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EDITORIAL

MINERALISATION IN THE PERMIAN ROCKS OF NORTHEAST ENGLAND

This issue celebrates localities of mineralogical interest in the Permian rocks of northeast England. The rocks, which crop out in a north–south ribbon between Nottingham and the mouth of the River Tyne, were deposited along the shallow western margin of the epicontinental Zechstein Sea in the late Permian. They include dolostones, evaporites, limestones, marls, mudstones, sandstones and siltstones, and are collectively described as the Zechstein Group. There are pronounced differences between the lithologies at the basin margin (where magnesian limestones, which host most of the mineralisation described in this issue, are conspicuous) and the centre of the basin, where thick evaporite sequences dominate.

The Magnesian Limestone has provided building stone for millennia. It was used in the Roman walls around the City of York, and in countless medieval buildings in northeast England (Lott and Cooper, 2005). Its architectural reputation was such that it was selected for the Houses of Parliament in the mid-nineteenth century. The purest dolostone began to be used in refractory production in the 1880s and demand from the steelmaking industry increased to such an extent that kiln-grade dolostone became the principal product of two of the localities described in this issue.

The Permian outcrop was surveyed by William Smith at the beginning of the nineteenth century and mapped in detail by Adam Sedgwick in the early 1820s (Sedgwick, 1829). The ‘Great Break’ between the folded Carboniferous and flat-lying Permian rocks attracted considerable interest. Fortunes were made once it was understood that it was an unconformity which concealed the Coal Measures.

John Farey and Adam Sedgwick made early records of minerals in the Permian rocks, but they lacked the prospectivity of the underlying Carboniferous strata, and later accounts are sparse and sporadic. Descriptions of mineralisation along the southern part of the outcrop (south of the River Tees) were collated by Gillian Harwood in the early 1980s. The first comprehensive review of the northern area is provided by Brian Young and colleagues in this issue.

Mineralisation along the northern outcrop (north of the River Tees) includes crystallographically fascinating fluorite from Old Towns Quarry near Newton Aycliffe, cannonball calcite concretions from quarries around Sunderland, baryte from localities around Ferryhill and rose quartz at Hawthorn Quarry near Easington. Minor copper mineralisation is associated with the Butterknowle Fault. Molybdenum minerals (ilsemannite and powellite) have been reported at the Billingham Anhydrite Mine and Whin Houses Borehole. One of the functions of the *Journal of the Russell Society* is to publish articles which describe mineralisation across a wide area. The review of mineralisation along the northern outcrop of the Permian rocks of northeast England admirably fills this niche. It suggests numerous avenues for further study and provides a key reference for future topographic research.

Detailed studies of the mineralisation at particular localities are another important facet of the *Journal of the Russell Society*. The three localities in the southern part of the Permian outcrop described in the remainder of *JRS* 24 fall into this category. They would be unknown but for fortunate chains of circumstance which alerted local collectors. The most mineralogically diverse is Whitwell Quarry where a remarkable supergene assemblage was uncovered by Peter Briscoe in the mid-1980s (Fig. 1).

The primary mineralisation at Whitwell Quarry can be understood by comparison with two nearby localities: Armstrong Quarry and the Sunnyside Deposit. Richard Bateman and co-workers use specimens rescued over a period of thirty years by the late Ray Richardson to describe disseminated mineralisation in the basal Permian rocks at Armstrong Quarry northeast of the village of Whitwell. The minerals occupy cavities and fractures left by the dissolution of calcium sulphates. Base-metal sulphides appear to have formed in a reaction between microbially reduced sulphur and syngenetic lead and zinc.



Figure 1. Transparent tabular pseudohexagonal leadhillite with brown Type 1 scotlandite in highly oxidised galena from Whitwell Quarry, north Derbyshire. Specimen GC4 in the Peter Briscoe Collection. The field of view is 1.5 mm across. Photo John Chapman.

The Sunnyside Deposit at the northern edge of the village of Whitwell is also re-examined using specimens rescued by Ray Richardson. Richardson's notebooks and catalogue include a wealth of information. They incorporate sketches and plans where less creative temperaments might have used photographs. Most of the sketches are simple, but they have an attractive interpretive quality which photographs cannot easily convey (Fig. 2). They illustrate the value of record-keeping; without them it would have been impossible to properly contextualise the mineralisation.

At the localities in north Derbyshire calcium sulphates appear to have played an important role in the mineralising process. Gypsum alters to anhydrite expelling sulphate-rich brines as it is buried and the temperature increases. Anhydrite alters back to gypsum during uplift and inversion, driving further fluid flow. Subsequent dissolution releases yet more calcium and sulphate. Sulphate ions may be immobilised in less soluble minerals such as baryte and celestine where brine streams interact. They can be reduced by microbial action, precipitating highly insoluble copper, lead and zinc sulphides. Calcium ions may drive dedolomitisation. Readers who wish to investigate these processes might be interested in John Warren's research. His summary of the styles of evaporite deposit generated in environments with differing fluid chemistries provides an excellent introduction and a list of useful references (Warren, 2016).

A long time gap between fieldwork and publication (as at the three localities in Derbyshire) is far from ideal, but it is not without advantage. Advances in mineralogical knowledge in the decades since the specimens were collected include the description of phosphohedyphane, which is one of the most important supergene minerals at Whitwell Quarry. Developments in 'focus-stacking', which generates images with a high resolution and depth of field, mean that specimens can now be documented far more effectively.

Focus-stacking has been adopted with enthusiasm by the mineralogical community. It is the only way to generate an image which records all of the visible detail on small specimens. The images are generated by algorithms which abstract the sharply focused areas from a stack of images and combine them in a single layer. The technique is still evolving and, as yet, there is no standard methodology. Many different lens combinations produce worthwhile results and the most expensive systems are not always the best. Respectable images can be obtained using antique objectives. The tabular pointed anglesite shown in Figure 3 was photographed using a microscope objective made in 1858 by James Swift. Swift learned his trade from Andrew Ross who manufactured the very first achromatic (two-colour corrected) microscope objectives in the 1830s. He would no doubt be pleased to find that one of his hand figured 'two inch' objectives (Fig. 4) was still capable of generating publication-quality images two centuries later.



Figure 2. A field sketch of the workings at Armstrong Quarry by Ray Richardson, dated May 1975, reveals that the workings had not reached the Marl Slate Formation but records dark marly limestone in the Lower Subdivision of the Cadeby Formation. The field notebooks were invaluable in deciphering the history and geology of the site.



Figure 3. Anglesite crystal from Whitwell Quarry imaged using the microscope objective shown in Figure 4. The field of view is 1.4 mm across. Photo John Chapman.



Figure 4. An antique two-inch achromatic microscope objective manufactured by James Swift & Son of London in 1858 which was used to create the image in Figure 3.

In later life James Swift manufactured polarising microscopes. They became an essential tool in mineralogical research in the early twentieth century but have fallen from favour in recent years. Thin section photographs are included in two of the articles in this volume. They illustrate facets of the mineralisation that would otherwise have remained obscure. One of the obstacles to private use is the need to prepare thin sections. A number of small companies and university geology labs currently offer this service at reasonable cost and David Copestake has written a guide to preparation as an appendix to the Sunnyside article.

Some readers may recall that stereo pairs were occasionally published in *The Mineralogical Record*. Two images taken from slightly different angles are set side-by-side and appear three dimensional when examined with a simple viewer. Stereoscopy can be combined with focus stacking to produce a three-dimensional representation at a depth of field and resolution which cannot be visualised in any other way. Images may be viewed as anaglyphs, which require red-cyan spectacles and do not faithfully reproduce every colour, or as stereo pairs with an appropriate viewer. Some of the specimens figured in this journal really come alive when they are examined in this way (Fig. 5).

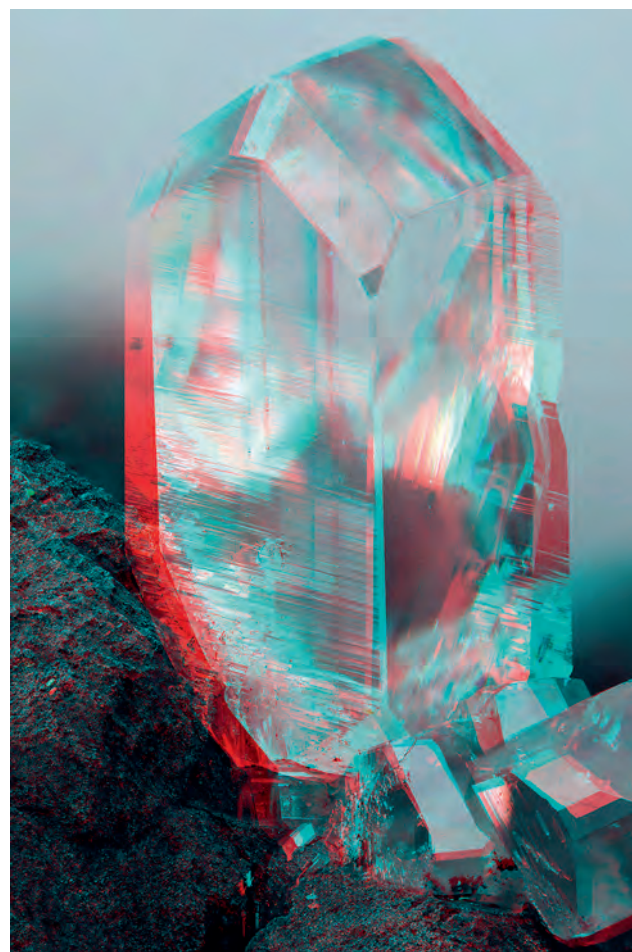


Figure 5. Red-cyan anaglyph of a transparent blocky anglesite crystal, 4.5 mm from top to bottom, with a complex pyramidal termination (see also Figure 10 in *The Mineralogy of Whitwell Quarry, Derbyshire* in this issue). Specimen Y20 in the Max Freier Collection from Whitwell Quarry, Derbyshire. Red-cyan spectacles are required to reveal the specimen in three dimensions.

Stereo viewers and red-cyan spectacles are inexpensively available on the internet. They provide a gateway into a fascinating miniature world. Printed media are not ideal for stereoscopy. The red-cyan anaglyph (Fig. 5) is included here in the hope that readers will acquire an appropriate viewing aid and visit the Society website, where many of the specimens figured on the pages of this journal can be viewed in three dimensions.

In common with focus-stacking and stereoscopy, fluorescence has the potential to reveal hidden detail in specimens. There has been a resurgence in interest in the last decade as bright LEDs have become available. In combination with a stereomicroscope, modern long-wave LED torches commonly reveal overlooked inclusions or hidden zonation. A few focus-stacked fluorescent images are included in *JRS* 24 (e.g. Fig. 6). In some cases they bring structures that are otherwise invisible to light, in other cases they are included to show particular fluorescence colours or simply for their visual appeal. After all, who has ever seen scotlandite illuminated by fluorescing leadhillite?

Reproducing the colour perceived by the human eye can be challenging. Fluorescence responses are commonly weak and require careful filtration to remove wavelengths which may compromise the colour balance. Even then it is not always possible to replicate the visual stimulus. Nonetheless, LED torches provide an inexpensive opportunity to study specimens in a 'different light'. They deserve a place in every mineralogist's toolkit.

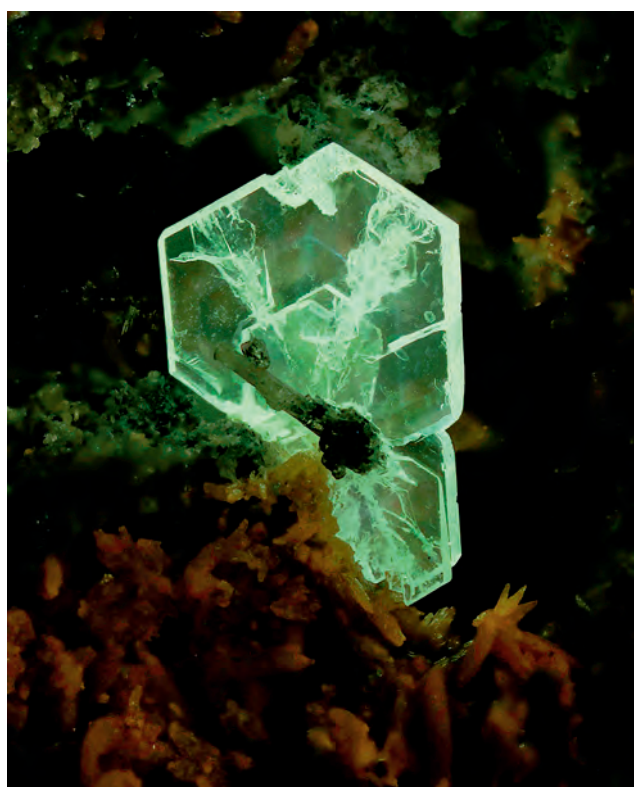


Figure 6. Fluorescence response of the pseudo-hexagonal leadhillite on scotlandite shown in Figure 1. Specimen GC4 in the Peter Briscoe Collection. The field of view is 1.5 mm across. Photo John Chapman.

Mineralisation in the Permian in northeast England will almost certainly feature in future editions of this Journal. Descriptions of the minerals from Wistow Shaft near Selby and the nineteenth century celestine from the Nidd Gorge near Knaresborough are part-prepared and it would be remiss not to mention, at least in passing, the minerals from the deeply buried Permian evaporite sequences in northeast Yorkshire. Boulby Mine is well known for remarkable specimens of boracite, hilgardite and trembathite. In the years since the publication of *Minerals of Britain and Ireland* (Tindle, 2008) a considerable number of minerals new to Britain, including howlite, hydroboracite, kalistrontite, starkeyite, volkovskite and uklonskovite, have been identified (Smith *et al.*, 2014; Genis *et al.*, 2015; Kemp *et al.*, 2018). This assemblage clearly has considerable potential for further discovery.

It is hard to avoid the conclusion that in a mineralogical context the Permian rocks of northeast England have been relatively overlooked. Many of the localities described in this volume are only known because someone with an appropriate interest was in the right place at the right time. The positive way to look at this is that a great deal remains to be found!

This brings us in a roundabout way to the next edition of the Journal. In 2022 the Society celebrates its golden jubilee. In our fiftieth anniversary year it seems appropriate to look back. The next *JRS* will feature articles with a historical context. And with the nation's health improving, we may even get out and enjoy a little more field work.

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MINERALS OF THE PERMIAN ROCKS OF NORTHEAST ENGLAND: A REVIEW

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The Permian rocks of northeast England are world renowned for the cyclic succession of marine carbonate rocks and evaporites which have long attracted, and continue to attract, research and which are the subject of a voluminous technical literature. In addition to the variety of minerals of authigenic origin, much less well known is the variety of minerals of epigenetic origin found within these rocks. In this paper we review the area's remarkable mineralogical diversity as recorded both in the published literature but also drawing upon numerous unpublished records and reports in addition to the authors' observations made over many years of familiarity with these rocks. The significance of some of the epigenetic mineralisation in the wider context of mineralisation across northern England is discussed.

INTRODUCTION

The area described in this review comprises the outcrop of Permian rocks adjacent to the North Sea coast between the rivers Tyne and Tees, together with small outliers immediately north of the Tyne between Whitley Bay and Tynemouth. It embraces parts of North and South Tyneside, County Durham, the City of Sunderland, Hartlepool, and Stockton on Tees.

Since the earliest days of geological science and their first stratigraphical classification by Sedgwick (1829), these rocks have attracted great research interest, particularly in the second half of the twentieth century with the recognition of their relevance to offshore hydrocarbon exploration. The marine limestone succession, originally known collectively as the Magnesian Limestone and today classified as the Zechstein Group, comprises a complex assemblage of varied carbonate lithologies. Many are without parallel in Britain and most of Western Europe and many sites are today scheduled as Sites of Special Scientific Interest (SSSIs). Although extensively concealed beneath a mantle of Quaternary deposits, numerous natural exposures and quarries, an almost continuous line of coastal cliffs and numerous borehole records, have enabled these rocks and their associated mineralisation to be studied in detail, culminating in a voluminous technical literature. This paper presents a review of the area's mineralogical diversity as revealed by published descriptions together with a number of new records and the authors' observations made over many years of familiarity with these rocks.

GEOLOGY

Detailed descriptions of the area's rocks and their stratigraphic relationships are out of place here: excellent summaries of these, in which references to more detailed sources are cited, include those of Pettigrew, (1980); Smith (1994; 1995); and Stone *et al.*

(2010). However, the following very brief outline clarifies the modern stratigraphical nomenclature and places the rocks in a regional context.

The Permian rocks of northeast England form the northernmost extremity of an almost continuous outcrop of these rocks which extends south from the River Tyne to Nottinghamshire. They rest unconformably upon various divisions of Carboniferous rocks and dip gently beneath a conformable cover of Triassic rocks, extending eastwards beneath the North Sea. The overlying Triassic rocks of the Teesside area are not considered in this review. Figure 1 provides a simplified geological map of the area's Permian rocks. The modern stratigraphical classification, together with traditional names previously used, is shown in Table 1.

Above the Yellow Sands which are today assigned to the Rotliegend Group, modern nomenclature has replaced formal use of the term 'Magnesian Limestone' with 'Zechstein Group' for the succeeding marine limestones, evaporites and marls. However, because much of the following review is concerned with the carbonate units of this group, and for ease of understanding, or where precise stratigraphical positions are not clear from the sources cited, the term 'Magnesian Limestone' is employed informally where appropriate in this review.

The Yellow Sands Formation, generally regarded as being of Early Permian age, comprises a succession of up to 70 m of aeolian desert sands typically composed of well-rounded 'millet seed' quartz grains. Records of numerous shafts, boreholes and wells reveal that these sands comprise a series of WSW–ENE trending self dunes and that where they are locally absent the overlying marine succession rests directly upon the basal unconformity. Rotliegend sandstones are one of

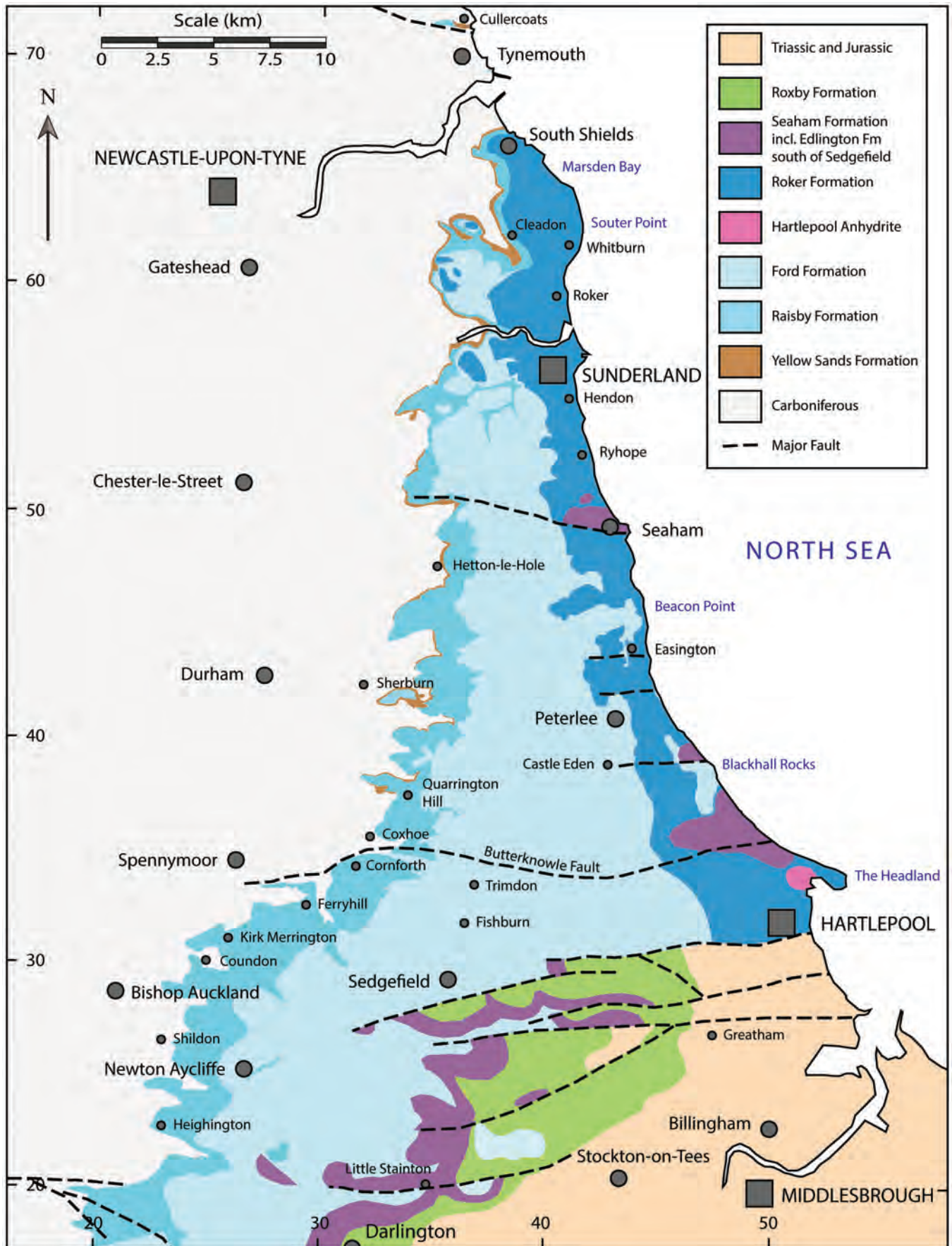


Figure 1. Simplified geological map of the Permian rocks of northeast England.



Figure 2. Trow Point, South Shields. The arrow points to the residue of the Hartlepool Anhydrite which comprises a few centimetres of clay here resting on pale yellow dolomitic limestones. The pale grey limestones above the residue are severely collapse brecciated. Photo Brian Young.

Formation has, like the Hartlepool Anhydrite, suffered total dissolution onshore and is represented by the Seaham Residue bed composed of up to 9 m of limestone and dolomitic clay. South of Sedgefield this is represented by up to 10 m of siltstones, mudstones and anhydrite known as the Edlington Formation, though these beds are almost completely concealed beneath superficial deposits. The overlying Seaham Formation which crops out on the coast at Seaham and Blackhall, comprises a succession of dolomitic limestones, in which spherulitic concretionary structures are also conspicuous. The succeeding Billingham Anhydrite and Boulby Halite formations do not crop out at the surface, though both were formerly exploited from beneath the cover of Triassic rocks as the original basis for the Teesside chemical industry. Anhydrite was mined from beneath the Billingham chemical works. Halite was worked haphazardly in the nineteenth and early twentieth centuries by solution mining at several places in Middlesbrough and north of the Tees (Marley, 1863), and then intensively and in a more controlled fashion in the Greatham and North Tees Salt Field by companies including Cerebos and ICI. Production ended in 2002. Above these evaporite units the Permian succession is completed by red-brown silty mudstones of the Rotten Marl and Roxby formations, though these are concealed by a thick mantle of superficial deposits and are known principally from boreholes.

The Zechstein evaporites thicken considerably southwards out of the area covered by this paper, and a host of additional, and sometimes exotic, evaporite minerals appear and have been described from potash mining at Boulby and polyhalite exploration at Whitby (Smith *et al.*, 2014).

MINERALS

The area is host to a remarkably wide range of minerals both of authigenic origin, e.g. evaporite, carbonate and clastic minerals, and those of epigenetic deposits emplaced within these rocks, e.g. baryte, fluorite and sulphides. Accordingly, as several species share more than one mode of origin, the minerals are reviewed here in simple alphabetical order with discussion of their origins and wider significance reserved for the discussion section. Although most of the minerals recorded in published texts are reliably confirmed species, a number (e.g. garnet) have been identified only to group level. Moreover, a number of records relate only to tentative identifications and a handful of published reports are suggested here to be unlikely or unreliable.

Brief summaries of the reported occurrence of each mineral are given below with, in a few instances, quotations from the sources cited. Descriptions

without citations are new and hitherto unreported records. Following the normal convention for this journal, species subtitles are in uppercase if there is no doubt about their identification and in lowercase if doubt remains. Subtitles are italicised if the balance of evidence suggests the claims are unreliable.

As older published descriptions pre-date the National Grid, the references quoted here have been added by the present authors. Grid references in more recent texts are quoted from the sources cited. Most are given to either 6 or 8 figure accuracy, though where reference is made to a general location or a wide area, for example a village name, they are quoted to four figure accuracy.

ANHYDRITE, CaSO_4

Anhydrite is the principal component of the area's main Zechstein evaporite units.

Smith (1994) speculated that the lowest of these, the Hartlepool Anhydrite, may have originally been up to 120 m thick over a large area between Sunderland and Seaham. However, subsequent dissolution has completely removed it from the inshore area save for a small subcrop around Hartlepool where it has been preserved beneath an impervious seal of up to 28 m of Quaternary deposits (Smith and Francis, 1967). The residue left from dissolution of this bed is exposed at Trow Point, South Tyneside, where it is overlain by severely collapse-brecciated limestones (Fig. 2). At Hartlepool the anhydrite is up to 110 m thick but thickens to 152 m a short distance offshore where it was penetrated in offshore borings for coal exploration (Magraw, 1975) and hydrocarbons. It is typically a hard, bluish grey fine- to coarsely-crystalline rock, locally with scattered gypsum porphyroblasts and cut by an extensive network of fine-grained grey to brown dolomite stringers (Trechmann, 1931, 1932; Sherlock and Hollingworth, 1938; Smith and Francis, 1967) (Fig. 3). Cores of this anhydrite, recovered from offshore boreholes between the Tyne and Tees revealed it to be a fine-grained crystalline pale greyish blue rock, commonly with a 'chickenwire' mesh of fine-grained buff dolomite. It was mined underground from a single 65 m deep shaft at the Warren Cement Works [NZ 516 345] from 1924 to 1930. Nothing remains of the workings today and there are no surface exposures.

Nodules of anhydrite were recorded by Smith and Moore (1973) from dolomitic mudstones within gypsum beds thought to be equivalent to the Hartlepool Anhydrite, at depths of around 60 m in a borehole at Hurworth Place, south of Darlington [NZ 29023 09532]. The outcrop between Little Stainton, Neasham and Darlington is known only from boreholes, some of which were sunk by ICI for gypsum exploration in the 1960s ('G' series holes at Little Stainton). It is mostly either converted to gypsum that now displays karst features, above residual layers of anhydrite, or is dissolved, so that the original thickness is hard to determine (Cooper and Gordon, 2000). Overlying collapse breccias are common

and the surface is characterised locally by subsidence depressions and rare sinkholes, for example at Hell's Kettles, near Croft [NZ 2811 1090] (Cooper, 1995).

The Billingham Main Anhydrite has suffered total dissolution over much of the area, though it remains at up to around 19 m thick at depth in the Billingham area where it is typically a grey to buff fine-grained crystalline rock. It was mined extensively underground beneath the former ICI Billingham works [NZ 477 227] via two 259 m deep shafts between 1926 and 1971 and used as a feedstock for the making of ammonium nitrate fertilizer and sulphuric acid (Anon., n.d.). Since the shafts were capped in 1978, proposals to reopen the abandoned workings for the storage of medium to low level radioactive waste have not been pursued. Little remains of these workings today and there are no surface exposures. The anhydrite is mostly dissolved away from the southern outcrop between Billingham and Darlington. Residual patches of anhydrite within beds of gypsum correlated with the Billingham Main Anhydrite were recorded at depths of around 40.5 m in the Hurworth Place Borehole, south of Darlington (Smith and Moore, 1973). Similar conditions are present in several boreholes around Darlington beneath foundered strata, but Cooper and Gordon (2000) note that in the area southeast of Darlington, where there is cover of the Sherwood Sandstone Group, gypsum passes rapidly to anhydrite down-dip to the east.

Anhydrite, accompanied by gypsum, is a minor constituent of siltstones and mudstones in the Roxby



Figure 3. Cut section of a core of the Hartlepool Anhydrite from the Wearmouth Offshore Borehole. Fine-grained bluish grey to white anhydrite includes prominent porphyroblasts of grey gypsum. Note also the patchy network of pale buff dolomite. Specimen No. BY3876 in the Brian Young Collection. The section is 8 cm across. Photo Brian Young.

Formation, cut in brine wells in the Greatham area [NZ 49 27] (Fowler, 1956).

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

Land (1974) noted the widespread occurrence of narrow veins containing ankerite, together with pyrite, in the Permian rocks of the area covered by BGS Sheet 15 (Tynemouth), though without further descriptions or locations. No other reports of ankerite from the area's Permian rocks are known.

Aphthitalite, $(\text{K}, \text{Na})_2\text{Na}(\text{SO}_4)_2$

Raymond (1959) noted the presence of tiny rectangular prismatic crystals, tentatively identified as aphthitalite, within blue efflorescent crusts of ilsemanite in the underground workings of the Billingham Anhydrite Mine [NZ 477 227].

ARAGONITE, CaCO_3

Smith (1994) noted an internal Geological Survey report in which J. Phemister recorded traces of aragonite, replacing calcite in calcite spherulites within the concretionary limestones in the lower part of the Roker Formation at Whitburn [NZ 40 62]. Al-Rekabi (1982) found no evidence of the past or present occurrence of aragonite in these rocks, except in fossilised mollusc shells. No other records of aragonite are known from the area's Permian rocks.

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

In a detailed investigation of copper mineralisation in brecciated dolomitic limestones of the Ford Formation adjacent to the Butterknowle Fault in the abandoned Raisby Railway Cutting, [NZ 3502 3492] Young (2001) described abundant azurite both as small spheroidal aggregates of crystals up to 2 mm long within calcite-lined cavities and forming bright blue stains on fracture surfaces of the limestone (Fig. 4). Small spheroidal masses of azurite up to a few millimetres across were also noted in the loose debris covering the sides of the cutting. The exposures here are now heavily overgrown.

Arsenopyrite, FeAsS

Arsenopyrite was tentatively identified by Raymond (1959) as a minor constituent of blue post-mining ilsemanite-rich efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

BARYTE, BaSO_4

Baryte mineralisation has long been known to be common within the Permian carbonate rocks of north-east England (e.g. Smythe, 1922; Fowler, 1943, 1956; Jones and Hirst, 1969).

Before reviewing these occurrences, it is necessary to mention Steele's (1981) record of authigenic baryte in

the Yellow Sands Formation, though without any descriptive or locality details. It is also appropriate to note that on the foreshore at Cullercoats [NZ 3668 7170], the Ninety Fathom Fault juxtaposes the Yellow Sands against the sandstone above the Hutton Seam of the Middle Coal Measures which is here veined and partly replaced by baryte together with calcite and pyrite, though this mineralisation is not known to affect the adjoining Yellow Sands (Land, 1974).

The Marl Slate at Raisby Quarry [NZ 345 353] is often flecked with millimetre scale pink and orange baryte.

Smythe (1922) recorded a 0.6 m wide 'band' of baryte "dipping gently N with the bedding" within what may now be assumed to be Raisby Formation limestones at Marden Old Quarry (now backfilled), near Cullercoats [NZ 355 715], though without further description.

Fowler (1943, 1956) recorded abundant mineralisation, including baryte, within limestones today recognised as belonging mainly to the Raisby Formation in several cored coal exploration boreholes drilled in the 1940s between Rushyford [NZ 284 288] and Fishburn [NZ 365 320], though not all borehole sites were identified. In these boreholes baryte-rich mineralisation, sometimes accompanied by fluorite, pyrite, calcite, dickite and/or galena, was found to be concentrated within roughly 7 m of limestones towards the top of the Raisby Formation. Various forms of baryte were described, including pinkish white to flesh coloured slender rod-like crystals locally aggregated into tufted groups, aggregates of fibrous curved platy crystals and as radiating sheaves of milky white radiating crystals.



Figure 4. Azurite forming pale blue crystalline patches, with small dark blue spheroidal aggregates (bottom left) on grey limestone from the Raisby Railway Cutting. Specimen No. BY5485 (5 cm across) in the Brian Young Collection. Photo Andy Hopkirk.

Minor veinlets of baryte, pyrite and occasional galena were seen in iron-metasomatised limestone at Bishop Middleham Quarry [NZ 334 320] and in limestones at Hartlepool Waterworks Borehole [NZ 507 334] (Fowler, 1956). Water-clear tabular crystals of baryte, accompanied by sphalerite and galena were found in cavities in Raisby Formation limestones in the nearby Whin Houses Borehole, near Butterwick [NZ 3997 3058] (Fowler, 1943). In the Ten O’Clock Barn No. 2 Borehole, near Butterwick [NZ 3916 3035] baryte mineralisation was concentrated within the topmost 21 m of this formation, beneath which a 9 m interval separated it from a 12 m thick zone rich in fluorite mineralisation. The mineral here typically occurred as white to very pale pink compact or fibrous crystalline masses up to at least 13 cm across, some of which appeared to replace the host limestone: a few platy crystals of baryte were also recorded from the zone of fluorite-rich mineralisation at a depth of 122 m in this borehole.

Fowler (1956) also reported compact fibrous and locally platy crystallised baryte coating joint planes in Ford Formation limestone cores from the Hesledon Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698] where, in addition, Dunham *et al.* (1948) identified carbonate-bearing fluorapatite (collophane), dickite, fluorite, galena, pyrite and sphalerite. An unpublished manuscript by Sir Kingsley Dunham and Denys Smith of specimens collected by W. Anderson records baryte with calcite and pyrite in a sample from a depth of 84 m, and baryte and galena at 85 m. Fowler’s unpublished manuscript log of Hesledon Dene No. 3 Water Borehole records platy baryte in a joint at 40 m, again from 45 to 47 m, and “some baryte in joints and finely striped bands” from 47 to 50 m. Skins of baryte on joint faces are recorded again between 69 and 77 m, with many scattered crystals of galena in the uppermost metre. Denys Smith’s unpublished manuscript description of Fowler’s core specimen from 65 to 66 m records innumerable small cavities, some empty and some filled with baryte and fluorite.

In the same general area, the Tinklers Gill Borehole [NZ 4157 3054] log records baryte on joints below 156 m and baryte, fluorite, calcite, and pyrite impregnating a suspected faulted section at 171 to 174 m. The manuscript log of Cole Hill Farm Borehole [NZ 4229 3110] records limestone with abundant cavities with baryte and calcite, and, less common fluorite, galena and sphalerite from the start of coring at 115 to 121 m, and from 126 to 129 m abundant small cavities with white baryte and “black blende” and some small cubes of fluorite.

Raymond (1959) reported that the most southerly (G7) of the boreholes drilled for gypsum exploration by ICI at Little Stainton proved “Lower Magnesian Limestone carrying nests and veins of calcite, gypsum or anhydrite and abundant baryte”.

Baryte veinlets are recorded in brecciated dolostone at 143 to 145m in the log of Dalton Nook Plantation Borehole

[NZ 4811 3144], probably in the Raisby Formation; and with pyrite and calcite in the Raisby Formation at 177 to 183 m in the Low Throston Borehole [NZ 4890 3316].

In their comprehensive investigation of baryte mineralisation in the Ferryhill area Hirst and Smith (1974) described abundant baryte as irregular patches, stringers and cavity fillings within Raisby Formation host rocks from the following surface locations: Chilton Quarry [NZ 300 314], Rough Furze Quarry [NZ 318 324], Mainsforth Limeworks Quarry [NZ 303 321] and several old quarries in Thrislington Plantation [NZ 318 327 and 312 324]. Smaller amounts of the mineral were also described from old quarries, now the Ferryhill Carrs Nature Reserve, west of the main east coast railway [NZ 300 330, NZ 303 323 and NZ 300 332], West Cornforth Quarry [NZ 318 345], Raisby Quarry [NZ 345 353] and Running Waters Quarry, near Shadforth [NZ 334 404]. Most of this baryte occurs as dense, opaque, finely crystalline white or pale pink masses, commonly forming spherical or hemispherical aggregates and similar to that previously described by Fowler (1943, 1956) and reminiscent of the ‘cawk’ variety of Derbyshire.

In almost all occurrences the baryte was seen to be overgrown by crusts of colourless or slightly amber rhombohedral or scalenohedral calcite crystals (Fig. 5). Hirst and Smith (1974) applied the term ‘Ferryhill Type’ to this morphology to distinguish it from the less abundant more coarsely crystalline and locally water-clear variants of the mineral they described from Raisby Hill, Running Waters and West Cornforth quarries and the opaque arborescent crystals of baryte, overgrowing calcite in vugs in the dolostone host rock at the latter location. In all these locations the baryte either fills



Figure 5. Nodular white ‘cawk’ type baryte coated with pale buff crystalline calcite. Rough Furze Quarry, Ferryhill. Specimen No. 4074 in the Brian Young Collection. The field of view is 4 cm across. Photo Andy Hopkirk.

cavities in the host rock or fills interstices in the matrix of brecciated limestones.

At Chilton Quarry, Fowler (1956) noted that the form of baryte, later termed 'Ferryhill Type' by Hirst and Smith (1974), typically formed lenses up to 15×8 cm, balls and nodules up to 10 cm across, and narrow veinlets in the host limestone. Hirst and Smith (1974) estimated that in parts of this quarry baryte of this sort accounted for between 10 and 20% by volume of the rock seen in the faces and noted a similar concentration of the mineral in parts of the nearby Rough Furze Quarry [NZ 319 325]. Such was the abundance of baryte at Chilton that Fowler (1956) reported that significant amounts of the quarried rock were rendered useless for lime-burning, though the amounts present and its mode of occurrence were unsuitable for its recovery as a saleable product. Consequently baryte-containing Magnesian Limestone is sometimes now to be found to have been used as walling stone in the Ferryhill and Sedgfield area. Baryte in occasional cavities and "hairline veins" has been logged from the Raisby Formation in the Surtees Arms Borehole [NZ 3030 3091] near Ferryhill and Hope House Borehole [NZ 3395 2541] near Sedgfield, but without further detail (Jones, 1969). The same author noted baryte from the "Lower Magnesian Limestone" in Easington Colliery West Drift [approx. NZ 4357 4418] and Mill Hill Borehole, Easington [NZ 4122 4248].

More recently, nodular aggregates of dull white finely crystalline baryte of 'Ferryhill Type', up to 8 mm across with minute 'cocks comb' like crystalline outer surfaces, embedded in greyish white crystalline calcite have been found in Raisby Formation dolomitic limestones at Thrislington Quarry, [NZ 317 330] (A. Bowden, *personal communication*, 2011) (Fig. 6) and one of the authors (BY) has also found a few discontinuous veins composed of rounded masses of radiating crystalline salmon pink baryte up to 1 cm across, the outermost zones of which are white or colourless, in Raisby Formation limestones at Cornforth Quarry [NZ 320 344].



Figure 6. Rounded masses of very pale pink 'cawk' type baryte embedded in greyish white calcite. Thrislington Quarry, Ferryhill. Specimen No. BY8833 (5 cm across) in the Brian Young Collection. Photo Brian Young.

Baryte was formerly exposed in a 1 m band of vuggy limestone with calcite and fluorite in a road cutting on the A689 near Coundon, at NZ 2550 2925, and in a 1.3 m high roadside exposure cutting at Leasingthorne [NZ 2555 3000]. It has often been found in temporary exposures in the village of Kirk Merrington, for example by the Methodist Chapel [NZ 2615 3130] and with fluorite in foundation excavations for the new Primary School [NZ 2630 3115]. Rounded, residual pebbles of pink 'cawk' baryte are locally widespread in superficial soils in the village.

Pink baryte was reported, together with dolomite, pyrite and possible chalcopyrite, from cavities within Raisby Formation limestone in the NCB Windlestone 'B' Borehole [NZ 2667 2834] (Mills and Hull, 1976) who also recorded the mineral, accompanied by sphalerite and magnetite within a Raisby Formation dolostone exposed in an old quarry southwest of Heighington [NZ 2325 2161]. These authors also noted the presence of baryte and sphalerite within the lowest beds of the Raisby Formation exposed in Old Towns Quarry, Newton Aycliffe [NZ 257 246] where Bridges and Pettigrew (2013) subsequently found crusts of white 'cockscomb' crystals up to 5 mm across, and locally stained brown by iron oxides, commonly lining cavities in dolomitic limestones. Here, as elsewhere in the area, baryte post-dates the associated fluorite. Further south, grey and brown limestones, correlated with the Raisby Formation, cut in a water borehole at Coldsides Farm, approximately 6 km northwest of Darlington, contained patches of white to very pale pink massive baryte up to 5 cm across (Fowler, 1956).

Baryte, similar in appearance to that described from the Raisby Formation of the Ferryhill area is also present locally in collapse-brecciated limestones of the Roker Formation on the coast at Frenchman's Bay [NZ 3892 6613] and the small inlet of Man Haven to the south east [NZ 3941 6605] (Smith, 1995; Young, 2008a). The mineral occurs here mainly as compact fine-grained masses up to 4 cm across filling interstices in the breccias. Within a number of open voids the mineral exhibits mammillated or locally distinctly botryoidal surfaces up to 1 cm across (Fig. 7), the outer surfaces of which locally show very small 'cocks comb' crystals, commonly encrusted with a layer of colourless calcite rhombohedra up to 2 mm thick. Comparable pale pink baryte mineralisation is also present in exposures of similar limestones approximately 3.5 km further south, at Souter Point, Whitburn [NZ 4152 6272]. No other minerals have been observed in any of these exposures.

Smith (1995) described widespread replacive patches and thin veins of white and pink cawk type baryte and some chert in all beds of the Raisby Formation below the Trow Point Bed on the flank of a small anticline just south of Frenchman's Bay, and in the Trow Point Bed itself at Velvet Beds Bay, Marsden [NZ 3980 6560].

Veinlets, of 1 cm width, of pink cawk type baryte and traces of pyrite were sampled by one of the authors (FWS) in the Ford Formation at Wingate Quarry [NZ 372 378].



Figure 7. Mammillated mass of compact pale pink 'cawk' type baryte from Man Haven, South Tyneside. Specimen No. 8311 in the Brian Young Collection. The field of view is 4 cm across. Photo Andy Hopkirk.

Baryte was recorded from the Upper Anhydrite and also, accompanied by gypsum and anhydrite, as a minor constituent of siltstones and mudstones in the Roxby Formation cut in brine wells in the Greatham area [NZ 49 27] (Fowler, 1956).

BITUMEN

Substantial parts of the Roker Formation, especially the extremely thinly bedded 'Flexible Limestone' and overlying concretionary limestones, are notable for emitting a very strong oily smell when freshly broken. Although some of the concretions are a mid to dark brown colour, the smell is common even in very pale cream to almost white lithologies and Smith (1994) noted that 'mineral oil' has not been recorded from these rocks in the onshore area but commented that bitumen may be concentrated in stylolites where it may be a dissolution residue. The concretionary limestones in the lower part of the Roker Formation are the correlatives of the Stinkdolomit of the North Sea, Germany and Poland which has been regarded as a hydrocarbon source rock (Smith, 1994). A similar strong oily smell has been found in deep purple fluorite at Marsden and the unusual botryoidal form of fluorite at Rough Furze Quarry near Thrislington (see below).

CALCITE, CaCO_3

Whereas dolostones and dolomitic limestones comprise a high proportion of the Magnesian Limestone succession, much purer limestones, albeit with smaller but generally significant magnesium contents, are also present and have been worked at many locations for burning to quicklime.

Although at outcrop the Yellow Sands are normally incoherent and uncemented, impregnations of coarsely crystalline calcite give rise to irregular beds known as 'sand rock', which is particularly common in the uppermost beds immediately beneath the Marl Slate (Smith and Francis, 1967). This 'sand rock' locally exhibits conspicuous lustre mottling with anhedral cementing calcite crystals commonly >2 cm across. In addition, spherical concretions of calcite-cemented sand up to 2 cm across are common in the Yellow Sands exposed in numerous quarries (Sedgwick, 1829, Smith and Francis, 1967). Calcite forms a patchy cement, and locally replaces quartz, in the Yellow Sands Formation of the Tynemouth area (Land, 1974).

Land (1974) noted the widespread occurrence of narrow veins of calcite, together with ankerite and pyrite, in the Permian rocks of the area covered by BGS Sheet 15 (Tynemouth), though without further descriptions or locations.

The bedded dolomitic limestones and dolostones of the Raisby Formation commonly exhibit an abundance of irregular open drusy cavities, mostly up to 15 mm across, good examples of which may be seen in most exposures. These are typically lined with closely packed white or colourless scalenohedral calcite crystals which are commonly capped by rhombohedral faces (Fowler, 1943). Small amounts of a variety of other minerals, described below, also occur locally.

It has been suggested that these cavities may represent original nodules of evaporite minerals (Harwood, 1980; Lee and Harwood, 1989; Lawrence *et al.*, 2004). Mills and Hull (1976) noted that the calcite in such cavities in Raisby Formation dolostones exposed in an old quarry at Southfield House, south of Shildon [NZ 2240 2479] displayed yellowish green phosphorescence under long wave (366.5 nm) ultraviolet light, whereas the host rock dolostone exhibited yellowish cream fluorescence, a phenomenon they observed in all specimens of Raisby Formation dolostones with secondary calcite in the area covered by BGS Sheet 27 (Durham). No records of comparable fluorescence or phosphorescence in these minerals are known from the area.

Porphyroblastic clusters of bladed calcite crystals within Raisby Formation dolostones exposed in the south bank of the River Tees near Piercebridge [NZ 2093 1544] were assumed by Mills and Hull (1976) to be pseudomorphous after anhydrite. Although these authors do not employ the term, their description resembles the 'felted texture' in dolostones described from the Durham area by Smith and Francis (1967).

Calcite in the form of small (<5 mm) white rhombohedral crystals is the only gangue mineral recorded from the copper mineralisation within the Butterknowle Fault system exposed in the Raisby Railway Cutting (Young, 2001).

Bridges and Pettigrew (2013) describe calcite as irregular trigonal crystals up to 15 mm long, locally cementing fragmented fluorite, in cavities in dolomitic limestones near the base of the Raisby Formation at Old Towns Quarry, Newton Aycliffe.

The lowest beds of the Roker Formation, known as the Concretionary Limestone Formation in older stratigraphical classifications, are remarkable for the curious and often bizarre concretions found within them. As the nature and possible origins of these rocks have been the subject of research from a very early date, resulting in numerous descriptive papers, notably those by Sedgwick (1829), Abbott (1903, 1907, 1914), Holtedahl (1921) and more recently Braithwaite (1988) and Smith (1994, 1995), only a brief summary of their essential features, drawn from this literature and the authors' personal field observations, will be given here. Details of features and variations seen in individual locations may be found in Smith (1994).

A very varied range of concretionary structures are present. In the Sunderland area the simplest and perhaps best known are the rounded concretions, known locally as 'Cannon Ball Rock' (Fig. 8). Although commonly erroneously labelled as being composed of dolomite, the concretions typically comprise finely crystalline pure calcite (Browell and Kirkby, 1866; Garwood, 1891; Trechmann, 1914; Al-Rekabi, 1982). Striking, though in places much water-worn, exposures of these are conspicuous in the low sea cliffs at Roker beach [NZ 4071 5960]. Particularly fine examples, together with a great variety of other more complex structures, were a notable feature of the extensive Fulwell and Carley Hill quarries [NZ 38 59] on the northern outskirts of Sunderland (Smith, 1994, 1995; Lane, 2014). Magnificent specimens from these and

other locations are held within the collections of Sunderland Museum, with a small number on permanent display. Substantial parts of these former workings have been backfilled or obscured by vegetation and, although today protected as Sites of Special Scientific Interest (SSSIs), the remaining exposures are a shadow of those that were visible until as recently as the 1960s. Today, the finest and most readily accessible exposures of these remarkable rocks are those in the cliffs at Hendon Beach, south of the mouth of the River Wear [NZ 4126 5480] (Fig. 9). Other good exposures can be seen in coastal cliffs between Marsden and Ryhope, north and south respectively of Sunderland. Typical 'cannon ball' concretions comprise rounded, and generally mutually interfering, pale buff spherical structures which range in size from around 5 mm to 0.2 m in diameter, though more exceptionally up to >0.3 m. They are typically in point contact with one another or occur as mutually interfering masses: isolated single 'cannon balls' are rare. Internally the concretions commonly exhibit a crude concentric banding, occasionally with a small stellate central cavity, though many appear homogenous. Eastwood (1953) and Smith and Francis (1967) suggested that these cavities may represent twinned gypsum crystals subsequently removed by dissolution. Also common are elongate finger-like concretions (Fig. 10), in places in curious radial groups together with highly complex fan-like and reticulate coral-like structures, with which they have in the past been confused (Fig. 11). Good examples of these may be seen in several abandoned quarries e.g. at Building Hill in Mowbray Park, adjoining Sunderland Museum [NZ 399 565] and in coastal exposures, but fine examples are also to be seen in many older buildings and boundary walls in the Sunderland area where these comparatively hard rocks were once much used as local building stones (Lane, 2014).



Figure 8. Typical spherical 'cannon ball' calcite concretions from Fulwell Quarry, Sunderland. Specimen No. BY3346 in the Brian Young Collection. The field of view is 4 cm across. Photo Andy Hopkirk.



Figure 9. Mass of typical spherical 'cannon ball' calcite, with remnants of powdery pale yellow dolomite matrix between some concretions from Hendon Beach, Sunderland. Specimen No. BY7680 in the Brian Young Collection. The field of view is 5.5 cm across. Photo Andy Hopkirk.



Figure 10. Mass of rod-like calcite concretions from Fulwell Quarry, Sunderland. Specimen No. 3341 in the Brian Young Collection. The field of view is 5 cm across. Photo Andy Hopkirk.

More widespread than these ‘cannon balls’, especially in the South Shields area and County Durham south of Sunderland, are spectacular spherulitic concretions composed of radiating calcite crystals and superficially reminiscent of the Triassic ‘Daisy Bed’ gypsum of the Kirkby Thore area, Cumbria (Symes and Young, 2008). These striking rocks may be seen in numerous old quarries in the Cleadon, Whitburn and Marsden areas.

Particularly clear and readily accessible exposures are those in Marsden Old Quarry [NZ 396 645], a Local Nature Reserve managed by South Tyneside Council to protect both its geological features and its rich and distinctive associated Magnesian Limestone flora. Whereas the character of the spherulitic rock varies slightly in detail across the faces of this large quarry, the following descriptions are typical of the main features described by Young (2006). Spherules exposed here during stripping of topsoil to encourage re-growth of the associated Magnesian Limestone flora are typically spherical and range from <5 mm to >50 mm in diameter (Fig. 12), though a few much larger spherules, up to 120 mm across, have been seen locally. In places the rounded form is replaced by finger-like spherulitic structures apparently elongated along vertical joints or fractures. Individual spherules consist of coarse calcite crystals radiating outwards from a central point



Figure 11. Complex radiating calcite concretions at Hendon Beach, Sunderland. The hammer shaft is 30 cm long. Photo Brian Young.



Figure 12. Spherulitic concretions of pale brown calcite with pale yellow powdery dolomite matrix from Marsden Old Quarry, South Tyneside. Specimen No.7973 (7 cm across) in the Brian Young Collection. Photo Brian Young.

comprising either a small mass of granular calcite with no obvious internal structure or a small cavity, presumably from which the original calcite has been leached. Nucleation of spherules around fossil bivalve shells has been recorded by Woolacott (1912) and Smith (1994) though examples are rare. The calcite crystals commonly exhibit sharp or rather rough pointed scalenohedral terminations on the outer margins of the spherules, seen as groups of sharp and locally lustrous pyramids on some weathered faces. Although the calcite is mostly uniformly pale brown in colour, faint banding in varying shades of brown, at right angles to the long axes of the crystals, is seen locally. All these spherulitic limestones yield a strong oily smell when struck and, although no separate hydrocarbons have been observed, it seems likely that the calcite owes its brown tint to disseminated bituminous matter. An appreciably stronger oily odour was noted from several much darker brown larger spherules, perhaps indicative of a higher hydrocarbon content (Young, 2006). The distinctly paler outer portions of partially weathered spherules and the generally paler buff colour of many of the long-exposed quarry faces may reflect partial leaching or degradation of included hydrocarbons.

Remnants of original bedding and perhaps joints, commonly preserved in the concretionary structures, have long been cited as evidence of their secondary nature, resulting from recrystallisation of the originally deposited limestones (Sedgwick, 1829; Garwood, 1891; Smith, 1994). More intense recrystallisation has completely eliminated such original features.

In natural exposures, weathered quarry faces and blocks seen in buildings, spaces between all of these concretionary structures are generally open voids. However, fresh samples reveal that these interstices are typically filled with un-cemented silt-grade, and commonly powdery, dolomite, accompanied by up to 25% of calcite, which is readily removed by weathering

(Smith, 1994). Twinned euhedral calcite scalenohedra up to 50 mm long were noted from within the dolomitic matrix of these rocks at the Fulwell and Carley Hill quarries, Sunderland [NZ 38 59] by Trechmann (1914) and Smith (1994) reported similar crystals in such material at Marsden and several other un-named locations.

Thin lenses and tongues of complex upward-radiate 'Christmas-tree' patterns of white blocky calcite crystals with sharply pointed feathery terminations were illustrated from laminated limestones within the concretionary limestones at Southwick [NZ 382 592] and Fulwell and Carley Hill quarries [NZ 38 59] by Smith (1994).

Limestones of the Seaham Formation exposed in coastal cliffs adjoining the harbour at Seaham [NZ 4326 4952] contain an array of spherulitic calcite concretions similar to those seen in the concretionary limestones of the Roker Formation (Smith, 1994: p. 110). Ranging from a few millimetres to >20 cm in diameter these are composed of radiating curved brown calcite crystals. They are accompanied by much smaller finely crystalline calcite spheroids, some of which have hollow centres and a weak concentric colour banding. Similar concretionary structures in partially collapse-brecciated limestones are exposed in coastal cliffs at Blackhall Rocks [NZ 472 392] (Smith, 1995).

The calcitic limestones of the Roker Formation are usually described as 'dedolomites', and the conversion was thought by Jones (1969) to have occurred by reaction with sulphate-rich solutions flushing through from the dissolution of anhydrite evaporites, probably whilst still at significant depth.

Calcareous tufa, associated with springs arising from different horizons within the Zechstein Group carbonate rocks, is known from the side of a small valley [NZ 4104 3991] at Shotton, near Dropswell; Trimdon [NZ 395 344]; and at Sharpley Burn near Burdon [NZ 389 509] (Smith, 1967, 1994). However, the area's most spectacular example of this material is at North Dock, Sunderland [NZ 4064 5852] where a stalactitic curtain of creamish white tufa >1.5 m thick and covering many square metres has encrusted a boundary wall built in about 1837 (Lane, 2014). In a shallow pool beneath this curtain, crudely rounded white 'cave pearls' up to 1 mm across have formed. Although known in the 1950s, the occurrence was re-discovered during demolition work in the 1990s and has since been incorporated into a publicly accessible feature in the Marine Activities Centre. The deposit was actively accumulating until recently, though the flow has now declined, probably as a result of local property developments and associated drainage, and this striking feature is today at risk of collapse.

Discontinuous sheets of travertine and stalactites up to 0.3 m long were recorded by Smith (1994) coating the walls of small caves and joints in the Raisby Formation in

an old quarry at Houghton-le-Spring [NZ 358 508]. Pale fawn and cream banded calcite flowstone occurs in joints in the Raisby Formation at Old Towns Quarry, Newton Aycliffe [NZ 256 245]. Similar material can be found at Wingate Quarry [NZ 372 378] and many recent quarry workings around Bishop Middleham and Cornforth.

CELESTINE, SrSO_4

Sedgwick (1829) commented briefly on the presence of celestine near Hartlepool, though without description or precise location details. No specimens are known to survive. More recently, Smith and Francis (1967) reported celestine in the Raisby Formation from several quarries on the escarpment, with no further descriptive or location details. The single confirmed onshore occurrence known to the authors is at Cornforth Quarry [NZ 320 344] where it was found rarely as very small (<2 mm) very pale blue crystalline masses associated with colourless gypsum in calcite-lined cavities in Raisby Formation dolomitic limestone (Malcolm Woodward, *personal communication*, 1996).

Smith (1994) reported small amounts of celestine dispersed through the Roker Formation of the Sunderland area, without descriptions or locations. It was found as faintly bluish white to colourless saccharoidal crystalline pockets, locally with a few indistinct crystal faces, associated with calcite in grey limestones from this horizon in drill cores recovered from the NCB North Sands No. 2 offshore Borehole drilled approximately 3 km north of Hartlepool [NZ 50227 35383] (Denys Smith, *personal communication*, 1985) (Fig. 13).



Figure 13. Bluish white celestine crystals in vein in dolomitic limestone from North Sands No. 2 Offshore Borehole, 3.3 km northwest of Hartlepool. Specimen No. BY3350B in the Brian Young Collection. The field of view is 1.5 cm across. Photo Andy Hopkirk.

CERUSSITE, PbCO_3

Bridges and Pettigrew (2013) noted thin coatings and small (<1 mm) crystals of cerussite coating heavily oxidised galena in association with baryte, calcite and the unusual 'reticulated' fluorite in cavities of Raisby Formation dolomitic limestones at Old Towns Quarry, Newton Aycliffe [NZ 256 245].

CHALCOPYRITE, CuFeS_2

Smith and Francis (1967) noted the presence of chalcopyrite in the Marl Slate Formation and the Raisby Formation at several quarries along the Magnesian Limestone escarpment, with no further details.

Lebour (1902) reported veins of chalcopyrite, weathered externally to malachite, in the Magnesian Limestone at Garmondsway, again without further description. It is likely that this refers to copper mineralisation seen in Raisby Formation limestones at Raisby Quarry [NZ 345 353] (Smythe, 1924; Smith and Francis, 1967; Dunham, 1990) where the present authors have found the mineral in detached blocks in the waste heaps. Mills and Hull (1976) reported possible chalcopyrite with baryte and dolomite, from a cavity in Raisby Formation dolomitic limestone in the NCB Windlestone 'B' Borehole [NZ 2667 2834]. The mineral was also reported by Smith (1994) as a minor constituent dispersed through the Roker Formation of the Sunderland area, with no descriptions or precise locations.

COPPER, Cu

Dunham (1990) noted native copper from Raisby Quarry [NZ 345 353] but gave no further description. Young (2001) reported rare tiny (<1 mm) irregular masses of native copper accompanied by small patches of cuprite in the assemblage of copper minerals within brecciated dolomitic limestone of the Ford Formation in the Butterknowle Fault zone exposed in Raisby Railway Cutting [NZ 3502 3492].

CUPRITE, Cu_2O

Young (2001) described small (<2 mm) patches of reddish-brown crystalline cuprite, associated with tiny masses of native copper, within the assemblage of copper minerals in brecciated dolomitic limestone of the Ford Formation in the Butterknowle Fault zone exposed in Raisby Railway Cutting [NZ 3502 3492].

DICKITE, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Dunham *et al.* (1948) recorded dickite as cream-coloured flaky coatings composed of sheaf-like or radial clusters of hexagonal plates up to 0.5 mm in diameter, on joints in an impure dolomitic mudstone in cores from between 75 and 76 m from the Hesledon Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698]. Associated minerals were baryte, carbonate-bearing fluorapatite

(collophane), fluorite, galena, sphalerite and pyrite. The precise stratigraphical horizon of this occurrence is unclear: Dunham *et al.* (1948) refer to it as “resembling the Marl Slate”, though Smith and Francis (1967) classify the entire Magnesian Limestone sequence penetrated here as belonging to the Middle Magnesian limestone (i.e. the Ford Formation).

DJURLEITE, $\text{Cu}_{1.97}\text{S}$

Young (2001) described pockets of djurleite up to 5 mm across closely associated with, and locally much altered to malachite, in Ford Formation brecciated dolomitic limestones within the Butterknowle Fault zone in the abandoned Raisby Railway Cutting near Coxhoe [NZ 3502 3492] (Fig. 14). No other copper sulphides were observed here, though chalcopyrite was noted from the workings of the adjacent Raisby Hill Quarry.

DOLOMITE, $\text{CaMg}(\text{CO}_3)_2$

Steele (1981) recorded dolomite as an authigenic mineral in the Yellow Sands Formation.

Turner *et al.* (1978) and Vaughan and Turner (1980) reported dolomite, accompanied by pyrite, in small authigenic chert lenses within the Marl Slate, though cited no locations.

Dolostones are present within all the carbonate-rich formations of the Zechstein Group and dolomite is a conspicuous, though minor component of most of the evaporite units. Smith and Francis (1967) and Smith (1994, 1995) have shown that the dolostones include well bedded fine grained earthy-looking rocks, fine-to

medium-grained crystalline dolostones and a variety of oolitic and locally pisolitic lithologies. Dolostones and dolomitic limestones, mainly from the Raisby Formation, have been worked from several large quarries for the making of refractory products.

From an old quarry near Southfield House, southwest of Shildon [NZ 2240 2479] Mills and Hull (1976) describe a fine-grained buff Raisby Formation dolostone which exhibits yellowish cream fluorescence under long wave (366.5 nm) ultraviolet light, whereas the calcite in 1 cm wide drusy cavities here displays momentary yellowish green phosphorescence. They note that this phenomenon is widespread in specimens of Raisby Formation rocks with secondary calcite in the area covered by the BGS Barnard Castle Sheet.

Sub-spherical aggregates of sand-grade dolomite rhombs were described by Smith and Francis (1967) in Ford Formation dolomitic limestones exposed in an old quarry at South Hetton [NZ 3759 4507]. These authors also described distinctive dolomitised limestones composed of sheaf-like or semi-radial aggregates of platy dolomite crystals up to 5 mm long which they termed ‘felted texture’, within dolomitised limestones of the lagoonal facies of the Ford Formation at numerous locations. However, Jones (1969) found that in many instances calcite rather than dolomite was the main carbonate mineral represented by this texture which he interpreted as a replacement of gypsum or anhydrite.

As noted above, pale yellow powdery dolomite fills interstices between the calcite concretions in the concretionary limestones of the Roker Formation in fresh examples of these rocks, though it is readily removed by weathering.

Perhaps surprisingly, despite the abundance of both dolomite and magnesium-rich calcite in these rocks, dolomite appears to be rare in cavity fillings or in any of the epigenetic mineralisation. However, Fowler (1943) recorded small flesh-coloured aggregates of dolomite crystals lining cavities in Raisby Formation limestones from boreholes in the Fishburn area and Smith and Francis (1967) noted dolomite, accompanied by hematite, coating joint faces on thickly-bedded dolomitic limestone of this formation at High Moorsley Quarry [NZ 334 455], though without further description. Mills and Hull (1976) reported dolomite, accompanied by baryte and possible chalcopyrite filling cavities in Raisby Formation dolomitic limestone in the NCB Windlestone Borehole [NZ 2667 2834].

Mesh-like networks of fine-grained pale buff dolomite (‘chicken wire’ texture) have been widely reported from gypsum and anhydrite in both the Hartlepool and Billingham Main Anhydrite formations, as for example in the Hurworth Place Borehole [NZ 29023 09532] (Smith and Moore, 1973).

Dolomite, accompanied by gypsum and locally baryte, is a minor constituent of siltstones and mudstones

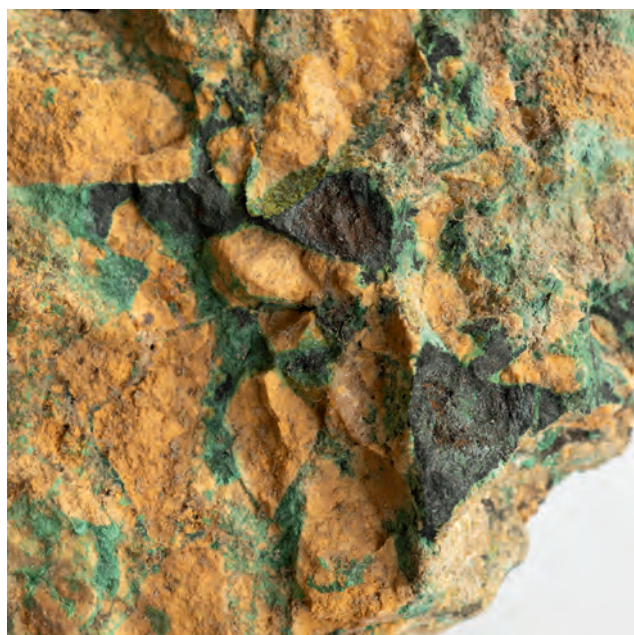


Figure 14. Massive grey djurleite with malachite staining in brecciated dolomitic limestone. Raisby Railway Cutting. Specimen No. BY4130 in the Brian Young Collection. The field of view is 3 cm across. Photo Andy Hopkirk.

in the Roxby Formation, cut in brine wells in the Greatham area [NZ 49 27] (Fowler, 1956).

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

Epsomite was reported from the Permian rocks of northeast England as a minor constituent of post-mining efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227] (Raymond, 1959).

It was briefly noted as granular efflorescent crusts on exposures of Ford Formation dolomitic limestones at Hesleden Dene, Peterlee [NZ 443 373] by Bridges and Young (1998). Young (2008b) described the mineral from Marsden Old Quarry Local Nature Reserve, South Shields [NZ 3965 6450] where it was found, together with gypsum, as ephemeral crystalline crusts covering several square metres of thinly bedded concretionary dolomitic limestones of the Roker Formation (Fig. 15). Similar efflorescent crusts were also reported from dolomitic limestones of the Ford Formation as, for example, at Aycliffe Quarry [NZ 288 223] and the Seaham Formation at Seaham Harbour [NZ 433 493]. With the exception of that at Billingham Mine, these are all characteristic of the mineral's common occurrence as ephemeral efflorescences in sheltered places on outcrops of dolomitic rocks (Gaines *et al.*, 1997).

The presence of efflorescent crusts of epsomite on medieval masonry at Durham Cathedral has been cited as evidence that at least some of the medieval mortar used here was made from the magnesium-rich Permian limestones of eastern County Durham rather than the mainly magnesium-free limestones of the North Pennines (Jackson and Young, 2016).

FLUORITE, CaF_2

Although detrital fluorite was reported from the Yellow Sands Formation in Yorkshire by Versey (1925), it has not been recorded from the area reviewed here.



Figure 15. Efflorescent crusts of epsomite on dolomitic limestone at Marsden Old Quarry, South Tyneside. The hammer shaft is 30 cm long. Photo Brian Young.

Fowler (1943) described fluorite from cored coal exploration boreholes drilled in about 1940 between Rushyford [NZ 284 288] and Fishburn [NZ 365 320] where it was abundant in the topmost 7 m of the Raisby Formation limestones in all four boreholes and ranged in colour from colourless to pale yellow, amber, violet, brown, black and cream. Of particular note is his description of a curious crystal morphology in which thin tabular plates occur in rectangular contact with one another creating what he referred to as 'echeloned' parallel growth. Fowler's description from an examination by J. Phemister of material from the hole at Rushyford deserves to be quoted:

"... the brown fluorite occurs occasionally as cubes, but is mainly developed as hollow octahedra or hopper crystals in which platy septa, parallel to the principal cubic planes, are prominent. The three-sided cups formed by these septa are occupied by small cubes of fluorite which are orientated in conformity with the walls of the cup ..." [In one cavity the mineral] "... forms small diversely orientated cubes on free surfaces of the cavity but the main fluorite infilling shows simultaneous reflections from a large number of small faces indicating a general tendency to uniform crystallographic orientation ...".

This morphology is very similar to the form reported from Old Towns Quarry, Newton Aycliffe [NZ 256 245], approximately 4 km southwest of Rushyford, by Bridges and Pettigrew (2013) who, rather surprisingly, appear to have been unaware of Fowler's descriptions (Fig. 16). Elsewhere in these cores Fowler (1943) notes fluorite as shapeless areas which he interprets as fine-grained replacements of the host limestone, as a white to cream-coloured powdery or as earthy masses locally with an



Figure 16. Colourless 'reticulated' fluorite crystals in cavity in dolomitic limestone from Old Towns Quarry, Newton Aycliffe. Specimen No. BY5502 in the Brian Young Collection. The field of view is 1.5 cm across. Photo Andy Hopkirk.

internal radiate structure, and as oval or circular cavity fillings composed of what he referred to as a 'horny' texture composed of finely granular crystalline fluorite, resembling anhydrite. More recently this form of fluorite, has been seen by one of the authors (FWS) in a road cutting [NZ 2550 2925] near Coundon, accompanied by pink and white 'Ferryhill Type' baryte, and again in excavations for the foundations of the new Primary School at Kirk Merrington [NZ 2630 3115] (Fig. 17).

In their description of 'reticulated' fluorite from cavities in Raisby Formation dolomitic limestones at Old Towns Quarry, Bridges and Pettigrew (2013) observed that although most examples were colourless, some exhibited a very pale yellow tinge, locally with a few purple spots, and a number of specimens exhibited a strong chocolate-brown colour. These authors speculated that interference in the crystallisation of the fluorite by a pre-existing mineral, perhaps gypsum, within the cavities may explain this strange morphology, though they provided no definitive evidence to support this and the origin of this odd morphology remains unexplained. This curious form is unknown in fluorite from the nearby Northern Pennine Orefield.

In the Ten O'Clock Barn No. 2 Borehole, near Butterwick [NZ 3916 3035] Fowler (1956) reported abundant fluorite mineralisation within a 12 m thick zone of Raisby Formation dolostones. Much of the fluorite here was described as forming threads and veinlets of a pale grey colour, locally with a few pale purple spots. Massive crystalline fluorite, apparently replacing dolomite, was also found, in places accounting for almost the full thickness of the cores (13 cm).



Figure 17. Colourless 'reticulated' fluorite crystal in a cavity in dolomitic limestone from excavations for the foundation of Kirk Merrington School, Kirk Merrington. Specimen No. BY9800 in the Brian Young Collection. The field of view is 2.5 cm across. Photo Andy Hopkirk.

Faint purple or violet fluorite was encountered with baryte in a thin crack in Raisby Formation dolomitic limestones at a depth of 65 m in the Hesleden Dene No. 3 Borehole [NZ 4660 3703] (Fowler, 1956). The manuscript log of Cole Hill Farm Borehole [NZ 4229 3110] records "limestone with abundant baryte, fluorite, black blende, and galena" from 115 to 121 m. Rare dark purple fluorite has been seen by one of the authors (FWS) lining cavities ca. 6 m above the Marl Slate at Middridge Quarry [NZ 247 255].

Fowler (1956) described thin lenses of fluorite up to 6 cm long and roughly circular nodules up to 3 cm in diameter from the dolomitic limestones of the Raisby Formation at Chilton Quarry, Ferryhill [NZ 3008 3137]. He noted that much of the mineral here occurred in a massive glassy form though with occasional pale amber coloured cubes in open cavities. One of the authors (BY) has observed very pale yellow cubes up to 1 cm across together with a few which exhibit a markedly thin plate-like form reminiscent of some of those described by Fowler (1943) and Bridges and Pettigrew (2013), though the reticulate form described by these authors has not been seen at Chilton. Thin sections of a 'grey rock' found by Fowler (1956) in contact with massive glassy fluorite at Chilton Quarry revealed this to consist of fine-grained fluorite in spherulitic growths up to 1.5 mm in diameter (Kingsley Dunham, *personal communication* in Fowler, 1956). Both Fowler (1956) and Hirst and Smith (1974) drew attention to the inconspicuous form and colour of much of this fluorite, pointing out that it was easily overlooked. Hirst and Smith (1974) also noted that here and elsewhere in the Ferryhill area fluorite concentrations within the host dolostone may reach as much as 3% by volume.

Hirst and Smith (1974) described a very finely crystalline form of fluorite in semi-radiate botryoidal aggregates within cavities of the Raisby Formation limestones (Fig. 18) from Rough Furze Quarry, approximately 2 km northeast of Chilton Quarry. When fresh these were black, though they faded to a pale grey colour on weathering. Upon crushing this material produced a strong oily odour, suggesting that the colour might be due to disseminated hydrocarbons. Specimens of this form of fluorite, collected here by one of the present authors (BY) from cavities in the limestone, show faint colour banding in shades of greyish brown with an overgrowth of rhombic crystals of white calcite up to 5 mm thick.

Dunham *et al.* (1948) recorded fluorite, though without description, in association with baryte, carbonate-bearing fluorapatite (collophane), dickite, galena, pyrite and sphalerite in dolomitic mudstone cores recovered from the Hesleden Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698]. As noted in the foregoing text, the precise stratigraphical horizon of this occurrence is unclear.

From two boreholes, the sites of which are unrecorded, in West Hartlepool, Trechmann (1941)



Figure 18. Greyish brown botryoidal fluorite encrusted with white calcite from Rough Furze Quarry, Ferryhill. Specimen No. BY4079 in the Brian Young Collection. The field of view is 1.5 cm across. Photo Andy Hopkirk.

recorded brown to violet fluorite in fractures and cavities in pisolitic and oolitic dolostones, likely to be within the Roker Formation, together with cores of ‘secondary’ fluorite in ooids of Roker Formation dolostones in the vicinity of Blackhall Rocks (Trechmann, 1913). Also at West Hartlepool, Fowler (1956) reported irregular grains of fluorite, together with a mineral assumed to be sphalerite, from a 44 m deep water well in Villiers Street. More recently one of the authors (BY) has also found granular crystalline fluorite, similar to that at Marsden Bay (see below), though of a paler purple colour and without any obvious bituminous content, as rare discontinuous lenses up to 7 cm across and around 7 mm thick within pale buff crystalline Roker Formation limestones at Hart Quarry, near Hartlepool [NZ 477 344]. Deep purple fluorite occurs within ooid and pisoid moulds in Roker Formation dolomites exposed at the Headland, Hartlepool [NZ 530 340] (M. Mawson, *personal communication*).

The manuscript log of North Sands Borehole [NZ 5027 3534] includes a note by Denys Smith of pale mauve and pink translucent minerals, that he thought were fluorite, baryte and calcite, making up 5% of the cuttings from between 36.6 and 38.1 m. Fluorite was reported by Smith (1994) as a minor constituent dispersed through rocks of the Roker Formation of the Sunderland area, though cited no locations. However, indistinct patches of fine-grained granular crystalline deep bluish purple fluorite up to 5 cm across, were noted within chert nodules in these rocks in the sea cliffs at Marsden Bay [NZ 3975 6515] (Brian Young, *personal communication* in Dunham, 1990) (Fig. 19). The colour resembles that of ‘Blue John’ and like the Derbyshire mineral, this fluorite emits a noticeable bituminous odour when struck. The cliffs at the northern end of

Marsden Bay [NZ 397 652] display a sequence of alternating turbidite and hemipelagic dolostone beds. The uppermost parts of the turbidites contain flake-like fragments eroded from hemipelagic units. These have commonly been leached and the resultant 1 to 5 mm voids filled by brownish glassy fluorite in irregular zones between 5 and 30 cm in thickness.

Fluorite and gypsum form part of the cement of sandstone specimens, assumed to be part of the Roxby Formation, recovered from brine wells in the Greatham area (Fowler, 1956).

FLUORAPATITE, $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$

Dunham *et al.* (1948) identified a brown carbonate-bearing fluorapatite, which is described as collophane, intergrown with sphalerite in a concretion or fissure filling in dolomitic mudstone cores recovered from between 75 and 76 m in the Hesledon Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698]. Associated minerals were baryte, dickite, fluorite, galena, pyrite and sphalerite.

Carbonate is widely recognised an important *T*-anion in apatite-supergroup minerals (Pan and Fleet, 2002) but it is never dominant and all carbonate-apatite species names have been discredited (Pasero *et al.*, 2010).

GALENA, PbS

Most descriptions of the Marl Slate and its European correlative the Kupferschiefer refer to the common occurrence within it of galena, pyrite and sphalerite, (e.g. Deans, 1950; Hirst and Dunham, 1963, Jones and Hirst, 1969), though few comment on the appearance, mode of occurrence or locations of these minerals.

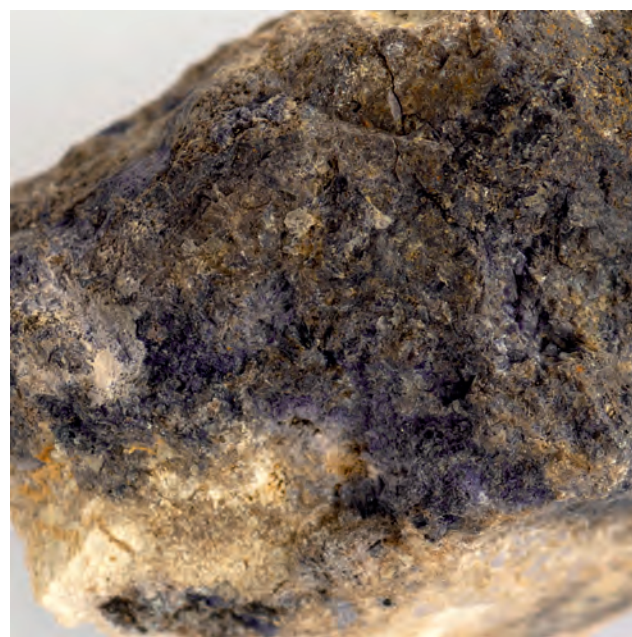


Figure 19. Deep purple granular crystalline bituminous fluorite from Marsden Bay, South Tyneside. Specimen No. 3314 in the Brian Young Collection. The field of view is 2.5 cm across. Photo Andy Hopkirk.

Fowler (1943) described small amounts of galena, locally accompanied by sphalerite, lining minute joints and forming films on bedding planes in the Marl Slate and lowermost few metres of the Raisby Formation limestones in boreholes near Rushyford and Fishburn, and in the Whin Houses Borehole, near Butterwick [NZ 3997 3058]. It is also recorded in the log of Elwick No.1 Borehole [NZ 4531 3117] a metre above the Marl Slate, and similarly at Tinkler's Gill Borehole [NZ 4157 3054], where the Marl Slate itself is described as showing finely crystalline galena and sphalerite on bedding planes and joints. Also from the Marl Slate Formation, Mills and Hull (1976) reported galena, locally accompanied by sphalerite, replacing quartz within dolomitic mudstones at Thickley Quarry, East Thickley [NZ 2407 2565]. They also note galena and pyrite on bedding planes and in veins in the NCB Eldon Moor No. 186 Borehole, Old Eldon [NZ 2676 2734]. North of the River Tyne, lustrous cleavages of coarse-grained galena up to 2 cm across and up to 3 mm thick, in places intergrown with mid brown sphalerite and a little massive pyrite, coating joint surfaces in thinly bedded bituminous siltstone were reported from temporary excavations in the Marl Slate Formation at Marden Pumping Station, Whitley Bay [NZ 3547 7135] (A. Newman, *personal communication*, 1986).

Winch (1817) and Haselhurst (1911) observed galena in veinlets in the Magnesian Limestone at Whitley Bay though gave no descriptions or more precise locality information. Fowler (1956) reported that galena was found within the baryte-fluorite mineralisation at Chilton Quarry, Ferryhill [NZ 3008 3137], where it was sufficiently abundant to have been employed by the quarrymen in making crystal radio sets. He also records an anonymous report of a 5 cm wide vein of galena in the lower part of the face of Raisby Formation dolomitic limestones at the nearby Bishop Middleham Quarry, now a local nature reserve. Smith and Francis (1967) noted the presence of galena, accompanied by baryte, in Raisby Formation dolomitic limestones at Ferryhill Cliff Quarry, now part of Ferryhill Carrs Nature Reserve [NZ 300 330] and in several small exposures nearby, though neither the mode of occurrence nor the form of the minerals were described. Twinned cubic crystals of galena up to 12 mm across have been found embedded in fine-grained white baryte at Rough Furze Quarry, Thrislington [NZ 319 325]. Polysynthetic cubes of galena in masses up to 7 cm across, associated with a little baryte and fluorite, have been found in Raisby Formation brecciated dolomitic limestone at Old Towns Quarry, Newton Aycliffe [NZ 256 246] where Bridges and Pettigrew (2013) noted the presence of cerussite-coated galena. Minor amounts of weathered galena are present with fluorite and baryte in the now-overgrown A689 road cutting at Coundon [NZ 2550 2925].

Dunham *et al.* (1948) recorded galena, though without description, in association with baryte, carbonate-bearing fluorapatite (collophane), dickite, fluorite, pyrite and sphalerite in dolomitic mudstone cores recovered from the Hesledon Dene No. 2 water borehole,

near Castle Eden [NZ 4654 3698]. The precise stratigraphical horizon of this occurrence is unclear, but the mineralised rock is described as "Marl Slate-like" and extends from depths of 71 to about 85 m. D.B. Smith's manuscript notes on Fowler's core specimens from the Hesledon Dene No. 3 Water Borehole record "traces of galena" present in samples from 59 and 62 m and describe a sample from 63 m as:

"unusually heavy and bears films of galena and blende. The bottom and top of the 3-inch specimen are bounded by thin bands of siltstone with a concentration of galena at the inter-boundaries".

The manuscript log of Cole Hill Farm Borehole [NZ 4229 3110] records limestone with baryte, fluorite, blende and galena" from 115 to 121 m.

Galena was reported by Smith (1994) as a minor constituent dispersed through the Roker Formation of the Sunderland area, though no descriptions or locations are given.

Smith and Francis (1967) and Dunham (1990) refer to the presence of galena in brecciated dolomites in a southern splay of the Blackhall Fault exposed in the coastal cliffs at Blackhall Rocks [NZ 4707 3918] where a trial adit of an unknown date was driven from the beach. Although the adit is no longer visible, the fault is exposed as a belt of intensely fractured dolomites at least 1 m wide within the Roker Formation in which a few vertical to sub-vertical bands of white chalky baryte up to around 4 mm wide are sparsely scattered. Following a storm, about 20 years ago, the fault zone was exposed on the foreshore a few hundred metres to the southeast where it contained scattered galena cubes up to 5 mm across within white chalky baryte (Fig. 20). The exposure has not been visible since as it was subsequently covered by beach sand (M. Mawson, *personal communication*).



Figure 20. Cut surface showing euhedral galena crystals embedded in white baryte in brecciated dolomite from Blackhalls Rocks, Blackhall. One pound coin for scale. Photo Brian Young.

GARNET

Garnet of unspecified composition was recorded as a constituent of the heavy minerals suite within the Yellow Sands Formation from West Boldon [NZ 349 602] and Claxheugh, Sunderland [NZ 363 575] by Pryor (1971).

GOETHITE, FeO(OH)

Iridescent coatings of presumed goethite, described as ‘limonite’, on fluorite and calcite were reported from cavities in Raisby Formation limestones in the Whin Houses Borehole, near Butterwick [NZ 3997 3058] by Fowler (1943) and black goethite pseudomorphs after pyrite were described from Chilton Quarry, Ferryhill [NZ 3008 3137] (Fowler, 1956). A few lustrous dark brown goethite pseudomorphs after spear-shaped crystals and aggregates of marcasite embedded in Raisby Formation dolomitic limestone were collected by one of the authors (BY) from High Moorsley Quarry, Hetton-le-Hole [NZ 334 455] (Fig. 21). Tiny needle-like inclusions of goethite (<10 µm) in calcite crystals were described from brecciated Raisby Formation limestones at Raisby Quarry [NZ 345 353] by Lee and Harwood (1989).

‘Limonite’ was recorded by Smythe (1924), Dunham (1990), and Smith and Francis (1967) from the copper mineralisation within the Raisby Formation at Raisby Quarry [NZ 345 353].

GYPSUM, CaSO₄·2H₂O

Woolacott (1919) noted the occurrence of the gypsum variety selenite within cavities in the limestones at Raisby Quarry [NZ 345 353] and more recently,



Figure 21. Goethite pseudomorphs after marcasite on dolomitic limestone from High Moorsley Quarry, Hetton-le-Hole. Specimen No. BY6123 in the Brian Young Collection. The field of view is 2 cm across. Photo Andy Hopkirk.

H. Wilkinson (*personal communication*, 2017) reported rounded masses of finely crystalline white gypsum up to 25 mm across partially filling calcite-lined cavities in Raisby Formation dolostones here. Anhydral crystals of colourless ‘selenite’ up to 45 mm across partly fill calcite-lined cavities in Raisby Formation limestones at Cornforth Quarry [NZ 320 344] (Fig. 22). In most of these specimens the gypsum shows signs of partial dissolution. A borehole near Wynyard [NZ 4166 2469] displayed gypsum as radiating clusters of needles, and thin fibrous veins in the Ford Formation (Jones, 1969).

Pseudomorphs after gypsum have been replaced volume for volume by dolomite, and then by calcite, and rarely minor pyrite, forming the ‘felted texture’ frequently found in the lagoonal limestones of the Ford Formation (Jones, 1969). Trimdon Grange Quarry [NZ 361 353] displays particularly good examples of this, where the depositional environment must have been almost sabkha-like, and the former “proportion of gypsum may have ranged from 10 to as much as 90%” (Smith, 1995).

Jones (1969) noted that “sulphates occur in the (Seaham Formation) throughout Durham” where in granular beds gypsum occupies the interstices, and elsewhere takes the form of scattered porphyroblastic blebs, replacement patches, joint and bedding-plane coatings, and thin fibrous beds, of secondary origin.

Tabular porphyroblasts of selenite up to around 7 mm long were described by Smith and Francis (1967) from cores of Hartlepool Anhydrite recovered from offshore boreholes in the Hartlepool area (Fig. 3).



Figure 22. Colourless cleavages of gypsum variety selenite in a calcite-lined cavity in dolomitic limestone from Cornforth Quarry, Cornforth. Specimen No. BY7127 in the Brian Young Collection. The field of view is 3.5 cm across. Photo Andy Hopkirk.

Young (2005) described a glacial erratic boulder of pale greyish white porphyroblastic alabastrine gypsum, 1.3 m across, that fell to the beach from boulder clay in the adjoining cliffs north of Beacon Point, Shippersea Bay [NZ 4435 4545]. It was interpreted as having been derived from an exposure of the Hartlepool Anhydrite several kilometres to the east and now beneath the North Sea (D.B. Smith, *personal communication* in Young, 2005). As it is very unusual to encounter a water-soluble rock of this sort as a glacial erratic, its survival here must reflect the impervious nature of the surrounding boulder clay. The boulder was completely destroyed by dissolution in sea water within months of its falling to the beach.

The outcrop zones of both the Hartlepool and Billingham anhydrites between Billingham and Darlington are largely hydrated to gypsum with a karstified rockhead surface. Rapid thickness variations from 8 to 20 m have been proved, in several boreholes around Darlington, over short distances (Cooper and Gordon, 2000). Much of the gypsification is believed to have occurred during interglacial periods when there was an abundance of water flowing over exposed surfaces. Minor dissolution does continue at the present day but generally only where boulder clay is thin or absent. Gypsum always passes down-dip to primary anhydrite. Although an area of shallow and consistent gypsum was explored by ICI around Little Stainton in the 1950s and 1960s as a potentially mineable deposit, it has not been worked.

In the Hurworth Place Borehole, south of Darlington [NZ 29023 09532], the Billingham Main Anhydrite, here 5.36 m thick, is almost completely hydrated to gypsum, though with some residual masses of anhydrite within its topmost 3 m (Smith and Moore, 1973). Fine-grained alabastrine gypsum is the dominant form, with some selenite porphyroblasts and a few veins of fibrous satin spar.

Large plates of colourless selenite >7 cm across were found within the Billingham Main Anhydrite at Billingham Anhydrite Mine [NZ 477 227] (Fig. 23). Gypsum also occurs in veins of up to 20 cm width of fibrous satin spar cross-cutting the anhydrite seam. Some loose blocks of anhydrite at the site of the former mine stockpile contain grey swallow-tail gypsum porphyroblasts up to 1 cm long that appear to be from 'as mined' rock and presumably originated from workings approaching the rockhead or some other source of water infiltration. Raymond (1959) recorded gypsum as a minor constituent of efflorescent crusts, formed by seepage of groundwaters, in the underground workings.

Fine-grained salmon-pink alabastrine gypsum within the Sherburn Anhydrite Formation was cut in an up-borehole drilled from the workings of Billingham Anhydrite Mine (D.B. Smith, *personal communication*, 1984).

HALITE, NaCl

Smith (1994) noted that halite was found filling narrow veins in Roker Formation cores recovered from a number of offshore boreholes.

In the onshore area beneath Teesside a bed of halite around 45 m thick was unexpectedly discovered immediately above the Billingham Main Anhydrite at depths of between 274 and 366 m below surface during drilling for groundwater in 1859 (Marley, 1863; Northolt and Highley, 1973). Originally named the 'Middle Halite' and now known as the Boulby Halite, this extends beneath a large area of east Yorkshire and the North Sea where its thickness increases significantly. Beginning in 1882 it was extensively worked by controlled solution mining both as a feedstock for the chemical industry and for the making of table salt until 2002. The large resulting solution cavities are today used for oil storage (Stone *et al.*, 2010).

Abundant lenses and patches of colourless granular halite, up to 80 mm long and 5 mm thick, were encountered within gypsum in the Billingham Main Anhydrite of the Hurworth Place Borehole, south of Darlington [NZ 29023 09532] (Smith and Moore, 1973). Raymond (1960) reported the presence of a thin bed of halite "a few feet" below the top of the Billingham Main Anhydrite at Billingham Anhydrite Mine [NZ 477 227] and also described intrusive masses of halite-anhydrite rock projecting downwards from the Boulby Halite into the anhydrite seam worked here. Halite was also reported by Raymond (1959) as a major constituent of post-mining efflorescent crusts, formed by seepage of groundwaters, in the underground workings of the Billingham Anhydrite Mine.

Smith (1993) described unusual alate (winged) halite crystals, distinguished by remarkably flared corners in silty mudstone cores from the Rotten Marl Formation recovered from several boreholes and brine wells in the Seal Sands area of lower Teesside [NZ 51 24 and NZ 51 25] (Fig. 24). These are typical of the displacive haselgebirge halite

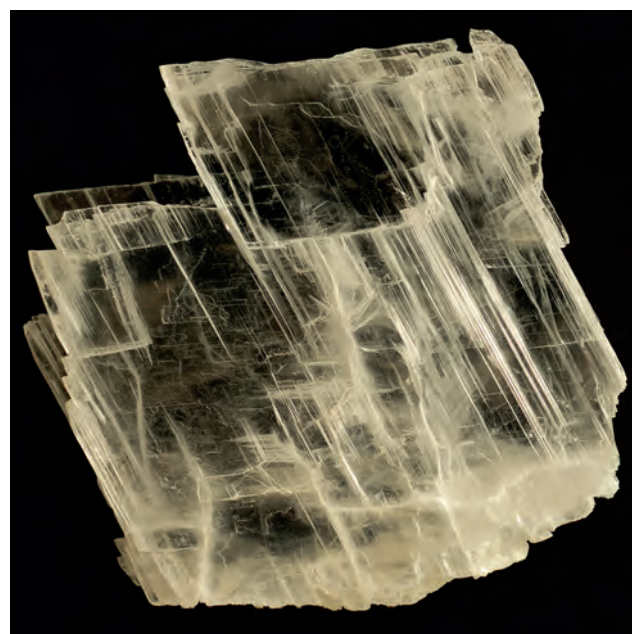


Figure 23. Colourless cleavage plate of gypsum variety selenite from the Billingham Anhydrite Mine, Billingham. Specimen no. BY9344 (6 cm across) in the Brian Young Collection. Photo Andy Hopkirk.

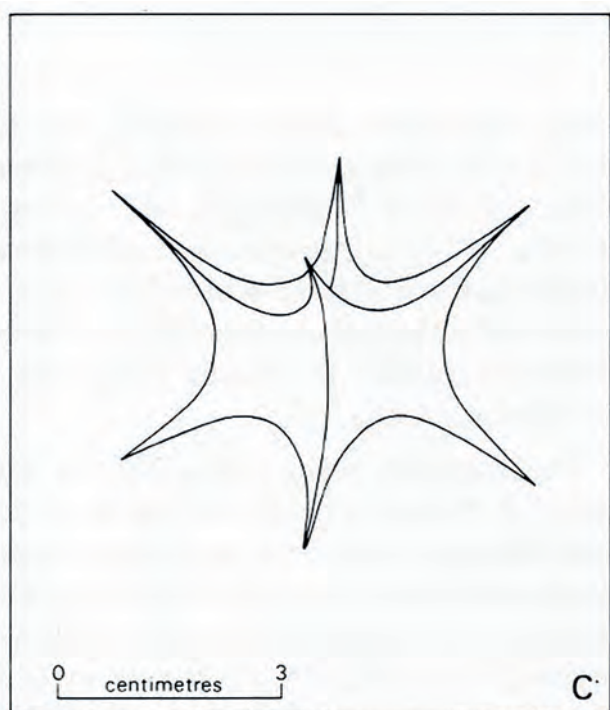


Figure 24. Outline sketch of an alate halite crystal from the Rotten Marl of the Teeside area. [Figure 1 C. reproduced from Smith (1993) with the permission of the Yorkshire Geological Society].

described from the Zechstein sequence of northeast Yorkshire by Smith (1971), where they are interpreted as the result of crystallisation during a late stage in the compaction of the enclosing sediment.

HEMATITE, Fe_2O_3

Anderson and Dunham (1953) attributed widespread reddening of Coal Measures rocks with hematite beneath the sub-Permian unconformity to sub-aerial weathering during late Carboniferous to early Permian times. A narrow pale grey zone which commonly lies between these red beds and the unconformity was interpreted by Smith and Francis (1967) as the result of bleaching by reducing waters of the advancing Zechstein Sea. These features are clearly exposed on the north bank of the River Wear near Castletown [NZ 357 576] (Smith, 1994).

Smith and Francis (1967) recorded hematite, accompanied by dolomite, on joint faces of Raisby Formation dolomitic limestones at High Moorsley Quarry [NZ 334 455], though they gave no descriptions of the mineral. Mills and Hull (1967) describe sparse discrete particles of hematite in a brecciated dolostone within the Raisby Formation exposed in an old quarry ESE of Elm Grange, southwest of Heighington [NZ 2325 2161] and also note the presence of hematite granules within an exposure of Raisby Formation dolostones on the south bank of the River Tees near Piercebridge [NZ 2093 1544].

ILLITE, $\text{K}_{0.65}\text{Al}_{2.0}\square\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}(\text{OH})_2$

Mills and Hull (1976) noted the presence of wisps of illite within the Marl Slate Formation at Eldon Drift

Mine [NZ 2526 2821]. It is the predominant phyllosilicate mineral in the Marl Slate (Hirst and Dunham, 1963) and the Magnesian Limestone (Jones, 1969).

Ilsemanite, $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$

Unusual blue post-mining efflorescent crusts on the walls of underground workings at Billingham Anhydrite Mine [NZ 477 227] were tentatively identified as ilsemanite by Raymond (1959). The source of the molybdenum was not established though the possibility of its derivation from chrome molybdenum drilling bits discarded in the workings was canvassed but dismissed as unlikely. However, in the light of the tentative identification of traces of molybdenite in these crusts (see below) and the suggested possible presence of powellite from mineralised Raisby Formation limestones in the Whin Houses Borehole, near Butterwick [NZ 3997 3058] (see below) the possible presence of molybdenum in these rocks is intriguing. Traces of molybdenum in the form of wulfenite have long been known from the Magnesian Limestone of Nottinghamshire (Deans, 1961) and more recently Smith (1981) has recorded molybdenum concentrations of up to 385 ppm in the Marl Slate of northeast England. It is therefore conceivable that concentrations of molybdenum, sufficient to form discrete minerals, may exist very locally within the area's Permian rocks.

KAOLINITE, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Microgranular kaolinite was reported as a constituent of the meagre matrix of the Yellow Sands Formation in the Tynemouth area (Land, 1974).

K-FELDSPAR

Land (1974) noted the presence of grains of orthoclase and microcline-microperthite within the Yellow Sands and Waugh (1978) reported authigenic overgrowths of K-feldspar of unspecified composition on quartz grains from these same rocks.

LEPIDOCROCITE, $\text{Fe}^{3+}\text{O}(\text{OH})$

Lepidocrocite was recorded by Raymond (1959) as a minor constituent of gypsum-rich rusty brown post-mining efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

Magnetite, $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$

Mills and Hull (1970) reported magnetite, accompanied by baryte and traces of sphalerite from a dolostone bed within the Raisby Formation exposed in an old quarry southwest of Heighington [NZ 2325 2161], though gave no other information on the occurrence or appearance of the mineral or the method of its identification. As this appears to be an unlikely situation to find magnetite, the report cannot be confirmed and should be viewed with caution.

MALACHITE, $\text{Cu}_2^{2+}(\text{CO}_3)(\text{OH})_2$

Both Smythe (1924) and Dunham (1990) commented on the presence of malachite accompanied by chalcopryrite and ‘limonite’ within fissures in the Raisby Formation at Raisby Quarry [NZ 345 353], though neither author gave further details. Smith and Francis (1967) also noted the presence of malachite and chalcopryrite at several quarries along the Magnesian Limestone escarpment, especially at Raisby Hill, also without details. Young (2001) described malachite as compact crystalline crusts and sprays of very small radiating acicular crystals within Ford Formation brecciated dolomitic limestone in the Butterknowle Fault zone at the abandoned Raisby Railway Cutting near Coxhoe [NZ 3502 3492] (Fig. 25) and also noted malachite encrustations on loose fragments of chalcopryrite collected from the adjacent Raisby Quarry [NZ 345 353].

Trechmann (1952) recorded malachite coating and impregnating cracks in magnesian limestone pebbles “in place since they were deposited” in a gravel working at Claxton, west of Greatham. Although the precise location is not given, the most modern BGS mapping (British Geological Survey, 1987) confirms the presence of glacial sand and gravel deposits around NZ 480 277. The occurrence, together with Trechmann’s note, is intriguing. As this lies above the mapped outcrop of the major east–west trending Greatham Fault it is tempting to speculate on the role of this fracture as a source of mineralisation. However, the occurrence is separated from bedrock by a substantial thickness of superficial deposits, almost certainly greater than Trechmann’s estimate of 13.7 m, and in the absence of evidence of any other mineralisation associated with this fracture, this



Figure 25. Cellular crystalline crust of malachite on dolomitic limestone from the Raisby Railway Cutting. Specimen No. BY4135 in the Brian Young Collection. The field of view is 5.5 cm across. Photo Andy Hopkirk.

seems unlikely. An anthropogenic origin involving some form of contamination is possible, but the occurrence remains unexplained. No samples of the material are known.

MANGANESE OXIDES

Roker Formation dolomites, exposed in the sea cliffs above the Gin Cave at Blackhall Rocks [NZ 4783 3897] have recently been found to exhibit patchy black mineralisation along joints and bedding planes over an area of several square metres above the northernmost entrance of the cave. Although mostly inaccessible from the beach the mineralisation can be seen in several large waterworn fallen blocks. Preliminary examination of samples taken from these suggest the black material may be an as yet unidentified manganese oxide mineral, perhaps accompanied by minor amounts of goethite, calcite and baryte (M. Mawson, *personal communication*). The occurrence is currently the subject of research and the nature and likely origins of the mineralisation await explanation.

MARCASITE, FeS_2

Bridges and Pettigrew (2013) suggested that tiny groups of flaky, iron-stained, crystals associated with pyrite within some fluorite-bearing cavities in Raisby Formation dolomitic limestones at Old Towns Quarry, Newton Aycliffe [NZ 256 245] may be marcasite, though they did not confirm its identity.

The presence of goethite pseudomorphs after marcasite at High Moorsley Quarry, Hetton-le-Hole [NZ 334 455] has been noted above.

Molybdenite, MoS_2

Molybdenite was tentatively identified by Raymond (1959) as a minor constituent of the blue post-mining ilsemanite-rich efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227]. The source and possible significance of the presence of molybdenum is discussed above in the description of ilsemanite.

NATROJAROSITE, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$

Fissures in collapse brecciated dolomitic limestones of the Roker Formation exposed in coastal cliffs at Hive Point [NZ 4433 4588] locally contain accumulations of pyrite-rich colliery spoil. Adjacent to these, open voids formed by in-weathering of blocks and open bedding planes within the breccia, contain compact masses of rather hard pale lemon yellow natrojarosite up to 10 mm across (Young *et al.*, 2008). The mineral here is part of an assemblage of iron sulphate and associated minerals, including sideronatrite (see below) actively forming by reaction of sea water with the abundant spreads of colliery spoil which remain on the adjoining beaches.

Powellite, CaMoO_4

Crushed samples of ‘limonite’ from Raisby Formation limestones in the Whin Houses Borehole, near Butterwick [NZ 3997 3058] contained “... very rare octagonal tablets of a greenish-yellow uniaxial mineral of very high refractive index and moderately low birefringence ...” which J. Phemister (*personal communication* in Fowler, 1943) suggested may be powellite or scheelite. As no further analytical evidence was provided the report cannot be confirmed. The source and possible significance of the presence of molybdenum is discussed in the description of ilsemanite.

PYRITE, FeS_2

Land (1974) noted the widespread occurrence of narrow veins containing pyrite, together with calcite and ankerite, in the Permian rocks of the area covered by BGS Sheet 15 (Tynemouth), though without descriptions, locations, descriptions or stratigraphical horizons.

Most descriptions of the Marl Slate Formation refer to the common occurrence within it of pyrite, galena and sphalerite. According to Smith (1994), citing Deans (1950), Love (1962) and Hirst and Dunham (1963), pyrite is the main sulphide disseminated through the Marl Slate, mainly as framboidal, spherical aggregates typically around 8 μm across. Small lenses of pyrite, associated with chalcedony and dolomite, have also been reported (Turner *et al.*, 1978; Vaughan and Turner, 1980).

Reports of pyrite at specific locations within this unit include those of Mills and Hull (1976) from Eldon Drift Mine [NZ 2526 2821] and the NCB Eldon Moor No. 186 Borehole, Old Eldon [NZ 2676 2734]. A few small anhedral masses of pyrite <2 mm across accompany galena and sphalerite on joint surfaces in thinly bedded bituminous siltstone collected from temporary excavations in the Marl Slate Formation at Marden Pumping Station, Whitley Bay [NZ 3547 7135] (A. Newman, *personal communication*, 1986). Fowler (1943) commented on the common occurrence of pyrite filling cavities in thin platy, limestones, interpreted here as part of the Marl Slate, and as small grains on calcite crystals which line joints in the overlying Raisby Formation limestones cut in boreholes in the Rushyford and Fishburn areas.

At Old Towns Quarry, Newton Aycliffe [NZ 256 245] Bridges and Pettigrew (2013) described small irregular, brown-stained crystals of pyrite up to 2 mm across, locally accompanied by thin crystals tentatively suggested to be marcasite, from some fluorite-bearing cavities in Raisby Formation dolomitic limestones. The mineral was also reported in association with baryte from interstices in Raisby Formation autobrecciated dolomitic limestone in the NCB Windlestone Borehole [NZ 2667 2834] (Mills and Hull, 1976). Dunham *et al.* (1948) recorded pyrite, though without description, in association with carbonate-bearing fluorapatite (collophane), dickite, fluorite,

galena, and sphalerite in dolomitic mudstone cores recovered from the Hesledon Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698]. The precise stratigraphical horizon of this occurrence is unclear.

Pyrite was reported by Smith (1994) as probably the most abundant of a number of minerals dispersed in very minor amounts throughout the Roker Formation of the Sunderland area, though no locations are cited.

Pyrite in the form of small anhedral and botryoidal masses, cubes, octahedra and pyritohedra was recorded by Raymond (1959) as a minor constituent of the blue post-mining ilsemanite-rich efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

Pyrolusite, Mn^{4+}O_2

Although Smith and Francis (1967) reported the presence of pyrolusite on Ford Formation limestones at Whelley Hill Quarry, now known as Hart Quarry [NZ 477 344], presumably as a weathering product, they offered no description of the mineral’s occurrence or of the means by which it was identified. It has not been possible to confirm this report.

QUARTZ, SiO_2

Whereas classic ‘millet seed’ grains of quartz comprise the bulk of the Yellow Sands Formation, there are few reports of quartz in its various forms from the area’s Zechstein Group rocks. Small lenses of authigenic chalcedony, accompanied by dolomite and pyrite were recorded from the Marl Slate by Turner *et al.* (1978) and Vaughan and Turner (1980) though they cited no locations. Trechmann (1954) recorded layers and nodules of chert in the Raisby Formation at Claxheugh, Sunderland [NZ 3620 5745]. Quartz is, however, remarkably abundant in cavities up to 10 cm across in Roker Dolomite Formation dolomitic limestones at Hawthorn Quarry, near Easington [NZ 437 462] as well crystallised rose quartz in the form of lustrous horizontally striated prisms with well developed pyramidal terminations (Fig. 26). Most are up to 0.5 mm across, though locally crystals up to 3 mm long have been found. They are typically translucent and pale pink to pale purplish pink in colour, commonly with patchy internal turbid white patches. The cause of the colouration has not been determined. In some cavities the quartz crystals rest directly upon the host limestone, though in many others they are underlain by a layer of colourless to white calcite scalenohedra <0.5 mm across. In places the pink crystals exhibit a patchy overgrowth of tiny colourless quartz crystals of similar morphology, each <0.3 mm long. No other minerals have been observed in these cavities. Calcite, together with generally minor amounts of other minerals described in this review, is the normal occupant of such cavities and the abundance of quartz at Hawthorn appears to be unique. The source of the silica and the reasons for its absence elsewhere in these rocks are not understood.



Figure 26. Doubly terminated crystals of pale 'rose quartz' in a cavity in dolomitic limestone from Hawthorn Quarry near Easington. Specimen No. BY3851 in the Brian Young Collection. The field of view is 2.5 cm across. Photo Andy Hopkirk.

Burton (1911) described a lens of chert, 9 m long and 0.15 m thick, within beds of the Roker Formation exposed in coastal cliffs at Ryhope [NZ 417 530], though the precise location is not recorded and it is likely that subsequent coastal erosion has destroyed these exposures. More recently, Smith (1994) reported quartz, chalcedony and chert as minor constituents occupying cavities within the Roker Formation in the Sunderland area, though without details of any locations. El-Rekabi (1982) considered that some of this quartz may replace original calcite and dolomite and that some chalcedony is probably secondary after anhydrite. Chert, accompanied by deep purple fluorite, has been found in Roker Formation limestones at Marsden Bay [NZ 3975 6515] (Brian Young, *personal communication* in Dunham, 1990) (see above).

RUTILE, TiO_2

Rutile was recorded as a constituent of the heavy minerals suite within the Yellow Sands Formation from West Boldon [NZ 349 602] and Claxheugh, Sunderland [NZ 363 575] by Pryor (1971).

Scheelite, CaWO_4

Crushed samples of 'limonite' from Raisby Formation limestones in the Whin Houses Borehole, near Butterwick [NZ 3997 3058] contained "... very rare octagonal tablets of a greenish-yellow uniaxial mineral of very high refractive index and moderately low birefringence ..." which J. Phemister (*personal communication* in Fowler, 1943) suggested may be scheelite or powellite. Whereas the possibility of traces of molybdenum within the area's Permian rocks has been discussed above in relation to powellite, scheelite is most unlikely to be present here.

SIDERONATRITE, $\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot 3\text{H}_2\text{O}$

Young *et al.* (2008) described efflorescent encrustations of bright deep yellow sideronatrinite covering an area of one to two square metres of Roker Formation dolomitic limestone about 2 m above beach level on the south side of Hawthorn Hive [NZ 4433 4588] in November 2000. The mineral here is part of an assemblage of iron sulphate minerals, including natrojarosite (see above) actively forming by reaction of sea water with the abundant spreads of pyrite-rich colliery spoil which remain on this beach and which locally fill fissures in the limestone of the adjacent cliffs. Although much of this small exposure has since been destroyed by cliff falls, it is possible that continuing reaction with the adjoining colliery spoil may create new accumulations of this mineral.

SPHALERITE, ZnS

Most descriptions of the Marl Slate and its European correlative the Kupferschiefer refer to the common occurrence within it of sphalerite, pyrite and galena (e.g. Deans, 1950; Hirst and Dunham, 1963, Jones and Hirst, 1969), though few comment on the appearance, mode of occurrence or locations of these minerals. Anhedral patches of mid-brown sphalerite up to 5 mm across and <2 mm thick accompanied by lustrous cleavages of coarse-grained galena and a little pyrite were found on joint surfaces of thinly bedded bituminous siltstones, reported from temporary excavations in the Marl Slate Formation at Marden Pumping Station, Whitley Bay [NZ 3547 7135] (A. Newman, *personal communication*, 1986). Galena and sphalerite occur on bedding planes and joints in Marl Slate at Tinklers Gill Borehole [NZ 4157 3054].

Dull brown bituminous limestones near the top of the Marl Slate Formation, formerly exposed in Cornforth Quarry [NZ 320 344], contain local concentrations of scattered lustrous complex euhedral sphalerite crystals characterised by markedly curved faces (Fig. 27). Whereas most are up to 1 cm across, a few examples >2 cm were seen. Although embedded within the limestone, fracturing along bedding planes commonly revealed the clear form of the crystals, and in some instances almost perfect euhedral terminated crystals fell freely from the rock upon breaking. Bedding parallel lenses up to 5 cm long and 15 mm deep, composed of anhedral coarsely crystalline sphalerite, accompanied by subordinate amounts of coarsely crystalline colourless calcite, also occur. These resemble the Type B vugs described by Harwood (1980) from the Yorkshire Zechstein and which she interpreted as replacements of displacive anhydrite nodules. Although superficially appearing very dark brown, the translucent edges and cleavage planes of this sphalerite exhibit a deep yellowish brown colour when viewed in a strong light.

A similar occurrence of sphalerite as scattered crystals and lining of joints, accompanied by galena, was described by Fowler (1943) from the lowest beds of

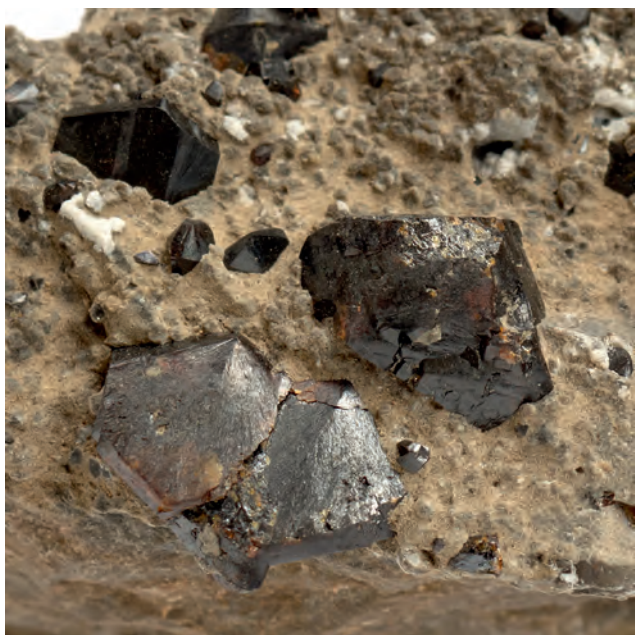


Figure 27. Euhedral crystals of dark brown sphalerite with curved faces embedded in bituminous limestone from Cornforth Quarry, Cornforth. Specimen No. BY6996 in the Brian Young Collection. The field of view is 2.5 cm across. Photo Andy Hopkirk.

the Magnesian Limestone in the Whin Houses Borehole, near Butterwick [NZ 3997 3058]. Sphalerite is recorded by Jones (1969) from joints and cavities, again low down in the limestones, at a depth of 95 m in Hope House Borehole [NZ 3395 2541]. The manuscript log of Cole Hill Farm Borehole [NZ 4229 3110] records limestone, with baryte, fluorite, black sphalerite, and galena from 115 to 121 m, and sphalerite again at 129 m.

Rare specimens of pale yellow to pale brown sphalerite, associated with calcite and baryte, were reported in associations with baryte and fluorite in Raisby Formation limestones at Chilton Quarry, Ferryhill [NZ 3008 3137] (Fowler, 1956). Mills and Hull (1976) noted sphalerite, accompanied by baryte, from dolomitic limestones near the base of Old Towns Quarry, Newton Aycliffe [NZ 257 246], though gave no descriptions of the mineral. Traces of sphalerite, accompanied by baryte and magnetite were also noted by these authors from a Raisby Formation dolostone exposed in an old quarry southwest of Heighington [NZ 2325 2161], again without further description.

Dunham *et al.* (1948) recorded sphalerite, though without description, in association with carbonate-bearing fluorapatite (collophane), dickite, fluorite, galena and pyrite in dolomitic mudstone cores of Ford Formation limestones, recovered from the Hesledon Dene No. 2 water borehole, near Castle Eden [NZ 4654 3698]. The precise stratigraphical horizon of this occurrence is unclear, but an unpublished manuscript log by Dunham and Denys Smith describe an irregular vein up to 1 cm wide containing yellowish sphalerite at a depth of 75 m.

Sphalerite was reported by Smith (1994) as a minor constituent dispersed throughout the Roker Formation of the Sunderland area, though no locations are given.

SULPHUR, S₈

Sulphur was recorded by Raymond (1959) as a minor constituent of the blue post-mining ilsemanite-rich efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

SYLVITE, KCl

Although post-depositional dissolution has removed soluble potassium minerals from the evaporite successions in the area being reviewed here, sylvite was noted as a minor constituent of some of the post mining efflorescent crusts formed by upward seepage of groundwaters at Billingham Anhydrite Mine [NZ 477 227] (Raymond, 1959).

Tachyhydrite, CaMg₂Cl₆·12H₂O

Raymond (1959) suggested that tachyhydrite may be a minor constituent of halite-rich post-mining efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

TALC, Mg₃Si₄O₁₀(OH)₂

Talc was recorded by Raymond (1959) as a minor constituent of the blue post-mining ilsemanite-rich efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227].

Tamarugite, NaAl(SO₄)₂·6H₂O

Small amounts of a rectangular prismatic mineral found in post-mining efflorescent crusts in the underground workings of Billingham Anhydrite Mine [NZ 477 227] were tentatively identified as tamarugite (Raymond, 1959).

THENARDITE, Na₂SO₄

White post-mining efflorescent crusts found in the underground workings of Billingham Anhydrite Mine [NZ 477 227] contained white to colourless prismatic crystals of thenardite up to 1 cm long which, upon removal from the mine, broke down to a white powdery form of the mineral (Raymond, 1959).

TOURMALINE

Tourmaline of unspecified composition was recorded as a constituent of the heavy minerals suite within the Yellow Sands Formation from West Boldon [NZ 349 602] and Claxheugh, Sunderland [NZ 363 575] by Pryor (1971).

TRONA, Na₃(CO₃)(HCO₃)·2H₂O

Raymond (1959) reported the widespread occurrence of efflorescent crusts of colourless needle- and plate-like crystals of trona in the workings of the Billingham Anhydrite Mine [NZ 477 227].

ZIRCON, ZrSiO_4

Zircon was recorded as a constituent of the heavy mineral suite within the Yellow Sands Formation from West Boldon [NZ 349 602] and Claxheugh, Sunderland [NZ 363 575] by Pryor (1971).

DISCUSSION

The minerals reviewed here are the products of a number of geological processes both during and subsequent to their deposition.

Minerals of sedimentary origin include the quartz grains that comprise the bulk of the Yellow Sands Formation, accompanied locally by minor amounts of detrital K-feldspar, the heavy minerals garnet, rutile, tourmaline and zircon, and authigenic kaolinite and K-feldspar.

The nature and origins of the high metal contents of the Marl Slate Formation, and its German correlative the Kupferschiefer, have long attracted research interest. Indeed, according to Smith (1994) because of its distinctive and abundant biota and unusual metal content, this unit has been studied in greater detail than any other part of the English Zechstein sequence. Papers relevant to its mineralogy include those by Howse and Kirkby (1863), Lebour (1902), Woolacott (1912; 1919), Trechmann (1914), Westoll (1943), Deans (1950), Dunham (1960), Love (1962), Hirst and Dunham (1963), Turner and Whitehouse (1978), Smith (1970; 1980), Vaughan and Turner (1980), Pettigrew (1980), Magaritz and Turner (1982), Harwood and Coleman (1983) and Sweeney *et al.* (1987). The current consensus view is that the metals reflect syngenetic mineralisation created by emanations of metal-rich brines via submarine springs into the stagnant basin in which the Marl Slate was being deposited. Scattered sphalerite crystals within the Marl Slate at Cornforth and Raisby quarries and scattered occurrences of pyrite and galena elsewhere are clear expressions of this syngenetic mineralisation. Small amounts of galena, sphalerite and pyrite, described from fissures both in the Marl Slate and lowest beds of the overlying Raisby Formation almost certainly reflect some minor post-depositional remobilisation of these sulphides. Analogous remobilisation of copper, lead and zinc from the Kupferschiefer has been proposed by Wagner *et al.* (2010) to account for some of the vein mineralisation in the Spessart area of Germany and it is likely that some of the minor concentrations of galena, pyrite and sphalerite found in epigenetic mineralisation within the lowermost parts of the Raisby Formation may have been sourced from the Marl Slate. There are insufficient data to allow any degree of reliable analysis of the geographical distribution of base (or precious) metals in the Marl Slate or to further define its prospectivity, but the absence of any report of significant mineralisation, on a par with the Kupferschiefer mining districts, is disheartening.

Based upon the report of detrital fluorite in the Yellow Sands of Yorkshire (Versey, 1925) Harwood (1980) suggested that vein deposits of the Northern Pennine

Orefield were undergoing erosion prior to the Upper Permian and therefore were a potential source of at least some of the metals found within the Zechstein sediments. As no other records of fluorite or any other minerals characteristic of the Pennine veins are known as detrital minerals in the area's Permian rocks, this seems unlikely to have been a major source of these metals. Harwood's suggestion (1980) of enrichment of metals by leaching of underlying Carboniferous sediments has some attraction.

Calcite and dolomite are the main components of the Zechstein Group carbonate succession with the evaporite units dominated by anhydrite, gypsum and halite, with small amounts of associated dolomite and locally celestine. Except for the single record of sylvite in post-mining efflorescences at Billingham Anhydrite Mine (Raymond, 1959) no primary potash minerals are known north of the Tees. Numerous cavities in the carbonate rocks are generally regarded as the result of dissolution of original anhydrite and/or gypsum, and the 'felted texture' commonly seen in lagoonal facies of the Ford Formation is believed to be represent calcite and dolomite replacing original gypsum (Jones, 1969). The diagenetic processes involved, including replacement of evaporite minerals with baryte, galena, pyrite and sphalerite, in the Zechstein carbonates of Yorkshire have been the subject of studies by Harwood (1980), Harwood and Smith (1983), and Lee and Harwood (1989). Across much of the present area the majority of these cavities are lined or filled with white or colourless calcite, though at one single location at Hawthorn Quarry, pale pink quartz is abundant: the reason for its abundance here is unknown. However, baryte and fluorite fillings are also common in parts of the region and reflect structurally controlled epigenetic mineralisation, as discussed below. The origin of enigmatic stratiform fluorite at Marsden Bay, may be in some way early diagenetically controlled, but it remains unresearched.

The apparent association of baryte with collapsed beds around solution residues locally in South Tyneside (and in offshore borings) suggests a reaction between sulphatic brines released during anhydrite removal in relatively recent times and upwards-moving, barium-enriched coalfield brines. The spatial association of baryte of this nature at Frenchman's Bay, with the Harton Dome in the underlying Coal Measures, is worth investigating.

The origin of the concretionary structures within the lower beds of the Roker Formation has attracted speculation since the nineteenth century (Sedgwick, 1829; Howse, 1848; Sorby, 1856; Garwood, 1891) and, despite more recent studies (e.g. Tarr, 1933; Shearman, 1971; Rickard, 1971; Braithwaite, 1988; Clark, 1980; Al-Rekabi, 1992), a fully satisfactory explanation of the processes involved in their creation has yet to emerge. However, segregation of calcite and dolomite from pre-existing dolomitic limestones and dolostones during dedolomitisation, a term first coined by Woolacott

(1912), is clearly involved. Smith (1994) has given a concise review this conundrum and attempts at its solution.

Whereas most of the discussion has so far focussed on diagenetic or syngenetic mineralisation, there are also significant clusters of structurally controlled epigenetic mineralisation.

Young (2001) demonstrated that copper mineralisation exposed in Raisby Railway Cutting is emplaced within Ford Formation brecciated limestones in the east–west trending Butterknowle Fault, the eastward extension of the syn-Carboniferous Lunedale Fault System which forms of the southern boundary of the Alston Block. The structural setting of this copper mineralisation closely resembles that of Farnham, North Yorkshire where similar copper mineralisation occurs in, and was briefly worked (Sedgwick, 1829; Marshall, 1829; Hunt, 1884; Harwood and Smith, 1986), from fractures associated with the Farnham Anticline, the eastward extension of the east–west Craven Fault Zone that marks the southern boundary of the Askrigg Block where it is associated with mineralisation in Carboniferous host rocks (Dunham and Stubblefield, 1945). A borehole close to the Farnham structure records galena and pyrite from the Lower Magnesian Limestone (Harwood and Smith, 1986). The proximity of the isolated occurrence of malachite within Quaternary gravels at Claxton, near Greatham, to the Greatham Fault, invites speculation on whether this fault, with its orientation and history similar to those of the Butterknowle and Farnham structures, may have been associated with copper mineralisation. However, the meagre evidence from this one small single occurrence remains unexplained and enigmatic.

Fowler (1943; 1956) highlighted the abundance of fluorite and baryte at numerous locations, mostly concentrated in a belt up to around 3 km wide between Ferryhill and Fishburn. Hirst and Smith (1974) subsequently demonstrated that this mineralisation coincides very closely both with the roughly east–west trending Trimdon Anticline in the underlying Coal Measures and with a buried seif dune of Yellow Sands, over the crest of which the Marl Slate thins appreciably, on the southern (downthrow) side of the Butterknowle Fault. They proposed that this structural situation enabled barium chloride-rich brines, known to be present in the Durham Coalfield (Sawkins, 1966; Solomon *et al.*, 1971; Edmunds, 1975), to be concentrated in the anticline from which they passed upwards into the Yellow Sands, through the very thin or absent Marl Slate and into the overlying Raisby Formation limestones. Here, they invoked mixing of these brines with sulphate-rich ground-waters resulting from anhydrite and gypsum dissolution, to precipitate baryte with the characteristic form seen here. The modern-day occurrence of small amounts of arborescent secondary baryte on the floor of Cornforth Quarry, observed by one of the authors (FWS) in the 1970s, suggests that the Fault is still capable of upwards transmission of barium-enriched brines. In

addition, Hirst and Smith (1974) considered the abundance of fluorite here and in neighbouring locations, concluding that, as in all locations, fluorite preceded the emplacement of baryte and that there were two different episodes of mineralisation. Fluid inclusion data suggested baryte formation temperatures of <70°C from fluids with equivalent salinities of 16.6–25.6% NaCl: fluorite indicated temperatures of between 104–108°C from fluids with an equivalent salinity of 23.35% NaCl. These authors were unable to identify the source of the fluorine but commented that the limited evidence of yttrium content suggested a dissimilarity between this fluorite and that of the Alston Orefield of the Northern Pennines. A large majority of the recorded occurrences of the region's fluorite, baryte, and galena lie in the lower part of the Magnesian Limestone, in South Durham, and spatially close to either the Butterknowle Fault, the West Hartlepool Fault, or the Seaton Carew Fault. It is reasonable to view them all as part of the same belt of multi-phase mineralisation post-dating the Alston Orefield mineralising event (now believed likely to be of early Permian age). The role of this fault belt, that hosts the Pennine Closehouse Mine baryte-galena deposit and forms the southern boundary of the Alston Block, as a likely long-term channel for base metal-, barium- and fluorine-bearing mineralising fluids is supported by the conclusions of Bott *et al.* (1972) who interpreted modern-day high heat flows from the Woodland Borehole [NZ 0910 2770], further west in this same structural belt, as due to the upward convection of thermal brines within it and its associated fractures. On a smaller scale, but still genetically significant, is the occurrence of baryte observed by FWS impregnating the Hutton Seam at Middridge Colliery, in workings approaching the east–west Middridge Fault, just on the north side of the Butterknowle system, again demonstrating the mobility of barium-bearing fluids, likely to have derived from the Coal Measures along faults in this area.

At the instigation of one of the authors (FWS) Consolidated Goldfields Ltd began an exploration programme in 1981 into the possibility of there being significant base metal mineralisation in the Raisby Formation along the Butterknowle Fault and in particular at its intersection with the highly porous, Ford Formation reef limestones, but it gained little traction and, despite acquiring ground for exploration, was shelved without significant new work being carried out. The present authors remain attracted, however, by the hypothesis. The sheer volume of baryte that must have been deposited in the Fishburn–Middridge area is colossal, albeit low grade wherever seen so far, and is clearly a record of major fluid movements.

The recently discovered manganese mineralisation at Blackhall Rocks, awaits further investigation.

Young *et al.* (1992; 2020) speculated on the possible role of the Stublick – Ninety Fathom Fault System as a potential channel for mineralisation both in north

Cumbria and the Northern Pennine Orefield. Baryte mineralisation in Coal Measures sandstones is described above at Cullercoats, where these rocks are juxtaposed against the Yellow Sands Formation by this fault. As the baryte occurrences at Marden Old Quarry, Frenchman's Bay, Man Haven and Souter Point (Smythe, 1922; Land, 1974; Smith, 1995; Young, 2008a), all lie within the footwall zone of this fault within 5 km of its the surface outcrop, they may also reflect the role of this structure as a significant channel for mineralising fluids, analogous to that of the Butterknowle Fault of South Durham.

Minerals reported from post-mining efflorescent crusts in the workings of Billingham Anhydrite Mine are interpreted as resulting from upward seepage of groundwater from the underlying Zechstein strata (Raymond, 1959). The presence of molybdenum minerals here introduces the possibility that, in common with the Zechstein beds of the Midlands (Deans, 1961), small concentrations of molybdenum may also be present in northeast England.

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Many of the sites mentioned in this paper lie on private land: their inclusion here does not imply any right of access.

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A RE-EXAMINATION OF THE MINERALISATION AT THE ‘SUNNYSIDE DEPOSIT’, WHITWELL, DERBYSHIRE

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Mineralisation associated with the ‘Sunnyside Deposit’ near Whitwell in north Derbyshire was described in 1972 in a collaboration between two amateur geologists (R. T. Richardson and G. H. Wood) and P. R. Ineson of Sheffield University. Baryte occurs as rhythmically banded veins, vein breccias, nodular masses and ooidal to pisoidal replacements of Cadeby Formation dolostone. Galena, goethite, malachite and manganese oxides were reported in the original article. A re-examination of specimens in the Ray Richardson Collection has added cerussite, hydrozincite, plumbojarosite, sphalerite and smithsonite. The primary mineralisation is thought to have formed in a reaction between invasive barium-rich Coal Measures brines and local sulphate-rich pore fluids. Baryte is orders of magnitude more abundant than galena in the exposures that are described, but the proximity of a small abandoned lead mine suggests galena may increase in abundance toward the Carboniferous–Permian unconformity.

INTRODUCTION

In the spring of 1968, baryte and galena were found while foundations were being dug during building work at the northern edge of the village of Whitwell in north Derbyshire. Specimens were collected by the late Ray Richardson¹ and the mineralisation was described in a collaborative article in the *Proceedings of the Yorkshire Geological Society* (Ineson *et al.*, 1972).

The baryte deposit is not given a name in the original article, but the Richardson specimens are labelled ‘Sunnyside Vein’, Sunnyside being the name of a cul-de-sac near the properties where the best material was collected. That name is modified to the ‘Sunnyside Deposit’ in this account because the majority of the baryte occurs as wall-rock replacements rather than fissure veins.

Peter Briscoe acquired the Richardson Collection in 2019. A re-examination of the Sunnyside specimens revealed five species that were not reported in the

original article. Field diaries record that additional material was collected in 1974, 1984 and 1995 during building projects (Richardson, 1970–1980; 1982–1985; 1987–1995). The new discoveries and advances in the modelling of mineral deposition in the last half century make a further record of the mineralisation worthwhile. The re-examination also provides an opportunity to compare the Sunnyside Deposit with epigenetic galena-baryte mineralisation on a northern splay of the Park Hall Fault at nearby Whitwell Quarry (Briscoe *et al.*, 2021).

LOCATION

The course of the ‘Sunnyside Vein’ is shown in Figure 1 based on the map reproduced in Ineson *et al.* (1972: p. 141). The map shows two separate veins, which unite where they cross the B6043 Worksop Road and continue as a single structure across undulating arable land and into Whitwell Wood.

A detailed investigation has revealed inconsistencies in the claimed localities of mineralised structures. Ray Richardson’s unpublished collection register, field diaries and sketchbooks cast doubt on the location of the ‘principal locality’ which is almost certainly not at SK 533 769 as claimed in Ineson *et al.* (1972: p. 142). Unfortunately, there are internal inconsistencies in

¹ Raymond Thornton Richardson (1930–2007) was an amateur geologist and mineral collector. A photo with members of the Doncaster Mines Research Group is reproduced in Briscoe and Green (2020: p. 7). The baryte mineralisation came to his attention because Eunice, his wife, worked with the wife of a local builder who had encountered ‘heavy rocks’ while ground was being prepared for a housing development. As Ray had an interest in geology, he was invited to examine the material.

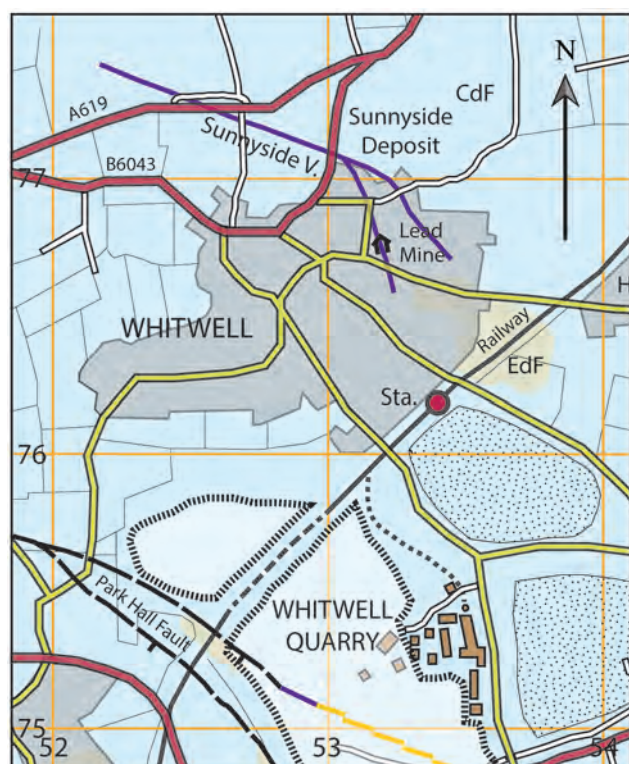


Figure 1. Small-scale map showing the position of the Sunnyside Vein (purple) based on the sketch in Ineson *et al.* (1972: p. 141). The course of the Park Hall Fault (dashed black) and location of the mineral deposit at Whitwell Quarry (purple and gold) are also shown. The geology is dominated by Cadeby Formation (CdF) dolostone (blue) with small outliers of Edlington Formation (EdF) mudstone (brown).

Ineson *et al.* (1972) and in the unpublished data. As the major mineralised localities currently lie beneath private housing there is no easy way to determine the truth (see Appendix 1).

GEOLOGY

The Sunnyside Deposit is hosted by dolostone of the late Permian Cadeby Formation² (Eden *et al.*, 1957; Smith *et al.*, 1973). The surface geology is relatively simple (Fig. 1; see also Briscoe *et al.*, 2021) and for the purposes of this summary it is sufficient to note that the dolostone lies unconformably above a thick sequence of Carboniferous Coal Measures sediments and dips at a shallow angle to the east where it is overlain by mudstone and calcium sulphate evaporites of the Edlington Formation. The Park Hall Fault, a major basement structure with a significant downthrow to the southwest, runs an approximately WNW–ESE course about 1.7 km to the south of the localities on Doles Lane.

² The Cadeby Formation is described as Lower Magnesian Limestone in many geological texts. The Lower Magnesian Limestone in Yorkshire, Derbyshire and Nottinghamshire was formally named the Cadeby Formation by Smith *et al.* (1986). It is highly dolomitic (>90% dolomite) in the area around Whitwell (Eden *et al.*, 1957; Smith *et al.*, 1973) and the term dolostone is used in preference to limestone in modern geological descriptions.

All of the Sunnyside exposures are near the top of the Cadeby Formation. They lie within dolostone which was formerly known as the Upper Member (e.g. Harwood, 1981: p. A1/2) or Upper Subdivision (e.g. Edwards *et al.*, 1950) and which is currently described as the Sprotbrough Member. The lithology is described by Ineson *et al.* (1972: p. 143) as follows:

“The wall-rocks comprise oolitic to pisolitic, and compact granular dolomitic limestones and compact shelly limestones”.

The matrix of Richardson Collection specimens is mostly ooidal to pisoidal³, but in some cases contains interlocking dolomite rhombs. This recrystallised saccharoidal texture is common in dolostone at nearby Armstrong Quarry (Bateman *et al.*, 2021) and may correspond to the ‘compact granular’ texture described by Ineson *et al.* (1972: p. 143). Only one specimen containing a shelly fossil was located (although fossil bivalves including *Bakevella* sp. are described in field notes).

There is a degree of ambiguity in the original lithological descriptions. The specimen illustrated in Figure 2 on Plate 9 of Ineson *et al.* (1972), is described as a “granular, shelly, dolomitic limestone with occasional pisoliths”. The dolostone on the counterpart to this specimen (catalogued in this study as SSV01) is made up of ooliths, pisoliths and ‘compound grains’ up to about 6 mm in diameter (Figs 2 and 3). It is neither ‘compact granular’ nor ‘shelly’ and it is hard to see why the original description includes these adjectives (which refer to three different lithologies). The mismatch between published description and observation shows the value of preserving specimens, especially figured specimens, for study.

Fluorescence images reveal textural details that are invisible in incident light (see Figs 2, 3 and 12). They have petrographic value and clearly differentiate dolostone from epigenetic baryte, which does not fluoresce in longwave ultraviolet light.

MINERALISATION

Economic base-metal mineralisation is sparse in the Permian rocks to the east of the Pennines (Harwood, 1981; Harwood and Smith, 1986b), but small-scale lead mining was recorded in the Whitwell area in an unpublished seventeenth-century manuscript (Ineson *et al.*, 1972) and Pilkington (1789: p. 102) records that lead ore was found:

“in the large bed of limestone on the eastern borders of the county [of Derbyshire], particularly in the neighbourhood of Bolsover, Barlborough and Whitwell”.

³ Recommended terminology for use in the description of oolitic and pisolitic rocks is outlined as a glossary to Young (1989). Ooids and pisoids refer to grains with recognisable concentric structures, ooids are less than 2 mm across and pisoids larger than 2 mm across.

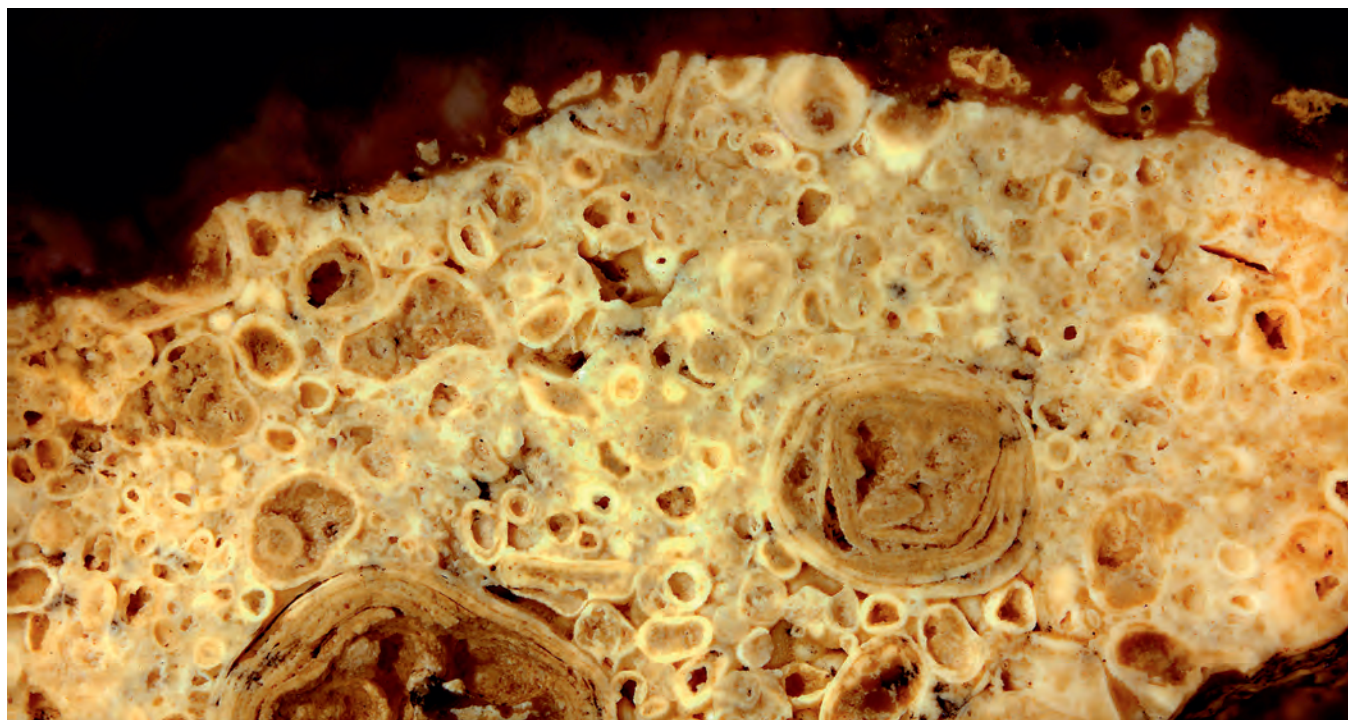
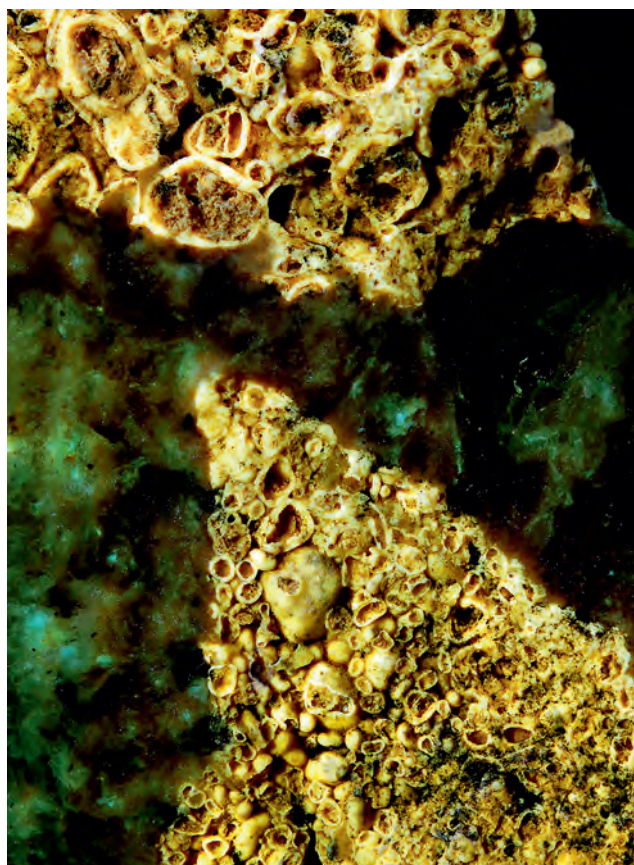


Figure 2. Fluorescence image of a part of a polished block of Cadeby Formation dolostone with a baryte vein (dark area at the top of the field). Dolomite oolites and pisoliths up to 6 mm in diameter commonly have hollow powdery centres, the larger ‘compound grains’ (see Smith, 2006: p. 137) have complex internal structures. The interface with the vein baryte is sharp and contains a few tiny dolostone clasts. Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire, illuminated by longwave ultraviolet radiation with a peak intensity at 370 nm. The field of view is 26 mm across. Photo John Chapman.

An adit and shaft are shown on the sketch map reproduced in Ineson *et al.* (1972: p. 141). The map is at too small a scale to identify the precise position of either feature, but an unpublished sketch (Fig. 4) shows that the



shaft lies between two houses on Doles Lane [SK 5310 7688]. The lead mine, therefore, lies within the area described as the Sunnyside Deposit in this article. The adit was driven from the south and given the early date it is unlikely to have been very long. The entrance is almost certainly concealed beneath housing near to the centre of Whitwell. The ground slopes downward at a gradient of about one in twenty for several hundred metres to the south of Doles Lane and Richardson makes a reference to discoveries of galena near the centre of the village in an undated note:

“There are known occurrences of Galena ... in foundation work for buildings on the north side of Whitwell Square. This is in direct line with the Barites vein and about 200 yds distant”.

Harwood (1981: p. 340) suggested that the ore mined in the seventeenth century may have been syngenetic galena concentrated near the base of the dolostone, but a vein deposit is more consistent with the information presented in Ineson *et al.* (1972). Recent studies show that the syngenetic base-metal mineralisation in the basal Permian rocks in the area around Whitwell is sparse and disseminated, even where it has been subject to local

Figure 3. (left) Fluorescence image showing clasts of Cadeby Formation dolostone in vein baryte. Somewhat etched oolites and pisoliths up to 6 mm in diameter, with hollow centres and strong creamy yellow fluorescence, are cut by non-fluorescent vein baryte. Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire, illuminated by long-wave ultraviolet radiation with a peak intensity at 370 nm. Photo John Chapman.

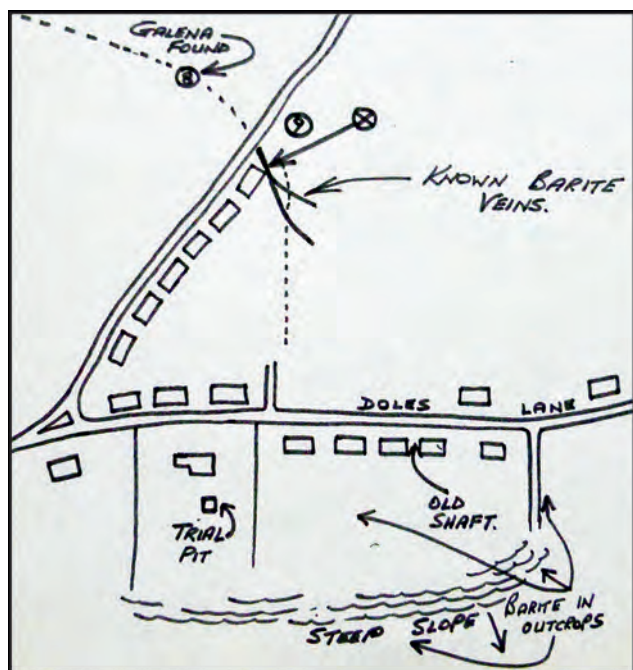


Figure 4. A sketch plan by Ray Richardson, dated 10 May 1970, showing the locations of some of the Sunnyside baryte excavations, particularly sites 8 and 9 (see Appendix 1), the possible site of an old shaft, and the site of the first excavation noted as a “TRIAL PIT” in the garden of a bungalow at the west end of Doles Lane. The steep slope with ‘baryte in outcrops’ now lies beneath the gardens of houses on the north side of Longcroft Lane. A baryte vein which is described as “10 FT WIDE” is present at the point marked with a cross in a circle, to the east of the B6043. The shape and course of the marked veins do not correspond with those recorded by Ineson *et al.* (1972: p. 141), which are traced on Figure 1.

remobilisation (Bateman *et al.*, 2021b). On the other hand, the epigenetic vein and replacement mineralisation associated with the Park Hall Fault at Whitwell Quarry is locally rich in galena (Briscoe *et al.*, 2021). Therefore, the balance of evidence favours an epigenetic vein and replacement deposit of the type that was encountered at Whitwell Quarry.

The ‘Sunnyside Vein’ was the only substantial lead-bearing baryte vein recorded anywhere in the local Permian rocks when it was described. Its unique geological context was the principal reason that the authors published their account. Ineson *et al.* (1972: p. 142) record:

“The best section (533769)⁴ showed that the mineralization was in the form of a vein with extensive metasomatic replacement of the wall-rock limestones. ... The width of the vein is taken tentatively to be between 0.45 and 0.60 metre, although the maximum width of baryte mineralization may extend 150 metres from the vein”.

“A pit (5305 7680) excavated 120 metres west of the section described above proved 1.2 metres of thin and thickly bedded limestone, partly dolomitic, with sporadic baryte, while farther east (5310 7688) limestone with galena and pink and colourless baryte was exposed. Small roadside exposures

(5315 7685) revealed baryte fragments in a dolomitic limestone outcrop, while indications of nearby mineralization were evident by the presence of baryte in rough pasture. Excavations (531772 to 527772) for a large water-pipeline in the fields to the north and north-east of the village, yielded in the bedrock both galena and baryte, similar to the previous examples”.

“The evidence here cited indicates that the mineralization is not sporadic in the bedrock, but is confined to a vein, ... However, no definite boundary is discernible. The strike of the vein is apparently parallel to the Park Hall Fault”.

These observations strongly suggest that the Sunnyside Deposit is a fault-controlled structure, containing baryte and minor galena in central veins with extensive replacements in the surrounding dolostone.

MINERALS

Minerals from the Sunnyside Deposit are listed alphabetically in the following text. Most of the species are common and identifications are visual. A few specimens were tested by wet chemistry and confirmatory analyses were made by X-ray diffraction (XRD) and energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM). Many of the images which accompany the mineral descriptions are available as red-cyan anaglyphs which can be examined in three dimensions on the Russell Society website.

BARYTE, BaSO₄

Baryte occurs as banded veins, vein breccias, nodules, replacements of ooidal to pisoidal dolostone and crystals in cavities. In the abstract to their article, Ineson *et al.* (1972: p. 139) record:

“Massive, crystalline, pink and purple varieties of baryte are the principal components of the vein. [And that] Extensive metasomatic wall-rock alteration of oolitic limestone to baryte-dolomite rock has occurred”.

Purple is an unusual colour for baryte. There are no previous reports at any other locality in the Permian rocks of northeast England⁵, where baryte is typically white to pink and may occasionally be pale blue; or in the South Pennine Orefield, where white and pink are the dominant colours (Ford *et al.*, 1993; Tindle, 2008; Young *et al.*, 2021). Purple bands are conspicuous in many Sunnyside specimens (a more detailed discussion of the colour, which is generated by red hematite inclusions in a pale blue groundmass, is included in the next section of the article).

Two distinct types of baryte vein are present among the Richardson specimens. Thick sub-vertical veins

⁴ All of the grid references refer to 100 km grid square SK.

⁵ Traces of purple baryte are described in this journal in polished blocks from nearby Whitwell Quarry (Briscoe *et al.*, 2021).

contain baryte with a complex layered structure. Fine-grained, opaque, brown to pink baryte is typically present close to the dolostone walls, it is overgrown by coarse tabular purple crystals, which give way to translucent white ‘cockscomb’ baryte (Fig. 5). Thin salmon-pink veins without obvious transverse structure or banding are commonly associated with replacement deposits. They form complex anastomosing networks around dolostone clasts and commonly contain cavities lined with colourless to white tabular crystals (Fig. 6).

The ooidal to pisoidal dolostone around the vertical feeder fractures is commonly replaced by baryte. This unusual texture is described in detail by Ineson *et al.* (1972). Further specimens were recovered from excavations made in 1974. Richardson (1970–1980) notes:

“The mineralisation here has produced some very good specimens of oolitic limestone which has had the ooliths replaced by Barites and still retains the original structure”.

Figure 5. (right) Polished section through one half of a thick sub-vertical ‘feeder vein’ from the Sunnyside Deposit showing a conspicuous centimetre-thick band of coarse purple tabular baryte. A millimetre-thick band of pale purple baryte overgrows the fine-grained reddish hematite-stained band next to the dolostone and there is also a hint of purple colour just below the outer edge of the vein. The field of view is 40 mm across. Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo David Green.

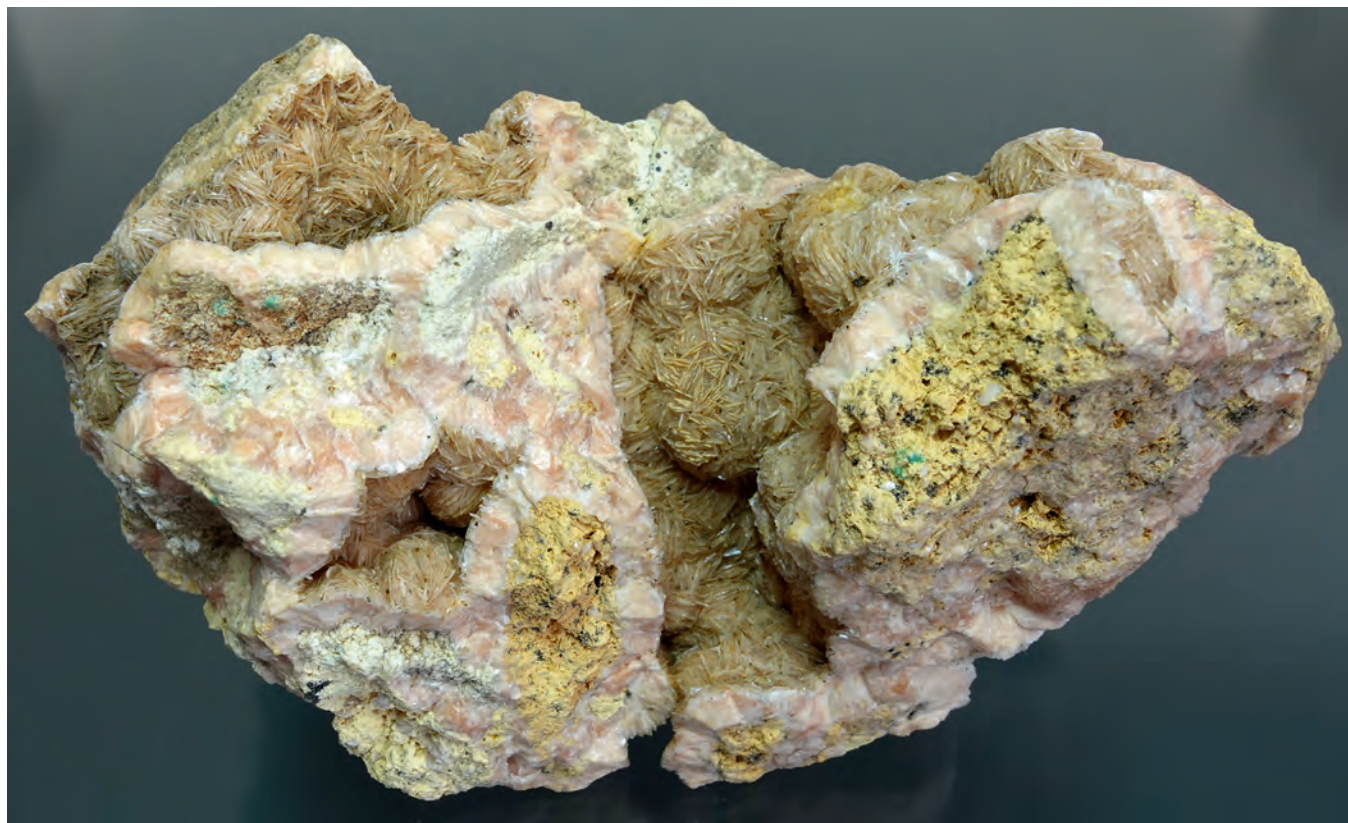
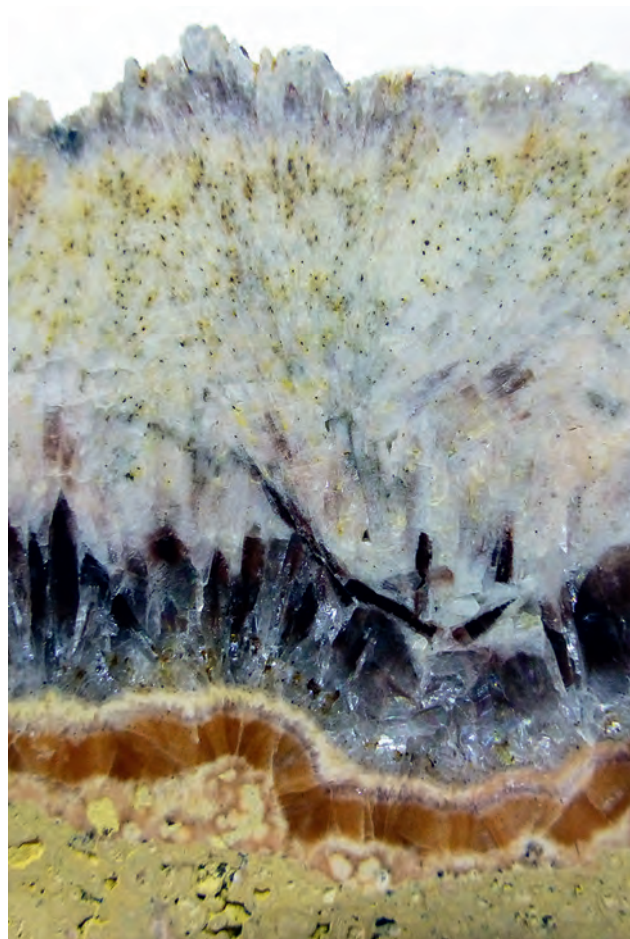


Figure 6. Bladed baryte in cavities between anastomosing pale pink veins surrounding porous sub-angular dolostone clasts. Traces of malachite are present in the dolostone clast on the right-hand side. Specimen SSV06 (100 × 60 mm), formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo David Green.

Cut and polished specimens from the 1974 find (catalogued as SSV11a–e) reveal concentrically zoned fine-grained baryte as spheroidal masses up to about 5 mm across (Fig. 7). The interiors of the spheroids are pale buff to yellow-brown and usually so poorly consolidated that they hollow out when cut and polished. The outer zones have more structural integrity and are pink to brown and concentrically banded. The baryte oololiths and pisoliths are usually embedded in a coarse colourless to pale blue baryte groundmass which contains small irregular cavities lined with tabular crystals (Fig. 8).

All of the baryte specimens that were present when the Richardson Collection was re-examined in 2020 are either fissure veins or dolostone replacements but field notes also record crystals lining cavities well away from the heavily mineralised exposures. For example, a trial excavation at No. 7 Doles Lane (probably near location 3 in Figure 31) revealed small cavities containing baryte crystals at two horizons (Fig. 9). Nodular infills, which are almost certainly direct pseudomorphic replacements of calcium sulphates (see Harwood, 1981), are also recorded.

Figure 7. (right) Concentrically banded buff to reddish brown baryte pisoids, up to 3 mm across, in a coarse white baryte matrix. Acid and fluorescence tests show that no dolomite remains in the centre of the pisoids. The colour banding is probably due to small quantities of iron minerals. The field of view is 30 mm across. Specimen SSV11c, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo David Green.

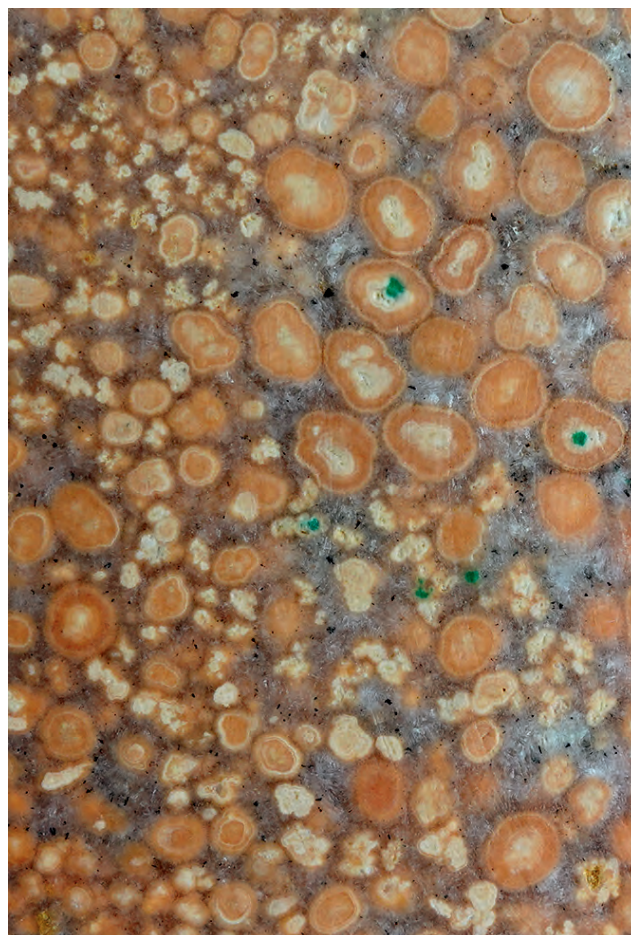


Figure 8. Tabular transparent baryte with preferential frosting around the crystal edges in a cavity in buff to pink replacement baryte. Specimen SSV20e, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. The field of view is 20 mm across. Photo John Chapman.

The morphology of crystals from the Sunnyside Deposit is described by Ineson *et al.* (1972: p. 142) as “of the typical (110) and (001) form”. Some of the best examples were collected 27 years after the original discovery in September 1995 at No. 8 Doles Lane:

“During a recent excavation at this site some very good quality Barite has been found at a depth of two feet. It shows chisel edged tabular crystals and very pure almost transparent Barite which occurs in alternate layers with a Pink variety” (Richardson, 1987–1995).

Specimens from this excavation could not be identified with absolute certainty when the Richardson Collection was re-examined, but two of the best specimens (SSV14a and b) (Fig. 10) have bands of colourless translucent baryte in the matrix.

Figure 9. (right) A sketch of a trial excavation with a depth of “about 4 ft” at No. 7 Doles Lane, Whitwell. House numbers on Doles Lane have changed since this excavation was made. The mention of a cable trench strongly suggests it was near to location 3 in Figure 31.

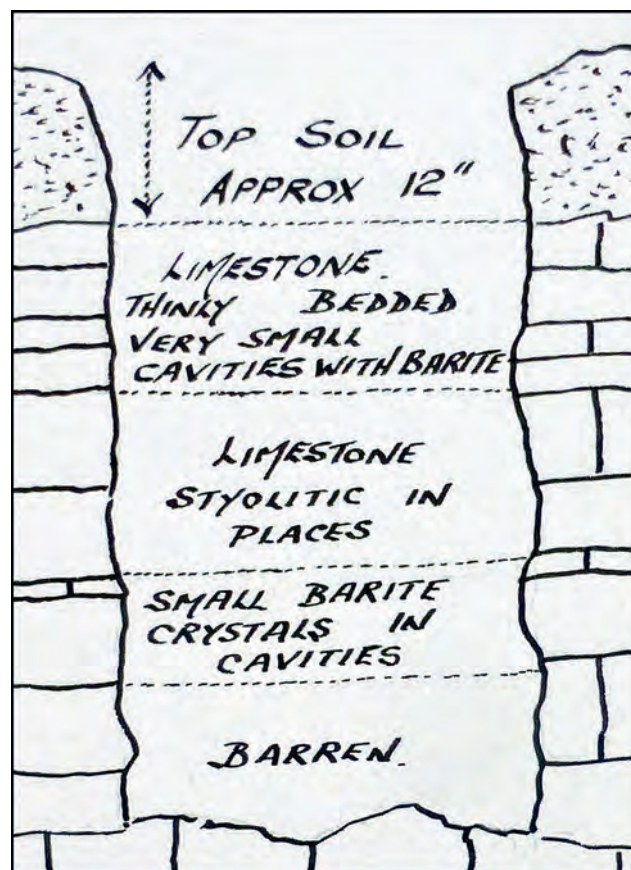


Figure 10. Pinkish criss-cross baryte blades, some with yellow-brown iron-stained edges on a baryte matrix with colourless to white bands. Probably one of the specimens collected from excavations at No. 8 Doles Lane in 1995. The broken crystal (right) has a somewhat purple interior. Specimen SSV014a (55 × 35 mm), formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo David Green.



Figure 11. Colourless tabular baryte, 1.2 mm across, in a small cavity in pisoidal matrix with preferential frosting along a rather ragged upper edge. Specimen SSV20e, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

Central fissures in the thick sub-vertical veins (see Fig. 5) are almost always lined with coarse white cockscomb baryte. Large cavities in vein breccias and replacement deposits may contain white to pale pink or yellow-brown criss-cross blades, some with pale blue to purple centres (see Fig. 10). Smaller cavities often contain colourless tabular to prismatic crystals (see Fig. 8), some with preferential frosting along the crystal edges (Fig. 11).

The extent to which dolostone clasts are replaced by baryte is revealed by their strong creamy yellow fluorescence in both longwave and shortwave ultraviolet light (see Figs 2 and 3). Vein baryte is not noticeably fluorescent in longwave ultraviolet light, but subtle growth banding is visible in cut and polished sections illuminated in shortwave ultraviolet light (Fig. 12).

CERUSSITE, PbCO_3

Cerussite occurs as dark resinous crusts around galena and as rare crystals in cavities in baryte. It has a pale yellow fluorescence in longwave ultraviolet light. On specimen SSV10a, a striated blocky 5×5 mm cerussite crystal in a cavity with partly oxidised galena is overgrown by smaller rounded tabular crystals and locally coated in translucent, pale grey smithsonite (Fig. 13).

DOLOMITE, $\text{CaMg}(\text{CO}_3)_2$

The Cadeby Formation in the area around Whitwell is made up of dolomite of near end-member composition and relatively little else (Eden *et al.*, 1957; Smith *et al.*, 1973). Cavities in the dolostone are commonly lined with rounded opaque white dolomite rhombs up to about 1 mm on edge, which are described as limpid dolomite by Harwood (1981). Although it is present in cavities in the wall-rock, there is no evidence that dolomite was deposited in the epigenetic baryte-galena mineralisation at the Sunnyside Deposit.

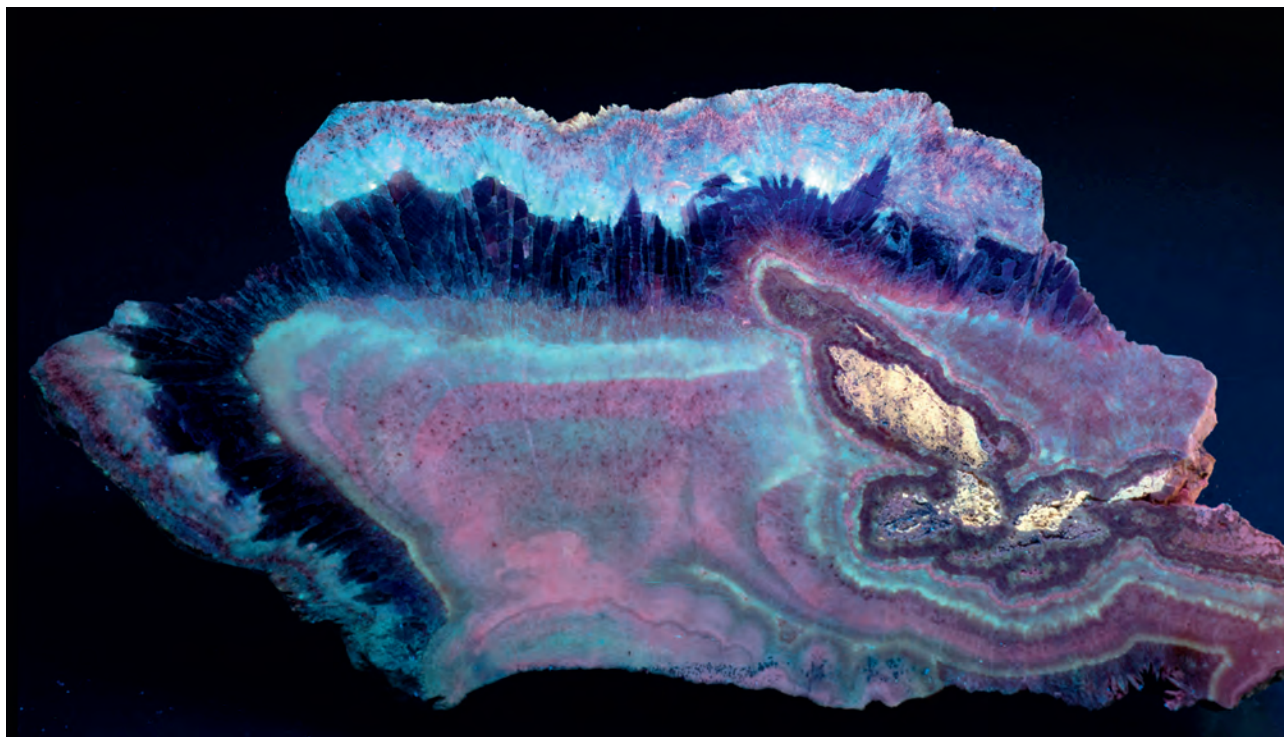


Figure 12. Cut and polished section through an unusually complex baryte vein showing growth banding revealed by illumination in shortwave ultraviolet light. There is subtle pink and white colour banding in the fine-grained baryte that underlies the weakly fluorescent purple band. The overlying laminar baryte has a medium white fluorescence which fades toward the outer surface where there are two pale pink bands. The strong creamy yellow fluorescence of the dolostone clast on the right-hand side is surrounded by layers of baryte with purple-brown, white and pink fluorescence. Specimen SSV28 (290×140 mm), formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo Peter Briscoe.



Figure 13. A crude striated blocky cerussite crystal, 5 mm across, with much smaller tabular crystals along its left-hand edge, in a cavity in baryte with slightly oxidised galena. Specimen SSV10a, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

GALENA, PbS

Galena is recorded at a number of the original Sunnyside localities by Ineson *et al.* (1972) and in unpublished notes by Ray Richardson. The first specimen listed in the Richardson Collection register was found in 1968 by a “Site Worker on [a] Water Main” and is described as “Crystals of Galena in Massive Barite” (Richardson, 1962–1983). Further discoveries were made in 1969 and 1970 and “Octahedral crystals of galena in specimens from the vein” are noted from excavations made in 1974 (Richardson, 1970–1980).

The octahedral crystals from the 1974 find were not found when the Richardson Collection was re-examined in 2020. They may have been donated to Gillian Harwood to support her research. Only two galena specimens, both collected in 1970, remained. In both cases, galena occurs as idiomorphic masses in a red baryte vein-breccia surrounding angular clasts of saccharoidal dolostone. On one specimen, crude pitted cuboctahedral galena crystals up to 11 mm across project into a small cavity.

GOETHITE, $\alpha\text{-Fe}^{3+}\text{O(OH)}$

Goethite replacements of idiomorphic marcasite are ubiquitous in vein baryte. The central cavities in the thick sub-vertical feeder veins are commonly lined with abundant millimetre-size pseudomorphs. Sharp replacements of goethite after marcasite are occasionally present in cavities in replacement baryte (Fig. 14). Rare cubic pseudomorphs found in the same situation are almost certainly after pyrite (Fig. 15). Pseudomorphs bounded by four triangular faces (Fig. 16) are probably after sphenoidal chalcopryite, although it should be noted that pyrite has also been recorded with a tetrahedral morphology (see Goldschmidt, 1920: Plate 132, Figs 493–495).



Figure 14. Goethite pseudomorph after blocky prismatic marcasite, 1.6 mm across, on tabular baryte. Specimen SSV05b, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.



Figure 15. Goethite pseudomorphs after pyrite, 0.2 mm on edge, on tabular translucent baryte. Specimen SSV21a, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.



Figure 16. Sharp goethite pseudomorphs after sphenoidal chalcopryite, the largest 0.4 mm on edge, in a cavity lined with tabular baryte, set within a pink pisoidal matrix. Specimen SSV20a, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

HEMATITE, Fe₂O₃

The pink to red colouration of much of the baryte from the Sunnyside Deposit is due to disseminated hematite. The distinctive purple bands in the thicker baryte veins contain clouds of larger inclusions (Fig. 17). Most are irregular, but some are crudely triangular and others hexagonal. They occasionally form linear arrays with relatively regular spacing and rarely develop into two-dimensional grids across small areas. This spatial ordering deserves further study. The inclusions are typically 10 to 30 μm across and less than 1 μm thick (Fig. 18). On rare occasions, thin faces with alternate inclinations can be distinguished around the hexagonal crystals.

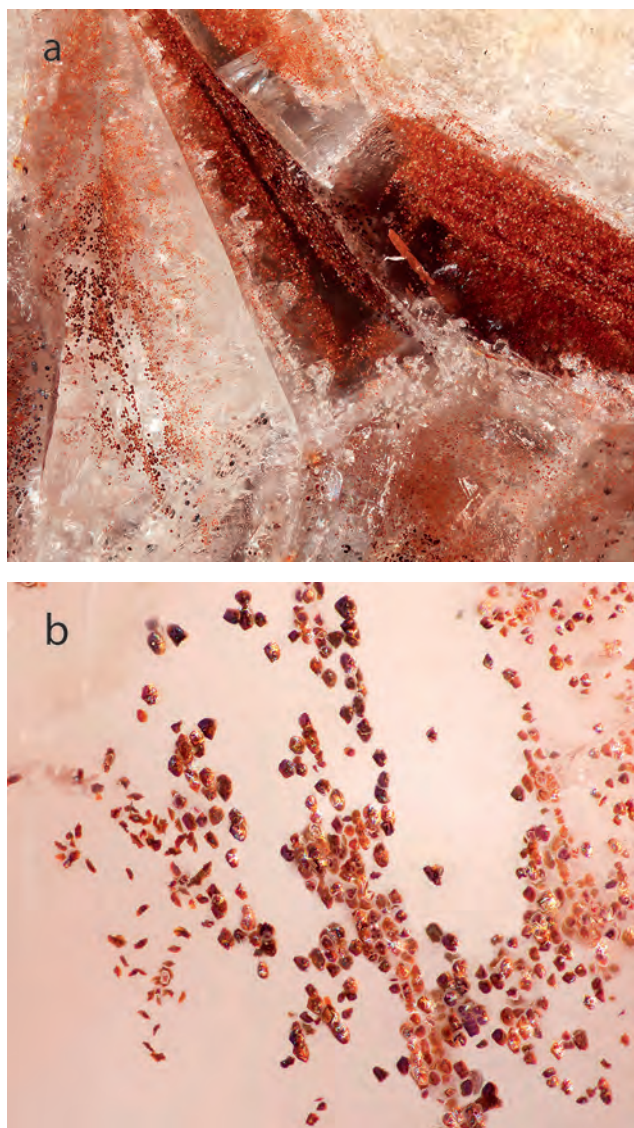


Figure 17. Two images of hematite inclusions in a purple layer of baryte (see Fig. 5). Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photos John Chapman.

a. At low magnification clouds of red hematite inclusions in layers which are parallel to the baryte crystal faces are visible. Larger black hematite inclusions are present at the left-hand side and along the bottom of the image. The field of view is 4 mm across.
b. At higher magnification some inclusions clearly form linear arrays. The field of view is 0.75 mm across.

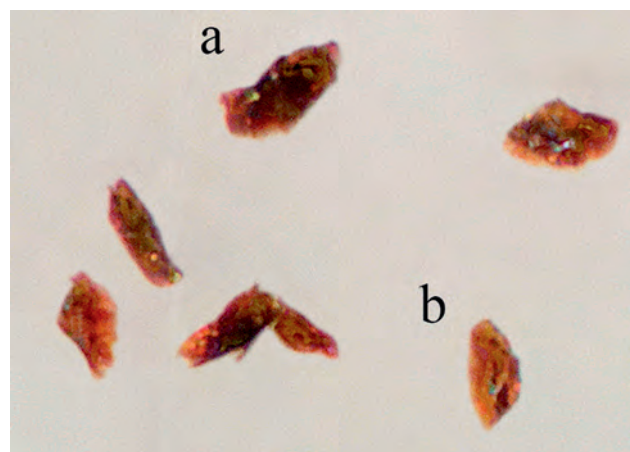


Figure 18. (right) High resolution image in oblique incident light showing the dark red hematite inclusions in one of the purple baryte bands in Figure 17. The field of view is 80 μm across. A thin crudely hexagonal morphology is evident on close examination of the inclusions labelled a and b. Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

Opaque spheroidal hematite inclusions up to about 100 μm across are less common but still relatively widespread in the purple baryte bands. Flashes of 'hematite red' are occasionally visible near their surfaces when viewed between crossed polars in transmitted light under a polarising microscope. They have a silvery grey metallic lustre when polished and exhibit typical bright blue-grey reflectance colours.

Unusual dendritic inclusions are present on a few specimens (Fig. 19). The reason for their unusual morphology (and precise nature) is uncertain but they almost certainly owe their red colour to hematite.

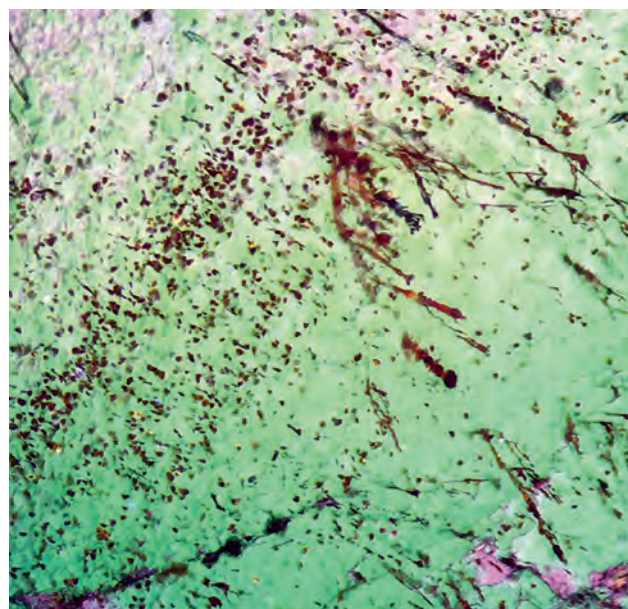


Figure 19. Clouds of red hematite inclusions, mostly with crudely triangular outlines, together with unusual branching dendrites in a layer of macroscopically purple baryte on specimen number SSV23.TS4. The green background colour in this image is produced by reflection birefringence in a transparent medium and is not representative of the true colour of the baryte. Image recorded in reflected light between crossed polars. Photo David Green.

HYDROZINCITE, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$

Thin white hydrozincite crusts line cavities near oxidising sphalerite on two specimens. They have the bright white fluorescence (excited by blue light) which is characteristic of the species.

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

Malachite is noted from the Sunnyside Deposit by Ineson *et al.* (1972). It occurs as dark green spherules in cavities lined with platy baryte (Fig. 20) and green stains and powdery coatings in oolitic to pisolitic baryte (see Fig. 6).

Malachite stains are common in cut sections of the replacement baryte collected in 1974 (see Fig. 7). They are distributed randomly through the rock, occurring in the buff centres of pisoids (Fig. 21), in the pink baryte around their edges, and in small polyhedral volumes between crystallites in the surrounding coarse baryte.

Primary copper sulphides have not been identified on any specimens, but the occasional presence of goethite pseudomorphs with a sphenoidal morphology (see Fig. 16), some in close association with malachite, suggests chalcopryite was originally present.



Figure 20. A malachite spherule, 1.8 mm across, overgrowing tabular pale pink baryte. Specimen SSV03, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

MANGANESE OXIDES

Manganese oxides are widespread in Cadeby Formation dolostone. They form when manganese held in solid solution in carbonates is released, oxidised and immobilised in cracks and fissures. Ineson *et al.* (1972: p. 142) record “dendritic pyrolusite” on tabular baryte at the Sunnyside Deposit. None of the dendrites examined to date have produced powder patterns when analysed by X-ray diffraction. They are unlikely to be

pyrolusite and are described using the catch-all term ‘manganese oxide’ in this account.

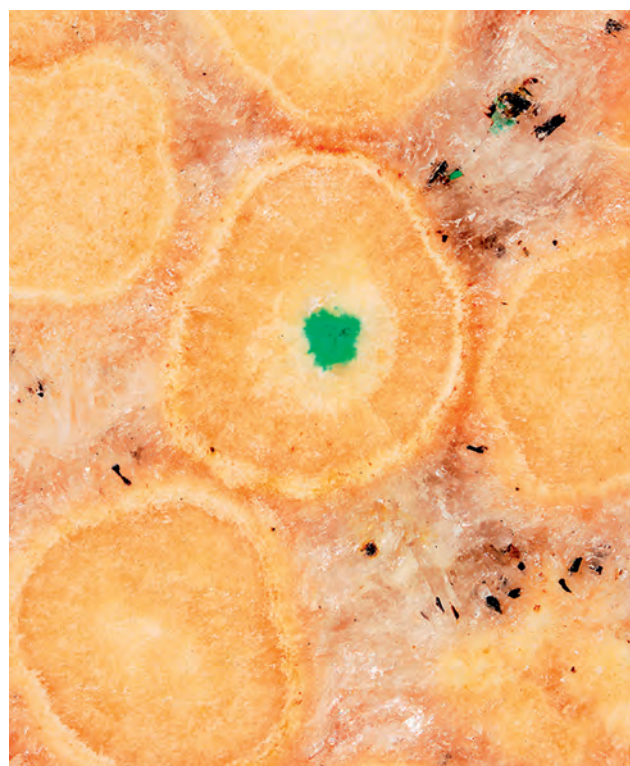


Figure 21. Dark green malachite in pisoidal baryte. The lobate patch in the central (3 mm diameter) pisoid is about 0.4 mm across. The tiny irregular green areas in the surrounding coarse colourless baryte are irregular polyhedral volumes between tabular crystals. Dark brown replacements of goethite, after either marcasite or chalcopryite, are common in the coarse baryte that surrounds the pisoids. Specimen SSV11c, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

MARCASITE, FeS_2

Goethite pseudomorphs after marcasite, up to about 2 mm on edge, are abundant in vein baryte (see Fig. 14). Alteration is usually complete, but residual marcasite has been identified in polished sections of well sealed grains. Marcasite is also found as silvery idiomorphic inclusions, up to about 0.5 mm across, in galena, sphalerite and smithsonite.

PLUMBOJAROSITE, $\text{Pb}_{0.5}\text{Fe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$

Sparse patches of a pulverulent sulphur-yellow phase, up to about 0.2 mm across, on goethite pseudomorphs after marcasite were examined by energy dispersive X-ray spectrometry, which revealed the presence of lead, iron and sulphur in the appropriate atomic ratios for plumbojarosite. None of the other minerals of the alunite-jarosite supergroup has a similar chemical signature.

Plumbojarosite is uncommon in the British Isles (Tindle, 2008). The first reliable occurrence in the Pennine orefields was reported by Young *et al.* (2020). The sparse patches described in this study appear to be the first record from Derbyshire.

SMITHSONITE, ZnCO_3

Millimetre-size cavities in dark red baryte on specimens SSV10a and b contain pale grey-brown, resinous, lenticular crystals, not generally exceeding 0.2 mm in length. They are soluble with effervescence in dilute mineral acid, and the only element with an atomic number greater than ten identified by energy-dispersive X-ray spectrometry is zinc. These data unambiguously identify smithsonite.

Smithsonite is usually the only supergene mineral present in the tiny cavities in which it occurs, but it is occasionally associated with other minerals. Rounded translucent pale grey smithsonite overgrows cerussite in a cavity with partly oxidised galena on specimen SSV10a (Fig. 22). In a small cavity on the same specimen it encloses silvery marcasite.



Figure 22. Rounded lenticular translucent drusy smithsonite (identified by energy-dispersive X-ray spectrometry) on striated cerussite. Specimen SSV10a, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. The field of view is 2.5 mm across. Photo John Chapman.

SPHALERITE, ZnS

Sphalerite is present on two specimens as millimetre-size black anhedral to idiomorphic grains in a red baryte vein-breccia surrounding angular dolostone clasts. Where they project into cavities, the crystal surfaces are complex and may be coated by hydrozincite.

In their description of the Sunnyside mineralisation, Ineson *et al.* (1972: p. 142) note that “No... sphalerite has been observed”. Both of the specimens found in this study (original Richardson catalogue number M235) were collected in 1970. The grains are small and easily overlooked without a stereomicroscope. They were probably mistaken for galena.

DISCUSSION

The Sunnyside Deposit is one of relatively few localities in the Permian rocks of northeast England where epigenetic baryte occurs in veins with base-metal sulphides. It provides a useful comparison with the lead-rich fault-zone mineralisation at nearby Whitwell Quarry (Briscoe *et al.*, 2021).

A considerable amount of material was rescued from the site but the whereabouts of the specimens figured in Ineson *et al.* (1972) is unknown⁶. They were catalogued as M159a–h in the Richardson Collection register (Richardson, 1962–1983) and appear to have been cut and polished at Sheffield University. They may have been retained in the departmental collection, but can no longer be traced. In any specimen-based science it is important that figured specimens are stored in safe and accessible repositories. Unfortunately, many research institutions and some museums appear unable to provide such facilities in the long term.

The only ‘figured’ specimen that was located when the Richardson Collection was re-examined is the cut and polished counterpart to the vein section shown as Figure 2 on Plate 9 of Ineson *et al.* (1972) (see Figs 2, 3, 5, 17, 18 and 23 in this article; probably part of M159h, which the collection catalogue records as ‘returned’). It was identified by comparing its banding pattern with the published image. No other figured specimens were found.

A new accession number and locality details were glued onto an inconspicuous area of every specimen when the collection was re-examined by the authors. Thirty numbers were used, each prefixed by the letters SSV. In some cases a number refers to a single specimen, in other cases a small group of related specimens have the same number and the individual pieces are distinguished by letters. The inconsistencies as to precise locations (see Appendix 1) mean that it is impossible to include an accurate grid reference on any of the labels. They simply record “Sunnyside Deposit, Whitwell, Derbyshire”.

The remainder of the discussion falls naturally into separate subsections which set the primary mineralisation in context, discuss the origin of the mineralising fluids, and describe the vein development, replacement petrography and unusual purple colour banding in the baryte.

Primary Mineralisation

The epigenetic baryte and associated base-metal mineralisation in the Permian rocks of northeast England was studied in considerable detail in the years

⁶ The authors have directed enquires to The University of Sheffield, where Richard Ineson worked, to Sheffield Museums and searched online without success. The Geology Department at The University of Sheffield had a difficult time in the late twentieth century and closed its doors in 2001 (Hunter, 2015).

following the description of the Sunnyside mineralisation. Indeed, the Sunnyside discovery (Ineson *et al.*, 1972) and a near contemporary account of mineralisation near Ferryhill in Co. Durham (Hirst and Smith, 1974) seems to have catalysed much of the research.

The various types of baryte deposit in the Permian limestones and dolostones that crop out between Nottingham and the mouth of the Tees are categorised by Harwood and Smith (1986b). Mineralisation in the Cadeby Formation is grouped into four areas centred on Farnham, Bramham, Edlington and Mansfield. The Sunnyside Deposit lies within the Mansfield area, where it is suggested that mineralisation can be “explained by upwards leakage, on a broad scale, of formation fluids from Carboniferous strata that overlie the South Pennine basement high”.

Harwood (1981: pp. 339–340) described the Sunnyside mineralisation as follows:

“Baryte occurs as a void fill and replaces Upper Member peloid and pisoid grainstones and packstones of the barrier facies ... Ineson *et al.*, note that “shelly limestones” have not been substantially replaced by baryte; there is thus some degree of facies control. Baryte mineralisation is after eogenetic dolomitisation and is also later than the formation of limpid dolomite overgrowths which line some vugs. Marcasite is present between some bladed baryte crystals but is not common; there is no hematite. Ineson *et al.*; found galena crystals (two!) in a central vein. ... Some coarse bladed concentrically banded baryte (e.g. Ineson *et al.*, 1972, Figs 4 and 7) contains ghosts of former dolomite structures, indicating these may not have been simple void-filling barytes, as previously deduced. Rapid crystal growth would allow incorporation of rare small dolomite inclusions in the baryte; other inclusions would “surf” in front of the growing crystals and may be later flushed away if not incorporated in the crystal itself”.

The use of inverted commas around the term ‘shelly limestones’ suggests some reservation about the description. This is corroborated by observations made during this study (see Figs 2 and 3). None of the dolostone preserved with baryte in the Richardson Collection is representative of shell-banks or coquinas, although these have been recorded at nearby sites in south Yorkshire (e.g. Smith, 2006).

There are minor inconsistencies in the account. The claim that just two galena crystals were found is at odds with the description published by Ineson *et al.* (1972) and also with Richardson’s unpublished accounts which identify several localities where galena was found (Table 1). Indeed, sufficient lead ore was discovered in the seventeenth century to warrant a mining trial (Pilkington, 1789: p. 102). The claim that no hematite is present is similarly problematic. Pink to red baryte is abundant in the replacement deposits and on the margins of veins, and hematite is visible as microscopic inclusions in purple baryte (see Figs 17–18).

Harwood (1981) is reluctant to describe any of the mineralisation at the Sunnyside Deposit as vein baryte but in later publications, Harwood and Smith (1986a,b) accept the presence of vein baryte in the Mansfield area. There can be little doubt that some of the baryte at the Sunnyside Deposit occurred as fissure veins. This style of mineralisation was familiar to Ineson *et al.* (1972), and they repeatedly describe it as such:

“mineralization was in the form of a vein with extensive metasomatic replacement of the wall-rock limestones. The core of this vein is fifteen to twenty-three centimetres wide and composed of tabular, purple baryte; the flanks are composed largely of both pink and colourless massive baryte”.

The Richardson specimens and field diaries are consistent with a central feeder vein in a sub-vertical fault or fracture surrounded by replacement deposits. An unpaginated field diary (Richardson, 1970–1980) records that Sunnyside was the “first major vein to be recorded in the Magnesian Limestone” and that baryte and galena were found “in the form of a vein with branch veins”. In this context it should be noted that sub-vertical baryte veins were also encountered at nearby Whitwell Quarry in the mid-1980s (Briscoe *et al.*, 2021).

Mineralising Fluids

Fluid-mixing has gained general acceptance as an explanation for the development of baryte deposits in the Permian rocks of northeast England (e.g. Hirst and Smith, 1974; Robinson and Ineson, 1979; Harwood and Smith, 1986b). With a solubility product of $1.1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$, baryte is relatively insoluble. At equilibrium concentrations, a very large amount of fluid would be required to produce a deposit of any size.

Fluids with higher barium or sulphate ion activities⁷ commonly develop where the concentration one or other ion is suppressed. Barium-rich aquifers are common in Coal Measures sandstones, where the slow decomposition of detrital feldspar releases barium into reduced (sulphate free, chloride-rich) pore fluids. Sulphate-rich aquifers develop where calcium sulphate evaporites form a significant part of basinal sequences and overwhelm any barium that is present (e.g. Downing and Howitt, 1969). Substantial baryte deposits can develop where such fluids mix. In an industrial analogue of this process, barium-rich Coal Measures brines (Smythe, 1922: p. 113–114) were used to produce ‘blanc fixe’, a white finely divided baryte pigment, at collieries in Northumberland (Gray and Judd, 2003).

A Carboniferous (Coal Measures) source for the barium-rich fluids which formed the baryte deposits in the Cadeby Formation in northeast England is uncontested (Hirst and Smith, 1974; Robinson and Ineson,

⁷ Activities and concentrations are used to describe the amount of a particular ionic species in solution; for a simple discussion of their use the reader is referred to Bridges (2015).

1979; Harwood, 1981; Harwood and Smith, 1986b). The source of the sulphate is more problematic. Sulphur isotope data are widely used to constrain fluid sources in hydrothermal ore deposits (Shanks, 2014), but their interpretation is far from straightforward.

Robinson and Ineson (1979) interpreted $\delta^{34}\text{S}$ values⁸ of between +15.7 and +19.3‰ in eight analyses of baryte from the Sunnyside Deposit to be indicative of Lower Carboniferous connate brines, which migrated up-dip from the east. This was challenged by Harwood (1981) who proposed that the values were consistent with diagenetically modified late Permian evaporite sulphate. In a later publication, however, Harwood and Smith (1986: p. 110) suggested an interaction between sulphate-rich groundwater with a Lower Carboniferous source and barium-rich groundwater with a Coal Measures source, somehow localised within Cadeby Formation dolostone. This remains the consensus view, but it is not entirely satisfactory.

Isotopic $\delta^{34}\text{S}$ values for Carboniferous and Permian calcium sulphate evaporites in northern England are typically in the ranges +15 to +22‰ and +8.5 to +11.5‰, respectively (Crowley *et al.*, 1997; Milodowski *et al.*, 1998). This provides the rationale for the analysis in Harwood and Smith (1986), which favours a Lower Carboniferous sulphate source.

Models which propose migration of sulphate-rich Lower Carboniferous brines give no explanation of how such fluids could migrate through the intervening kilometre-thick Upper Carboniferous sequences, where barium ion activities are locally high, without depositing substantial amounts of baryte. They also have no explanation of why baryte deposits would then be localised in basal Permian strata. Large baryte deposits are notably absent in the Coal Measures of South Yorkshire and north Nottinghamshire (Bateman *et al.*, 2018). These rocks were thoroughly mapped in the colliery workings beneath the Sunnyside Deposit. The Park Hall Fault and other basement structures in the vicinity are not mineralised in the Upper Carboniferous (Rippon in Ineson *et al.*, 1972). This is a challenge to the interpretations of Ineson *et al.* (1972), Robinson and Ineson (1979) and Harwood and Smith (1986b).

A local source of sulphate, as proposed by Harwood (1981), avoids the need for two different fluids to migrate from distal sources and provides a good reason for the localisation of baryte in the Cadeby Formation. It requires modification of the isotopic signature of the Permian sulphate, or a more local sulphate source with a Carboniferous signature. Mixing with recent groundwater cannot explain the discrepancy as recent sulphate is isotopically lighter (Gunn *et al.*, 2006). However,

isotopic fractionation as a result of sustained microbial reduction would enrich fluids in ^{34}S (e.g. Strebel *et al.*, 1990). The presence of substantial concentrations of sulphide minerals around former calcium sulphate nodules in nearby basal Permian assemblages provides evidence in support of sustained microbial reduction of evaporite sulphate (Bateman *et al.*, 2021b). Furthermore, baryte in the Cadeby Formation at Rock Cottage Quarry between Harrogate and Ripon has a $\delta^{34}\text{S}$ value of +17.88‰ (Harwood, 1981: p. 354). The baryte at this locality is thought to have a local sulphate source and the only reasonable explanation of the isotopic signature is sustained microbial reduction of Permian evaporite sulphate.

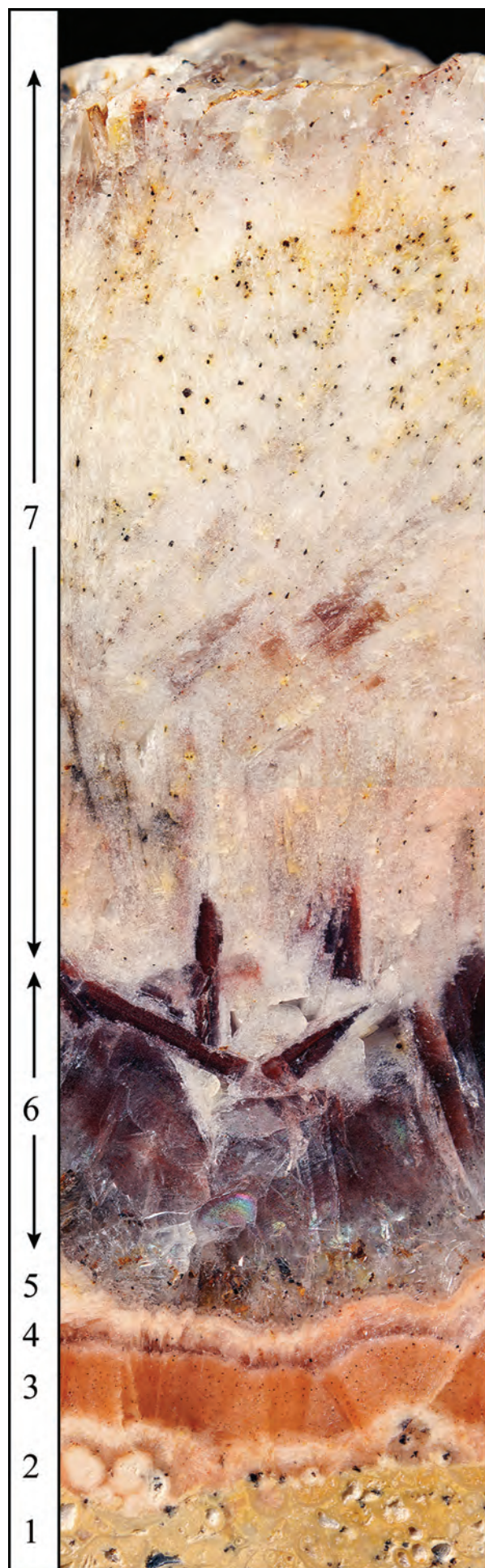
As a speculative aside, it is interesting to note that Versey (1925) recorded both detrital and authigenic baryte in the basal Permian Yellow Sands Formation. This poorly consolidated unit is made up of re-worked sediment with a broadly Carboniferous source. It averages about 7 m in thickness and lies close beneath the Cadeby Formation in the area around Whitwell (Ineson *et al.*, 1972). The detrital baryte (and any other detrital sulphate that was originally present in the Yellow Sands Formation) was derived from Carboniferous rocks, which had been subjected to gentle erosion for tens of millions of years prior to marine inundation and the onset of sedimentation in the late Permian. Whether remobilisation of such material could yield sufficient sulphate to produce a sizeable baryte deposit (and overwhelm local Permian evaporite sulphate) is unknown. Although it seems unlikely, it is suggested as an alternative to sustained microbial reduction because it represents a more local source of sulphate with a Carboniferous signature.

It is worthwhile reiterating that the interpretation of isotopic data is not straightforward. The model outlined by Ineson and Robinson (1979) for the South Pennine Orefield is complex and posits multiple fluid sources. A recent study of baryte from West Cumbria is similarly complex (Armstrong *et al.*, 2020). In this case, compartmentalisation of fluid sources at a kilometre-scale is advocated to explain the puzzling isotopic variability. A more detailed commentary is beyond the scope of this research and would, in any case, require additional analyses. If such a project was considered worthwhile, well provenanced baryte specimens from the Sunnyside Deposit and numerous other Permian locations are available from the authors.

Vein Development

Baryte veins at the Sunnyside Deposit fall into two distinct categories: one relatively wide with a complex banded internal structure, the other narrower with a less complex internal structure, forming anastomosing networks. The wide complex veins (see Fig. 5) are syntaxial infills. They occupy substantial sub-vertical fractures (the “central fracture” in unpublished field notes compiled by Ray Richardson) and appear to have acted as feeders for the solutions that formed the surrounding replacement deposits.

⁸ Values of $\delta^{34}\text{S}$ are quoted as values in parts per thousand difference (symbol ‰) from an international standard, which at the time of the measurement quoted herein was troilite (FeS) from the Canyon Diablo meteorite (Krouse and Coplen, 1997).



The narrow veins (see Fig. 6) form complex networks which enclose cavities containing baryte crystals. They commonly abut and sometimes merge into the replacement baryte and appear to have developed in the void spaces between dolostone clasts.

A close examination of the vein baryte provides evidence for a fluid-mixing model for baryte deposition. Polished sections through the wide and complex feeder veins (Fig. 23) commonly reveal a thin layer of fine-grained buff baryte coating dolostone walls (layer 2 in Fig. 23). The grain size suggests that this layer formed rapidly, covering the dolostone surface, and producing a slightly permeable barrier between the invasive barium-rich brines and sulphate-rich pore fluids in the dolostone. Further crystal development inward into the fracture appears to have been controlled by the slow diffusion of sulphate along crystal boundaries, allowing sufficient time for larger crystals to form nearer to the centre of the fracture (layers 6 and 7 in Fig. 23). If this model is correct, the occasional thin layers of fine-grained baryte (e.g. layer 5 in Fig. 23) in the veins are probably the result of distal crack-seal processes which allowed rapid (advective) mixing of the fluids for a short period of time until the cracks sealed and crystal development became diffusion limited once again.

Marcasite requires a pH of less than about 5 to crystallise (e.g. Kitchaev and Ceder, 2016). The abundance of marcasite (mostly now replaced by goethite) in the central cavities of the thick sub-vertical baryte veins shows that the invasive fluid was acidic. Dissolution by acidic fluids may have helped to generate the space for replacement deposits to form, particularly in the porous ooidal dolostone. Ford and Worley (2016) suggest this mechanism to account for some of the replacement deposits in the limestones of the South Pennine Orefield.

The distribution and oxidation state of iron minerals in the veins is noteworthy. Marcasite dominates the centres of

Figure 23. (left) Polished section showing the internal layer structure of a complex baryte vein from a near vertical fracture. The image (50 mm from top to bottom) shows one half of a fissure vein. A relatively sharp fracture divides the pisoidal dolostone wall-rock (layer 1) from a thin but complex layer of fine-grained white to pink baryte with replacement structures (layer 2). This gives way to a band of fine-grained reddish baryte about 2.5 mm thick (layer 3) and then a thinner (<1 mm) band of coarse faintly purple crystals, which clearly grew outward into an open space (layer 4). The purple crystals are coated by a layer of buff fine-grained laminar baryte about 1 mm thick (layer 5). A centimetre-thick band of transparent coarse tabular baryte with a distinctive purple colour and abundant inclusions follows (layer 6). It is clear that these crystals grew outward into open space (vertically upward as arranged on the page). A few of the crystals are broken and cemented into the overlying layer (layer 7). This consists of about 3 cm of coarse white laminar baryte with tiny idiomorphic inclusions of marcasite, mostly altered to goethite. Just below the outer edge a faint purple band is barely visible (also see Fig. 5). The central cavity, invisible in this image, is lined by cockscomb baryte with abundant millimetre-size goethite pseudomorphs after marcasite. Specimen SSV01, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo John Chapman.

the feeder veins (layer 7 in Fig. 23) and is also commonly present in the coarse baryte that forms the matrix for the pisoidal replacement deposits. Hematite nanoparticles (red-stained baryte) dominate the vein networks associated with the replacement deposits and the fine-grained baryte along the edges of feeder veins (layer 3 in Fig. 23). Larger crystals are present in the coarse purple bands (layer 6 in Fig. 23). In hematite, iron is present as Fe(III), in marcasite it is present as Fe(II). The source of the iron and the reason for the predominance of one or other oxidation state is unclear. A comparison of the isotopic signatures of iron in the two minerals might help to reveal their affinities (Johnson *et al.*, 2020), but is beyond the scope of this research.

Replacement Baryte Petrography

The bulk of the Sunnyside baryte occurs as roughly horizontal replacement-type deposits which are currently visible *in situ* at location 4 (Table 1; Fig. 31). Baryte often appears to replace the oolitic to pisolitic structure of the original dolostone. Cut and polished slabs make attractive specimens, and Ineson *et al.* (1972) describe their petrography in detail. Further discussion is worthwhile as a comparison with the original interpretation and in light of comments made in Harwood (1981), which notes:

“Baryte spherulites (Ineson *et al.*, 1972, Fig. 3) are similar to those at Oglethorpe⁹; centres of spherulites again are not always the centres of pisoids and some “pseudopisoids” result”.

Thin sections prepared for examination by polarised light microscopy are described at increasing magnification in the following text. Baryte is softer than the material normally prepared for thin sections and the poorly consolidated centres of the pisoids are fragile and susceptible to being hollowed out in the grinding process. Care is needed to produce good sections (see Appendix 2).

A typical group of baryte pisoliths in a matrix of coarse interlocking baryte is shown in plane-polarised light in Figure 24. Concentric banding is evident. The relatively dark regions of the section correspond to the buff to yellow-brown central regions of pisoids as seen in incident light. The pale brown surrounding regions correspond to the compact pink to brown outer zones of pisoids and the surrounding colourless mosaic to the interlocking crystal matrix in which they are embedded.

The same field is shown between crossed polars in Figure 25. Multiple ‘Maltese-cross’ extinction patterns in the centre of the pisoids indicate competitive spherulitic crystal growth. The paler surrounding area consists of larger crystals with a generally radial growth pattern. The pisoids are embedded in a coarse interlocking mosaic of randomly oriented tabular crystals, revealed by their bright first-order

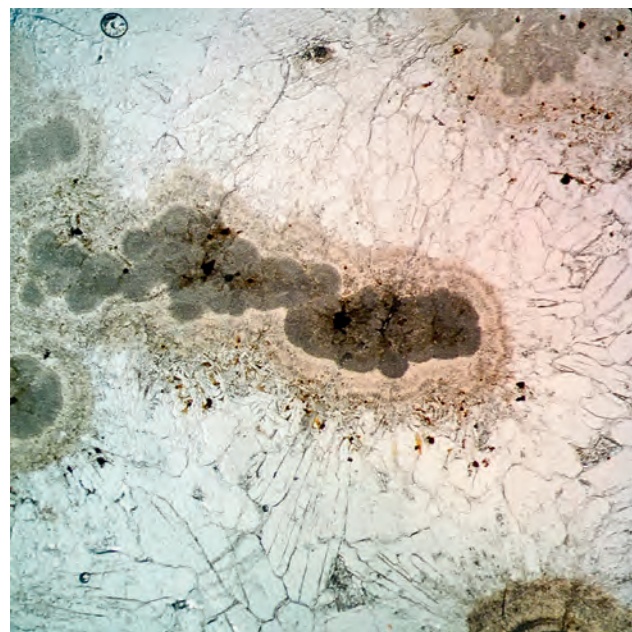


Figure 24. Image in plane-polarised light showing a section through a group of baryte pisoliths (dark grey to slightly pinkish brown in the centre of the field) in a matrix of coarse interlocking baryte (colourless). The field of view is 14 mm across. Section by David Copestake; SSV24.TS4. Photo David Green.

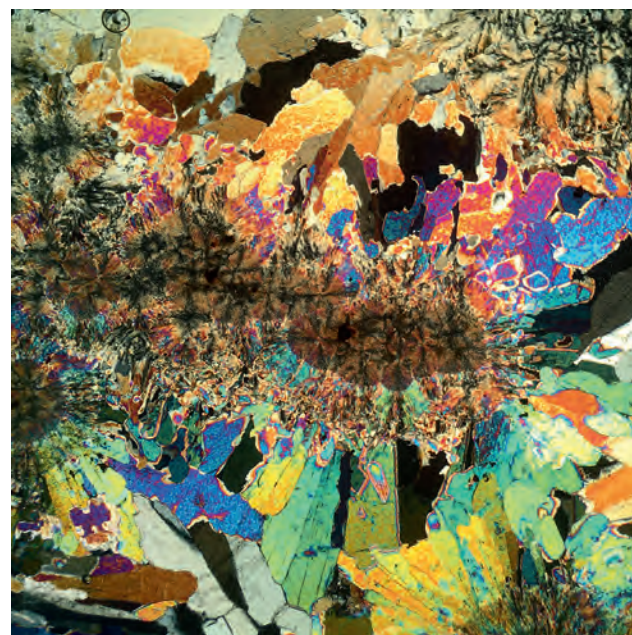


Figure 25. The area as shown in Figure 24 between crossed polars. ‘Maltese-cross’ extinction in the pisolitic aggregates indicates competitive spherulitic crystal growth. The surrounding coarse interlocking baryte crystals have bright first-order polarisation colours in this section, which is thicker than the normal 30 μm to provide birefringence colour contrast. The field of view is 14 mm across. Section by David Copestake; SSV24.TS4. Photo David Green.

interference colours. The fact that the coarse matrix occupies more than half of the area of the section strongly suggests that the replacement baryte is not a faithful replication of the structure of the original pisoidal dolostone. This is consistent with partial dissolution by invasive acidic fluids.

⁹ A baryte deposit in the Cadeby Formation near Oglethorpe Hall to the east of the village of Bramham in West Yorkshire uncovered during excavations for a gas pipeline and described in some detail by Harwood (1981).

Although the replacement baryte typically consists of central spherulitic cores, surrounded by radial overgrowths in a coarse matrix, the individual structural elements are not always well defined. A different group of baryte pisoliths is compared in Figures 26 and 27. Crude ‘Maltese-cross’ extinction reveals spherulitic crystal growth with numerous different nucleation points (Fig. 27). A comparison of the

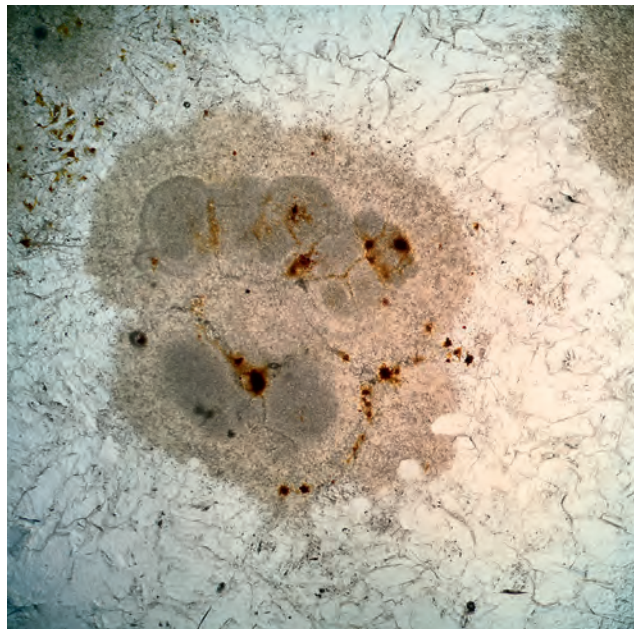


Figure 26. Image in plane-polarised light showing a section through an isolated group of baryte pisoliths (grey to pink in the centre of the field) in a matrix of coarse interlocking baryte (colourless). The field of view is 6.8 mm across. Section by David Copestake; SSV24.TS2. Photo David Green.

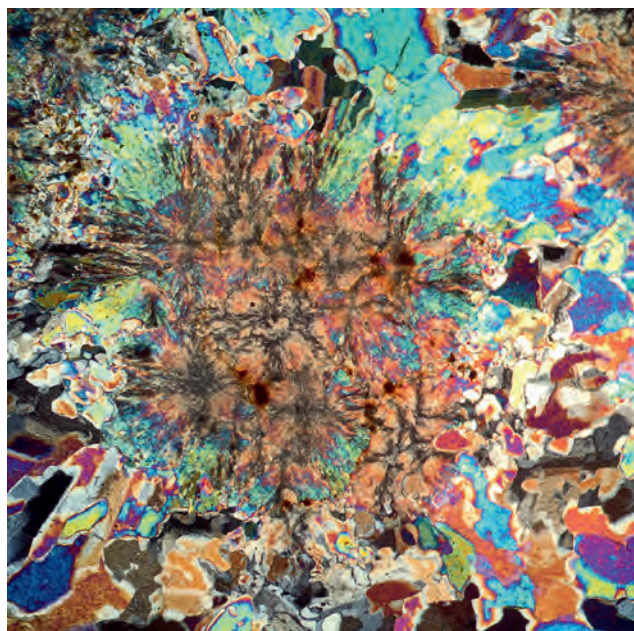


Figure 27. The area shown in Figure 26 between crossed polars. Crude ‘Maltese-cross’ extinction in the pisolitic aggregate indicates competitive spherulitic crystal growth originating at many different points. The surrounding coarse interlocking baryte crystals have bright first-order polarisation colours in this section, which is thicker than the normal 30 μm standard to provide birefringence colour contrast. The field of view is 6.8 mm across. Section by David Copestake; SSV24.TS2. Photo David Green.

images shows that, as noted in Harwood (1981), the centres of pisolids (dark spheroidal regions in Figure 26) do not all coincide with the nucleation points of spherulites (centres of the crosses in Figure 27). Thus, at a pisolidal level, the baryte does not consistently replicate the original structure of the dolostone.

Increasing the magnification and reducing the thickness of the sections allows the structure of individual spherulites to be examined in detail. The pattern is radial, indicating competitive growth from a single nucleation point, but as noted by Harwood (1981) the centre of the cross does not precisely coincide with the centre of the spherulite (Fig. 28). Spherulites are often considered to be indicators of rapid growth from supersaturated solutions. There is, however, no generally accepted theory of spherulite growth (e.g. Gránásky *et al.*, 2005) and factors such as the ionic strength and composition of the mineralising solutions may also be of importance.

Although it is hard to avoid the conclusion that ooids and pisolids in the dolostone provided ‘templates’ in which baryte spheroids nucleated, the petrographic data show that the pisolidal baryte is not a faithful replacement of the fabric of the rock. In most specimens there are too few pisolids and too much coarse baryte matrix. It seems likely that in the replacement process fragments of rock containing dolomite pisolids became detached, possibly as a result of dissolution by invasive acidic fluids. The dolomite in the more resistant fragments was probably replaced by baryte and cemented in a coarse matrix (Fig. 29).

Purple Baryte

The distinctive purple colour of some of the layers of vein baryte from the Sunnyside Deposit (Fig. 30) is mentioned several times by Ineson *et al.* (1972) without

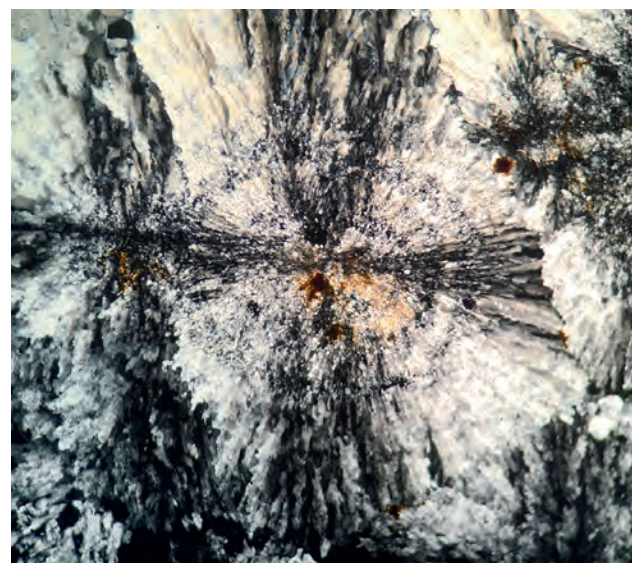


Figure 28. Well developed ‘Maltese-cross’ extinction indicates competitive growth of elongated baryte crystals (with parallel extinction) from a single nucleation point. Note that the centre of the cross and the centre of the concentric bands do not precisely coincide. The field of view is 3.4 mm across. Section made by David Copestake; SSV24.TS3. Photo David Green.

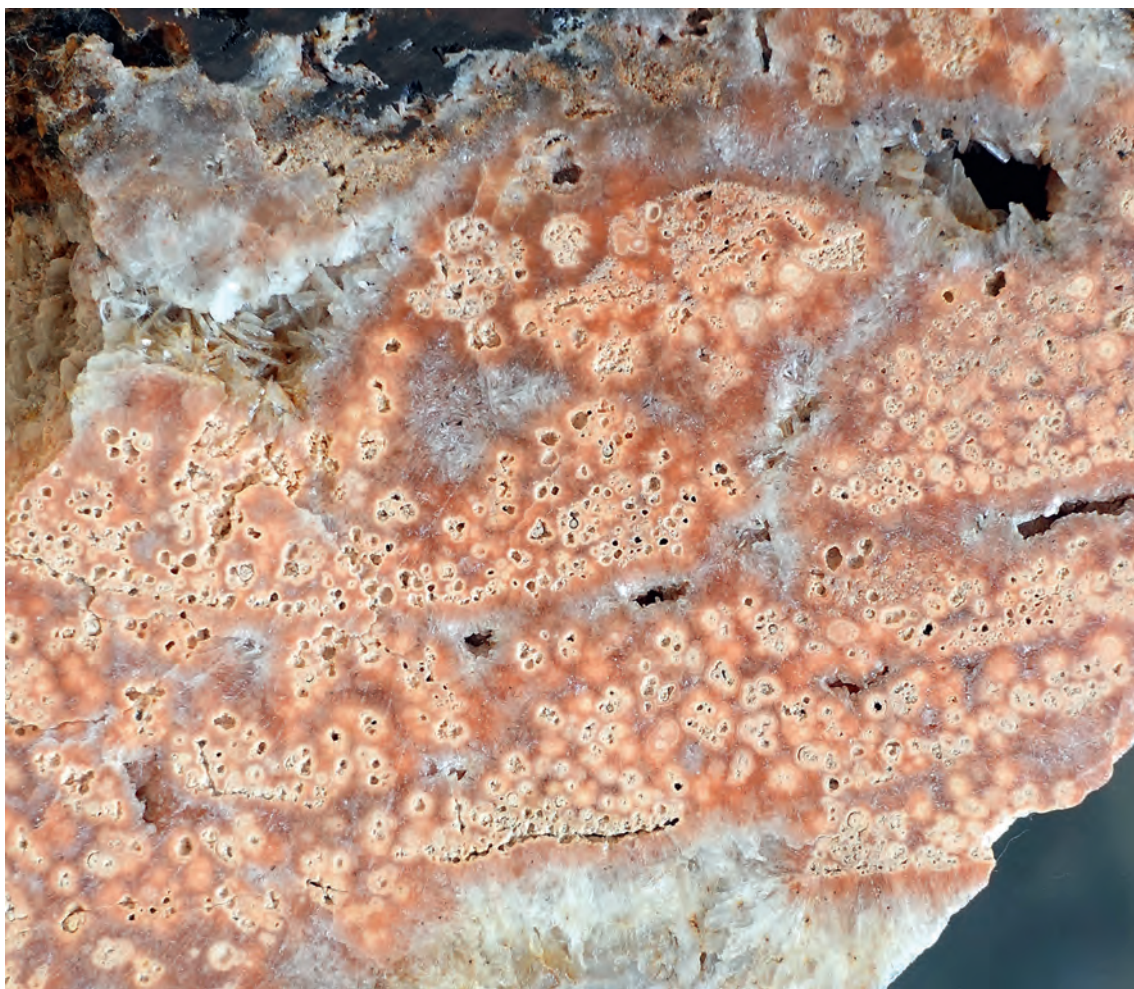


Figure 29. Red-brown to buff pisoidal replacement baryte. The poorly consolidated centres of the baryte pisoids have been hollowed out by grinding. Specimen SSV26, formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. The field of view is 80 mm across. Photo David Green.

any discussion of its origin. Purple is not a pure spectral colour. The impression is generated by the eye-brain complex when there is a relatively high stimulus of red and blue colour receptors in the eye and a significantly lower stimulus of green receptors (e.g. Williamson and Cummings, 1983).

The origin of colour in hematite is explored by Rossman (1996). Antiferromagnetic interactions result in a high absorbance in the visible range and this produces the metallic lustre and steel-grey colour of macroscopic crystals. The brick-red colour seen on the edges of very thin crystals and in micrometre-size particles and powder is produced by a transmission window centred in the extreme red at about 750 nm. The perceived colour of particles is a complex function of their size, shape and state of aggregation (Gonçalves *et al.*, 2012).

Figure 30. (right) A unique vein section with a conspicuous coarse purple band overgrowing fine-grained buff baryte. The purple band is overgrown by white laminar baryte which contains numerous brown goethite after marcasite inclusions and a thin faintly purple band toward the outer edge. Specimen SSV27 (120 × 180 mm), formerly in the Ray Richardson Collection, from the Sunnyside Deposit, Whitwell, Derbyshire. Photo David Green.



The purple colour appears to be generated by a combination of abundant red hematite inclusions and the faint blue colour (possibly due to Rayleigh scattering) of centimetre-thick crystals of transparent tabular baryte. The influence of the faint blue colour of the baryte groundmass is emphasised by a comparison of Figures 5 and 17. In Figure 5, the full thickness of the baryte is illuminated, the individual inclusions cannot be distinguished, and the band appears to be a somewhat reddish purple. In Figure 17, which shows the same specimen, only the topmost layer containing the hematite inclusions is illuminated, the individual inclusions can be resolved, and the influence of the groundmass is much reduced. Therefore, there is a sense in which the unusual and attractive purple colour of the Sunnyside baryte is an optical illusion.

Epilogue

Ray Richardson made what would generally be regarded as good decisions in his study of the Sunnyside Deposit, he obtained permission to collect specimens, made careful records, involved an expert from a local university, donated the more important material to their collection, and was involved with a publication in a respected journal. It is hard to avoid the conclusion that this chain of circumstance would be much less likely in twenty-first-century Britain. University geology departments have been subject to relentless cuts and many, including Sheffield, have closed.

Five university-based collection centres were set up to safeguard material from the earth sciences departments which were under threat of closure in the early 1990s. They lost support and funding over a surprisingly short period (Liston, 2011). The outlook for collections in the sector is bleak and their long-term safety cannot be guaranteed. In the absence of a safe home in a well curated public collection, the Richardson specimens and notebooks remain vulnerable. In the current uncertain times, and in the absence of engagement from local museums, where specialist geology curators are almost extinct, the responsibility for preserving such material rests with the collector community.

CONCLUSION

The Sunnyside Deposit is a rare example of baryte veins with surrounding wall-rock replacement and minor base-metal mineralisation in rocks of the late Permian Zechstein Group. It was considered to be locally unique when it was described by Ineson *et al.* (1972), but similar mineralisation was subsequently found at nearby Whitwell Quarry (Briscoe *et al.*, 2021). The primary baryte is notable for replacements of pisoidal dolostone and unusual purple colour bands. The associated supergene assemblage includes the first confirmed occurrence of plumbojarosite in Derbyshire.

Models of mineralising processes change as science advances and techniques improve. A different genetic model to those advanced by Ineson *et al.* (1972) and Harwood and Smith (1986b) is proposed in this article.

The mineralisation appears to have formed in a reaction between invasive, acidic, barium-rich but relatively metal-poor Coal Measures brines, and local sulphate-rich pore fluids. Near-vertical fractures, possibly generated by movement on the nearby Park Hall Fault, provided pathways through which the fluid flowed.

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APPENDIX 1 – LOCALITY DETAILS

A detailed investigation revealed inconsistencies in the localities of mineralised structures. Development is continuing along the northern edge of the village of Whitwell and it may afford further opportunities to study mineralisation in the area. The uncertainties associated with the original published data are presented here as they may have a bearing on future topographic studies

Ray Richardson's unpublished collection register, field diaries and sketchbooks are not in detailed agreement with the published map (Ineson *et al.*, 1972). In particular, there is doubt about the precise position of the 'principal locality', which is almost certainly not at SK 533 769 as claimed in Ineson *et al.* (1972: p. 142).

An entry into an unpaginated field diary, which describes excavations made in 1974 (Richardson, 1970–1980), records:

"The original locality where the vein was exposed in 1969/1970 has now been concealed by the drive and garden of the house which was built some time after the discovery of the main vein at this site".

"At some time in the future the roadway here is to be widened and a strip of ground is left unworked for this purpose. It is here that work has been started to

seek new specimens from the vein. A trench is being dug out about 8 to 10 yards long where it is known the vein passes underneath".

This locality appears to be in front of one of the houses on Doles Lane, an interpretation which is corroborated by an entry in another field diary (Richardson 1987–1995), which notes that material collected from a shallow excavation at No. 8 Doles Lane in 1995 was:

"from the same mineralisation which was seen and investigated here in 1968/69 and found to be a primary vein [with] some 15' of mineralisation seen *in situ* a short distance away. This find 27 years later [than the original discovery] is proof of the rich Barite zone in the area".

This evidence (and other notes and field sketches which suggest that the 'principal locality' was in the garden of one of the houses on the south side of Doles Lane) is at odds with Richardson's collection register (Richardson, 1962–1983: p. 24) which notes that specimens M159a–h (used in the original research) were not found on Doles Lane but from:

"[A] temporary exposure for building purposes on the B6043 road near Sunnyside, Whitwell, Derbyshire".



Figure 31. Large-scale sketch showing the claimed positions of mineralised localities associated with the Sunnyside Deposit. Locations 1–6 (blue circles) are from Ineson *et al.* (1972), location 1 being the claimed position of the 'principal section'. Location 1a (blue circle) is the grid reference for the 'principal locality' listed in the Richardson collection catalogue (1962–1983: p. 24). Locations 7–12 (magenta circles) are plotted from unpublished field sketches made by Ray Richardson. A detailed commentary is provided in Table 1.

Location	Comment
1. SK 533 769	Described by Ineson <i>et al.</i> (1972) as the ‘principal section’, showing the vein and extensive metasomatic baryte replacement. The quoted grid reference is almost certainly in error: there are internal inconsistencies in the original description [<i>vide infra</i>] and none of the unpublished field sketches indicate baryte in this area. A nearby site is currently (2020) being developed for housing, but there is no sign of any baryte in excavations for the foundations.
1a. SK 532 768	Described by Richardson (1962–1983: p. 24) as “[A] temporary exposure for building purposes on the B6043 road near Sunnyside, Whitwell, Derbyshire”, with the implication that the locality was the source of many of the studied specimens which were originally catalogued as M159a–h. The grid reference is nowhere near the B6043 and is clearly in error.
2. SK 5305 7680	Described by Ineson <i>et al.</i> (1972: p. 142) as an excavation 120 m west of the ‘principal locality’, this grid reference, now beneath houses on Longcroft View, is about 270 m WSW of location 1. There is currently no exposure, but Richardson (Fig. 4) marks baryte outcrops in this area on one of his field sketches.
3. SK 5310 7688	Ineson <i>et al.</i> (1972: p. 142) note galena with pink and colourless baryte at this locality. Richardson’s (1967–1968) unpublished sketch maps note baryte from a trench and a later sketch (Fig. 4) marks the position of an old shaft.
4. SK 5315 7685	Ineson <i>et al.</i> (1972: p. 142) note baryte in a roadside outcrop. This exposure is still extant below a garden retaining wall on the west side of Hangar Hill. It extends for about 5 m north of a lamp post at SK 53158 76857 and shows cream to red baryte as bedding-parallel replacements of Cadeby Formation dolostone.
5–6. SK 531 772 to SK 527 772	Ineson <i>et al.</i> (1972: p. 142) report galena and baryte in excavations for a pipeline. This runs across fields to the north of the village (indicated by a dotted line in Fig. 31), though sketches suggest it took an oblique course a little to the south of the claimed grid references. No baryte was obvious in ploughed fields in this area in late 2020.
7. SK 5314 7687	In an entry into a notebook dated 25 Mar 1968, Richardson (1967–1968) writes: “Recent trench excavations to only 2’ 6” depth at new bungalow next to corner [of Hangar Hill] as shown on sketch. Vein Barite, colourless to pink. Also natural exposure in roadside round corner with Barite <i>in situ</i> [location 4]”. Accompanying sketches show specimens of tabular baryte, galena and dolomite. It is possible that location 7 is the ‘principal locality’; it is roughly 120 m east of the excavation at location 2.
8. SK 5298 7711 (approximately)	An early sketch plan (Fig. 4) notes that galena was found in a field to the west of the B6043 Worksop Road. Further material was found when the field was ploughed in 1985, but the precise locality is not recorded (Richardson, 1982–1985).
9. SK 5305 7708 (approximately)	A baryte vein which is described as “10 FT WIDE” is present at a point marked with a cross in a circle, next to the B6043 (Fig. 4). Accompanying text notes: “Some examples of nodular barites were obtained and these are the best seen anywhere to date. All the baryte is first class material. Oolitic Limestone replaced by barite and showing clearly the original structure is present in the trench sections. ... the vein appears to originate somewhere near to or at “Sunnyside” Doles Lane”. Specimens registered as M159a–h in the collection catalogue are from a “Temporary exposure for building purposes on the B6043 road near Sunnyside” (Richardson, 1962–1983: p. 24) but the accompanying grid reference “SK 532 768” (location 1a) is more than 300 m away and clearly in error. It is possible that location 9 is the ‘principal locality’.
10. SK 5302 7688	The first discovery of baryte noted by Richardson (1967–1968) was at excavations in the garden of a bungalow owned by Mr and Mrs J. Proffitt at the west end of Doles Lane. There are now three houses on this site. The current No. 6 Doles Lane is near the site of the original bungalow (now demolished). Well crystallised baryte was found in shallow excavations at No. 8 Doles Lane in September 1995. Richardson (1987–1995) records that “a primary vein [with] some 15’ of mineralisation” was seen and investigated nearby in the late 1960s.
11 and 12. SK 5273 7720 and SK 5265 7723	Field notes in Richardson (1967–1968) record that baryte was found in spoil from a pipeline excavation near Whitwell Wood. Fragments of loose baryte were visible near the café in the lay-by on the A619 west of location 12 in late 2020 [SK 5260 7724 to SK 5238 7725]. No material was obvious in the field at location 11.

Table 1. A summary of claimed and estimated Sunnyside Deposit localities compiled from the article by Ineson *et al.* (1972) (locations 1–6, but not 1a), and unpublished field sketches made by Ray Richardson (locations 7–12).

To complicate matters, the grid reference listed in the collection register (Richardson, 1962–1983: p. 24) and card index for specimens M159a–h is “SK 532 768”, which is a little to the north of Mill Lane (well away from Doles Lane and Worksop Road) and more than 300 m from the point at which the Sunnyside Vein is marked crossing the B6043 on the sketch map reproduced in Ineson *et al.* (1972). This grid reference is nowhere near any of the mineralised localities marked on the sketches in Ray Richardson’s field diaries (Richardson, 1967–1968; 1970–1980; 1982–1985; 1987–1995) and is clearly in error.

Internal inconsistencies in grid references quoted in the published text (Ineson *et al.*, 1972) add to the confusion. In particular, a pit at SK 5305 7680 is described as “120 metres west” of the ‘principal section’ at SK 533 769. In fact, these two locations are 270 m apart.

The foregoing summary shows that the positional data cannot be relied upon. The grid references reported by Ineson *et al.* (1972: p. 142) [location 1, Fig. 31] and Richardson (1962–1983: p. 24) [location 1a, Fig. 31] for the ‘principal locality’ are either inaccurate or mistaken. In the absence of first-hand knowledge any attempt to correct them has the potential to introduce further errors. A large-scale sketch map which plots all of the published data in Ineson *et al.* (1972) and Richardson’s unpublished field sketches, together with information gathered on a site visit in 2020, is provided as Figure 31. Detailed comments on the locations where mineralisation has been reported are included in Table 1. The balance of evidence suggests that the ‘principal locality’, where most of the specimens used in the original study were found, is either near location 7 or location 9.

APPENDIX 2 – THIN SECTIONS

Particular care is needed to produce thin sections which preserve the poorly consolidated centres of the ooidal structures in the replacement baryte (see Fig. 28). A procedure developed by David Copestake is outlined in the following text.

Rectangular blocks, 6 to 8 mm in thickness and about 18 × 20 mm across, are cut from selected areas of the specimen using a thin-bladed diamond saw. A flat surface is prepared using progressively finer (220, 325 and 600 grade) silicon carbide grit. The grinding is done by hand using a gentle figure-of-eight motion in a silicon carbide slurry on plate glass. Care must be taken to keep the surface perfectly flat. The blocks are thoroughly cleaned after each stage, as the presence of a single grain of a coarser grit can ruin the next stage. Separate glass plates are used for each grit to avoid cross contamination. At the end of the process, the prepared blocks are arranged with their ground surfaces uppermost and left to dry, protected from dust.

As the baryte is soft and the centres of the ooids are friable the specimens must be impregnated. Canada Balsam is used, following a method modified from the old literature. The prepared blocks are soaked in pure turpentine overnight and then immersed for a day or so in fairly thin solution of Canada Balsam in xylene. They are removed with tweezers and left to drain on a wire gauze, which is moved a few times to prevent sticking. The drying can be accelerated in a warm oven at about 40°C. Once the balsam has set hard, the blocks are carefully rubbed down once again with 600 grade grit, washed and dried.

In the next stage of the process, the blocks are bonded to microscope slides. A block is selected and lightly pressed into plasticine in a plastic petri dish, keeping the prepared surface clean and level. Loctite 358 (an adhesive which cures in ultraviolet light) is applied. A clean glass slide is carefully placed on top and moved around to expel any air bubbles. The slide is secured using four long pins stuck into the plasticine at the edges of the slide. It is placed under an ultraviolet lamp and left for sufficient time for the adhesive to cure (usually between thirty seconds and two minutes depending on the intensity of the lamp).

After a day or more, when the adhesive has completely set, the preparation is placed in a jig designed specially for the purpose and its thickness reduced on the diamond saw so that about 1.5 mm remains on the slide. The remaining material is ground with a succession of silicon carbide grits until the required thickness is reached. It is finished with 800 grade silicon carbide. Considerable care is needed to keep the section parallel. In the initial stages the thickness can be monitored with an engineer's micrometer, but once the thickness reduces to less than about 100 µm it must be inspected under a polarising microscope.

Once grinding is complete, the section is cleaned around the edges with a cosmetic bud, dipped in acetone to remove surplus glue, and washed in warm water containing a little detergent. After a rinsing in clean water it is left on a tray to dry.

If required, a cover glass is applied using natural Canada Balsam. A hotplate is set at 70–80°C to warm the slide and cover glass. Air bubbles commonly form in the balsam at this stage and these should be pricked or moved using a heated needle. The cover glass is moved gently down at an angle using cover-glass forceps, and when the balsam has run under it, the slide is placed on a tile or cold surface for a while to set. It is then placed on an aluminium slide tray in a laboratory oven at 100°C for about 75 minutes to cook the balsam. A quick check is made at the end of the process to ensure the cover glass has not moved: if it has it is usually possible to re-align it while the preparation is still hot using a needle. The slide is then left to go cold at which point it is ready to be labelled. A diamond-writer may be useful to put a code on slides at an early stage to facilitate later labelling.

The polarised light microscope is a valuable if somewhat neglected tool in the study of mineral deposits. This appendix shows that it is possible to prepare thin sections of difficult subjects with equipment which is within the reach of determined amateurs.

THE MINERALOGY OF WHITWELL QUARRY, DERBYSHIRE

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Fine specimens of anglesite, cerussite, descloizite, lanarkite, leadhillite, phosphohedyphane and vanadinite along with rare species such as cotunnite, mattheddleite, plattnerite and scotlandite make Whitwell Quarry one of the most interesting mineralogical localities in the British Isles. There are two distinct primary assemblages. Baryte, calcite, galena, marcasite, pyrite and sphalerite occur in cavities and fractures near the base of the late Permian dolostone. They are part of a disseminated basal assemblage associated with calcium sulphate dissolution which is widespread at this horizon across northeast England. Baryte and galena occur as veins and replacement deposits along a northern splay of the Park Hall Fault. This mineralisation is interpreted as a small and locally unusual epigenetic deposit. Oxidation of the epigenetic sulphides has produced a diverse suite of secondary minerals with a broadly consistent zonation and paragenesis. There are striking similarities with the classic supergene assemblage at Leadhills–Wanlockhead in southern Scotland. Anglesite and sulphur are the sole occupants of well sealed cavities in massive galena. Cerussite is common toward the outer edges of galena blocks. Cavities in this ‘infiltration zone’ contain minerals of the ‘Leadhills suite’ (particularly lanarkite, leadhillite, mattheddleite, susannite and scotlandite) where the carbonate ion activity was unusually low. Hydrocerussite, cerussite and phosphohedyphane dominate the oxidation rinds between galena and the dolostone wall-rock. Hydrocerussite is overgrown and replaced by cerussite, which, in turn, is overgrown and replaced by phosphohedyphane. Descloizite, hydroxylapatite, phosphohedyphane and vanadinite are common in the surrounding fractures.

INTRODUCTION

Whitwell Quarry, between the villages of Whitwell and Creswell in north Derbyshire, is one of the most unusual mineral localities in the British Isles. There was no indication of complex supergene alteration at any deposit in the Permian rocks of northeast England prior to the discovery of mineralisation along a northern splay of the Park Hall Fault in the mid-1980s. Rescue collecting over the next few years revealed one of the most important localities in Britain.

There are scattered occurrences of base-metal mineralisation in the local area. Lead was mined on a small scale near Whitwell in Elizabethan times (Pilkington, 1789). Epigenetic baryte and galena from the Sunnyside Deposit to the north of the village are re-examined in this journal (Bateman *et al.*, 2021a). Disseminated baryte, galena and sphalerite occur in calcite nodules at the base of the Permian sequence at Armstrong Quarry between Whitwell and Worksop (Bateman *et al.*, 2021b). These localities provide interesting comparisons with Whitwell Quarry.

Diaries compiled by the late Ray Richardson¹ show that the quarry site was visited by field parties from 1962 onward. The only minerals recorded on early forays are dolomite, calcite and ‘pyrolusite’² in cavities and fractures in thick monotonous dolostone (Richardson, 1967–1968; 1970–1980). The first reports of baryte and galena date from the late 1970s (Harwood, 1981) but there is no indication that any unusual supergene minerals were recognised before 1985, when the quarry manager asked Peter Briscoe (who was employed by the operating company) to investigate material that had appeared on blast piles. Ray Richardson, who also worked for the Steetley Group, was present on the early field trips and on 12 August 1985 his diary records:

¹ Further information about Ray Richardson (1930–2007) is included in Bateman *et al.* (2021a,b)

² Although they are commonly described as ‘pyrolusite’ (e.g. Ineson *et al.*, 1972) all of the manganese dendrites examined in this study are amorphous.



Figure 1. A grainy image showing Whitwell Quarry as it stood following heavy rain in the spring of 1987. Flood water, which reached 1.5 m deep, provided no obstacle to the quarry vehicles but exceeded the specification of the footwear worn by two of the authors (David Green and Peter Briscoe) and rendered the productive area inaccessible. Photo David McCallum.

“Visit with Peter to investigate the occurrence of Galena in the quarry. Large blocks were found and appear to be associated with a fault ... on breaking many cavities are seen with crystals of Cerussite – Anglesite and Pyromorphite ... The galena is very bright on fresh fracture surfaces and displays a radiating structure” (Richardson, 1982–1985).

Richardson’s diary goes on to note that these “rather unusual formations ... require further investigation”. This article, which was begun in earnest more than thirty-five years after those words were written, records the results of those investigations.

The reserves of refractory-grade dolostone on the two upper benches in the southwestern corner of the site were quarried away in the early 1980s. The epigenetic mineralisation described in this article was exposed along a strike length of a few hundred metres in a complex fault zone on the shallow bottom bench. The dolostone at this horizon contained too much silica for refractory production and was sold as aggregate or used on the site. Fortunately, from a field-collecting perspective, it was extracted relatively slowly.

The fault zone extended across the southwest of the quarry site from SK 528 752 to SK 535 749 (see Fig. 6). Mineralisation at the northwest end was sparse, but galena became abundant as the fault began to break up. Oxidation was locally intense. Hand specimens of anglesite, cerussite, descloizite, phosphohedyphane and vanadinite were relatively common and rare minerals of the ‘Leadhills suite’³ were found in a few places.

³ The ‘Leadhills suite’ of supergene minerals was originally described by Heddle (1901b: p. 178) as “special Leadhills minerals”. It includes caledonite, leadhillite, lanarkite and susannite, and the more recently described chenite, macphersonite, mattheddleite and

The importance of the supergene assemblage was recognised as a result of rapid analyses by staff at the Natural History Museum in London. Their encouragement was such that a small band of enthusiasts organised regular rescue collecting (Fig. 1). Members of the Doncaster Mines Research Group, including Max Freier, David Green, David McCallum, Ray Richardson and Steve Uttley made regular visits between 1985 and 1990.

By 1987, when staff from the Natural History Museum visited, quarrying had removed most of the fault zone. The mineralisation that remained lay beneath a shallow haulage ramp (Fig. 2). Specimens were recovered from this area until 1990, when the internal roadways were realigned and the ramp was removed. Visits were made on a weekly basis while there was a chance that new material might be uncovered. If no interesting material was exposed, ‘lead piles’ were sorted (Fig. 3). Repeated examination of blocks of galena with the aid of a hand lens, especially after rain had washed away rock flour and clay gouge, revealed specimens that would otherwise have been lost.

The exposures that remained at the end of the 1980s had been buried by 1992 when Steetley PLC was broken up. Sporadic field visits in the years until 1997 failed to locate any further mineralisation and the group eventually lost touch with the operation.

scotlandite. Modern geochemical studies show that these minerals crystallise in low-carbonate environments near to oxidising galena (e.g. Bridges, 2015). They are found in close association at the Leadhills–Wanlockhead mines in southern Scotland and at a number of localities in the Caldbeck Fells, Cumbria (Cooper and Stanley, 1990).



Figure 2. Highly brecciated dolostone at the base of the Cadeby Formation exposed by a shallow haulage ramp. One of the authors (David McCallum, left) and Chris Stanley of the Natural History Museum are examining the mineralisation. Photo Max Freier.

News of the discovery gradually leaked out as duplicate material was exchanged among collectors. The first published description of the supergene assemblage appeared fifteen years after the last specimens were collected in a note which briefly mentions cerussite, lanarkite and leadhillite (Green *et al.*, 2005). The rare lead sulphite scotlandite was reported in the following year (Neall *et al.*, 2006). Descloizite and phosphohedyphane are figured in *Minerals of Britain and Ireland* (Tindle, 2008). The most comprehensive account of the minerals to date is in the Derbyshire chapter of *Minerals of the English Midlands* (Starkey, 2018: pp. 135–139), where most of the supergene minerals are described and fifteen specimens are figured.

Collections were donated to the Natural History Museum in the late 1980s, and subsequently to Manchester Museum (where David Green was Keeper



Figure 3. One of the ‘lead piles’ at Whitwell Quarry. Galena from the fault zone was gathered in a safe area for leisurely investigation. The handle of the lump hammer, which is just visible on the right-hand side of the image, is 25 cm long and provides a scale. Photo Peter Briscoe.

of Mineralogy) and to Sheffield Museum. A considerable number of specimens ranging from cabinet to micro-mount size remain in the authors’ collections and many duplicates have been dispersed into the collector community. Two recent field visits confirm that the mineralised section of the fault zone has been completely quarried away. Readers should note that Whitwell is a large working quarry and access is not allowed without prior permission.

LOCATION

Whitwell Quarry, centred at SK 53 75, occupies most of the land between the villages of Whitwell and Creswell in northeast Derbyshire (Fig. 4). It extends across significant parts of four Ordnance Survey kilometre grid squares in the parish of Whitwell with Steetley. The eastern boundary of the site is close to the border with Nottinghamshire, and the nearest town, Worksop, is the administrative hub for the Bassetlaw District of that county. The workings are surrounded by arable fields and scattered woodland.

The quarry complex covers 191 hectares and is about 1.5 km from north to south and 2 km from west to east. It is bordered to the south by the famous prehistoric site at Creswell Crags, to the north by the village of Whitwell, and to the southwest by the village of Creswell. Former colliery spoil heaps to the east are being removed to expose dolostone reserves (see Fig. 4) and the eastern site boundary will eventually lie along the line of the A60 trunk road, close to the Nottinghamshire border.

The site chimney, which serves the calcining plant operated by Steetley Dolomite, is a prominent local landmark (Fig. 5). The operation is listed as two separate entities in the most recent edition of the *Directory of Mines and Quarries*, Whitwell Quarry [SK 531 750] and Whitwell Quarry North [SK 526 757]: both are controlled by Cement Roadstone Holdings, the parent company of Tarmac Aggregates (Cameron *et al.*, 2020).

HISTORY

The limestone which crops out around Whitwell village has been quarried for centuries. For much of that time, the locus of activity was at the Steetley Quarry Complex between Steetley and Darfoulds (see Bateman *et al.*, 2021b), but small quarries had developed near to the modern Whitwell Quarry site in the late nineteenth and early twentieth centuries (Ordnance Survey, 1885; 1922; 1950). A working with limekilns beside Southfield Lane [SK 5308 7612] is now occupied by an industrial estate. Smaller workings northeast of Whitwell Station [SK 5365 7627] and northeast of Creswell [SK 5282 7470] have been reinstated.

The chain of circumstance that led to the development of Whitwell Quarry is intimately linked to refractory production at the Steetley Quarry Complex. Reserves of kiln-grade dolostone (which were considered to be of strategic national importance in the twentieth century)

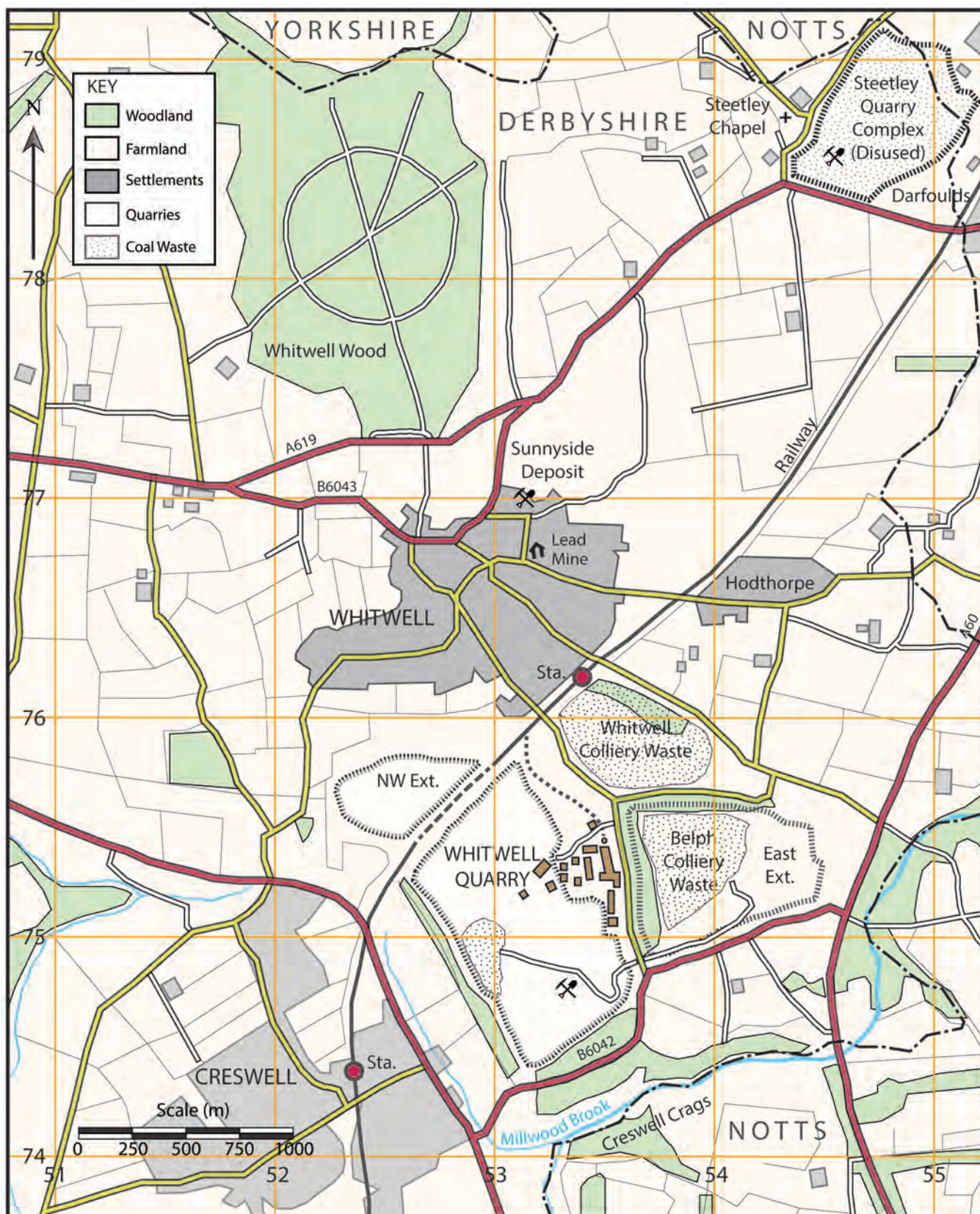


Figure 4. Map showing Whitwell Quarry in relation to major roads, the nearby villages of Whitwell, Hodthorpe and Creswell, and the famous prehistoric site at Creswell Crags. Two nearby sites of mineralogical interest, the Sunnyside Deposit to the north of the village of Whitwell and the disused and partly restored Steetley Quarry Complex, are also shown (Bateman *et al.*, 2021a,b). The approximate site of the Elizabethan lead mine is copied from Ineson *et al.* (1972) and further discussed in Bateman *et al.* (2021a). Four million tonnes of waste from Belpit Colliery are currently being moved into disused areas of Whitwell Quarry to expose dolostone reserves in the eastern quarry extension. The ‘haul road’ in the main quarry void runs along the former course of the mineralised fault zone.



Figure 5. Panoramic image of the quarry buildings in 2021, with the prominent chimney which serves the calcining plant on the left. Photo David Green.

had been exhausted at the quarries adjacent to the site by 1957. They were replaced by stone from Whitwell Quarry, where large additional reserves had been identified. The reserves at Whitwell Quarry were thick and homogeneous (Fig. 6) and easier to work than those at Armstrong Quarry, where marl bands in the Upper Subdivision of the Cadeby Formation had to be avoided and the Lower Subdivision was too contaminated to be used for refractory purposes (Bateman *et al.*, 2021b).

Whitwell Quarry had developed into an extensive site by the early 1990s (Fig. 7), when Steetley PLC⁴ was subject to a hostile takeover. The product range included DOLOFRIT[®], which was used to repair furnace hearths; DOLOMET[®], which was used to aid slag formation in steelmaking; DOLOPEL[®], which was used to make high-temperature furnace bricks for the steel and cement industries; ‘maglime’, which was used by farmers as a soil conditioner; and aggregate for use in construction and concrete manufacture (Redland, n.d.).

In 2016, the last year for which records are publicly available, Whitwell Quarry had 32 direct employees and contributed about six million pounds to the local economy (Tarmac, 2016). It supports more than 220 jobs, including those at Steetley Dolomite (now a subsidiary of the Lhoist Group), which operates two rotary kilns at its on-site works and processes 400,000 tonnes of kiln-grade dolostone annually.

GEOLOGY

The rocks which crop out in the area around Whitwell (Fig. 8) are part of a sequence of dolostones, evaporites, limestones, marls, mudstones, sandstones and siltstones collectively described as the Zechstein Group (Smith,

1989). They were deposited in shallow water at the western margin of the epicontinental Zechstein Sea. Conventional interpretations suggest that the sea was periodically cut off from an oceanic source over a period of about six million years in the late Permian. Evaporites (with varying amounts of fine-grained clastic sediment) were deposited in order of their solubility as the seawater evaporated.

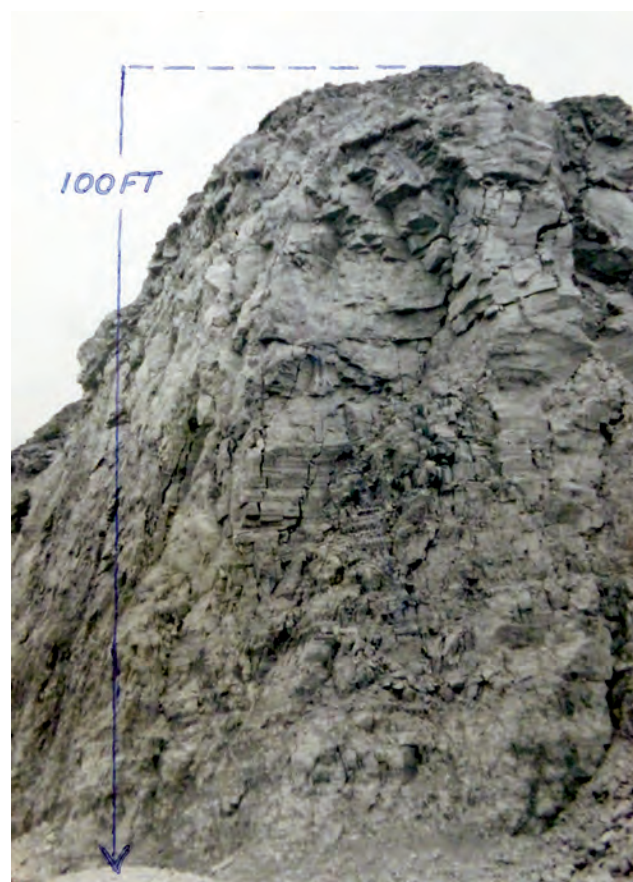


Figure 6. The south face of Whitwell Quarry on a field trip on 21 May 1967. About 30 m of pure dolostone is exposed. Photo Ray Richardson.

⁴ The ‘Steetley Minerals’ company name subsequently became available and was acquired by Peter Briscoe. It is currently registered as a mineral dealership.



Figure 7. Misty image of Whitwell Quarry, looking to the southeast, in 1992. Quarries in Cadeby Formation dolostone are necessarily shallow and the vast scale of the operation is evident. Photo Peter Briscoe.

At a regional scale, Zechstein stratigraphy is complex, with pronounced lithological variation between the basin margins and centre, and up to six major cycles of evaporite deposition (Smith and Taylor, 1992; Smith, 1995). The central areas of the basin beneath the North Sea have been mapped in detail as they contain major hydrocarbon reservoirs. The marginal sequence which crops out between Nottingham and the mouth of the River Tyne has attracted the attention of geologists for more than two centuries and is reasonably well understood (Stone *et al.*, 2010). The palaeogeography is described by Smith and Taylor (1992) and overviews are provided by Smith (1995), Ruffell and Shelton (2000), and Ruffell *et al.* (2006).

Unconsolidated regolith and wind blown dune fields which were present when the land was inundated form the base of the Permian sequence. This unit is described as the Yellow Sands Formation and is assigned to the Rotliegend Group. It is continuous in the area around Whitwell with an average thickness of about 7 m (Ineson *et al.*, 1972). Heavy mineral analyses show that the sand was derived from the surrounding Carboniferous rocks (Eden *et al.*, 1957).

The Marl Slate Formation overlies the Yellow Sands Formation and includes rock that was formerly described as Lower Permian Marl. It is a grey, finely laminated, silty, argillaceous dolostone with local accumulations of gypsum. The principal non-carbonates are detrital quartz, authigenic clays and pyrite. Trace-element analyses reveal high concentrations of lead, zinc and molybdenum in comparison to typical crustal abundances (Smith *et al.*, 1973: p. 114). Fine-grained galena and sphalerite occur as syngedimentary accumulations in the fabric of the rock. Remobilisation has produced more coarsely crystallised assemblages which extend into the overlying Cadeby Formation dolostone (Bateman *et al.*, 2021b).

The Marl Slate Formation is rather variable on a kilometre scale: it ranges between 0 and 20 m in thickness in the area covered by geological sheet 101 (Smith *et al.*, 1973: p. 121). In some sections the marly lithologies grade imperceptibly upward into the overlying dolostone; in others the boundary between the two formations is marked by a sharp upward change from soft grey marl to hard buff dolostone.

The Cadeby Formation, which was formerly described as the Lower Magnesian Limestone, overlies the Marl Slate Formation. It was deposited as reefs and ooidal shoals along the western margin of the Zechstein Sea (Eden *et al.*, 1957: p. 151). The type section at Cadeby Quarry reveals three distinct lithologies: dolomitised bryozoan-rich patch reefs with domed algal stromatolites of the Wetherby Member (formerly known as the Lower Subdivision) are separated from cross-bedded oolitic limestones of the overlying Sprotbrough Member (formerly known as the Upper Subdivision) by a thin sequence of interbedded mudstones and dolomitised oolitic limestones known as the Hampole Beds (Smith *et al.*, 1986). These divisions can be seen at some outcrops in the area around Whitwell (Eden *et al.*, 1957; Smith *et al.*, 1973).

The Cadeby Formation is the host rock for most of the mineralisation described in this article. The composition of the dolostone in the East Retford district is described by Smith *et al.* (1973: p. 123) as follows:

“In addition to dolomite and calcite and, locally, quartz, the Lower Magnesian Limestone contains a little ankerite⁵ in places, and there are accessory clay minerals, feldspars, micas, rock particles and oxides and hydroxides of iron. The last-named are

⁵ There is no evidence of ankerite in the modern mineralogical sense, this probably refers to iron-bearing dolomite (Bridges *et al.*, 2014).

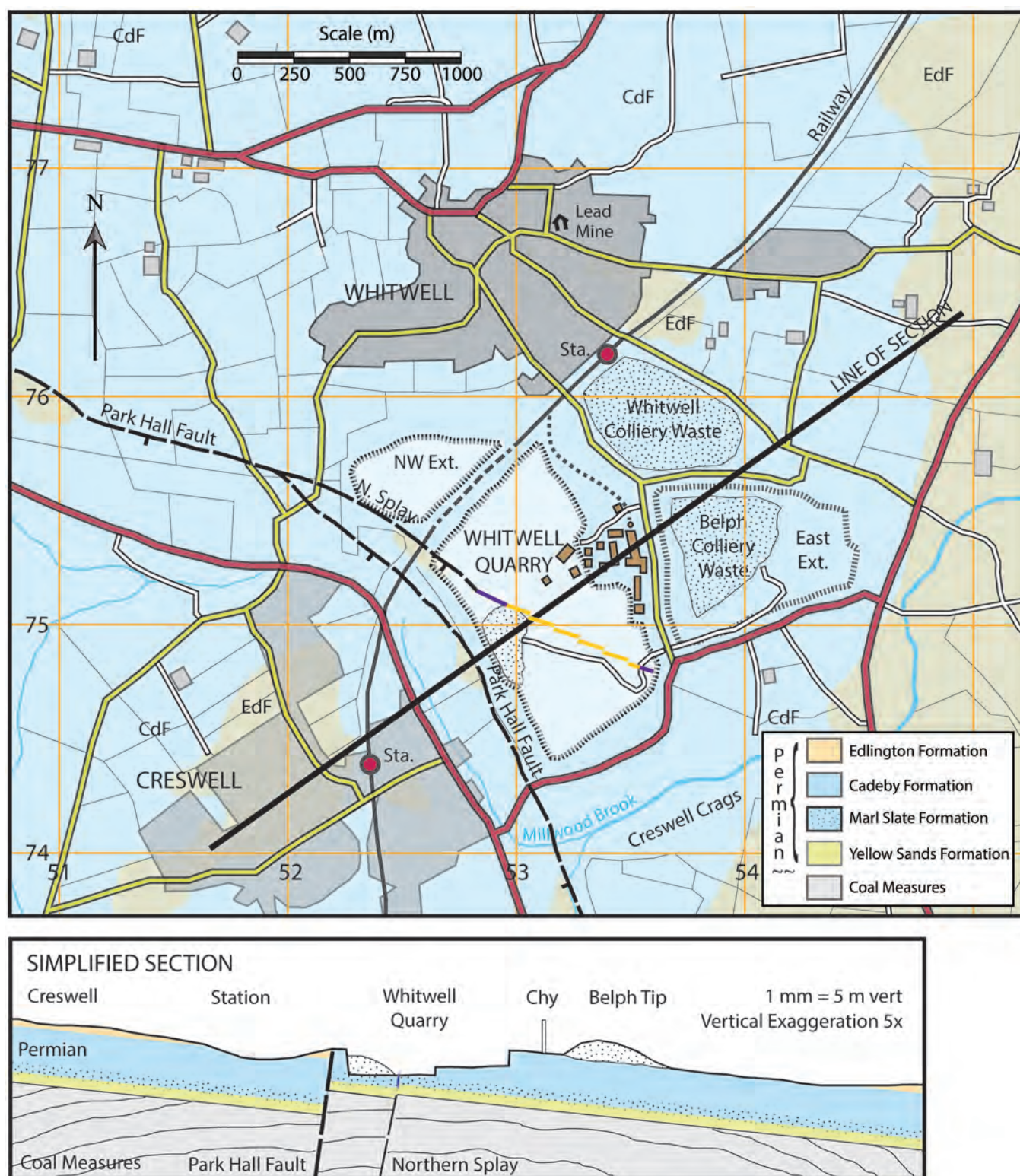


Figure 8. Geological sketch map and simplified section of the strata in the area around Whitwell Quarry. The map shows the outcrop of Cadeby Formation dolostone (CdF) and Edlington Formation mudstone (EdF). The course of the Park Hall Fault (dashed line) is shown with tick marks on the downthrow side. The northern splay of the fault has a smaller throw. It cuts obliquely across Whitwell Quarry, breaking into stringers and dies out to the southeast. Mineralised sections are indicated in purple and the presence of base-metal sulphides (mainly galena) in gold.

The simplified section is 4 km in length. It is exaggerated by a factor of five in the vertical direction. This gives a better idea of the topography and relative thickness of the strata, but exaggerates the shallow dip. The Marl Slate Formation is indicated on the section by the dotted shading at the base of the Cadeby Formation, but it is not included on the sketch map as its thickness varies and it can be difficult to differentiate from the overlying Cadeby Formation in the field. The section cuts across the large erosional outlier of Edlington Formation Mudstone beneath Creswell village and the small fault bounded outlier west of the Whitwell Quarry.

Contains British Geological Survey material © NERC [2021].

responsible for local pink or red coloration of the dolomites. Heavy minerals recorded include, in addition to iron ores, garnet, tourmaline and zircon. Pyrite occurs as specks and aggregates, and is also reported in pellet form: it is found most commonly in the lower part of the Limestone, and particularly at the base. Epigenetic pyrite, calcite and sphalerite occur in thin veins and as crystals infilling vughs, and small amounts of galena are recorded as specks and joint-coatings”.

“Anhydrite and gypsum have been noted in several underground sections, usually occurring as streaks, sometimes associated with red or grey mudstone bands”.

Dissolution has removed calcium sulphates from all of the exposures in the area around Whitwell, but their former presence was an important factor in the development of the basal mineralisation in the area.

Eden *et al.* (1957: p. 146) surveyed the area between Whitwell and Creswell before Whitwell Quarry was developed and describe the geology as follows:

“Between Whitwell and Creswell Crags crystalline granular wedge-bedded limestone is exposed at several localities. It is seen to a thickness of 40 ft in the crags flanking the dry valley at Whitwell, and is well exposed in the cuttings at Whitwell Station half a mile S.E. of the village. The limestone at the south-west end of the tunnel near here is referred to the lower subdivision ... There are quarries in crystalline and granular rock on both sides of the road at Hangingbank Wood threequarters of a mile S.S.W. of Whitwell; and at Creswell, 500 yd N.E. of the church, a quarry shows 20 ft of pink and buff finely-crystalline limestone in flaggy beds with

many stylolites, strongly false-bedded towards the north. These beds are close below the base of the Middle Permian Marl”.

“Between Whitwell and Creswell Crags, the belt of elevated ground on the upthrow side of the Creswell Fault shows numbers of knolls or ‘dome structures’ ... These are not ‘reefs’ for they consist, like the rock in the rest of the area, of granular crystalline false-bedded limestone”.

The rock is an unusually pure dolostone. Eden *et al.* (1957: p. 170) note that samples collected at outcrop contained “96.5 to 98.1 percent dolomite”, the principal contaminants being calcite and silica. Subsequent studies have shown that detrital quartz, clay minerals and authigenic silicates increase toward the underlying Marl Slate and are also concentrated in areas where the dolostone thins, and that iron oxides increase in abundance near to the land surface. Thin horizontal bands of red-brown clay and vertical fractures filled with a fine-grained red gouge are the only obvious contaminants in quarry faces (Fig. 9).

Recrystallisation had obliterated the original sedimentary structures in exposures along the fault zone. In the Cadeby Formation, saccharoidal recrystallisation fabrics are generally considered to have developed during pervasive dolomitisation not long after the sediments were deposited (Harwood, 1981). It is difficult to avoid the suspicion that fluids channelled along the Park Hall Fault had a local influence at Whitwell Quarry.

The shallow regional dip of between 1° and 2°, slightly to the south of east, takes the Cadeby Formation beneath the Edlington Formation to the east of the quarry



Figure 9. Whitwell Quarry looking toward the southeast from an internal roadway in 1988. The boundary face rises about 25 m above the quarry floor. Horizontal clay partings in the face, parallel to the original bedding, are occasionally displaced downward to the south by minor faults. The central axis of the fault zone is obscured in the boundary face at the far left by tipped overburden. Epigenetic galena was concentrated in dolostone in a shallow internal face below and to the right of where the photographer is standing (see Fig. 2). Photo Peter Briscoe.

site. This unit, which was formerly known as the Middle Permian Marl, consists of red to brown carbonate-rich mudstone with subordinate siltstone and sandstone. Gypsum and rock salt are present in buried sequences but absent at outcrop due to dissolution. Surface exposures typically reveal residual red mudstone or unconsolidated mud up to about 10 m in thickness.

The Edlington Formation crops out as a kilometre-wide north–south strip to the east of Whitwell Quarry. Thin erosional outliers remain for several kilometres to the west on topographic highs. The northwest part of Creswell village is built on one such outlier and two small fault-bounded outliers are present along the southwest boundary of the quarry site (see Fig. 8).

The Zechstein Group at Whitwell Quarry unconformably overlies folded and faulted Coal Measures sediments which had been eroded to low relief before the onset of sedimentation in the late Permian. The Whitwell Anticline, an asymmetric structure with an amplitude of about 300 m and a more steeply plunging northern limb, lies beneath the quarry site. The Park Hall Fault, a major basement structure with a downthrow of as much as 140 m in the Carboniferous (Rippon, 1985), runs near to the axis of the anticline southwest of the quarry boundary (see Fig. 8).

The Carboniferous fault pattern in the Whitwell area was mapped by the National Coal Board. It is described by Rippon (1985) and summarised as an inset to the most recent geological map of the area (British Geological Survey, 2011). The fault pattern is more complex in the Coal Measures than in the overlying Permian sequence. Small Coal Measures faults typically terminate at the unconformity. Some movement on the larger faults (including the Park Hall Fault which is of particular relevance to this discussion) post-dates Permian deposition.

The Park Hall Fault divides at about SK 520 756 to the west of Whitwell Quarry (British Geological Survey, 2011), with one limb (the main fault) running along the southwestern boundary of the site and the other (the northern splay) extending obliquely across the quarry floor (see Fig. 8). The major downthrow is on the southern limb, which changes from a WNW–ESE to a NNW–SSE course to the west of the quarry and extends for many kilometres in both directions. The northern splay maintains a WNW–ESE course with a small downthrow to the south. It reduces as it crosses the quarry floor and breaks into a series of *en échelon* stringers toward the southeastern boundary. The epigenetic mineralisation described in the following text is associated with this structure.

ANALYSIS

Initial analyses were conducted by X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) at British Coal's research laboratories in Wath-upon-Deane. Fragments of the less common supergene minerals were subsequently identified using Debye-Scherrer powder cameras at the Natural History Museum

and Leeds University. Specimens submitted for analysis at Manchester University between 1996 and 2010 were analysed by X-ray diffractometry and energy-dispersive X-ray spectrometry on a scanning electron microscope (SEM-EDS). When the authors' collections were re-examined in preparation for this article, a few further specimens were selected for XRD and SEM-EDS and the composition of a few bulk samples was determined by X-ray fluorescence spectrometry (Table 1).

SPECIES	IDENTIFICATION
ANGLESITE	XRD
BARYTE	XRD, XRF
Bindheimite	SEM-EDS
CALCITE	Wet Chemistry
CALEDONITE	SEM-EDS
CERUSSITE	XRD
COTUNNITE	XRD, SEM-EDS
<i>Covellite</i>	SEM-EDS
DESCLOIZITE	XRD, SEM-EDS, WDS
DOLOMITE	XRD, SEM-EDS
GALENA	XRD, SEM-EDS
GOETHITE	Visual
GYPSUM	SEM-EDS
HEMATITE	Visual
HEMIMORPHITE	SEM-EDS
HYDROCERUSSITE	XRD
HYDROXYLAPATITE	XRD, SEM-EDS
HYDROZINCITE	Visual
LANARKITE	XRD
LEADHILLITE	XRD
MALACHITE	Visual
MARCASITE	XRD, SEM-EDS
MATTHEDDLEITE	XRD, SEM-EDS, WDS
MIMETITE	SEM-EDS
<i>Periclase</i>	XRD
PHOSPHOHEDYPHANE	XRF, XRD, SEM-EDS, WDS
PLATTNERITE	XRD
PYRITE	XRD
PYROMORPHITE	WDS, SEM-EDS
QUARTZ	XRD
SCOTLANDITE	XRD, SEM-EDS
SMITHSONITE	Visual
SPHALERITE	Visual
SULPHUR	XRD
SUSANNITE	XRD, Optics
VANADINITE	XRF, XRD, IR, WDS.

Table 1. Species identified in the course of this study with the principal techniques used. The identification is considered beyond reasonable doubt for those species listed in upper case. Further analysis is required for those listed in lower case. An italic font indicates species that are not part of the natural assemblage. Abbreviations are: IR infra red absorption spectroscopy; SEM-EDS, energy-dispersive X-ray spectrometry on a scanning electron microscope; WDS, wavelength-dispersive X-ray spectrometry on an electron microprobe; XRF, X-ray fluorescence spectrometry on bulk samples; XRD, powder X-ray diffraction.

The quantitative data required to differentiate phosphohedypthane, pyromorphite and vanadinite was collected by wavelength-dispersive X-ray spectrometry on an electron microprobe at the Open University. Grains of descloizite, hydroxylapatite and mattheddleite were also studied by this technique. Measurements were typically made at an accelerating voltage of 20 kV and beam current of 20 nA with a 10 µm defocused beam.

MINERALS

The minerals of Whitwell Quarry are listed alphabetically in the following text. Species subtitles are in uppercase if there is no doubt about their identification and in lowercase if doubt remains; those in italic font are not part of the natural assemblage or otherwise erroneous. If the identification process was complex it is discussed in the relevant description.

The disseminated mineralisation is described before the epigenetic mineralisation where the same species occurs in both assemblages. Some discussion and interpretation, especially of the minor mineralisation, is included in the mineral descriptions to avoid repetition. Many of the images which accompany the mineral descriptions are available as red-cyan anaglyphs which can be examined in three dimensions on the Russell Society website.

ANGLESITE, PbSO_4

Anglesite is one of a handful of species that distinguish Whitwell Quarry as an important specimen locality. The finest crystals, though typically no more than a few millimetres in size, have remarkable transparency, lustre and perfection (Fig. 10).

Anglesite was almost always present in the larger blocks (>100 mm) of galena that were exposed on blast piles on early visits to the quarry. The crystals commonly spanned the cavities in which they had formed and shattered with perverse frequency. Anglesite was only present in blocks of sufficient size to shield the developing mineralisation from carbonating solutions. Where carbonating fluids have penetrated cavities during oxidation, anglesite is replaced by saccharoidal cerussite (see Fig. 25).

In the centre of large galena blocks, anglesite is commonly associated with sulphur and occasionally overgrown by colourless to yellow-brown cerussite crystals characterised by unusual asymmetric development and a high surface area in comparison to their volume (see Figs 27 and 28). It is sometimes coated by granular supergene galena, deposited during a local return to reducing conditions (Green *et al.*, 2005).

In association with minerals of the Leadhills suite, anglesite is usually early. Blocky crystals are commonly overgrown by leadhillite, mattheddleite and susannite. Distinctive 'ridge-back' and chisel-shaped crystals are occasionally intergrown with lanarkite and commonly associated with leadhillite and susannite (Figs 11 and 12; see also Fig. 52).



Figure 10. A small but exceptional transparent blocky anglesite crystal, 4.5 mm long, with a complex pyramidal termination and conspicuous striations on one pair of prism faces. Specimen Y20 in the Max Freier Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 11. Unusual 'ridge-back' anglesite, well shown in the crystal along the bottom of the image. The vertical crystal groups on the right-hand side have a similar morphology and strange asymmetric 'terminations'. The blocky leadhillite-like crystals in the bottom left-hand corner have been confirmed as susannite by X-ray diffraction. Specimen WQ041 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 2.8 mm across. Photo John Chapman.



Two generations of anglesite are present in some cavities: bladed prismatic first-generation crystals, with striations along their elongation direction; and blocky, tabular or prismatic second-generation crystals, with striations perpendicular to their elongation direction. First-generation crystals, which often span the cavities in which they have formed, are common and occasionally reach 30 mm in length. They are usually opaque and white, but sometimes grey to black due to galena inclusions. First-generation anglesite is not generally lustrous or transparent, although there are occasional exceptions (Fig. 13). It is commonly dotted with pale yellow sulphur crystals.

Blocky to tabular or prismatic second-generation crystals are often exquisite under magnification (Figs 14–16; see also Fig 10). They are usually no more than a few millimetres in length and more crystallographically complex than the first-generation crystals which they overgrow. Sulphur is conspicuously absent in cavities which contain second-generation crystals.

Figure 12. (*left*) Sharp pointed anglesite crystals are abundant in the bottom third of the image and their 'chisel-blade' habit is shown by a diffuse specular reflection from one of the smaller crystals in the upper right-hand corner. In common with the ridge-back crystals (Fig. 11) this crystal habit is most commonly associated with minerals of the Leadhills suite. The central rather rounded prismatic-tabular crystal contains diffuse dark brown phantoms, probably produced by nanoparticles of supergene galena. Specimen WQ041 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 1.5 mm across. Photo John Chapman.



Figure 13. Unusually lustrous prismatic first-generation anglesite, showing the typical crystal habit with light striations along the elongation direction. Specimen E102 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 6 mm across. Photo John Chapman.



Figure 14. Colourless tabular anglesite crystal, 2.5 mm in length, with a pointed termination. Specimen E101 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 15. Transparent prismatic anglesite, 3.5 mm from top to bottom, with conspicuous coarse striations on one pair of prism faces. Specimen WA21 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 16. Transparent equant anglesite with mirror-bright faces overgrowing pitted galena. Specimen MM1955 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.



Dark grey ghosts in anglesite are produced by galena deposited during local reversions to reducing conditions (Green *et al.*, 2005). Pale ghosts produced by void spaces in perfect continuity with the surrounding anglesite are less easy to account for. They provide a crystallographic conundrum which defies obvious explanation (Fig. 17).

BARYTE, BaSO_4

Baryte occurrences in the Cadeby Formation in northeast England are listed by Harwood (1981) and the various different types of primary deposit are categorised by Harwood and Smith (1986).

At Whitwell Quarry baryte occupies a variety of 'mineralogical niches'. It occurs as nodular replacements of calcium sulphates at the base of the dolostone; scattered crystal groups with base-metal sulphides in cavities and fractures left by the dissolution of calcium sulphates. It is also the principal primary gangue mineral in the fault-zone, where it occurs as veins, vein breccias, irregular replacement deposits and relatively rarely, as well formed crystals in cavities.

Figure 17. (left) A prismatic second-generation anglesite, 1.6 mm from top to bottom, containing a pale ghost in perfect crystallographic register with the surrounding crystal. The ghost has a few dark patches of supergene galena near the top but is otherwise hollow. The presence of a void was confirmed on a nearby crystal which was removed for inspection. Specimen MM1958 in the David Green Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 18. Curved translucent baryte overgrowing complex grey sphalerite on pale buff recrystallised dolomite. The field is 4.5 mm across. Specimen E153 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

The first definite record of baryte at Whitwell Quarry is a private communication between Richard Ineson and Gillian Harwood, which is recorded as ‘location 41’ in an appendix to Harwood’s PhD thesis (1981: p. A1/2) as “Baryte replacing dolomite with some galena in crystal vein”. It is probably from the northern half of the quarry, but impossible to place accurately as the grid reference “SK 5307542” has seven figures. The description suggests that baryte occurred in a mineralised fracture (i.e. “crystal vein”) and also replaced dolostone. This is consistent with mineralisation at the nearby Sunnyside Deposit and later discoveries along the fault zone at Whitwell Quarry, where epigenetic baryte veins are surrounded by replacement deposits.

The baryte which replaces calcium sulphate nodules at the base of the dolostone belongs to a regional assemblage which formed when invasive barium-rich brines replaced soluble calcium sulphates. Similar nodules are abundant in the area around Bramham in West Yorkshire and at other localities across northeast England (Barrett, 1975; Harwood, 1981; Harwood and Smith, 1986). Coarse opaque white to pale pink tabular baryte replaces ovoid nodules up to about 100 mm in size at the base of the Cadeby Formation at Whitwell Quarry. The composition is close to ideal end-member baryte, the only minor substituent being 1.0 wt% SrO.

Colourless to very pale blue tabular to prismatic baryte crystals and crystal groups accompany calcite, galena, pyrite and sphalerite in cavities and fractures near the base of the dolostone (Fig. 18). The cavitation is associated with dissolution and replacement of calcium sulphates (Harwood, 1980; Bateman *et al.*, 2021b). In this assemblage, baryte is always later than galena and sphalerite, but earlier than calcite. It commonly co-crystallises with pyrite. The crystals have a weak white to pale yellow fluorescence in longwave ultraviolet light; some contain small unidentified rounded inclusions with a strong yellow fluorescence.



Figure 19. Fine-grained hematite-stained baryte, replacing rounded dolostone clasts, embedded in a coarse white matrix. Specimen in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire, polished by Kelvin Betts. The field of view is 30 mm across. Photo Peter Briscoe.

Baryte is the principal primary gangue mineral in the epigenetic deposits along the Park Hall Fault. It occurs as veins and vein breccias and replaces dolostone (Fig. 19). There are strong similarities with baryte mineralisation at the Sunnyside Deposit to the north of Whitwell (Bateman *et al.*, 2021a). The primary vein and replacement textures at both sites have conspicuous similarities and there is minor development of the unusual purple bands which are characteristic of the Sunnyside Deposit on a few specimens from Whitwell Quarry.

Baryte crystals and crystal groups were found in fractures and cavities in the fault zone on early field trips to the quarry. There is considerable crystallographic variation; specimens include rosettes and fan-shaped crystal groups, some with complex white surface ornamentation, and transparent pale blue prisms (Figs 20 and 21).



Figure 20. A baryte rosette with minor iron staining on a 50 × 42 mm specimen from the fault zone. Specimen GB8 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo David Green.



Figure 21. Fan-shaped baryte crystal groups with oriented overgrowths on cellular dolostone. Specimen GC0 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 40 mm across. Photo David Green.

Bindheimite, $\text{Pb}_2\text{Sb}_2^{5+}\text{O}_7$

Bindheimite was renamed oxyplumboroméite in a standardisation of pyrochlore nomenclature (Atencio *et al.*, 2010) but it proved impossible to find the type specimen and its mineralogical status was changed from 'discredited' to 'questionable' pending further research (Christy and Atencio, 2013). It seems reasonable to retain the original name until this issue is resolved.

Bindheimite occurs rarely as pale yellow crusts and powdery masses in cavities in galena. It is tentatively listed on the basis of energy-dispersive X-ray spectroscopy, which confirmed the presence of lead and antimony.

CALCITE, CaCO_3

Although it is an important component of some Cadeby Formation dolostone (Eden *et al.*, 1957), pervasive dolomitisation has removed most of the rock forming calcite at Whitwell Quarry. Calcite is, nonetheless, widespread in a variety of mineralogical niches.

Millimetre-size curved rhombohedral crystals line cavities in dolostone from the northern quarry extension well away from the fault zone (Paul Nicholson, *personal communication*, 2021). This late-stage calcite is widespread in the Cadeby Formation (Harwood, 1981). Similar specimens occur in the Upper Subdivision of the Cadeby Formation at the Steetley Quarry Complex and many other nearby localities (Bateman *et al.*, 2021b).

Calcite occurs as rhombohedral and squat-prismatic hexagonal crystals with baryte, dolomite, galena, iron sulphides and sphalerite in the basal assemblage (Fig. 22). In some cases the crystals are conspicuously etched. Calcite post-dates all of the basal minerals with the exception of minor late-stage pyrite.



Figure 22. A white, translucent, etched calcite rhombohedron on pale buff recrystallised dolomite with lustrous galena and minor brown sphalerite. The field of view is 2.5 mm across. Specimen E126 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

Early field notes made by Peter Briscoe record veins containing calcite and baryte at the northwest end of the mineralised section of the fault zone, but calcite was not a major part of the primary gangue. Pale grey to white translucent tabular hexagonal and blocky pseudo-octahedral calcite crystals were found in a few fractures and cavities in fault-zone dolostone (Fig. 23).



Figure 23. Translucent hexagonal calcite crystals up to 1 mm across overgrowing sharp cuboctahedral goethite pseudomorphs after pyrite. Specimen MM1994 in the David Green Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

White sub-millimetre-size calcite rhombohedra occur rarely with supergene minerals in fractures in saccharoidal dolostone surrounding the fault zone. Most of the calcite occurs as isolated crystals and crusts which cannot be assigned a definite paragenetic position, but the hollow drusy calcite balls illustrated as Figure 24 are clearly late-stage supergene as they overgrow phosphohedyphane.



Figure 24. Rhombohedral calcite aggregates on pale green phosphohedyphane in an oxidation rind around massive galena. Initial suspicions that the white crystals might be an alunite-jarosite group mineral were dispelled by their vigorous effervescence in dilute acid. Specimen WQ056 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 14 mm across. Photo John Chapman.

CALEDONITE, $\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_6$

Copper minerals are rare at Whitwell Quarry. Diffuse patches of a pale blue fibrous supergene phase were identified by wet chemistry and energy-dispersive X-ray spectrometry as caledonite. The acicular to lath-like crystals are typically less than $1\text{ }\mu\text{m}$ thick, up to about $10\text{ }\mu\text{m}$ across, and several hundred micrometres long. They cover an area of about $7 \times 4\text{ mm}$ on an otherwise unremarkable specimen.

CERUSSITE, PbCO_3

Cerussite can be expected wherever galena oxidises. It is particularly common in carbonate host-rocks where it is occasionally found in sufficient quantities to be exploited as an ore. It is one of the most abundant supergene minerals from the fault zone at Whitwell Quarry.

Saccharoidal cerussite occasionally replaces anglesite where carbonating solutions have infiltrated cavities in galena in the course of oxidation (Fig. 25). In cavities containing minerals of the Leadhills suite, cerussite commonly overgrows and replaces leadhillite and susannite (see Fig. 98). In the oxidation rinds around galena it overgrows and replaces hydrocerussite and is overgrown and replaced by phosphohedyphane.



Figure 25. Anglesite with many of the smaller blocky crystals around the unaltered transparent central pair overgrown and replaced by saccharoidal cerussite. Specimen GA7 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 22 mm across. Photo David Green.

Epitaxial overgrowths of cerussite on hydrocerussite typically extend as acicular crystals parallel to the *c*-axes of the hydrocerussite plates. The two minerals are readily distinguished in longwave ultraviolet light: cerussite usually has a strong pale yellow to orange-yellow fluorescence but hydrocerussite has no discernible response. Epitaxial overgrowths of cerussite on leadhillite and susannite also extend at right angles to the ‘basal section’ but the cerussite tends to occur as prismatic rather than acicular crystals (Fig. 26). Both overgrowths are consistent with oxidation at increasing carbonate ion activity, which stabilises cerussite at the

expense of hydrocerussite and leadhillite (Williams, 1990; Bridges, 2015).



Figure 26. Transparent colourless twinned prismatic cerussite as an epitaxial overgrowth on leadhillite. Specimen E113 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

There is a marked variation in crystal habit moving outward from the centre of massive galena blocks. Colourless to honey-brown cerussite forms isolated groups of acicular to platy crystals deep within galena blocks where small amounts of ‘carbonating solution’ have infiltrated into cavities (Fig. 27). Strange lath-like crystals a few micrometres in thickness, thin ‘snow-flakes’ with patterned surfaces, pseudohexagonal reverse sceptres, and blocky crystals with acicular



Figure 27. Jumbled, irregular, acicular to lath-like cerussite crystals, typical of cavities deep within blocks of galena. Specimen E104 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

overgrowths and projections are sometimes present (Fig. 28). These unusual crystal habits are the result of non-equilibrium crystal growth probably produced by local supersaturation when a limited carbonate supply is introduced into a cavity with a relatively high lead ion activity (e.g. Raz *et al.*, 1999). Cerussite is usually the only supergene mineral in otherwise empty cavities in this situation, although it is occasionally associated with earlier anglesite and rarely with sulphur.

Translucent to transparent, tabular to prismatic cerussite crystals are common in cavities near to the surface of galena blocks. Tabular crystals often form complex twinned latticeworks (Fig. 29), and occasionally occur as isolated, lustrous, centimetre-size vee-twins. Blocky prismatic twins are common and usually asymmetric. Isolated translucent pale brown pseudo-hexagonal prisms occur rarely on pitted cuboctahedral galena (Fig. 30).

Cerussite is most abundant in the centimetre-thick oxidation rinds that surround masses of fault-zone galena. The crystals are typically dull, opaque and white with varied tabular to blocky pseudohexagonal

habits. Cavities typically follow the contour of the underlying galena. They range up to 10 cm across, and contain crystals up to 10 mm on edge, providing the largest, if not the finest, examples of the species from Whitwell Quarry (Fig. 31).

There is a transition from a carbonate-dominated to a phosphate-dominated supergene environment in the outer edges of oxidation rinds. Cerussite crystals are commonly replaced by phosphohedyphane, producing pseudomorphs with widely varying morphologies (e.g. Fig. 32). They are described in more detail under phosphohedyphane.

Blocky white cerussite occasionally overgrows phosphohedyphane in the outer edges of the oxidation rinds, but this reversal of the normal paragenetic sequence is unusual. The supergene assemblage in fractures in the dolostone is dominated by phosphates and vanadates. Blocky translucent white to pale yellow-brown cerussite crystals are occasionally present and, perhaps surprisingly, where they occur they generally show no sign of replacement by phosphohedyphane.



Figure 28. A cavity from the centre of a galena block containing cerussite in a variety of unusual crystal habits typified by high surface area to volume ratios. The central rocket-shaped crystal is a reverse sceptre, a habit which is less well developed in a smaller crystal at the left-hand side. There are several lath-like chisel blades, a couple of acicular crystals, and a thin pseudohexagonal plate at bottom centre. Specimen MM1946 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 3.4 mm across. Photo John Chapman.



Figure 29. A group of striated tabular vee-twin cerussite crystals in a galena cavity lined with platy leadhillite. Note the gentle curvature of the edge face on the thin crystal which joins the central twin group to the upper crystal and similar curvature on the thin crystal at bottom centre. Specimen E147 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 6 mm across. Photo John Chapman.



Figure 31. A typical cavity lined with white blocky cerussite in an 80 × 60 × 20 mm fragment of an oxidation rind which surrounded massive galena. Specimen E295 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo David Green.

Figure 30. (left) A columnar pseudo-hexagonal cerussite crystal on pitted galena. Specimen WQ037 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

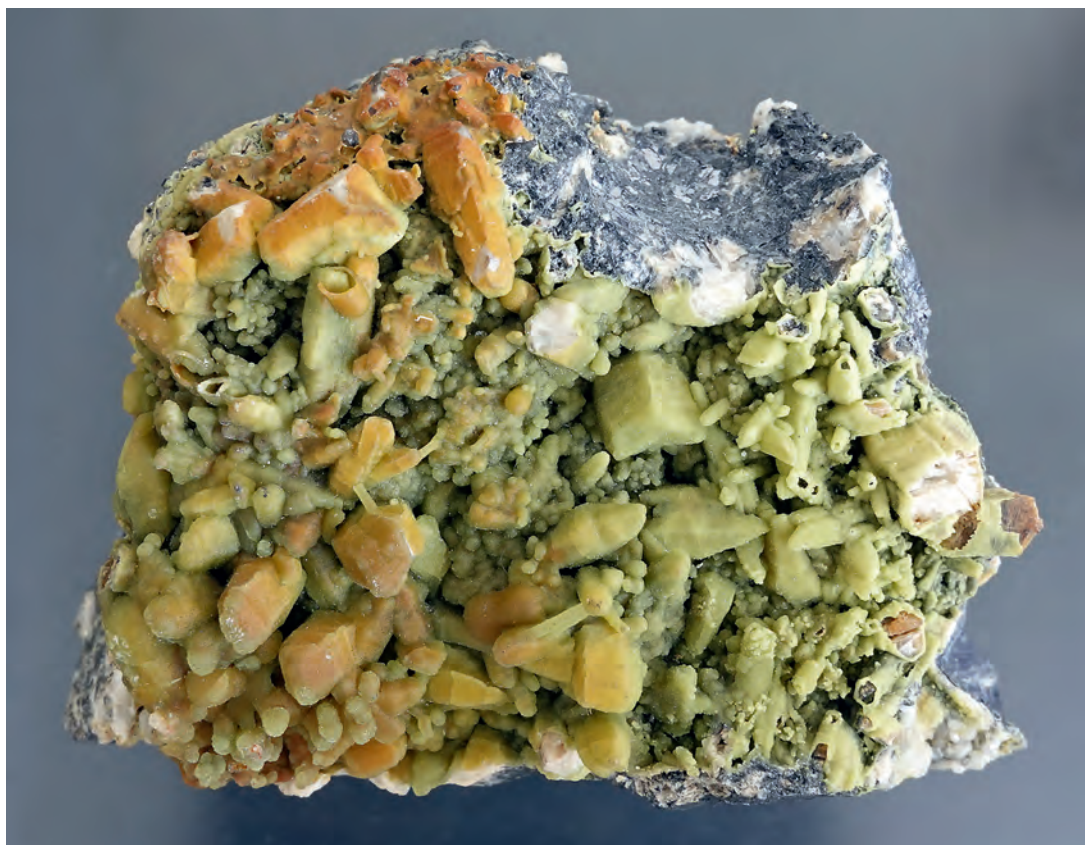


Figure 32. Sharp minutely drusy green to brown phosphohedyphane pseudomorphs after cerussite in a variety of blocky pseudo-hexagonal prismatic and pyramidal to acicular crystal habits on a 40 × 30 mm piece of galena. Some of the pseudomorphs have a conspicuous kernel of etched white cerussite, whilst others are hollow. Specimen E130, in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo David Green.

COTUNNITE, PbCl_2

Cotunnite is rare in the British Isles (Tindle, 2008). It was identified on a single specimen as interlocking bladed crystals (up to about 10 μm in length) in thin fractures in galena. A speculative discussion of its significance is included in the next section of this article.

Covellite, CuS

A whiskery covellite-like phase, which is almost certainly post-collecting in origin, was identified by energy-dispersive X-ray spectrometry. Similar copper-sulphide whiskers are commonly reported as post-collecting crusts on Leadhills-type supergene assemblages (e.g. Bridges *et al.*, 2008: p. 36).

DESCLOIZITE, $\text{PbZn}(\text{VO}_4)(\text{OH})$

Uncertainty surrounds many British records of descloizite due to confusion with mottramite and misleading claims of provenance (Tindle, 2008: p. 178). Identifications based on colour (orange-red = descloizite and black = mottramite) are untrustworthy and X-ray diffraction cannot reliably differentiate descloizite from other members of the adelite-descloizite group. Chemical analysis is generally required.

Examination by wavelength-dispersive X-ray spectrometry on an electron microprobe, and energy-

dispersive X-ray spectrometry on a scanning electron microscope show that the yellow, orange, red, brown and black crystalline crusts from Whitwell Quarry are descloizite. Bright orange-red to orange-brown crusts are associated with vanadinite on specimens which reach large cabinet size (Fig. 33).



Figure 33. A dense orange-brown descloizite crust with spots of manganese oxide and brown globular vanadinite in a fracture in dolostone. Specimen E127 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 35 mm across and the crust covers an area of 60 × 100 mm. Photo David Green.



Figure 34. Vibrant curved orange descloizite crystals in acicular white phosphohedyphane (identified by energy-dispersive X-ray spectrometry). Specimen E079 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field width is 1 mm. Photo John Chapman.



Figure 35. Dense orange-red descloizite overgrown by brown globular vanadinite in a fracture in dolostone around an oxidised galena mass. Specimen in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 10 mm across. Photo David Green.

Descloizite occurs as scattered crystals on the outer surfaces of oxidation rinds around massive fault-zone galena, where it commonly overgrows vanadinite and phosphohedyphane. This sequence may be reversed in fractures in the surrounding dolostone where vanadinite overgrows drusy orange-red to orange-brown descloizite (see Fig. 33). Isolated orange-brown crystals and crystal groups embedded in white acicular phosphohedyphane or (visually indistinguishable) lead-rich hydroxylapatite make attractive micromounts (Fig. 34; see also Fig. 101).

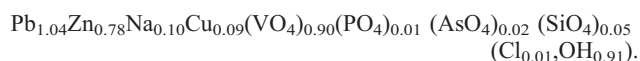
Descloizite occurs farther from the locus of mineralisation than any other lead-bearing supergene mineral. Crusts in fractures close to primary galena are commonly an intense, almost monochromatic, orange-red (Fig. 35). This shades toward chrome-red and brown away from the sulphide mineralisation, and yellow in the most distal occurrences. Coarse dark brown to black drusy crystalline crusts are present on a handful of specimens (Fig. 36). Quantitative analyses show that up to 27 mol% copper substitutes for zinc in one analysis of dark brown to black descloizite.



Figure 36. Black copper-rich descloizite as a dense drusy crust of sharply pointed crystals. Specimen MM1894 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

Individual descloizite crystals are commonly lanceolate with curved faces and sharp edges (see Fig. 34), and they may also be plane faced and tabular (Fig. 37). They rarely exceed 0.5 mm in their maximum dimension. Angular offsets around a common axis occasionally generate fan-like groups, but most of the clusters are rather random, with one dominant boat-shaped crystal and smaller haphazard offsets.

Chemical substitutions in the adelite-descloizite group are complex and extensive. The mean empirical formula, based on four oxygen atoms per formula unit, obtained from ten analyses of two different grains is:



This is consistent with the general formula for the adelite-descloizite group and close to the ideal end-member descloizite formula. Hydroxyl, calculated to maintain charge balance, is close to 1.0 and the cation and anion sums of 2.01 and 0.98, are very close to the ideal values of 2.00 and 1.00, respectively. The only significant substitutions are copper and sodium at the cation sites and arsenate anions (a more detailed discussion of the chemistry is included in the next section of the article).



Figure 37. Ultra-high magnification image showing a plane-faced orange-brown descloizite crystal group 0.2 mm across. Specimen E096 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

DOLOMITE, $\text{CaMg}(\text{CO}_3)_2$

Pervasive dolomitisation has obliterated depositional structures and replaced the original sedimentary carbonate at Whitwell Quarry (Eden *et al.*, 1957; Lott and Cooper, 2005). Fracturing and fluid migration has had an additional effect on the rock around the fault zone, locally reducing the dolostone to a powdery infill. A coarsening saccharoidal texture near to some fractures suggests that the fluids they contained facilitated local recrystallisation, but despite this local coarsening, drusy dolomite does not line mineralised fractures. In common with the nearby Sunnyside Deposit, dolomite does not appear to be part of the epigenetic primary mineralisation at Whitwell Quarry (Bateman *et al.*, 2021a).

Drusy dolomite recorded in cavities well away from the fault zone in undated field notes compiled by Ray Richardson is part of a widespread assemblage in the Cadeby Formation of northeast England (see Harwood, 1981; Bateman *et al.*, 2021b).

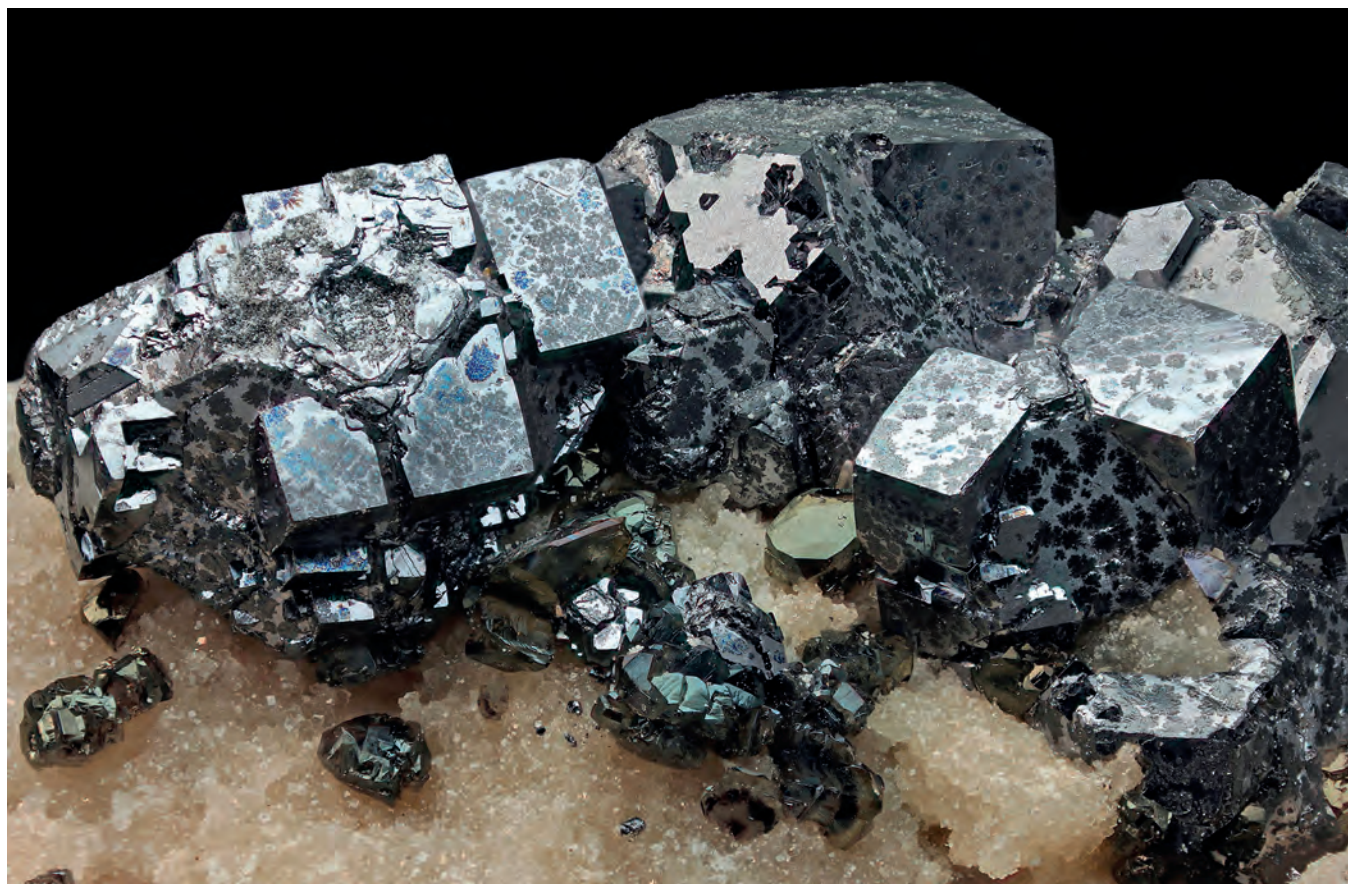


Figure 38. Octahedral to cuboctahedral galena crystals up to 2.5 mm across, with cubic offsets, overgrown in a few places by brown sphalerite in a fracture in saccharoidal dolomite. The crystal faces are covered in dendritic and occasionally somewhat iridescent features, which may be associated with the onset of oxidation. Specimen MM 1983 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 6.5 mm across. Photo John Chapman.

GALENA, PbS

The distribution of galena in the Permian rocks of northeast England is summarised by Harwood (1981) and the different types of deposit are classified by Harwood and Smith (1986).

In addition to syngenetic smears in the Marl Slate Formation and coarser accumulations in the overlying dolostone, galena is a component of two distinct assemblages at Whitwell Quarry. It occurs as isolated crystals with baryte, calcite and sphalerite in cavities and fractures left by the dissolution of calcium sulphates at the base of the Cadeby Formation; and as isolated blocks, discontinuous veins, vein breccias, and reniform masses along a northern splay of the Park Hall Fault.

In the basal assemblage galena occurs as lustrous cubic to cuboctahedral crystals up to about 6 mm on edge (Fig. 38). Some are plane faced, others skeletal. They are commonly associated with translucent sphalerite. The base-metal sulphides are commonly overgrown by baryte and calcite.

Galena was more abundant than any other primary mineral in the section of the fault zone studied by the authors. Quarrying occasionally uncovered isolated masses up to half a metre across in brecciated dolostone near the centre of the fault zone (Fig. 39). They were typically



Figure 39. A loose galena block mantled in a thin layer of red clay on a blast pile at Whitwell Quarry. The broken surface exposes massive galena and a little cerussite. This block, like most others from the fault zone, contains massive galena and very little else. The lump hammer handle is 25 cm long. Photo Peter Briscoe.

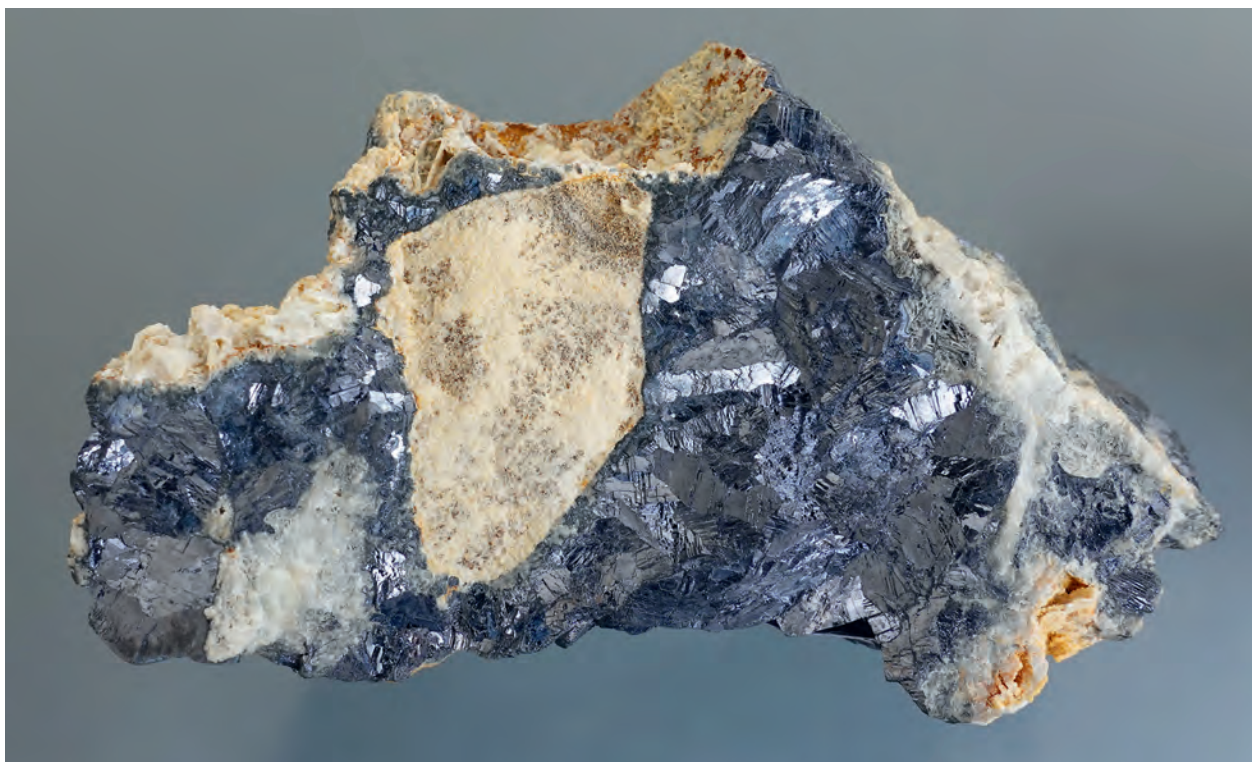


Figure 40. Galena as a vein breccia, 55 mm across, with a prominent subangular dolostone clast patterned with dendritic manganese oxides. Alteration along the top right-hand edge has produced a patch of grey hydrocerussite, but an examination in longwave ultraviolet light shows that the platy 'hydrocerussite' on the rest of the specimen has been replaced by cerussite. Specimen WQ043 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo David Green.

composed of a mosaic of galena and no other primary minerals. Discontinuous galena veins and vein breccias (Fig. 40), some with associated baryte, were concentrated in and around fractures that bounded the fault zone. Most of the galena in this situation was massive, but cubic crystals, some pseudomorphed by cerussite and phosphohedyphane, were found in fractures in the dolostone and cavities lined with crude cuboctahedra were occasionally present in massive galena.

Spectacular specimens of botryoidal galena (Fig. 41) were discovered early in 1986 in replacement deposits near the edge of the fault zone. Their curved surfaces were bright and lustrous despite extensive local oxidation. One flat-lying cavity, up to about 20 cm high, extended for about 3×1 m horizontally; an irregular cavity nearby was about 2 m high and defined by vertical fractures. Loose masses of botryoidal galena were found in a sandy dolomite infill with abundant cerussite, hydrocerussite and phosphohedyphane.

The botryoidal galena has morphological similarities to 'kidney hematite'. Its curved cleavage planes are locally parallel to (100). Broken cross-sections reveal a radiating internal structure in which subparallel domains a few tenths of a millimetre square extend for several millimetres along (100) until they are interrupted by curved discontinuities (Fig. 42). The discontinuities contain thin overlapping plates which lie perpendicular to the growth direction. They have an interlocking fish-scale texture which is best seen on their convex outer surfaces (Fig. 43).

It is unusual for galena to develop a botryoidal habit. No similar specimens are known from the Permian rocks of northeast England (Harwood, 1981; Tindle, 2008; Young *et al.*, 2021). Fine-grained botryoidal masses of sphalerite intergrown with wurtzite, galena and pyrite, described as 'schalenblende', occur at a number of European localities. They are believed to form by rapid crystallisation from low-temperature sulphide gels (Fleet, 1977). Unlike schalenblende, the botryoidal galena from Whitwell Quarry is relatively coarse. The only similar occurrence of which the authors are aware is at Larkin's Quarry, Co. Galway, Ireland (Sweeney and Unitt, 2021). This occurrence, in a high-temperature fluorite-rich vein plexus in granite, has few geological similarities with the low-temperature carbonate-hosted deposit at Whitwell Quarry.

Supergene galena occurs as thin granular overgrowths on anglesite, cerussite, hydrocerussite, lanarkite and leadhillite (Fig. 44). They indicate a limited and local return to reducing conditions (Green *et al.*, 2005). The brown colour of some supergene lead minerals, particularly cerussite from deep within galena blocks, is probably due to nanoscale inclusions of galena. Larger inclusions are responsible for the dark grey to black colour of some cerussite, hydrocerussite, lanarkite and leadhillite.

In addition to granular supergene galena (which was identified by X-ray diffraction) jet-black lead sulphide spherules (<0.2 mm) occur rarely on anglesite, cerussite and leadhillite. Their surfaces are smooth without any obvious cleavage even under a scanning electron microscope. They



Figure 41. A 55 × 80 mm mass of botryoidal galena with reniform domains divided by thin white hydrocerussite-cerussite septa. A broken area at the top left shows that the curved cleavage extends through the mass. Specimen E152 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo David Green.

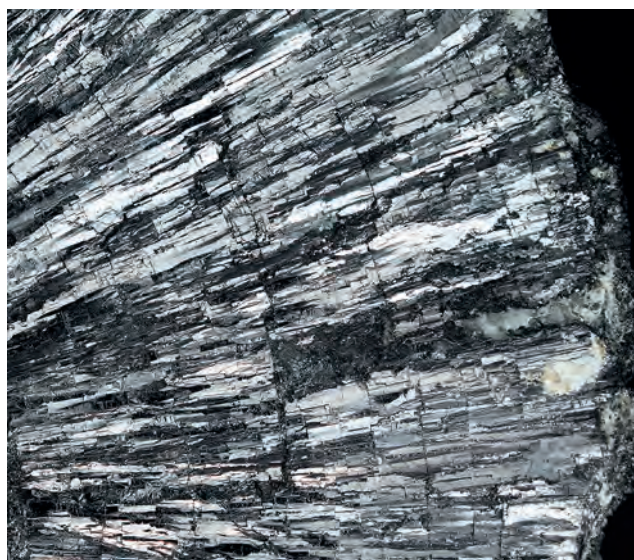


Figure 42. Transverse section through a mass of botryoidal galena showing elongated subparallel domains extending along the (100) growth direction for several millimetres until they are interrupted by curved discontinuities. Specimen WQ051 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 19 mm across. Photo John Chapman.



Figure 43. The convex outer surfaces of a mass of botryoidal galena with an interlocking fish-scale texture made up of thin curved galena plates. A developing septum is visible at the lower left. Specimen WQ048 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 9 mm across. Photo John Chapman.

may be related to a botryoidal silver-bearing lead sulphide described at the end of this section (see Fig. 91). Insufficient material was available for a complete characterisation with the techniques available to this study.



Figure 44. A thin crust of granular galena on a relatively unaltered anglesite crystal, 0.2 mm across, from Whitwell Quarry, Derbyshire. SEM photo by Christian Rewitzer.

GOETHITE, $\alpha\text{-Fe}^{3+}\text{O(OH)}$

Goethite and hematite are the end-points of most supergene alteration sequences which involve iron minerals (Cornell and Schwertmann, 2003). Goethite is responsible for the attractive pale yellow-brown colour of weathered Cadeby Formation dolostone (Smith *et al.*, 1973). Dark limonitic patches are common on exposed surfaces where specks of authigenic iron sulphide have oxidised.

Goethite does not occur in the basal assemblage, except perhaps as films on the tarnished surfaces of iron sulphides. In the fault-zone it is present as pseudomorphs after pyrite (Fig. 45) and as brown patches in pale green phosphohedyphane. In its powdery limonitic form it is commonly associated with cellular hemimorphite.

GYPSUM, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$

Mineralisation in the basal dolostone at Whitwell Quarry is concentrated in and around voids produced by the dissolution of calcium sulphates [which remain in the more deeply buried sequences to the east (Smith *et al.*, 1973: p. 123)]. Problems of stability and metastability make it impossible to be sure whether they were anhydrite, gypsum or a mixture of the two (van Driessche *et al.*, 2019). Direct evidence of the former presence of gypsum is provided by



Figure 45. A sharp goethite pseudomorph after pyrite, 0.7 mm on edge. Specimen MM1994 in the David Green Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

six-sided prismatic voids in baryte on a single specimen from the basal assemblage. Such structures are described using the Swiss term *narben*, which refers to the impressions left when crystals are removed by dissolution (Kloprogge and Lavinsky, 2017).

Supergene gypsum occurs rarely as clusters of monoclinic blades in fractures in galena. It appears to have formed recently in a reaction between sulphuric acid generated by pyrite decay and calcium-bearing carbonates.

HEMATITE, Fe_2O_3

The red to pink coloration of some vein and replacement baryte is due to submicroscopic hematite inclusions. Larger inclusions are almost certainly responsible for the rare purple tinge in bands of coarser baryte (cf. Bateman *et al.*, 2021a). The red gouge in the fault zone is probably also coloured by traces of fine-grained hematite.

HEMIMORPHITE, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$

Hemimorphite occurs in cellular limonitic boxworks and as fan-like crystal clusters with cerussite and hydrocerussite (Fig. 46). Dark vitreous masses containing residual sphalerite are occasionally associated with lead carbonates in the oxidation rinds around galena.

Hemimorphite was once plentiful in the fault zone. It is commonly etched and the limonite-coated crystals in some fractures are so badly pitted that they are barely recognisable. Crystal groups were sometimes coated by drusy phosphohedyphane before they dissolved and, in these instances, the former presence of hemimorphite is betrayed by hollow pseudomorphs (Fig. 47). They are described in more detail under phosphohedyphane.



Figure 46. Unusually large brown translucent hemimorphite with well developed negative terminations in white platy hydrocerussite which has been overgrown and replaced by cerussite. Specimen E298 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 6 mm across. Photo John Chapman.



Figure 47. White to pale brown phosphohedyphane pseudomorphs after hemimorphite. Specimen WQ065 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 4 mm across. Photo John Chapman.

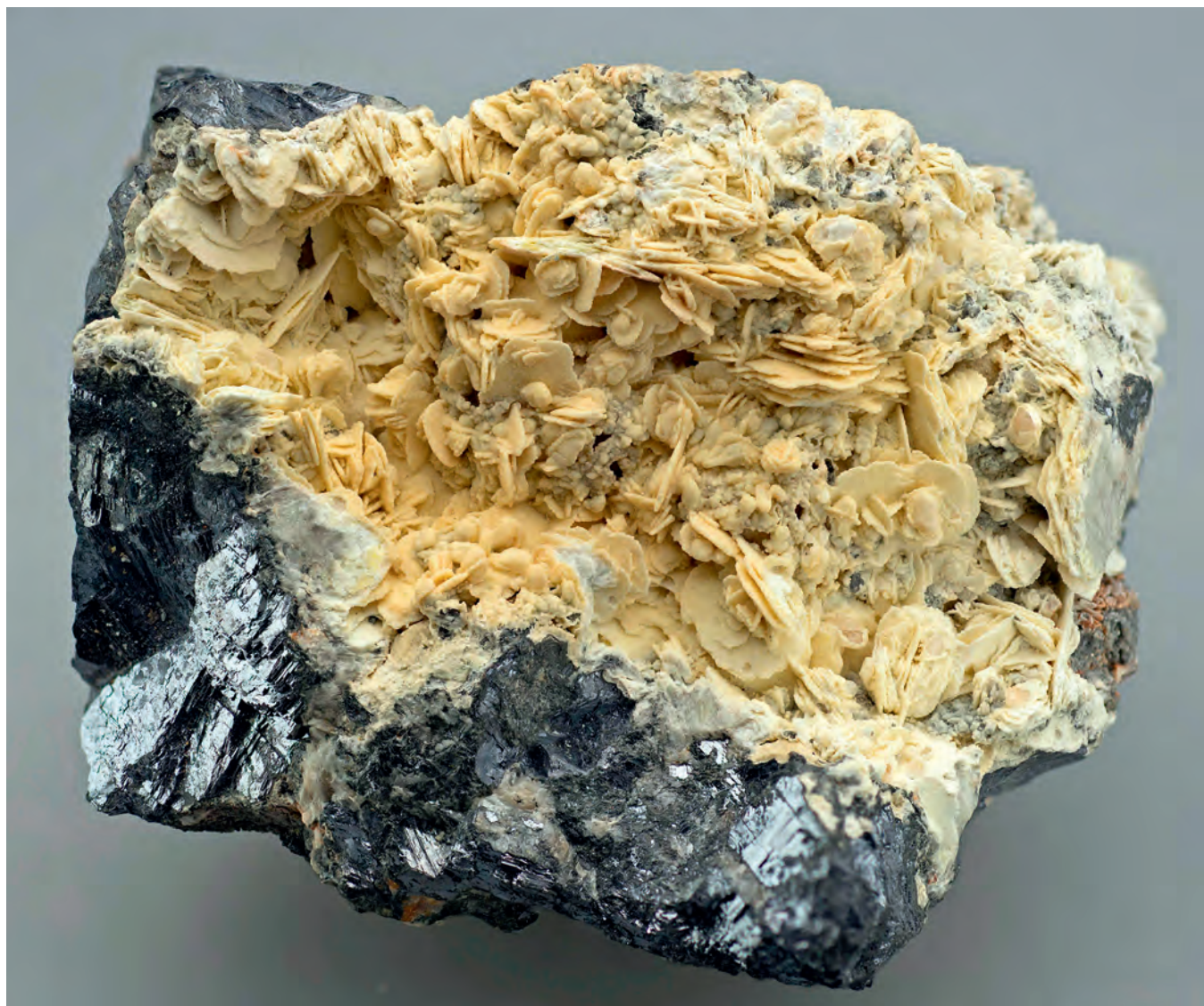


Figure 48. Discoidal hydrocerussite crystals up to 8 mm across with surface alteration to buff cerussite in a cavity in galena. Specimen GD3 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo David Green.

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

In the normal course of alteration, microbial activity and the presence of soluble carbonates raise the carbonate ion activity around galena into the cerussite stability field. Hydrocerussite requires a relatively low carbonate ion activity to form (Williams, 1990; Bridges, 2015). It is widespread in small amounts in the Caldbeck Fells (e.g. Bridges *et al.*, 2008; Green *et al.*, 2008) and at Leadhills–Wanlockhead (Temple, 1954), but rare in carbonate-hosted deposits in the Pennine orefields (Ford *et al.*, 1993; Bridges and Young, 1998; Tindle, 2008).

Hydrocerussite is readily identified in all but its most compact forms by its perfect cleavage, curved platy habit and lack of fluorescence. Hydrocerussite is abundant in the oxidation rinds around massive galena, where it forms the innermost layer in direct contact with the sulphide. Crystals are commonly white, rarely mint green or pale custard yellow, and occasionally dark grey due to inclusion of supergene galena. They range up to about 12 mm on edge and usually have a rounded platy

habit, occasionally occurring as rosettes or jumbled intergrown masses, and rarely as ‘poker-chip’ aggregates, stacked along the *c*-axis (Fig. 48).

Lustrous white to dark grey discoidal crystals are rarely associated with columnar leadhillite and susanite in cavities containing minerals of the Leadhills suite (Fig. 49). Stability field calculations show these minerals share a phase boundary at relatively low $p(\text{CO}_2)$ (Bridges, 2015: pp. 10–11). In most cases the paragenetic sequence is hydrocerussite followed by leadhillite followed by cerussite.

When specimens were re-examined in preparation for this article, there was concern that the revalidation of plumbonacrite and recent description of the pale green hydrocerussite-like mineral somersetite (Siidra *et al.*, 2018a,b) made the original identifications unreliable. Material from the core of a green blade was sampled and proved to be a perfect match for hydrocerussite. Further analyses gave no indication that any of the rare hydrocerussite-like minerals occur at Whitwell Quarry.



Figure 49. Dark discoidal hydrocerussite, possibly due to included galena, overgrown by pseudo-hexagonal leadhillite and possibly a little rhombohedral susannite at the bottom centre. An asymmetric horizontally striated cerussite crystal overgrows both species. The paragenesis is hydrocerussite–leadhillite–cerussite. Specimen E146 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 10 mm across. Photo John Chapman.

HYDROXYLAPATITE, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$

Lead-bearing hydroxylapatite is commonly intergrown with phosphohedyphane in nondescript white crusts associated with brown botryoidal vanadinite [the specimens are very similar those reported from Leadhills–Wanlockhead by Livingstone (1994)]. It also occurs in white acicular crusts with descloizite (see Fig. 101). Hydroxylapatite cannot be visually differentiated from phosphohedyphane in either of these associations (compare Figs 34, 87 and 101). Analyses suggest that it is rarer than phosphohedyphane and that it usually occurs at the end of the phosphate crystallisation sequence. On every example examined in this study it is associated with lead-bearing vanadate minerals. Precipitation of vanadinite or descloizite may remove sufficient lead from solution to favour the formation of hydroxylapatite rather than phosphohedyphane. In this situation white acicular hydroxylapatite overgrows green to white phosphohedyphane.

Quantitative analyses are consistent with an empirical formula:



based on five cations per formula unit. A more detailed discussion of the chemistry is included in the next section of the article.

HYDROZINCITE, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$

Hydrozincite occurs as thin coatings. Its presence in the supergene assemblage at Whitwell Quarry is probably the result of recent alteration of smithsonite or hemimorphite.

LANARKITE, $\text{Pb}_2(\text{SO}_4)\text{O}$

Lanarkite is the quintessential Leadhills-suite supergene mineral. It requires a very low carbonate ion activity ($p\text{CO}_2=7.2$) and relatively alkaline conditions to form (Bridges, 2015: pp. 10–11). Remarkable specimens are known from Leadhills–Wanlockhead in southern Scotland (Livingstone, 2002); micro-crystalline aggregates have been identified at a number of localities in the Caldbeck Fells (Green *et al.*, 2008; Green *et al.*, 2019). Lanarkite is otherwise rare in Britain: there are a few minor localities in central Wales but none in the Pennine orefields (Tindle, 2008).

The presence of lanarkite distinguishes Whitwell Quarry as geochemically unusual. In a British context, the specimens are second only to those from the Susanna Mine at Leadhills in terms of their size and quality. Most were found in cavities in galena, or between galena and baryte, in a vein on the southwest side of the fault zone in October 1986. Lanarkite was restricted to small areas where the assemblage had been protected from ‘carbonating fluids’. There are no other British localities in carbonate host rocks.

Lanarkite typically occurs as yellow to yellow-brown translucent prismatic crystals with chisel-shaped terminations (Fig. 50). Colourless to pale honey-brown cleavages (Fig. 51) and opaque white lath-like crystals, some with ragged terminations, also occur. Terminated crystals are usually less than 10 mm in length, but masses of poorly terminated buff to yellow-brown prisms, filling cavities in galena or between baryte and galena, reach 50 mm across.



Figure 50. Translucent to transparent, yellow prismatic lanarkite crystals (identified by X-ray diffraction), possibly with Type 2 scotlandite. Specimen E107 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

Lanarkite is usually the only major supergene mineral that is present in the cavities in which it occurs. It is sometimes associated with scotlandite; occasionally overgrown by leadhillite, mattheddleite and susannite; and rarely associated with 'ridge-back' anglesite crystals (Fig. 52).



Figure 51. Colourless to pale honey brown lanarkite cleavages on oxidised galena, identified by X-ray diffraction. Specimen E105 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 12 mm from top to bottom. Photo John Chapman.



Figure 52. Well formed prismatic pale brown lanarkite crystals (one on the left-hand side with an unusual pale sceptre) associated and intergrown with colourless striated 'ridge-back' anglesite crystals. Specimen WQ063 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 6.5 mm across. Photo John Chapman.



Figure 53. The leadhillite specimen found on 5 July 1986, with tabular to equant pseudo-hexagonal crystals up to 6 mm overgrowing discoidal stacked poker-chip hydrocerussite, and with later white tabular vee-twin cerussite. Specimen GB7 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo Peter Briscoe.

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

The first indication of good specimens of leadhillite at Whitwell Quarry came in mid-1986. A record maintained by two of the authors notes:

“It was from the centre of [the] vein that the most exciting discovery so far was made on the 5th July 1986 when LEADHILLITE was found as hexagonal plates and prisms up to .5 cm long. The Leadhillite is accompanied by Anglesite and an as yet unidentified platy [*sic*] mineral”.

The unidentified platy mineral was later shown to be hydrocerussite (see Fig. 49) and the plates and prisms were confirmed by X-ray powder diffraction as leadhillite. Further discoveries were made later in 1986 and 1987, but the find of 5 July 1986 (Fig. 53) was never surpassed.

Leadhillite typically occurs as thick pseudo-hexagonal plates, up to about 10 mm across, some with opposing chamfers around the girdle (Fig. 54). Less common habits include thin platy crystals, pseudo-hexagonal prisms (see Fig. 49). Large crystals are invariably opaque and white, whereas crystals smaller than about 2 mm are commonly colourless and transparent. In longwave ultraviolet leadhillite has a strong pale yellow fluorescence (Fig. 55).

Leadhillite occasionally overgrows anglesite, is often intimately associated with mattheddleite, is commonly overgrown by cerussite and rarely coated by

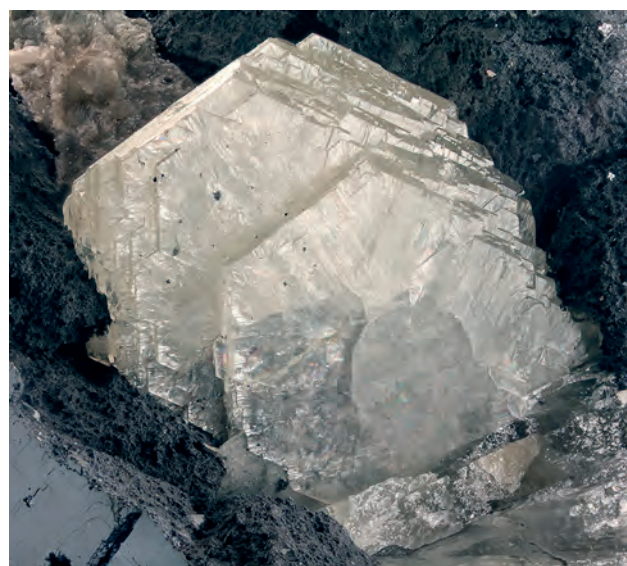


Figure 54. Tabular pseudo-hexagonal leadhillite, 5 mm across, with characteristic offset chamfers around the girdle, in a cavity in pitted galena. Specimen E115 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

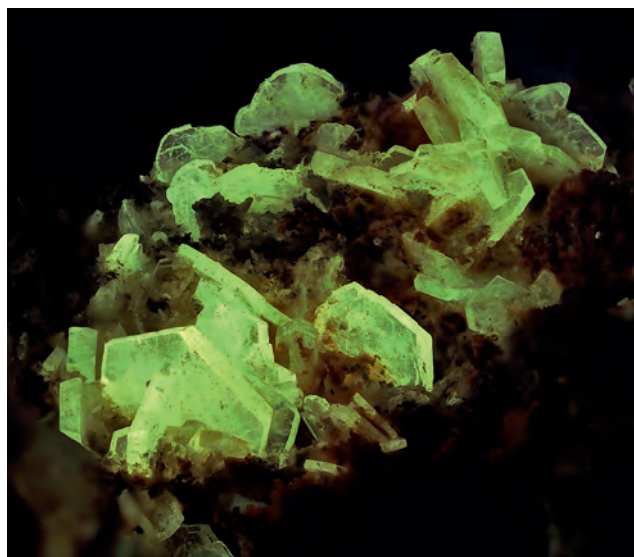


Figure 55. Tabular pseudo-hexagonal leadhillite crystals with strong pale yellow fluorescence in longwave ultraviolet light (370 nm peak) overgrowing scotlandite, which has very weak fluorescence (see also Editorial: Figure 6). Specimen GC4 in the Peter Briscoe Collection. The field of view is 6 mm across. Photo John Chapman.

phosphohedyphane (see Fig. 72). In direct association with cerussite, leadhillite is sometimes corroded whereas cerussite is fresh and lustrous (see Fig. 98). This suggests a gradual change in conditions as the minerals crystallised, increasingly favouring cerussite rather than leadhillite.

Limited analyses suggest that leadhillite is more common than susannite at Whitwell Quarry. Livingstone (1993: p. 11) notes that the two polymorphs commonly occur as intergrowths and this may account for the inconclusive results of some determinations. As discussed in the description of susannite, crystal morphology does not provide a reliable guide to identification (see also Fig. 11).

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

Most records of copper minerals from the Cadeby Formation in northeast England are from the Upper Subdivision (Deans, 1961; Barrett, 1975; Harwood, 1981; Bateman *et al.*, 2021a). The presence of copper-bearing descloizite (see Table 6), copper sulphide whiskers, traces of caledonite and possible linarite show that a small amount of copper was present in the supergene system. Malachite is surprisingly rare. It has been identified as pale green spherules on two specimens.

MANGANESE OXIDES

Manganese oxides are widespread in Cadeby Formation dolostone. They form when manganese held in solid solution in carbonates is released, oxidised and immobilised in cracks and fissures. Black dendritic manganese oxides are common in dolostone at Whitwell Quarry (see Fig. 40). The first such specimen listed from the site in Ray Richardson's collection catalogue is dated 8 November 1965 and described as pyrolusite (Richardson,

1962–1983). None of the dendrites examined to date have produced powder patterns when analysed by X-ray diffraction. They are unlikely to be pyrolusite and are described using the catch-all term 'manganese oxide' in this account. The brittle manganese dendrites in the Cadeby Formation dolostone are not directly associated with oxidation of the epigenetic mineralisation, but a soft sooty cobalt-bearing manganese oxide associated with descloizite appears to be part of the supergene suite.

MARCASITE, FeS_2

Marcasite is widespread in the Cadeby Formation in northeast England (Harwood, 1981). It is usually unaltered in basal assemblages. Its former presence in epigenetic baryte is betrayed by sharp goethite pseudomorphs.

Marcasite is relatively rare in the basal assemblage at Whitwell Quarry. It occurs as irregular groups of silvery to pale golden yellow metallic crystals up to about 0.5 mm on edge (Fig. 56). They pre-date baryte and are overgrown by cuboctahedral pyrite. No definite goethite pseudomorphs after marcasite have been identified in the vein assemblage. Silvery metallic inclusions in epigenetic galena generally have isometric outlines and are likely to be pyrite.

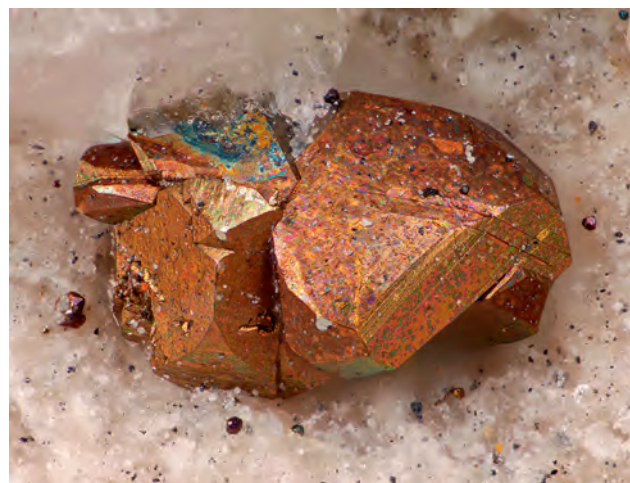


Figure 56. Tarnished irregular asymmetric marcasite, identified by XRD on this specimen, with a scattering of minute cuboctahedral pyrite crystals in a cavity in saccharoidal dolostone. Specimen WQ013 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 1 mm across. Photo John Chapman.

MATTHEDDLEITE,



Mattheddleite is a rare member of the apatite supergroup of minerals. It has a complex structure which has been refined on two occasions since it was first published by Livingstone *et al.* (1987). The later studies raise almost as many questions as they answer (Steele *et al.*, 2000; Essene *et al.*, 2006).

The best known British localities are at Leadhills–Wanlockhead (which is regarded as the type locality) and in the Caldbeck Fells (Cooper *et al.*, 1988; Bridges *et al.*, 2008; Green *et al.*, 2008; Neall and Green, 2009; Green *et al.*, 2012;

Green *et al.*, 2019). There are a handful of occurrences in Central Wales (Tindle, 2008; Rust, 2019) and a minor occurrence at Penberthy Croft Mine in Cornwall (Betterton, 1996).

The first report of mattheddleite from Whitwell Quarry is in Tindle (2008: p. 339). It occurs in the Leadhills suite of minerals as dense carpets of colourless to white prismatic crystals up to about 0.3 mm in length (Figs 57–59). Mattheddleite is always later than anglesite; commonly overgrows and sometimes replaces lanarkite; usually overgrows leadhillite; and is never associated with either hydrocerussite or cerussite. This rather restricted mineralogical niche is typical of other British localities.

An early analysis of a specimen submitted for identification to the Natural History Museum produced a powder pattern between mattheddleite and pyromorphite (Chris Stanley, *personal communication*, 1987).

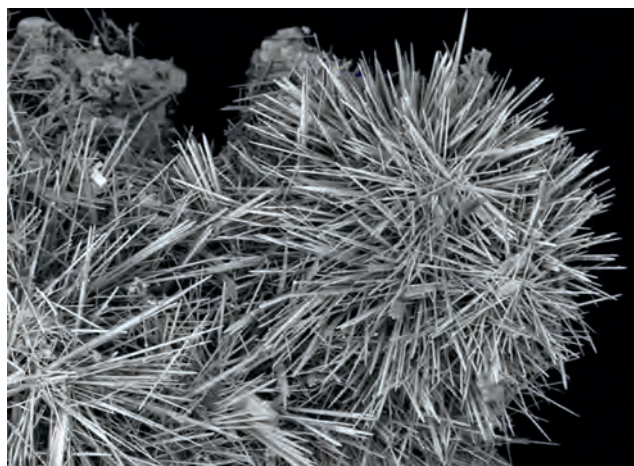


Figure 57. Dense radiating groups of acicular mattheddleite from Whitwell Quarry, Derbyshire. The field of view is 0.5 mm across. SEM photo by Christian Rewitzer.



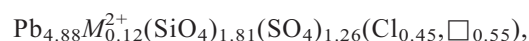
Figure 58. Acicular mattheddleite as a dense overgrowth on anglesite with minor transparent tabular leadhillite. Specimen E121 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.



Figure 59. Ultra-high resolution image of acicular mattheddleite showing the typical pencil-point terminations. A tabular co-crystallising leadhillite is visible at the top left. Specimen E120 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 0.4 mm across. Photo John Chapman.

More recent research has identified curved prismatic crystals of a carbonate-bearing variety with a similar unusual diffraction pattern (Fig. 60).

Analyses show that at least some of the more elongated prismatic crystals have a more normal composition. Their empirical formula on the basis of a single analysis is:



where *M* is a placeholder which represents sundry divalent cations (mostly barium and calcium). Further discussion is included in the next section of this article.



Figure 60. Hexagonal prisms of carbonate-bearing mattheddleite, curving slightly toward the terminations, on etched lanarkite from Whitwell Quarry, Derbyshire. The field of view is 0.7 mm across. SEM photo by Christian Rewitzer.

MIMETITE, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$

Lead-bearing members of the apatite supergroup from Whitwell Quarry generally contain 1 wt% As_2O_5 or less. Golden yellow prisms associated with leadhillite, lanarkite and scotlandite (Figs 61 and 62) provide the single exception. Semi-quantitative energy-dispersive X-ray spectrometry indicates a molar As:P ratio of approximately 4:1. Even allowing for the inaccuracies of analyses on unpolished surfaces (Newbury and Ritchie, 2013) this is well within the mimetite composition field.



Figure 61. Hexagonal prismatic mimetite with conspicuous pyramid faces and pinacoid terminations from Whitwell Quarry, Derbyshire. The field of view is 0.2 mm across. SEM photo by Christian Rewitzer.



Figure 62. Broken golden yellow prismatic mimetite embedded in leadhillite with lanarkite blades and minor scotlandite along the top edge. A broken prismatic crystal, 0.25 mm in length, with slight curvature is shown in the inset. Specimen WQ054 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 1.8 mm across. Photo John Chapman.

Periclase, MgO

The best match to an X-ray diffraction pattern produced by “black lustrous spheres” on cerussite was “dolomite plus periclase” (John Fuller, *personal communication*, 1986). Subsequent analyses of black lustrous spheres on cerussite or anglesite by energy-dispersive X-ray spectrometry have identified lead and sulphur, but no magnesium or calcium. The original specimen was re-examined in 2021: a black mineral on cerussite contains lead and a little iron, a result which is not consistent with dolomite or periclase.

Periclase is typically found in thermally metamorphosed dolostones. It is not typically black and would not be expected in a supergene mineral assemblage. The brief report in Starkey (2018: p. 136), although given in good faith, is based on the foregoing analysis which seems likely to be in error. It is possible that a particle of kiln-dust blown across the site from the nearby refractory plant was mistakenly sampled as periclase is a common component of furnace-bricks.

PHOSPHOHEDYPHANE, $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$

Early attempts to identify the green pyromorphite-like mineral (Fig. 63) which occurs around oxidising galena and commonly replaces cerussite at Whitwell Quarry (Fig. 64) were inconclusive. Bulk analysis by X-ray fluorescence spectrometry at British Coal’s research laboratories showed that lead, calcium and phosphorus (as phosphate) were present, but ascribed the calcium to contamination from the surrounding dolostone (A. J. Allinson, *personal communication*, 1986). The best match to a specimen analysed by X-ray diffraction at the Natural History Museum later in the same year was “possibly near svabite” (John Fuller, *personal communication*, 1986).

Subsequent studies by energy-dispersive X-ray spectrometry revealed the presence of lead, phosphorus, chlorine and calcium in every specimen that was analysed. X-ray powder diffraction patterns were distinct from pyromorphite, but specimens were labelled “pyromorphite” or “calcian pyromorphite” because it was the best match to the chemistry and structure at that time. These labels and any text which relies on them (e.g. Klopogge and Lavinsky, 2017: p. 204) are incorrect. Pyromorphite in the strict sense is extremely rare at Whitwell Quarry.

The ‘pyromorphite problem’ was resolved when phosphohedyphane, ideally $\text{Pb}_3\text{Ca}_2(\text{PO}_4)_3\text{Cl}$, a related lead-bearing apatite supergroup mineral, was described as a new species (Kampf *et al.*, 2006). The first British occurrences, from the Leadhills–Wanlockhead district and Whitwell Quarry, were reported in Tindle (2008: p. 391). Phosphohedyphane was subsequently identified from Roughton Gill and Short Grain in the Caldbeck Fells (Green *et al.*, 2008; Neall and Green, 2009). Its distribution is surprisingly coincident with the Leadhills suite of minerals.



Figure 63. Drusy crusts of green prismatic hexagonal crystals, originally labelled pyromorphite, but subsequently identified as phosphohedyphane. Five analyses by wavelength-dispersive X-ray spectrometry show that this specimen has a mean empirical formula (with undetected carbonate calculated) of $\text{Pb}_{3.46}\text{Ca}_{1.56}\text{Zn}_{0.04}(\text{PO}_4)_{2.66}(\text{AsO}_4)_{0.05}(\text{SiO}_4)_{0.07}(\text{CO}_3)_{0.26}(\text{Cl}_{0.87}\text{OH}_{0.13})$. More than 1.5 atoms of calcium replace lead which places the formula well within the phosphohedyphane composition field. Specimen MM1928 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 3.5 mm across. Photo John Chapman.

Phosphohedyphane is found in two distinct situations at Whitwell Quarry. Thick cellular crusts overgrow cerussite in the oxidation rinds surrounding blocks of fault-zone galena. Thin crusts are associated with descloizite, lead-rich hydroxylapatite and vanadinite in mineralised fractures in the surrounding dolostone. Phosphohedyphane is typically pale green in close proximity to galena and cerussite, and white in close proximity to vanadinite and descloizite. It is rarely brown, yellow, yellow-brown or orange-brown. The colour range is similar to pyromorphite, but phosphohedyphane tends toward more pastel shades. Late-stage white finely fibrous crystals in association with lead vanadates cannot be visually distinguished from lead-rich hydroxylapatite (compare Figs 34 and 101).

The alteration sequence in the oxidation rinds around massive galena is almost always hydrocerussite followed by cerussite followed by phosphohedyphane. Pseudomorphs after cerussite generally occur closest to galena. They may be surrounded by cellular crusts up to 50 mm thick. Patches of earthy goethite are particularly common in cellular phosphohedyphane. Microbial oxidation plays an important role in supergene alteration, and commonly catalyses the decomposition of iron sulphides (Brierley, 2009). Web-like phosphohedyphane aggregates draped across drusy surfaces in the cellular crusts may have nucleated around microbial filaments (Fig. 65).



Figure 64. One of the iconic specimens from Whitwell Quarry, phosphohedyphane replacing a blocky vee-twin cerussite, 12 mm high. The image was used for the 2012 Bakewell Show poster and is included in both Tindle (2008: p. 391) and Starkey (2018: p. 139). Specimen GA4 in the Peter Briscoe Collection. Photo David Green.



Figure 65. Drusy yellow-brown phosphohedyphane with a curved columnar drapery, which may have nucleated around microbial filaments. Specimen MM1941 in the David Green Collection from Whitwell Quarry, Derbyshire. The field of view is 19.6 mm from top to bottom. Photo John Chapman.



Figure 66. Broken section through a phosphohedyphane pseudomorph after tabular cerussite. The internal mould contains late-stage phosphohedyphane which formed after the original cerussite had dissolved. A pale line (white arrow) indicates the original cerussite crystal surface. The field of view is 1.5 mm across. Specimen E131 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

Phosphohedyphane pseudomorphs, particularly after cerussite, are attractive. They vary from thin drusy crusts on relatively unaltered crystals, to thicker crusts surrounding a kernel of etched white cerussite, to rounded casts with hollow cores (Fig. 66). In some cases only a hint of the original crystal form remains (Fig. 67). The morphological variety of the pseudomorphs mirrors the diversity of the original cerussite: hexagonal prisms and pyramids are common; ‘stalagmites’ encrust jackstraw crystals; stacked plates are ‘sequential pseudomorphs’ where phosphohedyphane encrusts cerussite that has replaced hydrocerussite. The most attractive specimens are vee-twin replacements. The twins tend to be larger than the surrounding pseudomorphs and leave no doubt about the identity of the original crystal (Fig. 68).

Phosphohedyphane pseudomorphs after galena were found on early visits to the quarry (Figs 69 and 70). They are typically replacements of scattered cubes on dolostone.



Figure 67. A ‘fenestrated’ pale green drusy phosphohedyphane pseudomorph retaining the barest outline of the shape of the cerussite crystal it has replaced. The field of view is 4 mm across. Specimen E131 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 68. Drusy phosphohedyphane replacing a large cerussite vee-twin, surrounded by blocky pseudo-hexagonal and jackstraw crystals. Specimen E131 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 15 mm across. Photo John Chapman.



Figure 70. Crudely cubic phosphohedyphane pseudomorphs after galena, up to 3 mm on edge. Specimen E294 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

Figure 69. (left) Cubic phosphohedyphane pseudomorphs, up to 4 mm on edge, with sequential alteration of galena to cerussite to phosphohedyphane. Specimen Y27 in the Max Freier Collection from Whitwell Quarry, Derbyshire. Photo David Green.

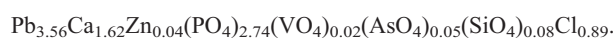


Figure 71. Phosphohedyphane pseudomorphs after hemimorphite. Sharp internal moulds show that the hemimorphite remained until after all of the phosphohedyphane had crystallised. Specimen WQ055 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 20 mm across. Photo John Chapman.

Pseudomorphs after hemimorphite were found at about the same time as the galena pseudomorphs. They are always casts, but unlike the casts after cerussite they have smooth internal surfaces which indicate that crystallisation of the phosphohedyphane was complete before the underlying hemimorphite began to dissolve (Fig. 71).

Phosphohedyphane replaces leadhillite on a few rare specimens (Fig. 72). In common with the pseudomorphs after galena and hydrocerussite, they are ‘sequential pseudomorphs’, with leadhillite followed by cerussite followed by phosphohedyphane, rather than direct replacements of leadhillite by phosphohedyphane.

The mean empirical formula of nineteen analyses of phosphohedyphane from Whitwell Quarry, calculated as recommended by Pasero *et al.* (2010: p. 173), is:



The excess cation charge is probably the result of a small amount of undetected carbonate, for which an empirical correction can be made. A more detailed discussion is included in the next section of this article.



Figure 72. Green drusy phosphohedyphane partly encrusting tabular white leadhillite, some of which has minor surface alteration to cerussite. Specimen GD8 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 32 mm across. Photo David Green.

PLATTNERITE, PbO_2

Plattnerite was described in the mid-nineteenth century from the Leadhills—Wanlockhead district. It is noted rather doubtfully by Greg and Lettsom (1858) as black hexagonal prisms, and more confidently by Heddle (1889; 1901a) as black botryoidal masses on pyromorphite and cerussite. More recently, well crystallised plattnerite has been identified with lanarkite at Susanna Mine near Leadhills (Steve Rust, *personal communication*, 2012). This association is consistent with geochemical predictions which show that the two minerals are stable in relatively alkaline oxidising conditions at low carbonate ion activities (Williams, 1990).

The plattnerite specimen from Whitwell Quarry which was identified by X-ray diffraction (at Leeds University in the late 1980s) was destroyed by sampling. Contemporary notes record that it was black phase associated with lanarkite and leadhillite. Tiny black crystals on lanarkite, identified in a recent re-examination on one further specimen, have not been confirmed analytically.

PYRITE, FeS_2

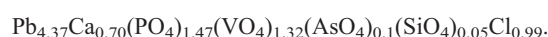
Pyrite is common in the basal Permian sequence in the area around Whitwell (Eden *et al.*, 1957; Smith *et al.*, 1973: p. 123). It is a minor component of the mineralisation in cavities and fractures left by the dissolution of calcium sulphates at the base of the Cadeby Formation. In this assemblage it overgrows marcasite and is commonly associated with baryte and calcite but is usually spatially separated from galena and sphalerite (cf. Bateman *et al.*, 2021b). The crystals may have a slight tarnish but they are never heavily oxidised. They commonly occur as inclusions in baryte and calcite. Minute cubes scattered on late-stage calcite suggest that pyrite was the last mineral to form in the basal assemblage.

The former presence of well crystallised pyrite in the epigenetic fault-zone mineralisation is revealed by sharp goethite pseudomorphs (see Fig. 45). Silvery metallic pyrite inclusions occur in epigenetic galena and baryte, and occasionally thin films line cavities in galena.

Supergene pyrite has been identified by X-ray diffraction as an overgrowth on leadhillite. In common with supergene galena, it probably signifies a late and local oscillation in the oxidation potential.

PYROMORPHITE, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$

A large number of lead-bearing apatite supergroup minerals, including the bright green crystals shown in Figure 63, were analysed in this study. The vast majority are phosphohedyphane or vanadinite. Pyromorphite in the strict sense is extremely rare at Whitwell Quarry. Most ‘lead apatite’ compositions extend in a coupled solid solution across the vanadinite composition field or are close to phosphate end-member phosphohedyphane. The vanadinite substitution vector cuts the corner of the pyromorphite composition field, and a pale brown calcium-bearing vanadinite crystal included a composition with the empirical formula:



This is phosphate-dominated and contains less than one atom of calcium per formula unit and therefore technically it is calcium-bearing vanadate-rich pyromorphite.

Acicular yellow crystals in a well sealed cavity in cerussite (Fig. 73) provided the single analysis of pyromorphite with a near ideal composition in this study. More detailed discussion is reserved for the next section of this article.

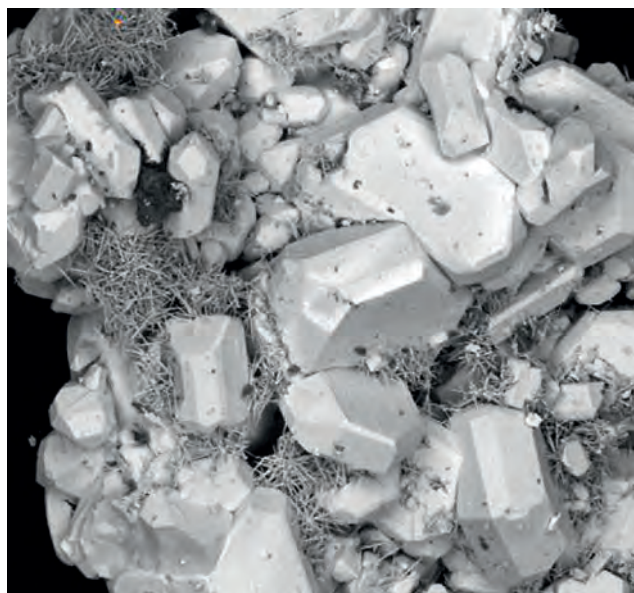


Figure 73. Acicular pyromorphite 'cobwebs' on blocky pseudo-hexagonal cerussite crystals up to about 200 μm across. The pyromorphite latticeworks are a bright cadmium yellow colour, but the individual crystals are difficult to resolve under a stereomicroscope. SEM photo by Christian Rewitzer.

QUARTZ, SiO_2

Thin sections show that detrital and authigenic quartz are present in Cadeby Formation dolostone at Whitwell Quarry, but the rock is relatively pure dolomite and total contaminants are usually no more than about 2%. Fine-grained detrital quartz is present at higher concentrations in the underlying Marl Slate Formation.

Quartz was identified by X-ray diffraction as a component of a brownish iridescent crystal mass on a fracture in dolostone (John Fuller, *personal communication*, 1986). It was identified more recently, by the same technique, in association with supergene pyrite as an overgrowth on leadhillite. Macroscopic crystals are not present in either the basal or epigenetic assemblages.

SCOTLANDITE, PbSO_3

Scotlandite is a rare species which marks the supergene assemblage at Whitwell Quarry out as geochemically interesting. It was described on an old specimen from the Susanna Mine at Leadhills (Paar *et al.*, 1984). British localities are restricted to Leadhills–Wanlockhead, a few localities in the Caldbeck Fells and Whitwell Quarry where scotlandite occurs as a rare member of the Leadhills suite of supergene minerals (Neall *et al.*, 2006).

Micro-crystalline scotlandite has been identified on about a dozen specimens from Whitwell Quarry. Drusy crusts of millimetre-size crystals line cavities in galena on specimens to small hand size. Scotlandite typically occurs in one of two characteristic crystal habits: Type 1 crystals are elongated and bounded by gently curved faces which terminate at a point to produce a pseudo-tetragonal habit (Fig. 74 and 75); Type 2 crystals are

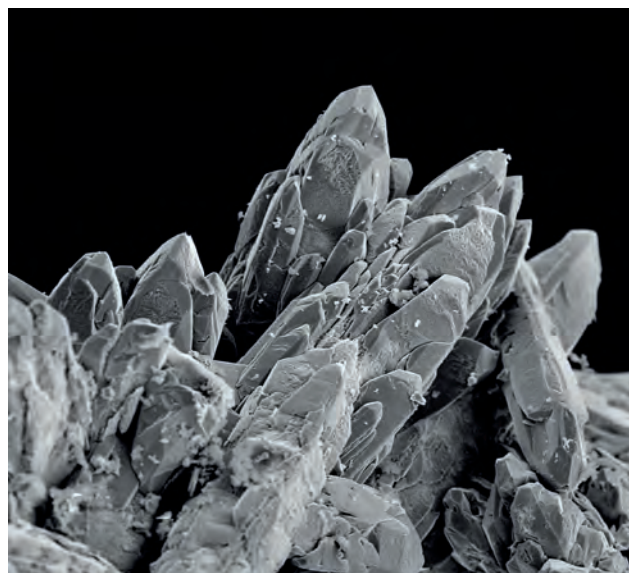


Figure 74. Pointed Type 1 scotlandite crystals up to about 200 μm in length, which taper to a four-sided point. SEM photo by David Green.



Figure 75. Intergrown pale brown Type 1 scotlandite crystals. Specimen GC4 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

prismatic, bounded by elongated prismatic $\{100\}$ and $\{010\}$, and have sharp chisel-shaped terminations (see Fig. 76). Type 1 crystals are more common than Type 2 crystals at Whitwell Quarry. The two habits are not found in close association on any specimen examined to date.



Figure 76. Type 2 scotlandite crystals in parallel growth with their distinctive somewhat asymmetric end-faces picked out in reflection (cf. Fig. 12). Elongated prismatic $\{100\}$ and $\{010\}$ are terminated by steep pinacoids to produce the acute chisel-shaped crystal habit figured by Paar *et al.* (1984). Specimen E123 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2 mm across. Photo John Chapman.

Type 1 scotlandite typically occurs as dense clusters on oxidised galena. It often dominates the cavities in which it occurs, covering areas of up to several square centimetres with haphazard groups of pale brown crystals up to about 1.5 mm in length (see Fig. 75). Type 1 crystals overgrow various unidentified phases; they are overgrown by lanarkite, leadhillite and rarely mattheddleite.

Type 2 scotlandite crystals up to about 2.5 mm in length are usually associated with lanarkite and anglesite. They can be distinguished from anglesite, which also occurs as chisel-shaped crystals, by the asymmetry of their pinacoidal terminations and faint striations running parallel rather than perpendicular to the elongation direction (see Fig. 76).

A previously undescribed scotlandite habit was identified when specimens were re-examined in preparation for this article. Translucent pseudo-orthorhombic prisms up to 1 mm in length (Fig. 77) produced a perfect match for scotlandite by X-ray powder diffraction. They occur in isolated cavities in galena on a specimen with leadhillite, lanarkite and a few tiny crystals of mimetite (see Fig. 62).



Figure 77. Radiating clusters of opaque pale buff pseudo-orthorhombic scotlandite up to 0.8 mm in length in cavities in galena. The X-ray diffraction pattern (obtained on a crystal cluster from this cavity) is a perfect match to scotlandite. Specimen WQ054 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

SMITHSONITE, ZnCO_3

White to pale brown and rarely lemon yellow botryoidal smithsonite crusts overgrow cerussite and cerussite pseudomorphs after hydrocerussite in cavities up to about 10 mm across in the oxidation rinds around epigenetic galena. The lemon yellow colour is almost certainly due to minute cadmium sulphide inclusions. Translucent honey brown lenticular smithsonite aggregates up to about 1 mm across with characteristic stepped faces are occasionally associated with cerussite and hemimorphite (Fig. 78).



Figure 78. Rounded smithsonite crystals with characteristic stepped faces on colourless cerussite. Specimen E125 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 3.2 mm across. Photo John Chapman.

SPHALERITE, ZnS

Sphalerite is a component of two distinct assemblages at Whitwell Quarry. It occurs with baryte, calcite and galena in cavities and fractures left by the dissolution of calcium sulphates at the base of the Cadeby Formation and as residual fragments in hemimorphite in the epigenetic assemblage.

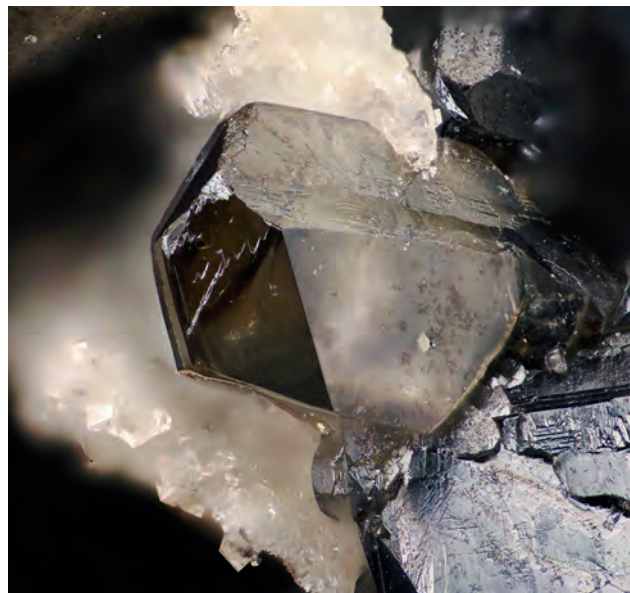


Figure 79. A brown translucent sphalerite crystal on galena in a cavity in pale buff dolostone. Specimen E126 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 0.75 mm across. Photo John Chapman.



Figure 80. Translucent sphalerite crystal groups with dark internal zones on pale buff dolostone. Specimen E153 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 6.5 mm across. Photo John Chapman.

Sphalerite is locally abundant in the basal assemblage. Translucent colourless to dark brown crystals up to about 1.5 mm on edge overgrow galena (Fig. 79) and are commonly overgrown by baryte (see Fig. 18). The smaller crystals are usually translucent to transparent except near to vertices where they may be dark and opaque (Fig. 80). On rare occasions they are pale transparent honey brown. Crystal groups are commonly complex, with numerous offset faces, but in most cases the underlying tetrahedral motif is still evident (Fig. 81). In the basal assemblage, sphalerite shows no evidence of oxidation. It has a weak orange fluorescence in longwave ultraviolet light.



Figure 81. Complex translucent sphalerite crystals overgrowing cuboctahedral galena on pale buff dolostone. Specimen E126 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 3 mm across. Photo John Chapman.

The descloizite-rich supergene halo and local occurrence of cellular hemimorphite suggests a significant amount of primary sphalerite was originally present in the fault-zone. It is impossible to be sure how much as oxidation has removed the evidence, however it is unlikely to have been present in the same quantities as galena.

SULPHUR, S₈

Small amounts of sulphur commonly occur with anglesite in well sealed cavities in and fractures in oxidising galena. Localities in the Pennine orefields are summarised by Ford *et al.* (1993) and Bridges and Young (1998).

At Whitwell Quarry, sulphur is widespread as inconspicuous crystals in blocks of epigenetic galena. Rounded crystals up to about 0.2 mm across commonly overgrow translucent white first-generation anglesite blades. Sulphur also occurs as isolated crystals (Fig. 82) and resinous infills in thin fractures in massive galena. Rarely, complex pale-yellow bipyramidal crystals up to about 0.6 mm across are associated with tabular leadhillite.

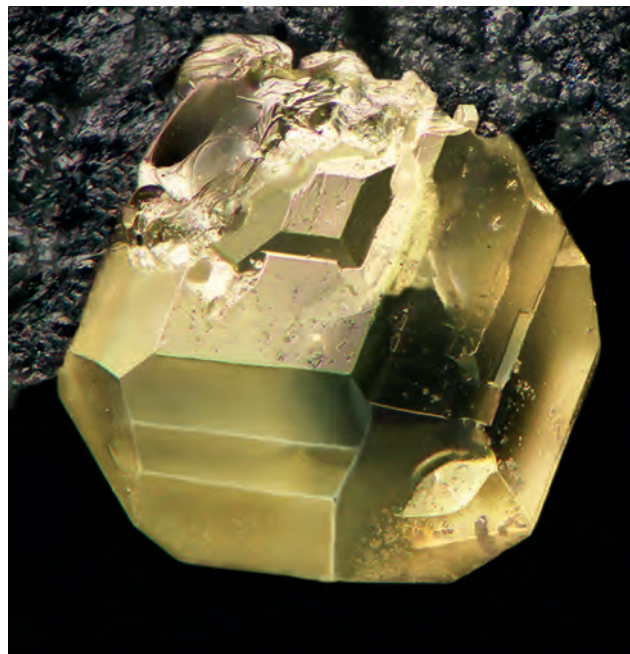


Figure 82. Ultra-high magnification image of a blocky sulphur crystal, 0.25 mm across, in a thin fracture in galena. Specimen E116 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.

SUSANNITE, Pb₄(CO₃)₂(SO₄)(OH)₂

Susannite, the trigonal polymorph of leadhillite and macphersonite, has a very similar structure to leadhillite and the two minerals are difficult to differentiate by X-ray powder diffraction (Steele *et al.*, 1999). The phase relationships are unclear (Livingstone, 1993). It seems likely that fluid chemistry has a strong influence on which polymorph develops.

Susannite is well known from the Leadhills–Wanlockhead district and the Caldbeck Fells (Tindle, 2008; Bridges *et al.*, 2008; Green *et al.*, 2008; Neall and Green, 2009; Green *et al.*, 2012). There are a number of localities in Central Wales (Tindle, 2008), notably Frongoch Mine, where susannite occurs in a wide variety of crystals habits (Rust, 2019).

At Whitwell Quarry, limited analyses by X-ray diffraction suggest that susannite is less common than leadhillite. An early analysis of a rhombohedral crystal provided a better match for susannite than leadhillite. Patterns from pseudohexagonal plates and columnar crystals are nearer to leadhillite. Studies of the optical interference figures produced by Whitwell specimens are inconclusive: uniaxial crosses, indicative of susannite, are produced by some optical paths, and biaxial figures, indicative of leadhillite, by others.

The two polymorphs commonly intergrow and this may account for the uncertainties in the optical determinations and some analyses by X-ray diffraction (Livingstone, 1993: p. 11). Crystal morphology does not provide a reliable guide to identification: the blocky crystals illustrated in Figure 11 are a better match to susannite than leadhillite by X-ray diffraction.



Figure 83. Lustrous toffee-brown vanadinite on a thin dolostone fragment, 55 mm from top to bottom, which was originally enclosed in a red clay gouge. Specimen E090 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo David Green.



Figure 84. Lustrous toffee-brown vanadinite on cellular phosphohedyphane, 36 × 30 mm, with traces of red clay gouge visible on the crystal group at top left. Specimen in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo Peter Briscoe.

VANADINITE, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$

The vanadinite specimens from Whitwell Quarry are remarkable in a British context (e.g. Fig. 83 and 84). The only other notable localities in the British Isles are in the Leadhills–Wanlockhead mining district, particularly the workings of High Pirn Mine on Belton Grain Vein, which produced globular orange-brown vanadinite associated with phosphohedyphane and lead-bearing hydroxylapatite (Temple, 1954, 1956; Livingstone, 1994; Livingstone, 2002; Tindle, 2008).

The first indication that the dark brown globular mineral surrounding partly oxidised masses of galena at Whitwell Quarry was vanadinite came in an early X-ray fluorescence analysis (Table 2). Chlorine was driven off when the sample was prepared, but the remaining elements are in the appropriate proportions for end-member vanadinite. Vanadinite was subsequently identified on specimens submitted to the Natural History Museum in London. Initial studies of curved, pale brown crystals by X-ray diffraction were inconclusive because calcium and phosphate substituting for lead and vanadate, respectively, changed the d -spacings. Vanadinite was subsequently confirmed by a combination of energy-dispersive X-ray spectrometry and infrared absorption spectroscopy (John Fuller, *personal communication*, 1986).

OXIDE	Wt%
Al_2O_3	1.38
SiO_2	1.08
SrO	2.08
P_2O_5	1.13
V_2O_5	17.50
PbO	73.30
CaO	0.5
Total	100.08

Table 2. Results of a bulk analysis by X-ray fluorescence spectrometry carried out in August 1986 by A. J. Allinson at British Coal's research laboratory at Wath-upon-Deane on "dark brown globular material on dolomite from a cavity filled with red mud with a conspicuous slickenside nearby". These data, which are consistent with vanadinite of near to end-member composition (ideally vanadinite contains 19.26 wt% V_2O_5 ; 78.8 wt% PbO and 1.94 wt% Cl). The strontium determination is based on the $\text{Sr L}\alpha$ peak at 1.806 keV which lies in a problematic spectral region for automatic peak detection software and is probably incorrect (Newbury, 2009). Very little strontium was detected in any of the analyses listed in Table 3.

Brown spheroidal vanadinite commonly overgrows phosphohedyphane and hydroxylapatite on the outer surfaces of the oxidation rinds around fault-zone galena. *In situ*, the richest specimens were almost always embedded in a thick layer of red clay gouge. The close association suggests it as a possible vanadate source, but its chemical and mineralogical composition are yet to be investigated.

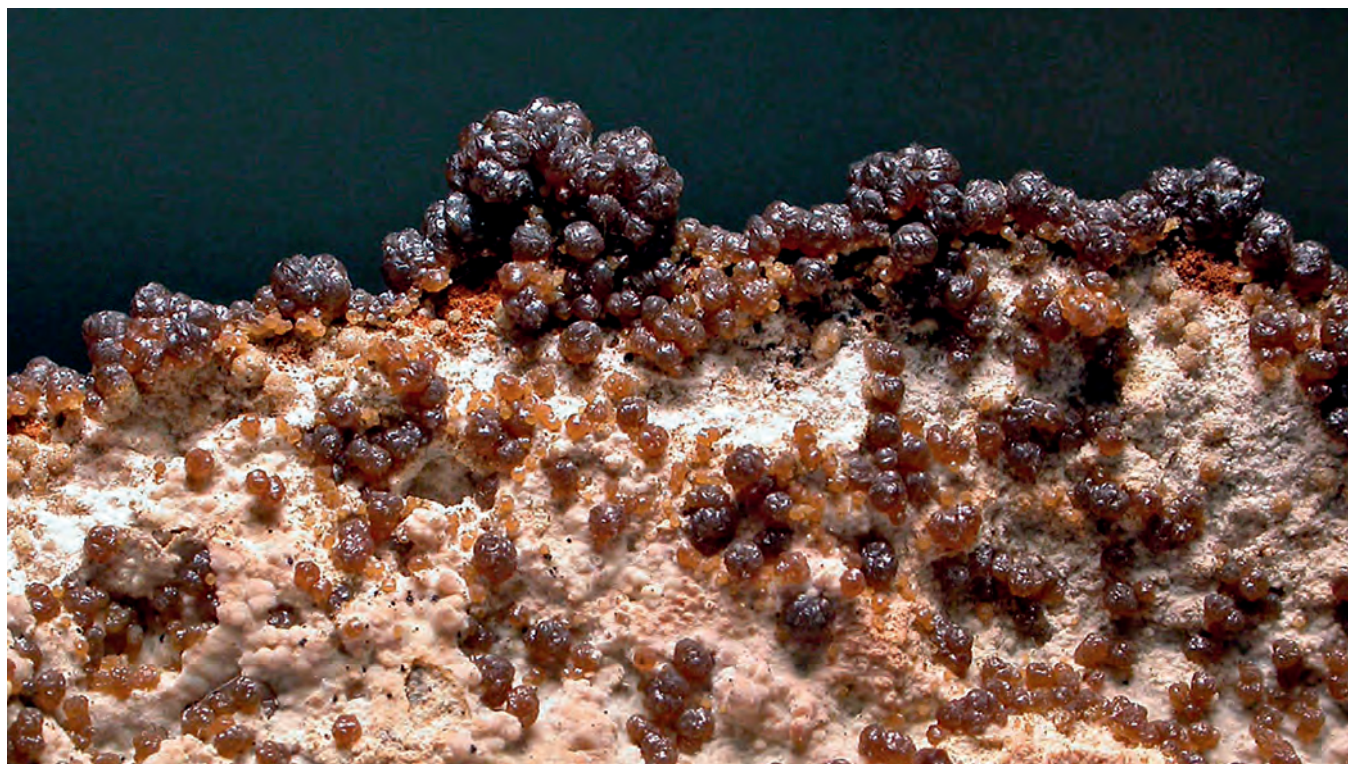


Figure 85. Lustrous millimetre-size globular dark toffee-brown vanadinite crystal groups on white phosphohedyphane on a thin dolostone clast which was originally mantled in a red clay gouge. The field of view is 30 mm across. Photo David Green.



Figure 86. Near spheroidal translucent brown vanadinite overgrowing unusual remnant pseudomorphs in which a central line of orange descloizite is overgrown by a white acicular phase (possibly lead-rich hydroxylapatite), pale green phosphohedyphane and a second generation of orange descloizite. Specimen E094 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 8.5 mm across. Photo John Chapman.

Vanadinite occurs in fractures in the dolostone as white to toffee-brown opaque to translucent globular crystals; colourless to yellow-brown hexagonal barrels; lenticular crystals with spicular to coralloidal overgrowths; and rarely as white to pale brown elongated prismatic crystals (Figs 85 to 90).

Analyses by wavelength-dispersive X-ray spectrometry show that a solid solution series extends from vanadinite toward phosphohedyphane, with a composition gap near the boundary between the two phases. The mean empirical formula for thirty-four analyses, calculated based on thirteen total anions as recommended by Pasero *et al.* (2010: p. 173), is:



This gives an idea of an average composition and shows that there is significant calcium and phosphate substitution for lead and vanadate, respectively. A more detailed examination of these data reveals that the compositions lie along a distinct substitution vector. Further discussion is included in the next section of the article.

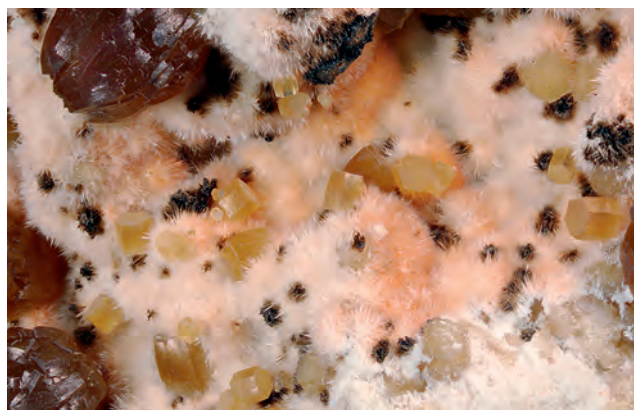


Figure 87. Small pale brown barrel-shaped vanadinite crystals with white acicular phosphohedyphane. The field of view is 5 mm across. Specimen E091 in the David McCallum Collection from Whitwell Quarry, Derbyshire. Photo John Chapman.



Figure 88. Opaque spicular to coralloidal overgrowths on curved lenticular vanadinite. Specimen E428 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 3 mm across. Photo John Chapman.



Figure 89. Rounded brown millimetre-size vanadinite crystals with bright orange descloizite on dolomite, one of the characteristic associations in fractures surrounding galena in the fault zone at Whitwell Quarry. Specimen E075 in the David McCallum Collection. Photo John Chapman.



Figure 90. Curved opaque white vanadinite with dark orange-brown descloizite. Specimen E428 in the David McCallum Collection (formerly in the Steve Uttley Collection) from Whitwell Quarry, Derbyshire. The field of view is 3.5 mm across. Photo John Chapman.

UNIDENTIFIED PHASES

In any complex mineral assemblage, especially one that has been investigated over a long period of time, data which does not fit into any obvious pattern accumulates. The early analyses of 'pyromorphite' and mattheddleite provide examples. The pyromorphite problem was resolved when phosphohedyphane was described as a new species. The unusual mattheddleite powder diffraction data is probably the result of carbonate substitution. Other anomalies remain.

In some cases, plausible inferences can be made. Traces of an azure-blue mineral between leadhillite cleavages are probably linarite, but they are too thin and disseminated for analysis by X-ray diffraction. A thin khaki-green crust on a small area of descloizite is suggestive of 'psittacinite', but its precise composition is yet to be determined. A soft black cobalt-bearing manganese oxide associated with descloizite may be asbolane, but it has not proved possible to separate sufficient pure material for analysis. A grey-green minutely botryoidal phase contains lead, zinc, chromium and silicon in roughly the correct proportions for hemihedrite, but requires further study.

Lead, iron and phosphorus were detected in a resinous, deep red, minutely botryoidal phase which was analysed in 2005. There were no known minerals with this composition and colour at the time and it was listed as "an unidentified phase with a superficial resemblance to carminite". The recent description of crimsonite, the phosphate analogue of carminite, which is named for its deep red colour (Kampf *et al.*, 2016) offers a possible solution. Crimsonite cannot be claimed with any certainty on the basis of colour and composition and unfortunately, the specimen could not be located when collections were re-examined in this study.



Figure 91. An unidentified black botryoidal phase with tabular leadhillite and possible susannite. Energy-dispersive X-ray spectroscopy revealed the presence of lead, sulphur and about 2 wt% silver on the surface of the spheres. This is the only silver-bearing phase identified to date at Whitwell Quarry. Specimen E124 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 2.5 mm across. Photo John Chapman.

A black botryoidal phase, intergrown with leadhillite and susannite contains lead, sulphur and about 2 wt% silver (Fig. 91). It has a soft matt outer surface which becomes brilliant shining black when touched with the point of a needle. There are some similarities with the black lead sulphide spherules that overgrow anglesite and cerussite (described under galena), which also remain to be properly characterised.

Examination at high magnification has revealed radiating sprays of white lath-like crystals, tiny colourless spherules made up of curved plates, blocky transparent tetragonal prisms and brown bow-tie aggregates (Fig. 92) in association with scotlandite. All are unidentified and await further study.

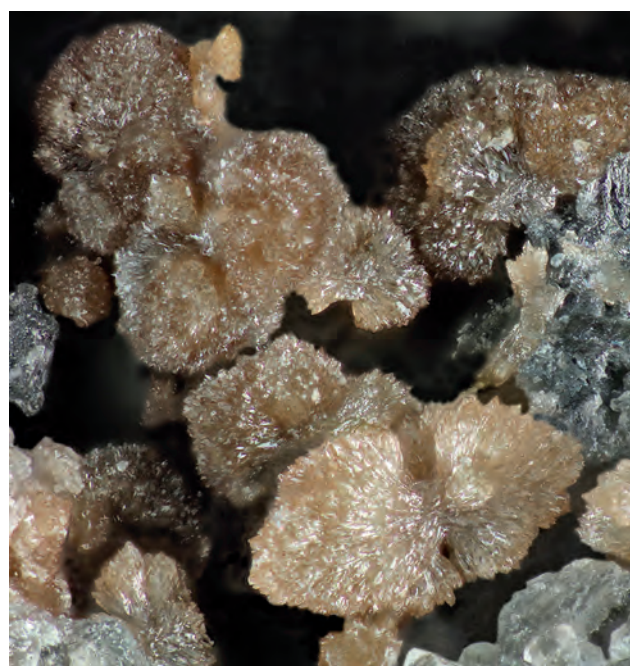


Figure 92. Unidentified bow-tie aggregates. Specimen GC4 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. The field of view is 0.5 mm across. Photo John Chapman.

DISCUSSION

Despite its mineralogical diversity, Whitwell Quarry's only formal geological notification is as a Regionally Important Geological Site (it is listed for its dolostone exposures and educational potential). The anomalous epigenetic deposit and unique supergene assemblage are not mentioned. Sadly, the mineralised section of the fault zone has been quarried away and the remnants are buried. The specimens that have been preserved at least provide an opportunity for future research.

There are two separate primary assemblages: disseminated mineralisation at the base of the sequence, and epigenetic mineralisation along a northern splay of the Park Hall Fault. These are contextualised and compared with mineralisation at the nearby Steetley Quarry Complex (particularly Armstrong Quarry) and the Sunnyside Deposit (Bateman *et al.*, 2021a,b), in the

first two subsections of this discussion. A holistic account of the supergene assemblage follows. Trends in the composition of the apatite-super group minerals are summarised in the penultimate subsection and a few suggestions for further research follow.

Basal Assemblage

The soft argillaceous rocks of the Marl Slate Formation (formerly the Lower Permian Marl) are of low commercial value and have the potential to contaminate kiln-grade dolostone. They were avoided by quarrying operations in the 1980s, but were occasionally uncovered in disturbed ground near the fault zone on the bottom bench. Most of the 'basal' specimens described in the foregoing text are from an irregular flat-lying deposit in buff saccharoidal dolostone just above the Marl Slate Formation. Field notes record that mineralisation extended into the marl, but it was sparse, exposures were poor and no specimens were collected.

Minerals present in the basal assemblage include baryte, calcite, galena, marcasite, pyrite and sphalerite. Sphalerite is more abundant than galena on most of the studied specimens. Baryte, calcite and pyrite are later than the base-metal sulphides. Pyrite overlaps and co-crystallises with baryte and calcite but is rarely associated with either galena or sphalerite.

The minerals occur in cavities and fractures produced by the dissolution of calcium sulphates. In their description of the buried and unweathered Cadeby Formation farther to the east, Smith *et al.* (1973: p. 123) record: "Anhydrite and gypsum ... in several underground sections, usually occurring as streaks". Calcium sulphate nodules are well known at the base of the sequence (e.g. Harwood, 1981; Bateman *et al.*, 2021b). Rock forming calcium sulphates no longer remain at Whitwell Quarry, but the former presence of gypsum is unequivocally indicated on one specimen from the basal assemblage by a six-sided prismatic *narben*. Replacement baryte nodules provide further evidence of the former presence of calcium sulphates (Harwood, 1981; Lee and Harwood, 1989). Mineralisation in ovoid cavities is probably associated with nodular calcium sulphate and 'fractures' are probably former calcium sulphate streaks.

The basal mineralisation was exposed for a relatively short time and therefore did not attract as much attention as the mineralisation along the fault zone. Although there is an almost complete overlap in the primary species that are present, a number of factors differentiate the two assemblages. The basal mineralisation was disseminated and horizontal unlike the fault-zone minerals which were concentrated in and around vertical fractures. The basal sulphide minerals occur as isolated crystals in cavities and fractures rather than polycrystalline masses. Unlike the fault zone, where galena is overwhelmingly dominant, sphalerite is the most abundant sulphide in the basal assemblage. The basal

sphalerite is translucent and fluorescent unlike the residual fault zone sphalerite which is opaque and does not fluoresce. Iron sulphides in the basal assemblage are generally later and spatially separated from the base-metal sulphides, unlike the fault zone deposit where the two are commonly intergrown. Finally, although it is not a distinguishing feature, the basal assemblage is almost entirely unaffected by supergene alteration.

Similarities between the basal assemblage at Whitwell Quarry and mineralisation at the same horizon at nearby localities suggest that it is part of a disseminated assemblage that is widespread across northeast England. A comparison with Armstrong Quarry, where the mineralisation is the result of geochemical processes associated with the local dissolution and replacement of calcium sulphate nodules, is helpful.

At Armstrong Quarry, Bateman *et al.* (2021b) suggest that dissolution of calcium sulphates increased the calcium ion activity, depositing calcite, at the same time as microbial reduction of sulphate raised the activity of reduced sulphur, immobilising lead and zinc as highly insoluble galena and sphalerite. Once the supply of lead and zinc had been exhausted, the activity of reduced sulphur increased until marcasite or pyrite began to crystallise. Rare late-stage baryte appears to have formed in a reaction between barium ions produced by slow diagenetic reactions in the local sediment and residual sulphate.

The similarities between the two basal assemblages suggest a common origin. At both localities the mineralisation is disseminated in cavities and fractures left by the dissolution of calcium sulphates. Galena and sphalerite are early and calcite, baryte and pyrite are late. Sphalerite is more abundant than galena and occurs as fluorescent translucent to transparent crystals. Marcasite is earlier than pyrite and the iron sulphides are spatially separated from the base-metal sulphides. The most significant differences between the mineralisation at the two sites are the relative abundances and paragenetic positions of calcite and baryte. Baryte is more abundant and earlier than calcite at Whitwell Quarry, but less abundant and later than calcite at Armstrong Quarry.

It is easy to account for the abundance of baryte in the basal assemblage at Whitwell Quarry. The exposure was close to a major fault which channelled barium-rich fluids from the underlying Carboniferous strata and fluid leakage is almost inevitable. In contrast, there are no faults in the Permian sequence at Armstrong Quarry and, as the Marl Slate Formation is unusually thick, the basal assemblage has been protected from upward-leakage of barium-rich brines.

The rarity of calcite at Whitwell Quarry in comparison to nearby basal assemblages is puzzling. The permeability of the recrystallised dolostone near the fault zone may have reduced the peak calcium ion

activity and inhibited calcite formation, perhaps due to increased advective flow. This is consistent with observations at Armstrong Quarry, where calcite is less abundant in cavities and fractures in the saccharoidal dolostone in comparison to the marly lithologies. The presence of etched calcite crystals in the basal assemblage at Whitwell Quarry (see Fig. 22) shows that some calcite has dissolved and this may also have a bearing on its scarcity.

Despite these differences it seems likely that the basal mineralisation at Whitwell Quarry is a variant of the disseminated mineralisation associated with the dissolution of nodules and streaks of calcium sulphate which is widespread across northeastern England (cf. Bateman *et al.*, 2021b). Comparison with buried sequences farther to the east, which still contain calcium sulphates, suggests that the mineralisation may be relatively recent. The ultimate origin of the base-metals appears to be syngenetic sulphides in the Marl Slate Formation but, as discussed by Bateman *et al.* (2021b), these may have been remobilised on more than one occasion.

Epigenetic Mineralisation

Epigenetic mineralisation in the Cadeby Formation is localised in four areas centred on Farnham, Bramham, Edlington and Mansfield according to Harwood and Smith (1986). It is dominated by baryte, which typically occurs as replacement deposits; mineralisation in veins is relatively unusual and substantial accumulations of galena are extremely rare. The fault-zone mineralisation at Whitwell Quarry is locally unique. In the absence of fluid inclusion, isotopic and trace-element data, the following discussion is speculative. It relies on field observations and limited comparisons with surrounding localities. It also highlights opportunities for further study.

The mineralisation at Whitwell Quarry was localised in a secondary fracture system (described here as the ‘northern splay’) which extends from the Park Hall Fault near to where it changes from a WNW–ESE to a NNW–SSE course (see Fig. 4). In the sections examined between 1985 and 1990, the mineralised zone was up to about 10 m wide and bordered by near-vertical faults with metre-scale downthrows to the south. Discontinuous vein-like galena-baryte mineralisation was concentrated along the faulted boundaries (Fig. 93) with replacement baryte and galena extending into the surrounding dolostone (see Figs 19 and 40). The heavily brecciated central dolostone contained irregular masses of galena, sometimes mantled in a red clay gouge, and generally without associated primary minerals (see Fig. 39). The fault zone was well mineralised along a strike length of a few hundred metres. In this area it typically extended for a few tens of metres along the strike before being displaced slightly to the southwest by conjugate fractures.

An impression of the structural complexity can be gained from field notes compiled by two of the authors



Figure 93. A near-vertical galena veinlet in heavily brecciated dolostone near the edge of the fault zone (left-hand side) with white powdery baryte and heavily brecciated dolostone to the right. The head of the pick is about 30 cm in length. Photo Peter Briscoe.

(Peter Briscoe and David McCallum) at the time:

“in May 1986 the main fault system in the north face was exposed with spectacular results. The vein occupies the fault zone in a very impersistent manner and the Galena may change from nothing to .5 metre of solid ore in a few centimetres, the vertical extent of the vein may also change very quickly ... The vein may also split into stringers, the main stringers always lie on the walls of the slickensided fault zone. The Galena is always mixed with Baryte at the extremities of the deposit, in the centre the Galena is more massive and may contain either good Cerussite, Anglesite or Vanadinite”.

They go on to record galena with subsidiary baryte as irregular masses in steeply dipping dolostone breccia zones; as discontinuous sub-vertical veinlets in fractures; as slickensided ‘steel ore’; as loose botryoidal masses in roughly horizontal cavities conformable with remnant bedding; and in irregular cavities controlled by vertical fractures.

Exposures of the fracture system to the northwest of the well mineralised section, nearer to the main course of the Park Hall Fault, contained a sooty gouge without obvious lead mineralisation. Fluid flow commonly bleaches the rock around major structural faults. In such situations, mineralisation is typically concentrated in ‘traps’ where the flow is reduced. The northern splay provided such a trap along a strike length of a few hundred metres as it became increasingly fractured and began to lose its identity.

The only nearby locality with mineralisation that is comparable with the fault-zone at Whitwell Quarry is the Sunnyside Deposit to the north of the village of Whitwell, where baryte veins are surrounded by extensive replacement deposits. It is generally agreed that the baryte deposits in the basal Permian formed in an interaction between invasive barium-rich Coal Measures brines and local sulphate-rich fluids. Bateman *et al.* (2021a) favour a scenario in which the invasive brines reacted with isotopically modified sulphate from local Permian evaporites.

It is tempting to use the Sunnyside Deposit as a model for the fault-zone mineralisation at Whitwell Quarry. There are similarities in the character of the primary baryte mineralisation but substantial differences in the bulk mineralogy and structural setting. The most important of these are that the mineralised fault system at Whitwell Quarry has a direct connection with a major fault in the Carboniferous basement and that galena is orders of magnitude more abundant at Whitwell Quarry than at any of the Sunnyside exposures.

The abundance of galena (and relative scarcity of baryte) at Whitwell Quarry poses a problem for a Coal Measures source. Lead minerals are uncommon in the Coal Measures (Bateman *et al.*, 2018) and there is no evidence that they have been a major source of base metals at any nearby Permian locality⁶ (Harwood and Smith, 1986). The proximity of the Park Hall Fault, a major basement structure, makes a source in the underlying metal-rich Lower Carboniferous shales more likely, though a more local source in the metal-rich Marl Slate Formation (analogous to the remobilisation proposed by Wagner *et al.* (2010) to account for some of the vein mineralisation in the Spessart area of Germany) cannot be discounted.

The epigenetic fault-zone mineralisation at Whitwell Quarry can be classified as a small and somewhat anomalous Mississippi Valley Type (MVT) deposit. It is dominated by galena and baryte and lies within a trap near a major structural fault in a carbonate host rock. It is unlikely to be a distal part of the Pennine suite. A late Carboniferous to early Permian age for the Pennine orefields is now generally accepted and this pre-dates the rocks of the late Permian Zechstein Group (Dunham, 1990; Dempsey, 2016; Ford and Worley, 2016; Bott and Smith, 2018; Dempsey *et al.*, 2021). The presence of detrital Pennine baryte and fluorite in the basal Permian Yellow Sands Formation in Yorkshire (Versey, 1925) shows that the Pennine mineralisation had been deposited and eroded away before the rocks of the Zechstein Group began to accumulate. A two-fluid model (see Wilkinson, 2014) similar to that proposed by Bateman *et al.* (2021a) for the Sunnyside Deposit is consistent with the structural setting and pattern of baryte deposition and seems worthy of further investigation.

Supergene Minerals

The species that distinguish Whitwell Quarry as an unusual and important locality are mostly supergene. Smears of slickensided galena on fault planes show that some fault movement post-dated the deposition of the primary minerals. The associated fracturing probably facilitated access to oxygenated groundwater when inversion and erosion raised the deposit above the water table.

The anomalous nature of the assemblage is highlighted by the fact that no similar mineralisation has been reported anywhere else in the Permian rocks of northeast England (Tindle, 2008; Young *et al.*, 2021). Supergene mineralisation at the nearby Sunnyside Deposit is sparse and comparatively simple; it includes cerussite, hydrozincite, malachite, plumbojarosite and smithsonite (Bateman *et al.*, 2021a). Traces of aurichalcite and malachite have been identified at Vale Road Quarry near Mansfield (Green and Spence, 1988). Cerussite is recorded at Sprotbrough Quarry, near the village of the same name, by Harwood (1981: p. 319), but no supergene minerals are noted in short summaries of thirty separate baryte-galena-sphalerite occurrences in Permian rocks in the Doncaster, Whitwell and north Nottinghamshire areas on page A1/2 of the appendix to her thesis.

Casting the net a little wider, cerussite, malachite and wulfenite have been identified across an extensive horizon at the top of the Cadeby Formation to the north of Nottingham (Deans, 1961; Harwood, 1981: p. A1/3). Supergene copper minerals (most commonly malachite) are present in the Cadeby and Brotherton formations around Bramham, Newton Kyme and Farnham in Yorkshire (Barrett, 1975; Harwood, 1981). They also occur in the Raisby and Ford formations (lateral equivalents of the Cadeby Formation) along the Butterknowle Fault near Coxhoe in Co. Durham (Young *et al.*, 2021). Surprisingly, a brief note of cerussite from Old Towns Quarry near Newton Aycliffe is the only record of a supergene lead mineral from the Permian rocks of this area (Bridges and Pettigrew, 2013).

With a solubility product of $2.3 \times 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$, wulfenite is a sensitive indicator of molybdate ion concentrations (Williams, 1990: p. 227; Smedley and Kinniburgh, 2017). Trace-element analyses reveal unusually high molybdenum concentrations in the Marl Slate Formation around Whitwell (Smith *et al.*, 1973: p. 114) and at the top of the Cadeby Formation in north Nottinghamshire, where wulfenite is widespread (Deans, 1961). It is surprising, therefore, that a thorough examination of numerous specimens from Whitwell Quarry has failed to reveal any trace of the mineral.

The supergene minerals have a consistent spatial zonation (Fig. 94). Cavities in massive polycrystalline galena beyond the influence of infiltrating carbonate contain anglesite with minor sulphur. Nearer to the edges, where carbonating solutions have penetrated along grain boundaries, cerussite is common. Cavities in the 'infiltration zone' contain minerals of the Leadhills suite where the carbonate ion activity was unusually low. Hydrocerussite,

⁶ The extent and character of the mineralisation at the Elizabethan lead mine in Whitwell village is unknown.

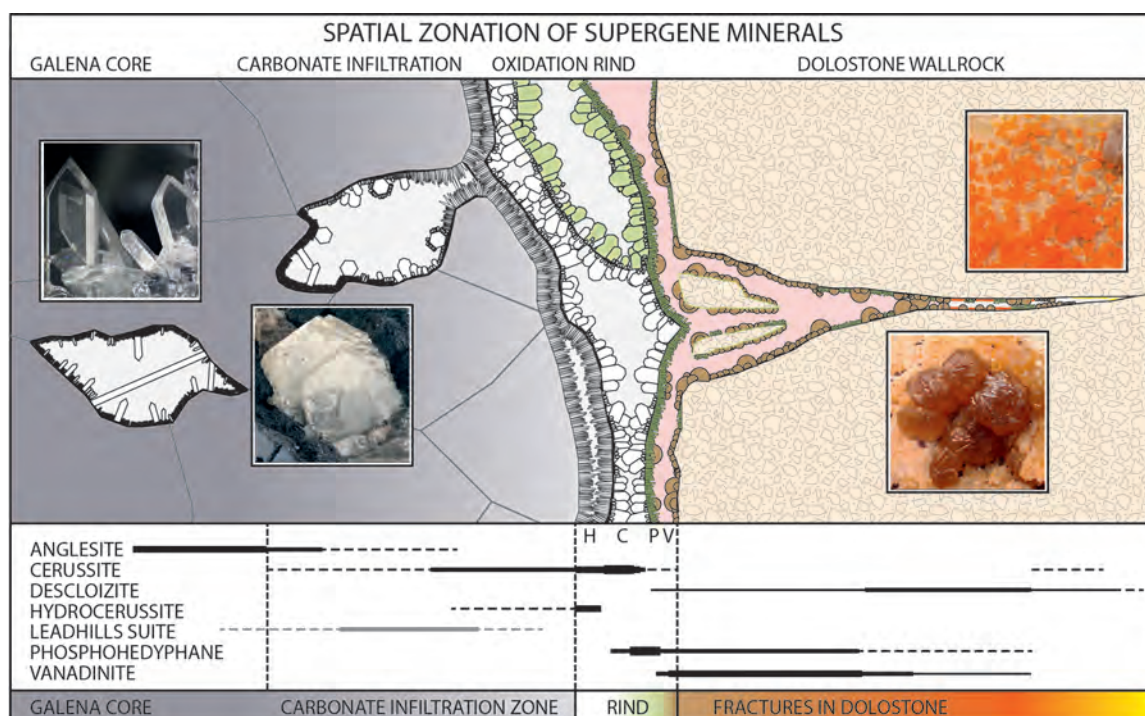


Figure 94. Simplified diagrammatic representation of the supergene mineralisation around fault-zone galena.

cerussite and phosphohedyphane dominate the ‘oxidation rinds’ between massive galena and the surrounding dolostone. The spatial sequence in the rinds is almost always hydrocerussite followed by cerussite followed by phosphohedyphane. The phosphohedyphane is overgrown by vanadates in the presence of a red clay gouge. Descloizite, hydroxylapatite, phosphohedyphane and vanadinite are the most common supergene minerals in fractures in the surrounding dolostone. Cerussite and calcite are also occasionally present.

The mineral zonation in and around massive galena appears to be controlled by the ‘carbonate ion activity’, which is usually expressed as $p(\text{CO}_2)$. Stability field diagrams provide a guide to the geochemistry (Williams, 1990; Bridges, 2015). The situation toward the outer edge of oxidation rinds where cerussite is stable [$p(\text{CO}_2) > 10^{-1.95}$], is illustrated in Figure 95.

Leadhillite occupies a stability field between cerussite and anglesite as the $p(\text{CO}_2)$ values fall and hydrocerussite eventually replaces cerussite as the stable lead carbonate (Fig. 96). Williams (1990) argues that hydrocerussite is the stable lead carbonate in fluids in equilibrium with atmospheric carbon dioxide and remains so up to a $p(\text{CO}_2)$ of $10^{-2.24}$. Bridges (2015) argues for a lower value of $10^{-3.82}$, which is a little less than atmospheric pressure. These geochemical details do not affect the overall thrust of this narrative.

The presence of hydrocerussite in the innermost layer of the oxidation rinds (see Fig. 94) is consistent with a reducing $p(\text{CO}_2)$ moving toward the underlying galena. On rare specimens where leadhillite is also present, the paragenetic sequence is usually hydrocerussite followed by leadhillite followed by cerussite (Fig. 97). These

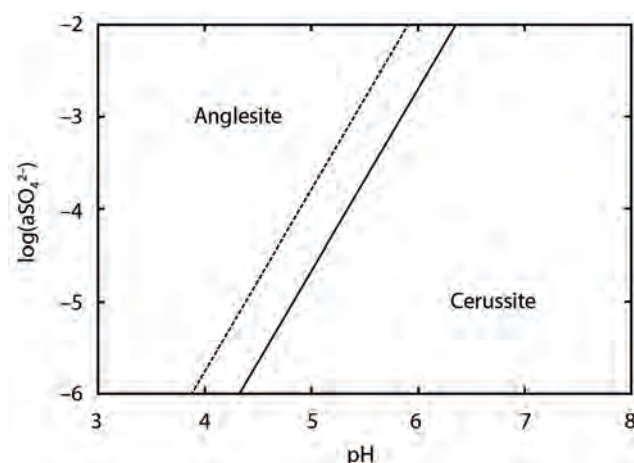


Figure 95. Stability field diagram for anglesite and cerussite calculated using the constants provided in Bridges (2015). The full line is for $p(\text{CO}_2) = 10^{-1.95}$, and the dotted line for $p(\text{CO}_2) = 10^{-1.0}$.

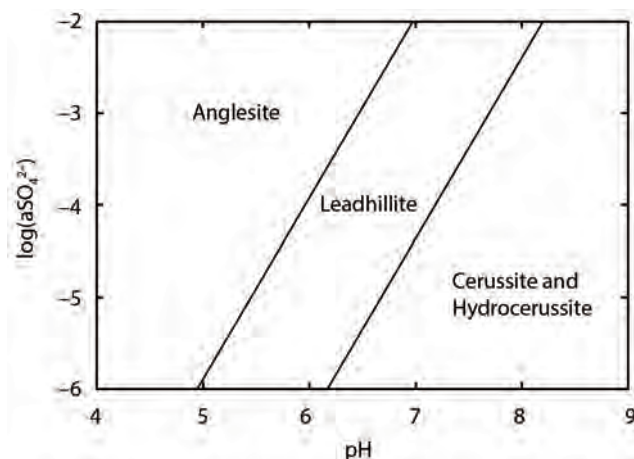


Figure 96. Stability field diagram calculated using the constants provided in Bridges (2015) for $p(\text{CO}_2) = 10^{-3.82}$. Above this value cerussite is the stable lead carbonate mineral and occupies the field at the right of the diagram; below it, hydrocerussite is stable.



Figure 97. Hydrocerussite overgrown by leadhillite with a very late and rather irregular tabular cerussite twin (middle left). It is unusual to find all three carbonate minerals in close association. In most cases the less stable species are replaced as conditions change. The paragenetic sequence, hydrocerussite followed by leadhillite followed by cerussite, is consistent with oxidation at increasing $p(\text{CO}_2)$ values (see Figs 95 and 96). Specimen E146 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 6 mm across. Photo John Chapman.

observations support a model in which carbonating solutions diffusing into massive galena gradually raise the $p(\text{CO}_2)$ value at a particular point as oxidation proceeds. In a carbonate-dominated environment, the

ultimate end-point of this process is the complete replacement of galena by cerussite. The oxidation rinds at Whitwell Quarry provide snapshots of this geochemical process in action.

The minerals of the Leadhills suite illustrate a more complex oxidation pathway beginning at low Eh and $p(\text{CO}_2)$ with a higher activity of sulphate (and rarely sulphite). Scotlandite, which contains sulphur in its intermediate S(IV) oxidation state as sulphite, requires a low Eh. It is restricted to relatively well sealed cavities in galena. Lanarkite requires a very low carbonate ion activity and relative alkaline conditions (Bridges, 2015: pp. 10–11) and is similarly restricted. Both minerals are overgrown by leadhillite and susannite, which are stable at higher $p\text{CO}_2$ (Bridges *et al.*, 2008; Bridges, 2015). Mattheddleite occupies a similar paragenetic window to leadhillite and susannite for reasons which remain to be explained. As conditions in the cavities containing Leadhills-suite minerals normalise, leadhillite and susannite are replaced by cerussite (e.g. Fig. 98).

The presence of a lead chloride in the supergene assemblage is intriguing. In Britain, cotunnite has been identified at a small number of coastal localities where galena has oxidised in the presence of seawater (Bridges, 2003; Hubbard and Green, 2005), at Leadhills–Wanlockhead (Temple, 1954; 1956) and in the Mendip Hills. The Mendip occurrences are in deposits with a very unusual chloride-rich geochemistry (Bridges *et al.*, 2012). The presence of cotunnite at Leadhills–Wanlockhead is anomalous as there is no obvious source of chloride.



Figure 98. A well formed lustrous vee-twin cerussite overgrowing etched white leadhillite. The dissolution of leadhillite and replacement by cerussite provides a graphic illustration of the effect of an increasing $p\text{CO}_2$. Specimen E113 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 10 mm across. Photo John Chapman.

The geochemical calculations used to explore the Mendip suite of lead chloride and oxychloride minerals (Bridges *et al.*, 2012) show that cotunnite requires acid conditions (otherwise lead oxychlorides are stable), with very little carbonate (otherwise phosgenite is stable) in a strong chloride brine (otherwise anglesite is stable). It is reasonable to conclude that a concentrated chloride brine attacked and altered the fault-zone galena at Whitwell Quarry. The Park Hall Fault brings the Edlington Formation into direct contact with the Cadeby Formation in an outlier along the southwest boundary of the site (see Fig. 4). Brines leaching into the fault zone from dissolving Edlington Formation evaporites during uplift provide a possible source.

Cotunnite is unstable in downward percolating rain-water and rapidly alters to lead carbonates. The crusts in fractures in galena from Whitwell Quarry are almost certainly residual. If more significant amounts of lead chloride were present early in the evolution of the supergene system, dissolution has the potential to generate very high lead ion activities. This may have had an influence on the unusual supergene assemblage that developed at the site.

The supergene assemblage in fractures in the dolostone surrounding the oxidising sulphides is dominated by phosphate and vanadate minerals.

Vanadinite occurs as remarkable cabinet specimens (e.g. Fig. 99). The richest examples were always mantled in a red clay gouge (Fig. 100), suggesting the latter as a possible source of vanadium. Vanadium-bearing phyllosilicates commonly accumulate in fine-grained clastic rocks in continental red-beds (Kelley *et al.*, 2017).

Some of the dark brown vanadinite crystals are slightly radioactive. Uranium and vanadium are often associated in continental red-bed deposits (one possible source of the red gouge). Inclusions of uranium-bearing hydrocarbon, which are associated with supergene minerals at the top of the Cadeby Formation in Nottinghamshire, are another possibility (Deans, 1961).

Unlike the supergene mineralisation in and around galena, there is no consistent paragenetic sequence in the fractures in the dolostone (Fig. 101; see also Figs 34, 86 and 87). Some general observations can, however, be made. Phosphohedyphane is the most common supergene phosphate and it is usually early. It may be overgrown by acicular white lead-bearing hydroxylapatite, and in some cases the relationship appears to be epitaxial. White radiating sprays of phosphohedyphane, or lead-bearing hydroxylapatite, or both, are commonly associated with vanadinite and descloizite. There is usually one generation of dark brown globular vanadinite on the outer edges of the

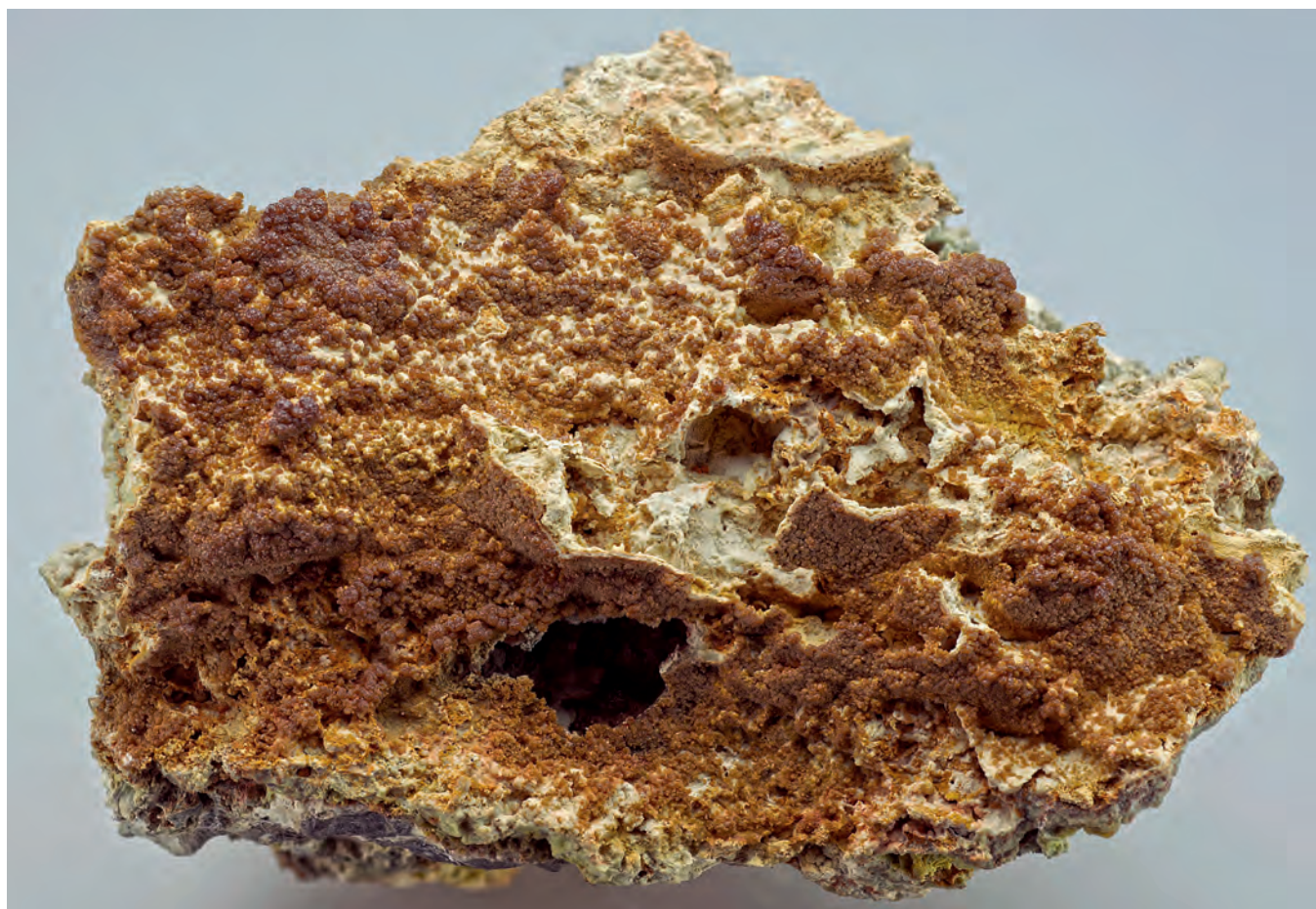


Figure 99. Cabinet specimen, 110 × 80 mm, richly coated in dark brown vanadinite on white to pale green phosphohedyphane (possibly with hydroxylapatite) which coats a rib of galena averaging about 20 mm in thickness. Specimen GA5 in the Peter Briscoe Collection from Whitwell Quarry, Derbyshire. Photo Peter Briscoe.



Figure 100. Galena in brecciated dolostone mantled by white lead carbonates and surrounded by pale green phosphohedyphane which is visible at the lower right. The galena is partly enclosed in a red gouge, which is most obvious at the top right. It conceals fragments of dolostone overgrown by globular vanadinite. The pick head in the image is about 10 cm in length. Photo Peter Briscoe.

oxidation rinds, but several generations, each with its own distinct crystal habit, may be present in the surrounding fractures (see Figs 87, 88 and 101).

The mineralisation in the distal fractures includes supergene calcite, cerussite, descloizite, hydroxylapatite, phosphohedyphane and vanadinite. The calcium and carbonate ion activities are likely to be buffered by the carbonate wall-rock. Phosphate may have been supplied by detrital apatite. Lead ions are clearly produced by the slow oxidation of primary galena but their activity is probably buffered by the surrounding supergene phases. Zinc ions are likely to be present in a supergene halo produced by the oxidation of sphalerite. Vanadium may be associated with fine-grained phyllosilicates in the red gouge. The concentration of hydroxyl ions is governed by the pH and chloride ions may be associated with residual evaporites. The interplay between the activities of these chemical species produced the distal assemblage, but there is no consistent paragenesis and a quantitative thermodynamic model is beyond the scope of this research.

The possible presence of a particle of periclase raises the prospect of anthropogenic influence on the supergene system. The calcining plant operated by Steetley Dolomite is the only likely source. The fault zone was



Figure 101. A specimen from the distal supergene assemblage showing the complexity of the mineralisation. Minor phosphohedyphane is overgrown by brown globular vanadinite, orange platy descloizite and white acicular hydroxylapatite (identified by energy-dispersive X-ray spectrometry). There are two generations of vanadinite the large early crystals are overgrown by descloizite but the slightly paler later generation (bottom left and right) overgrow descloizite. Specimen E096 in the David McCallum Collection from Whitwell Quarry, Derbyshire. The field of view is 3.5 mm across. Photo John Chapman.

No.	CaO	ZnO	PbO	V ₂ O ₃	SiO ₂	P ₂ O ₅	As ₂ O ₅	Cl	Total	MINERAL
P211	1.56	0.00	75.23	10.52	0.22	5.00	0.79	2.90	96.29	Vanadinite
P211	1.58	0.01	74.87	11.18	0.22	4.66	0.53	2.81	95.96	Vanadinite
P211	0.55	0.04	76.97	12.43	0.13	1.87	0.22	2.51	94.75	Vanadinite
P211	0.38	0.04	76.23	14.15	0.13	1.57	0.33	2.94	95.82	Vanadinite
P212	10.77	0.45	62.69	0.09	0.24	18.39	0.31	2.56	95.60	Phosphohedyphane
P212	8.99	0.48	64.52	0.08	0.20	17.65	0.29	2.65	94.92	Phosphohedyphane
P212	25.31	0.48	40.38	0.02	0.19	24.30	0.00	1.30	92.20	Hydroxylapatite
P212	8.39	0.44	66.06	0.04	0.18	17.32	0.32	2.61	95.46	Phosphohedyphane
P212	10.88	0.46	63.34	0.04	0.19	18.95	0.29	2.46	96.81	Phosphohedyphane
P212	8.10	0.44	67.82	0.09	0.22	17.63	0.35	2.78	97.51	Phosphohedyphane
P212	8.54	0.44	67.75	0.06	0.21	17.70	0.27	2.66	97.78	Phosphohedyphane
P212	22.25	0.53	47.12	0.06	0.24	22.95	0.03	1.66	95.15	Hydroxylapatite
P212	19.82	0.41	49.63	0.05	0.21	22.40	0.03	1.72	94.48	Hydroxylapatite
P213	1.74	0.07	74.70	9.65	0.26	5.60	1.16	2.74	96.00	Vanadinite
P213	0.59	0.01	77.21	13.83	0.13	2.00	0.18	2.72	96.75	Vanadinite
P213	1.27	0.00	76.15	12.01	0.11	3.68	0.46	2.86	96.61	Vanadinite
P213	1.05	0.03	76.57	12.64	0.14	2.88	0.40	2.84	96.74	Vanadinite
P213	1.78	0.00	75.85	9.22	0.23	6.17	0.99	2.84	97.22	Vanadinite
P214	1.13	0.02	77.41	12.46	0.23	3.14	0.44	2.85	97.82	Vanadinite
P214	0.94	0.02	76.98	12.38	0.20	3.06	0.46	2.78	96.95	Vanadinite
P214	1.10	0.03	76.09	12.30	0.19	3.48	0.54	2.77	96.68	Vanadinite
P214	0.86	0.03	77.19	13.05	0.20	2.79	0.24	2.84	97.29	Vanadinite
P215	2.74	0.03	74.33	8.09	0.25	7.54	0.95	2.76	96.85	Vanadinite
P215	3.00	0.01	74.66	7.56	0.24	7.98	0.86	2.70	97.10	Pyromorphite
P215	1.55	0.03	75.96	11.19	0.15	4.76	0.42	2.86	97.02	Vanadinite
P215	1.11	0.00	76.13	12.58	0.14	3.19	0.33	2.92	96.45	Vanadinite
P215	0.53	0.01	77.16	13.69	0.19	1.73	0.20	2.78	96.32	Vanadinite
P216	2.37	0.02	74.83	8.91	0.24	6.69	0.79	2.94	96.87	Vanadinite
P216	2.39	0.02	75.89	8.83	0.23	6.70	0.80	2.71	97.67	Vanadinite
P216	2.17	0.07	74.54	9.19	0.26	6.19	0.77	2.74	96.07	Vanadinite
P216	2.51	0.05	74.49	8.37	0.19	7.35	0.67	2.88	96.66	Vanadinite
P217	6.66	0.36	68.49	0.17	0.27	16.62	0.32	2.63	95.81	Phosphohedyphane
P217	7.21	0.39	66.85	0.12	0.23	16.56	0.21	2.43	94.11	Phosphohedyphane
P217	6.44	0.16	69.27	0.80	0.59	14.43	1.22	2.67	95.69	Phosphohedyphane
P218	1.17	0.03	76.37	12.14	0.17	3.47	0.48	2.95	96.82	Vanadinite
P218	1.14	0.00	76.68	11.94	0.21	3.36	0.55	2.78	96.70	Vanadinite
P218	1.14	0.02	76.58	11.95	0.20	3.42	0.56	2.82	96.79	Vanadinite
P218	0.86	0.01	76.52	12.38	0.16	2.83	0.72	2.76	96.27	Vanadinite
P221	7.14	0.23	69.25	0.03	0.49	16.19	0.97	2.95	97.45	Phosphohedyphane
P221	6.88	0.27	69.26	0.04	0.32	16.28	0.53	2.89	96.65	Phosphohedyphane
P221	7.43	0.38	69.47	0.01	0.34	16.84	0.55	2.83	97.93	Phosphohedyphane
P221	6.72	0.26	70.45	0.03	0.34	16.47	0.70	2.93	98.11	Phosphohedyphane

Table 3. Selected wavelength-dispersive X-ray analyses of lead-bearing apatite-supergroup minerals from Whitwell Quarry with results quoted as weight percent oxides. In addition to the elements listed, aluminium, barium, cobalt, copper, fluorine, iron, magnesium, manganese, sodium, strontium, sulphur and titanium were sought but were either below detection levels or rare with global mean values of less than 0.02 wt% and no outliers of more than 0.1 wt%. These data are disregarded in the table and subsequent calculations, but are included in the totals.

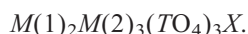
first exposed in the early 1980s and there was no kiln waste anywhere near it at the time the specimens were collected. The only way contamination could have been introduced is as wind-blown dust. Five years is a short time for solutions leached from wind-blown particulates to have had a substantial effect on a large supergene system, especially one that was well above the water table (effectively the quarry sump) and flushed by downward percolating rainwater. There is no evidence of minerals such as ettringite, the zinc hydroxide polymorphs ashoverite and sweetite, or the lead oxides and hydroxides which form in alkaline oxidising environments associated with lime burning. Therefore, there is little evidence to suggest significant anthropogenic modification of the assemblage.

Alkaline kiln dust is currently used as a component of a reactive engineered barrier around coal waste in the main quarry void. It is added to minimise any impact on the groundwater from sulphuric acid generated by pyrite decay (Hubbard, 2019). This process was not approved until the beginning of the twenty-first century, well after the last fault-zone minerals were collected.

Apatite-Supergroup Chemistry

Lead-bearing apatite-supergroup minerals, collectively described as ‘lead-apatites’, are a major component of the supergene assemblage at Whitwell Quarry (Table 3). A summary of their composition, nomenclature and structure provides a useful prelude to this discussion of their chemistry. Apatite-supergroup minerals have a flexible structure, which is generally hexagonal with unit-cell

parameters $a = 9.3\text{--}9.6$ Å and $c = 6.7\text{--}6.9$ Å (Pasero *et al.*, 2010). Their structural formula can be written:



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

The minerals of the apatite supergroup are currently divided into five groups on crystallographic and chemical criteria. Three are of importance to this discussion. Hydroxylapatite, pyromorphite and vanadinite belong to the apatite group, which has the same cation at the $M1$ and $M2$ sites. Phosphohedyphane belongs to the hedyphane group and has different cations at the $M1$ and $M2$ sites⁷. Mattheddleite is a member of the sulphate-silicate ellestadite group.

Selected analyses of lead-apatites from Whitwell Quarry are listed in Table 3. Empirical formulae were calculated from these data as recommended by Pasero *et al.* (2010: p. 173): ideally this should yield nine atoms per formula unit. Deviations in the expected totals are usually due to the presence of undetected light elements.

A plot of normalised calcium–lead versus phosphate–vanadate ratios (Fig. 102) shows that the compositions of vanadinite and phosphohedyphane fall into two groups. One group lies along a line which cuts obliquely through the vanadinite composition field, with one point lying slightly over the border in the pyromorphite field. These compositions correspond to the pale to dark brown rounded to barrel-shaped crystals. The second group lies near the y -axis in the phosphohedyphane composition field (and in two cases very slightly above it). These correspond to white to green drusy phosphohedyphane.

As the two groups are distinct, the first being calcium- and phosphate-bearing vanadinite and the second phosphate-dominated phosphohedyphane, they are considered independently.

⁷ A solid solution exists between pyromorphite, ideally $Pb_5(PO_4)_3Cl$, and phosphohedyphane, ideally $Ca_2Pb_3(PO_4)_3Cl$. In the absence of discontinuous structural changes, the boundary between the species lies where half of the lead at the $M(1)$ site has been replaced by calcium. This corresponds to one atom of calcium per formula unit and phosphohedyphane occupies the region of composition space $0.2 \leq Ca/(Ca+Pb) \leq 0.4$.

The vanadinite compositions (Fig. 102; Table 3) lie along a linear trend and have a mean empirical formula:



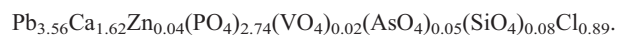
The mean composition and associated variances (Table 4) provide no information about trends in composition. They are nonetheless useful, as they give information about average site occupancy which provides a useful test of the reliability of the analyses.

The mean cation and anion site sums are close to accepted apatite-supergroup values without any requirement for correction: formula $Pb+Ca+Zn$ is 4.95 ± 0.12 ; formula $V+P+As+Si$ is 2.97 ± 0.08 ; and formula Cl is 1.08 ± 0.07 ⁸. These compare favourably with the ideal values of 5, 3 and 1, respectively. Charge balance is also reasonable, at -0.12 ± 0.49 electron charges per formula unit.

The standard error in the mean⁹ of the charge balance data of 0.08 indicates a small statistical difference between the measured mean of -0.12 and the expected value of 0.0 at 95% confidence level. This discrepancy could be eliminated by the undetected presence of an extra $0.06 M^{2+}$ ions per formula unit, a correction which would also rectify a similar discrepancy in formula $Pb+Ca+Zn$. It is well within acceptable limits.

The chlorine value gives more cause for concern: the site occupancy is 1.08 ± 0.012 which suggests a statistically significant chloride ion excess compared to the expected value of 1.00. As the charge balancing chloride ions are located in flexible channel sites there is probably room to accommodate such an excess in the structure. In terms of anionic charge, the excess chloride is balanced by a slight deficiency in T -anions and the net negative anion charge of 10.03 is very close to the expected value of 10.0. It is therefore reasonable to conclude that the analytical data are robust and reliable.

The mean empirical formula calculated from nineteen analyses of phosphohedyphane, using the method employed for vanadinite is:



The associated variances are listed in Table 5.

These data are more problematic: formula $Pb+Ca+Zn$ is 5.22 ± 0.09 ; formula $V+P+As+Si$ is 2.89 ± 0.08 ; and formula Cl is 0.89 ± 0.12 , which are all significantly different from the expected values of 5, 3 and 1. There is also a significant charge-balance error of 0.8 ± 0.12 electron charges per formula unit. This suggests the presence of undetected light elements.

⁸ These numbers are standard deviations at 95% confidence level, they provide a picture of the variability in the distribution of individual data points.

⁹ The standard error provides a guide to the reliability of the mean value at 95% confidence level.

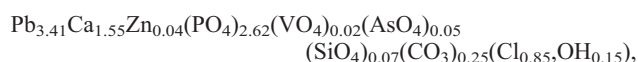
	Cl	Ca	Zn	Pb	V	Si	P	As
Mean	1.08	0.33	0.00	4.62	2.10	0.04	0.77	0.06
SD (2σ)	0.07	0.32	0.01	0.28	0.76	0.02	0.69	0.06
SE (2σ)	0.012	0.055	0.001	0.049	0.131	0.003	0.118	0.011

Table 4. Mean values as atoms per formula unit for all elements in the thirty four vanadinite analyses (plus one pyromorphite) shown in Figure 102. Standard deviations and standard errors in the mean ($n=35$) are quoted at 2σ (i.e. 95% confidence level).

	Cl	Ca	Zn	Pb	V	Si	P	As
Mean	0.89	1.62	0.04	3.56	0.02	0.08	2.74	0.05
SD (2σ)	0.12	0.42	0.04	0.40	0.06	0.08	0.22	0.05
SE (2σ)	0.031	0.105	0.009	0.100	0.014	0.019	0.055	0.014

Table 5. Mean values as atoms per formula unit for all elements in the nineteen phosphohedyphane analyses shown in Figure 102. Standard deviations and standard errors in the mean ($n=19$) are quoted at 2σ (i.e. 95% confidence level).

The charge balance error is too large to be addressed by adding hydroxyl to increase the mean X -anion sum to 1.0. The most likely cause is the presence of a small amount of carbonate. Adding 1.0 wt% CO_2 to the original datasets, suitable hydroxyl to increase the channel site occupancy to 1.0, and renormalising, produces a mean empirical formula:



with cation sums of 4.99, 3.02 and 1.0 which are very

close to the ideal values of 5, 3 and 1. The resultant charge balance error is 0.1 ± 0.12 electron charges per formula unit, which is within acceptable limits. The addition increases the mean oxide sum from 96.5 wt% to 97.5 wt%. There is no easy way to test whether this is correct, as small amounts of carbonate are difficult to detect by electron-beam techniques, however the suggestion that a small amount of carbonate might be present in an apatite-super group mineral in a dolostone host appears reasonable (Pan and Fleet, 2002; Pasero *et al.*, 2010).

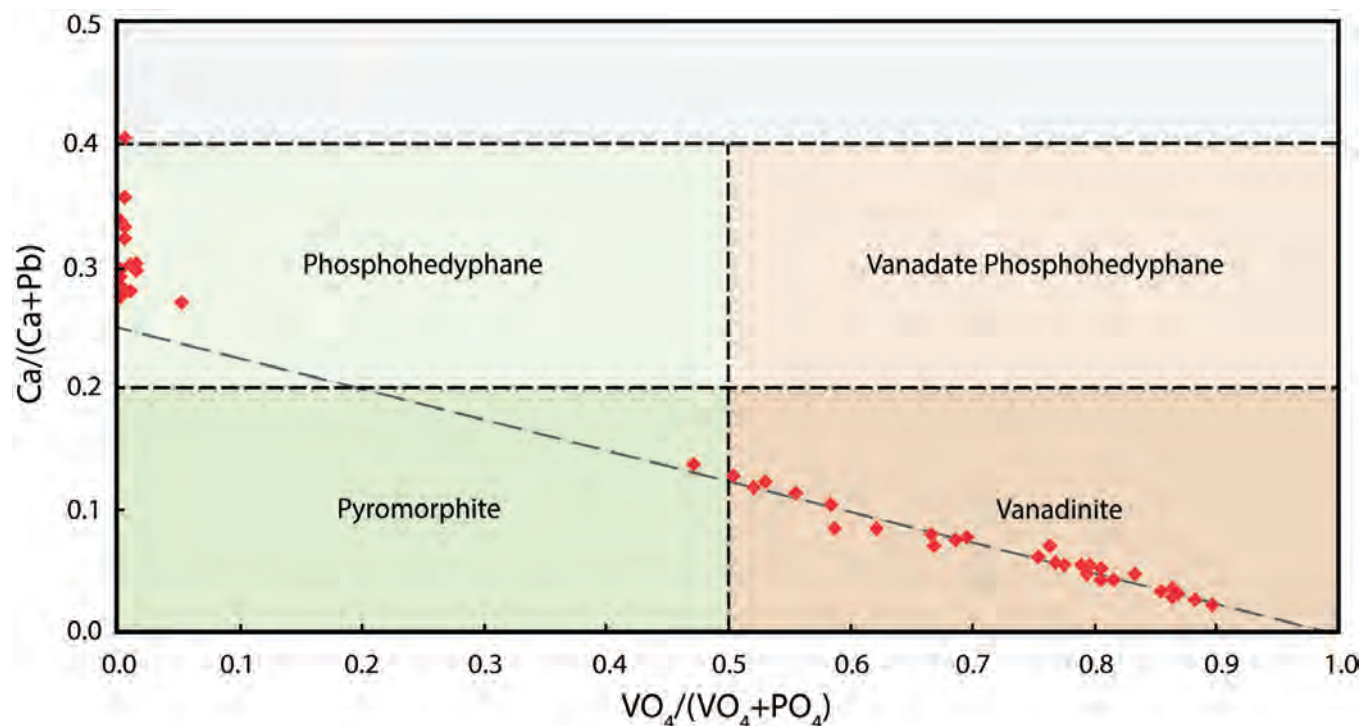


Figure 102. Plot showing fifty-four analyses of phosphohedyphane, pyromorphite and vanadinite by wavelength-dispersive X-ray spectrometry. The composition field of each species is indicated by dashed lines (based on the most simple interpretation of the rules of the International Mineralogical Association). Compositions at the bottom left and right hand corners correspond to end-member pyromorphite and vanadinite, ideally $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ and $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$, respectively. The composition at the top left of the phosphohedyphane composition field is end-member phosphohedyphane, ideally $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$. The 'vanadate phosphohedyphane' field corresponds to a potential vanadate analogue of phosphohedyphane (no such species has ever been identified). Compositions in the grey area at the top of the diagram require calcium substitution at the $M(1)$ and $M(2)$ sites in the structure. The dashed trend-line is a linear regression of the data for the analyses shown on the right-hand side of the diagram.

Calcium to lead ratios in phosphohedyphane, described as $\text{Ca}/(\text{Ca}+\text{Pb})$, vary between 0.27 and 0.41. The top of this range is very close to end-member composition, with two calcium atoms per formula unit. The lowest values lie slightly above the projection of the trend line in Figure 102. Unlike vanadinite, where there is a wide range of phosphate for vanadate substitution, there is very little vanadate substitution in phosphohedyphane: the maximum value of $\text{VO}_4/(\text{VO}_4+\text{PO}_4)$ is 0.05 and the mean value less than 0.01. This suggests a miscibility gap in the vanadinite–phosphohedyphane solid solution at Whitwell Quarry at about the point where half of the vanadate in the structure has been replaced by phosphate.

The minor element data in Table 3 shows that vanadinite and phosphohedyphane contain about the same amount of arsenate; that the silicate contents are highly variable with the mean value in phosphohedyphane being significantly greater than vanadinite; and that the mean zinc content of phosphohedyphane is greater than vanadinite.

There is insufficient information to make a statistically useful comparison with descloizite, which is commonly associated with phosphohedyphane and vanadinite, but the limited dataset suggests that copper and sodium preferentially partition into the cation sites in descloizite (Table 6). The maximum copper value of 4.32 wt% CuO is slightly more than a quarter of the way along the solid solution toward mottramite. The only noteworthy anionic substitution is 2.18 wt% As_2O_5 , which is a little higher than the maximum in the associated lead apatites (see Table 3).

The relationship between phosphate and calcium in Figure 102 is of crystal-chemical interest. Plotting formula calcium versus formula phosphate (Fig. 103) reveals a linear relationship ($r^2 = 0.97$) which can be expressed:

$$y = 0.463x - 0.029,$$

where y represents formula calcium and x formula phosphate. The trend line passes close to the origin, which shows that phosphate-free vanadinite from Whitwell Quarry should contain no calcium (a conclusion which is

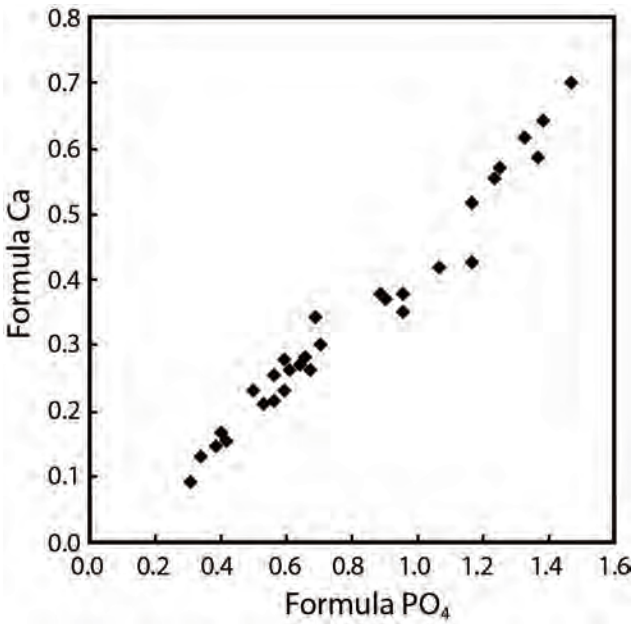


Figure 103. Plot of formula calcium versus formula phosphate for thirty-four analyses of brown vanadinite and one of pyromorphite from Whitwell Quarry. There is a clear linear trend in these data: the slope is 0.463 ± 0.028 with an r^2 -value of 0.97.

borne out by the analysis presented in Table 2). The calcium content increases linearly as a function of phosphate content adding nearly one calcium atom for every two phosphate groups across the vanadinite composition field.

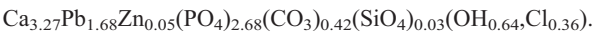
The fact that calcium and phosphate are restricted to a well defined substitution vector suggests that any potential vanadate analogue of phosphohedyphane is unlikely to be found at Whitwell Quarry. None of the points deviate far from the trend line, which does not intersect the appropriate composition field (see Fig. 102).

Relatively few acceptable analyses of hydroxylapatite and mattheddleite were obtained. The crystals of both species are invariably tiny and difficult to prepare. Three quantitative analyses of lead-rich hydroxylapatite are included in Table 3. The analytical totals are low (mean ~94 wt%) and the calculated empirical formulae do not charge balance even if suitable hydroxyl is added to increase the X-site occupancy to 1.0. In common with

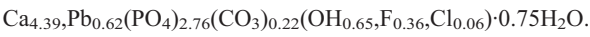
No.	Cl	Na ₂ O	CaO	CuO	ZnO	SrO	PbO	V ₂ O ₃	SiO ₂	P ₂ O ₅	As ₂ O ₅	Total
1	0.32	0.78	0.06	0.29	15.45	0.00	54.47	15.47	1.46	0.28	0.24	88.83
2	0.00	0.71	0.07	0.02	14.95	0.00	55.71	15.33	0.90	0.58	0.29	88.56
3	0.00	0.86	0.00	0.03	15.51	0.32	55.41	16.02	0.99	0.03	0.20	89.37
4	0.03	0.78	0.00	0.46	16.76	0.02	54.08	15.04	1.30	0.39	0.58	89.42
5	0.03	0.66	0.32	0.12	15.35	0.00	56.66	15.89	0.89	0.15	0.09	90.16
6	0.03	0.57	0.00	3.03	14.72	0.00	52.75	16.57	0.05	0.37	0.61	88.68
7	0.10	0.45	0.13	2.47	14.74	0.25	51.29	16.13	0.16	0.11	0.65	86.47
8	0.00	0.72	0.00	4.32	11.77	0.00	54.58	15.13	0.32	0.00	2.18	89.02
9	0.10	0.65	0.16	2.92	14.94	0.00	54.34	16.30	0.36	0.01	0.63	90.42
10	0.00	0.89	0.00	3.37	14.01	0.37	54.36	16.30	0.57	0.27	1.00	91.15

Table 6. Wavelength-dispersive X-ray analyses of descloizite from Whitwell Quarry with results quoted as weight percent oxides. In addition to the listed elements, barium, cobalt, iron, magnesium, manganese and sulphur were sought but are either below detection levels or rare with global mean values of less than 0.02 wt% and no outliers of more than 0.1 wt%. These data are disregarded in the table and subsequent calculations, but are included in the totals.

phosphohedyphane, the charge imbalance is probably due to undetected carbonate. If carbonate and hydroxyl are added, as described in the foregoing discussion, the mean empirical formula for the lead bearing hydroxylapatite from Whitwell is:

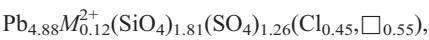


This is similar to the formula calculated by Livingstone (1994) for lead-rich hydroxylapatite from Wanlockhead:



Despite the close association between hydroxylapatite and vanadinite at both localities, neither contain any vanadate and it is interesting to note that vanadium does not substitute into the structure of the associated phosphohedyphane (see Fig. 102).

Only one analysis of mattheddleite was obtained from the tiny crystals that were available (Table 7). The empirical formula is:



where *M* is a placeholder which represents divalent cations (mostly barium and calcium). The occupancy of the *X*-site is assigned as a vacancy rather than hydroxyl to minimise the charge imbalance. Total silicate plus sulphate, at 3.08, is close to the ideal value of 3.0 and charge balance is reasonable for a single analysis, with 10.0 positive charges and 10.23 negative charges per formula unit.

In common with other members of the ellestadite group, the ideal formulae of mattheddleite is written $\text{Pb}_5(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}(\text{Cl},\text{OH})$, with a silicate to sulphate ratio of 1:1. There is good evidence that this is not the case: silicate is in significant excess in the analyses reported by Essene *et al.* (2006), at Whitwell Quarry and in the authors' data on specimens from the Caldbeck Fells (see Table 7). It is hard to avoid the suspicion that mattheddleite has been shoehorned into a general formula which it does not fit. If a proportion of the silicate was present as $(\text{Si}_2\text{O}_7)^{6-}$, or polymerised in some other way, the change in charge balance would allow the *X*-site to be filled with hydroxyl and carbonate, which was identified in some qualitative analyses.

Further Research

A few suggestions for further research have already been offered in the text. At a broad geological scale, trace-element, isotopic and fluid inclusion data would help to identify the source or sources of the epigenetic lead and baryte mineralisation. If suitable geochronometers could be found, age determinations would help to place it in the chronology of mineralisation in northern England. This would be especially interesting for the basal mineralisation which is associated with calcium sulphate dissolution as the presence of unaltered calcium sulphates in buried sequences to the east suggest it could be relatively recent.

The source of vanadium in the distal supergene assemblage remains to be established and uncertainties also surround minor associated uranium. The unusual cerussite crystals with high surface area to volume ratios suggest crystallisation in non-equilibrium conditions from supersaturated solutions. It seems likely that this cerussite formed during the slow ingress of a carbonating fluid into galena. The balance between the activities of lead and carbonate ions would be of interest.

The material listed as uncharacterised at the end of the mineral descriptions provides opportunities for further investigation. The uncharacterised lead iron phosphate would be new to Britain if it proved to be crimsonite. The same applies to the potential specimen of hemihedrite. Some of the tiny unidentified phases in close association with scotlandite may also contain sulphur in intermediate oxidation states.

From a crystal-chemical perspective, a detailed comparison of the composition of the lead-apatites, particularly vanadinite, with specimens from Leadhills–Wanlockhead would be interesting. Although the supergene mineralisation is superficially similar, there may be differences in the character and range of the chemical substitution. The linear relationship between calcium and phosphate content in vanadinite from Whitwell is intriguing and deserves further investigation. The composition of mattheddleite is similarly puzzling. The *X*-site occupancy in the single analysis that was obtained is slightly less than 0.5 and it could be argued that there might be 'keno' (with a vacancy dominant at the *X*-site) or hydroxyl variants of the species.

LOCATION	BaO	PbO	SiO ₂	SO ₃	Cl	Total	O=Cl	Total
Whitwell Quarry	0.80	79.97	7.99	7.43	1.18	97.54	0.27	97.27
Roughton Gill	0.01	81.81	8.90	6.61	0.74	98.27	0.17	98.10
Red Gill	0.01	82.26	8.67	6.86	1.17	99.09	0.27	98.83

Table 7. Wavelength-dispersive X-ray analyses of mattheddleite from Whitwell Quarry with results quoted as weight percent oxide. In addition to the elements listed in the table, aluminium, arsenic, calcium, cobalt, copper, fluorine, iron, magnesium, manganese, phosphorus, sodium, strontium, titanium and vanadium were sought but were either below detection levels or rare with global mean values of less than 0.02 wt% and no outliers of more than 0.1 wt%. These values are included in the totals but not reported as they have no effect on empirical formulae at two decimal places. Data for mattheddleite from two localities in the Caldbeck Fells are included for comparison.

CONCLUSION

The mineralisation that was exposed at Whitwell Quarry in the late 1980s includes an unaltered basal assemblage and an oxidised epigenetic assemblage. The disseminated basal mineralisation consists of early galena and sphalerite, and later baryte, calcite and iron sulphides, which occupy cavities and fractures left by the dissolution of calcium sulphates. It is a local variant of the disseminated basal assemblage that is widespread across northeastern England. Small mineralogical differences in comparison to nearby sites are almost certainly due to the geochemical disturbance caused by upward-leakage of barium-rich brines. The epigenetic fault-zone mineralisation consists of galena and baryte with minor calcite, iron sulphides and sphalerite. It is interpreted as a small Mississippi Valley Type deposit which post-dates the Pennine suite and does not fit into any obvious regional pattern. The primary minerals are likely to have formed in reactions between episodic pulses of metal-rich brine, channelled through the Park Hall Fault from the Carboniferous basement, and local pore fluids.

The species that distinguish Whitwell Quarry as unusual and important are mostly supergene. Their spatial zonation and paragenesis is consistent with oxidation at varying carbonate ion activity, with $p\text{CO}_2$ increasing with distance from the primary sulphides. Cavities in massive polycrystalline galena beyond the influence of infiltrating carbonate contain anglesite and minor sulphur. Where carbonating solutions have infiltrated along grain boundaries cerussite is the dominant supergene mineral unless the $p(\text{CO}_2)$ was unusually low, in which case minerals of the Leadhills suite occur. The oxidation rinds around galena contain hydrocerussite, overgrown and replaced by cerussite which, in turn, is overgrown and replaced by phosphohedyphane. Vanadinite is abundant on their outer edges in the presence of a red clay gouge. Phosphate and vanadate minerals dominate the distal assemblage. Descloizite, hydroxylapatite, phosphohedyphane and vanadinite are locally common and cerussite and calcite are occasionally present in fractures in the dolostone.

Whitwell Quarry includes the first occurrences of caledonite, cotunnite, descloizite, lanarkite, mattheddleite, phosphohedyphane, plattnerite, scotlandite, susannite, vanadinite and possibly also mimetite in Derbyshire. Anglesite, cerussite, descloizite, lanarkite, leadhillite, phosphohedyphane and vanadinite occur as hand specimens which would grace any museum cabinet. Mattheddleite and scotlandite compare favourably with the best from the British Isles. There are similarities with the classic supergene assemblage from Leadhills–Wanlockhead in southern Scotland, but there is no other locality that is remotely comparable in the British Permian.

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Readers should note that Whitwell Quarry is on private land and there is no right of access to any of the workings described in this article.

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MINERALISATION AT THE STEETLEY QUARRY COMPLEX ON THE DERBYSHIRE-NOTTINGHAMSHIRE BORDER NEAR WHITWELL

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Fine-grained synsedimentary lead and zinc sulphides are widespread in small quantities in the Marl Slate Formation (the base of the late Permian Zechstein Group) in northeast England. Remobilisation has produced more coarsely crystallised assemblages, which extend into the overlying Cadeby Formation. At Armstrong Quarry, baryte, galena, marcasite, pyrite and sphalerite are concentrated in and around calcite nodules and in cavities produced by the dissolution of calcium sulphate evaporites. A comparison with similar mineralisation at Rock Cottage Quarry in North Yorkshire, allied to a modern perspective on the calcium sulphate evaporite cycle, provides a framework for an interpretation of this assemblage. The nodules appear to have formed when calcium sulphates dissolved as the rocks rose back toward the surface. Dissolution increased the calcium ion activity, depositing calcite, which locally replaces the surrounding dolomite. Microbial reduction of evaporite sulphate raised the activity of reduced sulphur around the cavities, immobilising lead and zinc as highly insoluble galena and sphalerite. Once the local supply of lead and zinc had been exhausted, the activity of reduced sulphur increased until marcasite or pyrite began to crystallise. Minor late-stage baryte appears to have formed in a reaction between barium ions, produced by slow diagenetic reactions in the sediment, and residual sulphate.

INTRODUCTION

The Cadeby Formation in the area around the ancient settlement of Steetley on the Derbyshire-Nottinghamshire border between Whitwell and Worksop has produced durable yellow-brown building stone since the twelfth century. Toward the end of the nineteenth century, the purest beds of dolostone began to be used in the manufacture of refractory bricks. The market was considerable and production from Steetley Quarry was supplemented first by Wood Quarry and, as demand increased further, by Armstrong Quarry. This latter working had the most room to expand and dominated operations in the twentieth century.

Production transferred to nearby Whitwell Quarry in the late 1950s when refractory-grade dolostone in the Upper Subdivision of the Cadeby Formation at the Steetley Quarry Complex had been exhausted. Armstrong Quarry was re-opened for short periods in the last quarter of the twentieth century when dolostone from the Lower Subdivision of the Cadeby Formation, which was too contaminated to be worked for refractory purposes, was sold as aggregate. The reserves that were extracted in this phase of the operation were below the water table and pumps had to be installed. The base of the

Cadeby Formation and the underlying Marl Slate Formation were exposed in the quarry sump.

Disseminated lead-zinc mineralisation is well known at the base of the late Permian Zechstein Group in northeast England, but relatively few localities have been studied in detail. This account is based primarily on specimens collected from the area around the sump at Armstrong Quarry by the late Ray Richardson¹. Most of the mineralisation is in calcite nodules, which contain baryte, galena, marcasite, pyrite and sphalerite. The only locality where similar mineralisation has been subject to close scrutiny is Rock Cottage Quarry between Harrogate and Ripon in North Yorkshire (Harwood, 1980; 1981). The two sites make an interesting comparison. The mineralisation also provides useful insights into the genesis of the basal assemblage at nearby Whitwell Quarry (Briscoe *et al.*, 2021).

¹ Raymond Thornton Richardson (1930–2007) was an amateur geologist and mineral collector. Numerous visits to local sites including the Steetley Quarry Complex, are recorded in his field diaries.

LOCATION

The Steetley Quarry Complex lies between the village of Whitwell in north Derbyshire and the market town of Worksop which is the administrative hub of the Bassetlaw District of Nottinghamshire. The small but ancient settlement of Steetley² lies to the west of the site and the hamlet of Darfoulds is a little to the east. The complex includes the restored sites of Steetley and Wood quarries, which occupy the northern quarter in Nottinghamshire, and the large, derelict and partly infilled workings of Armstrong Quarry which extend to the south into Derbyshire (Fig. 1).

Armstrong Quarry is misidentified as ‘Steetley Quarry’ on many Ordnance Survey maps and is wrongly described as “Steetley Quarry” by Eden *et al.* (1957: p. 145). Smith *et al.* (1973: p. 129) record:

“The most extensive quarries in the district are at Steetley, where the Steetley Company formerly worked the Lower Magnesian Limestone ... The original quarry – Steetley Quarry [541 791] – extends northwards and westwards from the old Brickworks buildings; south-east and east of it is Wood Quarry, situated in and to the north-east of Steetley Wood; and to the south-west, extending almost to the main Worksop–Chesterfield road and lying partly in the adjacent Sheffield (100) district, is the vast Armstrong Quarry [547 787]”.

This interpretation is consistent with plans, sketches and field notes compiled by Ray Richardson, and is adopted in this article.

HISTORY

In the twelfth century, a private chapel was built for the occupants of a manor house near to the modern site of Steetley Farm. Its occupants fell victim to the Great Plague, and the house was demolished, but the chapel remains (Fig. 2). It was built using stone from Steetley Quarry.

In the medieval period the quarry was worked sporadically. There is documentary evidence to show that it was in operation in 1636 and again in 1730 when it supplied building blocks used in the construction of Worksop Manor (Whitehead and Barsley, 2002).

The Reverend Adam Sedgwick (1785–1873) visited in the early 1820s. His survey of the Magnesian Limestone (Sedgwick, 1829: p. 84) records:

“The ... quarries of Steetley are of considerable extent, and of great antiquity. The rock laid bare is not more than twenty feet thick. It is divided by a number of irregular horizontal partings into beds from one foot to three feet thick; and it is also

² Several rows of houses, a shop, off-licence and small school situated between Steetley, Wood and Armstrong quarries were originally part of the settlement of Steetley (Whitehead and Barsley, 2002). They were demolished in the 1970s. Herein, Steetley is taken to be centred at Steetley Chapel [SK 5436 7872] (see Fig. 2).



Figure 1. Sketch map showing the sites of Steetley Quarry (SQ), Wood Quarry (WQ) and Armstrong Quarry and the locations of the settlements of Steetley and Darfoulds. The area that was reworked for aggregate in the last quarter of the twentieth century at Armstrong Quarry is now flooded (the largest blue patch). The quarry sump, where the base of the Cadeby Formation and the underlying Marl Slate Formation were exposed, is close to the letter S according to Richardson (1987–1989).



Figure 2. Steetley Chapel, built by Gley le Breton during the Anarchy of Stephen (1135–1154), is Grade 1 listed and one of the most complete examples of Norman architecture in England. It fell into disuse in the late medieval period and an ivy-clad ruin was all that remained by the seventeenth century. The structure was restored and the roof replaced, beginning in the eighteenth century, under the direction of the Rector of Whitwell. The church was re-dedicated as All Saints in 1880. It is still in use and the chancel window, which was replaced in 1990, includes a representation of nearby Steetley Works. The exterior stone, which is from Steetley Quarry about 600 m to the northeast, has survived its 900 years of exposure and dereliction remarkably well.

intersected by a number of irregular transverse seams and fissures. The finest specimens are of a greyish white colour, crystalline, fine-grained, and of a beautiful shining pearly lustre. The top of the quarry is composed of thin soft yellowish beds much stained with the black spots”.

Cadeby Formation dolostone was selected for use in the Houses of Parliament which were finished in 1852 (Lott and Cooper, 2005). Shortly thereafter, Kirkby (1861: pp. 291–292) noted:

“For architectural purposes the limestone of this member is perhaps unequalled in England. It can be obtained in blocks of any moderate size, has a texture and hardness highly suitable for delicate mason-work, is of a beautiful tint, and will withstand almost any amount of weathering. It is therefore scarcely to be wondered at, that many of the finest edifices in England are constructed of it. Its quarries of Huddlestone, Bolsover, Steetly [*sic*], and Roche Abbey are amongst the most famous in the country”.

The purity of some of the beds of dolostone meant that they were an ideal feedstock for refractory production. Demand increased rapidly from the 1880s onward and came to dominate operations at the Steetley Quarry Complex in the first half of the twentieth century. Development in this period can be traced on Ordnance Survey maps. Steetley Quarry is marked as a comparatively small working (about 170 × 190 m) in the northwest corner of Steetley Wood on the first-edition six-inch map, surveyed between 1875 and 1884 (Ordnance Survey, 1885). The next survey, completed in 1897, shows tramways extending to the local railway line, kilns in Steetley Wood, and a small brickworks (for the manufacture of refractory bricks) at nearby Steetley Colliery (Ordnance Survey, 1899). A large-scale resurvey completed in 1914 reveals further expansion, including new buildings; a second working, Wood Quarry, to the east of the kilns in Steetley Wood; and the beginnings of development at Armstrong Quarry (Ordnance Survey, 1922). Armstrong Quarry extends for about 600 m from north to south and more than half that distance from east to west in the next major survey, which was completed in 1947 (Ordnance Survey, 1950). Almost all of Steetley Wood had been quarried away and a large calcining plant and brickworks built in Wood Quarry by this time. Armstrong Quarry was close to its modern boundaries along Steetley Lane and the A619 by the time of the next survey in 1955 (Ordnance Survey, 1956). It closed in 1957 and the full extent of the site is shown on the revised six-inch map completed in 1965 (Ordnance Survey, 1967).

All of the quarries had reached their natural boundaries by the summer of 1957 when refractory-grade dolomite production was transferred to Whitwell Quarry (Briscoe *et al.*, 2021). Handwritten notes, compiled by Ray Richardson, describe the working practices at Armstrong Quarry (Richardson, 1965). A few extracts of geological interest are included here:

“The thin limestone at the top of the face was about 6–8 feet thick and very seldom required blasting. It

was usually removed by a small excavator. Used for burning in earlier years but later discarded as waste ...”.

“[Armstrong Quarry was] worked as a single face until the marl³] (Blue Stone) became increasingly thicker as the workings advanced. The step face was then adopted to keep the unwanted marl separate. These steps were known as lenchings. At close of working the marl was about 8 feet thick. Stone was hand filled into wooden tubs and drawn by horses to the winch which hauled several tubs up the incline to the crushers. Horses were later replaced by small diesel locomotives. ... Eventually mechanical diggers took over and lorries ran direct to the crushers”.

“For a period the quarry was worked till 10 PM at night and was floodlit ... The aerial ropeways were also run at night. During this period the workings advanced very rapidly and led to the blasting out of a new deeper face at the opposite end of the quarry. This was about 20 ft in depth and was worked in the same direction as the earlier workings. ... the whole face was in the Lower Magnesian Limestone”.

“... The quarry was closed in 1957 and a new one opened at Whitwell. Slowly it is being filled in and will probably become farm land again with little to show of the former activity”.

An aerial photograph (Whitehead and Barsley, 2002: p. 222) shows the area in 1957 when quarrying ceased. Kilns and brickworks occupy most of Wood Quarry and the terraced houses built for the families of miners at nearby Steetley Colliery⁴ are conspicuous. Armstrong Quarry was used as a dumping ground for colliery spoil from the 1960s onward. Writing in 1972, Richardson (1970–1980) noted that little remained to be seen at Wood Quarry and “All of the exposures [at Armstrong Quarry] have now been obliterated owing to backfilling and tipping of colliery waste”.

The story might have ended at this point but for increasing demand for aggregate. Armstrong Quarry was re-opened and dolostone in the Lower Subdivision of the Cadeby Formation, which was too contaminated to be used for refractory purposes, was worked by the Steetley Denniff Division. In this final phase of operation, Armstrong Quarry was a satellite operation which produced aggregate when demand was high. The reworking began in the mid 1970s and continued sporadically until the late 1990s. The bottom 20 m of Cadeby Formation dolostone were removed and as the

³ The marl band which Richardson refers to here lies within the Upper Subdivision of the Cadeby Formation. It is definitely not part of the Marl Slate Formation, which lies beneath the underlying Lower Subdivision of the Cadeby Formation.

⁴ Steetley Colliery, which lies along the eastern boundary of the Steetley Quarry complex, was begun in 1873. It linked up with the nearby workings of Whitwell Colliery in 1894 and with Shireoaks Colliery soon thereafter. It was one of the most productive pits in the South Yorkshire Coalfield, employing almost 500 people when the coal mines were nationalised in 1947. It was amalgamated with Shireoaks Colliery in 1983 and the surface works abandoned. Coal was brought up at Shireoaks until it closed in 1990 (Whitehead and Barsley, 2002). Shallow lagoons to the east of Armstrong Quarry remain from recent coal-washing operations.

rock was mostly below the water table, pumps had to be installed. A sump was cut into the Lower Permian Marl (now known as the Marl Slate Formation). This soft argillaceous unit was of little commercial value and was avoided as it had the potential to contaminate production. A sketch plan, produced by Ray Richardson in 1989, shows that the sump had been excavated at about SK 549 787 and that the ‘marly spoil’ had been dumped to the southeast.

A brief epilogue may be of interest to readers who recall field trips to sites run by Steetley PLC before the group was broken up in the early 1990s. The quarry company would probably have remained a footnote in the history of building stones but for the purity of its dolostone and proximity to the great steelmaking centre of Sheffield. Bessemer converters, developed in the 1860s, required linings that were different to those used in earlier furnaces. Refractory bricks manufactured first from ganister and later from calcined dolomite provided the solution.

In 1885, Steetley Quarry, then a comparatively small concern, was purchased by Isaac Sharples, who began trading as the Steetley Lime and Building Stone Company. In 1888, Sharples perfected a continuous shaft kiln which calcined dolomite to produce a mixed oxide product for furnace linings. There was significant demand from the steel industry and the company expanded. By the outbreak of the First World War it was producing 50,000 tons annually at sites across the British Isles. Mergers and expansion in the interwar years led to the formation of the Steetley Lime and Basic Company. Conscious of the added value that research would provide, the company built a laboratory at its Steetley site. One of its first projects was a study of the release of magnesium from dolomitic lime. This resulted in a process which reduced British dependence on imported magnesia just before the Second World War.

The company recognised the need for innovation and in 1959 it built a substantial research facility in Worksop. By the 1970s, it had a global reach with interests in construction materials, facing bricks and clay tiles, minerals, refractory products, chemicals and engineering. It floated on the stock market in 1982 as Steetley PLC and became the world’s sixth largest quarrying company. It had acquired numerous British sites by that time, including mineralogically important localities such as Taffs Well Quarry near Cardiff and Llyncllys Quarry in Shropshire.

In 1992, shareholders approved a takeover by Redland aggregates by a narrow majority. Many former Steetley operations, including the original Steetley Quarry Complex, Whitwell Quarry and the brick-making and refractory facilities were sold off. The brickworks and associated buildings at the Steetley site were acquired by Baker Refractories. Despite full order books production ceased in April 2001 (Whitehead and Barsley, 2002). The buildings were subsequently demolished and the site redeveloped. It is currently occupied by a factory which produces items of pre-cast concrete.

GEOLOGY

The rocks exposed at the Steetley Quarry Complex are part of a sequence of dolostones, evaporites, limestones, marls and siltstones collectively known as the Zechstein Group (Smith, 1989). They were deposited on a faulted and folded Carboniferous basement in shallow water at the western margin of the epicontinental Zechstein Sea (Smith, 2006). The quarry complex is near to the edge of the old one-inch geological sheets 100 and 101, and descriptions of its geology are included in both sheet memoirs (Eden *et al.*, 1957; Smith *et al.*, 1973).

The stratigraphy and regional setting are outlined in a companion article (Briscoe *et al.*, 2021) and there is little value in repeating the details here. A small exposure of the Marl Slate Formation (formerly described as the Lower Permian Marl) in the now flooded sump at Armstrong Quarry [SK 549 787] and rocks at the base of the overlying Cadeby Formation hosted the mineralisation described in this article.

The Marl Slate Formation is a grey argillaceous dolostone with a high concentration of base-metal sulphides and local accumulations of gypsum. At a little less than 20 m it is unusually thick beneath the Steetley Quarry Complex (Smith *et al.*, 1973: p. 121). It is highly variable on a kilometre-scale, occasionally absent, and in some sections difficult to differentiate from the overlying Cadeby Formation (Ineson *et al.*, 1972). Carbonate minerals make up the bulk of the Marl Slate. The principal non-carbonates are fine-grained detrital quartz, clays and authigenic pyrite. Trace-element analyses reveal locally high concentrations of lead, zinc and molybdenum in comparison to mean crustal abundances (Smith *et al.*, 1973: p. 114). Galena and sphalerite are widely distributed in small quantities.

A discussion of the basal Permian in south Yorkshire and north Nottinghamshire in Smith (1974: pp. 123–125) illustrates the practical difficulties of categorising the rock units. At the time, Smith took the view that the Lower Permian Marl was distinct from the Marl Slate. The modern consensus, which was subsequently developed by Denys Smith⁵ and others, includes the Lower Permian Marl within the Marl Slate Formation. The current BGS lexicon of named rock units notes that the upper boundary of the Marl Slate Formation is the base of the overlying Cadeby Formation, without any practical petrological guidance (British Geological Survey, 2021). This may be a geological example of the aphorism ‘I know it when I see it’, but it adds a degree of uncertainty to this discussion.

In a description of Armstrong Quarry before the recent reworking for aggregate, Smith *et al.* (1973: pp. 129–130) record:

⁵ Denys Barker Smith (1929–2007) was internationally recognised for his expertise in the Permian System (McLean and Molyneux, 2007).

“A general section of ... [Armstrong] quarry, employing the divisions used by quarrymen is as follows:

[Lithology]	[Thickness ft]
<i>Top Rag</i>	
Weathered flaggy dolomite	6 to 8
Dolomite, pale brown massive; ripple-marked at top	3 to 7
Blue Stone, which passes laterally into greystone and thence into Crossly (see below).	0 to 10
<i>White Bed</i>	
pale brown dolomite, with clay-coated stylolitic bedding planes; beds up to 3 ft thick (the best quality stone)	8 to 10
<i>Bottom Bed</i>	
massive, pale brown dolomite	7

The Blue Stone, best seen in the south-east of the quarry, consists of pale grey, hard, compact, well bedded, impure dolomite with thin beds of grey clay between stylolitic surfaces. ... [It] is composed of dolomite grains (0.5 mm average diameter) with a few grains of quartz and calcite, the former interlocking with the dolomite. Accessory minerals are feldspar and muscovite. Up to 4 ft thick in the south, the Blue Stone thins and disappears to the north-east. Westwards it passes, apparently together with some of the overlying dolomite, into Greystone, a grey, less impure dolomite, up to 10 ft thick. This in turn passes, in the Steetley Farm [5443 7876] area, into Crossly, a grey or pale brown dolomite with abundant stylolites⁶ and a brecciated appearance. Like the Blue Stone, the Crossly dies out north-eastwards. In the abandoned western face of the quarry, southwards from Steetley Farm, Mr. D. B. Smith has identified the Hampole Beds, apparently within the Crossly described above; they consist of:

[Lithology]	[Thickness in]
Clay, green	0 to 2
Dolomite, grey to buff, porous (small horizontally elongated cavities), cross-laminated, granular	3 to 8
Clay, green	0 to 3
Dolomite, grey to buff, hard saccharoidal, fine sand grade, with many cavities and traces of ?shell casts; hard dense zone at top	2 to 8”

⁶ There is a possible ambiguity here. In the text accompanying sketches of geological structures at the Steetley Quarries, Richardson notes that it is the stylolitic structures (rather than the rock containing them) that are known as ‘Crossly’ where they are abundant.

This extract shows the lithological variability in the Upper Subdivision of the Cadeby Formation⁷, which includes substantial marl bands at Armstrong Quarry. It is consistent with Richardson’s description of working practices at the quarry site [*vide supra*] and underlines the care that was needed to produce refractory-grade dolostone.

There does not appear to be any published geological description of the rocks that were exposed in the Lower Subdivision of the Cadeby Formation during the reworking of Armstrong Quarry for aggregate. Records of a shallow drilling program associated with regeneration at the Steetley Quarry Complex are not currently in the public domain, and none of the logs of lithologies at Armstrong Quarry before the rock was quarried away⁸ are included on the *Geology of Britain Viewer* (British Geological Survey, 2020). Handwritten notes (Richardson, 1970–1980), dated May 1975, record:

“The quarries at Steetley which have been disused since 1957 except for the working of old tips etc., are now being reworked to a greater depth. The limestone is yellowish or buff coloured but a very dark grey bed is present in the lower parts of the workings. Most of the limestone seems to lack the lustre and sparkle of the higher beds which were worked before 1957”.

The ‘very dark grey bed’ is probably one of the thick bands of marly argillaceous dolostone that are present near the bottom of the Cadeby Formation (Smith *et al.*, 1986), rather than the Marl Slate Formation (see Figure 2 in the Editorial).

The sump in the Marl Slate Formation appears to have been dug in the early 1980s, when the aggregate workings reached the base of the dolostone. In an unpublished field diary, Richardson (1982–1985) records:

“In recent years (1983/1984/1985) part of the quarry has been worked again for aggregate and roadstone and at the deepest “SUMP” it has penetrated a grey mudstone in which cavities with nailhead and prismatic water clear Calcite crystals have occurred. There are small cubic crystals of Galena and Pale Blue Barite on some examples”.

In an account dated November 1989, Richardson (1987–1989) records:

“The minerals occur in dark grey limy marl, some friable, other [*sic*] very hard. This underlies the

⁷ The fact that the Hampole Beds are identified near the base of this sequence shows that the refractory working was largely within the Upper Subdivision of the Cadeby Formation, which is now described as the Sprotbrough Member. Subsequent aggregate production was largely from the Lower Subdivision, now known as the Wetherby Member. The older terms are retained in this account for consistency with the quotations.

⁸ Unfortunately this includes the data from a borehole at SK 548 788, mentioned in the discussion following Ineson *et al.* (1972), where baryte, calcite and galena were reported.

Lower Magnesian Limestone [Cadeby Formation] and is several feet thick”.

The depth of this horizon, a little more than 20 m below the original refractory quarry floor is consistent with the Marl Slate Formation.

It is impossible to precisely reconstruct the geology of the flooded and inaccessible areas of Armstrong Quarry where most of the specimens were found. The geology of Upper Subdivision (Sprotbrough Member) of the Cadeby Formation at the site is well described: marl bands up to about 3 m thick occur in relatively pure (refractory-grade) dolostone. Marl bands are also present in the Lower Subdivision (Wetherby Member), but their extent and thickness are uncertain. Field notes suggest that the boundary between the Cadeby Formation and the Marl Slate Formation in the quarry sump was relatively sharp, but detailed records were not made.

It is clear that base-metal mineralisation extended from the Marl Slate Formation into the base of the Cadeby Formation. The lithologies are obvious on most specimens, but it is not always possible to be sure of their precise stratigraphic positions.

MINERALS

Minerals from the Steetley Quarry Complex are listed alphabetically in the following text. Most of the species are common and identifications are visual unless otherwise stated. Many of the images which accompany the mineral descriptions are available as red-cyan anaglyphs which can be examined in three dimensions on the Russell Society website.

BARYTE, BaSO₄

Lustrous tabular baryte crystals are recorded in cavities in fine-grained dolomite from a borehole at SK 548 788 in Armstrong Quarry in the discussion which follows Ineson *et al.* (1972). The text does not state whether they are from the Marl Slate Formation or the Cadeby Formation, but the proximity of the borehole to the quarry sump, where baryte was restricted to the Marl Slate Formation, suggests the former.

“Pale Blue Barite” [*vide supra*] was identified in the sump at Armstrong Quarry in the mid-1980s. Richardson (1987–1989) recorded “tabular Barite - very fine” on a visit in November 1989, but it appears to have been



Figure 3. Tabular baryte crystals up to 12 mm on edge, with a hint of their original pale blue colour, overgrowing hexagonal calcite in a discoidal calcite nodule. Specimen STQ021, 140 × 120 mm, formerly in the Ray Richardson Collection, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. Photo David Green.



Figure 4. Stacked group of colourless to faintly brown subparallel tabular baryte crystals, 4 mm in length, on hexagonal calcite. Specimen STQ026, in the Peter Briscoe Collection, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. Photo John Chapman.

uncommon as on a second visit in the same month his notes record “No further Barite as yet”. An examination of the matrix and the accompanying field notes and catalogue entries leaves no doubt that the baryte specimens are from the Marl Slate Formation. Baryte overgrows calcite in flattened discoidal cavities left by the dissolution of calcium sulphates. It occurs as isolated groups of tabular crystals up to about 12 mm on edge, which always post-date calcite (Fig. 3).

The baryte crystals are invariably described as pale blue when collected but most have faded and some have changed colour to pale yellow-brown, possibly as a result of exposure to daylight⁹ (Fig. 4). All of the crystals have a strong white fluorescence and short persistent luminescence¹⁰ in longwave ultraviolet light (Fig. 5). Minute linear inclusion trails produced by co-crystallising pyrite are commonly present.

Baryte was identified by X-ray powder diffraction (to differentiate it from the similar looking celestine). Energy-dispersive X-ray analyses show that it is close to end-member composition with no major substitutions.

⁹ Light-induced colour changes are well known in specimens from Mowbray Mine in Cumbria (Sweet, 1930).

¹⁰ Modern scientific accounts use the term luminescence for inorganic material and minerals (e.g. Gaft *et al.*, 2005), but the term fluorescence is embedded in the mineralogical literature and widely understood. The difference between persistent luminescence (which applies to inorganic crystals) and phosphorescence (which applies to organic molecules) is outlined by Ince (2018) and the former is preferable in this case.



Figure 5. White fluorescence produced by tabular crystal of baryte excited by longwave ultraviolet light with a peak wavelength at 370 nm. Specimen STQ021, formerly in the Ray Richardson Collection, from Armstrong Quarry in north Derbyshire. The field of view is 35 mm across. Photo David Green.

CALCITE, CaCO_3

Rock forming calcite is widespread in Cadeby Formation dolostone. It is noted in small amounts at the Steetley Quarry Complex by Smith *et al.* (1973). Cavities in ‘oxidised’ yellow-brown Cadeby Formation dolostone lined with flattened rhombohedral crystals are common.

Most of the calcite specimens in the Richardson collection are from the basal assemblage at Armstrong Quarry. Field notes (Richardson, 1987–1989) record:

“Examination of material which was encountered whilst excavating the sump for the reworking of [Armstrong] quarry ... has revealed some very fine Calcite crystals associated with tabular Barite”.

The geological setting and morphology of the nodules leave little doubt that they are replacements of calcium sulphate¹¹ (e.g. Harwood, 1981; Tucker, 1991). The largest specimen in the Richardson collection is a 140 × 120 mm fragment of a flattened discoidal cavity from the Marl Slate Formation (see Fig. 3). On this example, translucent hexagonal calcite overgrows granular replacement calcite and sphalerite, which extend into the surrounding rock. At 30 mm, this ‘dedolomitised rind’ is unusually thick; calcite usually separates as a thinner shell (<10 mm thick) if specimens from the marly lithologies are soaked in water (Fig. 6).

¹¹ Richardson (1987–1989) also records calcite and marcasite in casts left by the late Permian productid *Horridonia horrida* Sowerby 1822. These are smaller (<40 mm) than typical evaporite nodule cavities. An illustration of this fossil is provided by Smith *et al.* (1973, pp. 126–127, Plate XI-9). Unfortunately, only one specimen survives.



Figure 6. A thin shell made up of interlocking translucent tabular calcite crystals up to about 3 mm across on argillaceous dolostone. Specimen STQ09, 60 × 50 mm, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo David Green.



Figure 7. Prismatic calcite crystals up to about 2 mm in length in cavities in dolostone. In the left-hand cavities, calcite forms a dense overgrowth on compact marly dolostone. In the right-hand cavity scattered calcite crystals overgrow minutely drusy dolomite in saccharoidal dolostone. Octahedral to cuboctahedral pyrite overgrows dolomite in the right-hand cavity. Specimen STQ02, 65 × 35 mm, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo David Green.



Figure 8. Tabular calcite crystals, the largest 3 mm across, with lobate growth patterns just visible on the rhombohedral faces and more linear features on the prisms. The tiny dots are pyrite. Specimen STQ012b, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.



Calcite is overwhelmingly abundant in the well sealed nodular replacements in marly lithologies, but not as ubiquitous in the more saccharoidal dolostone. This is illustrated by specimen STQ02 (Fig. 7), where two well sealed cavities in compact marly matrix sit directly beside a cavity in a more saccharoidal dolostone. The former contain thick continuous calcite crystal linings, the latter contains isolated calcite crystals on drusy rhombohedral dolomite. Cavities in porous saccharoidal dolostone generally contain less calcite and (unlike the marly lithologies) they are commonly lined with recrystallised dolomite.

The calcite crystals which project into cavities in the basal lithologies are typically equant short-prismatic to thick tabular and hexagonal, with shallow rhombohedral terminations (Figs 8 and 9). The largest reach about 10 mm. Most are translucent with subtle growth patterns which give their faces a slightly frosted appearance. They are occasionally opaque and white.

Ray Richardson's field notes [*vide supra*] describe "water clear Calcite", but none of his specimens could be described as such when they were catalogued in 2020. A small cavity which was exposed when one of the specimens was trimmed revealed gemmy glass-clear crystals. This suggests that some of the calcite has dulled in storage.

Figure 9. (left) Translucent calcite, the largest prismatic crystal 3 mm in length, with minute pyrite cubes. Specimen STQ012b, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.

DOLOMITE, $\text{CaMg}(\text{CO}_3)_2$

Dolomite is the principal rock forming mineral in the Cadeby Formation and the underlying Marl Slate Formation. Two analyses of refractory-grade dolostone from the Steetley Quarry Complex are quoted in Smith *et al.* (1973: p. 238). They are both close to ideal dolomite end-member composition, with 0.39 and 0.34 wt% FeO and 0.05 and 0.02 wt% MnO, respectively.

Field diaries compiled by Ray Richardson, dating from the early 1960s onwards, consistently note cavities lined with rhombohedral dolomite in the Upper Subdivision of the Cadeby Formation. On a field visit in 1976, Richardson (n.d.) records:

“The rock has the appearance of masses of sugar crystals which glisten when the specimen is turned about in the hand. ... Small cavities are lined with pure crystals of dolomite, the curved faces can clearly be seen”.

The manuscript goes on to note a large cavity containing intergrown saddle-shaped crystals (possibly Fig. 10).



Figure 10. A cavity in yellow-brown dolostone lined with drusy dolomite and traces of goethite. Specimen STQ04, formerly in the Ray Richardson Collection, from the oxidised Upper Subdivision of the Cadeby Formation at Armstrong Quarry in north Derbyshire. The field of view is 30 mm across. Photo David Green.

Minute dolomite rhombs are commonly intergrown with replacement calcite on the outer surfaces of ‘calcite shells’ from the marly basal lithologies at Armstrong Quarry. Thin sections show that replacement calcite grains enclose abundant residual dolomite (see Fig. 22).

Cavities in the more saccharoidal dolostone are commonly lined with drusy translucent to transparent dolomite rhombs up to about 0.5 mm on edge (Fig. 11). Rhombic ghosts with a creamy white fluorescence are commonly visible inside transparent crystals. They suggest crystal growth in two stages. The first produced opaque and relatively fluorescent rhombs, which are enclosed in later translucent to transparent overgrowths. Drusy dolomite is mostly earlier than the sulphide minerals, but galena occurs as inclusions in the outer edges of the translucent to transparent crystals and marcasite occasionally penetrates their surfaces (see Fig. 16).



Figure 11. Translucent rhombohedral dolomite crystals, a little less than 0.3 mm on edge, with minor marcasite. Specimen STQ013, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.

GALENA, PbS

Galena is recorded as minute cuboctahedral crystals and disseminations in fine-grained dolomite at a bore-hole at Armstrong Quarry [SK 548 788] in the discussion which follows Ineson *et al.* (1972). This is close to the area where the quarry sump was subsequently excavated.

Thin sections of specimens in the Richardson collection reveal occasional patches of galena in marly dolostone. This patchy disseminated mineralisation is probably part of the early syngenetic sulphide assemblage that was deposited in euxinic conditions on the Zechstein seabed. Richardson (1987–1989) also records galena as “odd isolated cubes here and there” (Fig. 12). Only one such specimen has survived. The crystal faces are rough and have an ingrained marly coating.



Figure 12. A free grown cuboctahedral galena crystal, 6 mm on edge, with minor octahedral overgrowths. Specimen STQ018, in the Peter Briscoe Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.



Figure 13. Galena cubes, up to 5 mm on edge, with abundant pale yellow sphalerite on colourless rhombohedral dolomite. Specimen STQ01, formerly in the Ray Richardson Collection, from basal Cadeby Formation dolostone above the Marl Slate Formation at Armstrong Quarry in north Derbyshire. The field of view is 18 mm across. Photo John Chapman.

Galena crystals in calcite nodules and cavities left by the dissolution of calcium sulphates are typically cubic. Some are plane faced, others skeletal. The faces are always mirror bright without any indication of subsequent oxidation (Fig. 13).

GOETHITE, $\alpha\text{-Fe}^{3+}\text{O(OH)}$

Thin films and microscopic particles of limonitic goethite give ‘oxidised’ Cadeby Formation dolostone its attractive yellow-brown colour. Dark brown spots, which mark the former position of crystals of pyrite or marcasite, are occasionally present in cavities lined with rhombohedral calcite or dolomite (see Fig. 10). Goethite is a sensitive indicator of supergene alteration and its absence from the grey basal lithologies shows they have not undergone any significant oxidation.

HEMATITE, Fe_2O_3

Hematite is noted incidentally in yellow-brown Cadeby Formation dolostone in early field trip reports compiled by Ray Richardson. The most notable occurrence is as irregular brick-red patches a few millimetres across in compact Cadeby Formation dolostone (Fig. 14). Thin sections reveal dense brick-red hematite stains in fine-grained dolostone (without any evidence of recrystallisation) with a little detrital quartz. The hematite spots are associated with structures (possibly trace fossils) which seem to connect to bedding-parallel surfaces, but in the

absence of more detailed field data their affinity and genesis remain uncertain.

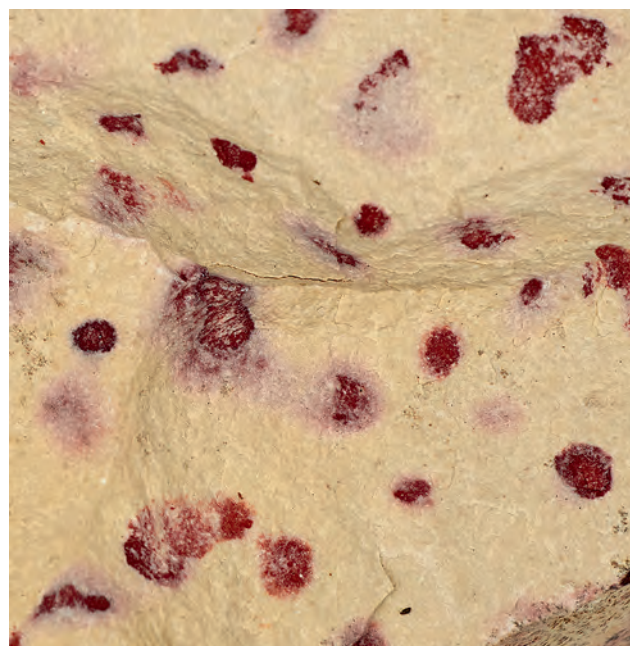


Figure 14. Irregular hematite spots in compact yellow brown dolostone. Specimen STQ020a, formerly in the Ray Richardson Collection, from an unspecified horizon, probably in the Upper Subdivision of the Cadeby Formation dolostone, at Armstrong Quarry in north Derbyshire. The field of view is 40 mm across. Photo John Chapman.

MANGANESE OXIDES

Uncharacterised manganese oxides are widespread in yellow-brown dolostone at the Steetley Quarry Complex. They form as dolomite weathers and manganese is released and deposited as insoluble oxides and oxyhydroxides in cracks and fissures.

MARCASITE, FeS_2

Marcasite is abundant in the Cadeby and underlying Marl Slate formations in northeast England (Harwood, 1981). Its former presence in oxidised assemblages is revealed by sharp goethite pseudomorphs.

Marcasite is less common than pyrite in the Marl Slate Formation at Armstrong Quarry. Crystal groups with reticulate offsets are scattered on colourless dolomite rhombs in cavities in compact grey dolostone on two specimens. Parts of some of the crystal groups are embedded in translucent to transparent late-stage dolomite (Fig. 15).

Blocky pyramidal marcasite crystals, overgrown in places by minute pyrite cubes, and partly enveloped in

later calcite, are present in a fossil productid cast. Some of the marcasite crystals have a thin brown tarnish which extends into the enveloping calcite (Fig. 16).



Figure 16. Blocky bipyramidal marcasite crystals, 0.35 mm across, with a brown surface tarnish, overgrown by tabular hexagonal calcite in a fossil productid cast. Specimen STQ011, formerly in the Ray Richardson Collection, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. Photo John Chapman.



Figure 15. A prismatic marcasite crystal, 0.3 mm long, tapering toward the termination, with a slight iridescent tarnish and numerous smaller twinned offsets, some of which are embedded in translucent rhombohedral dolomite. Specimen STQ013, formerly in the Ray Richardson Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.

PYRITE, FeS₂

Pyrite is common in fractures and cavities and as authigenic disseminations in Cadeby Formation dolostone in the area around Whitwell (Eden *et al.*, 1957; Smith *et al.*, 1973: p. 123). It is widespread in the underlying Marl Slate.

Pyrite is not usually found in close proximity to either sphalerite or galena in the mineralised nodules and cavities at Armstrong Quarry. It commonly overgrows dolomite and marcasite and co-crystallises with calcite and baryte. Tadpole-shaped inclusions in calcite, with long tails stretching along the growth direction, indicate the two minerals co-crystallised and that pyrite continued to form after calcite deposition ceased (Figs 17 and 18). Inclusion trails in baryte reveal co-crystallisation of the sulphate and sulphide, but unlike the calcite ‘tadpoles’, the inclusion trails are not generally capped, indicating that pyrite and baryte ceased to crystallise at about the same time.



Figure 17. A small shoal of tadpole-shaped pyrite inclusions with cubic heads, the largest a little less than 0.1 mm on edge, and long tails extending into the underlying calcite. Specimen STQ022 in the Peter Briscoe Collection, from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.

QUARTZ, SiO₂

Quartz is a minor component of Cadeby Formation dolostone. Smith *et al.* (1973: p. 129) note rare authigenic crystals interlocking with dolomite in a thin section from Armstrong Quarry. Two thin sections of Cadeby Formation dolostone prepared for this study show scattered authigenic crystals and detrital grains up to a few tens of micrometres across.

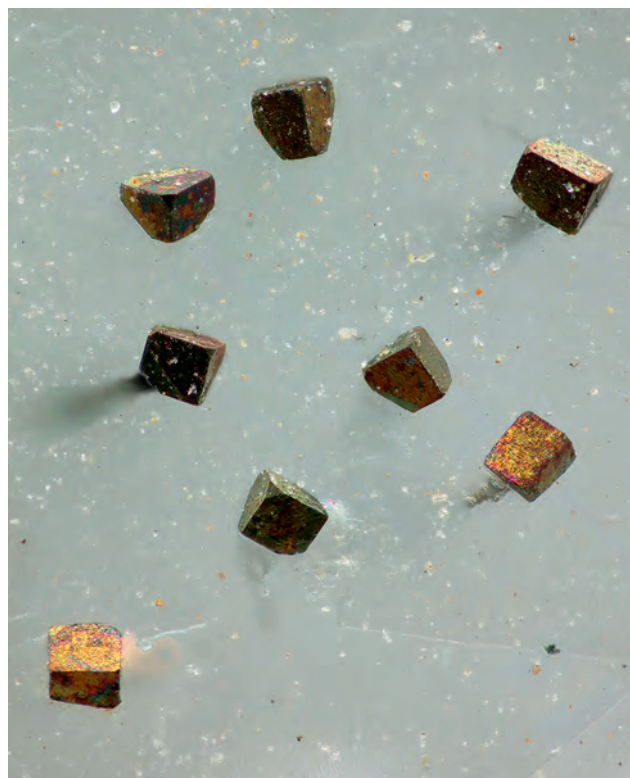


Figure 18. A high resolution image of the heads of the tadpole-shaped pyrite inclusions shown in Figure 17. They are typically about 80 µm on edge and have a cubic crystal form with barely discernible octahedral modifications. Specimen STQ022 in the Peter Briscoe Collection from the basal assemblage at Armstrong Quarry in north Derbyshire. Photo John Chapman.

SPHALERITE, ZnS

Sphalerite is briefly noted in cavities in fine-grained dolomite from a borehole at Armstrong Quarry [SK 548 788] in the discussion which follows Ineson *et al.* (1972). The stratigraphic horizon is not stated.

Sphalerite is locally abundant in the medium- to coarse-grained calcite around former calcium sulphate nodules in the Marl Slate. Colourless to pale yellow subhedral crystals and crystal groups, up to about 1 mm across, densely coat the outer surfaces of some dedolomitised rinds (Fig. 19). They pre-date the euhedral colourless to white calcite crystals which line the interiors of calcite nodules.

In cavities in the basal dolostone, complex lustrous pale yellow millimetre-size sphalerite crystals occasionally form dense overgrowths on drusy rhombohedral dolomite. They are commonly associated with galena and overgrown by later colourless tabular to prismatic calcite (Figs 20 and 21). Although they commonly crystallise in very close proximity, galena and sphalerite are rarely found in direct contact.

Sphalerite from Armstrong Quarry has an orange (in the dedolomitised haloes around calcite nodules) to pink (in cavities in the overlying dolostone) fluorescence in longwave ultraviolet light. Crystals from the dedolomitised rinds commonly have a more strongly



Figure 20. A drift of millimetre-size pale lemon yellow sphalerite crystals on drusy rhombohedral dolomite with three larger galena cubes and a little late-stage calcite. Specimen STQ01, 55 × 35 mm, formerly in the Ray Richardson Collection, from the basal dolostone at Armstrong Quarry in north Derbyshire. Photo David Green.

Figure 19. (*left*) Abundant pale yellow subhedral sphalerite on the outer surface of a thick calcite replacement shell. This area is on the reverse side of the calcite nodule shown in Figure 3. Specimen STQ021a, formerly in the Ray Richardson Collection, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. The field of view is 2.5 mm across. Photo John Chapman.



Figure 21. A small area of the specimen shown in Figure 20, with a pale yellow resinous sphalerite crystal group, a little less than 1 mm in the longest direction, beside a larger translucent blocky hexagonal calcite crystal. The calcite overgrows several pale yellow sphalerite crystal groups, which are just visible in outline. Specimen STQ01, 55 × 35 mm, formerly in the Ray Richardson Collection, from the basal dolostone at Armstrong Quarry in north Derbyshire. Photo John Chapman.

fluorescent ghost about halfway between the centre and edge faces. Patches of strong blue-white fluorescence, which are visible under a microscope within sphalerite crystals and at the interfaces with the underlying dolomite, are likely to be produced by a thin layer of recent hydrozincite.

DISCUSSION

Mineralisation in the yellow-brown dolostone which was quarried for refractory production in the Upper Subdivision of the Cadeby Formation at the Steetley Quarry Complex is relatively simple. It includes cavities lined with drusy calcite and dolomite, undifferentiated manganese oxides, widespread goethite and patchy hematite. This is typical of the Cadeby Formation across a wide area of northeast England and merits no further discussion.

Mineralisation in the basal Permian at Armstrong Quarry is more complex. Deposits at this horizon are more varied than the short descriptions of galena and sphalerite in many geology texts imply. In many cases, fine-grained synsedimentary sulphides have been remobilised into coarser disseminated deposits. Base-metal mineralisation in calcitised nodules is one variation on this theme. The nodules at Armstrong Quarry are similar to replacements reported from the Lower Subdivision of the Cadeby Formation at Rock Cottage Quarry between Harrogate and Ripon in North Yorkshire (Harwood, 1980; 1981). Less well studied occurrences include Vale Road Quarry near Mansfield Woodhouse in Nottinghamshire and Wistow Shaft near Selby in Yorkshire (Harwood, 1981; Starkey, 2018).

This account is based on the Ray Richardson Collection. It is impossible to be sure of the horizon at which every specimen was collected. Some are clearly from the Marl Slate Formation [an interpretation which is corroborated by field notes and catalogue entries which record 'Lower Permian Marl' (Richardson, 1983–2001)], whilst others are from the base of the overlying Cadeby Formation. The two units grade imperceptibly into one another in some places and the practical difficulties of distinguishing them are outlined in the foregoing text. In view of this uncertainty, the mineralisation is described as the 'basal assemblage' (more definite stratigraphic information relating to individual specimens is included in the figure captions where possible).

A summary of the origin of the synsedimentary mineralisation in the basal Permian in northeast England is a useful precursor to the next part of the discussion. It is generally agreed that metal-rich 'submarine springs' infiltrated poorly consolidated sediment and deposited fine-grained sulphides in euxinic (i.e. anoxic and sulphide-rich) conditions which developed on the seabed shortly after the Zechstein Basin flooded (e.g. Hirst and Dunham, 1963; Turner and Whitehouse, 1978; Young *et al.*, 2021). This synsedimentary assemblage is relatively simple in northeast England where the

principal sulphides are sphalerite and galena. Both minerals are widespread in the Marl Slate Formation in Yorkshire, Nottinghamshire and Derbyshire (Eden *et al.*, 1957; Aldred, 1969; Smith *et al.*, 1973; Harwood, 1981; Harwood and Smith, 1986).

Various (occasionally rather exotic) proposals have been advanced to account for mineralisation in the lateral European correlative of the Marl Slate Formation, the Kupferschiefer (e.g. Borg *et al.*, 2012; Keith *et al.*, 2018). The multi-stage deposits are much more complex than the mineralisation in northeast England. The synsedimentary galena and sphalerite in the Marl Slate Formation in northern England belongs to the earliest and least complex stage of base-metal mineralisation in the Zechstein Basin according to Vaughan *et al.* (1989).

The original synsedimentary sulphide mineralisation can be identified with reasonable confidence at some sites (e.g. Harwood, 1981; Sweeney *et al.*, 1987; Vaughan *et al.*, 1989). Galena remains as fine-grained patches which surround grains of rock-forming dolomite on one specimen from Armstrong Quarry¹². Polished sections show that it formed by non-displacive growth in relatively unconsolidated sediment.

The isolated matrixless galena crystals found in the Marl Slate Formation (see Fig. 12) are clearly displacive¹³. Rounded edges and pitted faces differentiate these crystals from the sharp lustrous cubes in calcite nodules (Fig. 13). Similar isolated crystals have been identified in the basal Permian at Vale Road Quarry near Mansfield Woodhouse (Harwood, 1981). They probably represent early remobilisation and coarsening of fine-grained synsedimentary lead sulphide by Ostwald ripening. Unfortunately, only one specimen from Armstrong Quarry has survived and there is insufficient contextual data for a more detailed commentary.

Remobilised base-metal sulphides are concentrated in and around calcitised nodules at some localities in the basal Permian. Harwood (1980, 1981) provides a detailed interpretation of the mineralisation in nodules at Rock Cottage Quarry between Harrogate and Ripon in North Yorkshire. This is the only detailed examination of this style of mineralisation in the current study area and it provides a valuable comparison with Armstrong Quarry. Harwood (1981: pp. 305–306) notes:

"Sphalerite and marcasite with some baryte and galena are present in calcitised displacive anhydrite nodules at Rock Cottage Quarry ... The displacive anhydrite nodules grew in low energy wackestones

¹² Galena was the only obvious fine-grained ore mineral noted in the rocks examined in this study, but patches of dark metallic galena are much more conspicuous in the fabric of the rock than pale translucent sphalerite.

¹³ In displacive growth, developing crystals move the surrounding sediment aside rather than passively enclosing it (e.g. Carstens, 1986). Displacive growth is commonly taken to indicate crystallisation in relatively unconsolidated sediment, although recent research suggests that supersaturation pressure can displace lithified material in some instances (Meng *et al.*, 2019).

and mudstones in lagoon facies of the Lower Member ... Petrological evidence suggests calcitisation and concurrent mineralisation took place shortly after penecontemporaneous dolomitisation and before substantial burial of the sediments (Harwood, 1980). Sphalerite is concentrated in nodules or parts of nodules rich in dolomite muds; these muds are contorted around subhedral sphalerite crystals, implying crystal growth took place whilst the muds were still soft. Sphalerite is honey-coloured with low iron content. ... Calcite-rich parts of the nodules show pseudomorphs after anhydrite (Harwood, 1980; Fig 5) and contain marcasite and some baryte (Harwood, 1980; Fig. 8). Galena is a rare accessory mineral and is also found on isolated joint faces at the same stratigraphic level”.

“The amount of sulphide mineralisation in the nodules is similar to that expected were the metals derived from the surrounding sediments”.

The research goes on to suggest that the sulphide minerals formed as a result of microbial reduction of displacive anhydrite during early diagenesis. The influence of microbial sulphate reduction is not in doubt (Harwood and Coleman, 1983), but subsequent investigations have shown that the calcitisation of anhydrite nodules post-dates lithification (e.g. Lee and Harwood, 1989). It is now generally accepted that Zechstein calcium sulphate was originally deposited as gypsum, altered to anhydrite at depth, and began to alter to gypsum once again as the strata rose back toward the surface during uplift and inversion (e.g. Warren, 2006). This provides a framework for the chronology proposed in this discussion. The hypothesis is otherwise similar to the scheme suggested by Harwood (1981) for the mineralisation at Rock Cottage Quarry.

It is worthwhile reiterating that it is the former presence of anhydrite in the nodules at Rock Cottage Quarry that makes a penecontemporaneous origin unlikely. Modern studies show that gypsum rather than anhydrite would have been stable when the nodules formed (van Dreissche *et al.*, 2019). Anhydrite forms during burial when the temperature rises sufficiently to destabilise gypsum (Warren, 2006). It should also be noted that the evidence for early sulphide mineralisation at Rock Cottage Quarry (the presence of displacive sphalerite crystals in the marl) is also consistent with crystallisation in poorly consolidated dedolomitised sediment around dissolving calcium sulphate nodules.

The similarities between the nodules at Rock Cottage Quarry and Armstrong Quarry are striking. The mineral assemblages, with galena, marcasite, sphalerite and minor late-stage baryte, are almost identical. In both cases, calcitised nodules contain pale coloured subhedral sphalerite in dolomitic mud (see Fig. 19). The mineralised nodules at the two sites appear to belong to a regional assemblage which also includes occurrences at Vale Road Quarry near Mansfield Woodhouse and Wistow Shaft near Selby (Harwood, 1981; Starkey, 2018) and can be extended to encompass the basal mineralisation at Whitwell Quarry (Briscoe *et al.*, 2021).

At Armstrong Quarry, calcitisation appears to have been initiated by the slow dissolution of calcium sulphates. This raised the $\text{Ca}_{(\text{aq})}^{2+}/\text{Mg}_{(\text{aq})}^{2+}$ ratio sufficiently to stabilise calcite rather than dolomite. In relatively well sealed marly lithologies, calcite replaced the dolostone host rock in a limited analogue of the well known process of dedolomitisation (Coniglio, 1978). Thin sections show that calcite grains in the dedolomitised rinds contain abundant residual dolomite (Fig. 22).

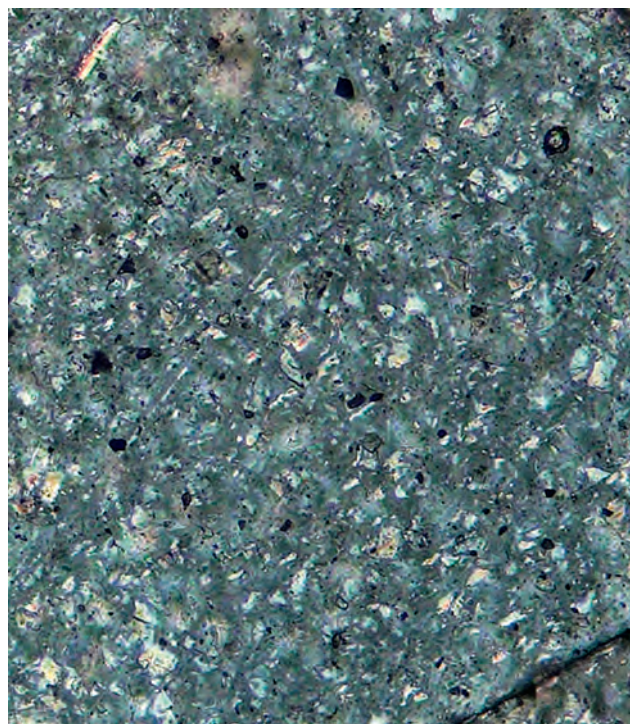


Figure 22. Thin section of a calcite grain from the dedolomitised rind around a calcite nodule. The grey calcite groundmass, which has been rotated close to extinction between crossed polarisers, encloses birefringent dolomite with high-order interference colours. Most on the dolomite inclusions are anhedral, but a few preserve a characteristic rhombohedral outline. Specimen STQ21a.TS1, prepared by David Copestake, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. The field of view is 0.3 mm across. Photo John Chapman.

Calcite is less abundant in the basal dolostone. In this lithology, the mineralisation occupies ovoid cavities and ‘fractures’. In deeply buried Cadeby Formation dolostone, calcium sulphate occurs as thin streaky infills and discoidal nodules. Smith *et al.* (1973: p. 123) record “Anhydrite and gypsum ... in several underground sections, usually occurring as streaks”. The thin planar fractures in the basal dolostone at Armstrong Quarry (and nearby Whitwell Quarry) may have been generated by dissolution of streaky calcium sulphate. Regardless of the way they formed, the relative absence of calcite in the dolostone is probably a reflection of a greater dilution factor during dissolution in a more permeable environment.

Pale yellow sphalerite is abundantly intergrown with replacement calcite in the dedolomitised rinds around former calcium sulphate nodules in the marly lithologies (see Fig. 19). It is also sometimes abundant in cavities

and fractures in the basal dolostone (see Fig. 20). Galena is less common and earlier than sphalerite in both of these situations. The sphalerite crystals in the outer edges of the rinds are displacive, but generally subhedral rather than euhedral (see Fig. 19). Thin sections reveal some idiomorphic outlines which indicate the crystals formed in relatively unconsolidated sediment and were subsequently enclosed by calcite (Fig. 23). Subhedral to anhedral outlines suggest that calcite and sphalerite co-crystallised in other areas.

There is good evidence that the base-metal sulphides in the calcite nodules formed in a reaction with microbially reduced sulphur (Harwood and Coleman, 1983). Base metals are surprisingly mobile in basinal environments and commonly form sulphide scales in oil and gas fields (Dyer *et al.*, 2006). Lead and zinc are recorded at up to 1000 ppm in the Marl Slate Formation in the area around Worksop (Smith *et al.*, 1973: p. 114). These are much higher than typical crustal abundances of 14 ppm for lead and 75 ppm for zinc, but the local reservoirs would have been exhausted more rapidly than the sulphur species generated by the slow microbial reduction of calcium sulphates, which were present in ‘rock forming’ rather than ‘trace-element’ concentrations.



Figure 23. Thin section showing sphalerite (black between crossed polarisers; the three largest crystals labelled Sp) in granular calcite in the dedolomitised rind surrounding a calcite nodule. Plane-faced idiomorphic sphalerite crystals lie within in a xenomorphic calcite matrix (grey to white) with residual dolomite (bright specks). Specimen STQ21a.TS1, prepared by David Copestake, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. The field of view is 3 mm across. Photo John Chapman.

Iron sulphides occur in small quantities on many specimens. They are almost always spatially separated from galena and sphalerite. Marcasite is generally early (Fig. 24). It is typically associated with rhombohedral dolomite, and overgrown by calcite, in cavities without any base-metal sulphides. It appears to have acted as a sink for reduced sulphur in the absence of lead or zinc.

Pyrite post-dates marcasite on all of the studied specimens. Marcasite requires $\text{pH} < 5$ to form (Kitchaev and Ceder, 2016) suggesting that the mineralising fluids evolved from slightly acidic toward neutral over time. Pyrite occasionally overgrows marcasite and commonly co-crystallises with late-stage calcite. Tadpole-shaped inclusions in the outer edges of calcite crystals show that it continued to form after carbonate deposition ceased (see Figs 17 and 18).

Baryte was the last major mineral to form. It overgrows calcite and occasionally contains pyrite inclusion trails. The source of the barium at Armstrong Quarry is clearly local rather than regional, it was probably generated by slow diagenetic reactions in the surrounding rock, which contains “accessory clay minerals, feldspars, micas [and] rock particles” according to Smith *et al.* (1973: p. 123).

Baryte from Armstrong Quarry has a strong white fluorescence (Fig. 25), unlike vein baryte from the nearby Sunnyside Deposit, which is not fluorescent in longwave ultraviolet (Bateman *et al.*, 2021). Luminescence in baryte is well known, but the activators which are responsible for the phenomenon remain obscure (Gaft *et al.*, 2005: p. 76). The differing fluorescence responses, which appear to be ‘locality specific’, may repay further study.

An examination of the specimens suggests the following chronology of mineralisation for the well sealed nodules in the Marl Slate Formation at Armstrong Quarry:

1. Dissolution of calcium sulphates raised the calcium and sulphate ion activities and produced void spaces. As the calcium ion activity increased calcite began to crystallise and replace the surrounding dolomite.
2. Slow microbial reduction of solution sulphate generated reduced sulphur, which immobilised the lead and zinc that was present in local pore fluids as highly insoluble galena and sphalerite. As crystallisation removed these elements from solution, concentration gradients developed which depleted the surrounding reservoir.
3. When the lead and zinc had been depleted, the activity of reduced sulphur increased until the solubility of iron sulphide was exceeded and pyrite began to co-crystallise with late-stage calcite.
4. Once the calcium sulphates had dissolved, calcite ceased to form. Isolated tabular baryte crystals developed as barium generated by the slow diagenetic reactions in the surrounding marl diffused into residual sulphate-rich fluids in the calcite-lined cavities.



Figure 24. Planar marcasite crystal groups, up to 0.5 mm in length, consisting of a large tapering prismatic crystal with numerous smaller offsets, some of which are embedded in translucent rhombohedral dolomite. Specimen STQ013, formerly in the Ray Richardson Collection, from the basal dolostone at Armstrong Quarry in north Derbyshire. Photo John Chapman.



Figure 25. White fluorescence in tabular baryte excited by longwave ultraviolet light with a peak wavelength at 370 nm (cf. Bateman et al., 2021: Figures 3 and 4). Specimen STQ026, in the Peter Briscoe Collection, from the Marl Slate Formation at Armstrong Quarry in north Derbyshire. Photo John Chapman.

This chronology can also be applied to cavities and fractures in the basal dolostone, where the lower abundance of calcite probably reflects greater local permeability, and some early carbonate was deposited as dolomite. It can be extended to account for the mineralisation in cavities or nodules from areas where the surrounding pore fluids contained no lead and zinc, where marcasite replaces galena or sphalerite as the early sink for reduced sulphur.

There are minor differences in the character of the mineralisation in dolostone and marl. Mineralisation in the dolostone is typically in ovoid cavities or fractures rather than nodules¹⁴. Calcite is less abundant, recrystallised dolomite is often present, and sphalerite is euhedral rather than subhedral and fluoresces rose-pink rather than orange-brown. These differences are outweighed by paragenetic and mineralogical similarities which strongly suggest a common origin.

Microbial reduction plays an important role in global geochemical cycles and it is the only way to reduce metastable solution sulphate in low-temperature sedimentary environments (Harwood and Coleman, 1983; Rickard, 2012). Isotopic fractionation as a result of sustained microbial reduction would be expected to enrich the remaining fluids in ^{34}S (e.g. Strebel *et al.*, 1990). This is the only credible mechanism by which baryte from the nodules at Rock Cottage Quarry could return a $\delta^{34}\text{S}$ value of +17.88‰¹⁵ (Harwood, 1981: p. 354). Permian evaporite sulphate normally lies within the range +8.5 to +11.5‰ (Milodowski *et al.*, 1998).

It should be noted that the isotopic signature of the baryte at Rock Cottage Quarry is not consistent with penecontemporaneous mineralisation in poorly consolidated sediment. It requires sustained microbial reduction in a relatively well sealed environment. In this context, measurements of $\delta^{34}\text{S}$ for baryte at Armstrong Quarry would be of interest. Positive values comparable to those from Rock Cottage Quarry would be expected if the mechanism outlined here is correct.

As outlined in previous paragraphs, the presence of anhydrite in the nodules at Rock Cottage Quarry suggests that calcitisation of the evaporite nodules and the associated remobilisation of base metals occurred during basin inversion (Lee and Harwood, 1989). This may have occurred as early as the late Mesozoic, which Smith (1972) suggested as the earliest date for dissolution of gypsum and foundering of the Roker Formation further to the north, or relatively recently

following re-activation of the Pennine Anticline in the Miocene, which Harwood (1981) suggested was consistent with observations of fluids in the mineralised nodules in the basal Permian at Wistow Shaft near Selby.

A direct determination of the age of the calcite would be valuable. The nodule calcite formed in a lead-rich environment and uranium–lead dating is unlikely to be reliable. The uranium–thorium system, which is currently accurate up to about 650 ka (Wendt *et al.*, 2021), would be able to test whether the process was recent. The authors would be happy to provide specimens if this or other geochronometers were considered viable.

CONCLUSION

At Armstrong Quarry, fine-grained synsedimentary lead and zinc sulphides, which are widespread in the Marl Slate Formation in northeast England, have been remobilised into a more coarsely crystallised assemblage, which extends into the overlying Cadeby Formation. Baryte, galena, marcasite, pyrite and sphalerite occur in and around calcitised nodules and in cavities produced by the dissolution of calcium sulphates.

A comparison with a similar assemblage at Rock Cottage Quarry in North Yorkshire, combined with a modern perspective on the calcium sulphate evaporite cycle, provides a framework for an interpretation of this mineralisation. The nodules appear to have formed as calcium sulphates dissolved when the rocks rose back toward the surface. Dissolution increased the calcium ion activity, depositing calcite, which replaced dolomite in a local analogue of the well known process of dedolomitisation. Slow microbial reduction of evaporite sulphate raised the activity of reduced sulphur, immobilising lead and zinc as highly insoluble galena and sphalerite. In the absence of these elements, reduced sulphur combined with iron to form marcasite (in acidic conditions) or pyrite as the solutions evolved toward a neutral pH. Isolated groups of tabular baryte post-date calcite in a few nodules from the Marl Slate Formation. They probably reflect a reaction between barium released by the slow diagenetic reactions in the marl and residual evaporite sulphate.

The minerals that formed in the calcite nodules reflect geochemical pathways in a relatively well sealed system, locally rich in lead and zinc, with no input of barium or other elements from underlying aquifers.

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Thanks go to the quarry operators, without their forbearance, the specimens described in this article would not have been collected. Thanks also go to the family of the late Ray Richardson, who took the time and trouble to rescue an important collection in difficult circumstances. Stephen Moreton is thanked for his analyses which confirmed that the blue bladed material

¹⁴ In this context, nodules and cavities exist in a continuum which ranges from almost completely solid calcite replacements with a small central cavity in the marly lithologies to crystal-lined vugs left by the dissolution of calcium sulphates in the saccharoidal lithologies.

¹⁵ Values of $\delta^{34}\text{S}$ are quoted as values in parts per thousand difference (symbol ‰) from an international standard, which at the time of the measurement was troilite (FeS) from the Canyon Diablo meteorite (Krouse and Coplen, 1997).

was baryte rather than celestine. The referees, David Alderton and Frank Ince, are thanked for comments which considerably improved the manuscript.

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MINERALS OF THE FRONGOCH MINE

by Steven A. Rust

First edition, published in 2019 by the author at

130 Elliots Drive Yeovil, Somerset, BA21 3NR

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Available from the author [steverust27@gmail.com] at the address noted above;

price £40 plus £5 postage and packing in UK.

There can be few collectors of British minerals who are not aware of the remarkable suite of rare supergene minerals from Frongoch Mine near Aberystwyth in Ceredigion. The mine was one of the richest in central Wales producing more than 60,000 tons of lead ore and 50,000 tons of zinc ore. It passed through the hands of numerous different companies in 146 years of virtually uninterrupted production.

Frongoch began to become popular with mineral collectors in the 1970s. Numerous interesting discoveries were made at the rather derelict site as the dumps were moved around and fresh material was exposed. The mine was known in the mid-nineteenth century for well crystallised brown pyromorphite, but Frongoch's mineralogical importance rests on the suite of unusual lead, copper and zinc minerals formed by post-mining oxidation. These include the basic lead copper thiosulphate steverustite, for which Frongoch is the type locality.

Minerals of the Frongoch Mine is divided into four chapters. A brief introduction sets the site in context and includes three maps which show its location about ten miles ESE of Aberystwyth. The following pages provide a brief history, beginning with the earliest record, a twenty-one year lease provided by Lord Lisburne at the end of the 1750s, and taking the reader through successive owners until the underground operations closed following a nine-month strike under the Belgian-financed Société Anonyme des Mines de Frongoch in 1903. Some reprocessing of dump material was attempted between the wars and the spoil heaps were used as a convenient local supply of aggregate until the 1980s. The historical description is supported by numerous figures including a three-dimensional representation of the workings, contemporary and recent surface photos, and a striking underground image of the pump-rods in the Engine Shaft by Roy Fellows.

The geological setting and mineral paragenesis are summarised in chapter three with some input from John Mason, whose expertise in Welsh mineralisation is well known to readers of this journal.

The longest section of the book (pages 22 to 179), provides an illustrated description of the minerals from Frongoch Mine. It is the result of more than thirty years of dedicated fieldwork. A total of 52 species plus three uncharacterised phases are described. Most of the valid species and the three uncharacterised phases are figured,

many more than once. The listing is alphabetic, and typically includes a short description, the identification technique and images of (mostly) micro-specimens. If a large number of illustrations accompany a particular species (there are, for example, 18 for anglesite) they are preceded by a tabular summary. The photos are all in colour and typically have a single-line caption which includes the field of view.

Minerals of the Frongoch Mine is a short-run publication (200 copies). Is it for your library? I am pleased to have a copy and have no hesitation in recommending it. Steve Rust is a remarkable collector and the book provides an illustrated record of the definitive collection of post-mining supergene minerals from the site. This is particularly important as recent developments have effectively sterilised the productive areas. Despite their cultural and scientific importance, attempts to preserve the mining remains and material of mineralogical value have not been successful. With the current lack of resources in the museum sector there is no guarantee that specimens (or collections) will survive indefinitely. Therefore published records are particularly valuable.

There are some spelling and grammatical errors. Mineral names are capitalised when they should be in lower case. There are a few scientific slips. Steverustite is described as a "lead copper sulphite" on page 118 and in other places when it is, in fact, a basic lead copper thiosulphate. These problems might have been reduced by an effective proof-reader.

Stacking photography has considerable potential to document micro-mineral assemblages. The images push the technique to, and sometimes a little beyond, its limit in a desire to record the nuances of tiny crystals. But where else would you find 16 images of bechererite from the same locality? The colour reproduction is of sufficiently quality to provide an impression of what the specimens look like, though some of the dark blues, particularly linarite, appear a little too saturated.

Minerals of the Frongoch Mine is a worthwhile acquisition for any collector who is interested in Welsh minerals, or the suite of rare basic copper, lead and zinc sulphates that form by post-mining oxidation at sites across the British Isles (and might encourage others to attempt similar projects).

David Green

THE PEAK DISTRICT: LANDSCAPE AND GEOLOGY

By Tony Waltham

First edition, published in 2021

160 pages, colour throughout, 236 × 165 mm, softcover, ISBN 978-1-78500-874-0

Available from The Crowood Press, Ramsbury, Marlborough, Wiltshire, SN8 2HR [www.crowood.com]; price £16.99 plus postage and packing in the UK.

Tony Waltham will be familiar to readers of the JRS as one of the contributors to the third edition of *Derbyshire Blue John* (reviewed in 2019). For readers who wish to place the Peak District's minerals in a geological context, *The Peak District: Landscape and Geology* is an excellent place to start. The book is one of a series produced by Crowood Press which describe the landscape and geology of selected regions of the British Isles. Tony is author of a companion volume: *The Yorkshire Dales: Landscape and Geology*, published in 2007.

The Peak District was Britain's first national park. The introductory chapter (of fourteen) sets the scene chronologically, geologically and topographically. It includes colourful and clear maps and diagrams, which are a feature of the volumes in this series. The remaining text concentrates on three broad themes: geology (Chapters 2–4), geomorphology (Chapters 5–9) and human impact (Chapters 10–14). Minerals and mining are addressed in Chapter 10, which at 19 pages is the longest in the book.

Most readers will be aware that the Peak District is 'a National Park of two halves'. Thick Carboniferous limestones, which define the White Peak, are surrounded by sandstone and shale of the Dark Peak. In Chapter 2, the limestones of the White Peak are described and placed in a modern stratigraphic context. Dinantian palaeogeography is summarised in a simple diagram, which shows the shallow seas of the Derbyshire Platform surrounded by the deeper water in the Edale Basin and Widmerpool Gulf. Reef and bedded lagoonal limestone, which give rise to different landforms, are differentiated, with photos of typical examples of each. There is a short description of characteristic fossils with a lovely photo of *Gigantoproductus in situ* in Carlsward Cavern. The text rounds off with a description of Derbyshire's volcanic rocks, which will be familiar to those readers who have visited Calton Hill.

The gritstone rocks of the Dark Peak are described in Chapter 3. The stratigraphy is outlined and a simple diagram illustrates typical sedimentary environments. The text goes on to describe the Coal Measures which will be familiar to readers of JRS through the account in volume 21. An excellent diagram in Chapter 4 provides a simple guide to the geological development of the Peak District. The text goes on to explain the faults, which began to develop in a Carboniferous basin and block topography, and subsequently provided channels for

mineralising fluids. An unusual horizontal slickenside at Ladywash Mine is illustrated and the effects of Variscan compression are discussed.

The development of the landscape is described in five chapters. The first few pages set the scene, with a scattering of data: valley incision in the Pennines is mostly at a rate of 10 to 20 centimetres per thousand years; there has been 75 m of uplift in the past 400,000 years; and uplift began in earnest about 10 million years ago when earth movements re-activated the Pennine Anticline. Most of the Peak District's landforms have developed in the last million years or so. They are fluvial rather than glacial. For the most part, water gently develops features such as the exhumed Carboniferous reef knolls of High Tor and Chrome Hill but in its more erosive incarnations it is responsible for 'anomalous gorges' including the spectacular Derwent Gorge between Matlock and Cromford. It also plays a critical role in landslides, which have become a tourist attraction at Mam Tor. The story of the landscape in recent glacial and interglacial periods is told in Chapter 6, which ends with two spectacular photos of 'valley bulges'. The karstic landscape of the White Peak is the focus of Chapter 7, which describes caves, dolines, dry valleys, gorges and risings associated with 'periglacial fluviokarst'.

Limestone caves have a chapter to themselves. The author is clearly at home underground and there are images of phreatic tubes and dripstone formations. Tall chambers which develop in vein cavities are shown and there is an excellent photo of Titan Shaft, which at 146 m is the deepest in the UK. The landscape chapters end with a discussion of the moorland and blanket bog of the Dark Peak, typified by Kinder Scout and Bleaklow, and the contrasting short cropped grassland of the White Peak.

A discussion of anthropogenic influences begins in Chapter 10, which describes mines and mineralisation in the Peak District. There is a nice image of a symmetrically banded fissure vein at Ladywash Mine and descriptions of the main types of orebody and the process of mineralisation. A summary of mining history extends to the modern-day; many readers will be familiar with the workings of Mill Dam Mine, which has been a venue for Russell Society field visits. No description of mineralisation in Derbyshire would be complete without a mention of Blue John, which receives more than a page of text and several figures including a nicely posed shot of underground extraction with a diamond chainsaw. Chapter 10 ends with a description of copper mining at Ecton in Staffordshire.

Chapter 11 looks at various forms of ‘stone for industry’. Derbyshire is well known for large limestone quarries, including the huge underground workings of Middleton Limestone Mine. There is also a remarkable variety of ornamental ‘marbles’, notably Ashford Black, Duke’s Red and attractive crinoidal limestones from several localities. As in Yorkshire, chert blocks were mined and quarried for use in the pottery industry. The Ashover Grit was used in building blocks, some of which contain attractive Liesegang rings. Local stones were pressed into service in built structures, particularly between the sixteenth and nineteenth centuries. They are described and illustrated in Chapter 12.

Dams and reservoirs are described in the penultimate chapter, and the book rounds off with a geological take on the recreational value of the landscape, which will inspire anyone with an interest in the outdoors. From a mineralogical perspective, *The Peak District: Landscape and Geology* is an ideal companion to the Derbyshire chapter of Roy Starkey’s guide to the *Minerals of the English Midlands*. The book is aimed at visitors who wish to understand the landscape and geology. It is written at about the same level as geological sections of the *Journal of the Russell Society* and is therefore readily comprehensible to the general reader and is highly recommended.

Richard Bateman