This is the main cause of the build-up of stalactitic formations in caves. It is worth noting that all carbonates become more soluble as $p\text{CO}_2$ increases. For example, the deposit of flowstone cerussite on the walls of the Bwlch Glas Mine, Ceredigion, Wales [SN 710 878] (Figure 2) indicates that deposition must have occurred from a solution with elevated $p\text{CO}_2$.



Figure 2. Powdery microcrystalline crusts of cerussite deposited as ‘flowstone’ on the walls of the upper adit, Bwlch Glas Mine, Talybont, Ceredigion, Wales. Specimen width 65 mm. Roy Starkey specimen (0505-114) and photograph.

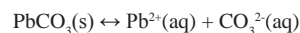
Stability Field Diagram Preparation

This is best explained by using an example. Anglesite and cerussite are often found together as pristine crystals in the same cavity implying that both minerals must have been able to crystallise from the same solution. Each mineral has a K_{sp} , that for anglesite being $10^{-7.8}$ (Robie *et al.*, 1978) and that for cerussite being $10^{-13.2}$ (Taylor and Lopata, 1984). These K_{sp} values are related to two equilibria and their associated equations. The equilibrium, and the equilibrium equation, for anglesite have already been given under Solubility Product (but are repeated here):



$$a\text{Pb}^{2+} \times a\text{SO}_4^{2-} = 10^{-7.8} \text{ or } a\text{Pb}^{2+} = 10^{-7.8} / a\text{SO}_4^{2-}$$

For cerussite the equilibrium, and the equilibrium equation, are:



$$a\text{Pb}^{2+} \times a\text{CO}_3^{2-} = 10^{-13.2} \text{ or } a\text{Pb}^{2+} = 10^{-13.2} / a\text{CO}_3^{2-}$$

Since $a\text{Pb}^{2+}$ must be the same for both minerals if they have formed from the same solution, the two equations above can be combined to give:

$$a\text{SO}_4^{2-} = a\text{CO}_3^{2-} / 10^{-5.4}$$

but Equation 2 above gives $a\text{CO}_3^{2-}$ in effect in terms of $p\text{CO}_2$ and pH and incorporating this into the above gives:

$$a\text{SO}_4^{2-} = 10^{11.29} \times a\text{H}_2\text{CO}_3^0 / a(\text{H}^+)^2 \text{ or } 10^{11.29} \times a\text{H}_2\text{CO}_3^0 \times a(\text{H}^+)^{-2} \text{ (Equation 3)}$$

To use Equation 3, use Equation 1 to calculate $a\text{H}_2\text{CO}_3^0$ and substitute this into Equation 3. Then for any pH, Equation 3 gives the $a\text{SO}_4^{2-}$ for that pH and the selected value of $p\text{CO}_2$. It should be noted that this is an equation for the demarcation line (hereafter called a fence) between the stability fields of cerussite and anglesite at the selected value of $p\text{CO}_2$. This relationship is best represented graphically and a typical example, in this case for anglesite and cerussite, is given in Figure 3 calculated at a $p\text{CO}_2$ of $10^{-1.95}$ (0.0112). It must be emphasised that this diagram is only valid at the selected value of $p\text{CO}_2$. If $p\text{CO}_2$ is changed, then the position of the fence will move.

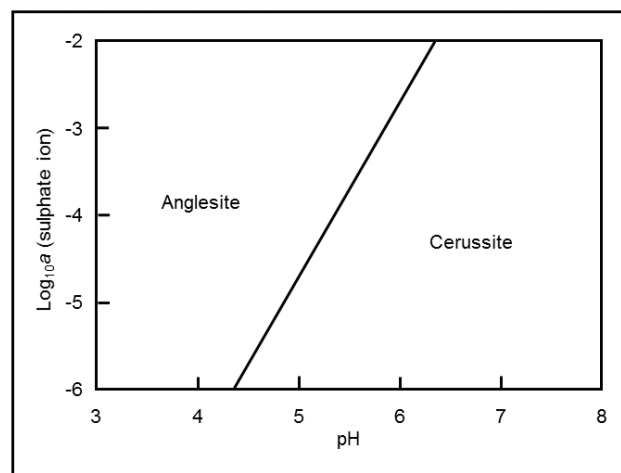


Figure 3. Stability field diagram for anglesite and cerussite at $p\text{CO}_2 = 10^{-1.95}$ (1.12% v/v CO_2).

There are several traps that have to be carefully avoided, or at least taken into consideration, when preparing stability field diagrams. It is quite possible to calculate a fence between two minerals that cannot form from the same solution; for example, anglesite and hydrocerussite, $\text{Pb}_3\text{CO}_3(\text{OH})_2$. The reason for this will become apparent later. The experimental work required to evaluate the Gibbs free energy of formation of a mineral is fraught with difficulty and has resulted in significantly different values for the same mineral in the literature; examples of this are also discussed below.

LEAD SUPERGENE MINERAL FORMATION

Anglesite and Cerussite

Anglesite and cerussite do not often occur together in cavities, which indicates that the chemical conditions in the solutions from which they individually formed lie somewhere in the large areas (or fields) on either side of the

fence in Figure 3. When the two minerals do occur together (Figure 4), the chemical conditions are actually as specified by the fence. It may seem that such conditions should be very rare, but there are chemical driving forces that move the solution chemistry towards the fence. As an example, the formation of cerussite from oxidising galena (Figure 5), removes carbonate ions from the solution, which lowers the pH and therefore moves the chemical conditions towards the fence. At the same time $a\text{SO}_4^{2-}$ is increased, which has the same effect.

Figure 3 shows the relationship between anglesite and cerussite at a $p\text{CO}_2$ of $10^{-1.95}$, a little above the atmospheric level ($\log a\text{SO}_4^{2-} = 2\text{pH} - 14.65$; see Appendix for the derivation of this equation from Equation 3). This is still relatively low; $p\text{CO}_2$ values well above 10^{-1} (0.1 or 10% v/v) are not unusual in an oxidising deposit, particularly in



Figure 4. Anglesite crystals, up to 0.5 mm long, on cerussite in a 'limonite'-coated cavity in galena. Killhope, Weardale. David Green specimen and photograph.



Figure 5. Small crystals of cerussite on cubes of oxidised galena (up to 15 mm). Breedon Hill Quarry, Breedon on the Hill, Leicestershire. Steve Warren specimen, David Green photograph.

carbonate rich terranes such as the Pennines. As $p\text{CO}_2$ rises above $10^{-1.95}$, the fence between the two minerals moves towards lower pH, while maintaining its orientation.

Leadhillite, $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$

If the $p\text{CO}_2$ is less than $10^{-1.95}$, then the fence of Figure 1 splits and a leadhillite stability field gradually opens up between the anglesite and the cerussite, becoming wider as $p\text{CO}_2$ falls. Figure 6 is a stability field diagram for lead supergene minerals at the atmospheric level of $p\text{CO}_2$ of $10^{-3.52}$, under which conditions the stability field for leadhillite is relatively wide. The K_{sp} for leadhillite is taken from Abdul-Samad *et al.*, (1982) and is $10^{-55.3}$. Note that the polymorphs of leadhillite (susannite and macphersonite) would occupy a similar stability field.

The relative rarity of leadhillite is one of several findings that support the view, expressed above, that elevated concentrations of CO_2 in oxidising veins are very common. Leadhillite is only common in deposits that contain very little carbonate mineralisation. Several localities in the Caldbeck Fells (Figure 7) and the Leadhills/Wanlockhead mining field meet this requirement, which is why the mineral is relatively common in these places. Leadhillite is quite rare in the carbonate rich Pennines.

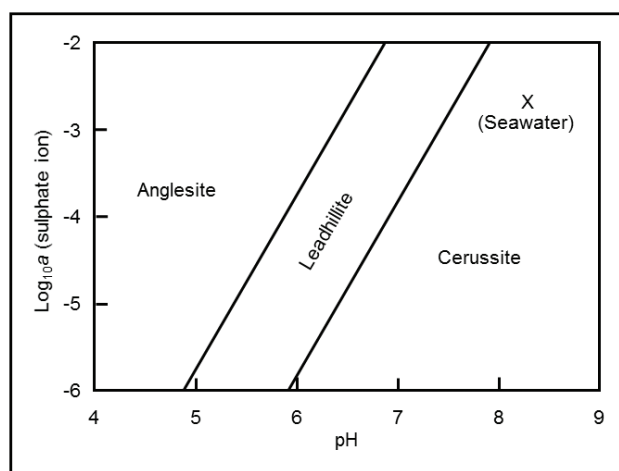


Figure 6. Stability field diagram for anglesite, leadhillite and cerussite at atmospheric $p\text{CO}_2$ ($10^{-3.52}$).



Figure 7. Tiny drusy crystals of leadhillite. Higher Roughton Gill, Caldbeck Fells, Cumbria. David Green specimen and photograph.

Perhaps the best studied example of its occurrence in the Pennines is at Closehouse Mine, Teesdale, [NY 850 228], (Young *et al.*, 1994) (Figure 8). This mine worked a massive baryte deposit and anglesite was very common here indicating low carbonate chemistry.

Seawater has a pH of approximately 8.3 and an $a_{\text{SO}_4^{2-}}$ of $10^{-2.7}$ (Garrels and Thompson, 1962) and the $p\text{CO}_2$ is atmospheric, so this point can be plotted on Figure 6. It clearly shows that cerussite is the stable lead supergene mineral in contact with seawater.

Hydrocerussite, $\text{Pb}_3\text{CO}_3(\text{OH})_2$

There is disagreement in the literature on the value of ΔG_f^0 and hence the K_{sp} for hydrocerussite. Williams (1990) argues the value is such that hydrocerussite is more stable than cerussite at the atmospheric value of $p\text{CO}_2$. However, this does not seem to match field observations, where cerussite appears to be perfectly stable on mine dumps. The author prefers the data evaluated by Taylor and Lopata (1984) who used the same technique to determine K_{sp} values for cerussite and hydrocerussite. Their data gives a K_{sp} for hydrocerussite of $10^{-45.63}$, which, when combined with their K_{sp} for cerussite ($10^{-13.2}$) gives a $p\text{CO}_2$ of $10^{-3.82}$, slightly lower than atmospheric for the value at which cerussite and hydrocerussite can form together from the same solution. Figure 9 is the stability diagram for the lead carbonate-sulphate system at a $p\text{CO}_2$ of $10^{-3.82}$. At any $p\text{CO}_2$ below this figure, hydrocerussite completely replaces cerussite in the cerussite stability field shown on Figure 6. Note, that the large stability field for leadhillite on Figure 9 explains the statement above, that anglesite and hydrocerussite cannot form from the same solution.

Lanarkite, Pb_2OSO_4

If $p\text{CO}_2$ is reduced to a value of $10^{-7.2}$ a stability field for the rare mineral lanarkite opens up between anglesite and leadhillite. Figure 10 shows a stability field diagram at the slightly lower $p\text{CO}_2$ of $10^{-7.4}$ at which lanarkite ($K_{\text{sp}} = 10^{-25.4}$) has a narrow stability field. It is interesting to note that a $p\text{CO}_2$ this low requires the presence of a relatively strong alkali, much stronger than could be developed from the dissolution of calcite at atmospheric levels. Lanarkite was relatively abundant in the Susanna Vein, Leadhills, Scotland based on its extensive presence as excellent specimens in museum collections. The country rocks of the area are a complex mixture of volcanic rocks and greywackes with much plagioclase feldspar (Temple, 1956). Personal observation of the Susanna Vein underground in 1984 indicated the presence of abundant clay. If some of this was derived from the weathering of feldspars or mafic minerals, then this might account for the relatively alkaline conditions, but this is very much an hypothesis, with no empirical evidence to support it. Lanarkite does occur in small amounts elsewhere in this mining field. It has also been reported from several localities in the Caldbeck Fells (Figure 11, see p. 12) (Bridges *et al.*, 2006; Green *et al.*, 2006; Bridges *et al.*, 2008; Green *et al.*, 2008; Neall and Green, 2009). In the Caldbeck Fells it is possible that the necessary low $p\text{CO}_2$ resulted from low carbonate

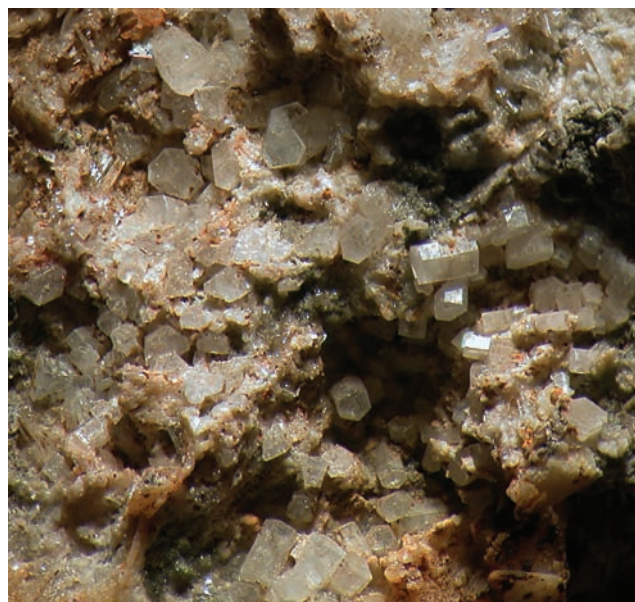


Figure 8. Small six-sided prisms of leadhillite with cerussite on galena. Closehouse Mine, Lunedale, Co. Durham. Field of view 11 mm. Frank Bouwerearts specimen (0523). Frank Ince photograph.

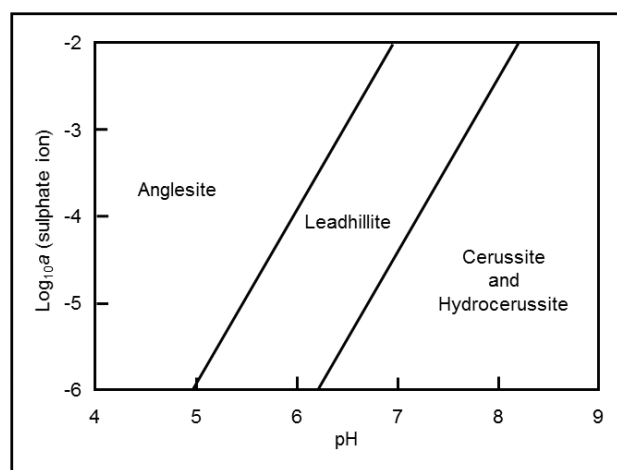


Figure 9. Stability field diagram at the $p\text{CO}_2$ ($10^{-3.82}$) at which cerussite and/or hydrocerussite can form from the same solution.

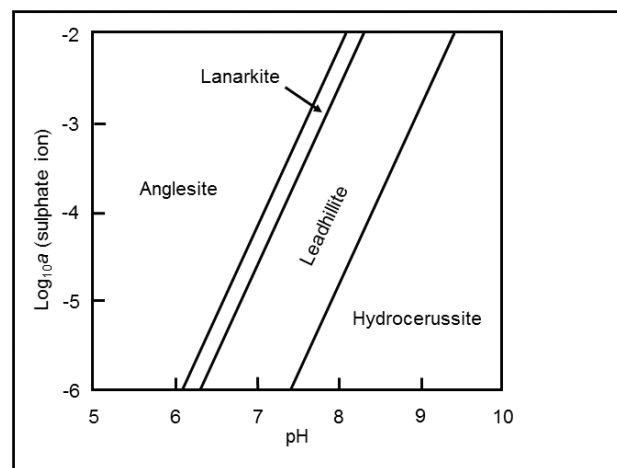


Figure 10. Stability field diagram at the $p\text{CO}_2$ ($10^{-7.4}$) at which lanarkite has a small stability field.



Figure 11. Bladed crystals of lanarkite (to 2 mm). Higher Roughton Gill, Caldbeck Fells, Cumbria. David Green specimen and photograph.

conditions combined with the weathering of mafic minerals in the lavas of the Eycott Volcanic Group, but again this is speculation.

Other Lead Supergene Minerals

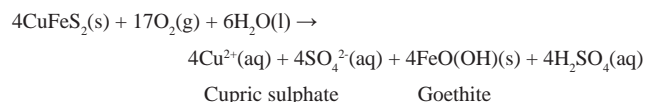
There are numerous other lead supergene minerals, many involving other metals e.g. dundasite, $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, but thermochemical data are rarely available for them. The most abundant lead secondary mineral after cerussite is pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, but this needs a different methodology to explain its occurrence and is worthy of a separate study; in this context Mason (2004) has described cerussite-pyromorphite assemblages from the Central Wales Orefield, and discussed the chemistry of their formation. The rare lead oxides such as litharge, PbO , are high pH minerals and would have stability fields off the right hand side of the diagrams in Figures 3, 6, 9 and 10.

Of considerable interest to British mineralogists are the lead minerals that contain the chloride ion, Cl^- , and a number of studies have already been published. A study on the long known rare assemblage of phosgenite, $\text{Pb}_2\text{CO}_3\text{Cl}_2$, and matlockite, PbFCl , at Bage Mine, Cromford, Derbyshire has been presented by Bridges (2013). This is a high $p\text{CO}_2$ assemblage as evidenced by the lack of leadhillite at the site. A study of the rare low $p\text{CO}_2$, relatively high pH assemblage of oxychlorides of the Mendips has been presented by Bridges *et al.* (2012). Both of these studies include stability field diagrams, but it must be stressed that both are based on plausible hypotheses, not hard facts. Phosgenite is well recorded from coastal localities such as Clevedon Beach, Avon, (Starkey, 1984) and Lossiemouth, Grampian Region, Starkey, (1988). It can form in cavities

with restricted access to seawater, if pH is slightly lowered by pyrite oxidation. More difficult to explain is the presence of cotunnite, PbCl_2 , at Clevedon (Bridges, 2003), which requires a higher $a\text{Cl}^-$ than that which occurs in seawater.

COPPER SUPERGENE MINERAL FORMATION

The first stage is the oxidation of a primary copper-containing ore mineral, e.g. chalcopyrite, CuFeS_2 . As with the other sulphides, this is a very complex, multi-stage process, with numerous transient intermediaries. The net result, however, is usually an acidic solution of copper sulphate (cupric sulphate) together with limonitic ochres related to goethite, $\text{FeO}(\text{OH})$. The reaction can be simplified to:



The copper and sulphate ions are then free to react with carbonate ions in solution to form a range of supergene copper sulphates and carbonates.

In some respects the copper system is simpler than that of lead, because $p\text{CO}_2$ typically only affects whether malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, or azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, forms. Figure 12 is a stability field diagram at the atmospheric $p\text{CO}_2$ of $10^{-3.52}$. This is based on thermochemical data from a number of sources, including Robie *et al.* (1978) and Williams (1990) and the K_{sp} values used to construct Figures 12, 13 and 15 are: chalcantinite $10^{-2.55}$, antlerite $10^{-46.9}$, brochantite $10^{-68.6}$, malachite $10^{-33.78}$ and azurite $10^{-45.96}$. Regrettably, as will be discussed later, there are considerable differences in the data for malachite and azurite, which results in some unreliability in the diagrams, but not enough to prevent some conclusions from being drawn. The minerals shown in Figure 12 are discussed in turn below.

Chalcantinite, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$

This mineral is denoted as Cu^{2+} and SO_4^{2-} (in the top left hand corner of Figure 12). Only in exceptionally arid conditions can this mineral crystallise and remain stable; normally Cu^{2+} and SO_4^{2-} ions remain in solution.

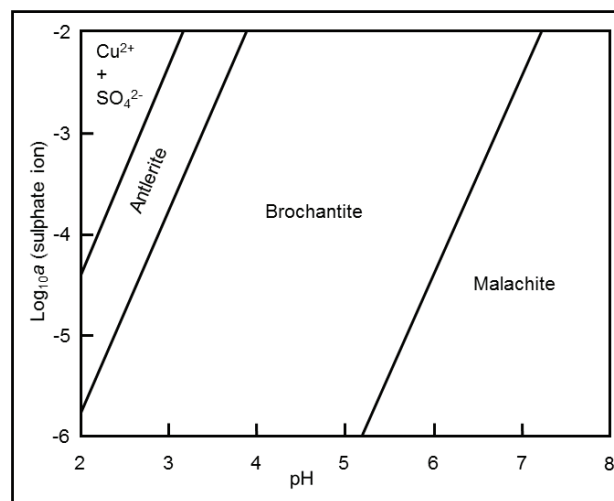
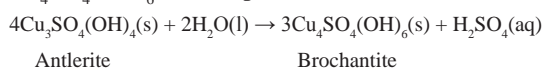


Figure 12. Stability field diagram for the copper system at $p\text{CO}_2 = 10^{-3.52}$ (atmospheric).

Antlerite, $\text{Cu}_3\text{SO}_4(\text{OH})_4$

Antlerite has a narrow stability field at slightly higher pH than chalcantite, but it is still only stable at what is really still quite a low pH range. It is a rare mineral, because normally in an oxidising deposit, pH will be too high for it to form. The walls of mines, where there is abundant pyrite, are where it has been mainly found in the UK (e.g. Parys Mountain). If the presence of antlerite is suspected, the specimen must not be washed in water, as the antlerite will react with water to form brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$, and sulphuric acid:



Brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$

At atmospheric $p\text{CO}_2$, brochantite has quite a large stability field, but at generally less than neutral pH. It should be noted that related minerals such as langite, $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, will occupy the same stability field. Unlike antlerite, brochantite is stable in water. It is relatively common in low carbonate environments such as the Caldbeck Fells, but much less so in the Pennines.

Malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$

By far the most abundant supergene copper mineral, malachite is widespread in ore deposits around the world, where it often forms a valuable resource. Less abundant in the UK, it was nevertheless an important ore in Cornwall and Devon and also in the Caldbeck Fells. It is essentially a relatively high pH mineral, in keeping with its requirement for carbonate ions in order to form.

Increasing $p\text{CO}_2$ has the effect of moving the fence between malachite and brochantite to lower pH. This is illustrated in Figure 13, calculated at a $p\text{CO}_2$ of $10^{-2.52}$ (0.3% v/v CO_2). Note that this narrows the brochantite field, expands that of malachite, but does not affect the lower pH minerals.

Azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Complications arise when trying to evaluate the $p\text{CO}_2$ at which malachite and azurite (Figure 14) can form from the same solution, and this is due to problems with the thermochemical data. Using generally accepted values for the solubility products (malachite $K_{\text{sp}} 10^{-33.78}$ and azurite $K_{\text{sp}} 10^{-45.96}$) gives a value of $p\text{CO}_2$ at the transition of $10^{-0.40}$. This equates to nearly 40% v/v CO_2 in the oxidising deposit, which seems very high indeed, considering that, while azurite is much less abundant than malachite, it is still a common mineral. Figure 15 shows a stability diagram at this $p\text{CO}_2$ and it can be seen that the brochantite stability field has virtually disappeared, bringing malachite and azurite close to antlerite. One small piece of evidence to show that this high $p\text{CO}_2$ might be feasible is the presence of a remarkable specimen of antlerite and malachite in the collections of the Natural History Museum (BM 1958,138) (Bridges *et al.*, 2005). The two fences on Figure 15 are close enough for this combination to occur in a metastable state as

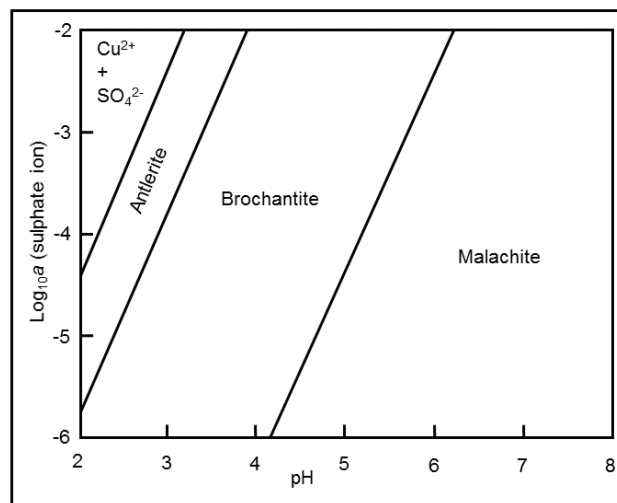


Figure 13. Stability field diagram for the copper system at $p\text{CO}_2 = 10^{-2.52}$.

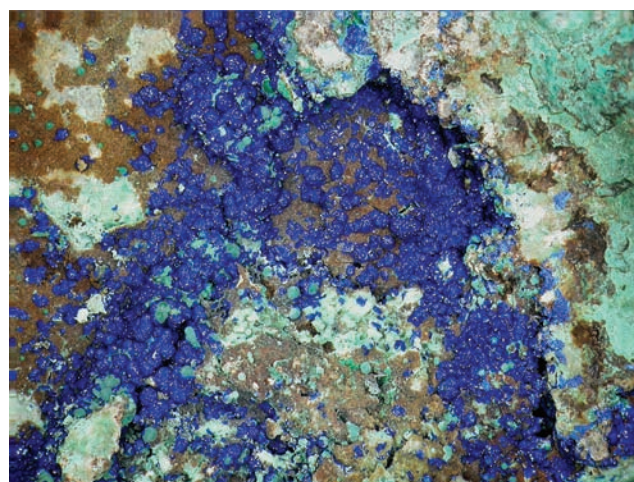


Figure 14. Deep blue azurite with green malachite and pale green chrysocolla (field of view 20 mm x 17 mm). Bardon Hill Quarry, Coalville, Leicestershire. Neil Hubbard specimen (1489). Frank Ince photograph.

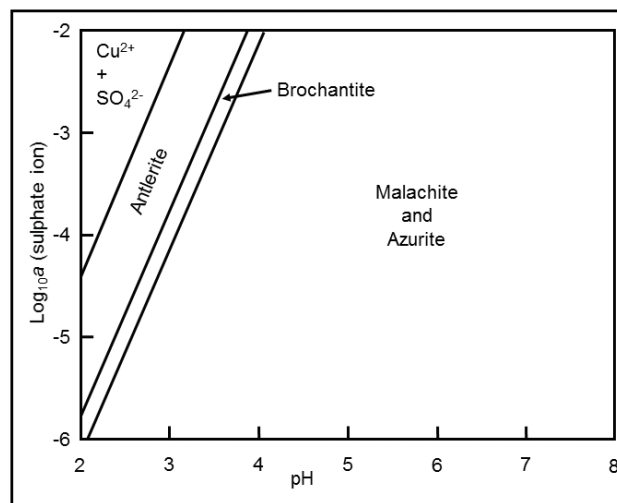


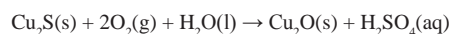
Figure 15. Stability field diagram for the copper system at $p\text{CO}_2 = 10^{-0.40}$ (circa 40% v/v CO_2).

a result of small variations in $p\text{CO}_2$. However, this is a most unusual occurrence and most malachite and azurite forms at a pH above neutral.

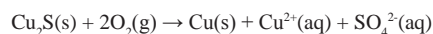
Other Copper Supergene Minerals

Two other copper-containing minerals, which are prized by mineralogists, are cuprite, Cu_2O , and native copper, Cu. It is theoretically possible to derive conditions of Eh and pH that would produce these minerals from oxidising chalcopyrite, but this is not the way they normally form. As stated in the Introduction, if acidic copper sulphate solutions pass through the *oxidation zone* to below the water table, conditions usually change to reducing and the dissolved copper ions react with sulphide ion (S^{2-}) to form copper (I) sulphides such as chalcocite, Cu_2S . The copper sulphides are so insoluble that they can replace minerals such as galena and sphalerite. They can also react with chalcopyrite to form bornite, Cu_5FeS_4 ; particularly in the *supergene enrichment zone*.

If the water table falls, allowing these copper (I) sulphides to be exposed to the *oxidation zone*, then the ideal conditions of Eh and pH for the formation of cuprite and native copper can occur readily. The equations can be written as:

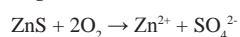


and



ZINC SUPERGENE MINERAL FORMATION

The first stage in the formation of zinc supergene minerals is the oxidation of sphalerite to zinc sulphate. The reaction is essentially the same as for lead and can be expressed as:



Zinc sulphate

Unlike lead and copper minerals, zinc sulphate, goslarite, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, is very soluble in water. The zinc hydroxy sulphates only form at high pH and stability field diagrams of the type shown in this paper are therefore not relevant to zinc. The main zinc supergene minerals include the two carbonates, smithsonite, ZnCO_3 , and hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, and the silicate hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$.

Hemimorphite forms when Zn^{2+} ions in solution react with a mobile source of silicate ions, such as silicic acid, H_4SiO_4 . Quartz is far too inert to provide a source of mobile silicate ions and the silicic acid is normally derived from the weathering of silicate minerals. Hemimorphite is therefore most abundant in areas where there is evidence of such a source, such as the Askrigg Block of the Northern Pennine Orefield, where there are numerous beds of chert.

Viewed geologically, hydrozincite is almost always found in the UK on the walls of mines and as an alteration product of sphalerite on surface dumps. In contrast, smithsonite is only found in oxidised ore deposits, where hydrozincite is very rare. This evidence suggests that the

$p\text{CO}_2$ that marks the demarcation between the two minerals should be very close to atmospheric, with higher $p\text{CO}_2$ favouring smithsonite. Regrettably it is not that simple. Research work by Alwan and Williams (1979) has shown that the critical $p\text{CO}_2$ is at about $10^{-1.5}$ (circa 3% v/v CO_2). This is quite high and implies that hydrozincite might be expected to be more common in ore deposits. The science is further complicated by the fact that in the laboratory, even with quite extreme conditions that would be expected to result in smithsonite, hydrozincite invariably forms. It seems that in natural systems there must be some ageing mechanism that results in hydrozincite gradually changing to smithsonite when $p\text{CO}_2$ is favourable. In some respects this seems to parallel the formation of dolomite group minerals, which also resist laboratory synthesis.

LEAD/COPPER SUPERGENE MINERAL FORMATION

The two key minerals are linarite, $\text{PbCuSO}_4(\text{OH})_2$, and caledonite, $\text{Pb}_5\text{Cu}_2(\text{CO}_3)(\text{SO}_4)_3(\text{OH})_6$. The solubility products reported are $10^{-31.6}$ for linarite and $10^{-110.7}$ for caledonite (Williams, 1990). Both minerals can be found alone in cavities although they can also occur together. However, both are often associated with simple lead and copper minerals such as cerussite (Figure 16) and brochantite. There are two possible processes for their formation.

The first is when low concentrations of Pb^{2+} ions build up in an environment dominated by copper minerals, such as brochantite. Based on the solubility product data above, the lead should form linarite and this is exactly what is found in natural systems. Linarite is commonly associated with minerals such as brochantite and, to a lesser extent, malachite, and can be found in such combinations in the carbonate rich Pennines.



Figure 16. Cerussite crystals, 2 mm long, with linarite and leadhillite. Roughton Gill mines, Caldbeck Fells, Cumbria. David Green specimen and photograph.

Regrettably, the same cannot be said for the situation where Cu^{2+} ions enter an environment dominated by lead minerals. Figure 17 is a stability field diagram based on the solubility products noted above and at atmospheric $p\text{CO}_2$ of $10^{-3.52}$. It shows a very large field for caledonite, which in effect means that caledonite should be much more common than linarite in lead-dominated systems, which is most certainly not the case. In addition, the difference in $a\text{SO}_4^{2-}$ between the leadhillite/caledonite fence and that of caledonite/linarite is several orders of magnitude. This means that linarite and leadhillite should not form together in the same cavity, but they do, and Figure 16 in Bridges *et al.* (2008), shows this association as pristine crystals.

As stated before, the experimental work required to determine ΔG_f^0 and solubility products is fraught with difficulty and it seems likely that the K_{sp} value of $10^{-110.7}$ overestimates the stability of caledonite and produces the large stability field seen in Figure 17, which cannot be reconciled with observed parageneses. Figure 18 shows a stability field diagram under the same conditions as above except that, following some preliminary investigations, the solubility product for caledonite has been set at $10^{-105.2}$;

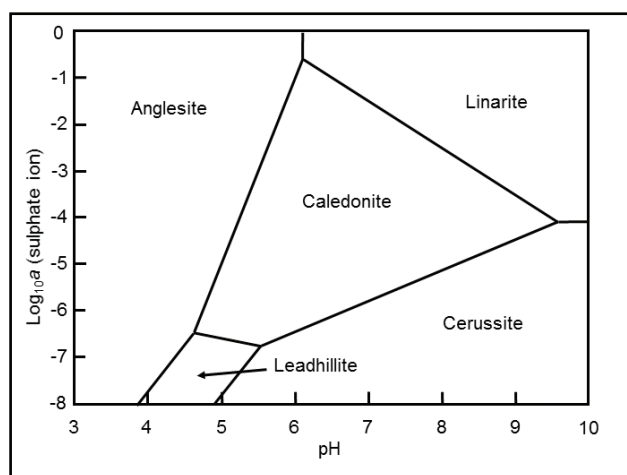


Figure 17. Stability field diagram for the lead system at $p\text{CO}_2 = 10^{-3.52}$ (atmospheric) and $a\text{Cu}^{2+}$ ion = $10^{-8.0}$ with K_{sp} caledonite = $10^{-110.7}$.

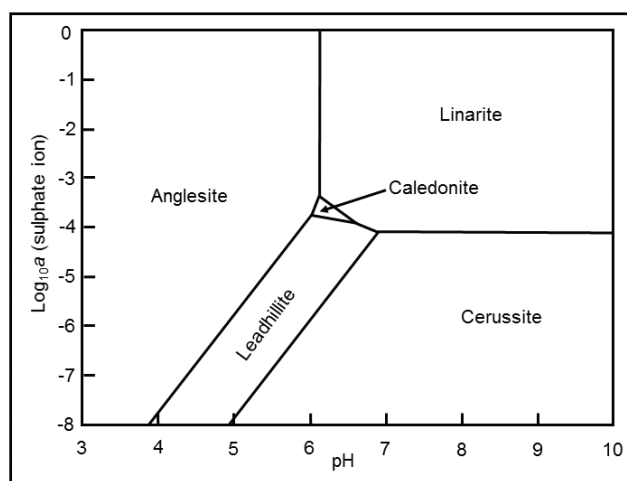


Figure 18. Stability field diagram for the lead system at $p\text{CO}_2 = 10^{-3.52}$ (atmospheric) and $a\text{Cu}^{2+}$ ion = $10^{-8.0}$ but with K_{sp} caledonite increased from $10^{-110.7}$ to $10^{-105.2}$.

the result is a diagram where caledonite still has a small field, adequate to explain its occurrence, but linarite has a small fence with leadhillite. Obviously, this suggestion is no more than an hypothesis, but it does give a possible explanation for what is seen in natural systems.

COPPER/ZINC SUPERGENE MINERAL FORMATION

The two minerals to be considered are aurichalcite, $(\text{Zn,Cu}^{2+})_5(\text{CO}_3)_2(\text{OH})_6$, and rosasite, $(\text{Cu}^{2+},\text{Zn})_2(\text{CO}_3)(\text{OH})_2$. The ratio of copper to zinc in these minerals is variable, which also alters their thermochemical properties and means that they are best considered qualitatively.

Based on the ratios of metal ions to CO_3^{2-} ions in the species, the formation of rosasite requires a higher $p\text{CO}_2$ than aurichalcite. Aurichalcite is more common and occurs in environments in contact with the atmosphere, so it is probably the mineral that is stable under these conditions. Rosasite is normally found in cavities in mixed oxidised copper and zinc ore. Both are far more common in the carbonate-rich Pennines than in carbonate deficient deposits.

FURTHER READING

Anyone with some knowledge of chemistry and wanting to become more familiar with the techniques outlined above is recommended to read: Krauskopf, K.B. and Bird, K.D. (1995). *Introduction to Geochemistry* (3rd edition). McGraw Hill Inc. New York.

The classic work on the subject, is: Garrels, R.M. and Christ, C.L. (1965). *Solutions, Minerals and Equilibria*. Harper and Row, N.Y. This work contains large numbers of stability field diagrams, but in order to plot many of them, chemical restraints have had to be used, which do not model the workings of natural systems.

With a very comprehensive treatment of supergene mineral formation: Williams, P.A. (1990). *Oxide Zone Geochemistry*. Ellis Horwood, N.Y. London etc., is a *tour de force* on the subject, it contains large numbers of stability diagrams and useful data. However, it is pitched at graduate chemist standard. An alternative advanced text is: Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice-Hall. New Jersey.

ACKNOWLEDGEMENTS

I decided that A-Level chemistry would be a suitable standard for an introductory text like this. I therefore sent the first draft to my grandson Matthew Bridges, a recent A-Level student, for comments. Thank you Matthew for your helpful comments which I have incorporated into the text. Once again I am indebted to Frank Ince for turning my computer generated paper diagrams into diagrams worthy of printing in the Journal.

The Editor would like to thank Frank Ince for his efforts in bringing this paper to publication and the two referees, Dr Robert Bowell and Professor Terry Seward, for their reviews and comments.

APPENDIX

The derivation of the fence equation for the anglesite-cerussite system at $p\text{CO}_2$ $10^{-1.95}$ (Figure 1).

Using Equation 1 (p. 6), convert $a\text{H}_2\text{CO}_3^0$ to the equivalent $p\text{CO}_2$, i.e. $\log(p\text{CO}_2) \times 10^{-1.46}$; substituting this value into Equation 3 (p. 8) gives:

$$a\text{SO}_4^{2-} = 10^{-11.29} \times \log(p\text{CO}_2) \times 10^{-1.46} \times (a\text{H}^+)^2,$$

substituting the $\log(p\text{CO}_2)$ of $10^{-1.95}$ into this equation gives:

$$a\text{SO}_4^{2-} = 10^{-11.29} \times 10^{-1.95} \times 10^{-1.46} \times (a\text{H}^+)^2,$$

combining the constants gives:

$$a\text{SO}_4^{2-} = 10^{-14.65} \times (a\text{H}^+)^2,$$

taking logs gives:

$$\log(a\text{SO}_4^{2-}) = -14.65 + [-2\log(a\text{H}^+)],$$

however $-\log(a\text{H}^+) = \text{pH}$; consequently:

$$\log(a\text{SO}_4^{2-}) = -14.65 + 2\text{pH},$$

following a rearrangement of terms, the fence equation for anglesite and cerussite at $p\text{CO}_2$ $10^{-1.95}$ is:

$$\log(a\text{SO}_4^{2-}) = 2\text{pH} - 14.65.$$

The slope of the straight line on Figure 1 being +2 and the intercept on the $\log(a\text{SO}_4^{2-})$ axis -14.65 (at $\text{pH} = 0$).

The fences shown in the other stability field diagrams are related to equivalent equations derived using the same process but with different starting conditions and/or combinations of minerals.

REFERENCES

- Abdul-Samad, F.A., Thomas, J.H., Williams, P.A. and Symes, R.F. (1982). Chemistry of formation of lanarkite, Pb_2OSO_4 . *Mineralogical Magazine*, **46**, 499–501.
- Alwan, A.K. and Williams, P.A. (1979). Mineral formation from aqueous solution. Part 1. The deposition of hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, from natural waters. *Transition Metal Chemistry*, **4**, 128–132.
- Bridges, T.F. (2003). Cotunnite from the beach at Clevedon, Avon, England. *Journal of the Russell Society*, **8**, 36–37.
- Bridges, T.F. (2013). Phosgenite and Matlockite in Derbyshire (Part 2). *Journal of the Russell Society*, **16**, 6–12.
- Bridges, T.F., Green, D.I. and Rumsey, M.S. (2005). A review of the occurrence of antlerite in the British Isles. *Journal of the Russell Society*, **8**, 81–84.
- Bridges, T.F., Green, D.I. and Rumsey, M.S. (2006). A review of the mineralogy of Brae Fell Mine, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **9**, 39–44.
- Bridges, T.F., Green, D.I., Rumsey, M.S. and Leppington, M. (2008). A review of the mineralisation at Red Gill Mine, Caldbeck Fells, Cumbria, England. *Journal of the Russell Society*, **11**, 29–47.
- Bridges, T.F., Green, D.I., Rumsey, M.S. and Leppington, M. (2011). A review of the mineralisation of the Roughton Gill Mines, Caldbeck Fells, Cumbria: Part 3 Roughton Gill Mine. *Journal of the Russell Society*, **14**, 3–23.
- Bridges, T.F., Turner, R. and Rumsey, M.S. (2012). A geochemical study of the lead oxychloride mineral assemblage of the Mendip Hills, Somerset, UK using a stability field model. *Journal of the Russell Society*, **15**, 18–28.
- Embrey, P.G. and Symes, R.F. (1987). *Minerals of Devon and Cornwall*. Natural History Museum, London and Mineralogical Record Inc., Tucson, Arizona.
- Garrels, R.M. and Christ, C.L. (1965). *Solutions, Minerals and Equilibria*. Harper and Row, N.Y.
- Garrels, R.M. and Thompson, M.E. (1962). A chemical model for seawater at 25°C and one atmosphere total pressure. *American Journal of Science*, **260**, 57–66.
- Green, D.I., Bridges, T.F., Rumsey, M.S., Leppington, C.M. and Tindle, A.G. (2008). A review of the mineralogy of the Roughton Gill Mines, Caldbeck Fells, Cumbria: Part 2, The Roughton Gill South Vein on Balliway Rigg. *Journal of the Russell Society*, **11**, 3–28.
- Green, D.I., Rumsey, M.S., Bridges, T.F., Tindle, A.G. and Ixer, R.A. (2006). A review of the mineralisation at Driggith and Sandbed mines, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **9**, 4–38.
- Moreton, S. (2007). Copper-bearing silica gel from the walls of the Tankardstown mine, Co. Waterford, Ireland. *Journal of the Russell Society*, **10**, 10–17.
- Krauskopf, K.B. and Bird, K.D. (1995). *Introduction to Geochemistry* (3rd edition). McGraw Hill Inc. New York.
- Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice-Hall. New Jersey.
- Mason, J. (2004). The Development of Supergene Lead Mineralisation in Central Wales. *UK Journal of Mines and Minerals*, **24**, 35–46.
- Neall, T and Green, D.I. (2009). The mineralogy of Short Grain Low Level, Caldbeck Fells, Cumbria. *Journal of the Russell Society*, **12**, 45–61.
- Oelkers, E.H. and Cole, D.R. (2008). Carbon dioxide sequestration: a solution to a global problem. *Elements*, **4**, 305–310.
- Robie, R.A., Hemmingway, B.S. and Fisher, R.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin No. 1452*.
- Starkey, R.E. (1984). Phosgenite from Clevedon, Avon. *Proceedings of the Bristol Naturalists' Society*, **44**, 13–14.
- Starkey, R.E. (1988). Phosgenite from Lossiemouth, Grampian Region: Confirmation of the first Scottish occurrence. *Scottish Journal of Geology*, **24**, 15–19.
- Taylor, P. and Lopata, V.J. (1984). Stability and solubility relationships between some solids in the system $\text{PbO}-\text{CO}_2-\text{H}_2\text{O}$. *Canadian Journal of Chemistry*, **62**, 395–402.
- Temple, A.K. (1956). The Leadhills-Wanlockhead Lead and Zinc Deposits. *University of Leeds manuscript accepted in 1955 and read in 1956*.
- Williams, P.A. (1990). *Oxide Zone Geochemistry*. Ellis Horwood, Chichester.
- Young, B., Bridges, T.F. and Hyslop, E.K. (1994). Leadhillite from the Northern Pennine Orefield. *Journal of the Russell Society*, **5**, 121–123.

MINERAL DEPOSITION IN A CAVITY IN SMALLCLEUGH MINE, NENTHEAD, CUMBRIA

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The contents of a cavity found underground in 1984 in Smallcleugh Mine, Nenthead, Cumbria are described. More than 100 specimens, none of which were attached to each other, were collected. It is suggested that these resulted from a process involving iron-rich dolomitic metasomatism, combined with dissolution of the limestone and brecciation of wall rock, and possibly in some cases fracturing of mineral crusts. This interpretation is in keeping with recent research on flat formation in the Alston Block of the Northern Pennine Orefield conducted by the British Geological Survey.

INTRODUCTION

Smallcleugh Mine is situated about 0.5 km east of Nenthead village, the entrance to the Horse Level being at NY 7877 4290. It was first worked in the late eighteenth century, but the main period of activity was during the nineteenth century when the leases were held by the London Lead Company, who worked the mine for galena. In 1882 the London Lead Company surrendered its Nenthead leases to the Nenthead and Tynedale Zinc Company; fourteen years later they passed to the Vieille Montagne Zinc Company, who worked the mine into the early twentieth century.

The insignificant entrance to the Smallcleugh Horse Level leads to miles of passages and stopes, many of the former being arched in yellow sandstone for stability. It is probably the greatest monument to the old miners of the United Kingdom that is still accessible. Figures 1 and 2 show typical examples of their workmanship.

The mine has long been a good source of mineral specimens, typical of much of the Alston Block of the

Northern Pennine Orefield (NPO), and has been useful in studying the processes that led to the formation of the extensive flat deposits (strictly strata bound replacement deposits) of the orefield. The British Geological Survey (BGS) have carried out extensive research into the origins and emplacement of the mineralisation in a number of flat deposits in the NPO including those in Smallcleugh Mine (Bouch *et al.*, 2008).



Figure 1. Stone arching in the Handsome Mea Flats near the area now called the 'Wheel Flats'. The image shows an area used to store ore trucks.



Figure 2. A junction of passages in the Handsome Mea Flats near the 'Wheel Flats'.

¹ Deceased. Correspondence relating to this paper should be addressed to Roy Starkey.

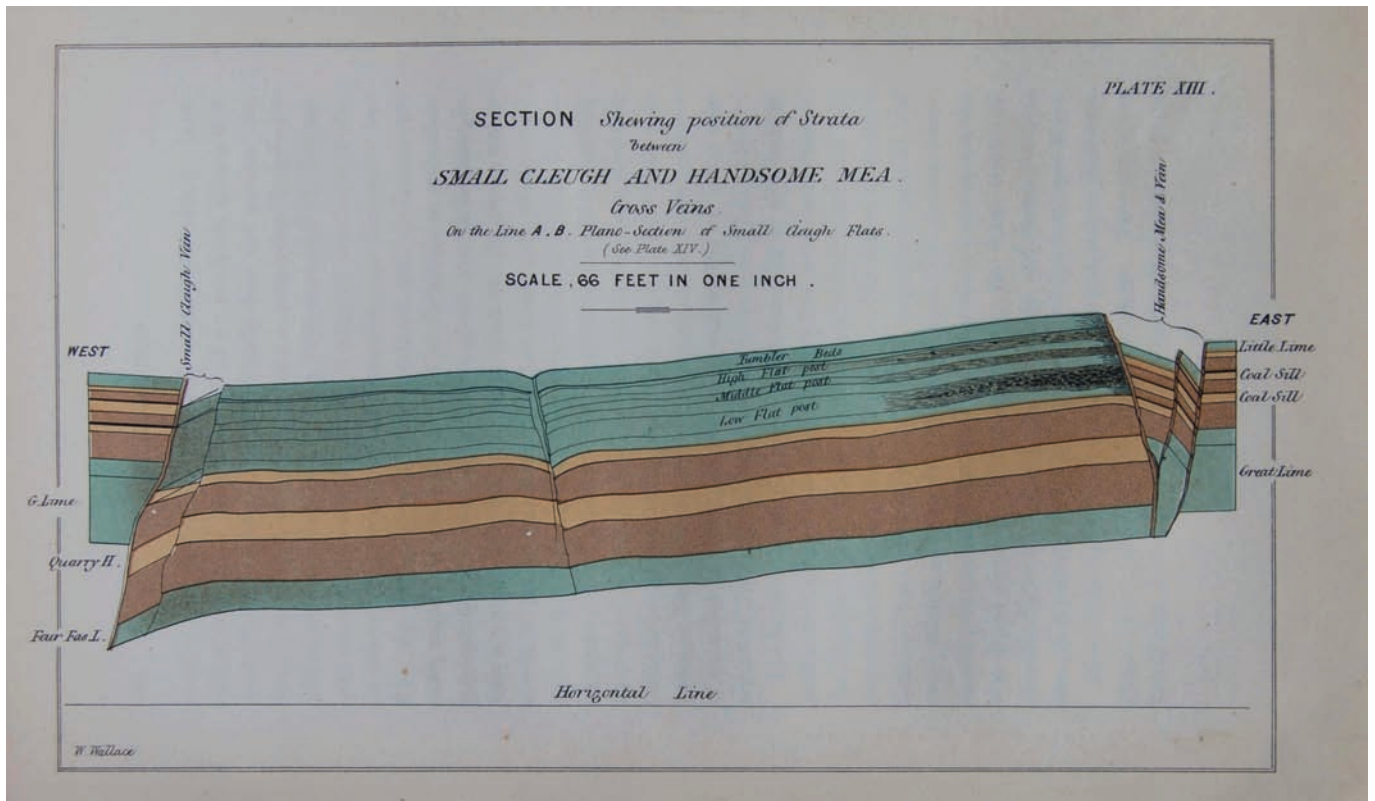


Figure 3. Diagram of the Smallcleugh horst structure; taken from Plate XIII, of Wallace (1861).

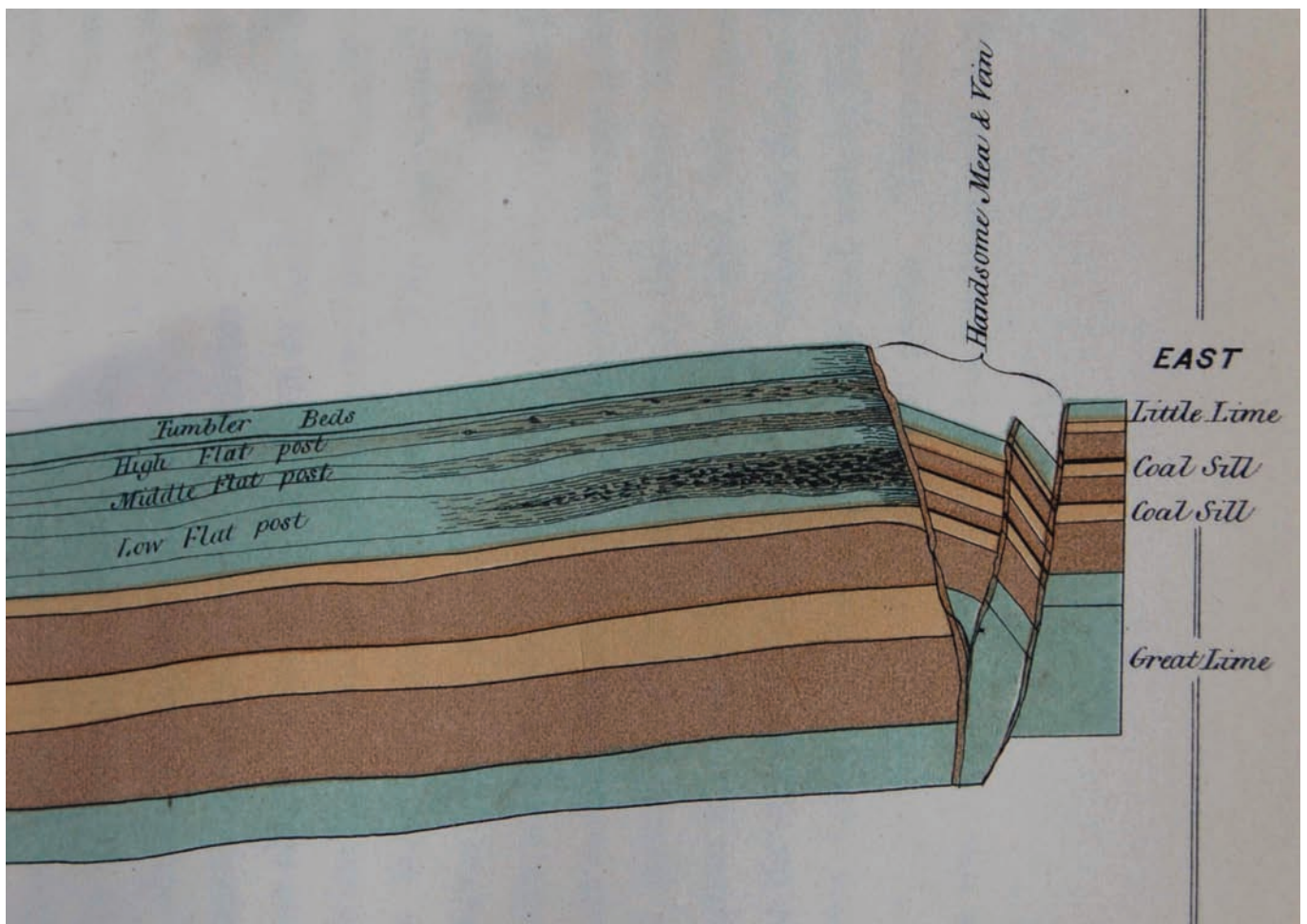


Figure 4. Detail of the Handsome Mea Vein side of Figure 3, showing the mineralised horizons; taken from Plate XIII, of Wallace (1861).

In 1984, the present authors discovered a pristine cavity full of specimen material in Smallcleugh Mine. It was decided to see how well this discovery could be interpreted using the results of the above research. That is the subject of this study.

GEOLOGY

The geological setting of the NPO consists of Lower Palaeozoic sedimentary and volcanic rocks, intruded by Caledonian granites, and overlain by Carboniferous limestones, sandstones, mudstones and thin coals. Mineralisation is hosted mainly in steeply dipping faults, with the greatest development of veins in hard competent rocks such as limestone or sandstone. The mineralisation of the Alston Block of the NPO is notable for the way in which the two main gangue minerals, fluorite and baryte, are zoned. The zonation shows a clear relationship to the underlying Weardale Granite. In an area roughly centred on Weardale, the main gangue mineral is fluorite, with very little barium mineralisation. The fluorite zone is surrounded by a zone in which barium minerals, particularly baryte, dominate and there is very little fluorite. The boundary between the two zones is quite sharp, with only minor overlap (Dunham, 1990, p. 80–81).

Smallcleugh Mine lies in an intermediate area where fluorite and barium minerals are uncommon or absent and 'ankerite' and dolomite are the most abundant gangue minerals. It is closer to the fluorite zone than the barium zone and minor amounts of fluorite are present in some parts of the mine. The mineralising fluids were predominantly high salinity brines of various compositions. Fluid inclusion data for the inner fluorite zone indicate homogenisation temperatures of up to 210°C, whereas those for the broader outer barium zone indicate lower temperatures of formation, between about 100°C and 125°C. The mineralisation is considered to have been initiated shortly after, or during the cooling of the Whin Sill *circa* 295 Ma, although radiometric data suggests that the main phase of mineralisation may have been restricted to the period between the late Permian (*circa* 250–260 Ma) and the end of the Triassic (*circa* 210 Ma) (Bouch *et al.*, 2006).

The main area of flat mineralisation in Smallcleugh Mine is housed in a horst structure between the Smallcleugh Cross Vein and the Handsome Mea Cross Vein. These veins are orientated approximately NW-SE, trending more to N-S further south where they join a vein complex consisting of the Middlecleugh First and Second Sun veins and the Longcleugh Vein. The whole horst structure is in the Great Limestone, a thickly bedded medium to dark grey bioclastic packstone with interspersed thin shaly mudstones, of Carboniferous (Namurian) age. An excellent diagram from Wallace (1861) is shown in Figure 3, with the Smallcleugh Vein to the left and the Handsome Mea complex of veins to the right.

Figure 4, taken from Figure 3, shows the mineralised areas relative to the veins and the position of the High, Middle and Low Flat mineralised horizons called 'posts' on the diagram.

The main area of flats is much nearer to the Handsome Mea Cross Vein than the Smallcleugh Vein and is named after that vein. The area in which the cavity was found is known to mine historians as the North End Flats.

The rock in the flats has been subjected to iron-rich dolomitic metasomatism and is partly silicified. It is very hard and produces sparks when hit with steel. Significant mineralisation remains exposed in the walls; it is commonly aligned with the original bedding. 'Ankerite' (see later) is abundant, and galena, quartz, sphalerite and patches of highly oxidised pyrite are also present.

THE CAVITY

The cavity is situated in the southwest side of the first of the Handsome Mea Flats, about 60 m away from the point at which the horse level from the entrance splits to run parallel with the veins. As discovered, it was accessible through a small letterbox shaped opening (Figure 5) and, when empty, the cavity measured 80 cm wide, 50 cm deep and 15 cm high, the width dimension being parallel to the wall of the flat.



Figure 5. The highlighted entrance to the cavity. Helen Wilkinson photograph.

The cavity contained more than 120 individual pieces of mineralised material, varying from a little less than 20 cm to no more than about 10 mm. All the pieces were lifted out one by one without the need for any force at all. Every piece was entirely covered with primary minerals (excluding a little oxidation) with no points of attachment to the cavity walls or to each other. Figure 6 (see p. 20) shows about half of the specimens. Regrettably, at the time the deposit was found, the potential relevance of the position of the specimens in the cavity was not appreciated and was not noted. Which way up specimens were found was also not noted and has had to be inferred from more recent work at other localities.

THE MINERALS

The minerals are typical of the Nenthead deposits and are described here in paragenetic order. Photographs are not included at this stage, as the main interest is in the structure of the specimens, not the appearance of particular species.

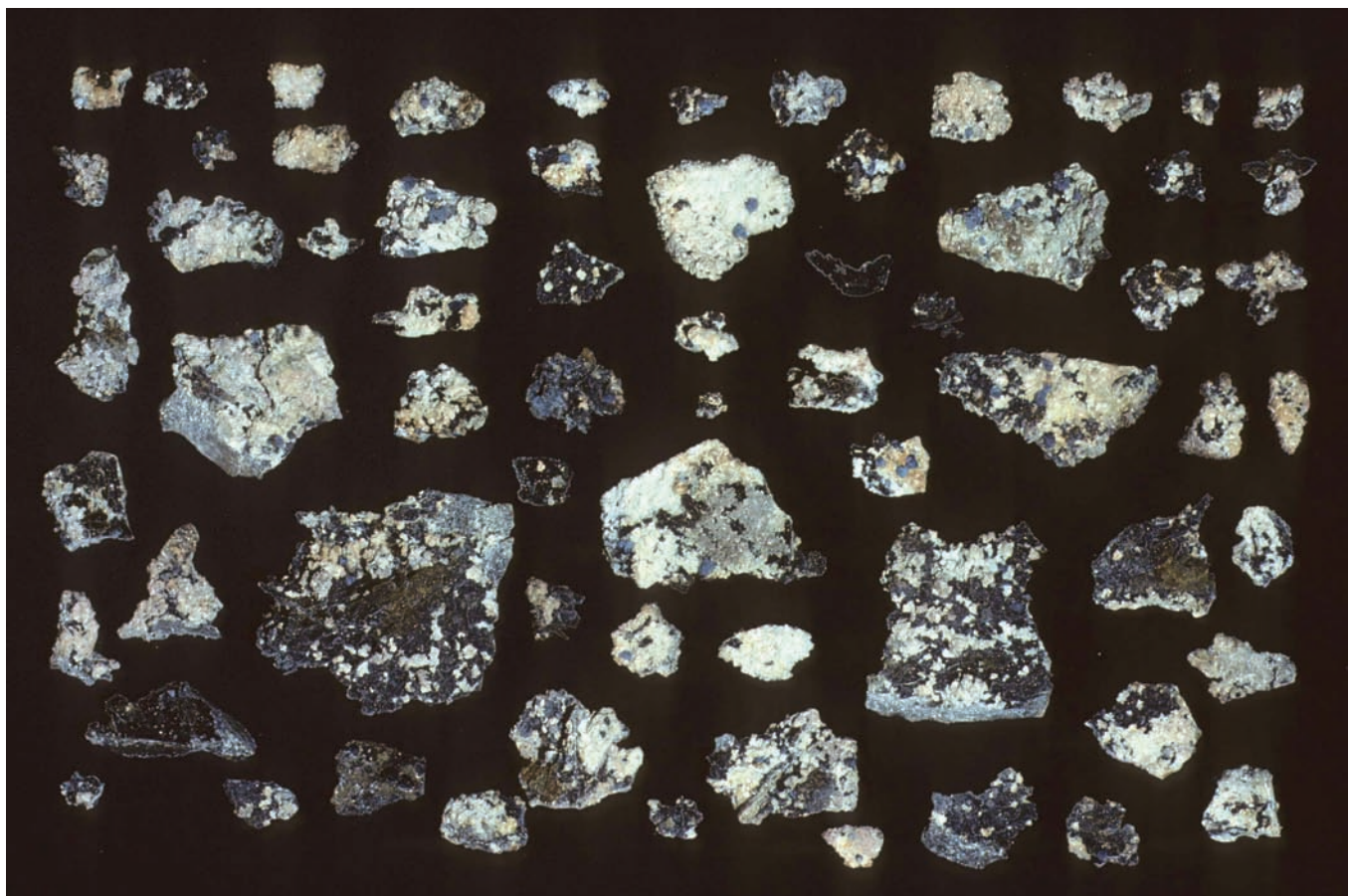


Figure 6. A photograph of about half the specimens from the cavity.

QUARTZ, SiO_2

As the first mineral to form, quartz commonly encrusts fragments of rock, and also occurs as thin pure laths. Individual crystals are pyramidal and rarely exceed 0.2 mm across.

PYRITE, FeS_2

Pyrite is described before sphalerite because rarely, the latter seems to have grown around the former. Both commonly occur directly on quartz. Pyrite occurs as crusts of mainly cubic crystals which seldom exceed 1 mm on edge. Although quartz is ubiquitous on all specimens, pyrite is not; if present it is usually on one side of a specimen only.

SPHALERITE, ZnS

In common with pyrite, crystals of black sphalerite have mostly grown on the microcrystalline quartz, described above. Rarely, however, sphalerite occurs entirely supported by 'ankerite'; it is not clear whether this is late-stage growth or whether crystals have detached from above and fallen onto the 'ankerite'. Sphalerite crystals are highly irregular and reach 12 mm across. Some show slight oxidation.

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

Traditionally, in the Northern Pennine Orefield, all saddle-shaped crystals of dolomite-group minerals, even those containing relatively small amounts of iron, have been described as 'ankerite' (e.g. Dunham (1990) where

analyses illustrate this point). However, using current IMA guidelines, to be described as ankerite (in a binary solid solution) the molar ratio of Fe:Mg must exceed 50:50 and this means that much of the material that has been described as 'ankerite' in the literature is iron-bearing or iron-rich dolomite; Bridges *et al.* (2014) provide a recent discussion of this problem. The current IMA accepted ideal formula for ankerite is $\text{CaFe}^{2+}(\text{CO}_3)_2$, a compound that does not exist in nature and has not been synthesised. The heading above uses a simplified formula that better reflects the composition. Throughout this paper, regardless of composition, iron-bearing or iron-rich dolomite-group minerals are described as 'ankerite'. The term is placed in inverted commas to reflect this usage; it should be understood that it may describe iron-bearing or iron-rich dolomite in the modern sense. 'Ankeritisation', also in inverted commas, is used to describe iron-rich metasomatism of the limestone.

'Ankerite' is very common on the specimens, occurring on almost every one. Crystals are saddle-shaped, mostly translucent cream in colour, and generally 2 to 3 mm across. Some show a slight brown colouration due to oxidation of the iron they contain. They can often be seen to have grown around sphalerite and pyrite, but both of these minerals also occur on ankerite.

CALCITE, CaCO_3

Calcite is the last mineral to form. It occurs rarely as crusts of minute nailhead crystals, which often have a mammillary form.

The minor oxidation referred to above has produced trace amounts of goethite, gypsum, hydrozincite and possibly brianyoungite on some specimens.

OBSERVATIONS AND DISCUSSION

The BGS research mentioned above and summarised by Bouch *et al.* (2006) on a number of sites in the Alston Block of the NPO, including Smallcleugh Mine, concluded that the first stage of the mineralisation was probably dolomitisation followed by ‘ankeritisation’ of the limestone adjacent to the vein. This process, which causes a reduction in the volume of the rock, resulted in cavity formation and the development of porosity, a process aided by brecciation and dissolution of the limestone. The dolomitisation-‘ankeritisation’ phase was followed by the deposition of sulphides, mainly sphalerite and galena in the cavities, together with quartz and ankerite. It is considered that this process provides a satisfactory explanation for the contents of the cavity.

Most of the smaller specimens are so heavily encrusted by primary minerals that it is not possible to see whether or not they have a core of rock. Figure 7 shows a typical small specimen. As they were loose in the cavity and it is most unlikely that they grew entirely unsupported, they almost certainly fractured off a surface at some time. It is noticeable that one side of the specimens is usually very different to the other, indicating which way up they were in the cavity.



Figure 7. A small specimen of ‘ankerite’ and quartz with minor sphalerite. Specimen width 6 cm.

On several of the larger specimens, rock cores are obvious. Figures 8 and 9 show two sides of such a specimen. It is probable that the complex mineralised structure shown in Figure 8 is the result of mineral growth and possible rock dissolution while the specimen was still attached to the wall of the cavity.

The mineralisation shown in Figure 9 is essentially a thin crust of ‘ankerite’ with minor pyrite on wall rock and must have formed after the specimen became detached from the wall.

It seems most probable that this specimen originally formed part of the roof of the cavity, as the more heavily encrusted side (underside in the cavity), is pristine (Figure 8), unlike the upper side in the cavity (Figure 9).

Figures 10 and 11 (see p. 22) show both sides of another specimen with a definite rock core and again the mineralisation is very different on the two sides. The upper side in the cavity (Figure 11) is similar to the above specimen in that it is coated with a thin layer of ‘ankerite’ crystals. Also note that, in the bottom left hand corner of the image, is a piece of rock that was nearly completely detached from the main part of the specimen. The underside in the cavity (Figure 10) is particularly interesting in that there are radiating ribs of quartz protruding from the surface. It seems most probable that the rock was stress-cracked in a radiating pattern and that the cracks became filled with quartz. Subsequently it is considered that the rock dissolved away allowing the quartz to stand free, followed by further minor growth. On both of these two specimens, after a period of growth while attached to the wall of the cavity, brecciation must have resulted in detachment from the surface. Again it seems likely that the specimen detached from the roof of the cavity.



Figure 8. A specimen of ‘ankerite’ with quartz and minor sphalerite (the underside in the cavity). Specimen width 14 cm.



Figure 9. The reverse of Figure 8 (the upper side in the cavity) showing rock with a thin crust of pyrite and ‘ankerite’.

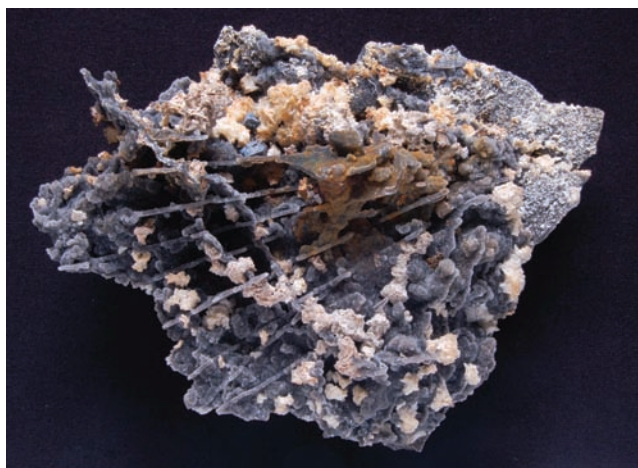


Figure 10. Radiating quartz ribs with 'ankerite' and minor sphalerite (the underside in the cavity). Specimen width 18 cm.



Figure 11. The reverse (upper side in the cavity) of Figure 10, showing rock encrusted with a thin coating of 'ankerite' crystals.

Figure 12 is a thin lath of quartz, partly encrusted with sphalerite. Again it seems probable that the quartz crystallised in a crack in carbonate rock, which later dissolved away, allowing the quartz lath to fall and later become coated with sphalerite.

Figures 13 and 14 show both sides of a specimen which is rather different to all of the above. It is very thin and it is not clear whether or not it has a very thin core of rock or whether it is just detached mineral growth. The mineralisation shown in Figure 13 is similar to Figures 8 and 10, with early quartz partly encrusted with 'ankerite' and with three crystals of sphalerite. The 'ankerite' on the left hand side of the image seems to have minute crystals of pyrite under the surface, some of which are partly oxidised. The clean 'ankerite' on the right of the image may have been sheltered from pyrite formation by another piece of mineral. The other side (uppermost in the cavity), of the specimen (Figure 14) shows quartz, with two upstanding ribs of quartz and is nearly completely encrusted with a layer of minute pyrite crystals and then minor 'ankerite' and calcite. It is suggested that the enormous number of pyrite crystallites in this layer were produced by rapid



Figure 12. A thin lath of quartz partly encrusted with sphalerite. Specimen width 6 cm.



Figure 13. A thin section of rock, encrusted with quartz and then 'ankerite' with minor sphalerite (the underside in the cavity). Specimen width 15 cm.



Figure 14. The reverse (upper side in the cavity) of Figure 13. The rock is encrusted with a layer of minute pyrite crystals and minor 'ankerite'.

crystallisation from a supersaturated solution, possibly triggered by strong shaking as a result of fault movement. A similar situation with regard to goethite is described from the adjacent Rampgill Mine by Bridges and Wilkinson (2003; 2005).

Not all specimens exhibit such markedly different upper and lower surfaces. Figures 15 and 16 show a thin specimen of ‘ankerite’ on quartz with minor sphalerite. The clean (probably upper side in the cavity) face (Figure 15) displays only minor oxidation. The other face of the specimen is similar to the left hand side of Figure 13, with a partial crust of minute pyrite crystals and some small areas of slightly larger pyrite crystals which pre-date the ankerite. The large sphalerite crystal is free from pyrite, but is partly encrusted with calcite. It seems likely that the clean side faced downwards in the cavity, protecting it from any debris falling from above. The cartoon below (Figure 17) illustrates schematically the inferred orientation of the specimens described in relation to the cavity. This is conjectural, and not to scale, but may assist with understanding the above descriptions.

It is interesting to note that the specimens were not attached to each other despite continued mineral growth. There must have been sufficient buoyancy in the strongly saline hydrothermal brines for crystal growth to lift specimens without adhering to those below.



Figure 15. A specimen of ‘ankerite’ on a quartz substrate with minor sphalerite (the underside in the cavity). Specimen width 9 cm.

Representative specimen material has been placed in the collections of the Great North Museum-Hancock and the Oxford University Museum of Natural History.

CONCLUSION

The most plausible explanation for the contents of the cavity is a combination of alteration, brecciation and dissolution of the limestone wall rock. The mineralising fluids were changing with time, much of the early mineralisation being dominated by quartz. Fault movement could easily account for the stress-cracking, the brecciation and the change in hydrothermal fluid flow and compositions to account for the different minerals in the cavity. This is in accord with recent research on flat formation in the Alston Block of the NPO reported in Bouch *et al.* (2006).

ACKNOWLEDGEMENTS

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Figure 16. The reverse (upper side in the cavity) of Figure 15, showing ‘ankerite’ with a thin partial crust of minute pyrite crystals and some areas of larger pyrite crystals.

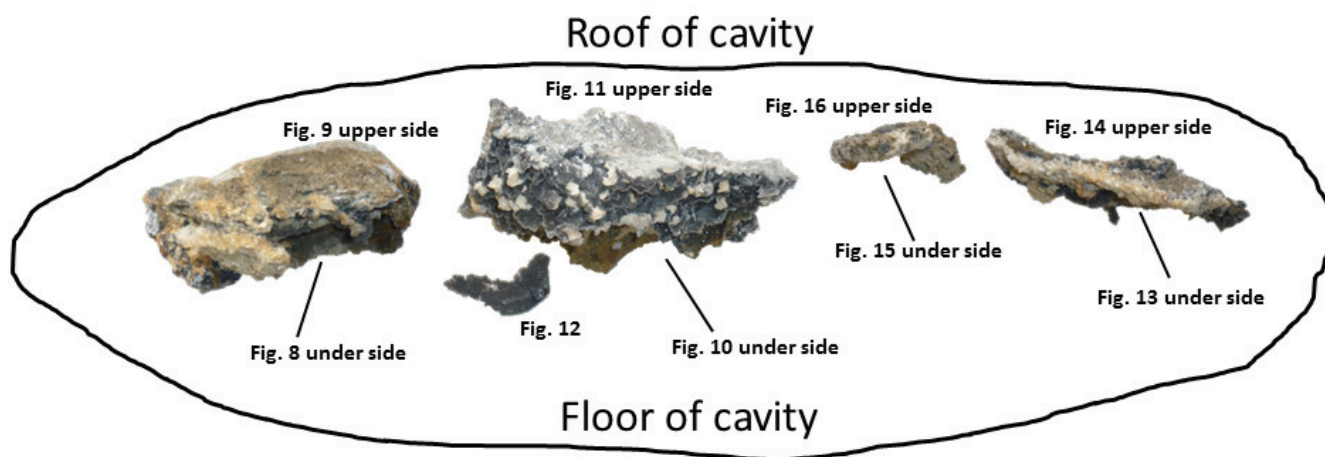


Figure 17. Cartoon illustrating the inferred orientation in the cavity of the specimens described. Not to scale.

REFERENCES

- Bouch, J.E., Naden, J., Shepherd, T.J., Young, B., Benham, A.J., McKervey, J.A. and Sloane, H.J. (2006). *Stratabound Pb-Zn-Ba-F mineralisation in the Alston Block of the Northern Pennine Orefield (England) - origins and emplacement*. Economic Minerals Programme of the British Geological Survey. Research Report RR/08/06.
- Bridges, T.F., Green, D.I. and Ince, F. (2014). Ankerite: its composition and formulae, and its status in the Northern Pennine Orefield. *Journal of the Russell Society*, **17**, 51–56.
- Bridges, T.F. and Wilkinson, H. (2003). Epimorphs of quartz after fluorite from the Rampgill, Coalcleugh and Barneycraig Mine System, Nenthead, Cumbria, England. *Journal of the Russell Society*, **8**, 38–39.
- Bridges, T.F. and Wilkinson, H. (2005). Epimorphs of quartz after fluorite from the Rampgill, Coalcleugh and Barneycraig Mine System, Nenthead, Cumbria, England - an update. *Journal of the Russell Society*, **8**, 112.
- Dunham, K.C. (1990). *Geology of the Northern Pennine Orefield. Vol. 1 - Tyne to Stainmore, 2nd edn*. Economic Memoir of the British Geological Survey.
- Wallace, W. (1861). *The Laws Which Regulate the Deposition of Lead Ore in Veins*. Edward Stanford, London.

THE HISTORY AND OCCURRENCE OF ‘BUXTON DIAMONDS’

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The presence of quartz crystals in the soils around Buxton has been known for centuries, and at one time these so-called ‘Buxton Diamonds’ were, from published sources, apparently relatively abundant, and well-known both to visitors and to commentators. However, few specimens survive in museum collections and there is considerable confusion in published accounts as to what exactly constitutes a ‘Buxton Diamond’. No satisfactory description or explanation of their origin and occurrence has hitherto been published. Attractive specimens of quartz and amethyst are known from various occurrences in the Peak District, associated with igneous rocks, but these are not true ‘Buxton Diamonds’. This paper presents the history of ‘Buxton Diamonds’ and confirms the occurrence of these, sometimes highly attractive, crystals of quartz in the limestone of Diamond Hill and the surrounding area.

INTRODUCTION

‘Buxton Diamonds’ are small, euhedral, doubly-terminated quartz crystals found weathering out from limestone in the soils south of Buxton. Like ‘Bristol Diamonds’ (Bradshaw, 1968), ‘Cornish Diamonds’ (Borlase, 1749), the Pecos Diamonds of New Mexico (Albright and Lueth, 2003), and the famous ‘Herkimer Diamonds’ of New York state (Ulrich, 1989), they represent an example of a mineral becoming part of local folklore and language. These crystals were collected as curiosities some 280 or more years ago, and gave rise to a popular tourist activity of crystal hunting, particularly in Victorian times.

Despite many references in contemporary tourist guides e.g. Bray (1783), Pilkington (1789), Glover (1845), and even forming the main thread of a children’s book by Agnes Strickland (Strickland, 1823), no formal scientific account has been presented of these interesting, and occasionally very beautiful quartz crystals. Remarkably few examples appear to have survived, and this is perhaps surprising in view of the apparent abundance of them at one time. Recent fieldwork has confirmed the occurrence of doubly terminated quartz crystals at Diamond Hill

(Figure 1; see also Figure 2). The presence of myriads of tiny (microscopic) euhedral quartz crystals in certain of the Derbyshire limestones is reported, and contrasted with the occurrence of ‘Buxton Diamonds’.

Historical accounts are rather confused and ambiguous, and we seek here to distinguish between what the authors consider to be true ‘Buxton Diamonds’, quartz crystals occurring in the limestones, and other occurrences of quartz and amethyst associated with the basaltic igneous rocks of the Peak District.

HISTORICAL ACCOUNTS AND LITERATURE

The attractions of Buxton and its environs have long been celebrated, and numerous guidebooks and travelogues have been published over the past few hundred years. William Camden’s *Britannia* (Camden, 1586) includes a description of Poole’s Cavern near Buxton, but does not mention ‘Buxton Diamonds’.

The earliest record of ‘Buxton Diamonds’ appears to be that of Dr Thomas Short, a physician from Sheffield, and one of the first to explain the effects of Buxton’s waters in

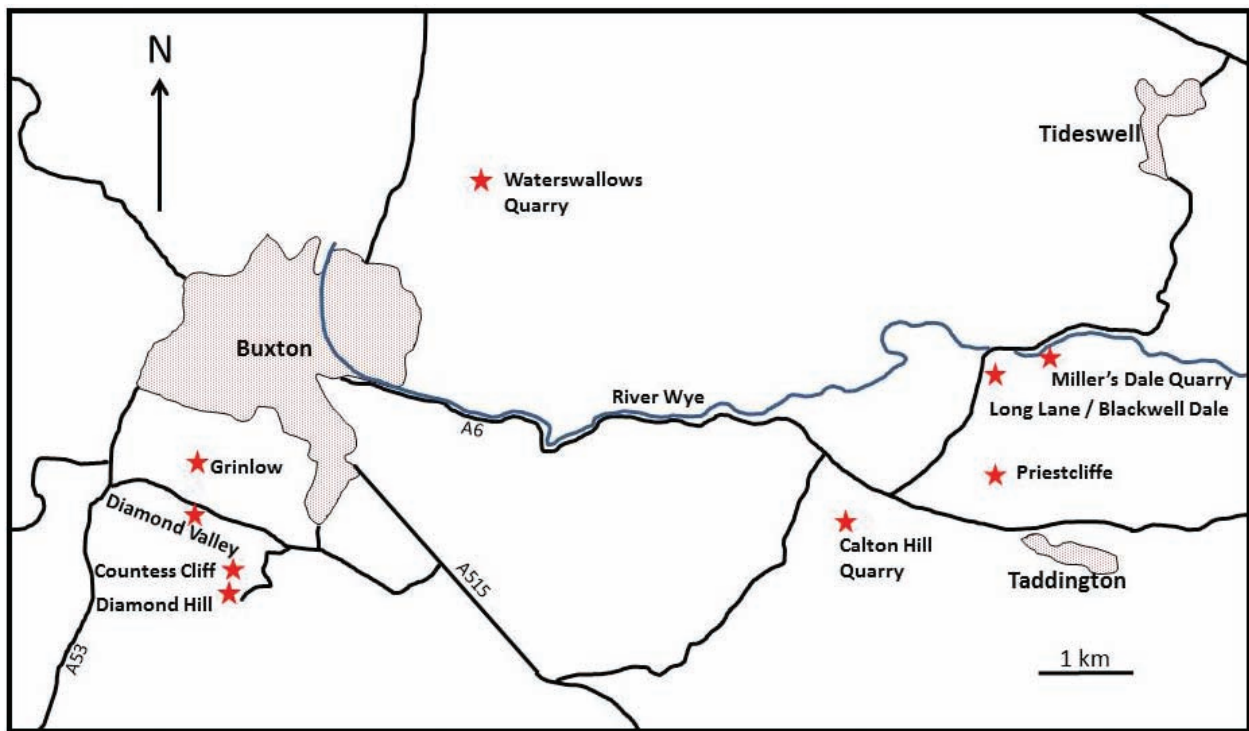


Figure 1. Sketch map showing the location of Buxton, Diamond Hill and other localities mentioned in the text.

improving health according to mechanist principles in his *Mineral Waters* (Short, 1734):

A little south of Pools [*sic*] Hole, (which is reckoned one of the Wonders of the Peak) and a Mile south West of Buxton, is a Cart Way, where in a bright Sunshine, immediately after a sharp Rain, the poor People gather small Crystals consisting of two Hexagonal Pyramids, and an intermediate Hexagonal Column, they are all of the same Figure, tho' of very different Magnitudes, and if any appear otherwise, they are either broken or imperfect; they naturally have all a most beautiful Polish, are of sundry Colours, as crystalline (which are the best) red, purple, brown, &c. The first are very fine, cut Glass two or three Times, and are therefore called Diamonds; Naturalists suppose them to proceed from nitrous Streams, for they are continually of the Shape of crystalized [*sic*] Salts of Nitre; some are small as wheat Corns, others large as a Child's Finger.

A curious account is provided by Bray (1783), who notes that:

... in the year 1756, a gentleman, in his walks, observed some little risings on the rocks, which appeared like ant-hills; he opened some, and found they consisted of a perfect arch, drawn up, as he imagined, by the exhalation of the sun; in them was first formed a thin bed of dirty-coloured spar, and upon that a regular cluster or bed of these crystals.

He then adds:

Dr. Short says, all these are formed in the winter, and the more stormy and colder it is, the larger and harder these petrifications. Our modern chymists [*sic*], I am aware, will not be altogether satisfied with Dr. Short's old-fashioned method of manufacturing crystals.

Unfortunately, Bray gives no clue as to the identity of the gentleman concerned, but his description bears some resemblance to that given by Ford (1969) in relation to the occurrence of quartz with fluorite at Treak Cliff.



Figure 2. Diamond Hill, with a solitary cow, viewed from the northeast, looking towards the wooded slopes of Turncliff Common in the distance. Roy Starkey image.

James Pilkington, Bishop of Durham, in his *A View of the Present State of Derbyshire* (Pilkington, 1789) includes the following notes:

Hexagonal crystals terminated by two pyramids of the same form, found in a yellowish red earth near Buxton. They have a slight reddish tinge, which they most probably derive from a small mixture of iron. These crystals are commonly called Buxton diamonds. Crystals of the same form, nearly an inch long, found in clay in a field between Mam-tor [*sic*] and Castleton. Small crystals of the same kind in an iron earth on Brassington moor. Iron earth is the only bed, in which I have found perfect crystals.

The importance of the tourist trade to Buxton is highlighted by Britton and Brayley (1802):

The principal, we might almost say only, dependence of the inhabitants, is on the expenditure of the crowds who assemble here. Several shops for the manufacture and sale of ornaments of fluor spar [*sic*], and alabaster, are established in this village [Buxton]. The most finished and

best assortment of articles of this description, are exhibited in the warehouse of Mr. Samuel Cooper. The place where the crystals, denominated Buxton diamonds, are found, is about two miles south-west from the village: it is a waste uneven piece of land, several acres in extent, and called the Diamond Hill. (Figure 2).

Of the Poole's Cavern Guides they note:

The money given by visitants is divided among ten aged women, who reside here, and act as guides by the permission of the Duke of Devonshire, to whom the ground belongs. Some of them are always ready to exhibit the wonders committed to their charge; and as the old ladies keep a watchful eye over each other's receipts, the spectator has generally three or four attendants more than are necessary. The extent of the cavern does not exceed 300 yards.

John Mawe (Mawe, 1802) refers only in passing to Poole's Cavern, and does not make reference to 'Buxton Diamonds' by name, but his description on page 85 is almost certainly based upon their occurrence:

In the siliceous order may first be mentioned topazine and rose coloured quartz, in hexagonal prisms, with double pyramids detached:

Amethystine [*sic*] quartz finely tinged; with perfect hexagonal prisms, also with double pyramids detached. Clear colourless quartz in fragments, and the same in bitumen: these varieties are loose in the limestone. Chert, hornstone, or petrosilex, forming thin laminated beds, near Bradwell, Buxton, Middleton, &c. &c.

Sowerby (1804) mentions quartz from Bristol, but does not comment on 'Buxton Diamonds', nor indeed, on rock crystal from Derbyshire.

By coincidence, two substantial publications appeared in 1811, both of which mention the occurrence of loose crystals of quartz.

White Watson, the renowned Derbyshire sculptor, marble-worker, pioneer geologist, writer and mineral dealer, may be considered a reliable and authoritative source. Cooper (2006) provides a detailed appreciation of White Watson. In his classic work (Watson, 1811) he provides the following detailed account:

At Counter's Cliff [*sic*], near Buxton, on a hill called Diamond Hill, Crystals of Quartz, called Buxton Diamonds, are disseminated in the Foxearth of flesh red colour, in hexagonal prisms terminating with an hexagonal pyramid at each end, sometimes in macles [French for twin] by two crystals crossing each other, and sometimes in clusters. With these crystals are found detached cubes of Fluete of Lime, frequently much corroded, and Tuberos balls of Sulphate of Baryte crystallized in mass into cuneiform crystals*; and in the incumbent black soil, colourless Quartz crystals are also disseminated; these crystals are most discernible after heavy showers of rain which wash the soil from them. It is probable, from similar crystals being found attached to the Cheeks of Veins, that these crystals were formed in Fissures of the Limestone.

*These balls have frequently the crystals of Quartz and Fluete of Lime imbedded [*sic*] in them.

Farey (1811) describes the occurrence of quartz crystals in "...cavities or tick-holes..." in limestone near Ashover, Matlock and Tideswell. He also draws attention to

Small detached and perfect Crystals of colourless Quartz, called by some, Derbyshire Diamonds, consisting of an hexagonal prism terminated by pyramids, with others of a light rose colour (see Mawe's "Mineralogy of Derbyshire," p. 85), [which] are found occasionally in the following places, *viz.*

Bakewell, NW, imbedded in Toadstone.

Brassington Common, loose in Corn Soil, on 4th Lime.

Buxton S (Sherbrook), imbedded in 3rd Toadstone: SW (Counters Cliff, and Grindon), loose in Peaty Soil, on 4th Lime.

Castleton NW (Tra-cliff Hill) [*sic*], loose in the Corn Soil.

Gateham W (Wetton Pasture), Staffordshire, in reddish Soil, on 4th Lime.

Millers Dale SW (Long-lane, near Priestcliff), imbedded in 3rd Toadstone, in great numbers.

It seems that quartz was a highly topical subject at this time. Jewitt (1811) includes a transcript of a letter dated 19th August 1810, written by a young lady who had visited Buxton, to her sister, in which she reports having spent a morning in Miller's Dale, and:

On the side of a hill, near the upper mill [probably the Long Lane occurrence], we picked up many specimens of the Derbyshire diamond. After rain they lie sparkling in the road. As you never mentioned these to me, it is probable you never saw them; you will, I hope, have that pleasure at my return.

A childrens' book, by the English historical writer and poet Agnes Strickland (1796–1874), *The Buxton Diamonds or Grateful Ellen* (Strickland, 1823), tells the story of a young girl and her adventures, including some apparently authentic details of the trade in 'Buxton Diamonds' and daily life in the Buxton area. The book (Figure 3) pre-dates her much better known multi-volume historical works on the *Lives of the Queens of England*, *Letters of Mary Queen of Scots* (research for which is perhaps the reason for her writing the *Buxton Diamonds or Grateful Ellen*) and the *Lives of the Queens of Scotland* (Strickland, 1840–1848; 1842–1843 and 1851–1859). Quite why Strickland should have chosen to produce such a work built around this theme is a mystery. It is recorded that she visited Chatsworth House at the invitation of the Duke of Devonshire in 1847 (Strickland, 1887), and also stayed at the Old Hall Hotel in Buxton whilst pursuing her interest in Mary Stuart (Mary Queen of Scots), wishing to see all of her prison-houses, so it is possible that she had made earlier trips to the region.

Rhodes (1824) mentions that Diamond Hill is

...a place often visited by strangers for the purpose of collecting these detached crystals of quartz that are here denominated Buxton Diamonds. These crystals are hexagonal, and their sides and angles are accurately formed, but in general they are of a bad colour, and but few of them are found perfectly transparent. They are hard, and their points, like the diamond, will cut glass; but this property is soon worn off.

He summarises information from Bray (1783) and Watson (1811), adding that

The right [north] bank of the Wye, which is made up of rock and wood, rises almost perpendicularly from the

water's edge to a considerable height. The left [south] affords a difficult passage amongst trees and underwood, brambles, and colt's foot, which is continued to within a few hundred yards of the bridge in Miller's-dale [sic]. At this bridge we crossed the river, for the purpose of exploring a contracted dell which leads from Diamond-hill [sic] to the village of Blackwell. [It is unclear to which locality Rhodes is referring as there is no valley which leads directly from Diamond Hill to Blackwell. It seems that he may be using the name "Diamond Hill", loosely, in reference to Priestcliff or possibly to Calton Hill]. While my companion was employed in sketching, from a jutting eminence at the base of Priestcliff, one of the finest scenes on the banks of the Wye, I amused myself in searching, amongst a stratum of loose toad-stone, near the road side, for Derbyshire diamonds. These crystals are here found in abundance, and they sometimes glitter in the pathway of the traveller and attract his attention: they are often defective in form, and generally they are of a dirty colour, slightly tinged with yellow, red, and purple. [Here, Rhodes clearly is referring to the Long Lane occurrence].

The Rev. R. Ward (Ward, 1826) reports that ...very small topazine and rose-coloured quartz, in hexagonal prisms, or with double pyramids detached,

are found in yellowish earth near Buxton, and are called Buxton diamonds

and in a later publication (Ward, 1827), he states that

Buxton also abounds with shops containing beautiful vases and other articles formed of the flour [sic] spar, alabaster, marble, &c. also curious specimens of minerals and fossils, similar to those exhibited for sale at Matlock and Castleton. Those quartz crystals, chiefly of the hexagonal form, called Buxton Diamonds, are found, especially after rain, on an uneven piece of ground by the Leek road, called Diamond Hill, two miles and a half from Buxton: they are also found near the village of Blackwell, at a short distance from Miller's Dale and the Wye.

Another clergyman, geologist and enthusiastic naturalist, the Rev. Leonard Jenyns, made a tour through Derbyshire in 1830 and documented his observations in a notebook (Jenyns, 1830). On 17th August 1830 he walked, in the rain, to Chatsworth, and in the evening he visited Mr White Watson, F.L.S. [W. Watson (1760–1835) sculptor, marble-worker and mineral dealer] in Bakewell, who had

...some extensive collections in the several departments of Nat: Hist [Natural History], particularly minerals and

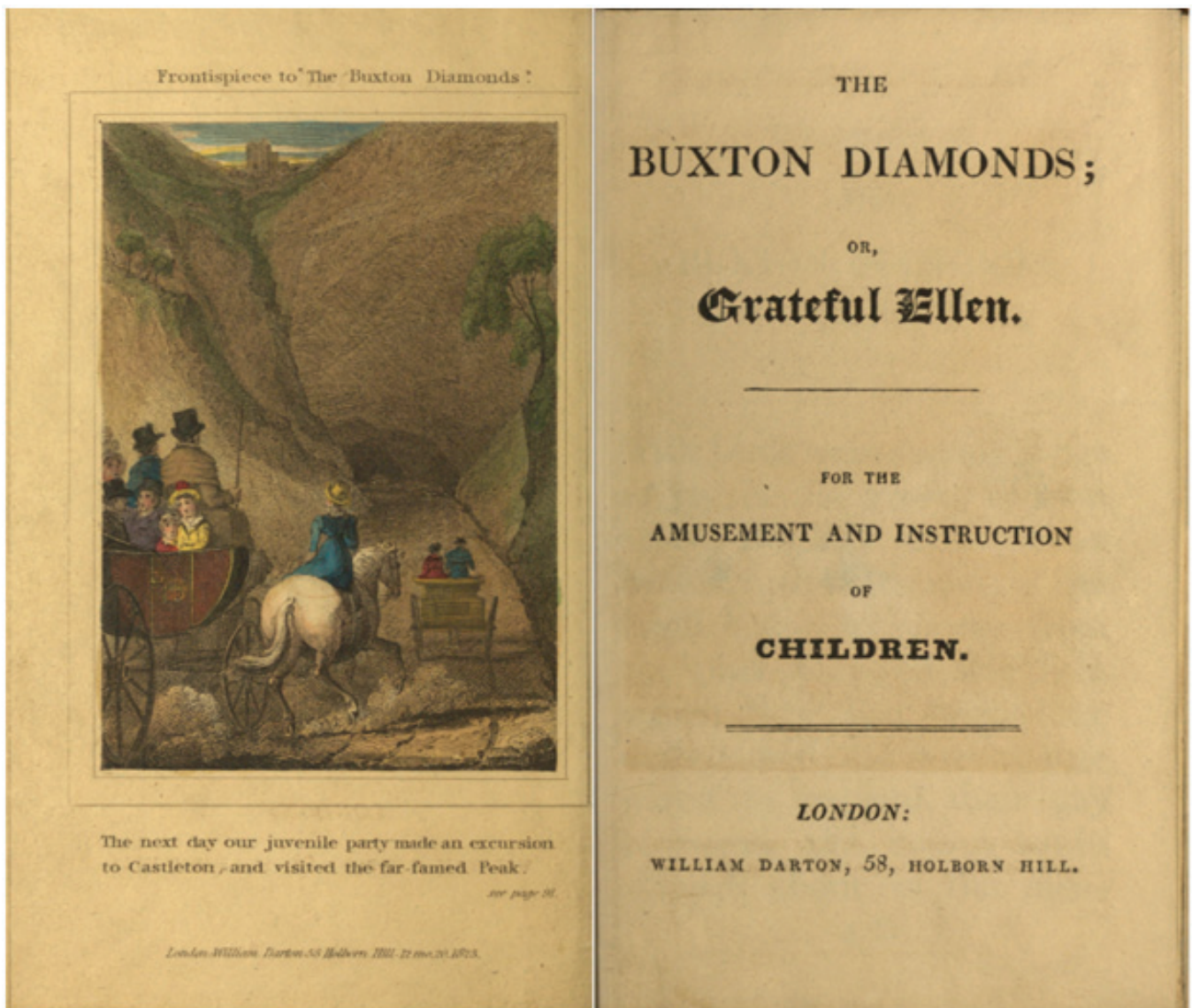


Figure 3. Frontispiece and title page from *The Buxton Diamonds or Grateful Ellen* (Strickland, 1823).

plants & remarkably well versed in the local details of the surrounding country. He showed me some very curious sections illustrating the Geology of Derbyshire.

Continuing his travels on the morning of Saturday 21st August, he walked about half a mile to the southwest of Buxton to Grin Low, and from there to Diamond Hill which he described as

...an elevated piece of pasture land a short distance from Grinlow, w^h [which] owes its name to the circumstance of quartz crystals being found there, or, as they are locally termed, - Buxton diamonds. These supposed rarities are met with just below the vegetable soil in a kind of sandy loam: - they are occasionally found seated on the surface, - but more commonly the poor people avail themselves of a hard rain w^h washes away the loose earth, after w^h they are easily scratched up: did not succeed in finding any myself."

Glover (1831) records the occurrence of quartz crystals (which he terms "Derbyshire Diamonds") associated with igneous rocks in

Sandy Dale S.S.E. of Wormhill, extending S.S.W. about 3/4m from Wye dale to near Blackwell village, in 3rd lime, and 3rd toadstone at its southern end; the 2nd toadstone skirts its eastern border at the northern end, and produces numerous quartz crystals, or Derbyshire diamonds. [It seems probable that Sandy Dale is the valley now called Blackwell Dale on the modern O.S. map, and thus that this description refers to the basalt-hosted toadstone occurrence at Long Lane].

Lewis (1831) reports that

About one mile and a half beyond the [Poole's] cavern is Diamond Hill, so called from the detached chrystals [sic] found there in profusion, denominated Buxton diamonds; their form is hexagonal, and their surface and angles well defined, but of bad colour; when first found they are hard, but they soon lose that property.

Tymms (1835) includes "...crystals, called Buxton diamonds" in his list of the mineral produce of Derbyshire, and the *New Buxton Guide* (Orme, 1837) also includes a passage under the title of

Diamond Hill – A little beyond the mountain, under which Poole's Hole is situated, is a place called Diamond Hill, which is much resorted to by the company who visit Buxton, to obtain crystallized matter, (quartz,) called Buxton diamonds, which are found in the soil and clay. The whitest of them are most esteemed; and their having the property of scratching glass, is the reason why the windows in most houses of Buxton are much injured by the experiments used to ascertain the power of these diamonds.

The Guide also provides the following advice for would-be visitors:

The old ladies who are employed to shew Poole's Hole, generally exhibit some of them for sale; but their demands are arbitrary, and often exceed the bounds of reason. It is therefore always best to bargain for those, and admission into the cave [combined], before you enter.

That Buxton supported a thriving tourist trade is beyond doubt, but the scale of the operation clearly meant that there was a ready market for souvenirs and "nick-nacks", as evidenced by Glover (1845), who notes that

The principal dependence of the inhabitants is more upon the crowds who assemble here during the bathing season than on any regular employment. It is computed that the public and private lodging-houses will accommodate from twelve to fifteen hundred persons at one time, besides the resident inhabitants. Several shops for the manufacture and sale of fluor spar [sic] and marble ornaments are established in the town, and the elegant repository of Mr Hall, for these articles, and that of Messrs. Bright and Sons, for hardware and jewellery, attract the visitors.

The diamonds procured in the neighbourhood may be seen here in great variety. They are made up in handsome ornaments, such as rings, brooches, and various articles of jewellery.

It is of course not unknown for such "fancy goods" to be imported, wholesale, from areas beyond their supposed place of origin, and it is entirely possible that jewellery and trinkets marketed as containing authentic 'Buxton Diamonds' may have contained quartz crystals from elsewhere.

Bagshaw (1846) includes a reference on page 20 to "The Derbyshire Diamonds, for which see Buxton", and later mentions that

On the western side of the lofty conical hill of Priestcliffe, in a dark-coloured ferruginous soil, are found a few quartz crystals similar to the Buxton diamonds.

The mineralogist, museum proprietor and author, William Adam, gives additional specific detail in his *The Gem of the Peak*, first published in 1838 (Adam, 1857), and provides perhaps the most informative contemporary account:

From hence we followed the narrow field-path up to Fern House (Mr. Needham's), Counter's Cliff; passing through the farm-yard and turning to the right. Under some low crags, we found the place where the Buxton Diamonds exist in abundance, in the hollow, or ravine, formed between Grinlow and Landman's Low. On descending the hill and examining this spot, we observed that it was traversed by the vein of the Grin-end Mine, the principal shaft of which is about a mile to the north-eastward, now worked for Sulphate of Barytes, or "Cauk" – and as it exhibits every appearance of having been worked throughout the course of this hollow, it may be presumed that the greater part of the loose matter here accumulated is the refuse of the workings, and may have been brought from considerable depths; and as I am informed that a mass of these quartz crystals aggregated was found in this mine,* it is probable that these detached and beautiful crystals belong to the limestone measures, which is often productive of fine quartz crystals. The crystals are often found in perfect hexagons, terminated by six-sided pyramids, sometimes perfectly clear, and in other cases "cankered," as the provincial phrase is, or reddish brown, being coloured with oxide of iron. The clear or transparent are found in the black soil, formed chiefly by the decay of vegetable matter, and the washing down of the peat from the moors, and the other in the red clay. They are from an eighth of an inch long to one inch: one that the author obtained was of a beautiful amethystine colour, and most perfect; but parties are not allowed to look for them as formerly, owing to the damage done to the pastures. These, like all quartz or siliceous crystals, scratch glass. Abundance of them are to be had in the shops of Buxton and Matlock. The author

has, since he examined this point, obtained a quantity of these beautiful crystals from one of the dells of the limestone near Winster, in a position which induces him to believe they originate in the Toadstone, and their present disattached state in the clay is the result of the destruction of the Toadstone, which proceeds rapidly wherever it is exposed. This measure often contains Geodes, the interior of which is lined with quartz crystals.

*This specimen is now in the Manchester Museum.” [A recent examination of the collection at Manchester Museum failed to identify it. David Gelsthorpe, *personal communication*, 2015].

Adam published an abridged version of his guide under the title *Description of Buxton, Chatsworth and Castleton* (Adam, 1847), which includes the following passage:

We observed to our right, and but a short distance from us, the towering hill of Priest Cliff, the giant base of which skirts the greater part of Blackwall Dale on the south side, and where quartz crystals, or what are termed “Derbyshire diamonds,” may be obtained among the loose matter on the side of the Cliff, in the long lane, leading to Taddington. [The term “Diamonds” here is being applied to a toadstone-hosted occurrence].

He also notes, in relation to Grin Low, that good views are to be obtained from the tower, and

Quartz Crystals found in the soil on the low side to the westward. These are beautifully crystalized [*sic*], and called Buxton Diamonds.

A tourist pamphlet, curiously titled *The Buxton Diamond* was published by John C. and Henry B. Bates (Bates and Bates, 1860), and describes various scenic attractions within the town, but strangely makes no mention of ‘Buxton Diamonds’ although the authors were clearly aware of the eponymous crystals.

White (1857) notes that

Diamond Hill, about a mile beyond Poole’s Hole, is a place mostly visited by strangers for the purpose of collecting those detached crystals which are here denominated Buxton Diamonds. These crystals are often hexagonal, and their sides and angles are accurately formed, and so hard that the points will cut glass.

and on page 524

On the western side of the lofty conical hill of Priestcliffe, in a dark coloured ferruginous soil, are found a few quartz crystals similar to the Buxton diamonds.

Although Greg and Lettsom (1858) do not mention ‘Buxton Diamonds’, they do report the occurrence of similar crystals, known as ‘British Diamonds’, from Clifton, Gloucestershire. The occurrence of these, so-called ‘Bristol Diamonds’ has been described in some detail by Bradshaw (1968).

Further re-working of earlier published material appears in William Adam’s *Dales, scenery, fishing streams* (Adam, 1861):

We now reached the two small corn mills, turned by the stream, at the other end of the dale, where it forms a junction with Chee-Tor dale and Blackwall [*sic*], to gain which you cross the river by a good bridge, and the road which leads to Buxton, and wind round the base of Priestcliff. A little above, a lane, literally paved with whinstone boulders*,

leads to the left towards Taddington, and in the south cliff which bounds it, you may dig in the loose and perished toadstone for Buxton Diamonds, (quartz crystals.) They often lie in clusters and are sometimes beautifully clear, or as we may be allowed to say, “of the purest water,” and sometimes they assume the hue of amethyst. But it is difficult to find a perfect crystal.

*The whinstone boulders are formed of the harder parts of the toadstone.

James Croston (Croston, 1868) remarks that

A field road from the Cottage [of Content] leads to the celebrated Diamond valley, the soil of which is productive of those detached crystals known as Buxton Diamonds, and which are often found aggregating in clusters in the dark ferruginous earth. The place has lately been closed against the public, and a notice-board now conveys a warning to acquisitive intruders.

This suggests that sufficient crystal seekers were active at this time as to present a nuisance to the land owner.

The name ‘Diamond Valley’ is also used by Heywood (1869) to describe the area to the south of Grin Low:

Below the height, on which stands Solomon’s Temple, is a ravine known as DIAMOND VALLEY, where among the loose debris and ferruginous earth, are found the detached crystals known far and near as Buxton Diamonds.

Interestingly, Traill (1870) does not refer to ‘Buxton Diamonds’ in his *Elementary Treatise on Quartz & Opal*, but Hyde (1893) keeps the story alive by mentioning that

Lying between the Temple and Harpur Hill is Diamond Hill, where, after a fall of rain, “Buxton Diamonds,” consisting of fine crystals of quartz, may be picked up from amongst the loose gravel.

Bulmer (1895) also states that

A little north of this place [Harpur Hill] is Counter’s Cliff. On a farm here, is the celebrated Diamond Hill where the crystals known as Buxton diamonds are found. If the turf be raised, particularly after rain, these stalactical [*sic*] formations are found a little distance below the surface. The crystals are hexagonal in form and shine with a brilliant lustre.

F.W. Rudler, in his excellent *Handbook to a Collection of the Minerals of the British Islands* (Rudler, 1905), notes that whilst quartz is by no means common among the minerals of Derbyshire, in the neighbourhood of Buxton there are small crystals of quartz, generally found loose in the soil, and known as “Buxton Diamonds”. He makes reference to a selection of crystals, exhibited as No. 961, which present the form of hexagonal prisms, terminated usually at each end by a hexagonal pyramid, some of which are perfectly colourless, others are tinted brown, with oxide of iron. He suggests that they

...appear to have been derived from such a source as is represented by No. 962, a specimen which shows similar doubly-terminated crystals in a matrix of flesh-coloured barytes.

It is possible that Rudler was referring to one of the specimens included here as Figure 23 or Figure 24. Rudler makes reference to a paper on the occurrence of quartz with calcite associated with the igneous rocks of Derbyshire by Holroyd and Barnes (1901), but the authors consider this

paper not to be of relevance to the formation of 'Buxton Diamonds'.

The literature, post-Rudler, pays scant attention to 'Buxton Diamonds', but they are mentioned in passing by Ford *et al.* (1993), and in a general review article about quartz in Derbyshire (Woore, 1978), which summarises much of the above historical information. Although the text is penned in an authoritative style, it is not clear whether the author is writing from personal experience or simply providing a distillation of earlier published works. The localities and descriptions which he lists, bear a striking resemblance to those given by Farey (1811):

Perhaps the best known are the 'Buxton Diamonds', found at 'Diamond Hill,' Counters Cliff, Buxton, where they are exposed sometimes on the surface of the soil, after heavy rain. They are much more numerous in the red sub-soil beneath the black surface layer, where they occur with some detached cubes of fluorspar, nodules of radiate-barite [*sic*], and 'brainstone' barite [*sic*]. These thin soils lie on limestone rock.

The quartz crystals are brilliant, under one inch in length, mostly clear, but some rose tinted. They are of regular crystalline form, with perfect prisms, doubly terminated. Similar quartz crystals also occur loose in soils at places farther away from Counters Cliff, and at Grindon, and occur loose in soil on the side of Grindlow Hill [it is unclear whether this refers to Grind Low [SK 205 674] to the south west of Bakewell, or Grin Low [SK 186 774] near Buxton, which seems more probable], and loose in soil on Brassington Common, and at Sherbrook in 'toadstone' rock, which term is a Derbyshire name for intrusive or volcanic rock.

They occur loose in soil at Treak Cliff, Castleton, and lie loose in a red soil by Gateham (Wetton Pastures).

They occur in toadstone north-west of Bakewell, and a great many by Long Low near Priestcliffe. They also occurred in iron ore mined in Fryden Dale. They occur in toadstone along the eastern side of the northern end of Sandy Dale, south-south-east of Wormhill, in clear crystals.

We have been unable to trace, or to confirm the identity of Mr Woore, and would be most interested to hear from any reader who may have known him.

Tindle (2008) and Braithwaite (1983) provide a review of the occurrence of quartz in Derbyshire, including a brief mention of 'Buxton Diamonds'.

GEOLOGY AND GENESIS

Buxton is recognised as the highest market town in England (altitude 303 metres) and lies on the western margin of the Peak District. The country rocks in the immediate vicinity of Diamond Hill are Dinantian (Carboniferous) Limestone, overlain to the northwest by younger Namurian sediments – the Millstone Grit (Figure 4). The area has attracted the attentions of generations of geologists and those seeking more detail on previous work will find a comprehensive reference listing in the sheet memoir (Aitkenhead *et al.*, 1985).

Although there are no permanent surface exposures in the proven quartz-producing area of Diamond Hill,

discontinuous outcrops west of Countess Cliff Farm, and along the north-eastern margin of Diamond Hill, mean that the geology of the area is well-constrained. The Bee Low Limestone Formation of the Peak Limestone Group makes up most of the hill, with the underlying Woo Dale Limestone Formation exposed in lower ground in the valley east of Countess Cliff. This sequence is structurally part of the Derbyshire Carbonate Platform, a geological "high" characterised by shallow seas, and periodic sub-aerial exposure and weathering during the late Viséan epoch (e.g. Vanstone, 1998).

The Bee Low Limestone Formation is dominated by grey, rather pure calcite calcarenites, with abundant (<0.5 m thick) layers of volcanoclastic material (bentonites), making up around 3% of the thickness (Waters *et al.*, 2009; Fox and Bridge, 1977). The unit also includes locally-developed basaltic lava (The Lower Millers Dale Lava Member), and a thicker tuff unit (the Ravendale Tuff Member). Within the limestones, accessory euhedral quartz may form up to 0.5% of rock volume, and locally up to 5% (Fox and Bridge, 1977).

Euhedral quartz crystals, mostly very small or microscopic, are a common minor component of limestone and evaporite rocks, and can form under near-surface conditions (e.g. Chafetz and Zhang, 1998), but only a few localities produce specimen-quality crystals (e.g. the 'Pecos Diamonds' of New Mexico (Albright and Lueth, 2003)). Limestones can contain quite large amounts of opaline silica, especially in the form of sponge spicules in the original sediment, and during diagenesis this dissolves and can recrystallize as chert, or, more rarely, as distinct quartz crystals. Silica can also be introduced into limestones by groundwaters moving through pores or fractures, or *via* hydrothermal activity.

All of these processes have operated, at least locally, within the Peak Limestone Group across Derbyshire (e.g. Orme, 1974). Biogenic opal and volcanoclastic material are both potential sources of silica within the limestones. Chert bands are abundant, especially within the Monsal Dale Limestone Formation (Waters *et al.*, 2009). Microscopic euhedral quartzes are a common accessory component of limestones in the area (Orme, 1974), and may locally become abundant, producing lithologies such as the "Quartz Rock" (Bemrose, 1898; Orme, 1974).

There is no good outcrop-scale evidence of the Diamond Hill occurrence, and thus many aspects of the geology remain uncertain. However, it is known that quartz crystals occur within limestone, and in the weathered regolith overlying the limestone. Furthermore, quartz crystals occur as isolated 'porphyroblasts' within limestone which preserves fine fossil structures (Figure 5), indicating that bulk recrystallization of the limestone has been limited. Hydrocarbon-brine fluid inclusions within the quartz crystals indicate a low-oxygen activity in the quartz-depositing fluids. Moser *et al.* (1992) and Hollis and Walkden (1996) record hydrocarbon-inclusions associated with main-phase mineralisation in Derbyshire, and this suggests that the 'diamonds' are part of this story. This is further supported by Watson (1811) who

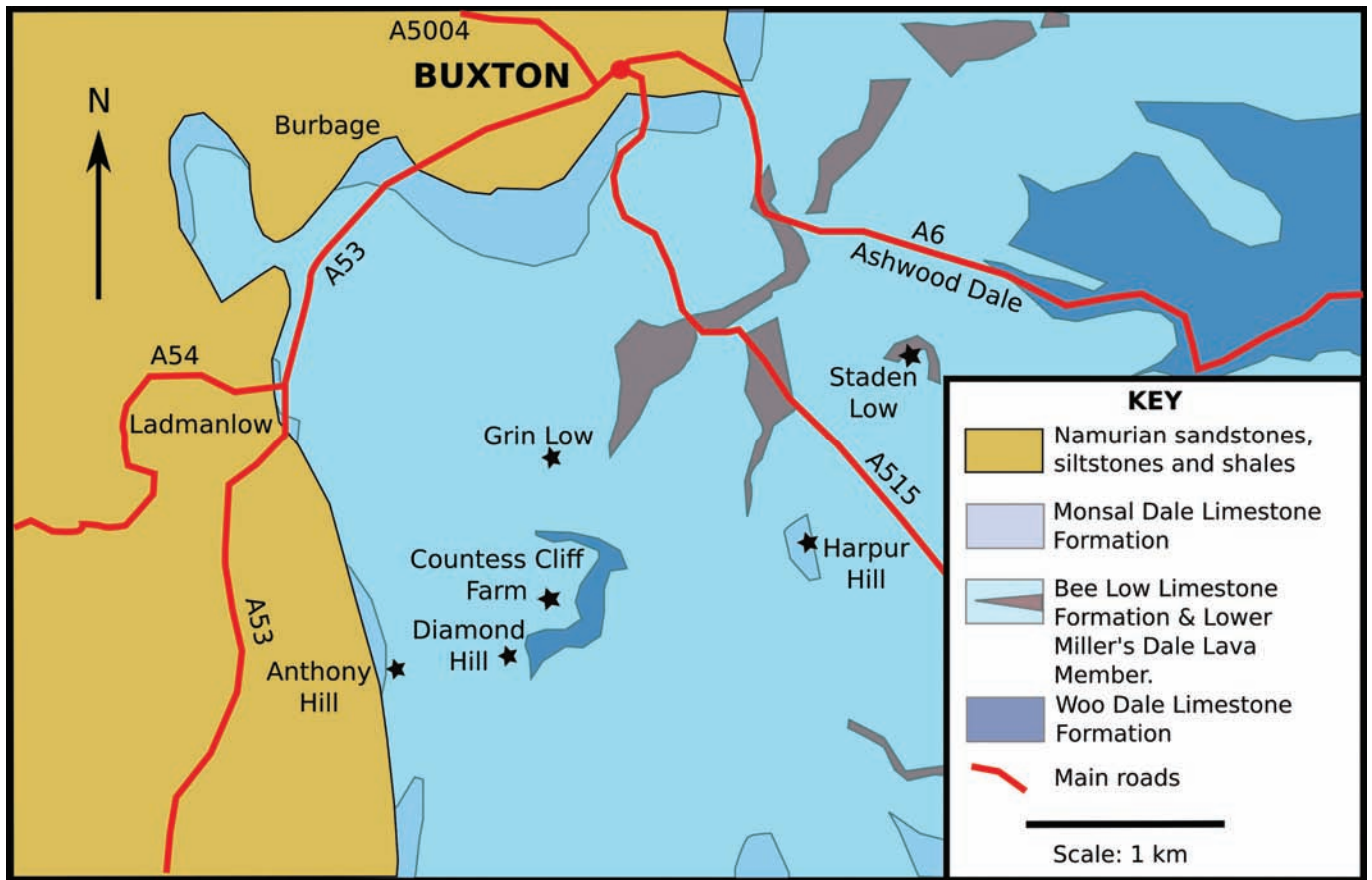


Figure 4. Simplified geological map of the area around Buxton (after Aitkenhead *et al.*, 1985).



Figure 5. Quartz crystals growing within a rugose coral, exposed by acid leaching of the enclosing limestone. The structure of the septa within the coral have been preserved within the quartz crystals. The largest crystal is 6 mm long. Roy Starkey specimen and image.

states that baryte and fluorite were locally associated with the ‘diamonds’ at Diamond Hill. Neither sieving of soil, nor our one sub-surface exposure has produced baryte or fluorite, so we suggest that such veins may be small, and of limited extent here, but that the quartz growth may be a low-temperature effect within limestone around such veins, similar to the silicification reported by Kanaris-Sotiriou *et al.* (1986) at Butts Quarry in Derbyshire. Ford (1967) notes that the silicified limestone ‘quartz rock’ is locally faulted-out by fluorite veins, so some of the silicification pre-dates at least some of the fluorite vein mineralisation.

Although the quartz crystals contain hydrocarbons, and grew from a relatively low oxygen fluid, many of the crystals from the Diamond Hill pit, and those preserved in museum collections, are turbid with abundant fine-grained hematite-stained clay inclusions. Such material must have been oxidised prior to quartz growth.

Limestones, and their associated bentonites, in this area were subaerially exposed, and subject to karstic weathering between the Dinantian and the Namurian. This weathering produced widespread reddish oxidised and residual deposits in Derbyshire (Vanstone, 1998). Such reddened, clay-rich lithologies are probably the source of the red inclusions in the turbid euhedral quartzes. Red residual rocks were also produced by Pleistocene weathering of the Peak Limestone Group but these post-date the quartz crystals (Piggott, 1962; 1965).

LOCALITIES

Diamond Hill [SK 052 707]

This small area of rough pasture, perhaps 0.25 km² in extent, is the ‘ancestral home’ of the ‘Buxton Diamond’ and is the place most frequently cited as being the source of ‘Buxton Diamonds’. Historical accounts are consistent in reporting the occurrence of quartz crystals loose in the soil, found especially after heavy rain, when they had been washed free of mud. A careful search of the area during the current project has confirmed the occurrence of doubly terminated crystals up to 16.5 × 7.5 mm, loose in the soil.



Figure 6. Quartz crystals recovered by washing and sieving soil. The assemblage shows a range of sizes and qualities of crystals, ranging from transparent, lustrous, euhedral crystals, to poorly-formed and heavily included examples, which is in good agreement with the variation seen in surviving museum specimens. The two largest crystals are 17 mm long. Roy Starkey specimens and image.

Examples of sparkling, euhedral, colourless crystals; milky; hematite stained; and poorly formed, inclusion-laden crystals have been noted (see Figure 6). All of the crystals collected, by wet sieving of soil samples, exhibit a very simple morphology – that of a hexagonal prism, terminated at each end by a hexagonal pyramid. Most of the crystals are only 3–4 mm or so in length, but several are larger.

A pit dug immediately beneath an area which yielded crystals in the soil, showed a profile of approximately 10 cm of dark topsoil, underlain by about 70 cm of brown clay, below which is corroded bedrock limestone (Figure 7). The limestone exhibits a very powdery surface which soils the hands, even after washing, and a marked colour difference between the typical dark grey core and a creamy white altered ‘crust’ approximately 1 mm thick. The surface of the limestone is noticeably rough to the touch, and here and there fossil fragments and tiny crystals of quartz are seen to protrude.

Five pieces of limestone recovered from the pit (total weight 2.7 kg), were leached in hydrochloric acid and the insoluble residue collected. The weight of limestone dissolved was 1,038 g, and the weight of the insoluble residue 1.45 g (0.14%). One sample shows 8 quartz crystals approximately 3 mm in length, still adhering to the enclosing matrix, and all growing from between the septa of a fossil coral (Figure 5). Some of these are compound crystals, but several exhibit the typical simple forms of a ‘Buxton Diamond’, although they are not colourless and transparent.

The insoluble residue is a broad mixture of clay particles from cavities and crevices in the limestone; pyrite as euhedral cubic and octahedral crystals and crudely arborescent aggregates; anhedral quartz fragments; ‘spongy’ masses of quartz from fossil replacements and thin fissures in the limestone; numerous microscopic euhedral quartz crystals; and about fifty, mainly milky, crystals and crystal aggregates of broadly ‘Buxton Diamond’ type. Interestingly, the type of residue from each of the pieces of leached limestone varies considerably, in spite of the fact that the rock samples all came from within a 50 × 50 cm area of subcrop.



Figure 7. Shallow pit excavated to expose the limestone subcrop on Diamond Hill (the white material is snow). The blade of the spade is resting on limestone at the bottom of the pit. Overall length of the spade is 0.9 m. Roy Starkey image.

Countess Cliff [SK 055 709]

Several early accounts give Countess Cliff as a locality for ‘Buxton Diamonds’. The steeply sloping area of turf-covered ground immediately to the east of Countess Cliff Farm was traversed at several different elevations, and the diggings from rabbit burrows and mole hills examined. No quartz crystals were noted on two visits by one of us (RES).

Grin Low [SK 054 717]

The Grin Low ridge, running roughly northwest–southeast from Grinlow Tower (also known locally as Solomon’s Temple), is typical turf-covered limestone country. Various scars, spoilheaps and depressions from earlier limestone quarrying and burning operations are scattered over the hillside, and there are exposures of limestone intermittently along the ridge. The spoil, soil and outcrops were examined and calcite veining noted in places, but no quartz crystals were observed.

Diamond Valley [SK 054 713]

The shallow valley between Grin Low Road, the B5053, and Diamond Hill has been called ‘Diamond Valley’ by some earlier workers, although this name does not appear on Ordnance Survey maps. The valley floor carries an ephemeral stream and is much obscured by waste from lime burning. Limestone crops out on both sides of the valley in low exposures. No quartz crystals were observed in the talus slopes below the limestone outcrops.

Long Lane / Blackwell Dale [SK 134 731]

Whilst not strictly anything to do with ‘Buxton Diamonds’ a brief mention of this occurrence is included for completeness. Early accounts mention the occurrence of quartz crystals associated with igneous rock just to the east of Long Lane which runs from Miller’s Dale up to Taddington. A small disused and overgrown quarry shows rotted toadstone veined by colourless to pale amethystine

quartz, some of which is crystallised. Richard Braithwaite (*personal communication*, 2015) visited this quarry in 1960 and found many small veins and cavities containing quartz crystals. These include near-colourless crystals to 15 mm, some of a peculiar “pagoda-like” habit consisting of repetitive parallel-growth intergrowths of bipyramids along the 3-fold axis (e.g. RSWB 60-109, Figure 8). These may grow directly on calcite, either massive or in scalenohedra to about 8 mm and/or on toadstone. Others, pinkish to hematite-red and 2–4 mm across, project between opaque pink platy baryte crystals to 5 mm on calcite on toadstone. The authors do not consider this occurrence to warrant the term ‘Buxton Diamonds’.

Priestcliffe [SK 135 719]

Bagshaw (1846) mentions the western side of Priestcliffe as a source of “...quartz crystals similar to the Buxton diamonds”. A member of the Peak Lapidary and Mineral Society apparently found a quartz crystal about 2.5 cm long on Priestcliffe in 2014 but it has not proved possible to verify this report (Paul Booth, *personal communication*, 2014). The western, southern and eastern slopes of Priestcliffe are formed of the Upper Millers Dale Lava, and the hill is capped by the Monsal Dale Limestone Formation. It seems probable that the crystal originated from the lava and is thus not of relevance to the present investigation.

Miller’s Dale Quarry [SK 141 730]

Wolverson Cope (1976) reports that the Priestcliffe Limestones exposed in a large disused quarry on the south side of Miller’s Dale contain authigenic crystals of quartz, many of which are visible to the naked eye. He also suggests that the presence of these crystals is responsible for the name ‘Diamond Hill’. One of us (RES) examined material from this quarry and several specimens showing crystals of quartz clearly visible with a hand lens were subjected to leaching with hydrochloric acid. The insoluble residue consists of large numbers of elongate euhedral quartz crystals, from about 100 to 400 microns in length (Figure 9), and a little tarnished pyrite. The crystals are too small to be of anything other than academic interest, but clearly demonstrate the occurrence of well-crystallised authigenic quartz within the limestones of Derbyshire. These too are not considered to warrant the term ‘Buxton Diamonds’.

Two quarries in igneous rocks, near Buxton, and which are often mentioned in connection with quartz from the Peak District, are at Waterswallows and Calton Hill. The occurrences are not considered to have anything to do with ‘Buxton Diamonds’ *sensu-stricto* but a brief note on each is included below for completeness.

Waterswallows Quarry [SK 082 748]

Waterswallows Quarry lies approximately 1 km to the north east of Buxton and is well-known in geological circles as an olivine-phyric dolerite sill which has been intruded into Dinantian limestone. When the quarry was working, back in the 1970s and 1980s small vughs of colourless to amethystine quartz were encountered from time to time (Figure 10).



Figure 8. “Pagoda” quartz crystal on toadstone fragment, Miller’s Dale. Specimen width 10 mm. Richard Braithwaite specimen (RSWB 60-109) and image.

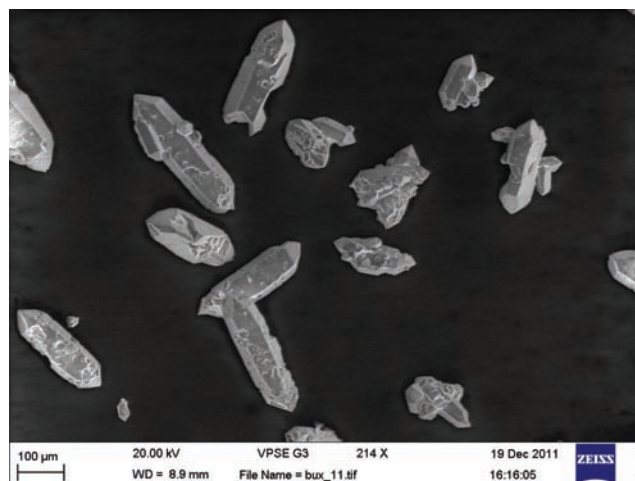


Figure 9. Scanning electron microscope image of elongate euhedral quartz crystals, 100 to 400 microns in length, obtained by dissolving limestone in hydrochloric acid. Miller’s Dale Quarry. Image J. Faithfull, University of Glasgow.



Figure 10. Amethyst. Waterswallows Quarry. 60 × 40 × 35 mm. Roy Starkey specimen (RES 0086-005) and image.

Calton Hill Quarry [SK 118 712]

The largely restored Calton Hill Quarry lies approximately 5.6 km east of Buxton. It is well-known to geologists because of the occurrence of nodules of spinel



Figure 11. Quartz. Calton Hill Quarry. 65 × 45 × 12 mm. Roy Starkey specimen (RES 2160-297) and image.



Figure 12. Quartz. Calton Hill Quarry. 95 × 65 × 50 mm. Roy Starkey specimen (RES 2160-440) and image.



Figure 13. Amethyst. Calton Hill Quarry. 75 × 70 × 50 mm. Roy Starkey specimen (RES 0086-010) and image.

herzolites and harzburgites which occur within the basalt lavas. The quarry produced specimens of well-crystallised quartz, and amethyst when it was working in the 1970s and 1980s, but as with Waterswallows Quarry and the Long Lane occurrence it is not considered that these constitute ‘Buxton Diamonds’, although the term ‘Derbyshire Diamonds’ may be considered to be appropriate by some workers (Figures 11 -15).



Figure 14. Quartz. Calton Hill Quarry. Specimen 50 × 35 × 35 mm, principal smoky quartz crystal 15 × 15 × 15 mm. Roy Starkey specimen (RES 2160-106) and image.



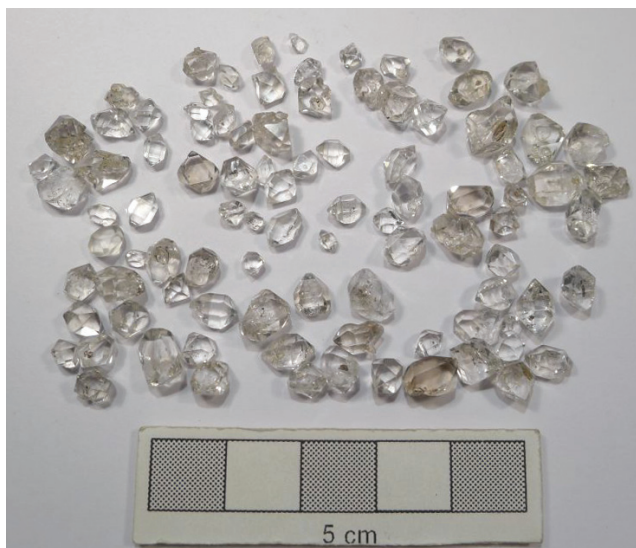
Figure 15. Quartz. Calton Hill Quarry. 25 × 23 × 20 mm. Roy Starkey specimen (RES 2160-460) and image.

SURVIVING SPECIMENS

Remarkably few examples of true ‘Buxton Diamonds’ have been found in museum or private collections.

Hunterian Museum (University of Glasgow)

The Hunterian Museum (University of Glasgow) has a jar of around 90 ‘Buxton Diamonds’, sparkling, colourless, euhedral, doubly terminated crystals of quartz mostly 3–9 mm and accessioned as GLAHM M691 (Figures 16a, b).



Figures 16a and 16b. ‘Buxton Diamonds’ – sparkling, colourless, euhedral, doubly terminated crystals of quartz mostly 3–9 mm. Found loose in soil, Buxton, Derbyshire. Presented by S. H. Needham, London, 1888. Hunterian Museum Collection specimens (GLAHM M691). Images J. Faithfull, University of Glasgow.

It is these crystals which provided the impetus for the current investigation. The crystals were acquired from Mr S.H. Needham, of London, in 1888 (Figure 17). Looking at these beautiful examples it is easy to understand why the name ‘Buxton Diamonds’ was coined, and also why so many people invested time and effort to go in search of them.

Samuel Henry Needham was elected to membership of the Geologists’ Association on 3rd October 1859, and became a Fellow of the Geological Society of London (No. 2970) at a meeting on 6 December 1876, at which time his address was stated to be “5 Mecklenburg Street, Mecklenburg Square, W.C. [London]”. He was subsequently elected to membership of the Quekett Microscopical Club on 22 February 1878, and at that time was listed as living at “33, Somerfield road, Finsbury Park, N”. At the Ordinary meeting of the Club on 22nd October 1880, he is reported as exhibiting

...a method of mounting Sections of Fossils and Minerals, Lepidoptera, &c., so as to exhibit the upper and under sides at one view. The specimens were mounted on a glass plate forming the lid of a shallow box, at the bottom of which was placed a flat mirror. The object could thus be seen both directly and reflected in the mirror, by which it was illuminated. Both the opaque and transparent portions of the specimens were thus seen remarkably well. (Anon., 1880).

Needham clearly felt that his technique was of considerable interest and he also demonstrated this at an Ordinary Meeting of the Geological Society on 20th November the same year (Anon., 1881).

Examination of the 1881 census reveals that he was born about 1825 in St Andrews parish, Holborn, Middlesex, and that, at that time he had the interesting trade of “commercial traveller (jewellery)” – which may perhaps explain his interest in ‘Buxton Diamonds’.

In 1882, at the Ninth Annual Meeting of the Postal Microscopical Society he exhibited microscope slides



Figure 17. Samuel Henry Needham. *Carte de visite* by W.S. Bradshaw, [1880s]. Reproduced by permission of the Geological Society of London.

of “...selected spicules, Polyzoa, etc., from weathered Carboniferous Limestone” (Anon., 1882). It is possible that his interest in the fossils of the Carboniferous Limestone may have led to him leaching quantities of this and in the

process of so doing, securing an unrivalled collection of quartz crystals.

A somewhat tenuous, but intriguing, possible link to the Buxton area is the briefest of mentions, in Adam (1857), which notes that “From hence we followed the narrow field-path up to Fern House (Mr. Needham’s)...”. Perhaps he lived for a time at Fern House, or maybe a relative of his was domiciled there. The *International Scientist’s Directory* (Cassino, 1885) lists “Needham, S. H., F.G.S., F.R.G.S., Mem. Quekett Mic. Club, 5 Mecklenburgh Street., Mecklenburgh Sq., London, W.”

Needham was still active in the Quekett Microscopical Society in the late 1880s. At a meeting on 10th December 1886 he exhibited the “Barbed spine of Sting Ray” (Anon., 1886); and “Nummulites from Mokattam Hills, Cairo” on 9th November 1888 (Anon., 1888). Needham’s membership of the Quekett Club appears to have lapsed after 1889, but during that year he exhibited “...a Collotype view of fossil trees, Victoria Park, Whiteinch, Glasgow” at a meeting of the Geological Society (Anon., 1889). A paper in *The Proceedings of the Zoological Society of London* (Hinton, 1905) describes a fossil deer specimen “...obtained by Mr S.H. Needham from a Pleistocene fissure-deposit in the isle of Portland, and it is now preserved in the Museum of Practical Geology.”

It has not been possible to establish conclusively what Needham’s standing was in the scientific community, but it seems probable that he was a talented and knowledgeable amateur microscopist and palaeontologist. He died on 17th April 1891 at his later residence, 3 Ella Road, Crouch Hill, Middlesex. His sole executor was Mr George Niven FGS, Director of the Commercial Bank of Australia, to whom he bequeathed his leasehold house, 20 Chiverton Street, Belgrave Road, S.W., and his collection of fossils, minerals and other specimens, microscopes, books and various other assets. The present whereabouts of his collection is unknown. Interestingly, Needham also bequeathed a sum of one hundred pounds to his “...friend Mr John Young FGS, Curator of the Hunterian Museum” which perhaps explains how the ‘Buxton Diamonds’ came to be in Glasgow. The authors would be pleased to have any additional information about Mr Needham.

Enquiries were made of several collectors, mineral dealers and academic researchers to establish whether they were aware of recent finds of ‘Buxton Diamonds’, or indeed whether they had ever seen any. Two key ‘witnesses’ here are the long-standing Derbyshire mineral dealer Don Edwards, and perhaps the leading figure of Derbyshire geology, Dr Trevor Ford. Neither had seen any crystals from Diamond Hill, although Trevor Ford recalled a single example found many years ago on Knotlow, nor to their knowledge had any examples come up for sale at local auctions over the years.

Natural History Museum, London

The specimens described by Rudler (1905) were, for many years, on display in the Ludlam Collection cases (Case VIII Div. 2) on the upper floor of the Geological Museum in South Kensington (sadly removed in the 1990s).

The accompanying display label states that the specimens were presented by C. Babington Sharpe. The crystals, 25 in number, and exhibiting a range of colours and sizes (up to about 15 × 6 mm) were formerly part of the Mineral Institute Collection and are now BM 1985,MI26284 (Figure 18). This accession is recorded in the register as having been acquired from C. Babington Sharpe around 1891, but accessioned in February 1936.

Sharpe also deposited crystals of “Quartz var. rock-crystal” from Buxton, Derbyshire, in 1885 - BM 1985,MI5467. This accession (Figure 19) numbers about 60 crystals of varying quality and clarity, ranging from small colourless crystals through to larger crudely formed and inclusion-laden examples. The largest crystal measures 17 × 8 mm.

A particularly interesting suite of crystals is BM 1913,64 (Figures 20a, b). The label states:

Quartz, found in a brown loamy soil about one foot below the surface near Buxton, Derbyshire. Presented by the Earl of Denbigh, 1913. (Pennant Collection). 12 isolated xls., pale pink doubly terminated; another similar crystal attached to lamellar Barytes (“Cawk”) with a cube of Fluor.

Sir Arthur Russell visited Buxton in June 1937, and his collection includes 28 crystals [BM 1964,R2164] from



Figure 18. ‘Buxton Diamonds’ – Presented to the Museum of Practical Geology by C.B. Sharpe. Natural History Museum specimens (BM 1985,MI26284). Roy Starkey image, reproduced with permission.



Figure 19. ‘Buxton Diamonds’ – Presented to the Museum of Practical Geology by C.B. Sharpe. Natural History Museum specimens (BM 1985,MI5467). Roy Starkey image, reproduced with permission.



Figures 20a and 20b. ‘Buxton Diamonds’ from the collection of Thomas Pennant (1726–1798), possibly the earliest collected examples identified during the project. Largest pink crystal 19×9 mm. The specimen of quartz on baryte measures $15 \times 13 \times 12$ mm, the quartz crystal is 12 mm long. Natural History Museum specimens (BM 1913,64). Roy Starkey images, reproduced with permission.

“Countess (Counter’s) Cliff and Turn Cliff Farm, Buxton, Derbyshire” (Figure 21). His hand written label indicates that some of these were collected by him personally, and others are recorded as coming from the Tennant-Jones-Paton Collection (No. 57). The label states:

Small loose colourless and reddish doubly terminated prismatic crystals found just below the turf in soil resting upon carboniferous limestone.

The crystals include one colourless, 7 milky to poor, 2 interpenetrant, 1 parti-coloured colourless and pale pink, with the remainder showing the typical pale pinkish to faintly smoky colouration.

The Natural History Museum collections also include BM 58330, a single crystal 17×8 mm in a glass phial, and 10 loose crystals, the largest of which is 15×7 mm. All of these exhibit the characteristic pink colouration. The Allan-Greg collection, acquired by purchase in 1860, contains two pinkish crystals 12×6 mm and 9×5 mm, accessioned as BM 92279 (AG64). In both cases the locality is recorded only as “Buxton, Derbyshire”.



Figure 21. ‘Buxton Diamonds’. Largest pink crystal 17×9 mm. Sir Arthur Russell Collection, Natural History Museum specimens (BM 1964,R2164). Roy Starkey image, reproduced with permission.

A number of ‘Buxton Diamonds’ in the Geological Museum exchange collection were acquired by Brian Young, *via* exchange in 1983. The crystals are recorded as being from “Buxton, Derbyshire”, and came originally from the Doneraile Collection. Brian Young Collection No. 2554 (Figure 22).

Two remarkable matrix specimens came to light in the latter stages of the investigation. Both show densely packed, pale pinkish “quartz crystals var. ‘Eisenkiesel’ in a matrix of fine-grained to crystallised cream coloured baryte”.

The first of these, BM 58412 (Figure 23, see p. 38), has no recorded history according to the register entry, and is listed only as from “Buxton, Derbyshire”. The reverse of the specimen shows an encrustation of yellowish, micro-crystallised baryte, typical of Derbyshire mineral deposits.



Figure 22. ‘Buxton Diamonds’ – Originally from the Doneraile Collection (Geological Museum, London). Brian Young specimens (2554). Roy Starkey image, reproduced with permission.



Figure 23. Quartz var. “Eisenkiesel” in a matrix of fine-grained to crystallised cream coloured baryte. Buxton, Derbyshire. 90 × 70 × 23 mm. Natural History Museum specimen (BM 58412). Roy Starkey image, reproduced with permission.



Figure 24. Quartz var. “Eisenkiesel” in a matrix of fine-grained to crystallised cream coloured baryte. Typical “cockscomb” baryte crystals occupy cavities in the matrix towards the top of the specimen. Purchased from Henry Heuland. Buxton, Derbyshire. 90 × 75 × 40 mm. Natural History Museum specimen (BM 92114). Roy Starkey image, reproduced with permission.

The second, somewhat larger, specimen of what looks like identical material, BM 92114 (Figure 24), was purchased from the legendary mineral dealer Henry Heuland (1778-1856).

Both of these specimens show extremely sharp casts of crystal faces where crystals have become detached. The quartz crystals are distinctly euhedral and show no sign of edge damage or transportation. It is difficult to conceive how such an assemblage could form, other than for previously crystallised euhedral crystals of quartz to have been washed into a void of some sort, and for the interstices to be subsequently infilled by the precipitation of baryte; or for the limestone matrix surrounding authigenic crystals of quartz to have been entirely replaced by metasomatic baryte.

No material resembling these specimens has been encountered in other collections, nor during fieldwork. The authors would be interested to learn of any similar occurrence known to readers.

National Museum Wales, Cardiff

The R.J. King Collection (now in National Museum Wales, Cardiff) contains nine ‘Buxton Diamonds’ accessioned as K899/1947. The accompanying label in Bob King’s handwriting states “Quartz, Diamond Hill, Harpur Hill, Buxton, Derbys.” (Figure 25) Bob’s hand-written field notes record the date of him collecting these as being 29 September 1947, when he journeyed from Leicester to

Buxton, *via* Derby, by train and walked to Diamond Hill. After seeking permission at Countess Cliff Farm, Bob was accompanied by an old shepherd who volunteered to show him where to dig. He wrote:

Business in hand was to cut through turf (six inches thick), layer of soil, (4 inches thick) to a dark yellow gritty clay. Diamonds occurred in transition zone between soil and clay, but best diamonds in clay, others in soil badly corroded. Very hard to find, but found 12, two very good ones ½” long. (Sally King, *personal communication*, 2015).



Figure 25. Quartz var. ‘Buxton Diamonds’, from Diamond Hill, Buxton, in the R. J. King Collection (K899/1947; now in National Museum Wales, Cardiff), collected by Bob King on 29 September 1947. Photo courtesy of Tom Cotterell, National Museum Wales, reproduced with permission.

Manchester Museum

Manchester Museum holds two collections of crystals. The first, N18500 consists of five colourless and transparent crystals about 7.5 mm long (Figure 26); and the second, N17700 which consists of twelve similar, colourless, doubly-terminated crystals with an accompanying label “Prisms of Silica from C. Limestone, Buxton. 1873. Plant.”, which was formerly in the Salford Museum Collection (Figure 27).

Buxton Museum

The collections at Buxton Museum and Art Gallery might reasonably be expected to contain representative local material, and there are examples of both quartz, labelled as from Diamond Hill, and the tiny fluorite cubes mentioned by White Watson. Accession Number 2007 M29 consists of three distinctly smoky, loose crystals (20 × 18 × 12 mm; 25 × 14 × 10 mm and 13 × 5 × 6 mm), mounted in a specially prepared wooden block (Figure 28). Two of the crystals are not a good match for other material from Diamond Hill and are reminiscent of specimens from Calton Hill Quarry (see for example Figure 14). The third crystal is a more typical ‘Buxton Diamond’ but rather smoky and dark compared to other examples seen. These specimens are of particular interest because they were formerly on display in The Douglas Museum (Randolph Douglas’s “House of Wonders”) in Castleton, Derbyshire (Figure 29, see p 40), which would suggest that they were considered at least ‘noteworthy’, if not fine, examples of ‘Buxton Diamonds’.



Figure 26. Buxton Diamonds – Five colourless and transparent crystals about 7.5 mm long. Manchester Museum specimens (N18500). Image courtesy of David Gelsthorpe, reproduced with permission.



Figure 27. Buxton Diamonds – Twelve colourless, doubly-terminated crystals with an accompanying label “Prisms of Silica from C. Limestone, Buxton. 1873. Plant.”, which was formerly in the Salford Museum Collection. Manchester Museum specimens (N17700). Image courtesy of David Gelsthorpe, reproduced with permission.



Figure 28. Three distinctly smoky crystals of quartz in a custom wooden mount. Buxton Museum and Art Gallery Collection (2007 M29). The specimen at the front right may be from Diamond Hill, but the others are somewhat similar to material from Calton Hill Quarry. Roy Starkey image, courtesy of Buxton Museum and Art Gallery, reproduced with permission.

Douglas (1895–1956) was a caver, collector of minerals, curator, escapologist, locksmith and miniaturist. He was a confidant to, and correspondent with, the great Harry Houdini (Dawes, 2005; Beedham, 2009). The ‘House of Wonders’ collection was purchased by Buxton Museum in 1984.

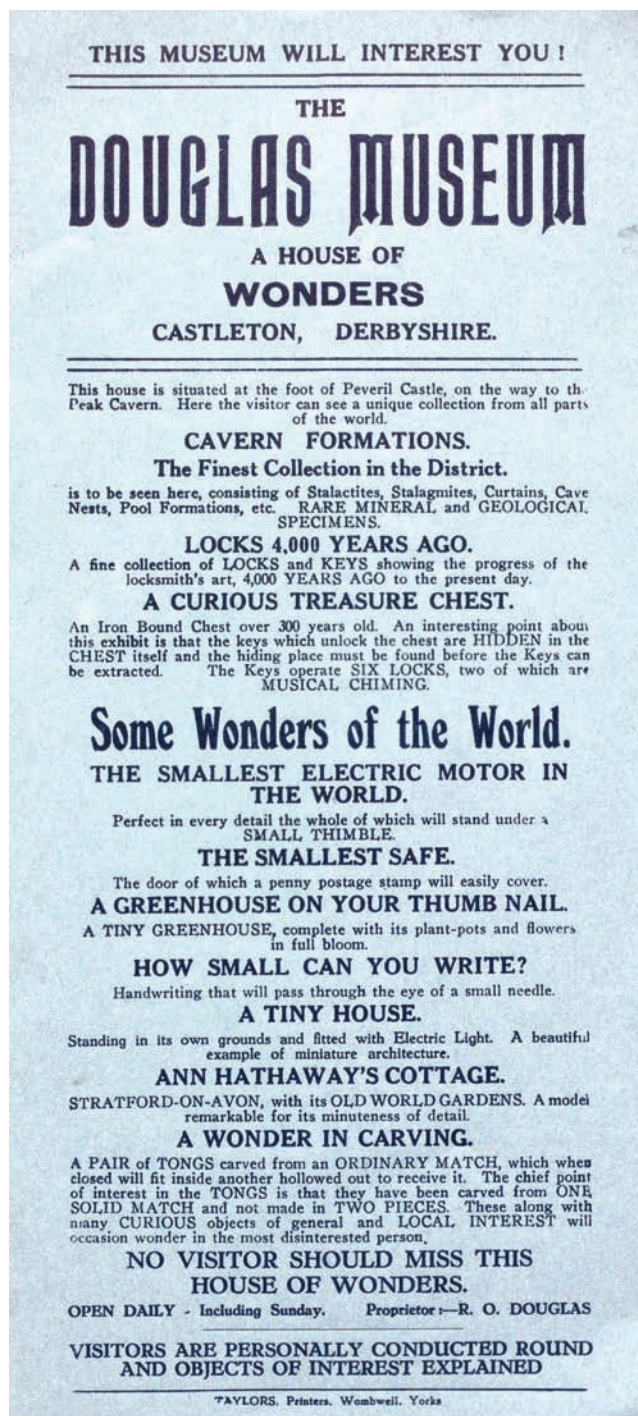


Figure 29. Advertisement for Randolph Douglas's "House of Wonders" in Castleton, Derbyshire. Reproduced by permission of Derbyshire County Council: Buxton Museum.

A round cardboard box with a glass lid contains 24 composite cubes of fluorite. The crystals are of broadly uniform size, about 2 mm on edge and pale yellow in colour (Figure 30). They are a good match for the specimens in the White Watson mineral cabinet owned by Peter Robinson (Figure 31).

Lapworth Museum (University of Birmingham)

Material in the Lapworth Museum (University of Birmingham) on long term loan from Birmingham Museums and Art Gallery, includes two groups of quartz



Figure 30. A round cardboard box with glass lid containing 24 composite cubes of fluorite, but labelled "barytes". The crystals are of broadly uniform size, about 2 mm on edge, and pale yellow in colour. They are a good match for specimens in a White Watson mineral cabinet owned by Peter Robinson. Buxton Museum and Art Gallery Collection (3582). Roy Starkey image, courtesy of Buxton Museum and Art Gallery, reproduced with permission.



Figure 31. Four crystals of quartz listed as No. "114 Quartz crystals, Buxton Diamonds" in a White Watson mineral cabinet dating from 1799. The crystal to the lower right is a typical, faintly pink 'Buxton Diamond' but the other three are of rather doubtful origin. Just visible to the right, are two small cubes of fluorite (2 × 2 × 2 mm and 5 × 5 × 5 mm), listed as No. "115. Fluorspar in detached cubes". Roy Starkey image, courtesy of Peter Robinson, reproduced with permission.

crystals which may be from the Buxton area. The first is from the Scholes Collection and is accompanied by a typed label "253. QUARTZ (double-pointed crystals) Scholes Collection, Buxton". These are very dark reddish brown, heavily included with hematite, and measure 13 × 7 mm and 13 × 5 mm respectively, which is comfortably within the typical size range of 'Buxton Diamonds' (Figure 32). The second suite of eight crystals is from the Wainwright Collection and is labelled "ROCK CRYSTAL double-ended LOCALITY UNKNOWN". These latter crystals range from colourless through to the typical pinkish red, and vary from about 10 × 4 mm to 15 × 8 mm, which again is in good agreement with the size distribution of 'Buxton Diamonds'. It seems very likely that these crystals originated from Diamond Hill, Buxton (Figure 33).

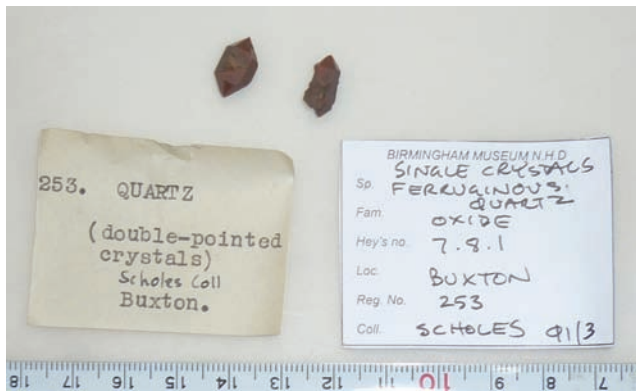


Figure 32. ‘Buxton Diamonds’ – Two very dark, reddish-brown crystals, 13 × 7 mm and 13 × 5 mm, heavily included with hematite, accompanied by a typed label “253. QUARTZ (double-pointed crystals) Scholes Collection, Buxton”. Birmingham Museum and Art Gallery specimens. Roy Starkey image, courtesy of the Lapworth Museum of Geology, University of Birmingham, reproduced with permission.



Figure 33. ‘Buxton Diamonds’ – Eight crystals from the Wainwright Collection, labelled “ROCK-CRYSTAL double-ended LOCALITY UNKNOWN”. The crystals range from colourless through to the typical pinkish red, and vary from about 10 × 4 mm to 15 × 8 mm. The physical characteristics suggest that these specimens probably originated from Diamond Hill, Buxton. Birmingham Museum and Art Gallery specimens. Roy Starkey image, courtesy of the Lapworth Museum of Geology, University of Birmingham, reproduced with permission.

White Watson specimens

A public appeal for information about ‘Buxton Diamonds’, published in the *Peak Advertiser*, a free newspaper distributed across the Peak District, with a fortnightly circulation of 30,000 copies (Starkey, 2011), elicited only one response, some three months later, from Peter Robinson, the owner of a White Watson cabinet. The cabinet includes four specimens (Figure 31) listed in the manuscript catalogue accompanying the cabinet (dated 1799) as “114. Quartz crystals, Buxton Diamonds” (Figure 34). One of these is a doubly terminated prismatic crystal with a slight reddish hue, typical of ‘Buxton Diamonds’.

Via Peter Robinson, we were able to contact another White Watson cabinet owner, Peter Maunder. His cabinet, dating from 1802, also contains four small pieces of quartz catalogue number “150. Quartz crystals, Buxton Diamonds”

(Figure 35), one of which is a typical, slightly smoky, ‘Buxton Diamond’ (Figure 36).

The quality, and number of the crystals which White Watson saw fit to include in his “Collection of Fossils the Production of Derbyshire” is interesting, and suggests that the better material was either scarce at the turn of the 18th century, or sufficiently valuable, not to be included in his “standard” assembled collections.

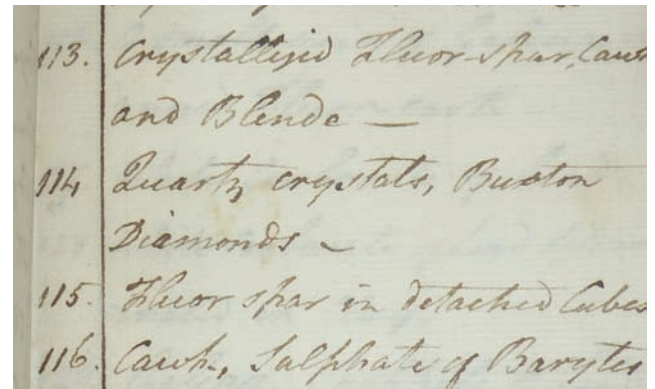


Figure 34. Extract from the manuscript catalogue accompanying a White Watson mineral cabinet. Roy Starkey image, courtesy of Peter Robinson, reproduced with permission.

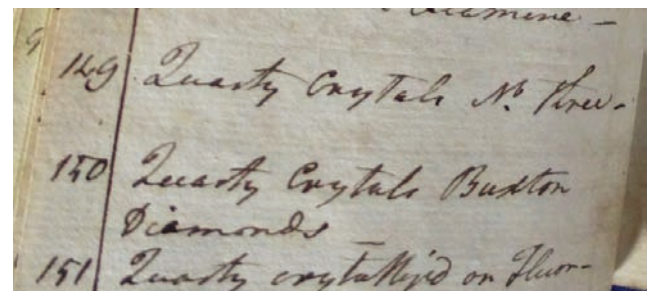


Figure 35. Extract from the manuscript catalogue accompanying a White Watson mineral cabinet. Image courtesy of Peter Maunder, reproduced with permission.



Figure 36. Four crystals of quartz listed as No. “150. Quartz crystals Buxton” in a White Watson mineral cabinet dating from 1802. The crystal at the centre of the picture is a typical, faintly smoky ‘Buxton Diamond’ but the other three are of rather doubtful origin. Image courtesy of Peter Maunder, reproduced with permission.

A third White Watson cabinet is held in the Booth Museum of Natural History, Brighton, but it is unfortunately incomplete and the remaining specimens do not include any 'Buxton Diamonds' (J. Cooper, *personal communication*).

Devonshire Mineral Collection, Chatsworth House, Derbyshire

The famous Devonshire mineral collection at Chatsworth House has been described by Cooper (2005) and Thomas and Cooper (2008). The historical associations with White Watson suggested that the collection might contain examples of 'Buxton Diamonds'. Examination of White Watson's catalogue (A) (Watson, 1804), reveals that the entry for specimen 376 is:

Quartz crystals in hexagonal prisms, with a double hexagonal pyramid – from Buxton – where they are called Diamonds.

Unfortunately the specimens do not appear to have survived (Franz Werner, *personal communication* 2015).

CONCLUSIONS

The well-documented historical occurrence of doubly terminated crystals of quartz in the Buxton area, 'Buxton Diamonds', has been investigated through a comprehensive literature review and by conducting a survey of museum collections, private individuals and mineral dealers. Recent fieldwork has confirmed both the occurrence of crystals of quartz in Derbyshire limestones, and the presence of euhedral crystals of quartz in the soil and in limestone at Diamond Hill, although these are neither common nor easy to find.

References to the quartz and amethyst found in certain of the Derbyshire igneous rocks are considered not to be true 'Buxton Diamonds' although the more general term 'Derbyshire Diamonds' may be applicable in some instances.

Authentic 'Buxton Diamonds' are of simple habit – a hexagonal prism terminated at each end by a hexagonal pyramid ranging in size from a few millimetres up to about 17 mm (the largest examples seen during the study), and varying considerably in colour and clarity. Some crystals are opaque and inclusion laden, others more typical milky quartz. The best examples are brilliantly clear and beautifully faceted, and a second variant shows a remarkably consistent pale red–pink colouration due to inclusions of an iron oxide, presumed to be hematite. It seems probable that some of the crystals are derived from the limestone, but that the ones of reddish hue may originate from later hydrothermal baryte infills as seen in two specimens at the Natural History Museum, London (Figures 23 and 24). The precise locality from which this material was collected remains a mystery.

Leaching of limestone from Diamond Hill produced a range of quartz fragments and crystals typical of the material in historical collections, but nothing to equal those in the Hunterian Museum collection acquired from S.H. Needham.

No examples of 'fancy goods' or jewellery containing 'Buxton Diamonds' have been located during the study and the authors would be pleased to hear from any reader who may have something to add to the story.

Finally, a public appeal for information regarding examples of 'Buxton Diamonds' or knowledge thereof, produced only a single response, which seems remarkable given the apparent abundance of them in past centuries, and hence the likely existence of examples amongst 'family treasures' and in attics and trinket boxes in the area.

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REFERENCES

- Adam, W. (1847). *Description of Buxton, Chatsworth and Castleton, abridged from Adam's Gem of the Peak*. Derby: Henry Mozley and Sons, and W. & W. Pike; W. Adam, Old Museum, & J.W. Adam, Library, Matlock Bath; W. Moore, Library, & J. Sutton, Herald Office, Buxton; and J. Goodwin, Bakewell.
- Adam, W. (1857). *The Gem of the Peak; or, Matlock Bath and its vicinity. An account of Derby; a tour from Derby to Matlock; excursions to Chatsworth, Haddon, Monsal Dale, Dovedale, Ilam, Alton Towers, Hardwick, Wingfield, Newstead Abbey, Ashbourne, Buxton and Castleton, Historical and Geological; Brief history of the fluor spar, from the earliest period down to the present time. A review of the geology of Derbyshire; catalogue of minerals and rocks, and of the flora of the High and Low Peak*. J. & C. Mozley, Derby. 6th Edition.
- Adam, W. (1861). *Dales, scenery, fishing streams, and mines of Derbyshire and surrounding counties, historical and geological*. W. Kent and Co., London.
- Aitkenhead, N., Chisholm, J.I. and Stevenson, I.P. (1985). *Geology of the country around Buxton, Leek and Bakewell*. Memoir of the British Geological Survey, Sheet 111. HMSO, London.
- Albright, J.L., and Lueth, V.W. (2003). *Pecos Diamonds - Quartz and Dolomite Crystals from the Seven Rivers*

- Formation Outcrops of Southeastern New Mexico. *New Mexico Geology*, **25**, 63–74.
- Anon. (1880). Report of Ordinary Meeting. *Journal of the Quekett Microscopical Club*, **6**, 222–223.
- Anon. (1881). Exhibits, in Proceedings of the Geological Society, *Quarterly Journal of the Geological Society*, **37**, 2.
- Anon. (1882). Annual Meeting 1882. *Journal of the Postal Microscopical Society: a miscellany of Natural and Microscopical Science*. Edited by Alfred Allen. **1**, 194 and 204.
- Anon. (1886). Report of Ordinary Meeting, 10th December 1886 – exhibit of the “Barbed spine of Sting Ray”. *Journal of the Quekett Microscopical Club*, Series II, Vol. III, no. 17, 30.
- Anon. (1888). Report of Ordinary Meeting, 9th November 1888 – exhibit of “Nummulites from Mokattam Hills, Cairo”. *Journal of the Quekett Microscopical Club*, Series II, Vol. III, no. 24, 350.
- Anon. (1889). Exhibits, in *Quarterly Journal of the Geological Society*. **45**, 86.
- Bagshaw, S. (1846). *History, gazetteer and directory of Derbyshire, with the town of Burton-upon-Trent; comprising a General Survey of the County etc.* Sheffield.
- Bates, J.C. and Bates, H.B. (1860). The Buxton Diamond. The Terrace, Gardens, Serpentine, and Corbar Wood Walks. Bates and Bates, Buxton.
- Beedham, A. (2009). Randini: The Man Who Helped Houdini. Youbooks, Sheffield.
- Bemrose, A. (1898). On a quartz rock in the Carboniferous Limestone of Derbyshire. *Quarterly Journal of the Geological Society*, **54**, 169–183.
- Borlase, W. (1749). An Enquiry into the Original State and Properties of Spar, and Sparry Productions, Particularly, the Spars, or Crystals Found in the Cornish Mines, Called Cornish Diamonds. In a Letter to Emanuel Mendez da Costa, Esq; F. R. S. from the Rev. Mr. Wm. Borlase. *Philosophical Transactions of the Royal Society, London*, **46**, 250–277.
- Bradshaw, R. (1968). Bristol Diamonds. *Proceedings of the Bristol Naturalists' Society*, **31**, (4), 439–450.
- Braithwaite, R.S.W. (1983). Minerals of the Derbyshire Orefield. *Mineralogical Record*, **14**, 15–24.
- Bray, W. (1783). *Sketch of a tour into Derbyshire and Yorkshire, including parts of Buckingham, Warwick, Leicester, Nottingham, Northampton, Bedford and Hertford-shires*. B. White, London.
- Britton, J. and Brayley, E.W. (1802). *The Beauties of England and Wales or Delineations, topographical, historical and descriptive, of each county*. Vol. III. Vernor & Hood, Longman & Rees, Cuthell & Martin, J. & A. Arch, W.J. & J. Richardson, and B. Crosby. London.
- Bulmer, T. & Co. (1895). *History, topography, and directory of Derbyshire: Comprising Its History and Archaeology : a General View of Its Physical and Geological Features, with Separate Historical and Topographical Descriptions of Each Town, Parish, Manor, and Extra-parochial Liberty*.
- Camden, W. (1586). *Britannia or a Chorographical Description of Great Britain and Ireland, together with the Adjacent Islands*. Written in Latin by William Camden and translated into English, with Additions and Improvements .Revised, Digested, and Published, with Large Additions, by Edmund Gibson.
- Cassino, S.E. (1885). *The International Scientist's Directory*. S.E. Cassino and Company, Boston, U.S.A.
- Chafetz, H.S. and Zhang, J. (1998). Authigenic megaquartz crystals in a quaternary dolomite. *Journal of Sedimentary Research*. **68**, 994–1000.
- Cooper, M.P. (2005). The Devonshire mineral collection of Chatsworth House, Derbyshire: an 18th Century survivor and its restoration. *Mineralogical Record*, **36**, 239–272.
- Cooper, M.P. (2006). *Robbing the Sparry Garniture – A 200 Year History of British Mineral Dealers 1750–1950*. Mineralogical Record, Tucson.
- Croston, J. (1868). *On Foot Through The Peak; or a Summer Saunter Among the Hills and Dales of Derbyshire*. J. Heywood, Manchester and Simpkin, Marshall & Co., London.
- Dawes, E.A. (2005). A Rich Cabinet of Magical Curiosities 280: Castleton's House of Wonders: Randolph O. Douglas, His Museum and His Houdini Collection. *Magic Circular*, **96**, Issue 1027, February 2002. See <http://conjuringarts.org/2010/10/bbc-features-randini/>.
- Farey, J. (1811). *A General View of the Agriculture and Minerals of Derbyshire; with observations on the means of their improvement*, Vol.1, (3 volumes). London. 532.
- Ford, T.D. (1967). A quartz-rock filled sink hole on the Carboniferous Limestone near Castleton, Derbyshire. *The Mercian Geologist*. **2**, 57–62.
- Ford, T.D. (1969). The Blue John fluorspar deposits of Treak Cliff, Derbyshire, in relation to the boulder bed. *Proceedings of the Yorkshire Geological Society*, **37**, Part 2, No. 7, 153–157.
- Ford, T.D., Sarjeant, W.A.S. and Smith, M.E. (1993). The Minerals of the Peak District of Derbyshire. *UK Journal of Mines and Minerals*, **13**, 16–55.
- Fox, F.C. and Bridge, D.McC. (1977). *The limestone and dolomite resources of the country around Monyash, Derbyshire*. Institute of Geological Sciences Mineral Assessment Report 26. HMSO, London.
- Glover, S. (1831). *The history and gazetteer of the county of Derby: drawn up from actual observation, and from the best authorities; containing a variety of geological, mineralogical, commercial and statistical information*. Vol.1. Ed. Thomas Noble. Longman & Co., London.
- Glover, S. (1845). *The Peak Guide containing the topographical, statistical and general history of Buxton, Chatsworth, Edensor, Castleton, Bakewell, Haddon, Matlock and Cromford*. Ed. Thomas Noble. Henry Mozley & Sons, Derby.
- Greg, R.P. and Lettsom, W.G. (1858). *Manual of the Mineralogy of Great Britain and Ireland*. John van Voorst, London.
- Heywood, J. (1869). *Pocket Guide to Buxton - A Guide to Buxton and its Environs. With an appendix and table of distances*. John Haywood, Manchester.

- Hinton, M.A.C. (1905). On Some Abnormal Remains of the Red Deer (*Cervus elaphus*) from the Post-Pliocene Deposits of the South of England. *Proceedings of the Zoological Society of London*, **1**, 210–212.
- Hollis, C. and Walkden, G. (1996). The use of burial diagenetic calcite cements to determine the controls upon hydrocarbon emplacement and mineralization on a carbonate platform, Derbyshire, England. In Strogon, P., Somerville, I. D. & Jones, G. L. (eds), 1996, *Recent Advances in Lower Carboniferous Geology*, Geological Society Special Publication No. 107, 35–49.
- Holroyd, W.F. and Barnes, J. (1901). On the Super-position of Quartz Crystals on Calcite in the Igneous Rocks occurring in the Carboniferous Limestone of Derbyshire. *Transactions of the Manchester Geological Society*, **26**, 46–49.
- Hyde, S. (1893). *Buxton: its baths and climate comprising a full account of the celebrated waters and climate of Buxton together with special chapters on baths, bathing and massage also excursions around Buxton and the Peak*. J. Heywood, Manchester, London and Bristol.
- Jenyns, Rev. L. (1830). *Tour into Derbyshire*. Manuscript notebook. Private Collection.
- Jewitt, A. (1811). *The History of Buxton: and Visitor's Guide to the Curiosities of the Peak: Including a Descriptive Itinerary of the Excursions Usually Made: and a Set of Botanical Tables, Exhibiting the Places of Growth, &c. of the Most Remarkable Plants Found Wild in the Neighbourhood of Buxton*.
- Kanaris-Sotiriou, R., Neves, R. and Gibb, F.G.F. (1986). Wall rock silicification associated with fluorite veins in Carboniferous limestone at Butts Quarry, Derbyshire, England. *Geological Magazine*, **123**, 569–579.
- Lewis, S. (1831). *A Topographical Dictionary of England*, Vol. 1 of 4 vols. London.
- Mawe, J. (1802). *The Mineralogy of Derbyshire: with a description of the most interesting mines in the North of England; in Scotland and in Wales; and an analysis of Mr. William's Work, intitled "The Mineral Kingdom"*. William Phillips, London.
- Moser, M.R., Rankin, A.H., Milledge, H.J. (1992). Hydrocarbon-bearing fluid inclusions in fluorite associated with the Windy Knoll bitumen deposit, UK. *Geochimica et Cosmochimica Acta*, **56**, 155–168.
- Orme, D. (1837). *New Buxton Guide, containing a concise account of the properties of its medical springs, so celebrated for Gout, Rheumatism and Bilious Complaints, and of the Recent, Elegant, and Convenient, Hot Baths; with a selection of Important and Valuable Medical Opinions on their Use; accompanied with descriptions of remarkable Curiosities of Nature and Art; in the vicinity of that elegant and fashionable resort; with a view of the Crescent and Castleton*. Buxton.
- Orme, G.R. (1974). Silica in the Visean limestones of Derbyshire, England. *Proceedings of the Yorkshire Geological Society*, **40**, 63–104.
- Pigott, C.D. (1962). Soil formation and development on the carboniferous limestone of Derbyshire. *Journal of Ecology*, **50**, 145–146.
- Pigott, C.D. (1965). The Structure of Limestone Surfaces in Derbyshire. *The Geographical Journal*, **131**, 41–44.
- Pilkington, J. (1789). *A View of the present state of Derbyshire; with an account of its most remarkable antiquities, illustrated by an accurate map and plates*. In Two Volumes. Vol.1 Derby.
- Rhodes, E. (1824). *Peak Scenery; or, The Derbyshire tourist*. Longman, Hurst, Rees, Orme, Brown and Green, London.
- Rudler, F.W. (1905). *A Handbook to a Collection of the Minerals of the British Islands, Mostly Selected from the Ludlam Collection, in the Museum of Practical Geology, Jermyn Street, London*. Printed for His Majesty's Stationery Office, by Wyman and Sons, Ltd, London.
- Short, T. (1734). *The Natural, Experimental, and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire and Yorkshire, particularly those of Scarborough*. F. Gyles, London.
- Sowerby, J. (1804). *British Mineralogy: Or Coloured Figures Intended to Elucidate the Mineralogy of Great Britain*, Vol. **I**, London.
- Starkey, R.E. (2011). Buxton Diamonds – can you help? *Peak Advertiser*, **30**, No. 24, 28th November, 50.
- Strickland, A. (1823). *The Buxton Diamonds or, Grateful Ellen*. William Darton, London.
- Strickland, A. (1840–1848). *Lives of the queens of England, from the Norman conquest; with anecdotes of their courts, now first published from official records and other authentic documents, private as well as public*. 12 volumes, H. Colburn, London.
- Strickland, A. (1842–1843). *Letters of Mary, Queen of Scots, and documents connected with her personal history*. H. Colburn, London.
- Strickland, A. (1851–1859). *Lives of the Queens of Scotland and English Princesses Connected with the Regal Succession of Great Britain*. 8 volumes. W. Blackwood and Sons, Edinburgh.
- Strickland, J.M. (1887). *Life of Agnes Strickland*. William Blackwood and Sons, Edinburgh.
- Thomas, I. and Cooper, M. (2008). The geology of Chatsworth House, Derbyshire. *Mercian Geologist*, **17**, 27–42.
- Tindle, A.G. (2008). *Minerals of Britain and Ireland*. Terra Publishing, Harpenden.
- Traill, G.W. (1870). *An Elementary Treatise on Quartz and Opal*. 2nd edition. Maclachlan and Stewart, Edinburgh; Simpkin, Marshall and Co., London.
- Tymms, S. (1835) *The Family Topographer being a compendious account of the antient and present state of the counties of England. Vol. V, Midland Circuit: Derbyshire, Leicestershire, Lincolnshire, Northamptonshire, Nottinghamshire, Rutlandshire, Warwickshire*. J.B. Nichols and Son, London.
- Ulrich, W. (1989). The Quartz Crystals of Herkimer County and its Environs. *Rocks and Minerals*, **64**, 108–122.
- Vanstone, S.D. (1998). Late Dinantian palaeokarst of England and Wales: implications for exposure surface development. *Sedimentology*, **45**, 19–37.
- Ward, R. (1826). *The Buxton, Matlock & Castleton guide, containing concise accounts of these and other*

- remarkable places and objects, chiefly in the northern parts of the interesting county of Derby. 6th edition. Birmingham.
- Ward, R. (1827). *A Guide to the Peak of Derbyshire, containing a concise account of Buxton, Matlock, and Castleton, and other remarkable places and objects, chiefly in the Northerly Parts of that very interesting County*. Birmingham. 7th edition.
- Waters, C.N., Waters, R.A., Barclay, W.J. & Davies, J.R. (2009). *A lithostratigraphical framework for the Carboniferous successions of southern Great Britain (onshore)*. British Geological Survey Research Report RR/09/01.
- Watson, W. (1804). *Catalogue of a Collection of Fossils, the Productions of Derbyshire, in Her Grace the Duchess of Devonshire's Cabinet at Chatsworth: Arranged According to the Order of the Respective Strata in which they are found; Accompanied with a Tablet Representing a Section of the strata in Derbyshire, with a Printed Explanation*.
- Watson, W. (1811). *A delineation of the strata of Derbyshire, forming the surface from Bolsover in the east to Buxton in the west, by a plate designed from a tablet composed of each stratum within the above line. With an explanatory account of the same, together with a description of the fossils found in these strata: and also of the nature and quality of the respective soils*. W. Todd, Sheffield.
- White, F. (1857). *History, Gazetteer and Directory of the County of Derby etc.*, in one volume, with a coloured sheet map of the County. F. White & Co., Sheffield.
- Wolverson Cope, E. (1976). *Geology Explained in the Peak District*. David & Charles, Newton Abbot.
- Woore, E. F. (1978). Quartz crystals in Derbyshire. *Gems*, **10**, No.1, Jan–Feb, 13.

AMETHYST FROM SCREEL HILL, CASTLE DOUGLAS, DUMFRIES AND GALLOWAY, SCOTLAND.

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Allanton, Castle Douglas, Dumfries & Galloway DG7 3EN

Amethyst has long been known from many locations in Scotland (e.g. Heddle, 1901) but few have been as prolific as a recently exposed occurrence on Scree Hill, approximately 7 km south of Castle Douglas, in Dumfries and Galloway, SW Scotland. Curiously, Heddle does not list Scree in his localities for amethyst, despite it being reported as early as 1844 that “rock-crystals of a pale purple colour and of the most perfect prismatic forms, abound in a small stream upon the hill of Scree, within the estate of Colonel Maxwell of Orchardton” (Thomson, 1844).

Scree Hill is on the western edge of the Criffel-Dalbeattie granodiorite complex which is known to host veins of coloured quartz (amethyst and smoky) in several locations. Todd and McMullen (1996) describe an occurrence of smoky quartz in Auchenlosh Quarry, Dalbeattie, (now landfilled) where it accompanies amethyst, and colourless and milky quartz crystals in a vein in granodiorite. Drusy amethyst is also known from Boreland of Southwick nearby. McCracken (1962–3) describes this as a “pocket” exposed in a stream, but the authors’ own unpublished observations are that it is a vein or breccia in granodiorite. McCracken also mentions smoky quartz in a fault in the Kinharvie Burn, a locality described in greater detail by McMullen and Todd (1990)

who also report amethyst there. Williams (1962–3) briefly mentions the Boreland of Southwick and Kinharvie Burn occurrences, adds Buittle to the list where amethyst occurs “in veins in a porphyrite”, and reports amethyst in drift at Glen Burn, New Abbey.

Scree Hill is steep-sided on its NE flank, partly covered in forestry plantation and drained on its SW side by the Glen of Scree Burn. Public access is provided by forestry tracks, and a car park at O.S. grid reference NX 7997 5471. Geologically the hill is composed of hornfelsed Silurian greywacke in the aureole of the Criffel-Dalbeattie granodiorite complex (Leake *et al.*, 1978).

In addition to Thomson (1844), previous reports of minerals on Scree Hill are of molybdenite and ferrimolybdenite by Williams (1973), molybdenite and amethyst by Lawson (1977), and disseminated copper mineralisation by Leake *et al.* (1978). The authors of this note have found molybdenite as fine-grained masses with pyrite in thin quartz veins in a trackside exposure low down the hill, and next to the Glen of Scree Burn at NX 7971 5457, very close to Williams’ grid reference [NX 797 546], although Williams found it as plates “up to ½ inch across”.

Thomson's amethyst location is imprecisely recorded but was almost certainly in the Glen of Scree Burn – the only significant stream on the hill. Amethyst was found in the 1970s in the bed of the burn a few hundred metres downstream of the new discovery, and the crystals there were larger, but paler (J. Lawson, *unpublished observation*). This location is now buried under sediment and vegetation, and no trace could be found when it was searched for in the course of this investigation.

The new discovery was made in about January 2009 by Sarah McKie, daughter of one of the authors (JL), while walking her dog. She observed fragments of crystalline quartz and amethyst beside a recently made forest track roughly 400 m SW of the summit of the hill. Her father and brother (RL) investigated, and narrowed the source down to grid reference NX 7822 5503.

Near this point the forest track crosses the burn and bends to the left (when ascending) before terminating in a turning point (Figures 1 and 2). A short spur of track, on the SW side of the burn, had impinged on a mineralised structure and scattered fragments of it along the edge of the track. Further visits, in company with other collectors (Stephen Moreton and Michael McMullen), found that the occurrence was

buried under more than a metre of overburden and would require excavation if it was to be studied properly.

After permission was secured from the Forestry Commission, some digging along the side of the end of the spur of track, where the concentration of amethyst fragments was greatest, revealed the source to be a brecciated zone, probably trending NW–SE in hornfels, running parallel to, and a few metres SW of, the Glen of Scree Burn

A few tens of metres uphill from this point, NW–SE trending quartz strings are exposed along strike of the amethyst, but are not amethystine. Further upstream still, in a gorge, further traces of amethyst, associated with quartz veining and breccia, have been reported (Davidson, 2015). The 1970s occurrence was also along strike, but much further downhill. This may imply that there exists a much larger NW–SE trending zone, mineralised intermittently along its length, beneath the overburden on this side of the hill, with the burn roughly following its course.

At the excavation site, crystallised quartz was abundant as drusy plates up to *circa* 20 cm across. These were nearly all loose and detached from the country rock, which itself was extensively fractured, making extraction of specimens relatively easy. A striking feature of the specimens was the presence, on their reverse side, of epimorphs up to *circa* 1 cm across, after a rhombohedral mineral (Figure 3). This had clearly been the first phase of the mineralisation, and its subsequent dissolution has resulted in the drusy quartz becoming separated from the host rock, making collecting it relatively easy.

A single specimen was found in which the epimorphs still contained a corroded relict of the mineral responsible. XRD and quantitative XRF analysis identified it as dolomite (2.3 % FeO, 0.7 % MnO, accurate to +/- 0.1 %), not siderite as suggested by Davidson (2015). The drusy quartz/amethyst itself comprises pyramidal crystals usually around 3–8 mm across, but a few exceptional ones reach

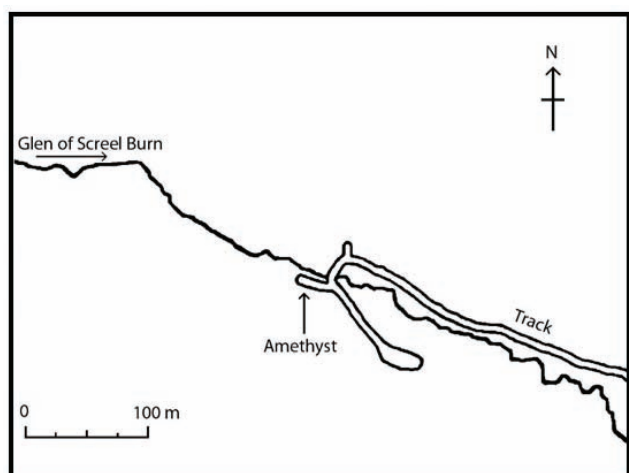


Figure 1. Sketch map of the amethyst locality at Scree Hill.



Figure 2. The amethyst locality at Scree Hill, in March 2012, viewed from the north. Stephen Moreton photograph.



Figure 3. Epimorphs after dolomite on the reverse of an amethyst specimen, 105 x 75 mm. Robert Lawson specimen. Stephen Moreton photograph.

around 2 cm. These last generally filled the largest cavities and did not form large drusy plates, most of the cavity space having been filled in by the time the crystals achieved their larger size.

The colour of the crystallised quartz ranges from colourless and milky, to light purple, the latter predominating at the excavation site. A few specimens were of smoky quartz, the smoky colour sometimes being unevenly distributed even on the same specimen and ranging from a pale smoky amethyst to intense dark brown. The fragments exposed by the trackside a few tens of metres to the SE, and which led to the original discovery, are mostly without colour, so the distribution of amethystine quartz may not be even along strike. Upwards facing sides are often impregnated by a reddish ferruginous material, which defies attempts at removal. Tiny (*circa* 1 mm) limonite pseudomorphs after pyrite, dotted over some specimens, and minute (0.1 mm, but sometimes covering areas up to 1 cm across) hematite rosettes on the epimorphs, complete the assemblage.

The amethyst, although not of faceting grade, makes attractive mineral specimens (Figure 4), and is remarkable for the profusion of such specimens obtained, doubtless with much more still in the ground. Many have been distributed with the appellation “Heights Lodge Pocket” after the home of one of the authors, from which Screel is visible, although it should be clarified that there is no single “pocket” as such, but rather a zone of mineralised breccia.

The occurrence was still open along strike at each end of the excavation, and was of unknown vertical extent and width, when digging ceased owing to depth of overburden, and time constraints. The locality has since been partially reinstated and is becoming vegetated and obscured, making a detailed record of it essential lest it becomes lost altogether.

ACKNOWLEDGEMENTS

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REFERENCES

- Davidson, J. (2015). North West branch visit to Screel Hill, *Newsletter of the Russell Society*, **66**, 28–29.
- Hedde, M.F. (1901). *The Mineralogy of Scotland* (ed. by J.G. Goodchild), Vol. 1. David Douglas, Edinburgh.
- Lawson, J. (1977). Galloway. *Gems*, **9**, 13–14.



Figure 4. Amethyst druse 15 cm across. John and Robert Lawson specimen. Peter Briscoe photograph.

- Leake, R.C., Brown, M.J., Date, A.R., Smith, T.K. (1978). A reconnaissance geochemical drainage survey of the Criffel-Dalbeattie granodiorite complex and its environs. *Mineral Reconnaissance Program Report*, No. 19, British Geological Survey.
- McCracken, A. (1962–3). The geological collections of the museum. *Transactions of the Dumfries & Galloway Natural History & Antiquarian Society*, **XLI**, 9–16.
- McMullen, M.J. and Todd, J.G. (1990). Mineralisation of the Kinharvie Burn, South West Scotland. *UK Journal of Mines & Minerals*, **8**, 43–45.
- Thomson, J. (1844). Parish of Rerrick. County of Kirkcudbright, in *The New Statistical Accounts of Scotland*, **4**, 354–368.
- Todd, J.G. and McMullen, M.J. (1996). Mineralogy of a quartz-hematite vein at Auchenlosh quarry, Dalbeattie, Dumfries & Galloway Region. *Transactions of the Dumfries & Galloway Natural History & Antiquarian Society*, **LXXI**, 159–160.
- Williams, J. (1962–3). The mineralogical collection of the Dumfries Burgh Museum. *Transactions of the Dumfries & Galloway Natural History & Antiquarian Society*, **XLI**, 201–215.
- Williams, J. (1973). The antimony, bismuth, molybdenum and tungsten minerals of south-west Scotland. *Transactions of the Dumfries & Galloway Natural History & Antiquarian Society*, **L**, 1–4.

CROOKESITE, TlCu_7Se_4 , FROM LITTLEHAM COVE, DEVON: THE FIRST MINERAL CONTAINING ESSENTIAL THALLIUM FROM THE BRITISH ISLES

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The rare thallium copper selenide, crookesite, occurs as dark grey metallic needles in at least two cavities in a nodule collected from cliffs at Littleham Cove, Budleigh Salterton, Devon. This is the first report of a thallium mineral from the British Isles. The small crystal size, confusion in the mineralogical literature and the need to preserve as much of the specimen as possible for future study, made the identification particularly challenging. Thallium minerals have a very limited worldwide distribution. They are almost entirely restricted to unusual low temperature epithermal deposits.

The discovery of crookesite in nodules in a Permian red bed environment is, therefore, of significant interest. Thallium minerals do not appear to have been reported in this geological setting before.

INTRODUCTION

Minerals which contain thallium as an essential component of their crystal structure are relatively rare in comparison to other elements with comparable or smaller crustal abundances; they number about 60, and account for less than 1.5% of the 5046 currently accepted species (www.ruff.info, retrieved 15/9/2015). Strong geochemical affinities with members of group I of the periodic table, and a comparatively low crustal abundance (0.07 ppm, according to Guberman, 2010) means that thallium most commonly substitutes for chemically similar but more abundant elements of similar charge and size, particularly potassium (Goldschmidt, 1954). As global demand for thallium and its compounds is relatively low, it is obtained as a by-product of the mining of lead, zinc and copper ores (Guberman, 2010).

Controversy surrounds the discovery of thallium. It is generally accepted that Sir William Crookes (1832–1919) of the Royal College of Science in London was the first to realise that a green line in the emission spectrum of impure sulphuric acid was produced by a new chemical element. He named it thallium, but was slow to investigate further. The French physicist Claude-August Lamy (1820–1878) made the same discovery and produced a small ingot of pure thallium metal in 1862. He was credited by the French Academy of Science as the true discoverer. Claims and counter-claims followed, but both men are now credited as co-discoverers (Brock, 2008). Trace quantities of thallium are widespread in the natural environment; it is commonly associated with potassium minerals in clays, soils and granite and found at low concentrations in natural spring water and in plants.

The first mineral with essential thallium was discovered at Skrikerum Mine in Sweden in 1866 and named crookesite in honour of Sir William Crookes (Nordenskiöld, 1867). Crookesite is one of the most common thallium minerals, but to put the general rarity of thallium species in context, it is noted from only 12 locations worldwide (www.mindat.org, retrieved 15/9/2015).

This paper describes crookesite from the central cavity of a dark coloured nodule found in argillaceous red beds of Permian age at Littleham Cove, Budleigh Salterton, Devon. This appears to be the first report from this geological environment and it is the first occurrence of crookesite (or any mineral containing essential thallium) from the British Isles.

GEOLOGY

Littleham Cove lies about 3 km west of Budleigh Salterton on the south coast of Devon (Figure 1). It is a significant and interesting locality due to the presence of vanadium- and uranium-rich nodules in the Permian red beds. The cove falls within the Jurassic Coast World Heritage Site and is situated just outside the Budleigh Salterton SSSI, which is designated for its Triassic pebble beds. It should be noted that nodules are present in many red bed deposits in the surrounding area; they are not restricted to Littleham Cove. There are reports of similar nodules from cliffs between Budleigh Salterton and Exmouth, from nearby inland clay-pits (Carter, 1931) and from similar sequences as far east as Sidmouth (DIG, *personal observations*). However, the specimens described herein were collected near Littleham Cove [SY 044 808] where nodules are very common.

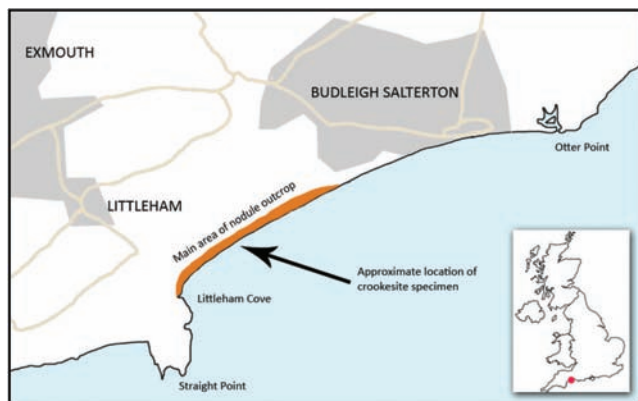


Figure 1. A map of the southern coast line in Devon showing the position of Budleigh Salterton, Littleham Cove and the approximate position of the nodules that were found to contain crookesite.

The nodules were first documented by local archaeologist and geologist George Carter (Carter, 1931) who noted the presence of significant concentrations of vanadium and smaller amounts of uranium, nickel and cobalt. Mineralogical investigations have been reported subsequently in a number of disparate publications and various mineral phases have been either identified or suggested, to account for their unusual geochemistry. The primary minerals within the nodules are typically poorly crystallised and are relatively difficult to identify even by modern techniques.

In a relatively recent study (Milodowski *et al.*, 2000), it was noted that in addition to 22 claimed species, the nodules contain a significant number of phases that have not been fully characterised. Unfortunately the characterisation of these phases was beyond the scope of their study and additional data is still required for the confident verification of some of their claimed 22 species. It is, therefore, impossible to describe the full mineralogical diversity of the nodules, which is clearly underestimated in current publications and warrants a detailed study in the future.

Milodowski *et al.* (2000) also note that the mode of formation of the nodules is poorly understood. The nodules have a global distribution and commonly contain significant concentrations of elements of geochemical interest, notably arsenic and uranium. As such, systematic examination of the mineral assemblages might provide insights into important geochemical questions.

CROOKESITE SPECIMEN

The crookesite-bearing specimen, now registered in the Natural History Museum (NHM) as BM 2013,125, was collected by one of the authors [ID] on a Russell Society field trip in September 2001. The specimen is one of two nodules that were found to contain dark grey, metallic needles. Both were collected *in situ* from an exposure in the cliff where they formed part of a band of nodules running approximately parallel to the local bedding, about 5 to 6 m above the beach (Figure 2). Unlike the nodules found on the beach, those collected *in situ* in the cliff exposure had a ‘fresher’ appearance, with fewer cracks and less



Figure 2. The Permian red beds, showing the distinctly lighter bands from which the crookesite containing nodules were collected. This photo was taken around the time of collection and it should be noted that this cliff face no longer exists as it is shown here, having suffered from considerable erosion during recent storms

surface alteration to supergene phases, which were visually identified as pinkish erythrite and yellowish pascoite.

The crookesite crystals occur in small cavities in the cores of the nodules. They are typically about 0.02×0.02 mm in cross-section with a maximum length of about 0.9 mm, although most are between 0.2 and 0.5 mm long. The needles are commonly slightly curved. They are present in two of the ten visually similar cavities that were exposed when the nodule was broken in half. Associated minerals in the cavity include unidentified black vanadium oxide(s), colourless prismatic calcite, yellow-orange crusts of pascoite, an unidentified brown vanadium-bearing clay mineral, an unidentified dark grey sub-metallic phase with a pale grey overgrowth and a platy micro-crystalline, blue-grey metallic tarnish on the crookesite needles, which is especially abundant on the larger needles towards their terminations. Unfortunately, the majority of these phases have not been characterised. Due to their small size and position, it was not possible to remove material satisfactorily from these phases for analysis without risking complete destruction of the specimen (Figure 3, see p. 50).

The other cavities on the specimen contain similar mineral assemblages, dominated by a brown vanadium-bearing clay mineral, black vanadium oxide(s) and colourless prismatic calcite crystals up to about 0.5 mm long. In some of the cavities in which crookesite is absent there are tiny (around 10μ) metallic, hexagonal plates that are rich in Cu and Se, it is likely that these are klockmannite crystals which we know have formed post-collection.

CHEMICAL ANALYSIS

Initial analyses by energy-dispersive spectrometry on a scanning electron microscope at the University of Manchester revealed the presence of Cu, Se, Tl and Mo in the metallic needles. Subsequent analyses at the NHM on a different set of needles revealed only Cu, Se and Tl; no Mo was detected, but traces of Ni were found. In view

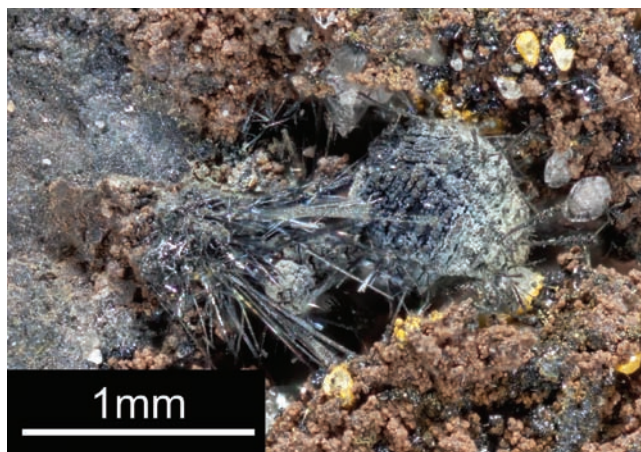


Figure 3. Crookesite specimen BM 2013,125. The crookesite occurs as thin grey metallic needles growing in and around a sphere of a pale grey unidentified mineral. The whole cavity is lined with a brown vanadium-bearing clay group mineral and crystals of calcite (white) and pascoite (yellow) can be seen in association. Tiny black specks throughout the clay group mineral are thought to be various (undetermined) vanadium oxides.

of the variation in elemental composition between the two analyses and the presence of an overgrowth on the metallic needles, it was decided that quantitative analyses on the interior of the crystals were required.

A number of needles were carefully removed, mounted in epoxy resin and polished using an aluminium oxide abrasive. The resulting probe block was carbon coated to ensure better conductivity and analysed by wavelength dispersive spectrometry (WDS) on a Cameca SX100 electron microprobe at the NHM. This probe block is registered in the collections as P16781 and is part of specimen BM 2013,125.

The analyses showed Cu, Se and Tl to be the dominant constituents of the metallic needles, and revealed a heterogeneous bimodal compositional variation. One cluster of results has Cu>Se>Tl and the other Se>Cu>Tl. The first cluster shows a good correlation with the composition of crookesite, while the second remains to be fully understood.

Although the data show a good match to crookesite, a literature review also revealed another phase with a similar chemical composition, sabatierite, Cu_6TlSe_4 (Johan *et al.*, 1978). It is recorded that crookesite can be Cu deficient, and has an empirical formula that is more usefully written as $\text{Cu}_{7-x}\text{TlSe}_4$ in which $x < 1$ (Berger, 1987a). Therefore, crookesite cannot be easily distinguished from sabatierite on the basis of chemical data alone. Furthermore, a number of synthetic Cu-, Se- and Tl- bearing phases are also known and complicate the identification yet further (Berger, 1987b).

STRUCTURAL ANALYSIS

To determine whether the metallic needles from Littleham Cove are sabatierite, crookesite, or equivalent to one of the synthetic Cu-, Se- and Tl-bearing phases noted in the foregoing text requires both structural and chemical data.

At this point, it is important to note that the published data on sabatierite has been called into question. Berger (1987a) suggested that sabatierite may be identical to a synthetic tetragonal phase with a formula, Cu_4TlSe_3 . Unfortunately the type sabatierite specimen has not been re-analysed and whether or not it corresponds to tetragonal Cu_4TlSe_3 , or something else, is not known.

Fortunately, the crystal symmetry and unit-cell parameters of crookesite are not disputed: crookesite is tetragonal, with $a = 10.435 \text{ \AA}$ and $c = 3.954 \text{ \AA}$ (Berger, 1987a) and importantly, these values are different from any of the synthetic or natural possibilities that might correspond to sabatierite.

Due to the paucity of material on the specimen (Figure 3), it was inappropriate to run an experiment using standard X-ray powder diffraction techniques as most of the unknown would be destroyed. The recent acquisition of a modern four circle diffractometer by the NHM presented an opportunity to make a more sophisticated structural analysis, including unit-cell parameters and crystal symmetry, from which powder diffraction data could be calculated.

A needle measuring $0.014 \times 0.017 \times 0.360 \text{ mm}$, with slight curvature along its length was removed from the specimen and mounted on a carbon fibre, which was in turn mounted on a glass fibre (Figure 4) for analysis. Data were collected for 51 hours on an XcaliburE, four circle diffractometer equipped with an Eos CCD detector. Analysis was not straightforward as the needle was found



Figure 4. The single crystal of crookesite that was mounted for study on the XcaliburE four circle diffractometer, note the small size of this specimen.

to be an aggregate of smaller crystallites, each with a slight angular offset. A detailed discussion of the data reduction is beyond the scope of this article; however, it proved possible to determine space group and unit-cell parameters which are almost identical to those reported for crookesite (Table 1). From these data, the relative intensity and position of the lines in the X-ray powder diffraction pattern could be calculated; these are compared to published data in Figure 5. The similarity to crookesite is striking.

DISCUSSION

Fourteen years after its collection and following eight years of intermittent study at two different institutions, a combination of chemical and crystallographic data has conclusively identified crookesite, the first mineral containing essential thallium from the British Isles.

	Space Group	"a" parameter	"c" parameter
Crookesite (of Berger 1987a)	I/4m	3.954	10.435
Crookesite (this study)	I/4m	3.926	10.430

Table 1. The symmetry and unit-cell parameters of crookesite from Budleigh Salterton, compared with reported data (Berger, 1987a).

Neither the chemical data nor the crystallographic data were sufficient to identify the mineral to species level. The task was complicated by uncertainty surrounding the closely related species *sabatierite*. Here problems of nomenclature were generated by improvements in instrumentation and subsequent new ideas, racing ahead of the confirmative analyses on the type specimen that is held as an ultimate reference for this exact reason. The nomenclature problems surrounding *sabatierite* could probably be resolved by a modern investigation of the type specimen. It is unfortunate that this specimen was not re-examined in 1987 when the *sabatierite* validity was first questioned; it is equally regrettable that a re-examination of this species was beyond the scope of this project. Fortunately, however, the type specimen has been preserved in the collections at the École de Mines in Paris and should be available for future re-examination (www.smmp.net/IMA-CM/ctms_s.pdf, retrieved 15/9/2015).

It is important that such specimens are conserved, recorded in the literature and held within safe, stable, internationally recognised museums. It is also important that these institutions and their curators are able to make competent value judgments to allow researchers access to such specimens so that scientific knowledge can develop in line with advances in instrumentation.

The analytical difficulties associated with the identification of crookesite from Littleham Cove also demonstrate the importance of patience. When the specimen was first submitted to the NHM an in-house

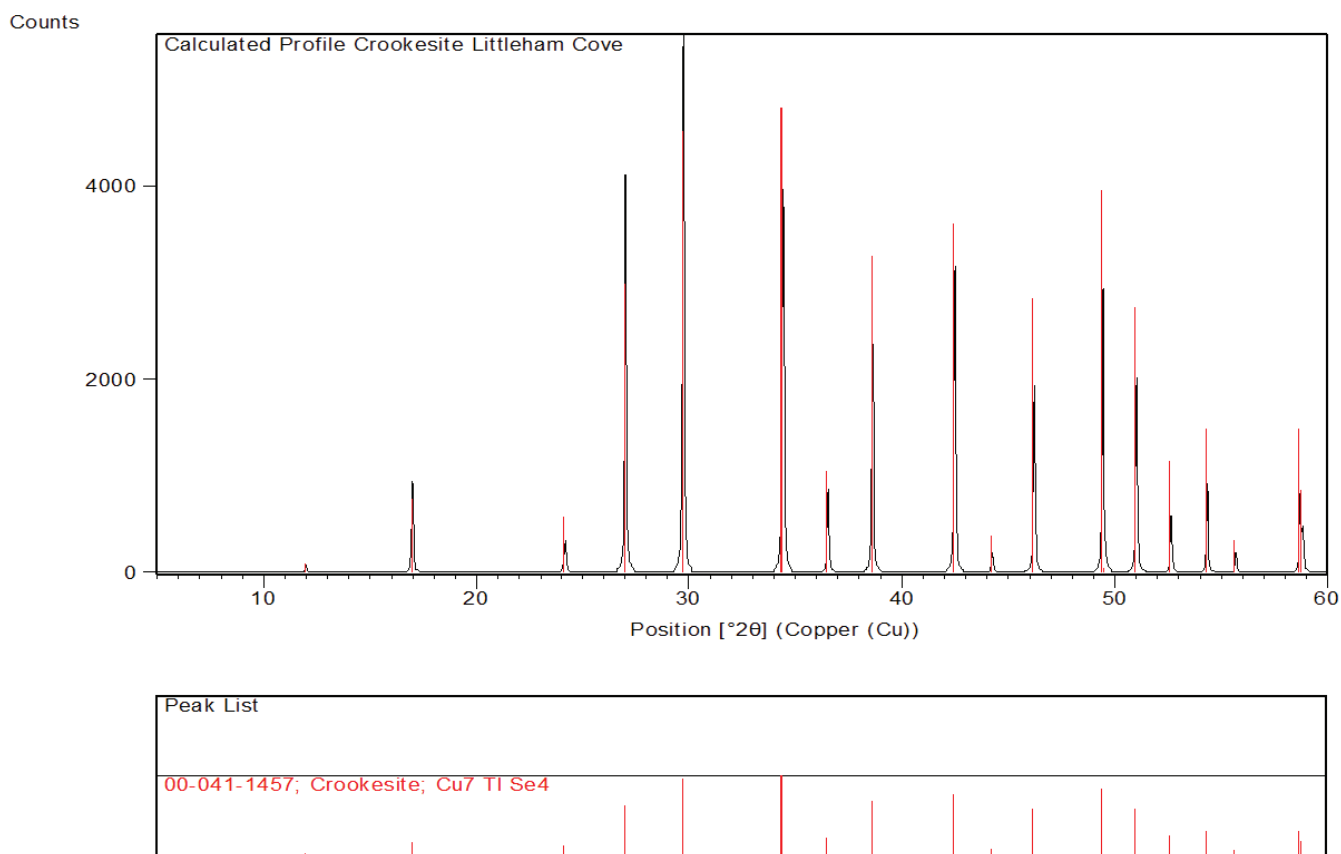


Figure 5. The diffraction pattern of crookesite, calculated from the single crystal data, together with the JCPDS crookesite reference pattern (00-041-1457)

identification by powder XRD would have required the near complete destruction of the unknown, leaving precious little available for future study. A decision was made to wait for a more appropriate technique, which was not available to the institution at the time due to operational constraints. When an appropriate instrument became available, the project was completed in the knowledge that most of the specimen would be preserved for future study.

The occurrence of a thallium mineral in the nodules at Littleham Cove is of significant geochemical interest. Thallium occurs in univalent and trivalent states; the first of these is most important in nature due to the high redox potential required to produce Tl^{3+} . Univalent thallium has considerable geochemical similarities to the larger alkali metals and it commonly substitutes for potassium in mineral structures. Similarities with potassium and other group I elements mean that, despite its crustal abundance, thallium almost always occurs as a substituent in common rock-forming minerals. It is only found as an essential constituent of minerals in very unusual circumstances. Thallium minerals are almost entirely confined to rare low temperature epithermal deposits. The mechanism by which the concentration of thallium has risen sufficiently to produce crookesite in a Permian red bed deposit is, therefore, of very considerable interest and deserves further study. It is hoped that a more complete mineralogical analysis of the locality, the nodules and all the mineral associations will produce a better geochemical understanding of this phenomenon.

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REFERENCES

- Berger, R. A. (1987a). Crookesite and sabatierite in a new light - A crystallographer's comment. *Zeitschrift für Kristallographie*, **181**, 241–250.
- Berger, R. A. (1987b). A phase-analytical study of the Tl-Cu-Se system. *Journal of Solid State Chemistry*, **70**, 65–70.
- Brock, W. H. (2008). *William Crookes (1832–1919) and the commercialization of science. (Science technology & Culture, 1700–1945)*. Ashgate, England.
- Carter, G. E. L. (1931). An occurrence of vanadiferous nodules in the Permian beds of south Devon. *Mineralogical Magazine*, **22**, 609–613.
- Goldschmidt, V. M. (1954). *Geochemistry*. Clarendon Press, Oxford.
- Guberman, D. E. (2010). Thallium. In: *USGS Mineral Commodity Summaries 2010*. United States Government Printing Office, Washington. p. 166.
- Johan, Z., Kvacek, M. and Picot, P. (1978). La Sabatierite, un nouveau seleniure de cuivre et du thallium. *Bulletin de Mineralogie*, **101**, 557–560.
- Milodowski, A. E., Styles, M.T. and Hards, V. L. (2000). *A natural analogue for copper waste canisters: The copper-uranium mineralised concretions in the Permian mudrocks of south Devon, United Kingdom*. Technical Report, TR-00-11. British Geological Survey, Keyworth, Nottingham.
- Nordenskiöld, M. A. E. (1867). Sur les minéraux sélénifères et thallifères de Skrikerum. *Bulletin Mensuel de la Société Chimique de Paris*, **7**, 409–414.
- Tindle, A. (2008). *Minerals of Britain and Ireland*. Terra Publishing, England.

“MATTHEW FORSTER HEDDLE: MINERALOGIST AND MOUNTAINEER”

By Hamish H. Johnston

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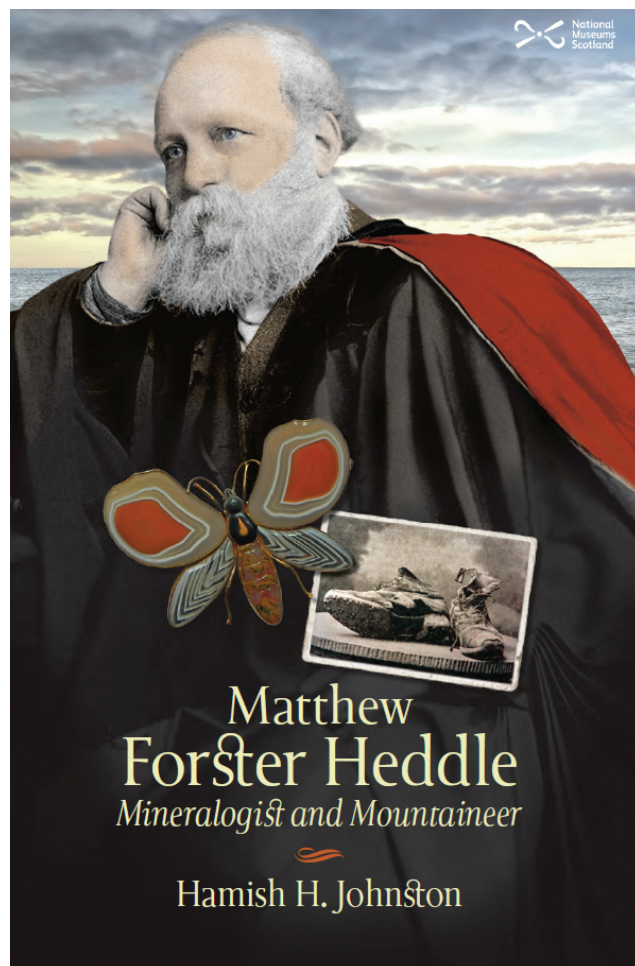
I should perhaps start this review by declaring a “vested interest”, firstly that of being a life-long fan of Matthew Forster Heddle (hereafter referred to as Heddle), and secondly that I have provided a certain amount of input to and support for the book during its preparation. However, I trust that this will not detract from the objectivity of the review, and indeed it perhaps adds weight to my being asked to undertake the task. My fascination with Heddle stems from a series of articles “*In the footsteps of Heddle*” by Peter Rogers, published in *Gems* magazine in the 1970s.

After settling in Birmingham in the late 1970s, I was a regular visitor to the Central Reference Library to research mineral localities. Delighted to find that they held a copy of Heddle’s *The Mineralogy of Scotland*, this was something which I examined frequently, painstakingly transcribing information and carefully working to trace localities on Ordnance Survey maps. This, of course, was in the days when photocopying was relatively expensive (certainly for my budget), and long before the internet and the wonderful book digitisation projects which we all take for granted nowadays. Some years later, I was able to purchase a two volume set of my own – certainly the most expensive book I’d ever bought at the time, and something which I still treasure and consult regularly.

As many readers will know, the mineralogy of Scotland has occupied much of my free time over the past 40 years or so, and I have spent many happy, and sometimes wet, days trudging along the coast, up glens and over Scottish mountains in pursuit of Heddle’s locations. A defining feature of *The Mineralogy of Scotland* is the fact that it was published before the Ordnance Survey National Grid Reference system was adopted, and for those of us interested in trying to trace the precise spot to which Heddle was referring, this adds an extra dimension to the “chase”. Heddle aficionados will be well-used to descriptions such as

Ben Ledi, in the channel of a burn on the east side; At Corriebuidhe Hill, 3 miles south, in limestone overlying mica slate at an elevation of about 2000 feet, about eighteen veins from 3 to 4 feet thick, running north and south for about 200 yards; On a hill north of Uya sound, in large crystals, in veins in Serpentine.

A consequence of this, of course, is that one gets to visit and explore tracts of country in more detail than would otherwise have been the case, and this can bring its own rewards, with new discoveries and previously unseen vistas on a clear day. Many modern collectors baulk at the thought of long walks in pursuit of an uncertain result, preferring instead to visit localities near the road, preferably not involving any great ascent or physical effort. Heddle,



however, was physically fit and strong, a lover of long walks, and had been brought up in the relatively untamed environment of the Orkneys. Self-reliance must have been a trait of his character from an early age, and his “skill-set”, in modern-speak, was ideally suited to strenuous days in the hills, or at sea exploring remote areas in his quest for interesting specimens.

This book, by Hamish H. Johnston (Heddle’s great-great-grandson) is not an account of Heddle’s scientific work but is about Heddle the man; it provides a much fuller picture of him than anything that has appeared before. The book has a substantial feel to it, weighing in at about 500 g, with a striking coloured image of Heddle in academic dress on the cover, and inset photos of a fine agate brooch in the form of a butterfly, made for Celia Heddle, and Heddle’s worn walking boots.

Structured into nine chapters, the book is arranged chronologically and has a thoughtful foreword by Alec

Livingstone, formerly Head of Department of Geology at National Museums Scotland. This is followed by a preface introducing the author's interest in his great-great-grandfather and the approach to researching material for the book. Family trees at the front of the book provide a useful point of reference to which the reader will doubtless return as they journey through the text, and the frontispiece is a picture of Heddle in scholarly pose, holding a magnifying glass and mineral specimen.

The first chapter outlines Heddle's parentage and sets out the family histories of the Heddles of Cletts on South Ronaldsay and the Moodies of Melsetter on Hoy, from whom Heddle was descended. There is much interesting background here and the author has done an admirable job of collating data from as far back as the sixteenth century. The many strands of military, commercial and family life are woven together into a coherent tapestry, tracing regimental adventures, slave trading, business activities in West Africa and international diplomacy. The varying fortunes of the family estate at Melsetter on Hoy, Orkney are summarised, and all of the historical sources are fully referenced in over 100 footnotes tabulated at the end of the chapter, an important resource for anyone wishing to pursue further research in the future, and an approach followed throughout the book.

Chapter two explores Heddle's childhood and schooling and it is interesting to learn of the family, political and business environment against which Heddle's education and formative years took place. Heddle was aged only four when his mother died in 1833, and with his father heavily involved in business activities and often away, Heddle and his brothers must have enjoyed many adventures during the summer holidays. He grew up surrounded by moorland, high cliffs and the expansive seas surrounding Hoy, becoming an accomplished sailor. His formal education at Edinburgh Academy began in 1837, and here it was reported that he

distinguished himself by his readiness to do battle on behalf of his weaker school-fellows. One or two stories told about him while there showed him to have been possessed of considerable self-control, fortitude and pluck.

In 1842, Heddle moved to the Merchiston Castle Academy, near Edinburgh where he helped found a school Natural History Society, and began his collecting career with sea shells, and also compiled a herbarium of pressed plants. His interests then turned to rocks and minerals which were to become his life's work.

In October 1844, then aged 16, Heddle matriculated at the University of Edinburgh to study Medicine. Chapter three reviews his time there and his progression towards a career as an Edinburgh doctor. His final year at the University of Edinburgh was 1850/51, and his thesis "*The Ores of the Metals*", was a mineralogical and chemical work, surely stretching the boundaries of acceptability for a medical degree.

Chapter four describes Heddle's mineralogical activities, which he pursued, to a greater or lesser extent, in parallel with his medical studies and his subsequent employment as a physician. This chapter, together with the two which

follow, (chapter five) on his time as an academic at the University of St Andrews, and (chapter six) describing his collecting and scientific papers, will probably be seen as the core of the book by Russell Society readers. The insights provided and historical links made by the author add much to our understanding of how, where and when Heddle undertook his scientific researches. Heddle's fieldwork was conducted both alone, and with various companions, most notably his good friends Patrick Dudgeon and John Harvie-Brown, but also in the company of clergymen such as Rev. David Webster, Charles Clouston and James Joass. Heddle also collected and undertook fieldwork with James Nicol and Archibald Geikie of the Geological Survey, and as a consequence his name is inextricably linked with the so-called "Highlands Controversy" of north-west Scotland. The author has made extensive use of Heddle's published papers to piece together something of a diary of his field exploits and researches.

As with so many contemporary collectors a love of minerals and geology is inextricably linked to a love of the outdoors and of mountains, and this was certainly true of Heddle. Chapter seven, "Heddle the Mountaineer" pays tribute to his activities in this realm, and in which his stamina leaves one simply breathless with admiration for his constitution.

Chapters eight and nine cover the period of Heddle's retirement from academic life and a searching review of his legacy, particularly the lengths to which he went in pursuit of a safe future for his beloved mineral collection, now part of National Museums Scotland in Edinburgh. One is left with the feeling that this wonderful man lived life to the fullest extent possible, and in spite of various setbacks along the way, that he made the most of every day, and touched many people's lives along the way. His influence continues to be felt to this day.

The book concludes with an appendix on relative monetary values, a list of sources, a bibliography, a list of his many publications and a useful index.

It is often said of notable characters that "we shall not see their like again" and this is especially true in the case of Matthew Forster Heddle. The book gives a fascinating and detailed insight to Heddle the man, presenting his character and his contemporaries in a way which nicely augments his many technical publications and his fabulous collection of minerals, now in the National Museum in Edinburgh. Viewed against all the difficulties and challenges which he faced in his personal and professional life, the terrain in which he worked, and the lack of adequate transportation when compared to the present day, his accomplishments seem all the more remarkable.

From a personal standpoint I would much prefer to have seen all the illustrations captioned as numbered figures and referenced in the text at the appropriate point, but this is a minor criticism. Likewise, the clustering of colour plates into two "art sections" seems a rather outmoded and unnecessary economy in this day and age, but doubtless this approach was adopted to reduce printing costs and hence the ultimate cover price of the book.

This is an excellent book which will have you itching to head for Scotland to visit some of the places mentioned, and to experience for yourself the magic of the countryside and the geology which inspired Heddle for almost seventy years. In the words of Alec Livingstone's foreword:

This scholarly biography superbly encapsulates Heddle's life with great empathy and is a fascinating, long-overdue tribute to Scotland's greatest mineralogist.

Highly recommended – go and buy a copy!

The book can be obtained directly from <http://shop.nms.ac.uk/products/Matthew-Forster-Heddle.html>, or through bookshops.

Roy Starkey

NOTES FOR CONTRIBUTORS

TYPESCRIPTS

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

FORMAT AND PRESENTATION

Papers should be submitted in the style and format of the Journal, and divided into appropriate sections and subsections. A recent issue of the Journal should be consulted for examples. Titles of papers should be adequately informative. Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST 40 71 and enclosed in square brackets where necessary, e.g.: [ST 4015 7185], [ST 401 718], [ST 40 71]). Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, microchemical analyses, etc.). It may not be necessary to reproduce such data in full in the text, but they should be supplied to the Editor if required by the referees in the course of their assessment. For mineral occurrences of particular note (e.g. new occurrences in the British Isles or at a particular locality) authors are strongly encouraged to record the specimen number and the institution or collection where the specimen is lodged.

FIGURES

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

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

TABLES

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

TERMINOLOGY

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

ABBREVIATIONS

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

REFERENCES

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

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

Bannister, F.A., Hey, M.H. and Claringbull, G.F. (1950). Connellite, buttgenschichtite and tallingite. *Mineralogical Magazine*, **29**, 280–286.

Dewey, H. (1923). *Copper Ores of Cornwall and Devon*. Memoirs of the Geological Survey: Special Reports on the Mineral Resources of Great Britain, Vol. **27**.

Hedde, M.F. (1901). *The Mineralogy of Scotland* (ed. by J.G. Goodchild), Vol. 1. David Douglas, Edinburgh. Any page numbers (e.g., p. 25) should be included in the citation in the text.

Jackson, N.J. (1977). *The Geology and Mineralization of the St Just District*. Unpublished PhD thesis, University of London.

King, R.J. (1973). Mineralization. In: Sylvester-Bradley, P.C. and Ford, T.D. (eds), *The Geology of the East Midlands*. Leicester University Press. Any page numbers (in this case: pp. 112–137) should be included in the citation in the text.

