Mineralization of England and Wales

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GCR Editors: L.P. Thomas and E.L. Durham

Chapter 5

Wales

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INTRODUCTION

Geological setting

Wales has a number of important metallogenic provinces, some of which are of only local extent and due to locally operating processes, while others represent facets of much broader metallogenic processes that affected large parts of the British Isles. A number of the major metallogenic provinces specific to Wales are linked genetically to processes associated with the evolution of the Iapetus Ocean during Lower Palaeozoic times (Kokelaar *et al.*, 1984). South-easterly subduction of oceanic lithosphere under the north-west continental margin of Gondwanaland generated episodic volcanism across Wales during Ordovician and early Silurian times, accompanied by periods of crustal extension, leading to basin development, and intermittent uplift, resulting in localized depressuring of volcano-sedimentary sequences, accompanied by diagenesis and low-grade metamorphism (Bevins and Rowbotham, 1983; Bevins and Robinson, 1993). In late Silurian to early Devonian times, closure of Iapetus and inversion of the existing basin resulted in the Acadian phase of the Caledonian Orogeny (Soper *et al.*, 1987).

Following the Caledonian Orogeny, compressive tectonics gradually gave way to an extensional regime which prevailed across the entire area, but was most strongly developed in south and north-east Wales where widespread subsidence was responsible for the re-establishment of marine conditions in early Carboniferous times, leading to the development of thick carbonate sequences, and in later Carboniferous times the development of coal swamps. By the end of Carboniferous times, a new phase of compression, related to the Variscan Orogeny, caused deformation and uplift across the southernmost part of Wales, and superimposed new structures on the previously deformed Lower Palaeozoic rocks of the area.

A further cycle of compression and extension resulted in new basin developments during Permo–Triassic and Jurassic times. The uplifted Caledonides and Variscides of Wales were, during this phase of tectonic activity, bounded by offshore basins in the Bristol Channel, in the Cardigan Bay–St Georges Channel–Liverpool Bay areas, and in Cheshire, once again imposing a series of extensional tectonic regimes across the Welsh uplands.

By Tertiary times much of Wales was subject to sub-tropical, terrestrial conditions, with the climate gradually cooling towards the end of that period and heralding the onset of a series of glaciations in Pleistocene times. Extensive erosion, due to glacial ice, and dumping of glacially transported material finally shaped the landscape of Wales into the now familiar picture. The final event of relevance to the mineralogy of Wales, and mineralogy is perhaps unique with respect to this, was the initiation, from the Early Bronze Age onwards, of prospecting for, and mining of, a variety of metals occurring in a diverse range of deposits, and the formation of spoil heaps associated with these activities. Surficial weathering of this spoil has led to the development of secondary mineral assemblages of anthropogenic influence.

A comprehensive, contemporary overview of the geological evolution of the region, both onshore and offshore, is provided by Howells (2007).

The sequence of mineralization through time – the basis for the GCR network

The sites selected to reflect the history of metallogenesis and mineralization in Wales are located on Figure 5.1. They cover all major aspects of Welsh mineralization, from deposits formed by seafloor exhalation in early Cambrian times through to rare supergene minerals developed in mine waste since the cessation of metal mining. Some sites constitute the type localities for a number of minerals described first from Wales, while the importance of some others is their role in age-constraining mineralizing events. Many of the finer mineral specimens collected in Wales are illustrated on the Amgeuddfa Cymru–National Museum Wales 'Mineralogy of Wales' website, at http://www.museumwales.ac.uk/en/977/.

Lower Palaeozoic iron and manganese exhalative mineralization in North Wales

The Lower Cambrian Harlech Grits Group is enriched in manganese throughout its thickness (Woodland, 1956). In the Hafotty Formation an ore-bed, averaging 0.4 m in thickness, has been worked extensively along its strike, while in the Gamlan Formation, a sequence of turbidites close to the top of the Harlech Grits Group, thin lenses of coticule, a quartz-spessartine rock,

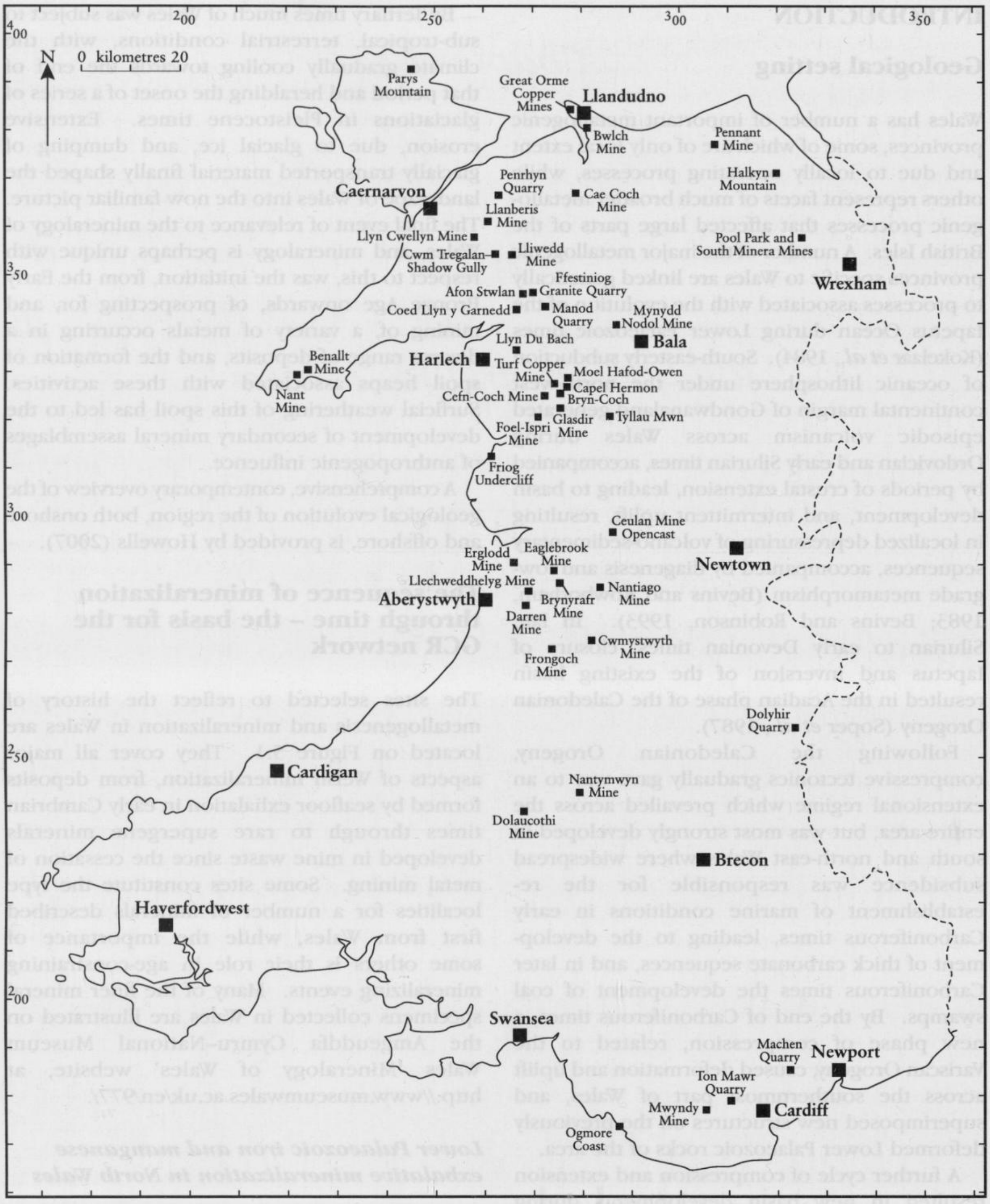


Figure 5.1 Map of Wales showing the location of the GCR sites described in this chapter.

represent metamorphosed manganiferous precipitates. At the **Llyn Du Bach Complex** GCR site in the northern Rhinogs, the ore-bed may be examined in its fresh, unweathered condition and consists of a hard, splintery, laminated, pinkish-red and cream rock consisting largely of manganiferous carbonates, spessartine and quartz, with a number of rarer accessory phases. The manganiferous sediments are interpreted as the distal facies of submarine exhalative systems (Bennett, 1987), the relatively high mobility of manganese permitting greater lateral travel away from source prior to precipitation. Following precipitation, the ores were modified by diagenetic through to metamorphic processes.

Extensive developments of ooidal ironstones and manganese ores once again formed in Arenig through to Caradoc times across North Wales (Trythall, 1989; Young, 1992, 1993), and have been worked at numerous sites. Relatively discontinuous, but extremely rich, manganese mineralization was exploited at the **Benallt and Nant Mines** GCR site near Rhiw in south-west Llŷn. These mines worked banded ores not dissimilar in some respects to those of the Harlech Dome, but which are mineralogically more complex: the Benallt Mine is the type locality for a number of rare Mn-bearing and Ba-bearing minerals (see Bevins, 1994). Mineralization is of sedimentary-exhalative-type, but a considerable amount of metamorphic remobilization appears to have occurred.

Ooidal ironstones, dominated by chamosite, have been worked widely across Gwynedd. The ironstones occur typically as discontinuous lenses within shallow-water siliciclastic sequences and the mineralization is of sedimentary-exhalative-type (Trythall, 1989). The ironstones comprise relatively fine-grained ooids through to pisoids. Alteration, due to both contact and regional metamorphism, is common, and has produced siderite, magnetite, pyrite, stilpnomelane and hematite in varying amounts. At the **Tyllau Mwn** GCR site, both original ooids and magnetite octahedra developed during contact metamorphism may be discerned in both hand specimen and thin-section (Matthews and Scoon, 1964).

Porphyry copper, intrusion breccia and epithermal sinter mineralization associated with Tremadoc volcanism – the Coed y Brenin porphyry copper system

Calk-alkaline volcanism, linked to subduction of Iapetus oceanic crust, occurred in Tremadoc times at Treffgarne, in Pembrokeshire (Bevins *et al.*, 1984), and at Rhobell Fawr, in southern Snowdonia (Kokelaar, 1979). In both cases there is associated mineralization. Igneous rocks in the Rhobell area chiefly comprise basic lavas and related breccias, accompanied by numerous high-level basic to intermediate intrusions, the latter being associated with widespread, mainly weak, porphyry-type mineralization. In one area, however, in rocks belonging to the Afon Wen Intrusive Complex, significant porphyry-style copper-molybdenum-gold mineralization was discovered and economically evaluated in the early 1970s (Allen *et al.*, 1976; Rice and Sharp, 1976). Mineralization consists of thin veinlets and disseminations of chalcopyrite, pyrite and tennantite in altered diorite and microtonalite. Fresh primary mineralization is rarely exposed; the Bryn-Coch exposure at the **Bryn-Coch and Capel Hermon** GCR site provides the best opportunity for its study. At the nearby Capel Hermon area, the mineralization is of a higher grade, but is partially altered to supergene phases. The sites combine to provide one of the best examples of porphyry copper mineralization in the British Isles, and in addition one of the oldest such deposits recognized anywhere worldwide.

At higher levels in this metallogenic environment, intrusive explosion breccias developed where large volumes of meteoric water came into contact with rising magmas. Some of these intrusion breccias, which form irregular pipes, are mineralized with sulphides. At the **Glasdir Mine** GCR site, copper was worked from such a body, which comprised a mass of brecciated Upper Cambrian sedimentary rocks, carrying, along thin interclast fractures, sulphide veinlets almost exclusively dominated by pyrite and chalcopyrite (Allen and Easterbrook, 1978). At still higher levels, sinter-like textures are developed in the breccia pipes, with accompanying silicification of the wall-rocks. These are well demonstrated at the **Moel Hafod-Owen** GCR site, where a breccia pipe is mineralized with banded, auriferous pyrite and quartz, which are interpreted as having been deposited during fumarolic activity at a late stage of the volcanic cycle (Miller, 1993).

An exceptional site occurs at the **Turf Copper Mine** GCR site, where copper, mobilized in Holocene times from the Coed y Brenin porphyry copper deposit, has been precipitated as the native metal replacing organic material in a peat bog. Historically, the peat was dug and burned to release the copper, for subsequent smelting. This site is unique in Great Britain.

Auriferous ribbon-vein mineralization spatially associated with Tremadoc intrusive rocks: the Dolgellau Gold-belt

Originally believed to be post-Caledonian in age (see Shepherd and Bottrell, 1993), the quartz-carbonate-sulphide-gold-bearing veins of the Dolgellau Gold-belt have recently been shown to be pre-tectonic in origin, as demonstrated by cliff-base and wave-cut-platform exposures of folded and boudinaged veins of this suite at the **Friog Undercliff** GCR site (Mason *et al.*, 1999). These distinctive veins are spatially restricted to Cambrian sedimentary rocks and highly altered intrusive rocks ('greenstones') of Tremadoc age. Typically they display book-and-ribbon textures in which intra-vein clasts have been sheared into thin streaks of white mica and chlorite, best seen at the **Cefn-Coch Mine** GCR site. A diverse sulphide assemblage is present, most aspects of which may be studied at the **Foel-Ispri Mine** GCR site. The mineralization is dominated by pyrrhotite, chalcopyrite, sphalerite, arsenopyrite, pyrite and galena; tetrahedrite, cobaltite and a range of bismuth and other telluride minerals are locally present (Gilbey, 1968; Naden, 1988). A four-stage paragenetic sequence has been defined recently by Mason *et al.* (2002). Gold occurs as inclusions in pyrite and arsenopyrite, or locally as coarse-grained developments in high-grade 'bonanza-shoots', which were responsible for the majority of production. The veins are thought to have been emplaced during depressurising and dewatering of the sediments during post-Tremadoc uplift of the basement-controlled Harlech Dome.

Mineralization genetically associated with Caradoc igneous activity in North Wales

Many of the diverse mineral deposits of North Wales relate to igneous activity in Caradoc times. During this time, Snowdonia was the focus of the most intense activity within the volcanic province, with major caldera development in central Snowdonia and associated vein mineralization (Reedman *et al.*, 1985; Fitches, 1987). Copper mineralization, occurring in quartz veins within and marginal to the Snowdon Caldera, is the dominant deposit of this area. The veins, features of which are well displayed at the **Lliwedd Mine** GCR site, are demonstrably pre-tectonic with respect to Acadian deformation, and consist of quartz and chlorite with chalcopyrite, sphalerite, galena, arsenopyrite, pyrrhotite, pyrite and rare bismuth-bearing phases. Evidence of zonation away from the caldera margin is present at a number of mines, including the **Llanberis Mine** GCR site. Here, the relatively high abundance of arsenopyrite and pyrrhotite, in comparison to that at sites within the caldera area, is well demonstrated.

In addition to the Snowdonia copper vein deposits, there are also a number of minor parageneses present in this area. At the **Cwm Tregalan–Shadow Gully** GCR site, magnetite and hematite mineralization, in veins and breccia zones, is enriched in tin and tungsten, occurring as cassiterite and scheelite respectively, and implying a magmatic input to the mineralizing process (Reedman *et al.*, 1985; Colman and Appleby, 1991). To the west of Snowdon, trials for copper were made on the margin of the Mynydd Mawr microgranite at the **Llyn Cwellyn Mine** GCR site. The trials exposed a vein dominated by fluorite, with significant magnetite along with a later chalcopyrite-dominated sulphide assemblage (Colman and Appleby, 1991) that also contains minor amounts of bismuth and lead tellurides. To the south of Snowdon, near Ffestiniog, another microgranite of Caradoc age, the Tan y Grisiau Microgranite, is exposed at the **Ffestiniog Granite Quarry** GCR site. Pipe-like bodies, which are believed to be a late-stage magmatic feature, are mineralized with allanite and molybdenite (Bromley, 1964). The microgranite is also cut by quartz-chlorite-sulphide veins, the age of emplacement of which is further constrained by the fact that they are pre-tectonic, as evidenced at the **Afon Stwlan** GCR site. Here, boudinage of quartz-chlorite-sulphide (sphalerite, galena, pyrite, pyrrhotite and chalcopyrite) veining is well exposed in a road cutting. Finally, well to the north-east of Snowdon, and related to a separate, small volcanic centre, lead-antimony mineralization was worked at the **Bwlch Mine** GCR site. At this locality, brecciated and highly altered nodular rhyolite contains a stockwork of quartz veins which carry stibnite, semseyite and a range of other rare lead-antimony sulphosalts (Bevins *et al.*, 1988).

Volcanic exhalative mineralization associated with this magmatic episode is also well developed in North Wales. In north-east Snowdonia, the **Cae Coch Mine** GCR site exploited a massive stratiform body of pyrite (with traces of molybdenite) lying at the junction between basaltic lavas and tuffs, and overlying slaty pyritic mudstones, all of Caradoc age. The mineralization, comprising massive framboidal pyrite and quartz, has strong affinities with the Kuroko-class of ore deposits (Ball and Bland, 1985), although a contrasting model of syn-diagenetic inhalation of fluids has been proposed more recently (Bottrell and Morton, 1992). The site is also of international importance for the unique biochemical system present in the old underground workings in which oxidation of the pyrite to iron sulphates is facilitated by the abundance of several species of chemolithic bacteria which form huge gelatinous growths, so-called 'acid-streamers' (Jenkins and Johnson, 1993).

On Anglesey, the **Parys Mountain** GCR site was once the largest copper mine in Europe. The deposit is believed to have formed as a result of the exhalation of metalliferous brines onto the seafloor (Pointon and Ixer, 1980) in Llandovery times (Tennant and Steed, 1997) during active volcanism; these deposits were subsequently remobilized to an extent during metamorphism and by Acadian deformation to produce epigenetic vein systems. The main deposit, worked in a system of huge opencuts and termed the 'Great Lode' by the miners (Greenly, 1919), is thus a modified exhalative stratiform body brought into its current steep inclination by folding. To the north of the Great Lode a second major deposit, the 'White Rock', has been interpreted as a siliceous sinter deposited on the seabed as a result of fumarolic activity (Pointon and Ixer, 1980). The ore-grade mineralization consists of finely intergrown pyrite and chalcopyrite with variable amounts of galena and sphalerite; quartz is ubiquitous, while ferroan dolomite and barite (possibly supergene) occur locally. The ores also contain a wide range of accessory phases, determined only by ore microscopy and electron microprobe analysis: these include tetrahedrite-tennantite, native bismuth, bismuthinite, lead-bismuth sulphosalts such as kobellite, and native gold (Thanasuthipitak, 1974). Secondary minerals are also present (Jenkins *et al.*, 2000), the most important species being anglesite, for which the site is the type locality. The anglesite occurred in a near-surface gossan and was not only abundant but also coarsely crystalline.

'Alpine-type' veins cutting Caradoc and older sedimentary and igneous rocks

Quartz-albite-chlorite veins, carrying important accessory anatase, brookite, rutile, titantite, hematite, chlorite, epidote, clinozoisite, monazite-(Ce), xenotime-(Y), synchysite-(Ce) and apatite, are a widespread regional feature in Snowdonia, but are particularly common in the area between Porthmadog and Blaenau Ffestiniog. They consist of partially open, vuggy fissures formed in competent and brittle lithologies: they occur in boudin necks in slate-hosted dykes at the **Penrhyn Quarry** GCR site, and in larger igneous intrusions at numerous sites across Snowdonia including the **Manod Quarry** GCR site. The constituent minerals are usually well-crystallized, and for this reason the veins have been targeted by mineral collectors for over a century. One locality, Prenteg, near Tremadog, where 'Alpine-type' veins are hosted by a dolerite sill, formerly produced brookite specimens that are still regarded as world-class (Starkey and Robinson, 1992). However, as a scientific study site for this suite of veins, the **Manod Quarry** GCR site near Blaenau Ffestiniog is of particular note (Green and Middleton, 1996), due to the quantity of material still remaining *in situ* and on the tips. Useful age-constraints have been recorded at the **Coed Llyn y Garnedd** GCR site, whilst, in addition to the typical 'Alpine-type' vein minerals, the mineralized boudin necks at the **Penrhyn Quarry** GCR site also carry an unusual assemblage of chalcocite, altered in places to chrysocolla and accompanied by siderite and calcite. The tendency for the veins to occur at structural sites where localized extensional brittle fracturing has occurred as a response to Acadian compression has lead to the suggestion that they are syn-tectonic with respect to that deformation.

Stratabound gold-arsenic mineralization associated with Upper Ordovician pyritic shales

Although recent exploration has indicated that more than one stratabound gold-arsenic deposit may occur along the south-eastern margin of the Welsh Basin (Brown, 1993), the only example currently recognized with certainty is at the **Dolaucothi Mine** GCR site, mined intermittently since Roman times (Annels and Burnham, 1995). The deposit is complex and its origin has long been debated; emplacement associated with Acadian uplift and deformation is the currently preferred theory. Hosted by tightly folded black-shales of Ashgill age, the gold occurs both in pyrite- and porphyroblastic arsenopyrite-rich bands in black shales, and is also associated with the same sulphides in a complex series of quartz veins which has been interpreted by Annels and Roberts (1989) as having saddle-reef forms.

Quartz-sulphide vein mineralization of Devonian and Variscan age in Central Wales

Numerous, mainly ENE–WSW-trending, quartz-carbonate-sulphide veins occur in the Central Wales Orefield, once of considerable importance as a source of lead, silver and zinc (Jones, 1922). The veins are now more renowned for their display of spectacular hydraulic fracture brecciation textures (Phillips, 1972). Recent investigations (Fletcher *et al.*, 1993; Mason, 1994, 1997) have suggested that there is compelling evidence for two or more phases of vein mineralization, evidenced both by paragenetic relationships and isotopic data. The first group of veins, the six A1 assemblages of Mason (1994, 1997), are characterized by their polymetallic nature and complexly intergrown sulphide minerals, while the second group of veins, the six A2 assemblages of Mason (1994, 1997), are characterized by their simple mineralogy in often coarse-grained crustiform assemblages. At many sites, different elements of both the A1 and A2 groups have occupied the same lode-fracture due to re-activation, allowing cross-cutting paragenetic relationships to be readily observed, such as at the **Brynyrafr Mine** GCR site and at the **Cwmystwyth Mine** GCR site, the latter being a site where copper ores of the A1 group were mined as long ago as the Early Bronze Age.

Prominent mineralogical features of the A1 mineralization are particularly encountered in the A1-c polymetallic assemblage, which is often extremely argentiferous. A sulphide assemblage consisting of galena, chalcopyrite, richly argentiferous tetrahedrite, and bournonite was worked at several mines, including at the **Darren Mine** GCR site, where silver grades approaching 1000 g/t were encountered at times. The A1-c assemblage also contains cobalt and nickel minerals, including abundant siegenite at the **Erglodd Mine** GCR site, and millerite, the extremely rare nickel-antimony sulphide tucekite, and electrum at the **Eaglebrook Mine** GCR site.

The crustiform texture of the A2 mineralization is well demonstrated by an exposure of the A2-a assemblage at the **Ceulan Mine Opencast** GCR site and by dump material comprising the A2-c assemblage at the **Nantiago Mine** GCR site. Both sites also demonstrate the simple mineralogy of the A2 assemblages. The A2 type of mineralization is not only restricted to the Central Wales Orefield, but is probably a reflection of metallogenic processes operating on a much wider scale during Variscan times. Similar mineralization, including an extraordinary development of the A2-d 'Giant quartz' assemblage, is to be seen at the **Nantymwyn Mine** GCR site, near Llandovery, in southern Central Wales.

Copper-lead-arsenic-barium vein mineralization in the Welsh Borderland

An apparently localized occurrence of barite-tennantite-galena-dominated mineralization is centred on the Dolyhir area of the Welsh Borderland and intermittently exposed at the **Dolyhir Quarry** GCR site. Simple extensional veins cutting both the Neoproterozoic Longmyndian basement (Strinds Formation and Yat Wood Formation) and the Dolyhir Limestone Formation, of Wenlock age, contain a primary assemblage locally featuring barite and massive tennantite with galena, chalcopyrite and a range of rare ore minerals including luzonite, primary greenockite (locally altered to otavite), proustite, enargite and rammelsbergite. The rare carbonate ewaldite has recently been recorded at this locality, being the first British and only the fourth worldwide occurrence. Supergene alteration has produced a diverse secondary assemblage including bornite, chalcocite, azurite, malachite, tyrolite, olivenite, zincolivenite, anglesite, beudantite and many other species. These primary and secondary parageneses are not seen elsewhere in Wales or in the adjacent regions of England.

Mississippi Valley-type lead-zinc-fluorite and copper-dolomite associations in north-east Wales

A major Mississippi Valley-type (MVT) orefield, hosted by limestones and sandstones of Carboniferous age, stretching from Minera to Prestatyn, constitutes one of the five major 'Pennine-type' orefields of Britain (Ixer and Vaughan, 1993). The coarse-grained, crustiform mineralization occurs in veins, pipes and metasomatic flats in favourable lithologies and is typified by simple galena-sphalerite-calcite-fluorite-chalcopyrite assemblages, accompanied by minor barite and uraniferous vein hydrocarbons (Parnell, 1988b), as in the **Halkyn Mountain** GCR site area. Southward, in the Minera district, fluorite and barite are virtually absent, sphalerite becomes more abundant and quartz is a major gangue phase, as at the **Pool Park and South Minera Mines** GCR site. At Minera, early studies indicated that the veins extended downwards into the underlying deformed Lower Palaeozoic rocks, supporting the contention that at least some of the veins yielding Variscan isotopic dates in other parts of Wales (e.g. some of the Central Wales A2 veins) may be related to this major phase of metallogenesis. Close to the **Halkyn Mountain** GCR site, at the **Pennant Mine** GCR site where barite-witherite-calcite-sphalerite-galena-chalcopyrite mineralization was mined, is an example of veining cutting Silurian turbiditic rocks, an occurrence which may serve to re-inforce the above contention.

The historically important copper deposits at the **Great Orme Copper Mines** GCR site belong to the copper-dolomite class of ore deposits (Ixer and Davies, 1996), an internationally recognized grouping typically formed by the interaction of late-stage fluids, from either Mississippi Valley-type Pb-Zn deposits or sedimentary exhalative Pb-Zn deposits, with copper-bearing rocks. Paragenetically, the Great Orme deposits are complex due to the fact that the primary chalcopyrite-dolomite mineralization has been extensively oxidized; abundant malachite, often pseudomorphing chalcopyrite, occurs in repeated generations with secondary calcite. Other secondary minerals are of limited occurrence but include covellite, chalcocite, azurite, cuprite, and various other copper and manganese oxides.

Upper Palaeozoic millerite-bearing ironstones of the South Wales Coalfield

Sedimentary ironstones are widely developed in the Upper Carboniferous (Westphalian) 'Coal Measures' of South Wales, and provided the majority of ore for Welsh iron production. Claystone–ironstone nodules occur throughout the Westphalian sequences, forming bands in the dark-grey mudstones adjacent to coal seams, while blackband ironstones are relatively restricted in occurrence.

Common throughout the British coalfields, the South Wales claystone–ironstones are of particular importance in mineralogical terms for the well-crystallized sulphide assemblage developed in septarian cracks within the claystone–ironstone nodules. This assemblage, accompanied by siderite, dolomite, calcite, quartz, barite, carbonate-fluorapatite, waxy hydrocarbons and clay minerals, comprises millerite, galena, chalcopyrite, sphalerite, pyrite, marcasite and siegenite. It is, however, the excellent acicular groups of millerite crystals, reaching several centimetres in length on occasion, which have chiefly made the South Wales ironstones internationally famous in mineralogical terms.

Recently, similar, and clearly structurally controlled mineralization, has been observed *in situ* encrusting open joint-surfaces in Westphalian sandstones in the north-western part of the coalfield (Bevins and Mason, 2000). Together with recent fluid-inclusion and isotopic studies (Alderton and Bevins, 1996; Alderton *et al.*, 2004), the new discoveries throw a considerable amount of light on the genesis of the mineralization, and may have connotations with regard to the overall evolution of the coalfield.

In the South Wales Coalfield the selection of a single representative site for conservation purposes is not practical. Hence, the millerite-bearing claystone–ironstone mineralization has not been allocated a specific GCR site, although it is of GCR importance.

Mesozoic Fe-Mn and Pb-Zn-Cu-Ba mineralization in South Wales

Four discrete types of mineralization characterize the Mesozoic to Recent mineral deposits of South Wales. Three of the mineralization events are of epigenetic origin with respect to their host rocks, whilst the fourth involved the supergene alteration of the earlier events. The epigenetic mineralization comprises oxide-facies iron and manganese ores (represented by the **Mwyndy Mine** GCR site) with superimposed, and often spectacular, metasomatic cavity-fill assemblages, well exposed at the **Ton Mawr Quarry** GCR site. Mississippi Valley-type (MVT) veins carry lead, zinc and minor copper sulphides with associated calcite, fluorite and barium- and strontium-bearing minerals, the age of which is constrained at the **Ogmore Coast** GCR site. The locally intense supergene weathering, which is particularly evident in the MVT veins, has produced mostly common secondary minerals, but locally some unusual assemblages have been recorded, the most complex of which is seen at the **Machen Quarry** GCR site.

Secondary mineralization

Secondary mineralization falls into a number of distinct categories, and the minerals present depend on the particular environment in which they developed. There are rich secondary mineral assemblages in Wales, some containing minerals that are very rare worldwide.

Firstly, there are those minerals that have developed in gossans linked to extensive oxidation of underlying mineral deposits. Although no longer exposed, there is ample evidence (Greenly, 1919) to suggest that there was an extensive gossan developed above the orebody at the **Parys Mountain** GCR site, which contained abundant anglesite, for which the site is the type locality. In Central Wales, the **Llechweddhelyg Mine** GCR site shows a range of secondary minerals, including goethite, malachite, chrysocolla, cerussite, pyromorphite and wulfenite. A similar mineral suite is seen at the **Frongoch Mine** GCR site, although this site is notable for the abundance of cerussite and the unusual (for Wales) presence of well-formed brown pyromorphite crystals (Green *et al.*, 1996).

A second suite of secondary minerals has developed in post-mining times on the mine tips and in old workings. At the **Llechweddhelyg Mine** GCR site, these include mattheddleite, susannite, schmiederite, caledonite, elyite and chenite (Bevins and Mason, 1997), while at the **Frongoch Mine** GCR site an extremely wide variety of post-mining minerals includes the recently described species ramsbeckite, schulenbergite, namuwite, lautenthalite, brianyoungite, redgillite, the second world occurrence of bechererite (Green *et al.*, 1996; Rust *et al.*, 2004), and the recently described new mineral steverustite (Cooper *et al.*, 2009).

A contrasting secondary deposit is developed at the **Mynydd Nodol Mine** GCR site, where botryoidal manganese oxides are developed in veins and joints cutting tuffs of Ordovician age. It is thought to represent the deep leaching of underlying Ordovician basic volcanic rocks (Bevins and Mason, 1998), possibly in a subtropical environment in Tertiary times.

A unique secondary mineral deposit in Great Britain occurs in the Dolgellau Gold-belt, at the **Turf Copper Mine** GCR site, where, in post-glacial times, copper leached from the Coed y Brenin porphyry-copper deposit has been precipitated as native copper replacing organic matter in the so-called 'Turf Copper' Mine (Rice and Sharp, 1976).

LOWER PALAEOZOIC IRON AND MANGANESE EXHALATIVE MINERALIZATION IN NORTH WALES

Bedded iron and manganese ores, inferred to be of exhalative origin, occur in Lower Palaeozoic rocks across a large area of North Wales. The earliest mineralization of this type to be worked is of Lower Cambrian age, and it outcrops on the St Tudwal's Peninsula and, more substantially, around the Harlech Dome, where it furnished a widespread manganese mining industry, particularly in the latter part of the 19th century (Figures 5.2 and 5.3). This mineralization, best

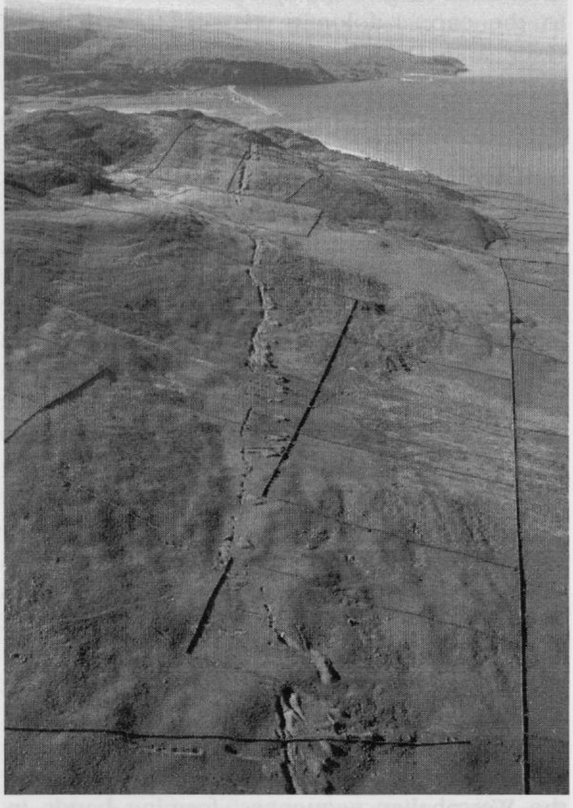


Figure 5.2 Nineteenth-century manganese workings on exposures of the Cambrian-age Hafotty Formation in the Harlech Dome, looking south towards the Mawddach Estuary. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

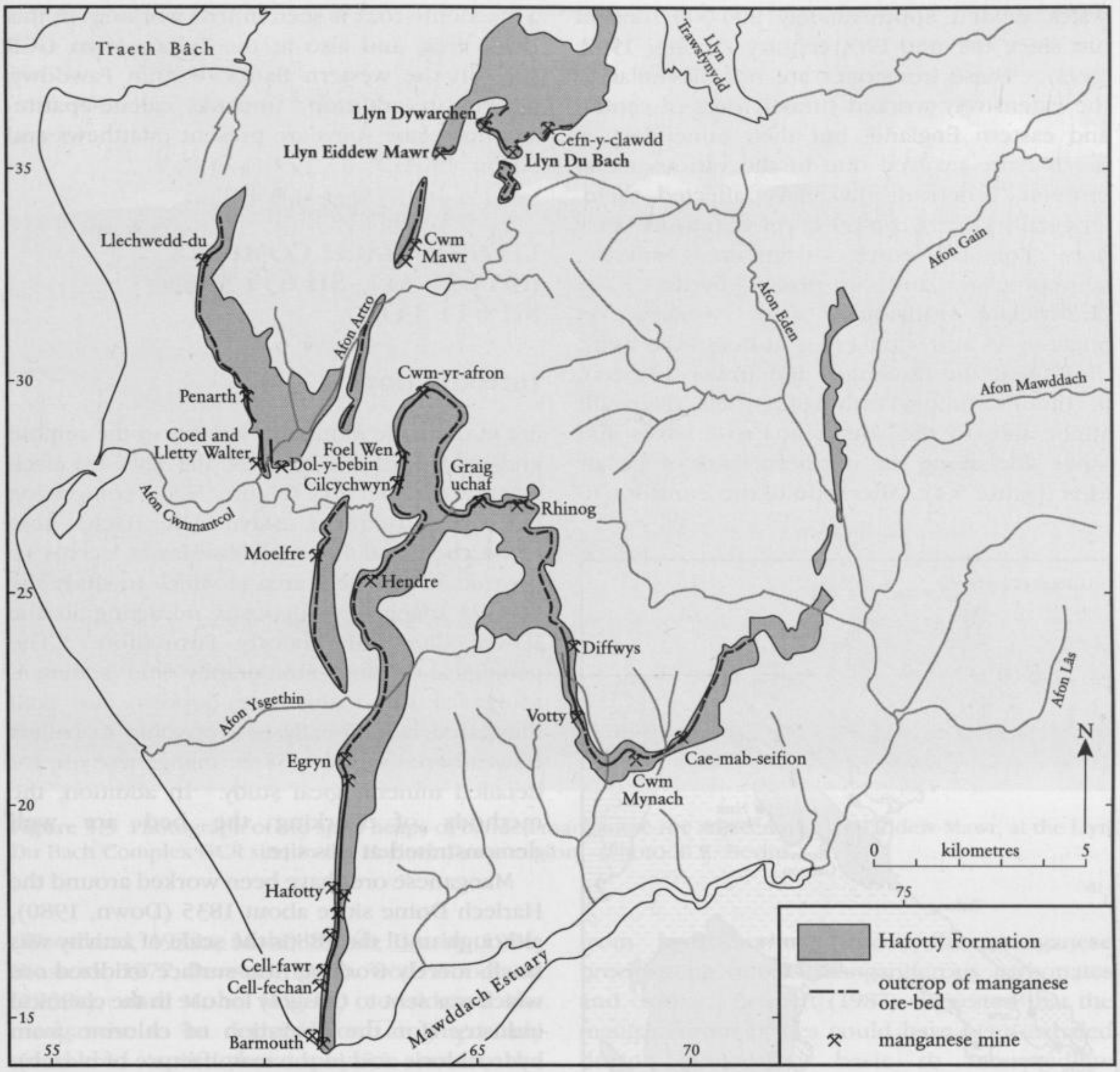


Figure 5.3 Map of the Harlech Dome region, showing the distribution of the Cambrian-age Hafotty Formation, the locations of the principal manganese mines, and the three mines which comprise the **Llyn Du Bach Complex** GCR site. Based on Down (1980), and Allen and Jackson (1985).

seen at the **Llyn Du Bach Complex** GCR site, consists of banded, stratiform manganese and iron silicates and carbonates, the contrasting colours of which give the ore, where unweathered, a streaky pink and yellow appearance. The ore has been interpreted by Bennett (1987) to represent the distal facies of a submarine exhalative system.

Iron and manganese deposits of Ordovician age are of widespread occurrence across North Wales, where, on Llŷn, they were mined in substantial quantity at the **Benallt and Nant Mines** GCR site. This site is of considerable scientific importance for the large number of rare, well-crystallized silicate minerals discovered while the mines were working, the genesis of which will be discussed in this chapter. This site is also the type locality for a number of Mn-bearing and Ba-bearing minerals.

Ooidal ironstones, deposited in shallow waters during Ordovician times, form part of a much larger ironstone province developed on the Gondwanan shelf (Young, 1992, 1993). Similar, but much larger deposits, have been mined through Europe, northern Africa and Canada, while the Ordovician ironstones of

Wales yielded approximately 200 000 tons of ore since the mid-19th century (Young, 1992, 1993). These ironstones are not dissimilar to the extensively worked Jurassic ores of central and eastern England, but their mineralogy is much more evolved due to the various metamorphic processes that have affected them. Originally largely composed of chamosite, they now contain much magnetite, siderite, stilpnomelane and, in places, pyrite. The Ordovician ironstones were worked on Anglesey, in Snowdonia (e.g. at Betws Garmon), on Llŷn (in the Llanengan and Trevor districts), in the Ffestiniog–Porthmadog belt (Penyrallt Mine) and, to the south, at Cross Foxes and other sites along the northern flank of Cadair Idris (Figure 5.4). Alteration of the ironstone to a magnetite-rock is seen in trial workings in this latter area, and also at the **Tyllau Mwn** GCR site, on the western flanks of Aran Fawddwy, where, in addition, unusual calcite-apatite-stilpnomelane veins are present (Matthews and Scoon, 1964).

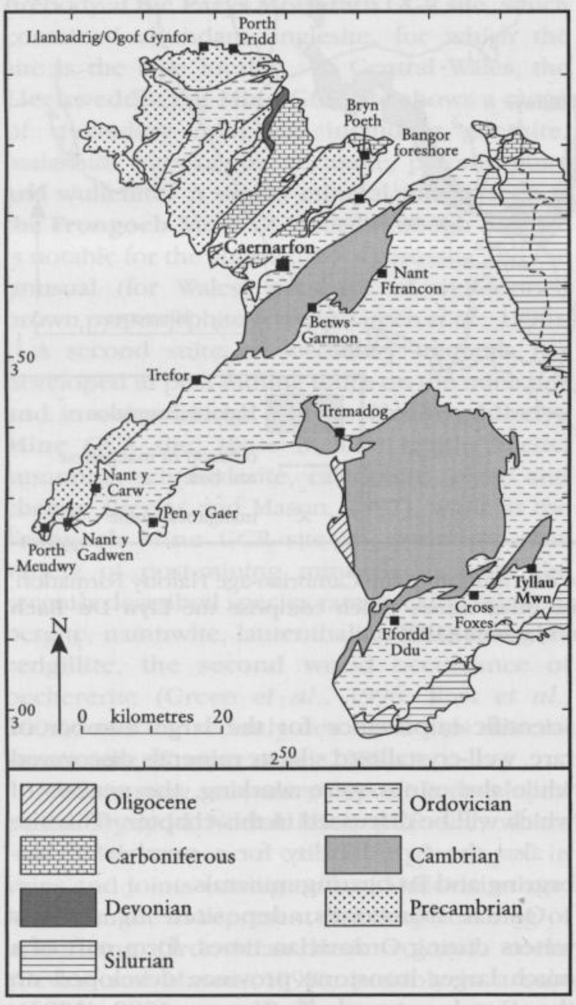


Figure 5.4 Map of North Wales, showing the distribution of Ordovician oolitic iron ore workings, and the location of the **Tyllau Mwn** GCR site. After Trythall (1988).

LLYN DU BACH COMPLEX (SH 657 341, SH 654 346, SH 644 341)

Introduction

Set in dramatic mountain scenery in the remote and wild northern Rhinogs, the Llyn Du Bach Complex GCR site (Figure 5.5), comprising three small mines (Llyn Du Bach, Llyn Dywarchen and Llyn Eiddew-Mawr), serves to provide an excellent area in which to study the bedded manganese deposits occurring in the Lower Cambrian Hafotty Formation. The geological setting, stratigraphy and sedimentology of the manganese deposits are well illustrated; additionally it is possible to collect unweathered samples of the manganese ore for detailed mineralogical study. In addition, the methods of working the bed are well demonstrated at this site.

Manganese ores have been worked around the Harlech Dome since about 1835 (Down, 1980), although until the 1880s the scale of activity was small, merely working near-surface oxidized ore which was sent to Glasgow for use in the chemical industry (for the liberation of chlorine from hydrochloric acid in the manufacture of bleach). The 1880s saw an upsurge as a consequence of the discovery of the wear-resistant, enhanced hardness properties of manganese steels, which created a great demand for the metal. This evaporated, however, following the end of the First World War, although the mines that constitute this GCR site had closed long before, apparently only being prospected again in wartime. Total recorded production from these sites from 1889 to 1897 was 6158 tons (Down, 1980), the ore grade almost never exceeding 35% Mn and frequently dropping to 25%. These low grades were difficult to work profitably in such remote areas, and one major reason for the industry's demise was the increasing availability of higher-grade ores from overseas.

The manganese ores of the Harlech Dome have been examined in considerable detail

Figure 5.5 Photograph of old spoil-heaps of banded manganese ore adjacent to Llyn Eiddew-Mawr, at the Llyn Du Bach Complex GCR site, in the Harlech Dome region. (Photo: R.E. Bevins.)

(Woodland, 1939a; Mohr, 1964b; Glasby, 1974; Binstock, 1977; Bennett, 1987). Both Woodland (1939a), and Mohr (1964b) considered the manganese to be derived from an intensively weathered 'spilitic/keratophyric' terrain, the manganese precipitating as a colloidal gel containing rhodochrosite and silica in a climatically controlled evaporitic basinal environment. Subsequently, the model was modified by Glasby (1974), and later by Binstock (1977), who both inferred that the mineralization was an early diagenetic rhodochrosite precipitate and could have formed in a marine environment.

These models were questioned by Bennett (1987), however, who suggested that the weathered terrain model required unusual climatic conditions and basin-water chemistry, while the diagenetic model could not account for the quantity of manganese present, both in the ore-bed and in the overall sedimentary pile. He concluded that the mineralization was syngenetic/syn-diagenetic, and was deposited from hydrothermal brines, the manganese precipitating out as manganiferous carbonates and oxides. Bennett (1987) suggested that the manganiferous brines could have been exhaled during submarine, basic to intermediate volcanism, and that a possible source area was either Anglesey or Llŷn, where such volcanic rocks, of possible Cambrian age, existed. Bennett (1987) also commented that many original depositional features were preserved, despite mineralogical alteration at lower-greenschist-facies metamorphic grades.

Description

Manganese mineralization in the Harlech Dome comprises a discrete bed near to the base of the Hafotty Formation, which is a member of the Lower Cambrian Harlech Grits Group. The group consists primarily of medium- to coarse-grained, occasionally volcaniclastic, sandstones derived from proximal turbidites deposited in relatively shallow waters (Allen and Jackson, 1985). The Hafotty Formation is enriched in manganese (Bennett, 1987), but one horizon, the 'manganese ore-bed', approximately 0.5 m thick, contains up to 35% Mn. This ore-bed is remarkably persistent across the Harlech Dome, although it is thickest (approaching 1 m) in the south-west and thins to sub-economic levels in the east (Allen and Jackson, 1985) and it represents a notable marker horizon.

At the Llyn Du Bach Complex GCR site (Figure 5.6), the ore-bed has been worked open-cast, the bed being removed and the waste being contained in pack-walled areas, between which tramways may be seen, along which the ore was conveyed from the working face. This method of working, common to many of the Harlech Dome manganese mines, is particularly well-displayed at the Llyn Eiddew-Mawr mine.

The ore-bed is a hard, dense, and splintery rock, cherty in appearance, with reddish and yellowish bands indicating mineralogical variation. Immediately below the ore-bed, in sharp contact, is a mudstone unit enriched in iron and containing magnetite and abundant pyrite. The upper contact of the ore-bed is gradational, and is overlain by a thick sandstone. This is well exposed on the miner's track from Llyn Eiddew-Mawr to Llyn Du Bach, as the track has been purposely excavated along the ore-bed in order to prospect it *en route*; along this track the overlying sandstones overhang spectacularly. At one point a fault crosses the bed, down-throwing it a small distance to the north-west; the track accordingly steps-up to follow the bed.

The best exposure of the ore-bed itself is situated at the end of this track, just beyond the Llyn Du Bach tarn, where a pile of ore has been blasted out but abandoned. In hand specimen, the alternating yellowish, pinkish-red, and reddish-brown banded nature of the finely laminated ore is readily seen.

The manganese ore-bed shows a number of original sedimentary features, including relict lamination, graded bedding, and flattened spheroidal microfossils (Bennett, 1987). Interbedded clastic units are also present, and a possible tuffaceous origin has been suggested by Bennett (1987), as they are widespread throughout the outcrop of the ore-bed and contain pseudomorphs after feldspar and vitric fragments. Carbonate microspherulites also occur in the ore, forming discrete layers; they are radially zoned with regard to their Fe and Mn content, zonation manifesting itself as concentric bands. The fact that at times one band is seen forming a zone around two touching microspherules indicates that they are in 'growth position'. Bennett (1987) commented that these small carbonate concretions are identical in many respects to those formed during the diagenesis of manganese-rich sediments in modern lacustrine and marine environments.

The yellowish bands, which contain more Mn than Fe, are composed mainly of micro-concretionary micritic calcian rhodochrosite but also contain pseudomorphs after probable authigenic gypsum or anhydrite. The red bands, which contain more Fe and less Mn, are composed of kutnohorite, spessartine, silica, hematite, magnetite and ferropyrophanite. Apatite, barite, rhodonite and pennantite have also been recorded (Bennett, 1987), while pyrite occurs as scattered 1–2 mm cubes, and irregular quartz veinlets are common. Interbedded thin clastic horizons have been altered by low-grade metamorphism into quartz-spessartine rocks, known as 'coticules', which also occur at several horizons within the Harlech Grits Group.

The limited extent of oxidation of the manganese ore at this site results in only thin films of grey manganese ores coating the primary ore, in contrast to many of the Harlech Dome manganese mines, where typically it has been oxidized extensively, with a deep-brown to greyish colour.

Interpretation

The diagenetic models of earlier authors to explain the origin of the Harlech manganese ore-bed were questioned by Bennett (1987) on a number of grounds. Firstly, the fact that manganese is enriched in the Harlech Grits Group relative to iron led Bennett (1987) to suggest that much iron must have been removed from the metallogenic system at source, rather than by localized, in-situ, diagenetic chemical fractionation. Such fractionation should theoretically lead to a relative depletion of manganese below the horizon of manganese mineralization, which is not the case in the Harlech deposit.

Secondly, Bennett (1987) noted the consistent positive correlation between manganese enrichment and the deposition of mud-facies sediments. This suggests that there existed an inverse relationship between manganese enrichment and sedimentation rates, such that,

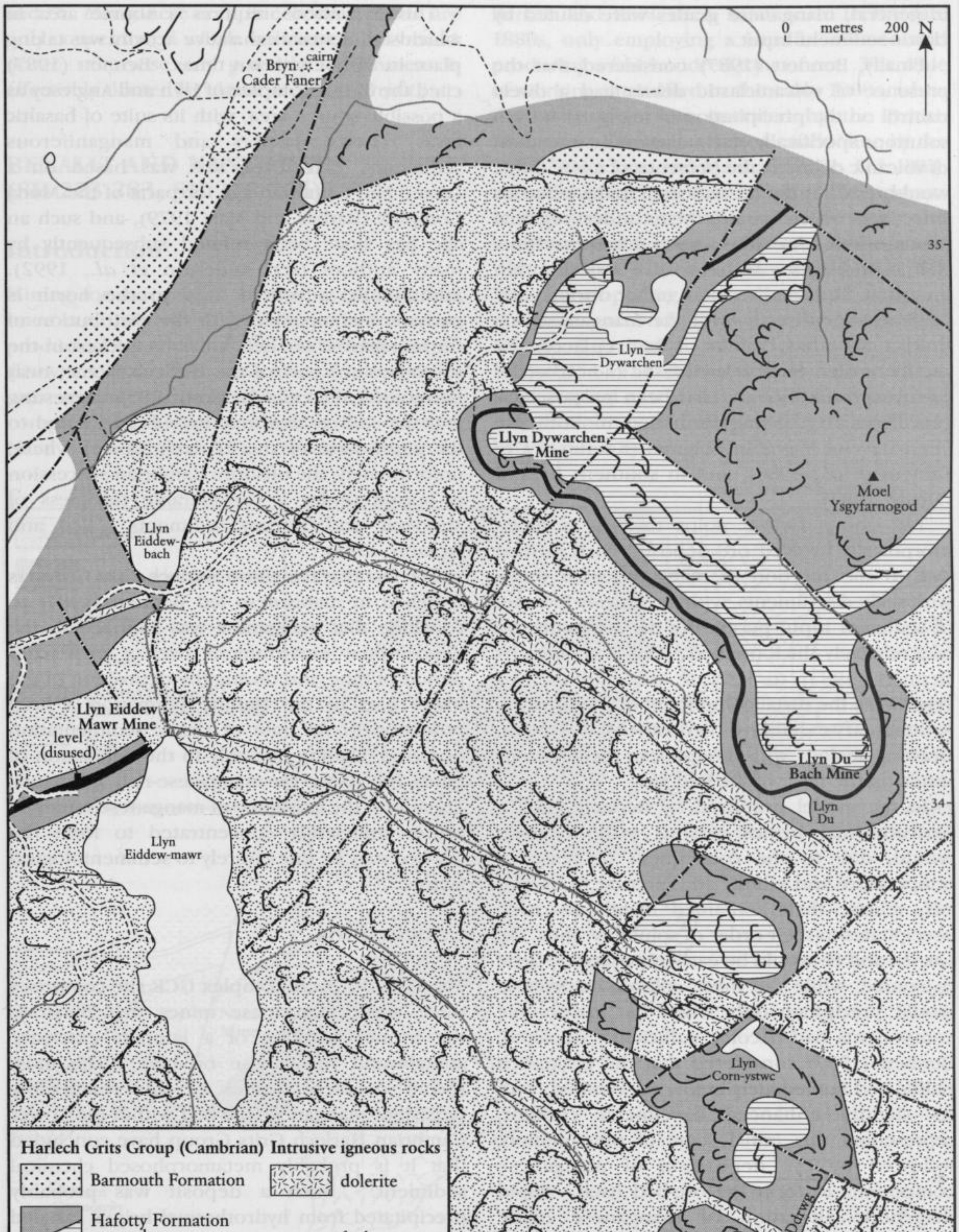


Figure 5.6 Map of the Llyn Du Bach Complex GCR site. After Institute of Geological Sciences 1:50 000 Sheet 135, Harlech (1982).

in general, manganese grades were diluted by clastic sediment input.

Finally, Bennett (1987) considered that the presence of volcaniclastic debris had a direct control on the precipitation of manganese from solution: specifically, early diagenetic alteration of volcanic debris in the presence of a Mn^{2+} flux would result in the formation of manganiferous smectites, which would then, under regional metamorphic conditions, evolve into spessartine-rich assemblages. An alternative was that thin limestone beds had reacted, either during early diagenesis or directly with the manganese-rich fluids, so that calcite was replaced by rhodochrosite. Such volcaniclastic and carbonate pre-ore protoliths have also been proposed as precursors to coticule formation in both the Venn-Stavelot Massif in Belgium (Kramm, 1976; Lamens *et al.*, 1986), and in southern Ireland (Doyle, 1984).

The above factors point towards a metamorphically evolved ore deposit which formed due to the reaction of manganese-rich fluids with seabed sediments, with a relatively low rate of sediment input permitting the accumulation of a relatively thick ore-bed. This was taken by Bennett (1987) to indicate that the ore-bed represents the distal component of a submarine sedimentary-exhalative hydrothermal system, drawing analogy with the modern metalliferous muds on the floor of the Red Sea.

In the model proposed by Bennett (1987), hydrothermal brines mixing with seawater would, due to the consequent decrease in temperature and salinity and increase in Eh and pH, release their contained metals as oxide precipitates in their order of solubility: thus, Pb, Cu, Zn and Fe would be early precipitates, close to source, while the more soluble manganese would precipitate only when the less-soluble components had become sufficiently depleted. Bennett (1987) considered that the pyrite-rich pelitic bed immediately below the ore-bed, with its slightly enhanced base-metal content, represented this initial stage of precipitation, followed by the deposition of manganese compounds to form the ore-bed itself. Rapid diagenetic alteration of manganese oxide precipitates to carbonates was cited in this model to explain the low Co-Ni-Cu content of the manganese ore, as the latter elements are generally highly enriched in seafloor manganese oxide nodules, the oxide being a strong scavenger of base-metal cations.

This hypothesis requires a source area in which sedimentary exhalative activity was taking place in early Cambrian times. Bennett (1987) cited the Mona Complex of Llŷn and Anglesey as a possible source area, with its suite of basaltic lavas, cherts, jaspers and manganiferous sediments. However, this was based on a Lower–Mid-Cambrian age for parts of the Mona Complex (Barber and Max, 1979), and such an age has since been refuted subsequently by many authors (see Anderton *et al.*, 1992). Additionally, a source area to the north is perhaps incompatible with the distribution of the manganese ore-bed, which is thickest in the south-western part of the Harlech Dome, near Barmouth (Allen and Jackson, 1985), suggesting that the source area may have been located to the south-west of the Harlech Dome, where, unfortunately, the offshore Cambrian succession is buried under a considerable thickness of Mesozoic and Tertiary sediments (Allen and Jackson, 1985).

The fact that the entire Harlech Grits Group is enriched in manganese led Bennett (1987) to conclude that manganese was supplied to the depositional environment over a protracted period of time, but during the deposition of the lower part of the Hafotty Formation a brief reduction in the rate of clastic sedimentation occurred, leading not only to the deposition of muds, but also to the manganese-rich sediments. Therefore, the existence of manganese mineralization sufficiently concentrated to form the ore-bed may be due entirely to sedimentological factors.

Conclusions

The Llyn Du Bach Complex GCR site comprises three small manganese mines that illustrate the former working of a laterally extensive stratabound manganese ore-bed. The most recent detailed studies of this remarkably persistent manganese ore-bed within the Lower Cambrian Harlech Grits Group have concluded that it is probably metamorphosed chemical sediment. Such a deposit was probably precipitated from hydrothermal brines exhaled onto the seabed, but the fact that the Harlech deposit is manganese-dominated implies that it was probably deposited at a considerable distance from the centre of fluid outflow. Closer to the source similar sedimentary deposits are likely to occur which are enriched in Pb, Cu, Zn and Fe. Manganese ores, in economic terms, are only concentrated where sediment input breaks occur; otherwise any potential enrichment is effectively diluted by clastic sediment input.

BENALLT AND NANT MINES (SH 223 283, SH 210 266)

Introduction

Mining for manganese in south-west Llŷn was once an important industry, these mines producing over half of the total Welsh output (Down, 1980). Two separate major orebodies were exploited, one by the Benallt–Rhiw mine complex and the other, close to the coast, at Nant Mine (Figure 5.7). Working began at Benallt and Rhiw on a small scale in the late 1880s, only employing a handful of men and producing a few hundred tons of ore. The scale of working intensified in the early 1900s, when the Rhiw Mine was operated by the British Manganese Co. Ltd, and the Benallt Mine by the North Wales Iron and Manganese Co. Ltd. With rich ores being raised in considerable amounts at that time, transport became an issue, and a railway was constructed down to the coast, where the ore was loaded onto ships from a pier. The major opening up by the Benallt company of another orebody, known as the 'Nant Mine' (Figure 5.8) and located close to this pier, followed in 1914. By this time, Benallt and Rhiw were worked extensively by opencast methods, with complexes of underground galleries linked by a maze of levels and shafts.

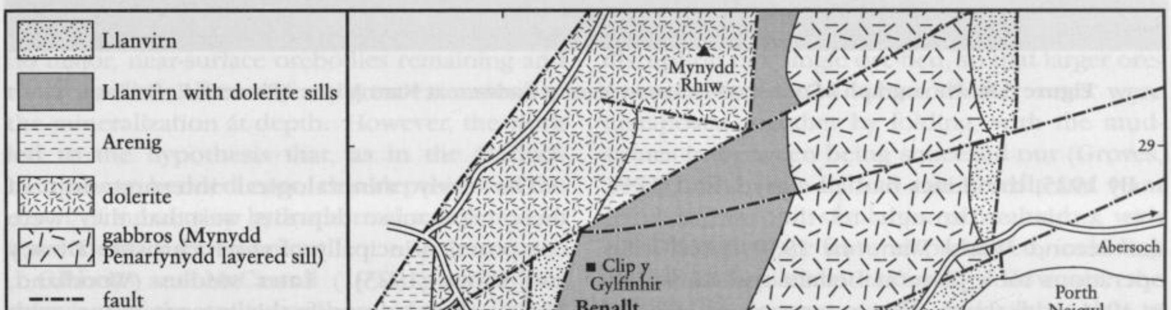


Figure 5.7 Map of the Benallt and Nant Mines GCR site. After British Geological Survey 1:10 000 Sheet SH22NW, Rhiw (1991).

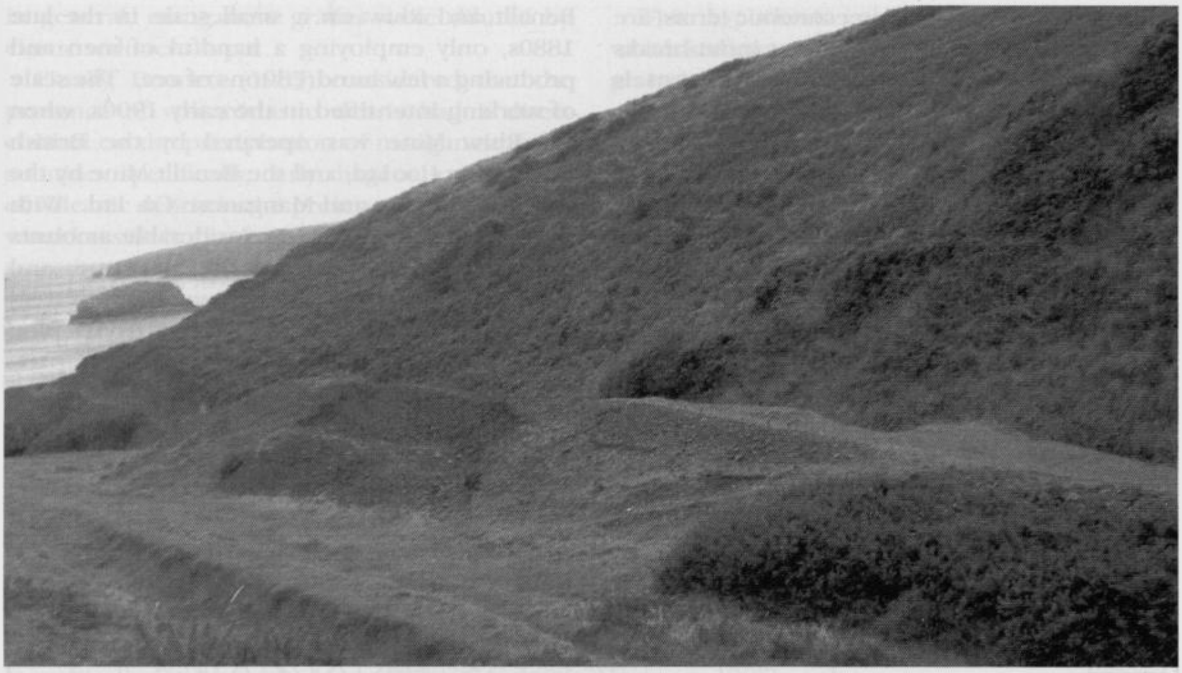


Figure 5.8 Photograph of old spoil-heaps in Nant y Gadwen at Nant Mine. (Photo R.E. Bevins.)

By 1925, the mines had all closed, and there was a hiatus through to the outbreak of the Second World War. In 1939, small-scale operations took place at Benallt and Rhiw, but in 1941, with the decline in manganese imports due to the war in the Atlantic Ocean, Benallt was requisitioned by the Ministry of Supply in a major development that involved the importation of colliers from South Wales and tin-miners from Cornwall. Development underground resulted in the location of a major ore-zone, which produced 30 000 tons of ore, a discovery ensuring the mine's operation through the war years. Additionally, the Royal Canadian Engineers drilled *c.* 2500 m of exploration boreholes, which considerably improved the geological interpretation of the orebody. This drilling programme was influenced partly by the results of magnetometry traverses, and the orebodies discovered as a result were an important early example of the successful application of this geophysical method in mineral exploration.

Benallt was finally abandoned at the end of 1945, by which time it had yielded 113 838 tons of manganese ore (although some output was combined with Nant). With the production from Nant, and the old Rhiw workings, the total output exceeded 150 000 tons (Down, 1980).

The early mineralogical interpretation of these manganese deposits was that they were composed principally of rhodochrosite (Dewey and Dines, 1923). Later studies (Woodland, 1939b) were to modify this interpretation, with the recognition of important quantities of manganese-bearing chlorite-group minerals. Groves (1952) finally established that the Benallt ore was in fact a complexly intergrown mixture of manganese silicates with manganese-iron oxides, with little carbonate present, except at Nant, where rhodochrosite is of some importance.

These mines attracted early attention from specimen mineralogists for the unusual and well-crystallized suite of manganese and other minerals (Russell, 1911), and the wartime re-opening presented the opportunity for further studies (Campbell Smith *et al.*, 1944a,b, 1946, 1949; Campbell Smith, 1945, 1948; Campbell Smith and Claringbull, 1947; Smith and Frondel, 1968). In addition to the discovery of a number of rare minerals new to Wales, these studies described type specimens of banalsite, pennantite, and cymrite, all new mineral species from the Benallt–Nant mining complex. Very few sites worldwide are a type locality for more than one mineral.

Exploration continued intermittently in the post-war years, and in 1971 a magnetic survey was carried out (Cornwell, 1979). This was more for mapping than economic purposes, and no indications of major blind orebodies were reported. In the 1970s, exploration was also carried out by Noranda-Kerr Ltd over layered basic intrusive rocks immediately to the east of the site, the targets being possible magmatic Cu-Ni mineral deposits, but concentrations were found not to be of economic interest (Brown and Evans, 1989).

More recently, an important exploration and research project was undertaken by the Mineral Reconnaissance Programme of the British Geological Survey (Brown and Evans, 1989), in which the areas between Nant and Benallt, and also the area to the north of Benallt, were examined. Methods included magnetometry, soil- and rock-sampling, and the drilling of five boreholes, the latter being collared over detected magnetic anomalies. The results of this programme led to the conclusion that there were no major, near-surface orebodies remaining and there was little chance of any great extensions to the mineralization at depth. However, the work led to the hypothesis that, as in the Harlech manganese bedded ores, this deposit was the result of submarine hydrothermal exhalation in a sedimentary environment.

Gibbons and McCarroll (1993) provided an overview of the earlier proposals for the origin of the Benallt and Nant manganese deposits. Finally, the previously unreported presence of reduced copper mineralization was noted by Bevins and Mason (1998).

Description

In the Benallt–Nant area, Ordovician strata unconformably overlie a complex suite of granitic to dioritic igneous rocks, which constitute the Sarn Complex (Gibbons, 1980). The manganese mineralization is hosted by turbiditic mudstones and siltstones, with associated ironstone bands, of Arenig to Llanvirn age. These rocks form part of a package of sedimentary rocks and intercalated basaltic and andesitic lavas, cherts and crystal tuffs. Recent evidence from drill cores suggests that the lavas were intruded into wet sediments just below the seafloor (Brown and Evans, 1989). A series of dolerite sills, which intrudes the package, are probably cogenetic with the lavas. The host rocks and included ore-beds have undergone polyphase Acadian deformation. A basic dyke, the Ty Canol Dyke (Groves, 1952), was intersected during wartime operations, and its WNW–ESE trend led Groves (1952) to interpret it as a member of the 'Tertiary' (Palaeogene) basic dyke-swarm of north-western Britain (see also Bevins *et al.*, 1996a).

The Benallt–Nant orebodies differ from the persistent stratabound horizon worked in the Harlech Dome in that they occur as strike-elongated, irregular, approximately ellipsoidal masses. A single such mass formed the sole ore-zone at Nant Mine, while at Benallt the ore occurred in a number of smaller zones. According to Groves (1947), the Benallt orebody lay between basalt in the hangingwall (the Lower Clip Lava) and an E-dipping dolerite sill (the Footwall Sill) in the footwall. The Nant orebody was entirely thrust-bounded and juxtaposed against dolerite on both sides.

Benallt Mine was an extremely complex mine in geological terms, due to the apparent tectonic disruption of a single ore-bed, so that larger ore-zones were created when smaller ones were juxtaposed together by folding, with the mud-stones in between being squeezed out (Groves, 1952). The ores at both the Benallt and Nant mines are broadly similar in textural terms, with relict sedimentary features preserved, including ooidal and pisoidal textures. However, the Benallt ore is more oxide- and silicate-rich in contrast to that at Nant, where the manganese carbonate rhodochrosite was important.

In addition to the fine-grained, silicate-oxide-carbonate ores, which consist of pennantite, jacobsite, hematite, rhodonite, rhodochrosite, collophane and rare strontianite, the deposits are cut by veins and breccia-zones carrying a wide range of minerals, well crystallized in places. Many fine specimens were recovered from the underground workings when the mine was active (Bevins, 1994). These include the principal ore minerals, such as pennantite and the magnetic Mn-Fe oxide jacobsite, the gangue barium feldspars celsian and paracelsian (the latter forming striking white, prismatic crystals exceptionally up to 5 cm in length) and the type samples of another barium feldspar, banalsite. A large number of often complex manganese silicates also occur in these veins, including clove-brown alleghanyite, often intergrown with tephroite, in crystals up to 2 cm, cinnamon-brown bannisterite, similarly coloured ganophyllite, bementite, and a number of hydrated silicates, some of which may be secondary, comprising braunite, cymrite (type locality), birnessite and neotocite. Recent significant discoveries include those of Cotterell (2006a) describing the first British occurrence of caryopilite and the first Welsh occurrence of pyroxmangite from Nant Mine, Dossett *et al.* (2007) reporting the first Welsh occurrence of powellite, and Cotterell (2008) describing the first British occurrence of the rare manganese oxide hydroxide feitknechtite at Benallt Mine.

Two zeolite-group minerals are also present, namely harmotome, which occurs as microscopic crystals with barite on banalsite, and natrolite which cements breccia-zones, and formerly yielded excellent crystals, exceptionally up to 5 cm. A number of complex Mn-Fe (Ti) oxides have also been recorded, comprising bixbyite, hausmannite, pyrophanite and the aforementioned jacobsite. Other Mn and Mn-Ba oxides may be secondary and comprise manganite, manganosite, pyrochroite, pyrolusite and romanèchite.

Previously unreported copper mineralization, comprising the secondary minerals chalcocite, native copper and cuprite, with minor malachite alteration, was noted recently occurring in small veinlets in a dark, cherty matrix on one of the tips at Benallt Mine (Bevins and Mason, 1998). The cherty material was almost certainly derived from the volcanic sequence overlying the manganese ore-bed.

Interpretation

The mineralization at Benallt–Nant is extremely complex, although comparison with other mineralized areas in North Wales serves to aid interpretation of the genesis of this diverse assemblage. It is clear from both earlier (Groves, 1952) and more-recent (Brown and Evans, 1989) studies that the original ore deposit consisted of a fine-grained sedimentary horizon comprising carbonates, oxides and possibly silicates of Mn, Fe, Ba and minor Sr. This then underwent a diverse range of changes.

Firstly, severe tectonism modified the morphology of the deposits, leaving the manganese ore as a series of juxtaposed lenses. Secondly, brittle fracturing, and probably concomitant chemical remobilization, resulted in the crystallization of a diverse suite of Mn-, Fe- and Ba-dominated silicates and oxides, as euhedral, coarse-grained crystals in veins accompanied by calcite and quartz. These veins were clearly tensile fractures, as considerable open spaces would have been required for the well-developed euhedral crystals to form. Thirdly, weathering caused modifications in the development of hydrated Mn and Mn-Ba oxides.

Veins, whose chemical composition strongly reflects that of their host rock, are widely reported from the Welsh Caledonides (Fitches, 1987; Mason, 1997). The so-called 'Alpine-type' veins, consisting of quartz, albite, TiO_2 polymorphs and rare-earth-element-bearing minerals, described from the **Manod Quarry** and **Coed Llyn y Garnedd** GCR sites, are interpreted as being the result of localized hydrothermal remobilization and migration of elements from host rock to adjacent tensile fractures, which constituted favourable sites for mineralization. The process resulting in the generation of such veins is interpreted as being operative under low-grade regional metamorphic conditions, varying from simple burial metamorphism through to combinations of regional and dynamic metamorphism connected with regional polyphase deformation (see Bevins and Robinson, 1993).

The fact that the minerals occurring within the veins cutting the deformed manganese ores at Benallt–Nant have compositions which reflect that of the ore itself strongly suggests that these veins may belong to the 'Alpine-type' suite, their different composition merely reflecting the source geochemistry. This interpretation does, however, require detailed assessment, in particular collection of fluid-inclusion data from the Benallt–Nant veins and a comparison made with that already obtained by Starkey and Robinson (1992) from the 'Alpine-type' veins from Prenteg, near Tremadog.

The original genesis of the ore is now interpreted as being of exhalative origin, in a subaqueous environment with hemipelagic sedimentation (Brown and Evans, 1989). This is the same model as was proposed by Bennett (1987) for the Harlech manganese deposit of Lower Cambrian age, and implies that early submarine exhalation of metalliferous brines was of frequent occurrence during Cambrian to early Ordovician times in this part of the Welsh Basin. Brown and Evans (1989) commented on the contrasting ore mineralogy between Benallt and Nant, suggesting that the relative abundance of carbonates at Nant, in contrast to silicates and oxides at Benallt, could reflect the positions of the two sites with respect to the exhalative centre. Clearly, however, further work is required to elaborate upon this model in such a complexly deformed terrain.

The genetic significance of the recently discovered copper mineralization remains to be established. The mineral species present are usually found as supergene replacements of existing chalcopyrite mineralization, for which there is little evidence at this site. However, drilling by the British Geological Survey, near to Tyddyn Meirion, about 350 m south of Benallt (BH 1A of Brown and Evans, 1989), intersected a black chert horizon which, upon analysis, revealed anomalous levels of copper (up to 99 ppm), with an associated Pb (233 ppm) and As (80 ppm) anomaly. This suggests that some base-metal enrichment is present in these cherty rocks, which locally may manifest itself as discrete minerals.

Conclusions

The Benallt and Nant Mines GCR site contains an unusual suite of manganese and barium minerals, including the type locality for a number of new species. In geological, mineralogical and metallogenic terms, the Benallt–Nant manganese ores compromise one of the most complex ore deposits in Wales. Originally deposited from hydrothermal brines exhaled onto the early Ordovician seabed during an episode of volcanism, they have been modified both by intense deformation and by metamorphic remobilization of manganese and other elements, leading to a wide range of rare minerals, sometimes occurring as well-formed crystals in tensional veins

TYLLAU MWN (SH 844 205)

Introduction

Lower Palaeozoic ooidal ironstones, dominated by chamosite, have been worked across a wide area of North Wales where Arenig- to Caradoc-age strata crop out. The ironstones occur typically as discontinuous lenses within shallow-water siliciclastic sequences, and they vary from relatively fine-grained ooids through to coarse pisoids (Trythall, 1989). Alteration, due to low-grade metamorphism, is common and has produced siderite, magnetite, pyrite, stilpnomelane and hematite in varying amounts. At the Tyllau Mwn GCR site (Figure 5.9), both original and metamorphic features can be observed, in contrast with other sites where the ore is either totally altered, obliterating all primary textures, or only slightly affected.

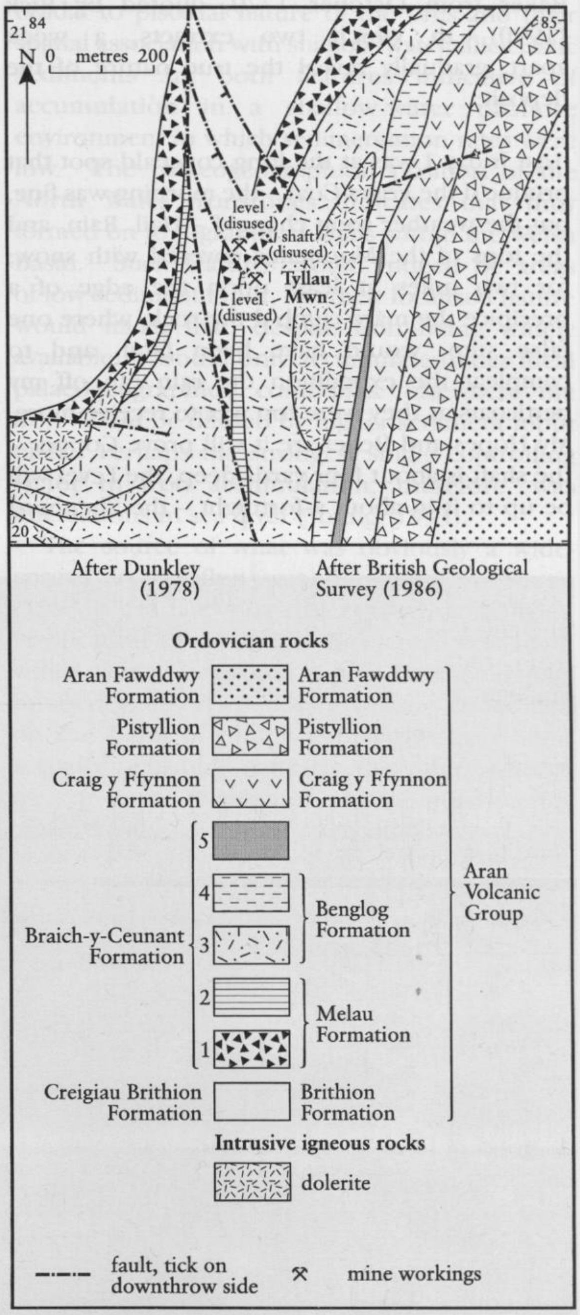


Figure 5.9 Map of the Tyllau Mwn GCR site. Based on Dunkley (1978), and British Geological Survey 1:50 000 Sheet 136, Bala (1986).

Tyllau Mwn mine lies in an extremely remote location at about 600 m OD on the western flank of the Aran Mountains (Figure 5.10). Here, shallow levels and opencuts (Bick, 1990) tried a lenticular mass of ironstone, which lies at a near-vertical attitude. This working, which was initiated in the late 1700s, was originally in search of copper, and there exists a fascinating record of the works in the diary of Elizabeth Baker from October 1770, quoted by Bick (1990), in which two extracts, a week apart, gradually reveal the true nature of the deposit:

'Last friday I was at the long conceald spot that produc'd the Friars Coat – the morning was fine, but the weather soon chang'd – Hail, Rain, and the tops of the Mountains covered with snow; for two miles at least upon the edge of a precipice the mare climb'd the rock, where one false step, would have been fatal, and to compleat the expedition the rain ran off my petticoats as they were too wet to receive more. My Hopes and Belief are it will prove Copper – the shaft is about four yards deep, the Level will be up to it in about a fortnight – the Shepherd told me by an interpreter they had found the stuff that made Gold that morning.'

'Now to the Friars Coat. We have sunk a Shaft five yards, the vein is about four feet wide and continues much like the sample you had from the Day; Ive drove a Level that will be up to the Shaft this week – when I hope to God it may prove a Copper Mine tho' the Magnet acts powerfully on what is raised – Clarksons Assayer was Fool or Knave to assay it for Lead – If it proves Iron and Silver, those are the Metals which constitute what is calld the Friars Coat.'

Perhaps not surprisingly, since the 'vein' was in fact a steeply dipping ironstone bed, little was heard of the site following this brief flurry of activity, until the late 19th and early 20th centuries, when intermittent extraction of ironstone took place. The remote situation must, however, have adversely affected the economics of iron mining, so that it was never of any real importance.

More recently, the site was reported on, following the discovery of well-crystallized stilpnomelane, occurring in calcite veins with fluorapatite, ilmenite and pyrrhotite (Matthews and Scoon, 1964).

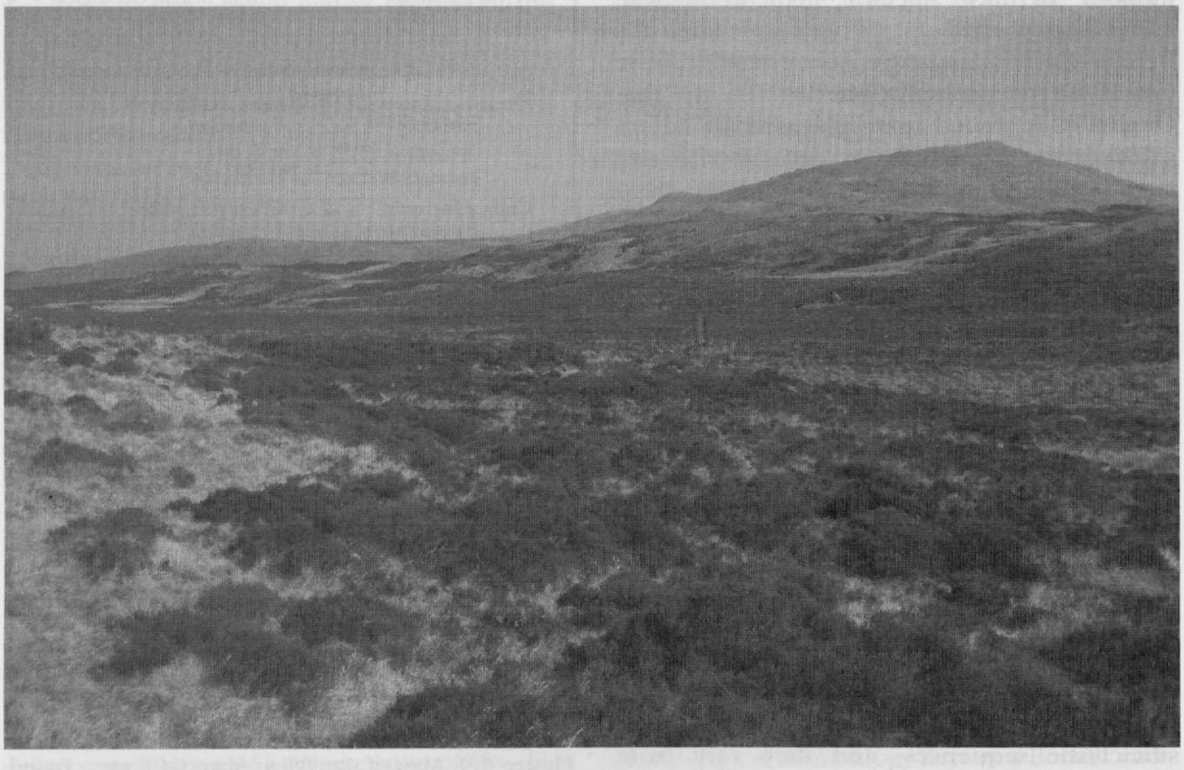


Figure 5.10 Distant view of spoil heaps at the remote Tyllau Mwn GCR site. (Photo: N. Smith.)

Description

The ironstone worked at Tyllau Mwn strikes north-east–south-west and is nearly vertical in attitude. It forms a lenticular mass over 100 m in length and averages 2.5 m in width. It is hosted by volcaniclastic rocks of Ordovician (Arenig–Caradoc) age, which belong to the Aran Volcanic Group. A rhyolite dome intrudes the sequence to the north of the site.

The ironstone, originally composed of chamositic ooids, has been altered by metamorphic processes into a highly distinctive rock consisting of magnetite octahedra (< 0.5 mm) packed in a pale, calcite-rich chloritic matrix. Dissolution of the calcite by rainwater since the mining of the ore has left the lustrous magnetite crystals standing proud from their matrix. In hand specimen, flattened pisoids, up to *c.* 5 mm, are still visible despite the degree of recrystallization.

The iron ore is attractive in polished section where the overprinting of relict chamosite ooids by euhedral magnetite octahedra is well displayed. As well as calcite in the ore groundmass, calcite occurring in veins is abundant on all scales up to an observed maximum thickness of 0.3 m (Matthews and Scoon, 1964). The calcite veins locally carry an interesting and unusual suite of accessory minerals, described in detail by Matthews and Scoon (1964). Stilpnomelane is the principal accessory phase, but it also occurs within the ironstone itself. In the veins, stilpnomelane occurs as plates aligned normal to the vein walls, which reach a maximum size of 20 × 20 × 2 mm. It occurs only in the marginal zones of the calcite veins, however, being absent from centres of the thicker veins. Its colour in thin-section is either yellowish-brown to dark brown (ferri-stilpnomelane) or light apple-green to pale yellow (ferro-stilpnomelane), the ferric variety constituting the bulk of the vein material and the ferrous variety occurring mainly in the ore.

Fluorapatite is also present within the assemblage, occurring as occasional tabular, isolated crystals in the range 1–10 mm in size embedded in calcite. Ilmenite is rare and forms flat rhombs, again 'floating' free in the calcite, while pyrrhotite is quite common, forming both small veinlets within the ironstone and thin strings within the calcite veins, where it is often intergrown with stilpnomelane.

Interpretation

Bedded ooidal ironstones of Ordovician age are widespread across North Wales, individual horizons being laterally persistent over considerable distances. However, they are only of sufficient thickness to be worked in localized areas, typically thinning out rapidly along strike to sub-economic widths (Trythall, 1989). The ooidal to pisoidal nature of the ores and their spatial association with shallow-water siliciclastic sediments are both features indicative of accumulation in a shallow-water offshore environment in which sedimentation rates were low. The palaeogeographical position of the North Wales ironstones indicates that they formed on topographical highs within the Welsh Basin. Such features would indeed be areas of low sediment input, but their localized nature would mean that, despite iron being widely available, it would only accumulate under ideal palaeogeographical conditions: elsewhere the iron would be diluted by higher sediment input rates. Perhaps the strongest single controlling factor in iron accumulation, therefore, was fluctuations in sea level (Young, 1993).

The source of what was obviously a widespread iron influx was discussed by Young (1993). A late diagenetic origin, involving ferrification of an ooidal limestone precursor, which was at one time a popular model (e.g. Kimberley, 1974), is now generally discounted on the basis of evidence that the iron ooids actually existed within the depositional environment. Kimberley (1989) subsequently modified the diagenetic theory to allow iron ooids to be formed directly from iron-rich fluids exhaling onto the seafloor, thereby supplying the metal to the sediment–water interface. Young (1993), however, commented that the topographical highs of the Ordovician seas in which these ores accumulated were extremely unlikely locations for such fluids to be available.

Another possible ore-formation mechanism, discussed by Young (1993), involves the enrichment of iron due to terrestrial weathering at the sediment source and transport of sediments with a high iron content, such as lateritic soils, to the marine environment. This is hard to reconcile, however, with the topographical-high palaeogeographical locations of these deposits, and additionally ooids with internal compositions indicative of a lateritic origin (i.e. iron oxides and kaolinite) have yet to be recorded from any marine ironstones.

Young (1993) considered the most likely genetic model for marine ooidal ironstone formation to be the early diagenetic re-distribution of iron, with the intense weathering of detrital phases and their replacement by authigenic aluminous and ferriferous clay minerals. Such sedimentary reworking would readily occur over the topographical highs of the Welsh Basin sea, where the other requirement, restricted sediment input over protracted time-periods in order to permit lengthy reworking, would be satisfied. Young (1993) suggested that the sedimentary reworking could be both biological and mechanical (e.g. in storms). The time factor is difficult to estimate, but Young *et al*. (1991) suggested a formational period in the order of 100 000 years for the Jurassic Cleveland ironstone, which, although much younger, is of a broadly similar nature to the Ordovician ironstones of North Wales.

The alteration of ooidal ironstone to a magnetite-dominated rock is not uncommon in North Wales. The ironstones occurring at Penyrallt Mine (SH 6285 4093) in the Ffestiniog–Porthmadog belt show the typical pattern of alteration, involving the growth of porphyroblastic magnetite euhedra, while vein stilpnomelane is locally present (Bevins and Mason, 1998). It is likely that this mineralogical alteration occurred on a widespread scale due to regional low-grade metamorphism. Alternatively, Trythall (1989) suggested that some of the secondary minerals (quartz, siderite and pyrite) occurring in the iron ore at Betws Garmon, in Snowdonia, might have been deposited from hydrothermal fluids, although these occur largely in veins, while the magnetite always occurs in the groundmass.

The stilpnomelane-calcite veins at Tyllau Mwn are clearly late-stage features, as they cut and contain clasts of the magnetite-dominated rock. Matthews and Scoon (1964) interpreted them as late, post-metamorphic features, although they noted that no precise data were available regarding the conditions under which they had formed. Their interpretation involved emplacement under low temperatures and hydrostatic pressures, via either an aqueous solution-vapour mix or a vapour. They proposed that stilpnomelane had formed directly from chamosite, while the vein ilmenite and apatite drew their titanium and phosphorus directly from the ore wall-rock.

It is more likely, however, that the Tyllau Mwn veins were formed during regional, burial-related metamorphism, in a similar way to the 'Alpine-type' veins of the Ffestiniog–Porthmadog belt (see **Manod Quarry** GCR site report). Veins with 'Alpine-type' characteristics are present elsewhere in the Aran Mountains area, although they do not contain the wide range of minerals recorded from the Ffestiniog–Porthmadog belt; they chiefly cut silicic, pyroclastic rocks of the Aran Volcanic Group and consist entirely of quartz with pink feldspar (authors' unpublished data). However, they too are interpreted as being formed by localized migration of fluids into fractures in rocks undergoing regional metamorphism, again reflecting the geochemistry of their source rock.

Conclusions

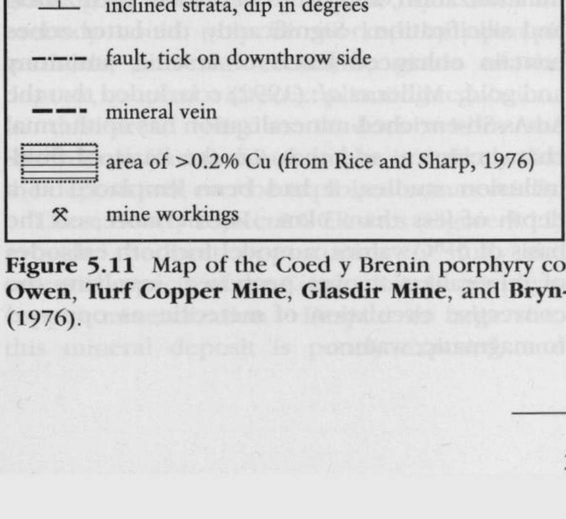
The Tyllau Mwn mine worked low-grade, bedded ooidal ironstones of Ordovician age. The ore deposits accumulated on topographical highs in shallow-water conditions in early to mid-Ordovician times. Originally composed of ooids and pisoids formed from iron-rich clay minerals, they were altered under regional low-grade metamorphism to chamosite-magnetite-rich rocks, the degree of mineralogical evolution being partly affected by the thermal affects of adjacent igneous intrusions. Local veining also formed during metamorphism, the vein constituents being derived from the ironstone host-rock and dominated by stilpnomelane and calcite.

COED Y BRENIN PORPHYRY COPPER SYSTEM

The Coed y Brenin disseminated copper deposit, with its associated breccia pipes, constitutes the best-known example of a porphyry copper system within the British Caledonides and is one of the oldest known examples of this class of deposit worldwide. Various styles of mineralization occur at different structural levels within the system, from mesothermal disseminated Cu-Mo-Au occurring mainly in intrusive rocks, up to high-level, epithermal Au-As-Sb-enriched assemblages occurring in breccia pipes emplaced in the overlying sedimentary succession. It has now been shown that these deposits are all linked genetically.

The Coed y Brenin porphyry copper system lies within the Dolgellau Gold-belt, and comprises the area in, and to the north of, the NE–SW-trending, fault-controlled Afon Wen valley, which is situated approximately 8 km to the NNE of Dolgellau (Figure 5.11). Copper has long been mined in the area, from the numerous 'gold-belt'-type veins (this volume) that are present, and which occasionally carry workable quantities of chalcopyrite, with local, rich concentrations of gold. Alluvial gold has historically been won from the gravels of the Afon Wen (Hall, 1990), while the most important copper producer in the first half of the 19th century was a group of workings situated about the hamlet of Capel Hermon, known as the 'Dolfrwynog Mine'. Several rich pockets of gold were discovered at this site in the 1850s (Hall, 1990), but mining had ceased by the end of the 1860s. However, by this time, the much bigger Glasdir copper deposit was being opened up. At the time, Glasdir was regarded as a 'lode' deposit, and it produced significant quantities of copper and gold in the late 19th and early 20th centuries.

The first allusion to the presence of a much larger disseminated copper deposit in Coed y Brenin came from the observations of Ramsay (1866), who investigated strongly enhanced copper levels in a peat deposit known as the 'Turf Copper' Mine, situated between the valleys of the Afon Wen and Afon Mawddach. This site



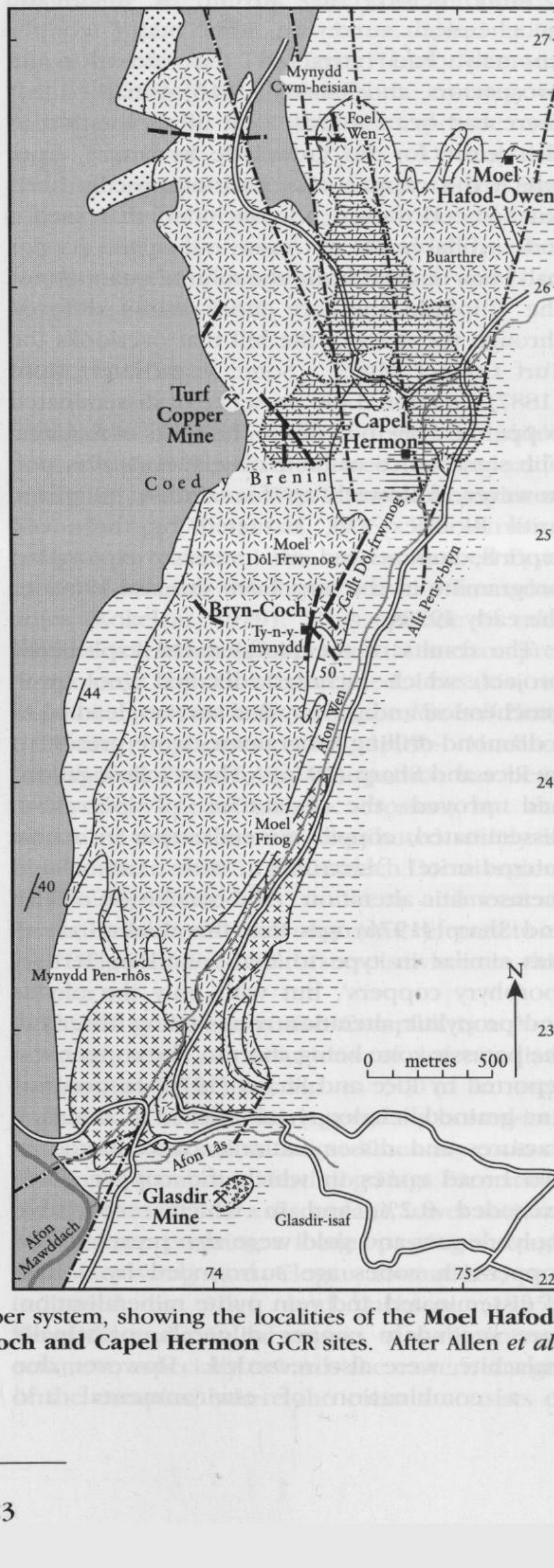


Figure 5.11 Map of the Coed y Brenin porphyry copper system, showing the localities of the **Moel Hafod-Owen**, **Turf Copper Mine**, **Glasdir Mine**, and **Bryn-Coch and Capel Hermon** GCR sites. After Allen *et al.* (1976).

is unique in the British Isles, in that copper-rich peat was exploited by stripping, burning in a kiln and smelting of the ashes thereby obtained. Operations were chiefly conducted in the early 19th century and were highly profitable at times. The richest 'ore' contained leaves and acorns that had been replaced by native copper (Henwood, 1856).

Long before the advent of systematic geochemical surveying, this major copper anomaly had attracted the attention of prospectors, and Ramsay (1866) remarked that there had been a great deal of exploration in the vicinity for the 'great lode, or bunch', from which the copper salts had supposedly been leached. However, he concluded that such a lode probably did not exist: rather, the copper had been derived from 'the minute quantities of the sulphide that are more-or-less diffused through the mass of the hill that overlooks the Turf Copper Mine'. Some years later, Hunt (1887) also noted the presence of disseminated copper-bearing minerals in the rocks of the area. The significance of their observations was not, however, followed up for almost 80 years, until Riofinex Ltd, attracted by these old reports, commenced an intensive exploration programme in the area from the mid-1960s to the early 1970s.

The results of the Riofinex Ltd exploration project, which included detailed geological, geochemical and geophysical surveys, leading to a diamond-drilling programme, were presented by Rice and Sharp (1976). These investigations had proved the existence of pervasive, disseminated, copper mineralization in a host microdiorite laccolith with associated metasomatic alteration. The conclusion of Rice and Sharp (1976) was that this mineralization was similar in type to that found in Tertiary 'porphyry coppers', but with only the phyllic and propylitic alteration zones being observed, the potassic zone being absent. The copper was reported by Rice and Sharp (1976) to occur as fine-grained chalcopyrite blebs in hairline fractures and disseminations, concentrated in two broad zones in which the copper grade exceeded 0.2%, and in which recoverable molybdenum and gold were also present. The copper-rich zones are surrounded by a halo of disseminated and vein pyrite mineralization. Rare secondary copper minerals, principally malachite, were also recorded. However, due to a combination of environmental and economic factors, the deposit has remained unworked.

Allen *et al.* (1976) provided geochemical evidence that showed that all of the microdiorites in the Coed y Brenin area, which they grouped together as the 'Afon Wen Intrusive Complex', have high Cu contents. Geochemical data presented by Allen *et al.* (1976) indicated genesis of the magmas in an island-arc system, and that the intrusions could be correlated with the Rhobell Volcanic Group, of Tremadoc age. Further investigations by Allen *et al.* (1979) showed the extent of microdiorite-hosted copper mineralization to be greater than previously reported, not only to the north and south, but also over the discordant feeder to the intrusive complex.

The intensive research undertaken in the Coed y Brenin area during the 1970s also included a re-interpretation of the Glasdir deposit (Allen and Easterbrook, 1978). The 'lode' at Glasdir was described by Allen and Easterbrook (1978) as a disseminated sulphide deposit occurring at the margin of a breccia pipe intruded into the Upper Cambrian Ffestiniog Flags Formation, the ore-grade zone taking the form of a flattened, inverted cone. A number of other, similar but unmineralized, breccia pipes were also described from the area by Allen and Jackson (1985). At the same time, a fluid-inclusion study of the mineralization within the gold-belt area in general concluded that the mineralization associated with the Coed y Brenin porphyry copper system was distinct from, and earlier than, the gold-belt veins (Shepherd and Allen, 1985).

More-recent investigations of the Coed y Brenin deposits were undertaken by Miller *et al.* (1991, 1992), and Miller (1993). Two styles of mineralization were noted by Miller *et al.* (1991), comprising weak stockwork, veinlet and disseminated copper-dominated sulphide mineralization, and zones of intense pyritization and silicification. Significantly, the latter zones contain enhanced levels of arsenic, antimony and gold. Miller *et al.* (1992) concluded that the Au-As-Sb-enriched mineralization has epithermal characteristics, and that, on the basis of fluid-inclusion studies, it had been emplaced at a depth of less than 3 km. Furthermore, on the basis of $\delta^{18}O$ values, a model for both episodes of mineralization was proposed, involving the convective circulation of meteoric, as opposed to magmatic, waters.

Four GCR sites represent the disseminated, porphyry-type copper deposit, its genetically related mesothermal to epithermal representatives, and its geochemical effects (see Figure 5.11). The porphyry-type mineralization can be seen in its unweathered state at Bryn-Coch, while ore-grade mineralization that has undergone moderate supergene alteration is exposed at the closely adjacent Capel Hermon area; these two areas together comprise the **Bryn-Coch and Capel Hermon** GCR site. At the **Glasdir Mine** GCR site, copper mineralization occurs in a contemporary volcanic explosion breccia pipe, while at a high structural level, epithermal Au-As-Sb-enriched pyrite mineralization in a siliceous sinter-like environment is magnificently exposed at the **Moel Hafod-Owen** GCR site. Finally, the remobilization and reprecipitation of copper in the near-surface environment in Holocene times is demonstrated at the **Turf Copper Mine** GCR site. This network of sites is unique in the British Isles, and superbly demonstrates the range of primary and secondary mineral deposits associated with a porphyry copper deposit and its subsequent alteration.

BRYN-COCH AND CAPEL HERMON (SH 744 246, SH 748 253)

Introduction

The existence of low-grade, disseminated mineralization in the Coed y Brenin area had been remarked upon by Ramsay (1881), but it was nearly a century later, following a systematic and detailed modern exploration programme, that drill targets were established. The drilling, often through thick drift, proved a zone of potentially ore-grade copper mineralization, comprising about 200 million tons grading at 0.3% Cu, with accessory molybdenum and low-grade gold (Rice and Sharp, 1976). Such an orebody could only be worked by open-pit methods, and the economic grade of the deposit, coupled with strict planning regulations in this area, lying as it does within the Snowdonia National Park, make it unlikely that the deposit will ever be exploited commercially.

These closely adjacent GCR sites (Figure 5.11) provide the best opportunity to study the essential aspects of the Coed y Brenin porphyry copper mineralization. Despite its large size, this mineral deposit is poorly exposed, and these forestry road cuttings represent the best examples of porphyry copper mineralization in Great Britain, a deposit that is unusually old (early Ordovician) in global terms. Bryn-Coch is in fact a marginal area to the main Coed y Brenin orebody as defined by Riofinex in the 1970s (Rice and Sharp, 1976), but is of similar grade. At Capel Hermon, the mineralization has been extensively altered by supergene processes, while at Bryn-Coch it may be examined in its unweathered state. The Capel Hermon site was cleared of fallen talus through the courtesy of Forest Enterprise in 1998 and exposure was vastly improved (Figure 5.12). During this clearing operation, the occurrence of the rare copper arsenate tyrolite was noted and subsequently confirmed by X-ray diffraction analysis (authors' unpublished data and also Armstrong *et al.*, 2003).

Description

Low-grade, disseminated copper sulphide mineralization pervades altered microtonalite belonging to the Afon Wen Intrusive Complex of Tremadoc age (Allen *et al.*, 1976). The intrusive complex is related to the nearby Rhobell Fawr subaerial volcano, which was active in Tremadoc times (Kokelaar, 1979). This episode of calc-alkaline volcanism is expressed at surface predominantly by flow-brecciated, basaltic to andesitic lavas and tuffs, as at the *Rhobell Fawr* GCR site (Stephenson *et al.*, 1999). Much of the Rhobell Fawr volcanic sequence has been removed by post-Tremadoc erosion, but the associated intrusions are distributed widely in the Cambrian strata in the Harlech Dome region, particularly around its southern and eastern flanks, in the broad tract of ground referred to as the 'Dolgellau Gold-belt' (see elsewhere in this chapter).

The Afon Wen Intrusive Complex is a N–S-trending suite of intrusions of intermediate composition reaching up to 500 m in total thickness. The complex is generally hosted in a concordant manner within sedimentary rocks of the Upper Cambrian Ffestiniog Flags Formation, but the presence of a discordant, lower section, possibly representing a feeder passing through the Maentwrog and Clogau formations, was indicated by Allen and Jackson (1985). Xenoliths and raft-like masses of sediment are common, especially towards the eastern margin of the complex, where the contact consists of

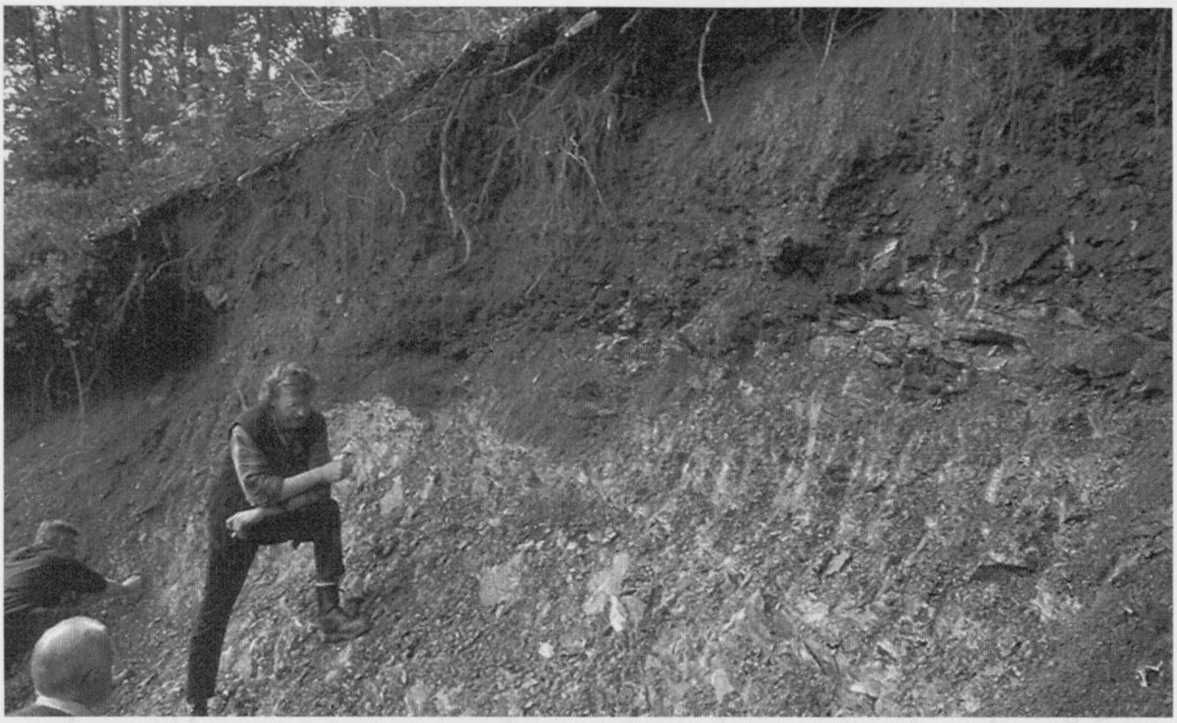


Figure 5.12 Photograph of an exposure of mineralization in the Coed y Brenin porphyry copper system in a forestry track cutting near Capel Harmon, at Capel Hermon. (Photo: R.E. Bevins.)

interfingered intrusive and sedimentary rocks. The western contact is steeply dipping and relatively sharp, a feature taken by Rice and Sharp (1976) to indicate 'forceful emplacement'.

Three principal types of intrusive igneous rocks, all hornblende-bearing diorites, were identified within the Afon Wen Intrusive Complex and described by Rice and Sharp (1976) following the Riofinex exploration programme. Further work by Allen and Jackson (1985) classified the rocks making up the complex as either quartz-microdiorite or microtonalite, both porphyritic in places. Rice and Sharp (1976) considered their 'older diorite' to be the most significant component of the complex in terms of its copper content. However, in the field these rocks are difficult to distinguish, due to the degree of alteration and, as with the other Cambrian-hosted intrusions in the area, they are commonly referred to as 'greenstones'.

Alteration of the various rocks of the Afon Wen Intrusive Complex, which is of the propylitic-phyllic-type, has resulted in the development of rocks consisting of relict phenocrysts of plagioclase and amphibole, often wholly pseudomorphed. The plagioclase crystals are usually replaced by albite, chlorite, sericite, calcite and quartz, while the amphibole crystals are replaced typically by chlorite, epidote, calcite, tremolite, sericite, quartz and titanite. The fine-grained, green-grey groundmass consists of a mosaic intergrowth of feldspar, quartz, calcite, chlorite and epidote (Allen and Jackson, 1985). The maximum intensity of copper mineralization occurs along the western edge of the phyllic zone, as identified by Rice and Sharp (1976), which constitutes the inner part of the porphyry copper system. Here, alteration is dominated by relatively high contents of sericite-quartz-carbonate compared relative to the contents of chlorite and epidote, which are more characteristic of the outer propylitic zone of such systems.

Commonly, porphyry copper bodies show a zonation pattern, with a copper-rich centre and a peripheral zone of intense pyritization, and Coed y Brenin conforms to this pattern. Away from the Bryn-Coch and Capel Hermon GCR site, exposures of pyritized intrusive rocks and sedimentary rocks of the Ffestiniog Flags Formation are common along the forest roads, and a fine example occurs on the road leading up to the **Moel Hafod-Owen** GCR site.

The unweathered primary mineralization of the Coed y Brenin porphyry copper deposit, as exposed at Bryn-Coch, consists of pyrite, accompanied by chalcopyrite, both of which occur as thin veinlets (< 1 mm wide) and as fine disseminations in the host rock. Thin quartz-carbonate veins, generally no more than 1–2 cm in width, occur along joints in the host rock but are laterally impersistent. These carry, in addition to pyrite and chalcopyrite, minor quantities of molybdenite (Rice and Sharp, 1976), and, in the exposure at Capel Hermon, lesser quantities of bornite and tennantite (Armstrong *et al.*, 2003). Molybdenite also occurs as thin, dark-grey, metallic smears on otherwise unmineralized joint-planes, and molybdenum concentrations are in the range 30–50 ppm. Gold is present at low levels (*c.* 0.1 ppm) and its paragenesis is uncertain. All of these ore mineral occurrences are typical of porphyry copper mineralization. Secondary malachite and covellite are locally conspicuous at Bryn-Coch, but are more abundant at Capel Hermon, where a layer enriched in supergene malachite can be seen at the base of the soil profile. In the Capel Hermon exposure, rare azurite and tyrolite (Armstrong *et al.*, 2003) also occur, the latter forming silky blue fans of lath-like micro-crystals to *c.* 1 mm, being an alteration product of tennantite.

Interpretation

The Coed y Brenin deposit, although often cited as the best example of porphyry copper mineralization in the British Isles sector of the Caledonian–Appalachian orogen (e.g. Rice, 1993), is problematic in that in some aspects it does not fit readily into current classification schemes for this important global type of ore deposit. In its setting, ore mineralogy and ore mineral textures, Coed y Brenin is typical of the porphyry copper style of mineralization. However, aspects of alteration assemblages, fluid-inclusion character, host-rock geochemistry and isotopic compositions of the sulphides and alteration phases sometimes conflict, perhaps due to the age of the deposit and the variety of processes that have affected the deposit since its formation. An example of this disparity relates to the K-Ar data obtained from micas in the deposit (Allen and Jackson, 1985), which yield two age populations, namely 409 ± 7 Ma and 374 ± 5 Ma. These ages are too young to be compatible with the geological age of the deposit obtained direct from geological constraints, and therefore must represent later resetting events, during which argon-loss occurred from the micas. A mineral deposit in which such resetting has occurred is likely to have been affected by events resulting in increased temperatures and/or stress, and it is clearly possible that such events could also cause overprinting of other aspects of the deposit.

Fluid-inclusion research by Shepherd and Allen (1985) has shown that sulphide-bearing quartz veins within the porphyry copper deposit were deposited from low-salinity (mean = 8 wt% NaCl equivalent), hot (160°–280°C) fluids, but data from minor quartz veinlets and fractured quartz phenocrysts led Shepherd and Allen (1985) to conclude that the initial Cu-Mo mineralization was deposited from relatively high-temperature, saline fluids. The effects of this initial high-temperature mineralization were subsequently overprinted by retrograde phyllic alteration as the intrusions cooled and the surrounding meteoric convective system collapsed inwards.

Conventionally, a magmatic fluid input is to be expected as an integral part of the process leading to porphyry copper deposit formation. In the case of Coed y Brenin, recent research (Miller *et al.*, 1992), involving a study of oxygen isotope distributions in quartz, has suggested that this may not be the case: $\delta^{18}O$ values from quartz veins within the deposit show a narrow range of values between +10.3‰ and +13.2‰ (SMOW), while combined oxygen and fluid-inclusion data indicate an original $\delta^{18}O$ for the mineralizing fluid of –3.5‰ to 0.0‰ (SMOW). These values, close to those that would be expected for meteoric hydrothermal waters, led Miller *et al.* (1992) to conclude that 'there is clearly no evidence for the involvement of magmatic fluids' in the porphyry copper mineralization.

However, caution is necessary in the selection of mineral samples for isotopic and fluid-inclusion studies, and in particular the paragenetic position of the sample selected should be established without doubt (Mason, 1997). This is a critical factor with quartz veins in a province such as the Dolgellau Gold-belt, which has been subjected to multiple phases of mineralization, regional metamorphism and deformation. In addition to the porphyry-type mineralization, the Coed y Brenin area is rich in gold-belt veins (this volume), which have recently been shown to be of pre-Acadian age

(Mason *et al.*, 1999), and which occur on all scales, from veinlets through to massive quartz sulphide lodes, such as that mined at Dolfrwynog. In addition, there are widespread white quartz-filled gashes which formed at an early stage in the metamorphism and deformation of both intrusive rocks and gold-belt veins, the so-called 'Late-Quartz Veins' of Platten and Dominy (1999), which also locally contain carbonates, sericite, epidote and sulphides. To identify quartz veins which can be confidently associated genetically with the porphyry copper mineralization, rather than with later events, is a difficult problem, which is well illustrated at these two sites.

Data which perhaps better reflect the characteristics of the fluids responsible for the Cu-Mo mineralization were obtained from sulphur isotope analysis in samples of chalcopyrite, pyrite and molybdenite, minerals genetically associated with the porphyry copper mineralization (Miller *et al.*, 1991). Values of $\delta^{34}S$ from these minerals have a range from +1.1‰ to +9.7‰, which are broadly similar to those from sulphides in the Dolgellau Gold-belt veins of −2.5‰ to +11.0‰ (Bottrell and Spiro, 1988). The sulphur isotope data obtained by Miller *et al.* (1991) were interpreted as representing the mixing of fluids containing light igneous and heavy sedimentary sulphur. This would be expected in a hydrothermal system in which permeable clastic sediments were intruded by high-level magmas; the resultant convective cell or cells would allow both late magmatic and abundant meteoric waters to mix and circulate through the sediments and intrusives, mobilizing and re-distributing metalliferous minerals into concentrated ore-zones.

In other parts of the world, zones of supergene enrichment often occur in the upper parts of porphyry copper deposits and carry particularly valuable ore-grades. At Coed y Brenin this zone is missing, and Allen and Jackson (1985) suggested that it was presumably eroded away during Pleistocene glacial activity. This assertion is strongly supported by the occurrence of rare nuggets (up to *c.* 2 cm) of intergrown native copper and cuprite, among the other placer minerals, in the drift-derived alluvium of the Afon Wen, downstream from the porphyry copper deposit (J.S. Mason, unpublished data). Post-Pleistocene supergene processes have superficially affected the deposit in places, such as at the Bryn-Coch and Capel Hermon GCR site, where malachite is present; conditions were clearly less favourable for azurite crystallization. The alteration of tennantite to tyrolite is remarkably similar in style to the supergene mineralization at the **Dolyhir Quarry** GCR site (this chapter), although at Coed y Brenin the supergene assemblage is much simpler.

The continuing supergene mobilization of copper is evident from the geochemistry of stream waters in the area (Rice and Sharp, 1976), and is well illustrated by the **Turf Copper Mine** GCR site, where copper in the native form has been precipitated in the near-surface environment in a peat bog, where the copper replaces organic matter.

Conclusions

The Coed y Brenin porphyry copper deposit, excellently exposed at the Bryn-Coch and Capel Hermon GCR site, is of particular interest since it represents a relatively ancient example of this style of mineralization and is the finest example of such a deposit in Great Britain. As a result of its antiquity, the deposit has been affected by a variety of post-mineralization processes. These include the overprinting of primary assemblages, further episodes of mineralization, regional low-grade metamorphism and deformation.

GLASDIR MINE (SH 740 223)

Introduction

Glasdir Mine GCR site (Figure 5.13), comprising waste tips and a cavernous, part-flooded opencast (Figure 5.14), was at one time the most important copper mine in the Dolgellau Gold-belt, eventually producing over 7000 tons of copper ore concentrates, grading *c.* 10% Cu, with 0.5oz Au/ton and recoverable silver, prior to closure at the outbreak of the First World War in 1914 (Hall, 1990). The ore at Glasdir, consisting principally of fine-grained pyrite and chalcopyrite impregnating host-brecciated sedimentary rocks, was difficult to concentrate using the conventional 19th century technologies, and experiments with oil flotation were carried out as early as the 1890s. In the late 1890s, William Elmore and Sons continued with this experimentation, with the construction of the

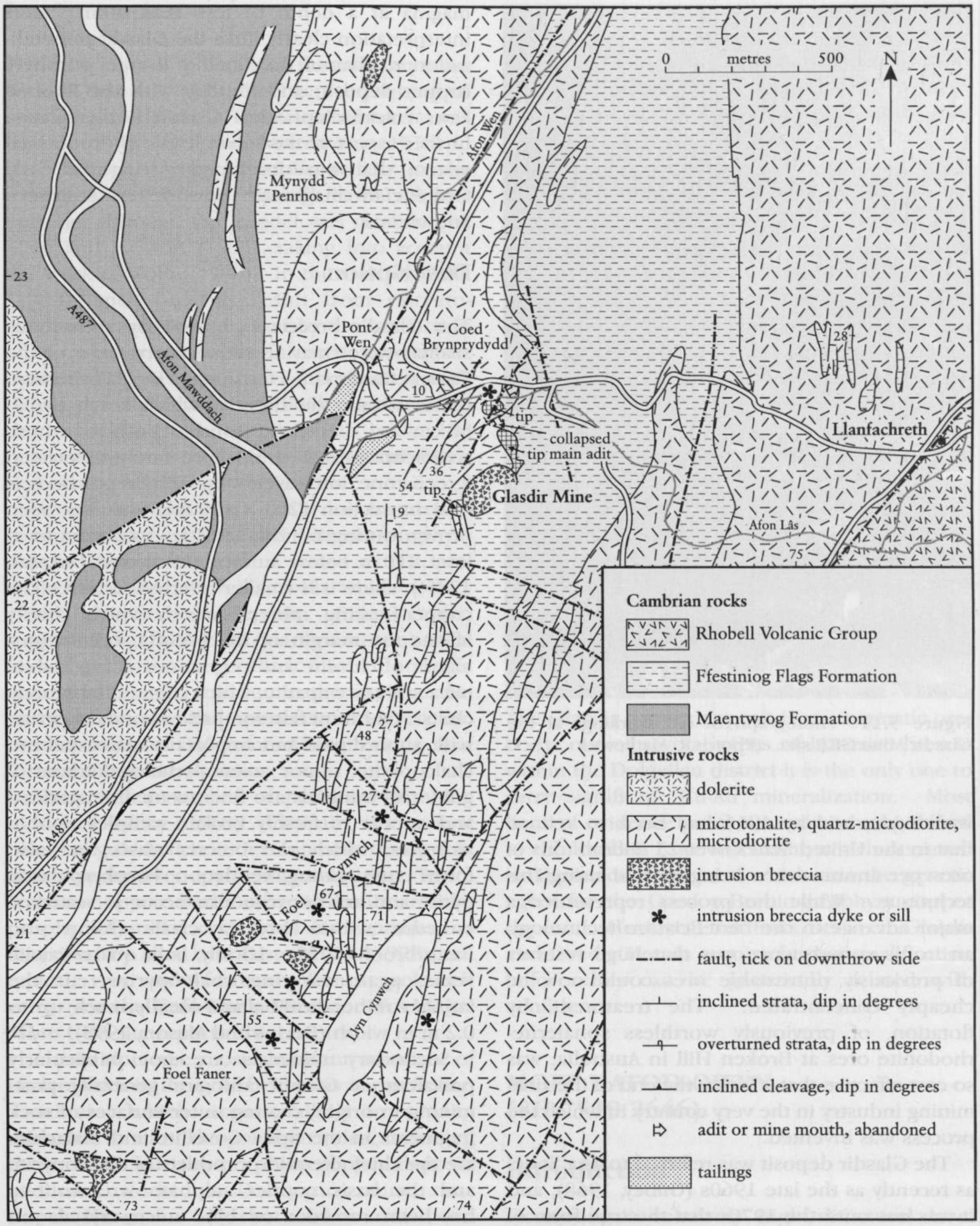


Figure 5.13 Map of the Glasdir Mine GCR site and the locations of other intrusive breccias. After Allen and Easterbrook (1978).

world's first practical flotation plant, inspired reportedly by Frank Elmore's observation that sulphides were adhering to greasy hand prints in areas of the mill circuit where the ore pulp had been splashed (Hall, 1990). This new technology, the Elmore Process, was to be rapidly adopted

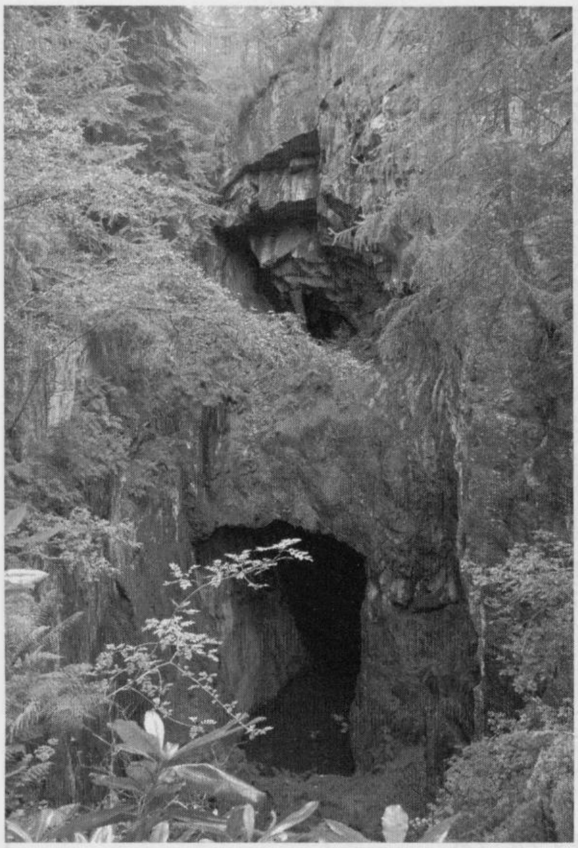


Figure 5.14 Photograph of old workings at the Glasdir Mine GCR site. (Photo: R. Mathews.)

worldwide, and by 1916 had been so refined that in the United States over 25 million tons of ores per annum were being treated using this technique. While the process represented a major advance in ore beneficiation technology, an ironic consequence was that huge reserves of previously untreatable ores could now be cheaply concentrated. The treatment, by flotation, of previously worthless sphalerite-rhodonite ores at Broken Hill in Australia, was so cost effective that it led to the end of the zinc-mining industry in the very country in which the process was invented.

The Glasdir deposit was referred to as a 'lode' as recently as the late 1960s (Gilbey, 1968), and it was not until the 1970s that the true form of the deposit was recognized (Allen and Easterbrook, 1978). Together with a number of other breccia pipes in the Coed y Brenin district, the Glasdir deposit was classified by Allen and Jackson (1985) as an example of an explosion breccia, formed by the violent reaction between large quantities of meteoric waters and hot magma at a depth of less than 4 km. This interpretation clearly links the Glasdir mineralization to that of the Coed y Brenin porphyry copper deposit, and thereby with the Rhobell Fawr volcanic episode. Glasdir is therefore a further aspect of the sub-volcanic hydrothermal system that was developed during the early Ordovician magmatic episode in southern Snowdonia.

Description

The Glasdir breccia is hosted by arenaceous shallow-water marine sedimentary rocks of the Upper Cambrian Ffestiniog Flags Formation. Clasts within the breccia, which reach up to 30 cm in diameter, consist both of these sedimentary rocks and, more rarely, associated 'greenstone' intrusive rocks. The breccia body is oval in section (200 × 100 m), and has been proven during mining activities to persist to at least 210 m below surface (Allen and Jackson, 1985), where it is smaller in cross-section. The copper-bearing mineralization, which chiefly affects the margin of the breccia, occurs in a matrix of chlorite and very minor quartz, white mica and trace apatite, which cement the breccia clasts. Ore minerals comprise abundant pyrite, with subordinate but important marcasite and chalcopyrite, minor arsenopyrite and traces of gold. All minerals are fine- to medium-grained and appear in freshly broken samples as thin stringers, which rim breccia clasts and also form cross-cutting veinlets. Porphyroblastic pyrite and arsenopyrite also occur as scattered euhedra within breccia clasts (Allen and Easterbrook, 1978). Locally, later quartz-calcite veins, again carrying chalcopyrite, cut the stringer mineralization and locally reach up to 0.2 m in width (Bevins and Mason, 1998).

Secondary minerals are not particularly prevalent at Glasdir and are generally post-mining in origin, coating outer surfaces of rock fragments in the tips. Covellite and malachite are the chief alteration products of chalcopyrite and the basic copper sulphate wroewolfeite has been recorded as blue micro-crystals on mudstone associated with malachite (Bevins, 1994). The secondary aluminium-bearing minerals gibbsite and allophane, and the rare basic hydrated calcium silicate-carbonate-sulphate, thaumasite, have also been reported (Bevins, 1994) and are also believed to be of post-mining origin.

Interpretation

The formation of mineralized intrusive breccias, such as that at Glasdir, has been the subject of considerable debate. The Glasdir breccia was considered by Allen and Easterbrook (1978) to have formed during fumarolic activity in the waning stages of the Rhobell Fawr volcanic episode, although that model was modified by Allen and Jackson (1985), taking into account the work of Wolfe (1980). In the view of Wolfe (1980), such breccias result from phreato-magmatic explosions, caused by the interaction of hot magmas with meteoric waters, causing the upward ballistic intrusion of brecciated rock debris. Allen and Jackson (1985) suggested that this model might be applied to Glasdir, but invoked the role of later hydrothermal fluids percolating up through the breccia.

Ore mineralization at Glasdir has features in common with both the Coed y Brenin porphyry copper deposit and, to a lesser extent, the Dolgellau Gold-belt veins, with which Gilbey (1968) classified the deposit. Gilbey (1968) suggested that the lack of quartz, a most unusual feature given that the gold-belt veins are strongly quartz-dominated, was due to the fact that this particular fracture had opened up relatively late in the sequence of mineralizing events that formed the gold-belt veins.

There are a number of problems with the model of Gilbey (1968). Critically, the earliest phase of gold-belt vein development resulted in quartz-pyrite-arsenopyrite mineralization. Pyrite and arsenopyrite both occur at Glasdir, and the porphyroblast-like crystals of both phases, as described by Allen and Easterbrook (1978), are typical, very early features of most gold-belt veins (see the **Cefn-Coch Mine** and **Foel-Ispri Mine** GCR site reports, this chapter).

In addition, the most abundant associate of chalcopyrite in the gold-belt veins is pyrrhotite, a mineral which occurs, albeit in varying amounts, in all of the gold-belt veins, including those which cut the porphyry copper deposit, and were worked at Dolfrwynog mine, near Capel Hermon. Pyrrhotite has not been recorded, either from Glasdir or from the Coed y Brenin porphyry copper deposit. Whether it is genuinely absent, or whether once it was present but has since been altered to pyrite, remains to be determined.

These mineralogical disparities with the gold-belt veins, plus the limited fluid-inclusion data from Glasdir (Shepherd and Allen, 1985) which link the deposit more with the porphyry copper system than with the gold-belt veins, tend to preclude against a common genesis for the Glasdir deposit and the gold-belt veins; rather, Glasdir appears to represent a further facet of the complex hydrothermal system developed around the Rhobell Fawr volcano in Tremadoc times. In particular it re-inforces the idea that this area is anomalous, on a regional scale, not only in Au (Shepherd and Bottrell, 1993) but also Cu and As, so that any localized centres of hydrothermal circulation might be expected to mobilize, transport and concentrate these elements in a variety of parageneses, although critically dependant on local conditions. Thus, the Coed y Brenin porphyry copper and Glasdir pipe mineralization may be genetically related to the same general system, but each with its own paragenetic features; for example As occurs in tennantite at Coed y Brenin but in arsenopyrite at Glasdir. However, further mineralogical work is required on both deposits in order to fully establish their genetic relationship.

Conclusions

The Glasdir copper deposit is an enigmatic ore-body: out of several pipes of intrusive breccia within the Dolgellau district it is the only one to carry significant Cu-Au mineralization. Most lines of evidence point towards it being linked to the Rhobell Fawr volcanism, which occurred in Tremadoc times, and which was the genetic agent for the Coed y Brenin porphyry copper deposit. However, the links between Glasdir and Coed y Brenin require further qualification before they can be genetically related with confidence.

MOEL HAFOD-OWEN (SH 7519 2646)

Introduction

Occupying a relatively high structural level above the Coed y Brenin porphyry copper deposit, the Moel Hafod-Owen site is another example of a mineralized breccia-zone formed during the waning stages of the Rhobell Fawr volcanism. What is of particular interest, however, is the evidence that this breccia represents the root zone of an ancient epithermal fumarolic system. This excellent exposure, forming a prominent boss on the northern side of a forest road, reveals strongly contrasting features between this and the Glasdir breccia (see **Glasdir Mine** GCR site report), situated farther to the south-west, in the Afon Wen valley and lying on the same line of structural weakness.

This site (Figure 5.11) has only been recognized relatively recently, and was not mentioned by Allen and Jackson (1985). Miller (1993) provided a first description of the site, although isotopic data concerning this style of mineralization were presented by Miller *et al.* (1991, 1992). Miller (1993) classified the mineralization, consisting of zones of intense pyritization and silicification enriched in Au, As and Sb, as epithermal in character.

The site is best approached from the west, along the upper forest road that leaves a minor tarmac road *c.* 1 km to the north-west of Capel Hermon. The first section along the road passes through the pyritized halo around the Coed y Brenin porphyry copper deposit, and pyritized sedimentary and intrusive rocks are exposed in frequent cuttings.

Description

The Moel Hafod-Owen breccia (Figure 5.15) is hosted by clastic shallow-water marine sedimentary rocks belonging to the Upper Cambrian Ffestiniog Flags Formation, which constitute the principal host to the Afon Wen Intrusive Complex (Allen *et al.*, 1976) and associated porphyry-style copper mineralization. The shape of the body is difficult to interpret in this exposure, but the breccia appears to form a lenticular pipe-like mass, with sharp, steeply dipping contacts, although the eastern contact is complicated by faulting. The site overlooks the Capel Hermon area, with a view down the markedly linear Afon Wen valley. It is along this lineament, termed the 'Afon Wen Fault' (Allen and Jackson, 1985), that both the Moel Hafod-Owen and the Glasdir mineralized breccia-zones occur.

Additionally, the view to the ESE, across the valley, shows the position of the base of the Rhobell Fawr volcanic succession, which lies unconformably upon the Ffestiniog Flags Formation. An obvious line of crags marks the outcrop of the volcanic rocks. The overall picture is complicated by the Bwlch Goriwared Fault, which has downthrown the volcanic rocks relative to Moel Hafod-Owen, the volcanic rocks therefore lying at a lower topographical level than the Moel Hafod-Owen GCR site.

Figure 5.15 Photograph of the Moel Hafod-Owen GCR site. (Photo: S. Campbell.)

The breccia consists of highly bleached, silicified and pyritized clasts of siltstone and mudstone, set in a mineralized matrix. The mineralization cementing the clasts comprises, in hand specimen, clear to white, locally drusy quartz carrying aggregates of cubic pyrite. In places, quartz and pyrite show rhythmic banding, the pyrite bands being 2–4 mm in thickness, in a crustiform arrangement about the clasts. Some of the quartz has a porous, clinkery appearance, although this is partly due to the dissolution of pyrite by weathering. In general, however, the pyrite is very fresh, and secondary limonite is limited in occurrence, although it is abundant along the eastern, fault-bounded margin. Elevated levels of arsenic, antimony and gold, detected by geochemical analysis, suggest the presence of other ore minerals.

To either side of the breccia, rocks belonging to the Ffestiniog Flags Formation are poorly exposed along the track. Although pyritic, as indeed this formation is in many exposures, they lack the pervasive pyritization seen along the earlier section of the track, being outside the pyrite-halo of the Coed y Brenin porphyry copper deposit. The contrast in hardness between the 'normal' rocks of the formation and the pyritized and silicified variety constituting the breccia is the reason for the relatively high relief of the breccia outcrop and for its boss-like shape.

Interpretation

The most important feature of the Moel Hafod-Owen deposit to be seen *in situ* is the locally developed sinter-like texture, with banded, porous quartz and pyrite formed about silicified and pyritized rock-clasts. Such a feature, combined with the epithermal geochemical signature of the mineralization obtained by Miller (1993), strongly suggests that the mineralization and alteration were developed within an active fumarolic system during the Rhobell Fawr volcanic episode. Sinter-like deposits also occur at the **Parys Mountain** GCR site (this chapter) and are strikingly similar to the Moel Hafod-Owen examples.

Hydrothermal fluids, driven by the convective heat engine of the intrusive complex emplaced beneath the Rhobell Fawr volcano, would, whether of igneous, sedimentary or meteoric origin, be driven upward through the sedimentary pile overlying the intrusive rocks, interacting *en route* with minerals contained within those rocks, and eventually, in some cases, escaping to surface as fumarolic geysers. Such features are common-place in modern-day volcanic terranes, such as in North Island, New Zealand; indeed, excellent exposures of explosion breccias and alteration assemblages at Ohakuri have been linked to hydrothermal activity which ceased only 42 000 years ago (Henneberger and Browne, 1988). Thus the Moel Hafod-Owen breccia is best interpreted as a site where such fumarolic waters have repeatedly pulsed up through an open fracture-system, causing pervasive silicification and pyritization of rock clasts, and depositing siliceous, banded, sulphidic sinter deposits within the open spaces between them.

Miller *et al.* (1991) examined sulphur isotope ratios in pyrite from Moel Hafod-Owen and found them to contrast strongly with those of the host rocks ($\delta^{34}S$ = −3.9‰ to −2.9‰ in pyrite, +15‰ to +20‰ in whole-rock) and also with those of the porphyry copper sulphides (+1.1‰ to +9.75‰). The contrast was explained by Miller *et al.* (1991) to be due to the mixing of igneous- and meteoric-derived fluids; as with the Coed y Brenin porphyry copper deposit, this is perhaps to be expected in such a metallogenic environment, although the contrasting data obtained from the pyritic breccia and porphyry copper mineralization require further consideration.

The Moel Hafod-Owen breccia contrasts strongly with the Glasdir deposit; while Moel Hafod-Owen, with its more epithermal signature, is interpreted as a representative of the same overall system, it is thought to have been emplaced at a higher structural level. In common with Glasdir, however, the site is situated along the line of a major, NNE–SSW-trending structural weakness. This lineament, the Afon Wen Fault, marks the hinge of the tilting and folding which occurred immediately prior to Rhobell Fawr volcanism (Allen and Jackson, 1985) and appears to have been a deep-seated fracture that controlled and channelled much of the hydrothermal activity in Tremadoc times.

Conclusions

The Moel Hafod-Owen GCR site exposes a mineralized breccia-zone that is thought to represent the root zone of an ancient epithermal fumarolic system. This system may well have had a surface expression in the form of fumaroles and geysers, as seen today, for example, on North Island, New Zealand. The mineralization is dominated by pyritization and silicification, and is thought to have developed as part of the Rhobell Fawr volcanic episode in Tremadoc times.

TURF COPPER MINE (SH 741 255)

Introduction

The famous Turf Copper Mine (Figure 5.11) has many features of importance in both metallogenic and environmental terms. Copper, leached since the end of the last Pleistocene glaciation from the nearby 200 million-ton-plus Coed y Brenin porphyry copper deposit, travelled downslope in solution, to precipitate at this site in the native metal form, replacing organic debris in an accumulating peat deposit in boggy, deciduous, woodland, developed over low-permeability glacial drift.

Historically, the peat was dug and burned here so that the ashes could be smelted for their copper content: the operation was said by Henwood (1856) to have been highly lucrative, who had been informed of one year in which 2000 tons of peat ash had been sold at a profit of about £20 000. Most of the work was done early in the 19th century, and Henwood (1856) provided interesting details of the working. The conversion of the peat to ash was done with extreme care to avoid the peat bursting into flames, as the consequent slagging would make the contained copper difficult to smelt. Apart from the peat cutters, all utensils employed in the works had to be made of copper, as iron tools were rapidly destroyed. Ashing of the peat required a slow burn over an 8- to 10-day period, and any peat containing less than 2.5% copper was left undug, being uneconomic at the time.

In geochemical terms, the area remains highly anomalous. The remaining peat and underlying drift still carry very high copper levels and a distinctive copper-tolerant flora has developed, characterized by abundant thrift (*Armeria maritima*), whose pink flowers, usually seen on sea-cliffs, cover the site in early summer. Turf Copper Mine is of major botanical importance and is a key site in the study of metal-tolerant plant communities.

Figure 5.16 Photograph of sea thrift (*Armeria maritima*) growing as a copper-tolerant plant at the Turf Copper Mine GCR site. (Photo: S. Campbell.)

Description

Turf Copper Mine consists of a low-lying, boggy area surrounded by coniferous forest on all sides. Due to the removal of the 'ore', only the residual low-grade peat remains in places; elsewhere the site has been stripped down to the glacial drift. The best time to visit the site is in May or June, when drifts of the copper-tolerant thrift flowers colour the landscape and bear testimony to the anomalous geochemistry (Figure 5.16).

Henwood (1856) visited the site when its workings were still relatively fresh, and he provided a detailed description of the deposit. The peat bed was 'eighteen inches to two feet' in thickness (*c.* 0.45–0.6 m), and lay upon several centimetres of stony debris derived from the local rocks, which evidently included pyritized sedimentary and intrusive rocks. Below the stony layer lay a second peat bed, which was also cupriferous, but not to an economic extent. The peat beds lie on glacial till, which was proved, in the immediate vicinity of Turf Copper Mine, by drilling during the porphyry copper exploration programme, to be greater than 30 m in thickness (Rice and Sharp, 1976).

According to Henwood (1856), the richest part of the deposit occurred at the base of the upper peat bed. Here, the peat, consisting of a mixture of grass and rotten oak and hazel wood, was sometimes dug and sent direct for smelting. In this rich peat, native copper was observed coating leaves, and replacing acorns and hazelnuts: occasionally it preferentially replaced certain layers in wood, so that upon being cut it would exhibit alternating layers of metal and wood.

Interpretation

The origin of the copper impregnating the peat at the Turf Copper Mine site perplexed prospectors for many years, and the slopes around the site are riddled with trial diggings in search of some conjectured 'Mother-Lode', from which the copper was supposed to have been derived. Ramsay (1866), however, gave the first clue as to its genesis by remarking that the rocks in this part of Coed y Brenin contain minor copper mineralization diffused throughout. The mineralization to which Ramsay (1866) was referring is the now-famous Coed y Brenin porphyry copper deposit, seen at the **Bryn-Coch and Capel Hermon** GCR site (see GCR site report, this chapter).

It was suggested by Allen and Jackson (1985) that the original zone of supergene enrichment in the Coed y Brenin porphyry copper deposit had been removed by glacial erosion during Pleistocene times. This would have had the effect of exposing fresh sulphides to weathering agents. Groundwaters would thus have become strongly enriched in leached copper, subsequently re-deposited in a chemically favourable environment within the peat bog at this site, where hollows in clay-rich glacial till impaired drainage. Precipitation of the copper involved complex replacement of humifying organic matter.

The thick overburden proved by the Riofinex drilling programme is worthy of note. Two holes drilled in the Turf Copper area indicated grossly different overburden thicknesses, of 4.5 m and 36.8 m, and further research led to the recognition of a buried valley, running through the area in an approximately east–west direction (Rice and Sharp, 1976). Rice and Sharp (1976) deduced from their data that the upper reaches of the Afon Wen formerly flowed along this valley into the Afon Mawddach approximately 1 km below Ferndale. During Pleistocene times, a glacier flowing southward from the Trawsfynydd ice-divide (Allen and Jackson, 1985), followed the Mawddach valley but overflowed in the narrow section of that valley below Cefn-Deuddwr, forcing moraine up into the palaeo-Wen valley, thereby blocking it. In the post-glaciation environment, the Wen was turned to the SSW to flow along its present, steep-sided valley. The fact that the Turf Copper deposit rests upon the till of the buried valley therefore confirms its post-glacial age.

Several other areas in Coed y Brenin contain peat with high copper concentrations, but they tend to be more restricted in size. A good example is a small tract of bog in a field, *c.* 450 m south-west of Bryn-Coch, but small areas covered in thrift are encountered throughout Coed y Brenin, indicating that copper anomalies are widespread in this pervasively mineralized area.

Conclusions

Recent mobilization of copper, where groundwaters have reacted with highly disseminated bedrock sulphides exposed by glacial erosion, has resulted in the formation of local secondary copper concentrations in the reducing, humic environments of peat bogs in the Coed y Brenin area, the largest example of which constitutes the Turf Copper Mine. The occurrence of a metal-tolerant flora, epitomized by abundant thrift, is of particular note and its use as a geochemical prospecting tool is important.

DOLGELLAU GOLD-BELT

Introduction

Gold is present as an economically significant component of a major series of quartz veins that outcrop in a curved belt of ground to the west and north of Dolgellau, flanking the Harlech Dome. This geographically well-constrained metallogenic province (Figure 5.17) is known as the 'Dolgellau Gold-belt'. The first documented discovery of gold in this part of Wales was in 1843 (Dean, 1845), in contrast to the demonstrably earlier Roman workings at the **Dolaucothi Mine** GCR site. However, the Romans were active militarily in the Dolgellau Gold-belt area, and a major Roman road, Sarn Helen, passes close to a number of gold localities and crosses rivers in which alluvial gold has long been panned (Crew and Musson, 1996).

Initial gold-mining attempts in the early 1850s were met with public scepticism, but following a significant discovery at Clogau Mine, the area experienced a major gold rush, and by 1862 virtually every vein outcrop was being explored, with highly variable results (Hall, 1990). Activity continued apace throughout the latter half of the 19th century and into the early 20th century, during which period 18 mines

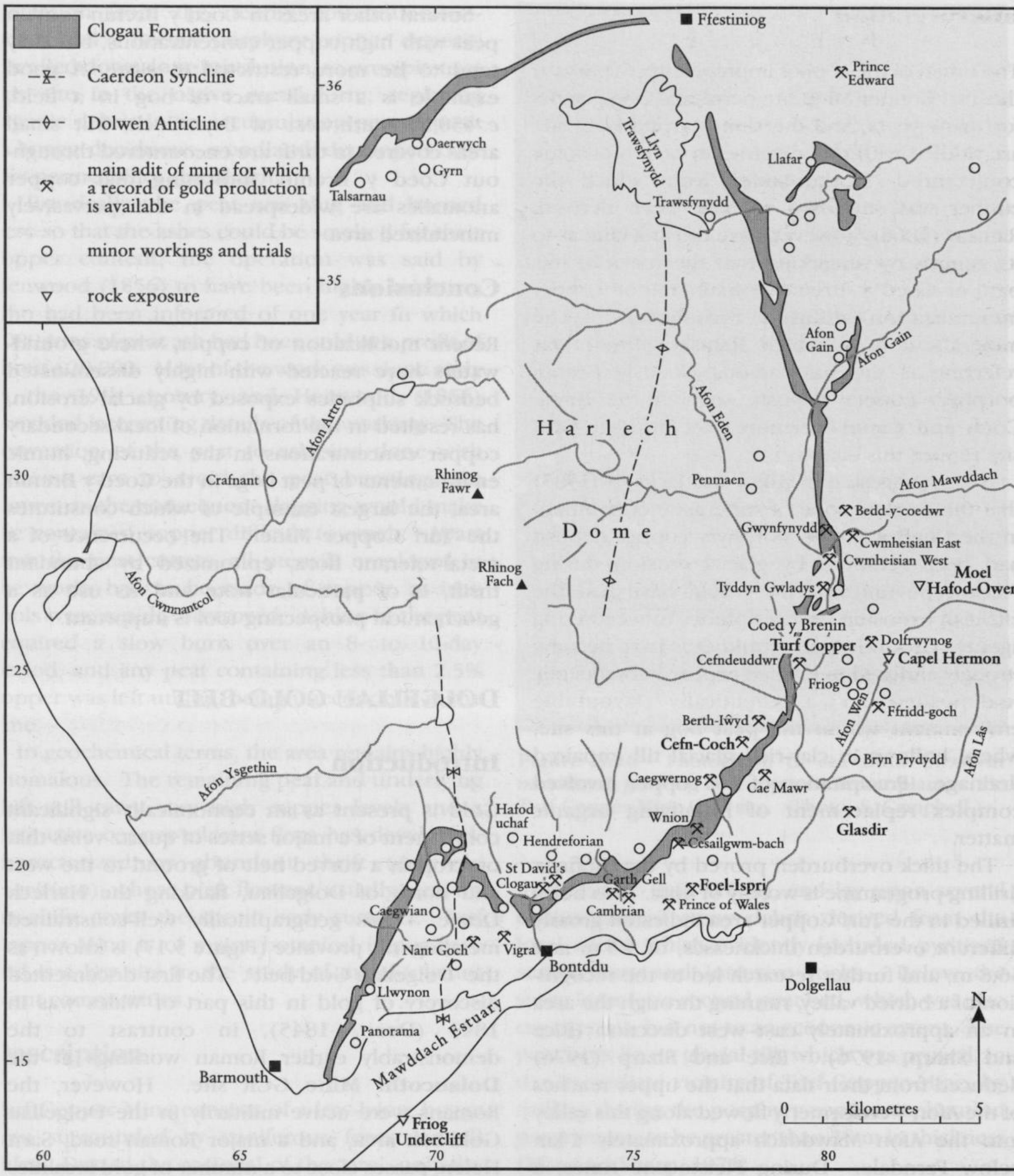


Figure 5.17 Map of the Harlech Dome region, showing the locations of the principal gold mines and the Dolgellau Gold-belt GCR sites. After Institute of Geological Sciences 1:50 000 Sheet 135, Harlech (1982).

yielded approximately 4 tons of gold (Hall, 1990), the majority of production coming from the Clogau and Gwynfynydd mines, near Bontddu and Ganllwyd respectively. Production peaked in 1904, when Clogau Mine produced a record 18 417 oz of gold. The area saw a renaissance in 1931, following Britain's abandonment of the gold standard, but mining again declined with the outbreak of the Second World War. More recently, intermittent operations have been centred on the Clogau and Gwynfynydd mines, the gold being entirely used in specialist, provenanced jewellery. Currently, although the mines are all closed, the area is being re-appraised by an exploration company.

The rocks of the Dolgellau Gold-belt comprise marine shallow-water clastic to deeper basinal hemipelagic sedimentary rocks of Middle to Upper Cambrian age, based on Allen *et al.* (1981), and Allen and Jackson (1985). The area underwent uplift, with local folding, at the end of Cambrian times, prior to the Rhobell Fawr volcanism in early Tremadoc times. The igneous activity, in an island-arc setting (Kokelaar, 1977, 1979), was triggered by south-easterly subduction of ocean floor to the north-west of Wales (Dewey, 1969). The Rhobell Fawr volcanic episode resulted in the subaerial eruption of a thick pile of basic lavas, and these, together with associated autoclastic breccias, lie unconformably upon the eroded Cambrian palaeosurface. Contemporaneous intrusive magmatic phases resulted in the emplacement of a series of dioritic to doleritic dykes and laccoliths (with associated porphyry-type mineralization) and numerous sill-like minor intrusions (Allen and Jackson, 1985). Many of the intrusive rocks have undergone intense hydrothermal alteration to a quartz-calcite-sericite-chlorite-dominated assemblage that gives them a typical green-grey colour (so-called 'greenstones'). The final phase of intrusion resulted in the emplacement of a group of thin basaltic dykes that, in some cases, occupy fissures that have later been re-activated to host gold-belt-type veins.

Following the Rhobell Fawr volcanic phase, the area again underwent uplift and local folding, with movement being centred on the rising Harlech Dome, a basement-controlled crustal block of north–south orientation. This resulted in mélange development on its northern flanks during Arenig to Llanvirn times (Smith, 1987). The folds produced during the pre- and post-Rhobell Fawr episodes trend north–south, an anomalous orientation in the Welsh Caledonides where the pervasive structural trend is north-east–south-west. However, end-Caledonian (Acadian) compression related to the final closure of the Iapetus Ocean (see Woodcock and Soper, 2006) accentuated these earlier structures and imposed more typical NNE–SSW- to NE–SW-trending folds on the Ordovician cover in the east of the area (Allen and Jackson, 1985).

The numerous quartz veins of the Dolgellau Gold-belt form branched and anastomozing zones of mineralization that generally trend in an east–west to ENE–WSW direction and persist over several kilometres of strike length. They vary in width from thin strings up to massive bodies of quartz several metres wide. The veins are generally discordant to bedding, and dips are variable, a feature that is partly due to later deformation. Typically, and especially where hosted by shales, the veins display multiple book-and-ribbon textures, indicative of repeated fissure opening, although massive pods of quartz and breccia cements also occur, particularly where the veins are hosted by competent greenstones or arenitic units. Frequent intra-vein partings, sometimes stylolitic in section, carry abundant sericite and chlorite. Veins are usually 'welded' to their walls, although gouging along some vein walls indicates re-activation of suitably orientated veins as loci for faults. Wall-rocks are variably altered, the most frequent additions being pyrite, arsenopyrite and sericite.

The veins consist of quartz with calcite, chlorite, sericite, sulphides (major pyrite, pyrrhotite, chalcopyrite, galena, sphalerite, arsenopyrite; and minor acanthite, bismuthinite, boulangerite, bournonite, cobaltite, cubanite, matildite, mackinawite, pyrargyrite and tetrahedrite), tellurides (aleksite, altaite, hedleyite, hessite, nagyagite, pilsenite, tellurobismuthite and tetradymite), electrum and gold (Forbes, 1867; Readwin, 1888; Gilbey, 1968; Naden, 1988; Bevins and Stanley, 1990; Bevins, 1994; Mason *et al.*, 2002). The sulphides occur in massive, complex intergrowths enclosed by milky quartz. A generalized paragenetic sequence was described by Gilbey (1968), with initial pyrite-arsenopyrite being succeeded by chalcopyrite-pyrrhotite-pyrite; followed by sphalerite-galena-chalcopyrite-pyrite, with all stages accompanied by the gangue species. More recently, Mason *et al.* (2002) have reported a four-stage paragenetic sequence comprising early Fe-Co-As followed by localized bonanza-style Au-Ag-Bi-Te-Pb mineralization. Stage three is dominated by a Cu-Fe association, whilst the final stage is a Pb-Zn association.

Gold occurs in two generations: firstly as microscopic inclusions in pyrite/arsenopyrite/cobaltite, and secondly as often coarse-grained visible masses associated variably with Bi, Ag and Pb tellurides, Ag-Sb minerals, and/or galena (Gilbey, 1968; Naden, 1988; Mason *et al.*, 2002). The main gold-telluride assemblage is extremely localized within the overall vein environments. Indeed a recurrent problem in mining for gold in this area has been that the bulk gold grade of the mineralization is usually sub-economic, the vast majority of the gold being restricted to localized high-grade 'bonanza-shoots'. For example, at Clogau Mine in 1867, over 500 oz of gold was produced from 'a section of vein six feet long, 4 ft 6 inches high and 9 inches wide' (Hall, 1990). This 'bonanza' was discovered by mining engineer Arthur Dean, who, with an early use of geological modelling, successfully targeted areas in which the veins passed from a greenstone host into black shale in his search for gold (Hall, 1990). However, the exact mechanism for the development of the localized gold 'bonanzas' is not totally understood, and is the subject of continuing research. Bottrell *et al.* (1988) concluded, from fluid-inclusion studies on samples from Clogau Mine, that the gold was precipitated when externally derived hydrothermal fluids reacted with the wall-rocks (and particularly graphitic horizons within the Clogau and Maentwrog formations), an argument first put forward by Gilbey (1968).

Within the gold-belt there also occurs a generation of veins which are distinctive in their banded, crustiform nature and carry a coarse-grained, mineralogically simple assemblage dominated by calcite (often pinkish), marcasite, sphalerite and galena. These veins are a late-stage feature, and cross-cut the gold-belt-type veins where they intersect them. They are of widespread occurrence, not only in the gold-belt, but also throughout the Snowdonia district.

The emplacement of the gold-belt veins has, until recently, been assigned to a post-Caledonian (early Devonian) mineralizing event, based largely on K-Ar ages of 410 ± 13 Ma to 390 ± 12 Ma obtained from wall-rock micas (Allen and Jackson, 1985). The interpretation of the K-Ar data was influenced by the inference that the gold-belt veins were emplaced after end-Silurian deformation because the veins cut across the trends of axial traces and cleavage.

Data obtained from fluid inclusions and isotopes of sulphur, oxygen and hydrogen (Bottrell and Spiro, 1988; Bottrell *et al.*, 1988, 1990; summarized by Shepherd and Bottrell, 1993) pointed towards a metamorphic origin for the mineralizing fluids of the gold-belt. An estimate of the P–T conditions of formation of the gold-belt veins (Bottrell *et al.*, 1988) was given as 1.8 ± 0.3 kbar at 320° C. The mineralizing fluids, it was proposed, were produced during deep groundwater permeation during the final stages of uplift of the Harlech Dome.

In those studies, it was inferred that the emplacement of the gold-belt veins post-dated the timing of peak metamorphism. The metamorphic peak was put at 420–400 Ma, quoting Fitch *et al.* (1969). However, with regard to the timing of peak metamorphic P–T conditions, it has been argued by Bevins and Rowbotham (1983), and Robinson and Bevins (1986) that the metamorphism of the Lower Palaeozoic strata in parts of the Welsh Caledonides was directly related to depth of burial, the metamorphic grade increasing downwards through the stratigraphical column. Indeed, the values for conditions of formation of the gold-belt veins quoted above (Bottrell *et al.*, 1988) could represent the lowermost greenschist metamorphic conditions that would have affected the Cambrian rocks of the area. However, in the Dolgellau Gold-belt, with its polyphase history of uplift throughout the Lower Palaeozoic, the point in time when burial depth (and hence metamorphic grade) reached a maximum is not known. It cannot, however, be assumed that burial metamorphism peaked coincidentally with the Acadian deformation and strain-related metamorphism to which the K-Ar data of Fitch *et al.* (1969) pertain. Additionally, the K-Ar isotope systems upon which this age range was based would, in all likelihood, have been reset by the Acadian deformation, thereby losing the isotopic signatures of earlier metamorphic processes.

The problem of K-Ar resetting in micas during tectonic disturbance also applies to the model ages of the gold-belt veins presented by Allen and Jackson (1985). In fact, isotopic data discussed by Bottrell *et al.* (1990) suggested that isotopic disequilibrium between quartz and calcite in the gold-belt veins was the product of a widespread resetting event after the formation of the veins. Additionally, it was suggested by Fitches (1987) that the relationship of the veins to fold axes does not necessarily mean that they post-dated the Acadian deformation. Given that the main folds within the Dolgellau gold-belt were likely to have been initiated in the phases of uplift associated with the Rhobell Fawr volcanic episode, veins cutting across their axes could in fact have been pre-tectonic with respect to the Acadian deformation. This would make them analogous with the quartz-sulphide veins developed during Caradoc times in the vicinity of the Snowdon Caldera (Reedman *et al.*, 1985), seen for example at the **Lliwedd Mine** and **Llanberis Mine** GCR sites. Indeed, recent work has re-appraised structural evidence superbly exposed at the **Friog Undercliff** GCR site and concluded that the gold-belt veins are, in fact, pre-tectonic in age (Mason *et al.*, 1999).

Three GCR sites have been selected to represent the mineralization of the Dolgellau Gold-belt, namely **Foel-Ispri Mine**, where the sulphide mineralogy of the gold-belt may be readily studied, **Cefn-Coch Mine**, a site which demonstrates the variations in vein textures according to the nature of their host lithology, and **Friog Undercliff**, where wave-cut-platform and cliff-base exposures provide a vast, naturally polished section with critical evidence for constraining the age of the gold-belt veins.

FOEL-ISPRI MINE (SH 703 201)

Description

Despite its rich mineralogy, Foel-Ispri Mine (Figures 5.17 and 5.18) was never a major producer. Gold mining met with little success, producing only 88 oz in the period between 1890 and 1899, and while small quantities of lead and zinc ore concentrates were also produced, the mine was finally abandoned in 1903 (Morrison, 1975; Hall, 1990).

Siltstones and mudstones, locally pyritic, belonging to the Middle Cambrian Maentwrog Formation, are intruded by a number of 'greenstone' sills. Numerous steeply dipping quartz-sulphide veins up to several metres in width transect the succession; the largest vein trends east–west with a change to north-east–south-west at its eastern end, while a cross vein runs down the hillside in a gully-like working. The main vein frequently branches, with intra-vein 'horses' of country rock. The wall-rocks are frequently sericitized, pyritized and arsenopyritized, typical wall-rock alteration features of the gold-belt (Mason *et al.*, 2002).

Massive sulphides occur in large blocks on the waste tips of the mine, and a visual inspection of hand specimens reveals their complexity of intergrowth. The textural complexity of the sulphide mineralization is due at least in part to the deformation suffered by the gold-belt veins during the Acadian folding and cleavage

Figure 5.18 Photograph of the Foel Ispri Mine GCR site. (Photo: R. Mathews.)

development. However, the chief sulphide species characteristic of the gold-belt may all be studied on the macroscopic scale at this locality.

Arsenopyrite and pyrite are both abundant and are early in the paragenesis, occurring as small euhedra in altered wall-rock and in larger aggregates in quartz, close to vein margins; Stage 1 of Mason *et al.* (2002). The second stage in the paragenesis of the overall gold-belt mineralization, here involving gold and tetrahedrite is only locally developed, as evidenced by the small output figure, while Stage 3 resulted in the crystallization of abundant, massive and closely intergrown pyrrhotite and chalcopyrite, the latter containing cubanite and mackinawite inclusions. A further phase of mineralization, Stage 4 of Mason *et al.* (2002) led to crystallization of abundant sphalerite associated with galena, both containing inclusions derived from earlier stages. All stages of mineralization were accompanied by quartz, carbonates, chlorite and white mica.

As noted above, coarse-grained, 'bonanza-shoot' gold was once present at Foel-Ispri, although production figures (Hall, 1990) indicate that it was of extremely localized occurrence. However, some specimens from this mine were preserved during working, and are held in the collections of the National Museum of Wales.

Secondary mineralization, as at most gold-belt sites, is widespread but developed only on a superficial scale. Scorodite is the commonest species present, forming yellowish encrustations on altered arsenopyrite. Iron oxides cement pyritic waste material in places.

Interpretation

The paragenetic sequence pyrite + arsenopyrite, followed by 'bonanza-shoot' mineralization, then by chalcopyrite + pyrrhotite, followed by sphalerite + galena is repeated throughout the Dolgellau Gold-belt, reflecting a phased metallogenic process operating on a regional scale. However, the proportions of the various minerals vary from site to site, suggesting that the degree of vein re-opening during each phase of mineralization varied considerably from one vein to another. Foel-Ispri Mine is one of a small number of sites where all stages of activity are represented.

Two principal gold parageneses, described by Mason *et al.* (2002), are represented at Foel-Ispri. These comprise: microscopic gold associated with early pyrite and arsenopyrite; the second being coarse-grained 'bonanza' gold occurring in limited pockets where it lines microfractures in quartz and may replace pre-existing sulphide minerals.

The age of the veins at Foel-Ispri, and elsewhere in the Dolgellau Gold-belt, is constrained by the Upper Cambrian strata that they cut, and by their Acadian deformation, as revealed at the **Friog Undercliff** GCR site. The mineral assemblages that they contain are in many ways similar to those of the Snowdon Caldera veins (see **Llanberis Mine** and **Lliwedd Mine** GCR site reports, this chapter), which were formed during the waning stages of caldera development in Caradoc times. Within the immediate area of the Dolgellau Gold-belt, major Tremadoc volcanism was genetically associated with porphyry and breccia-pipe metalliferous mineralization (Rice and Sharp, 1976; Allen and Easterbrook, 1978; Allen and Jackson, 1985; Miller, 1993) (see the **Coed y Brenin Porphyry Copper System** GCR site reports, this chapter). By indirect analogy with the Snowdon Caldera deposits, it is not unreasonable to assign the genesis of the veins of the Dolgellau Gold-belt to uplift and unloading of the Harlech Dome during the waning stages of the Tremadoc Rhobell volcanic episode, the mineralizing fluids being derived by burial-related dewatering of Cambrian and older sediments.

CEFN-COCH MINE (SH 717 231)

Description

Mining at Cefn-Coch (Figure 5.17) commenced in the 18th century, when the vein was reportedly tried for lead (Lewis, 1967), but the main phase of activity began in the 1860s gold rush. Since then, the mine produced a recorded 1234.25 oz of gold intermittently over a 49-year period commencing in 1863 (Hall, 1990). Grades varied up to 30 oz Au/ton of quartz.

The mineralization at Cefn-Coch (Figure 5.19) is hosted by sedimentary rocks of Cambrian age, belonging to the Gamlan Formation (of the Lower Cambrian Harlech Grits Group) and the Clogau Formation (of the Middle Cambrian Mawddach Group), which dip to the ESE and lie on the eastern flank of the Harlech Dome. The

Figure 5.19 Photograph of the Cefn-Coch Mine GCR site. (Photo: R. Mathews.)

Gamlan Formation consists of turbiditic siltstones with a coarse quartzose unit, the Cefn Coch Grit Member, occurring near the top. In contrast, the Clogau Formation consists of black carbonaceous and sulphidic mudstones. Sills of altered dolerite ('greenstone') intrude the succession. Two principal veins occur at Cefn-Coch, which both strike north-east–south-west and dip steeply to the north-west. Normal fault movement along the vein-hosted fractures has occurred to a limited extent.

The southern vein, less than 0.5 m wide and hosted entirely by the Clogau Formation, consists of quartz, dolomite and white mica with minor sulphides (galena, sphalerite, chalcopyrite and arsenopyrite), which occur as small, fine-grained intergrowths. The waste tips from the workings on the southern vein are composed of blocks of black shale with classic developments of quartz-dominated ribbon-veining (Figure 5.20). The texture is indicative of repeated phases of fracture re-activation, fluid injection and mineralization. Cut sections from this vein show important additional features, in particular folding in thin cross-veins at right-angles to the main vein, and the development of intra-vein

Figure 5.20 Quartz-dominated ribbon-veining, Cefn-Coch Mine GCR site. (Photo: J.S. Mason.)

stylolitic partings parallel to the vein walls where former thin ribbon-edge veneers of wall-rock occurred. Both features are consistent with the interpretation, based on exposures at the **Friog Undercliff** GCR site, that the gold-belt veins are pre-tectonic with respect to maximum Acadian compression and cleavage development.

The northern vein is a much wider (over 3 m locally), more intensively worked structure. The vein lies partly within the Clogau Formation and associated 'greenstones' and partly along the boundary between the Clogau Formation and the underlying Gamlan Formation. It is recorded (Hall, 1990) that the vein became barren with respect to gold upon entering the flaggy sandstones of the Gamlan Formation. The contrasting textures of the vein mineralization within different host-rocks are clearly demonstrated in this area. Blocks of veinstone on the waste tips show the development, below the Clogau Formation, of massive vein quartz with included brecciated fragments of 'greenstone' and Gamlan Formation turbiditic sandstone.

Sulphides are more abundant in the northern vein and chiefly comprise chalcopyrite, pyrrhotite, pyrite, arsenopyrite, sphalerite and galena. Cobaltite and tellurobismuthite have also been recorded (Gilbey, 1968). As at other gold-belt workings, the sulphides occur in complex intergrowth. Gold is of localized occurrence and was particularly associated with sphalerite (Gilbey, 1968). An old specimen (NMW83.41G.M131) in the collections of the National Museum, labelled 'Cefn-Coch', shows spectacular developments of coarse gold in a quartz matrix with associated sphalerite.

A cross-structure transects the northern vein (but apparently does not displace it) at the site of the old Engine Shaft. Gold was reportedly particularly enriched at this junction (Hall, 1990) and the large amount of stoping undertaken supports this contention. The dumps immediately to the north-east of this major working contain much wall-rock that is heavily impregnated with rhombs of fine-grained arsenopyrite. Oxidation of the arsenopyrite to scorodite is locally intense. Pervasive arsenopyritization is one of the most conspicuous features of wall-rock alteration in conjunction with the development of the gold-belt veins.

Interpretation

Where gold-belt veins traverse varying host lithologies, marked differences in vein texture occur. Veins entirely hosted by black shales tend to exhibit well-developed, composite book-and-ribbon textures. Veins developed within more competent arenaceous facies and in 'greenstones' commonly consist of breccia cements in which the repeated injections of mineralizing fluids during successive fracturing episodes are less clearly demonstrated, although in paragenetic terms the mineral associations and depositional sequences are either similar or identical.

Such features indicate that vein development was strongly influenced by host-rock composition and rheology. Under the extensional tectonic regime in which the regional series of normal fault-hosted veins was emplaced, fracturing was initiated by crustal tension and propagated by the hydraulic action of hydrothermal fluids that readily migrated into the developing fracture-zones (Ashton, 1981). Within the black shales, ribbon-veins, comprising multiple leaves of quartz intercalated with veneers of streaked-out argillite wall-rock, were formed by repeated fracturing accompanied by ductile shear along the wall-rock veneers. In contrast, the more competent arenites and 'greenstones' underwent brittle deformation, including hydraulic brecciation (Phillips, 1972), resulting in the emplacement of vein quartz containing randomly orientated angular rock-clasts.

The impoverishment in terms of gold grade with depth is in accordance with the widely held view that gold-shoots were localized where veins passed through black-shale–'greenstone' contacts. Upon entering the more arenaceous facies of the Gamlan Formation, this critical factor was no longer present, and the gold-shoots died out. The association of gold-rich ore-shoots and black-shale host-rocks is a worldwide phenomenon, and is attributed to constituents particular to the black shales (e.g. graphite, pyrite or pyrrhotite) being capable of precipitating gold from hydrothermal fluids by destabilizing gold complexes in solution. The black shales of the Clogau Formation contain both carbonaceous material and sulphides, and it has been proposed that gold was precipitated by destabilization of the $Au(HS)_2^-$ complex due to reactions between the hydrothermal fluids and constituents of the black-shale wall-rocks (Brand *et al.*, 1989).

FRIOG UNDERCLIFF (SH 610 119)

Description

The coastal section running south from the southern end of the beach at Fairbourne, termed the 'Friog Undercliff', features numerous veins occurring within E-dipping Middle to Upper Cambrian strata on wave-cut platforms and in the water-worn cliff-bases (Figure 5.21). The section comprises, from north to south, pyritic shales and sandstones (Maentwrog Formation), black carbonaceous shales (Clogau Formation), and rhythmically layered semi-distal turbidites with manganiferous segregations (Gamlan Formation). The sedimentary sequence has been intruded by minor sills, generally < 0.5 m in width. These belong to the regional gold-belt suite of intermediate to basic intrusives ('greenstones'), all of which have been pervasively hydrothermally altered, with replacement of the primary igneous assemblage by a secondary assemblage of calcite-chlorite-white mica-quartz.

Veins, ranging from millimetre-scale stringers to massive quartz-carbonate ribs > 2 m in width, occur abundantly throughout the section (Figure 5.22). Textures vary from simple ribs of inclusion-free quartz-carbonate to complex ribbon-rock zones in which multiple veins are separated by thin screens of sheared wall-rock. Quartz and calcite (in places manganoan) are accompanied by abundant sericite and chlorite. Sulphides are patchy in occurrence and are

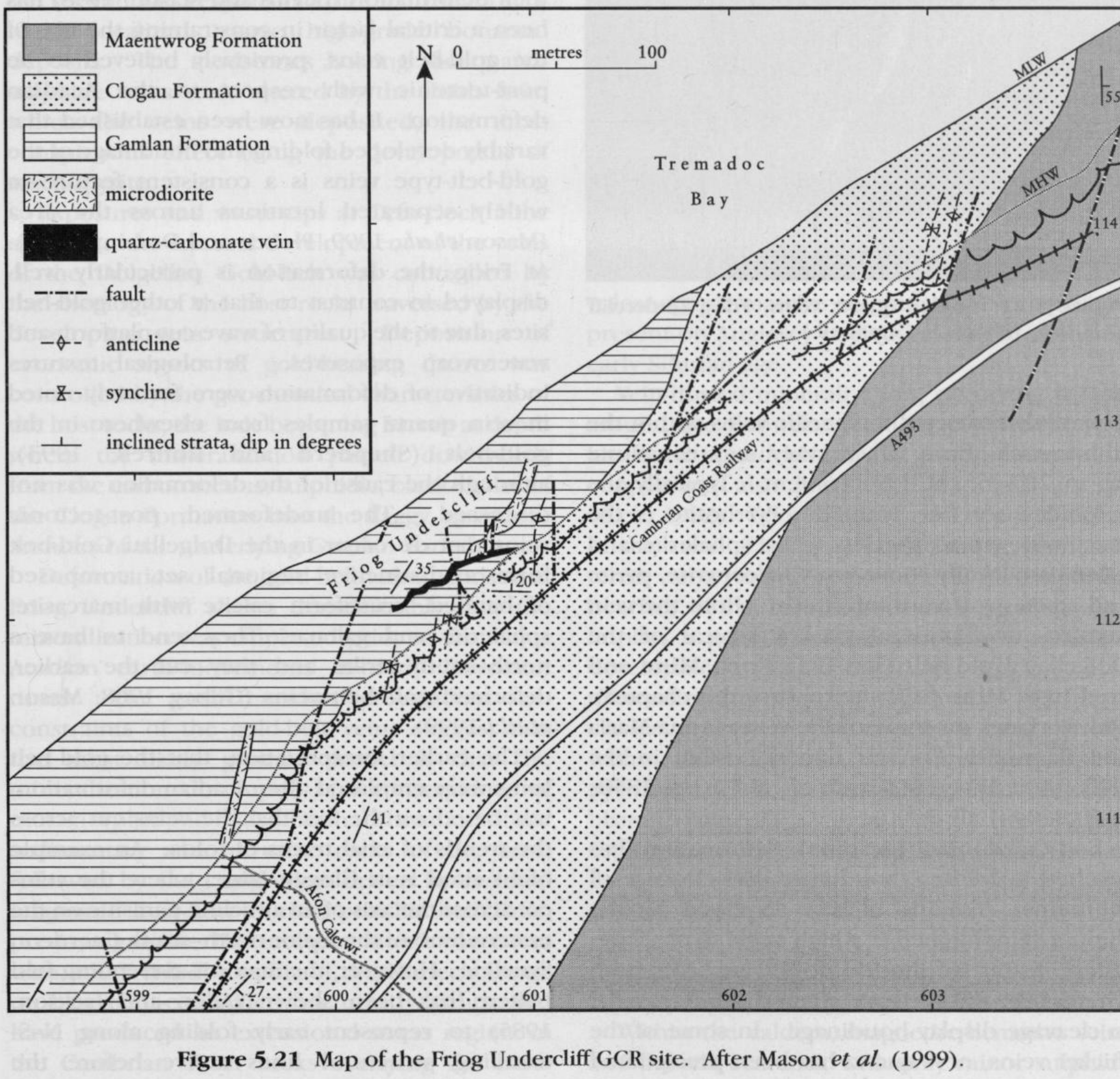


Figure 5.21 Map of the Friog Undercliff GCR site. After Mason *et al.* (1999).

Figure 5.22 Folded quartz veins, Friog Undercliff GCR site. (Photo: S. Campbell.)

frequently restricted to specific veins within the ribbon-rock zones, where they may constitute up to 20% of the vein content. Typically the sulphides are fine grained. Pyrrhotite is the most widespread species, while sphalerite and galena are locally common. Chalcopyrite, pyrite and arsenopyrite are infrequent. Both the vein textures and mineralogy are typical of the Dolgellau Gold-belt (see **Cefn-Coch Mine** and **Foel-Ispri Mine** GCR site reports, this chapter). Old workings on some of the veins (Anna Maria and Barmouth Consols mines), visible in the cliffs, were driven in search of gold in the 1850s and 1860s (Hall, 1990).

End-Caledonian (Acadian) deformation has resulted in folding, boudinage and cleavage of the veins. Folding is best displayed by the thinner veins aligned at a high angle to cleavage, where trains of buckle folds are common, whereas the thicker veins aligned nearly parallel to cleavage display boudinage. In some of the thicker veins, new quartz has been precipitated in the boudin necks (Mason *et al.*, 1999). Cleavage, which is well developed in the argillaceous components of the host rocks, manifests itself in the vein quartz as groups of parallel fractures that are most prominent at fold crests. Locally, the sedimentary rocks have been deformed plastically around the larger, relatively competent veins. Within the veins, ribbons of included wall-rock have commonly been deformed into thin intra-vein partings of sericite and chlorite that, in profile, frequently display a stylolitic texture. In thin-section, vein quartz displays mosaic textures with strain shadows and other signatures of lattice deformation.

Interpretation

The discovery, in 1997, of the Friog veins and their deformation (Bevins and Mason, 1998) has been a critical factor in constraining the age of the gold-belt veins, previously believed to be post-tectonic with respect to the Acadian deformation. It has now been established that variably developed folding and boudinage of the gold-belt-type veins is a consistent feature in widely separated locations across the area (Mason *et al.*, 1999; Platten and Dominy, 1999). At Friog, the deformation is particularly well-displayed in contrast to that at other gold-belt sites, due to the quality of wave-cut-platform and water-worn exposures. Petrological textures indicative of deformation were formerly noted in vein quartz samples from elsewhere in the gold-belt (Shepherd and Bottrell, 1993), although the cause of the deformation was not discussed. The undeformed, post-tectonic veins that do occur in the Dolgellau Gold-belt form a distinctive regional set, composed of banded, crustiform calcite with marcasite, sphalerite and galena. They tend to have a north–south strike and they cut the earlier, deformed gold-belt veins (Gilbey, 1968; Mason *et al.*, 1999).

The earlier interpretation, that the gold-belt veins were emplaced after Acadian deformation, was based on the fact that the veins cut across the trends of axial traces of folds. An example often cited is at Clogau Mine, where the veins cut across the axis of an anticline parasitic on the eastern limb of the major north–south Caerdeon Syncline. However, the major N–S-trending fold pattern has been shown (Allen and Jackson, 1985) to represent early folding along N–S-trending structural lines active before the

Rhobell Fawr volcanism, and accentuated during further, including Acadian, episodes of deformation. Therefore, in places, the gold-belt veins cut across the axial traces of much earlier folds.

Conclusions

Gold has been extracted from quartz veins in the so-called Dolgellau Gold-belt for over 150 years. Abundant, sulphide-rich vein material at Foel-Ispri Mine shows that the gold-bearing quartz veins of the area principally contain arsenopyrite, pyrite, chalcopyrite, pyrrhotite, sphalerite and galena. The minerals typically form massive, complex intergrowths. Two generations of gold mineralization are present: one occurs as microscopic grains in early pyrite/arsenopyrite while the second was responsible for the formation of highly localized, coarse, high-grade 'bonanza' deposits. The mudstones hosting the quartz-sulphide veins were altered by the fluids from which the veins were deposited, the most conspicuous effect being the development of arsenopyrite.

Exposures and waste tips at Cefn-Coch Mine show that the textural development of the veins of the Dolgellau Gold-belt was controlled by the rheology of the host rocks traversed by the developing vein structures. Deposition of economic shoots of gold-bearing quartz was controlled by the geochemical characteristics of the host rocks, the lode becoming barren at depth where the mineralization passed downwards from the carbonaceous, sulphidic, black-shales of the Clogau Formation into the flaggy, quartzose arenites of the underlying Gamlan Formation.

Deformation of the gold-belt veins exposed at Friog Undercliff shows demonstrably that the mineralization was emplaced prior to the major Acadian earth-movements in early Devonian times. The post-Tremadoc, pre-Acadian age-constraints of the gold-belt veins suggest that the most likely genetic model is that the mineralization developed as a consequence of metamorphic and hydrothermal alteration of the sedimentary and intrusive rocks of the area, followed by fluid migration driven by residual magmatic heat-flow during post-Rhobell Fawr, pre-Arenig uplift. This interpretation is consistent with end-Tremadoc uplift of the Harlech Dome on basement-controlled fractures, which would have produced an extensional stress regime in the Cambrian cover rocks overlying the basement of the dome. Under extension and the depressurizing caused by uplift and unloading, fluids would have risen through the Cambrian sedimentary rocks, creating hydraulic fracture-systems and depositing the gold-belt veins. Incremental uplift would have repeatedly re-activated the fractures hosting the gold-belt veins, with the addition of successive quartz-sulphide ribbons, and the development of the paragenetic sequence described for the area.

MINERALIZATION ASSOCIATED WITH CARADOC IGNEOUS ACTIVITY IN NORTH WALES

A range of mineralization occurs in North Wales in direct association with volcanic, pyroclastic and intrusive rocks of Caradoc age (Reedman *et al.*, 1985; Howells *et al.*, 1991). Vein mineralization exposed in and around the Snowdon massif is linked to the development of a caldera which was associated with eruption of a thick volcanic sequence of bimodal acid-basic composition (Figures 5.23 and 5.24). Away from the caldera, a number of other, relatively minor mineral deposits occur in association with Caradoc volcanic rocks, although a major volcanogenic massive sulphide (VMS) deposit is present on Anglesey in a succession of probable early Silurian age.

Vein-hosted mineralization, occurring in and around the Snowdon Caldera of Caradoc age, has been mined historically, predominantly for copper but also locally for lead and arsenic (Bick, 1982). Four types of vein deposits occur in the area. The most important in economic terms is a major series of quartz-sulphide-bearing veins, developed in a setting that implies a genetic association with the caldera development (Reedman *et al.*, 1985). This mineralization may be subdivided into two classes, represented by two GCR sites. Firstly, within the caldera-fill, the veins carry pyrite, pyrrhotite, chalcopyrite, galena, sphalerite and bismuth minerals, as seen at the **Lliwedd Mine** GCR site. Secondly, within older Lower Palaeozoic sedimentary rocks peripheral to the caldera there is a belt of veins of similar mineralogy, but with far more abundant pyrrhotite as well as substantial arsenopyrite, represented by the **Llanberis Mine** GCR site.

Within the caldera, magnetite-hematite veins and breccia cements, with only minor sulphide

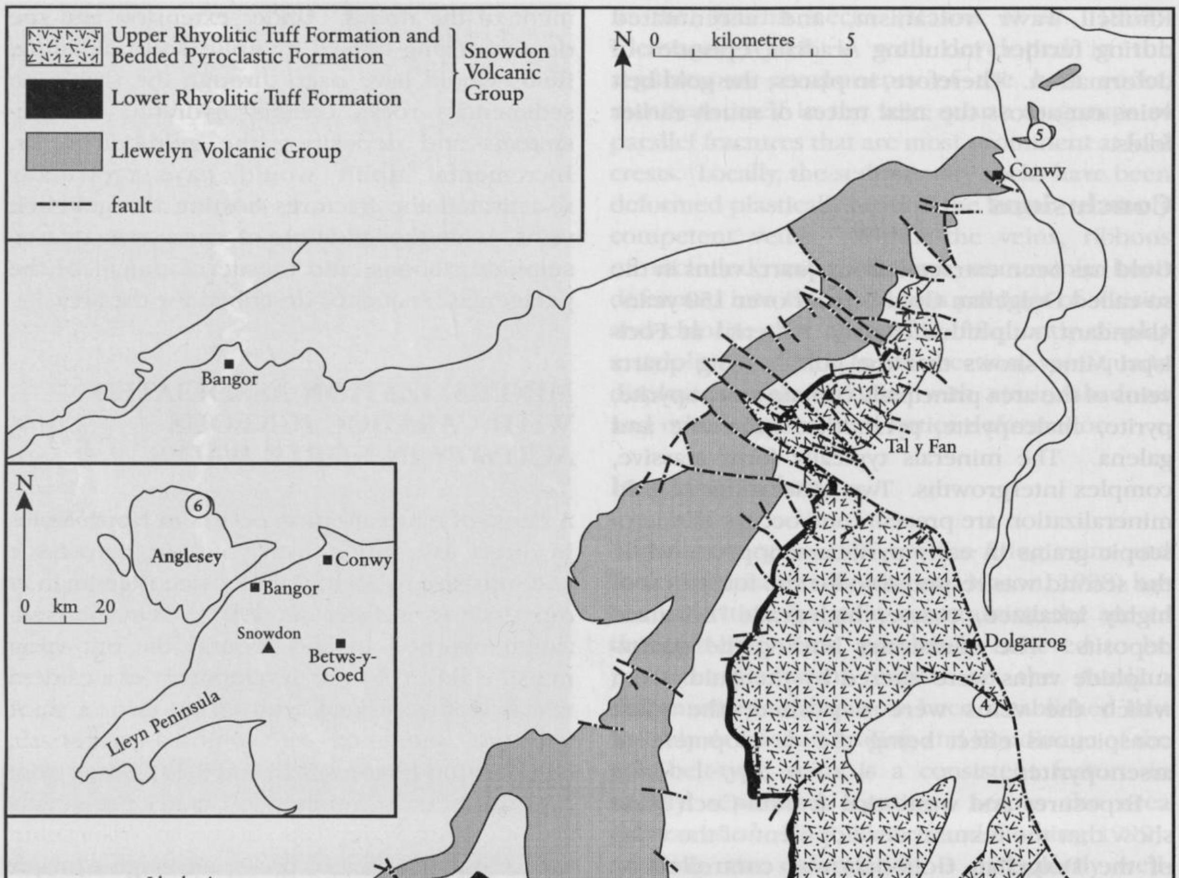


Figure 5.23 Map showing the distribution of the GCR sites in relation to mineralization associated with the main Snowdon Caldera. After Howells *et al.* (1991).

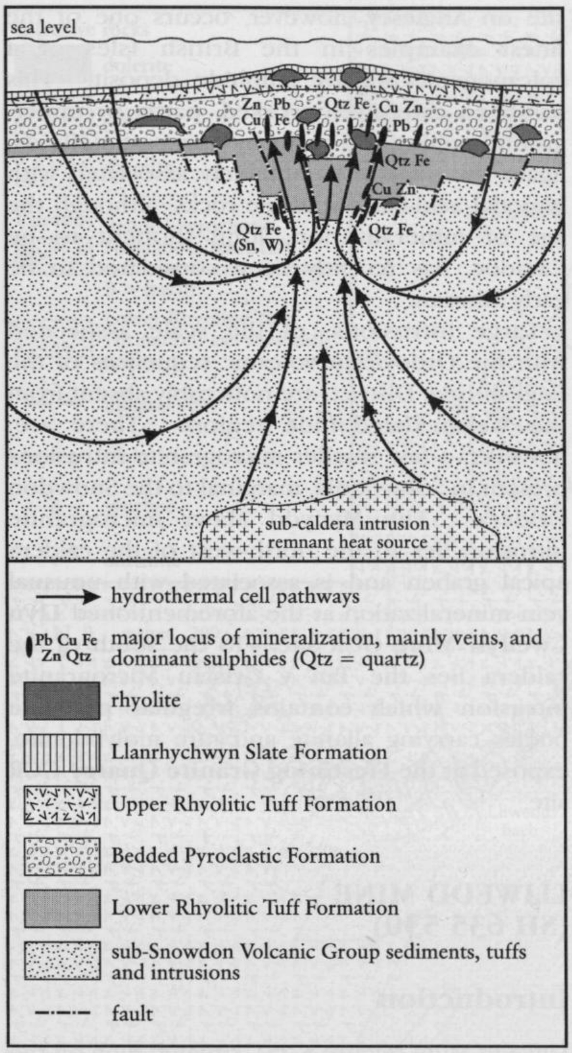


Figure 5.24 Schematic cross-section through the hydrothermal cells responsible for the Snowdon mineralization. After Reedman *et al.* (1985).

content, represent a second type of mineralization. These veins carry minor scheelite and cassiterite, as seen at the **Cwm Tregalan–Shadow Gully** GCR site. Thirdly, an isolated but extremely unusual vein, outcropping to the west of the caldera at the margin of the Mynydd Mawr microgranite and tried at the **Llyn Cwellyn Mine** GCR site, contains fluorite and an associated quartz-carbonate-chalcopyrite-dominated assemblage which includes a number of rare, as yet undetermined, telluride minerals. The fourth type of vein mineralization consists of regional, probably Variscan, crustiform fissure-fill calcite-marcasite veins, although no site shows sufficient genetic importance to warrant GCR status.

The Snowdon Caldera developed in mid-Ordovician times (Howells *et al.*, 1991) within an ensialic back-arc setting (Kokelaar *et al.*, 1984). The products of extensive volcanic activity were deposited within a marine basin in which the predominant pattern of sedimentation involved the accumulation of fine- to coarse-grained siliciclastic sequences. Initial volcanism resulted in the deposition of the Llewelyn Volcanic Group (the '1st Eruptive Cycle' of Howells *et al.*, 1991), which crops out to the north and east of Snowdon. This consists of a number of localized acid to basic volcanic deposits, derived from a set of eruptive centres, with associated intrusive rocks, again with a wide compositional range. Welded ash-flow tuffs in the upper part of the sequence are interpreted as having been erupted subaerially to the north of the area, flowing southward to encounter a marine depositional environment (Howells and Leveridge, 1980: Howells *et al.*, 1985, 1991).

The Snowdon Volcanic Group (the '2nd Eruptive Cycle' of Howells *et al.*, 1991), with which the metalliferous mineralization is genetically linked, is separated from the Llewelyn Volcanic Group by a thick sequence of marine clastic sedimentary rocks. The coarsening of this sequence towards the top indicates a gradual shallowing of the sea immediately prior to the onset of volcanism. At the base of the volcanic sequence, basaltic pillow lavas and hyaloclastites are indicative of submarine eruption.

The Snowdon Volcanic Group is strongly bimodal, lacking the intermediate compositions present in the Llewelyn Volcanic Group. Associated intrusives include dolerites, rhyolites and microgranites, and the volcanic rocks are either acidic or basic. Early major acidic volcanism led to the eruption of the Lower Rhyolitic Tuff Formation. This comprises acidic ash-flow tuffs, rhyolite lavas, and marine sedimentary rocks including slumped or reworked tuffs. The sequence is interpreted (Reedman *et al.*, 1985) as the products of a massive eruptive event involving the production of approximately 60 km^3 of ash-flow tuffs and their ponding within a volcanotectonic depression termed the 'Lower Rhyolitic Tuff Caldera'. The caldera had an estimated surface area of 130 m^2 and was asymmetrical, with the greatest subsidence in the north, where almost 500 m of ash-flow tuffs accumulated. Subsidence, controlled by faulting, occurred primarily around the caldera margin and along a NE–SW-trending apical graben (Beavon, 1980). The lack of intercalated sedimentary rocks within the Lower Rhyolitic Tuff Formation indicates that it was deposited from effectively continuous volcanic activity.

After a break in activity, caldera resurgence occurred with the eruption of the basic volcanic rocks which comprise the Bedded Pyroclastic Formation, consisting of basaltic lavas, hyaloclastites and basic tuffs with associated volcaniclastic rocks containing a shallow-water shelly marine fauna (Reedman *et al.*, 1985; Kokelaar, 1992). Rhyolite domes, representing waning acidic activity and indicating the availability of both acid and basic magmas to the system at this time, locally intruded the Bedded Pyroclastic Formation. Acidic activity finally returned with the eruption of the Upper Rhyolitic Tuff Formation. Following the final cessation of volcanism, the area returned to an environment of marine clastic sedimentation.

The various volcanic and sedimentary rocks underwent Acadian deformation in early to mid-Devonian times, and were folded along a north-east–south-west axial trend, with an associated axial planar cleavage. Metamorphism to lowermost greenschist facies occurred at some time prior to final deformation (Bevins and Robinson, 1988). In addition, with the exception of the crustiform fissure-fill veins, the mineralization was emplaced prior to Acadian deformation, as there is clear evidence for vein deformation (Fitches, 1987).

To the north of Snowdonia, at the **Bwlch Mine** GCR site, near Llandudno, an unusual mineral deposit comprising thin veinlets containing sulphantimonide mineralization occurs in highly silicified, nodular ash-flow tuffs of the Llewelyn Volcanic Group. A number of rare antimony-bearing minerals are present.

At the **Cae Coch Mine** GCR site a massive stratiform pyrite orebody occurring in black mudstones associated with basic lavas and tuffs is thought to represent contemporary volcanic exhalative mineralization, although an alternative syn-diagenetic fluid inhalation model has been proposed. At the **Parys Mountain** GCR site on Anglesey, however, occurs one of the finest examples in the British Isles of a volcanogenic massive sulphide deposit. This has been extensively worked, partly by underground mining and partly by opencast methods. Again the deposit is intimately associated with bimodal acid-basic volcanic rocks, although the age of mineralization, long thought to be Caradoc, has recently been considered to be early Silurian.

Large intrusions, of the scale associated with the Ordovician volcanic sequences of the English Lake District, are noticeably absent from the Welsh Caledonide region. There are, however, a few smaller microgranite intrusions present in Snowdonia, marginal to the Snowdon Caldera. The Mynydd Mawr microgranite intrusion lies to the north-west of the caldera apical graben and is associated with unusual vein mineralization at the aforementioned **Llyn Cwellyn Mine** GCR site. To the south of the caldera lies the Tan y Grisiau Microgranite intrusion which contains irregular pipe-like bodies carrying allanite and rare molybdenite, exposed at the **Ffestiniog Granite Quarry** GCR site.

LLIWEDD MINE (SH 635 530)

Introduction

Lliwedd Mine (Figure 5.25), situated high on the shoulder of Lliwedd, one of the four summits which form the famous 'Snowdon Horseshoe', is one of a group of copper workings in the Cwm Llan district on the southern side of Snowdon, the others being Hafod-y-Llan, Braich-yr-Oen (or Y Geuallt) and Hafod-y-Porth. All these mines worked similar mineralization in a series of veins known as the 'Cwm Llan veins'. Lliwedd, however, is the most representative site because not only is mineralized material abundant in its dumps, but also because the opencut system reveals crucial evidence regarding the geometry of the mineral deposit.

Lliwedd Mine is said to have been first worked in the late 17th century (Bick, 1985), and was worked intermittently, with varying success, throughout the first half of the 19th century, before closing in the late 1860s. Much later, in the early 1900s, the site was re-appraised by the South African Gold Mining Syndicate.

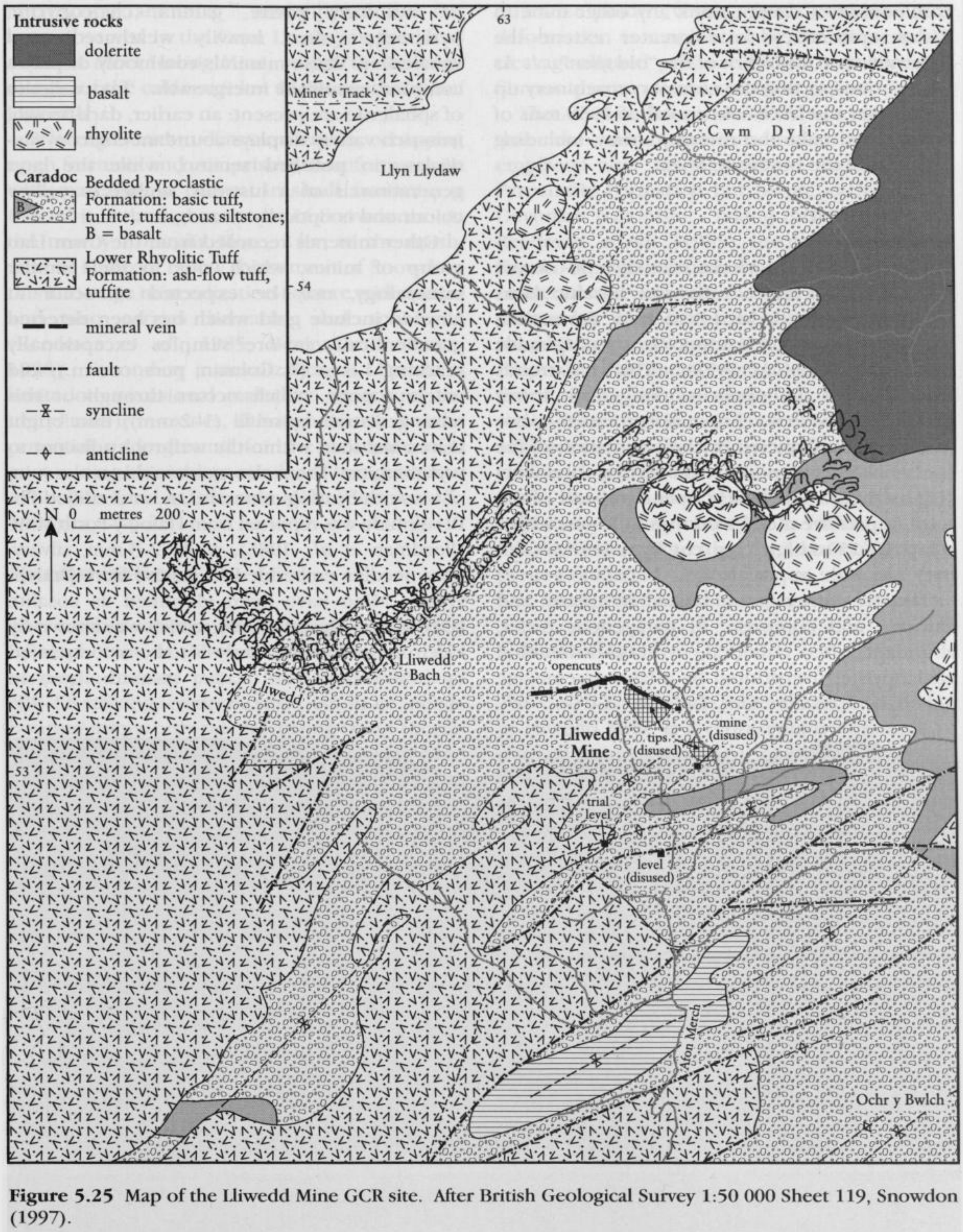


Figure 5.25 Map of the Lliwedd Mine GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

In its working years, ore from Lliwedd Mine was hand cobbed (the extensive areas of finely broken veinstuff bear testimony to this) and crushed on site, using iron roll crushers and a stamp mill. The remoteness of the site, on a steep hillside between 450 m and 600 m OD, and accessible only via a steep, rough cart track, must have caused problems. As Bick (1985) commented: 'I do not think any other mine in Wales epitomizes to a greater extent the determination and spirit of the "old men"....'. As well as transporting the necessary machinery up to the site, the track saw a total of 1938 tons of copper ore make the return journey, including 303 tons in the best year, 1842.

Description

The mineralization worked at Lliwedd occurs entirely within basic tuffs and basaltic lavas belonging to the Bedded Pyroclastic Formation, within the Snowdon Volcanic Group of Caradoc age (Howells *et al.*, 1991). The vein trends ENE–WSW in the upper workings, but lower down the hillside it veers sharply to north-west–south-east, as depicted by the orientation of the spectacular, cavernous, near-vertical opencuts (Figure 5.26). The lowest opencut is one of the most impressive metal-workings in Wales, with a steep 10–15 m-high crag cut by a vertical slot over 2 m wide in places.

The ore minerals are hosted by quartz and chlorite, and comprise, in paragenetic order, abundant, often euhedral, pyrite and anhedral chalcopyrite, overprinted by a later assemblage of colloform pyrite, galena, chalcopyrite, pyrrhotite (often heavily weathered) and sphalerite. These minerals commonly display a complex, emulsoid intergrowth. Two varieties of sphalerite are present: an earlier, dark-brown, iron-rich variety displays abundant chalcopyrite-disease in polished section, while the later generation is of a lustrous, amber to yellow colour and is optically clean.

Other minerals recorded from the Cwm Llan group of mines, which, due to their similar mineralogy, may be expected to occur at Lliwedd include gold which has been detected geochemically in ore samples exceptionally reaching 1.8 g/t (T. Colman, pers. comm.), and native copper, which occurs throughout this mining district as small (1–2 mm), thin bright leaves included within the wall-rock adjacent to vein margins. There also exists in this area a suite of bismuth-bearing minerals; an unidentified Pb-Bi sulphide was reported from Hafod-y-Porth Mine (Reedman *et al.*, 1985), while 2–3 mm, silvery-grey needles embedded in galena from Braich-yr-Oen Mine have been identified as cosalite (Bevins and Mason, 1998), which was shown by electron microprobe analysis to be accompanied by bismuthinite and native bismuth, both in

Figure 5.26 Photograph of the Lliwedd Mine GCR site. (Photo: T. Colman.)

microscopic amounts. Arsenopyrite has not been observed in the Cwm Llan veins, but does occur at Moel Hebog Mine, within the western margin of the caldera, 9 km to the south-west of Lliwedd.

A later generation of mineralization, occupying open fractures and comprising crustiform calcite with marcasite, is present in small amounts, as indeed it is throughout most of Snowdonia. At the nearby Britannia Mine, 2 km to the north-west of Lliwedd, below the summit of Snowdon, this late-stage mineralization is more widespread and also carries hematite and sphalerite (Reedman *et al.*, 1985; Bevins and Mason, 1998). Secondary mineralization at Lliwedd is limited to occasional malachite spots and the ubiquitous iron oxides, although there exists the potential underground for the existence of a post-mining assemblage similar to that described in Sneyd's Level at Britannia Mine (Bevins *et al.*, 1985).

Interpretation

The marked change in strike of the worked mineral vein at Lliwedd is indicative of a conjugate fracture pattern with ENE–WSW- and NW–SE-striking components. At most neighbouring mines only one fracturing trend (north-west–south-east at Britannia, and north-east–south-west at Hafod-y-Llan, Braich-yr-Oen and Hafod-y-Porth) is dominant, yet at Lliwedd there is clear evidence for the mineralization having been emplaced along both structural directions at the same time. The ENE–WSW trend at Lliwedd is somewhat anomalous, as most other veins within this structural set in the area trend north-east–south-west. However, this orientation falls within the field of fault orientations reported along the apical graben of the Snowdon Caldera, which is the structure genetically associated with the mineralization in the current model for emplacement (Reedman *et al.*, 1985).

The model of Reedman *et al.* (1985) is supported by the fact that the veins are pre-tectonic in origin, as demonstrated by Fitches (1987). Both barren minor quartz veins (which are locally extremely common) and the larger, sulphide-bearing veins have suffered deformation, the nature of which varies according to vein orientation, so that veins with an initially high angle to cleavage have been folded, while those in a cleavage-parallel or sub-parallel orientation have been boudinaged. Within the massive quartz-sulphide veins, firm evidence for deformation is manifested by the existence of cleavage-aligned pressure fringes, composed of fibrous quartz, around sulphide grains.

The Acadian deformation of the veins implies that the mineralization must have been emplaced after the deposition of the Bedded Pyroclastic Formation but before early to mid-Devonian tectonism. Taking this into account, Reedman *et al.* (1985) invoked a modified Kuroko-type genesis, involving the hydrothermal convection of seawater through the caldera fill, driven by heat from the high-level magma chamber from which the volcanic sequence was erupted. The metals were leached by these fluids from the surrounding volcanic and sedimentary rocks, and were deposited as sulphides along the fracture system controlling caldera development, at an estimated depth of 2 km. Reedman *et al.* (1985) also suggested that in places such fluids escaped to surface, to form exhalative deposits, citing the Cae Coch massive pyrite-dominated deposit as an example (see **Cae Coch Mine** GCR site report, this chapter).

Conclusions

The Cu-Pb-Zn sulphide mineralization occurring at Lliwedd Mine is a representative example of mineralization developed within the Snowdon Caldera linked to extensive volcanic activity in Caradoc times. Quartz-sulphide veins were emplaced within the caldera along two conjugate fracture-sets trending in a ENE–WSW and north-west–south-east direction, during volcanotectonic extensional movements associated with caldera resurgence at a late stage within the volcanic cycle. Lliwedd Mine is situated along the axial zone of a NE–SW-trending apical graben which developed along the central zone of the caldera.

LLANBERIS MINE (SH 598 586)

Introduction

The rocky hillside overlooking the south-east shore of Llyn Peris is honeycombed with the old workings of the once important Llanberis Mine (Figure 5.27), which is one of a number of mines developed on veins carrying Snowdonia copper-type mineralization, but occurring outside of the Snowdon Caldera area (see Howells *et al.*,

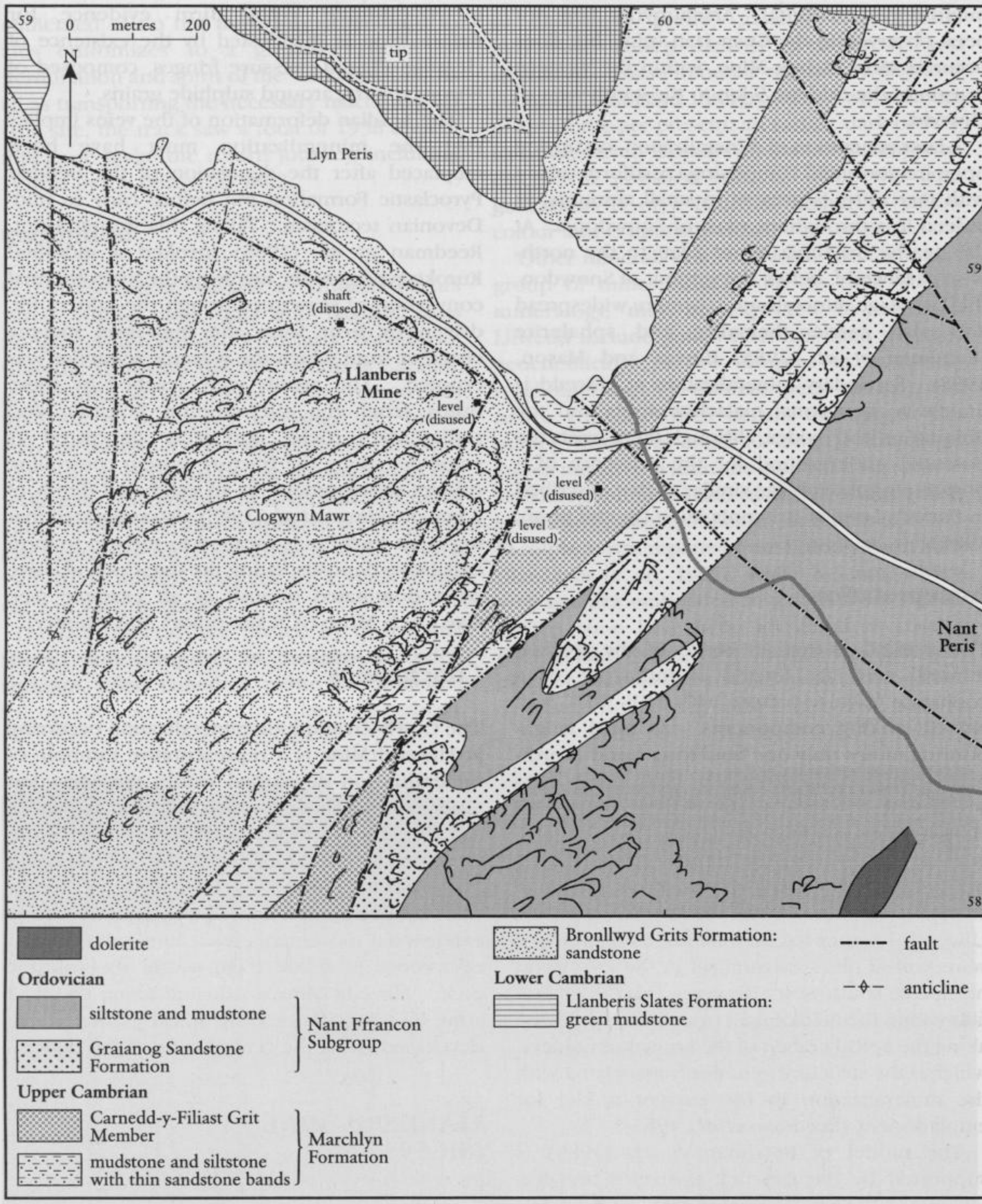


Figure 5.27 Map of the Llanberis Mine GCR site. After British Geological Survey 1:50 000 Sheet 106, Bangor (1985a).

1991). These deposits, in pre-Caradoc rocks, have a mineral assemblage with consistent differences from that within the caldera, possibly reflecting a hitherto unidentified zonation pattern to the Snowdon volcanic-related mineralization.

According to Bick (1982), the Llanberis Mine was commenced around the middle of the 18th century, and Vaynol Estate papers from 1760, described by Bick (1982), indicate that by then work had started in earnest. At this time, the ore was carted down to the valley floor and then conveyed by boat along Llyn Peris, as commemorated in a 1792 watercolour painting by John 'Warwick' Smith. Activity continued into the 19th century, with good results at times; in 1832 ore production amounted to 1169 tons, albeit at an apparently low grade (Bick, 1982). However, by the latter half of the 19th century, the mine was struggling, and in 1873 it fell victim to a share promotion venture, accompanied by glowing reports of the richness of the mine. Although the promotion raised a considerable sum of money, the company went into liquidation in 1885, having sold no ore whatsoever. This was not an unusual pattern in late 19th-century Welsh metal mining, and gave the industry a tarnished reputation from which it never really recovered.

Despite this inauspicious end, Llanberis Mine was one of the more productive of the Snowdonia copper mines, yielding, between 1804 and 1885, 7499 tons of copper ore, the vast majority of which was produced prior to 1847 (Bick, 1982). Production figures for the 18th century remain unknown.

Description

Llanberis Mine (Figure 5.28) lies beyond the north-west margin of the Snowdon Caldera, and the mineralization has been emplaced at a much lower stratigraphical level than that worked within the caldera area, described under the **Lliwedd Mine** GCR site. The mineralization at Llanberis Mine is hosted by W-dipping clastic marine sedimentary rocks, belonging to the Bronllwyd Grits Formation and the Marchlyn Formation, of Merioneth (Upper Cambrian) age (British Geological Survey, 1985a), and approximately equivalent to the Ffestiniog Flags and Maentwrog formations of southern Snowdonia and the Dolgellau Gold-belt. Quartzose grits are a feature of the sequence, and are intercalated

Figure 5.28 Photograph of the Llanberis Mine GCR site. (Photo: R.E. Bevins.)

with mudstones and siltstones. This sequence is the host to a series of quartz-chlorite-sulphide veins up to several metres in width. The steeply dipping veins generally trend WNW–ESE to north-west–south-east, and form an interconnecting network in which the geometry of the open workings suggests that rich sulphide deposits occurred as massive lensoid bodies within the vein structures.

The vein mineralization consists of quartz, accompanied by chlorite and massive sulphides. However, the paragenesis is somewhat different to the veins within the caldera area. Early mineralization comprises abundant rhombic arsenopyrite associated with pyrite. The arsenopyrite and pyrite occur both in vein quartz (which cements clasts of wall-rock) and also as porphyroblastic growths within a chloritized grit matrix. Arsenopyrite-pyrite deposition was followed by pyrrhotite, which is particularly abundant at the south-east margin of the site. Abundant chalcopyrite, associated with traces of sphalerite, occurs in veins in the pyrrhotite, and in addition forms peripheral rims to, and veinlets within, arsenopyrite. Chalcopyrite also occurs as massive aggregates in the quartz-chlorite matrix.

Deformation, which post-dated the vein emplacement, resulted in the development of cataclastic textures in arsenopyrite, while pyrrhotite often occurs with an equigranular mosaic-like texture, a feature suggestive of recrystallization. Secondary mineralization is of restricted occurrence at the surface and is of a superficial nature. Yellow scorodite forms thin coatings on corroded arsenopyrite while pyrrhotite is commonly altered to limonite. Thin, blue to green copper stains are not uncommon on chalcopyrite-bearing veinstone.

Interpretation

The primary paragenesis at Llanberis Mine is representative of a group of pre-tectonic veins which occur around the margins of the Snowdon Caldera within Cambrian and Lower Ordovician strata. They are interpreted here as being connected to the mineralization associated with hydrothermal convection centred on the Snowdon Caldera. This means that they were emplaced at a much greater depth than the intra-caldera veins, occurring stratigraphically more than 500 m below the veins at the **Lliwedd Mine** GCR site.

The arsenopyrite-pyrrhotite-rich paragenesis at Llanberis Mine is characteristic of the veins occurring within these older strata. Other occurrences of the paragenesis occur in the Gwaith–Ceunant area, to the south-east of Bethesda, where arsenic was a mining product (Bick, 1982), in the Drws-y-Coed district, south of the Mynydd Mawr microgranite, at various mines in Cwm Pennant, and to the south-east of the caldera at Moel Fleiddiau (Bevins and Mason, 1998). Proportions of arsenopyrite and pyrrhotite vary: at Blaen-y-Pennant mine arsenopyrite occurs as inclusions in massive pyrrhotite, while at Drws-y-Coed coarse-grained arsenopyrite and massive pyrrhotite are common. Pyrite, chalcopyrite, sphalerite and galena are frequent associated minerals, although the quantities of these minerals vary from minor to major occurrences without any particularly obvious pattern, except that sphalerite and galena seem to be more abundant the further the site is from the caldera margin. As in the caldera area, native copper occurs as flakes within the wall-rock in places.

The distribution and stratigraphical position of this paragenesis strongly suggests that the mineralization in and around the Snowdon Caldera exhibits a pattern of depth, and perhaps lateral, zonation. In this zonation, the deepest-formed veins contain more arsenopyrite and pyrrhotite, while those closer to surface contain more galena and sphalerite, with chalcopyrite and pyrite occurring ubiquitously. However, further work is required to qualify this, in particular examination of crystallization temperatures of the various assemblages, as arsenopyrite-pyrrhotite mineralization passing up into galena-sphalerite-rich deposits is suggestive of a higher-temperature zone existing at depth. This is a reasonable expectation given the model of Reedman *et al.* (1985) for the caldera mineralization, in which the hydrothermal fluids were driven around a convective cell by a magmatic heat source, which would have resulted in a steep geothermal gradient in the Snowdon Caldera and adjacent areas in Caradoc times.

The total extent of the Snowdon Caldera convective hydrothermal system is worthy of examination, for if the proposed model is correct, it extended well beyond the caldera rim, and was operative, as indeed hydrothermal cells tend to be, on a regional scale. Reedman *et al.* (1985) suggested that the Cae Coch massive sulphide deposit, almost 15 km to the north-east of the caldera (see **Cae Coch Mine** GCR site report, this chapter), might represent the same hydrothermal system exhaling onto the seabed. In addition, numerous veins carrying chalcopyrite but dominated by sphalerite and galena occur in Lower to Middle Ordovician strata in the Ffestiniog–Porthmadog belt (see Bevins and Mason, 1998); these are demonstrably pre-tectonic and cut the Tan y Grisiau Microgranite and related intrusions of Caradoc age, as at the **Coed Llyn y Garnedd** GCR site, 4 km to the south-east of the southern margin of the caldera. Clearly, further detailed research is required in order to fully classify the metalliferous vein mineralization of Snowdonia.

Conclusions

The mineralization worked at Llanberis Mine, and at a number of other localities peripheral to the margin of the Snowdon Caldera, was emplaced at a stratigraphically lower level than the caldera-fill mineralization as seen at the **Lliwedd Mine** GCR site. The mineralization is similar to that of the caldera-fill in many respects, but differs in that it contains abundant arsenopyrite, a greater abundance of pyrrhotite, and lesser quantities of Pb-Zn sulphides. These features, observed at many sites peripheral to the caldera, suggest that the mineralization exhibits a degree of depth, and possibly lateral, zonation.

CWM TREGALAN–SHADOW GULLY (SH 612 531, SH 6064 5345)

Introduction

Natural exposures at the head of Cwm Llan reveal an unusual facet of the vein mineralization within the Snowdon Caldera of Caradoc age. While this vein mineralization, described under the **Lliwedd Mine** and **Llanberis Mine** GCR site reports, is sulphidic in nature, at Cwm Tregalan oxide-dominated iron mineralization, accompanied by minor tin and tungsten, is developed.

Mineralization at the head of Cwm Llan (Figure 5.29) was first noted by Williams (1927), who reported 'dolerites' at the locality which were 'rich in copper where purple-coloured in streaks and patches, and include chalcocite, plush-red cuprite and occasional copper-pyrites and malachite'. To date this occurrence has never been confirmed, and it may prove to be more correctly identified as the red to steel-grey hematite, occurring with chlorite among the pillowed basalts immediately underlying the Lower Rhyolitic Tuff Formation in Cwm Tregalan.

The mineralization in this area, noted by Reedman *et al.* (1985), was first described in detail by Colman and Appleby (1991), who reported enhanced tin and tungsten contents, and identified cassiterite accompanying the abundant magnetite of Shadow Gully. Colman and Appleby (1991) also drew the important distinction between these localized deposits and the more typical Cu-Pb-Zn sulphide-bearing veins of the Snowdon Caldera. They noted that the mineralization was pre-cleavage in age, and suggested that the presence of tin and tungsten indicated a magmatic input to the mineralization. More recently, the tungsten-bearing phase from Shadow Gully has been identified by electron microprobe analysis as scheelite (Bevins and Mason, 1998).

Description

Mineralization at Cwm Tregalan–Shadow Gully is developed along syn-volcanic fractures, and the host rocks overlie sandstones rich in detrital magnetite. The host rocks comprise pillow basalts and welded tuffs which lie at the base of the Lower Rhyolitic Tuff Formation of Caradoc age (British Geological Survey, 1997). The mineralization, therefore, occurs at a relatively low stratigraphical level compared to the sulphide-rich veins, which, within the caldera, tend to occur close to the junction between the Lower Rhyolitic Tuff Formation and the overlying Bedded Pyroclastic Formation.

The Cwm Tregalan deposit comprises NW–SE- and NE–SW-trending veins dominated by quartz, hematite and magnetite, often with a banded texture. Veins reach 70 cm in width; thinner veins are often deformed into tight, convoluted folds. Vesicles in the host basalts, where in proximity to the veins, also contain the same mineral assemblage, suggesting that mineralization of the veins and vesicles was synchronous. Coarse-grained, specular hematite (< 2 cm) forms bladed aggregates in milky quartz, accompanied by minor euhedral magnetite in a quartz matrix. In polished section, the magnetite can be seen to have been deposited

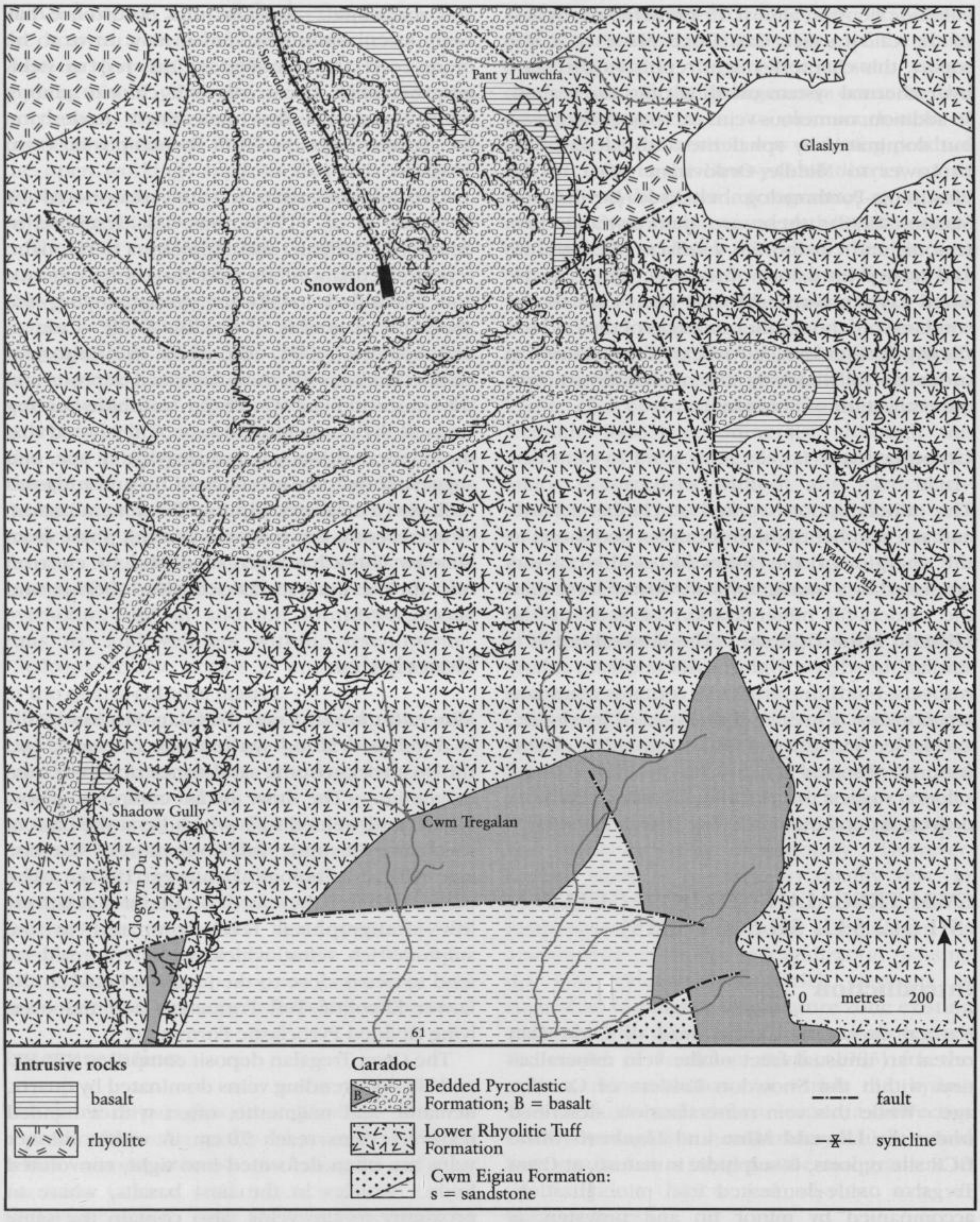


Figure 5.29 Map of the Cwm Tregalan–Shadow Gully GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

after the hematite, locally pseudomorphing it. Chlorite, associated with minor pale-pink to white albite, occurs intergrown with the quartz, while pyrite is a minor, early phase. Secondary alteration has resulted locally in the formation of purplish-red hematite staining.

Shadow Gully is a pronounced NW–SE-trending gully in the crags forming the head of Cwm Tregalan (Figure 5.30), funnelling debris down from the upper slopes. It is floored by brecciated volcanic rocks of the Lower Rhyolitic Tuff Formation, which are cemented by a mineral assemblage similar in some respects to that of the aforementioned vein, but with a number of important additions. The breccia, which is best exposed in the lower part of the gully, is of considerable width, reaching 10 m from wall to wall in places, although it pinches in the upper part of the gully into a network of thinner quartz-magnetite-pyrite veins.

The Shadow Gully mineralization comprises abundant octahedral magnetite up to 2 mm in an interlocking groundmass with occasional areas of quartz and ovoid pyrite growths (the latter replaced by magnetite). Hematite is later in the paragenesis than magnetite, and forms rims on magnetite crystals and thin cross-cutting veinlets, both visible in polished section. Ore microscopy also reveals the presence of minor chalcopyrite, which forms inclusions in magnetite and fills cracks in the pyrite. Cassiterite has been observed as minute inclusions in magnetite, and scheelite occurs as small (80–150 μm) grains interstitial to the magnetite. Secondary covellite forms rims to chalcopyrite crystals, while limonite is a ubiquitous weathering product.

Interpretation

These two spatially close mineral deposits contain an assemblage which is in marked contrast to the quartz-chlorite-sulphide veins within the remainder of the Snowdon Caldera area. The two occurrences are in many respects similar, except that at Shadow Gully, magnetite is earlier and much more abundant than hematite, chalcopyrite is present, and pyrite is relatively common. However, the similarity of the mineralization at both localities led Colman and Appleby (1991) to interpret the two occurrences as facets of the same mineralizing event, with fracture-hosted veins in the pillowed basalts of the Cwm Tregalan locality passing up into mineralized breccia within the Lower Rhyolitic Tuff Formation in Shadow Gully and finally pinching out in the quartz-pyrite-magnetite veins in the upper part of the gully.

The mechanism invoked by Colman and Appleby (1991) for this upward transition was the lowering of the confining pressure as the hydrothermal fluids moved upwards, allowing

Figure 5.30 Photograph of Shadow Gully. (Photo: T. Colman.)

them to permeate rocks of the Lower Rhyolitic Tuff Formation, which were then hydraulically brecciated by the mechanism proposed in the model of Phillips (1972). Colman and Appleby (1991) also commented that it was difficult to draw a comparison with the Cu-Pb-Zn mineralization of the Snowdon Caldera veins, as the two styles of mineralization do not occur in contact with one another.

The breccia cement nature of the Shadow Gully mineralization makes it distinct from the Snowdon Caldera veins, which, albeit locally, do contain clasts of wall-rock, but do not constitute breccia cements *sensu stricto*. Furthermore, the oxide-dominated mineralogy (containing only 2.56 wt% S) and very low levels of base-metals, with maximum recorded values of 35 ppm Cu, 126 ppm Pb and 157 ppm Zn (Colman and Appleby, 1991), contrast markedly with the Snowdon Caldera mineralization, despite Shadow Gully lying little more than 1 km away from the major copper-producing Britannia Mine, situated mainly within the Lower Rhyolitic Tuff Formation to the north-east, on the opposite side of Snowdon summit.

Colman and Appleby (1991) inferred that the elevated levels of tin and tungsten, occurring as cassiterite and scheelite respectively, are suggestive of a direct magmatic input to the mineralization, as are the elevated fluorine contents in the wall-rocks. They suggested that the magnetite-rich sandstones underlying the pillowed basalts of Cwm Tregalan were so different in their magnetite geochemistry to the Cwm Tregalan–Shadow Gully mineralization that the juxtaposition of the two magnetite occurrences was coincidental.

Given that the mineralization at Cwm Tregalan–Shadow Gully is so different from that of the Snowdon Caldera Cu-Pb-Zn veins, and also that it occurs at a lower stratigraphical level, near the base of the Lower Rhyolitic Tuff Formation, it is probable that these oxide-dominated deposits represent a separate and distinct mineralizing event, although whether this event pre- or post-dated the widespread Cu-Pb-Zn mineralization remains to be established.

Conclusions

The oxide-dominated Fe (Sn-W) vein and breccia-zone mineralization of Cwm Tregalan–Shadow Gully is unique within the overall context of the Snowdonia volcanogenic mineralization. The geochemistry of the mineralization suggests that there has been a direct magmatic input, but the age relationship of this mineralization to the more widespread Cu-Pb-Zn vein mineralization within the Snowdon Caldera has yet to be determined, and provides scope for further research.

LLYN CWELLYN MINE (SH 5486 5569)

Introduction

A small trial working on the shore of Llyn Cwellyn (Figure 5.31), only recently described in any detail (Colman, 1990; Colman and Appleby, 1991), is unique in the Welsh Caledonides. A narrow vein, which was prospected by a trial level, lies within the metamorphic aureole of the Mynydd Mawr microgranite intrusion and contains abundant fluorite with subsidiary magnetite. A late-stage injection of quartz-carbonate-sulphide mineralization is also present, and the trial was most likely made in order to assess the copper content of this mineral assemblage. A further unusual feature of this mineralization is that the sulphide assemblage contains a number of Pb- and Bi-bearing telluride phases.

Description

The mineral vein at Llyn Cwellyn Mine (Figure 5.32) is not accessible due to the working being flooded. However, blocks among the tip debris show that it was up to 50 cm in width and the shape of the working suggests a NNW–SSE-striking steep or vertical structure. The host rocks are coarse clastic marine sedimentary rocks belonging to the Upper Cambrian (Merioneth) Marchlyn Formation (British Geological Survey, 1997), situated in a position proximal to the northern margin of the Mynydd Mawr intrusion.

The mineralization comprises early magnetite-pyrite-chlorite aggregates as impregnations of rock clasts, which have a swirling, almost spinifex-like texture in polished section. Massive fluorite, predominantly white but also purple and green, with a purple UV fluorescence, cements the magnetite-bearing clasts. The fluorite is cut and locally brecciated, with a quartz-ferroan carbonate cement which contains

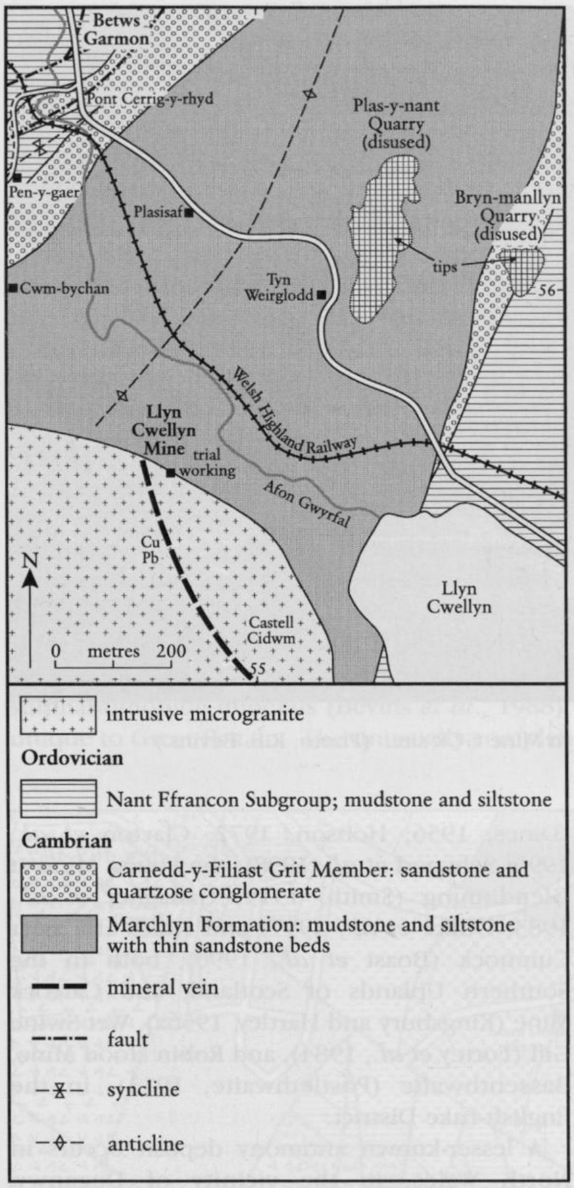


Figure 5.31 Map of the Llyn Cwellyn Mine GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

areas of chalcopyrite and pyrite. In polished section, pyrrhotite (enclosing pyrite), rare sphalerite and galena accompany the chalcopyrite in minor quantities.

Accompanying the quartz + ferroan carbonate + sulphide assemblage, and visible in polished section, are small quantities of lead- and bismuth-bearing telluride minerals. These tend to form composite grains, which are generally 20–50 μm in size, with the appearance of a myrmekitic intergrowth. Tellurides also form intergrowths with pyrrhotite. To date, the telluride phases from this locality have not been identified, largely because of their complex intergrowth textures.

Interpretation

The mineral assemblage occurring at Llyn Cwellyn Mine is unique within the overall picture of the Snowdonia mineralization. The quantity of fluorite and the site's position marginal to the Mynydd Mawr intrusion are suggestive of a partially or wholly magmatic origin. Colman (1990), and Colman and Appleby (1991) discussed the rare-earth-element profile of fluorite from Llyn Cwellyn, concluding that the rare-earth-element distribution patterns in the microgranite and in the vein fluorite are similar, suggesting a genetic relationship between the intrusion and the fluorite mineralization.

The Mynydd Mawr intrusion is a peralkaline intrusion (Howells *et al.*, 1991), which contains fluorite as an accessory phase (Bevins, 1994); additionally a number of rare Nb-Ta and rare-earth-element-bearing minerals are present, which are currently under investigation (A. Tindle, pers. comm.).

The metalliferous mineralization associated with the fluorite is in some respects similar to that of the Snowdonia district as a whole, with common pyrite and chalcopyrite. However, the occurrence of pyrrhotite intergrown with a number of lead- and bismuth-bearing telluride phases is an unusual feature not seen elsewhere within this province, although pyrrhotite is locally common. The pyrrhotite-telluride mineralization, which post-dates pyrite formation, is indicative of late-stage fluids containing tellurium but with a relatively low sulphur content; under such conditions, all remaining sulphur would be taken up in pyrrhotite, while lead and bismuth would combine with tellurium.

The source for the tellurium is unclear, except that it should be noted that elsewhere in the Welsh Caledonides bismuth and lead tellurides have been recorded from the Dolgellau Gold-belt, in southern Snowdonia (Bevins, 1994; Mason *et al.*, 2002), where they are again a late-stage mineral within the primary paragenesis. It may prove to be the case that the basement which underlies the whole Snowdonia area represents a tellurium-enriched source province, so that elevated levels of tellurium,

Figure 5.32 Photograph of the Llyn Cwellyn Mine GCR site. (Photo: R.E. Bevins.)

either substituting for sulphur in sulphides or occasionally occurring as discrete telluride minerals, may be detected geochemically over a wide part of North Wales.

Conclusions

The Llyn Cwellyn trial working constitutes a unique occurrence of fluorite mineralization in the Welsh Caledonides, and the geochemistry of the fluorite is consistent with a magmatic input to the mineralization, probably from the nearby Mynydd Mawr microgranite intrusion. The metalliferous minerals, which were deposited later than the fluorite, include unusual lead and bismuth tellurides, the identification and genesis of which is the subject of ongoing studies.

BWLCH MINE, DEGANWY (SH 787 794)

Introduction

Antimony mineralization is comparatively rare in Great Britain. Amongst the better known antimony deposits are those in the Padstow, Tintagel and Port Isaac areas of north Cornwall (Dines, 1956; Hobson, 1972; Clayton *et al.*, 1990; Selwood *et al.*, 1998); the Louisa Mine at Glendinning (Smith, 1919; Gallagher *et al.*, 1983; Duller *et al.*, 1997) and Hares Hill near Cumnock (Boast *et al.*, 1990), both in the Southern Uplands of Scotland; and Carrock Mine (Kingsbury and Hartley, 1956a), Wet Swine Gill (Fortey *et al.*, 1984), and Robin Hood Mine, Bassenthwaite (Postlethwaite, 1913), in the English Lake District.

A lesser-known antimony deposit occurs in North Wales, in the vicinity of Deganwy, Gwynedd, where a complex sulphantimonide assemblage has been identified recently (Bevins *et al.*, 1988), following the earlier record of stibnite and semseyite from this mine by Russell (1944), in samples he examined from the collections of the Museum of Practical Geology and of the Royal Geological Society of Cornwall.

The history of mining is uncertain, as is the amount of ore extracted. The occurrence is not even mentioned in the Geological Survey '*Special Reports on the Mineral Resources of Great Britain*' volume covering antimony (Dewey, 1920). Neither is the mine mentioned in the regional geological memoir (Warren *et al.*, 1984), although a disused shaft is marked on the most recent 1:50 000 geological sheet (British

Geological Survey, 1989b). Perhaps the earliest reference to the mine is that on a geological map dated 1837, which refers to a 'Mine of Antimony' (see Bick, 1982). The deposit is almost certainly that referred to in the description of stibnite from 'Castell Diganwy, near Conway' by Smyth *et al.* (1864).

Sulphantimonide mineralization at Bwlch Mine is hosted by extensively recrystallized acidic ash-flow tuffs of Ordovician age. This volcanic activity was related to the 1st Eruptive Cycle of volcanism in North Wales in Ordovician (Caradoc) times, associated with the subsequent development of a major caldera subsidence structure during the 2nd Eruptive Cycle (see Howells *et al.*, 1991). It has been proposed by Bevins *et al.* (1988) that the antimony mineralization was genetically linked to the magmatic activity associated with the 1st Eruptive Cycle.

The Bwlch Mine mineral deposit (Figure 5.33) is included in the Wales GCR mineralogy network because it contains a suite of rare lead sulphantimonide minerals (Bevins *et al.*, 1988), unique to Great Britain. The unusually complex assemblage is replicated at only a few deposits worldwide, such as at Vall de Ribes, in the Spanish Pyrenees (Ayora and Phillips, 1981).

Description

Bwlch Mine is a small site which is visible from a distance due to the yellow antimony-ochres which pervade the dumps. The mine was driven into a hillside, although there are no records of the mine layout. The shaft is now blocked, and the only source of specimens is from the small overgrown dumps near to the former mine entrance, which represent a strictly limited mineralogical resource.

The host rock comprises a highly silicified ash-flow tuff, considered to be of Caradoc age, belonging to the Capel Curig Volcanic Formation (British Geological Survey, 1989b), part of the Llewelyn Volcanic Group (the 1st Eruptive Cycle in Snowdonia). The ash-flow tuff is extensively silicified and more locally carbonatized. As a consequence, original textures are almost entirely overprinted and determination of the

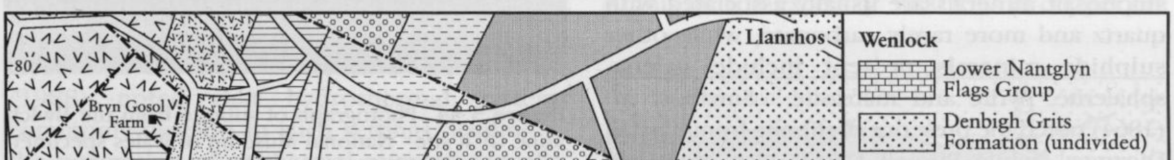


Figure 5.33 Map of the Bwlch Mine GCR site. After British Geological Survey 1:50 000 Sheet 94, Llandudno (1989a).

original character of the silicic volcanic rocks is difficult. The rock is nodular and shows a variety of spherulitic textures in thin-section. The most common spherulites are up to 1.5 mm across and are composed of radiating aggregates of fine-grained quartz; other spherulites have a structure more reminiscent of orbicules, with concentric layers of fine-grained quartz. A third type of spherulite is composed of coarse-grained aggregates of randomly orientated quartz crystals, some of which have a hollow core. These latter spherulites may represent former lithophysae. The only primary textures which are recognizable are poorly preserved glass shards, now replaced by fine-grained, recrystallized quartz aggregates. It is thus most likely that the Bwlch siliceous volcanic rocks are in fact ash-flow tuffs, which are widely developed in the Ordovician sequences representative of the 1st and 2nd Eruptive Cycles across Snowdonia (Howells *et al*., 1991).

The antimony-bearing minerals at Bwlch Mine, dominated by stibnite (Figure 5.34) occur in irregular patches and veinlets up to 2 cm (but more typically around 0.5 cm) wide. The sulphosalt minerals are usually associated with quartz and more rarely carbonate, while other sulphide minerals present include galena, sphalerite, pyrite and marcasite. Smyth *et al*. (1864) noted the presence of stibnite from 'Castell Diganwy', while Russell (1944) also identified semseyite and jamesonite from Bwlch Mine. The most detailed account of the Bwlch Mine sulphosalt assemblage, however, was by Bevins *et al*. (1988) who confirmed the previous identifications and additionally reported the presence of zinkenite, jamesonite, and plagionite, along with possible robinsonite and boulangerite. Recent unpublished studies (J. Cleverley and R.E. Bevins) have subsequently confirmed the presence of the latter two phases.

Various secondary minerals are also present, although their identification is mostly uncertain. Russell (1944) considered that a brownish-yellow crust on stibnite and other sulphosalt minerals was bindheimite, while Bevins *et al*. (1988) suggested that cherry-red coatings on stibnite were kermesite. Anglesite was also recorded by Russell (1944). Recently, Ryback and Francis (2001) have described rosiaite from Bwlch Mine, occurring as a very thin, light orange-brown crust on stibnite and buff-coloured bindheimite. Rosiaite itself was only recently described as a new species by Basso *et al*. (1996) from

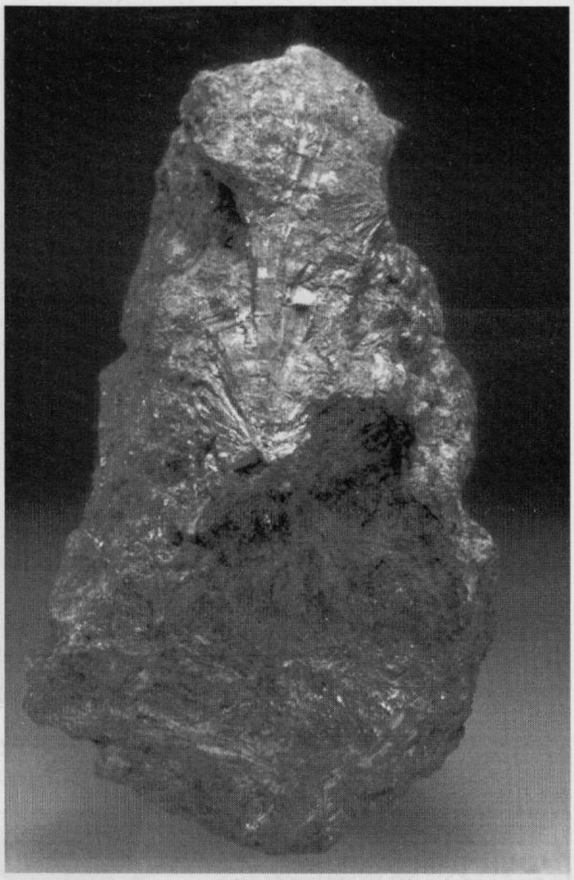


Figure 5.34 Photograph of stibnite from the Bwlch Mine GCR site. National Museum of Wales specimen NMW85.70G.M34. (Photo: M.P. Cooper, © National Museum of Wales.)

Cetine Mine, in Tuscany, Italy. Finally, as yet unpublished studies on secondary minerals from Bwlch Mine (J. Cleverley and R.E. Bevins) have identified a secondary Sb-Al-Zn oxide hydrate forming acicular crystals as overgrowths on boulangerite and as coatings on dolomite occurring as intergrowths with jamesonite. It is thought that this phase is the zinc analogue of cualstibite, described from the Clara Mine, Germany (Walenta, 1984).

Interpretation

Antimony mineralization at Bwlch Mine is directly associated with altered silicic volcanic rocks, contrasting with other occurrences of antimony mineralization in Great Britain. At Glendinning, the antimony mineralization is thought to be epigenetic, with three stages of mineralization, comprising an early pyrite-arsenopyrite assemblage, overprinted by stibnite-sphalerite-galena, followed by a late, minor galena-sphalerite-chalcopyrite-barite assemblage (Gallagher *et al.*, 1983; Duller *et al.*, 1997). At Wet Swine Gill, where the mineralization is located in the contact aureole of the Skiddaw Granite, the genesis of the antimony mineralization has been linked to the remobilization of primary antimony (Fortey *et al.*, 1984). In both cases described above, there was an early episode of arsenopyrite mineralization; in contrast, no such early arsenic-rich phase of mineralization has been recognized at Bwlch Mine.

Potentially, a closer similarity is seen with the antimony mineralization in north Cornwall, which also occurs associated with volcanic rocks, although in this latter case they are of basic composition (Dines, 1956; Hobson, 1972; Clayton *et al.*, 1990; Selwood *et al.*, 1998). Accordingly, there appears to be no deposit in Great Britain which is directly analogous to the Bwlch Mine occurrence.

It is widely accepted that the Ordovician volcanic rocks of Snowdonia were erupted in an ensialic marginal basin setting, a basin which developed at the margin of Gondwanaland in relation to subduction of oceanic crust linked to closure of the Iapetus Ocean. Bevins *et al.* (1988) noted that hydrothermal systems commonly develop in such settings, leading to the generation of epithermal mineral deposits; by analogy with North Island, New Zealand they suggested that the Bwlch Mine antimony mineral deposit was of epithermal character also, linked to acidic ash-flow tuff eruption during the 1st Eruptive Cycle of Snowdon volcanism in Ordovician (Caradoc) times. Other episodes of mineralization in Snowdonia, for example the Cu-Pb-Zn-As and Fe-Sn-W oxide parageneses, have also been linked to the Ordovician volcanic activity (Reedman *et al.*, 1985), exposed, for example, at the **Cwm Tregalan–Shadow Gully**, **Llanberis Mine** and **Lliwedd Mine** GCR sites.

Conclusions

Antimony mineralization at Bwlch Mine, near Deganwy, is unique in Great Britain. It is associated with silicic ash-flow tuffs of Ordovician age and is thought to have been derived by hydrothermal activity associated with the contemporaneous eruption and alteration of the ash-flows. The site is also of importance for the rare primary and secondary minerals present, a number of the antimony-bearing minerals being the first, and in specific cases only, occurrence in Great Britain.

PARYS MOUNTAIN (SH 433 903–SH 449 907)

Introduction

Parys Mountain, on Anglesey (Figure 5.35), is the site of one of the finest examples of a volcanogenic massive sulphide (VMS)-type deposit in the Caledonides of the British Isles. Mining at Parys Mountain began in the Early Bronze Age (Jenkins, 1995), and it is thought likely that the Romans also worked the deposit (Manning, 1959). However, the most important phase of activity commenced in the early 1760s, with a major stimulus in 1768 following the discovery of a major orebody. This orebody came to be known as the 'Great Lode', sometimes referred to as the 'Opencast Lode', and made Parys Mountain Europe's premier copper producer. At this time in excess of 3000 tons of copper ore

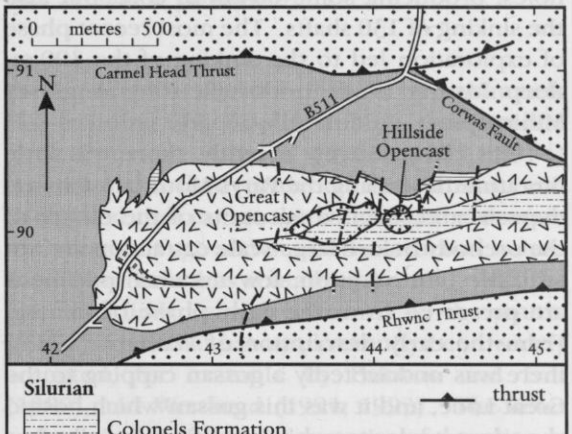


Figure 5.35 Map of the Parys Mountain GCR site. After Westhead (1991, 1993).

were being recovered per annum. At the end of the 18th century Parys Mountain was the largest copper mine in the world.

Several other orebodies were discovered following depletion of the Great Lode in the 1790s, the most significant being termed the 'North Discovery Lode', which provided considerable profit for the mine in the 1820s. Other notable discoveries included the Golden Venture Lode, the Carreg-y-doll Lode, Charlotte's Lode and the geographically more remote Morfa-du Lode (Greenly, 1919). Interestingly, it is thought that precipitation of copper in pits using scrap iron was trialed at Parys Mountain as early as 1579 (see Rowlands, 1981).

By the 1890s most mining at Parys Mountain had ended and it finally ceased in 1911, although copper precipitation continued until the 1950s. Although the full figures are not known precisely, Manning (1959) estimated that a total of more than 130 000 tons of copper metal were extracted from 2.6–3.7 × 10^6 tons of ore. The most recent phase of exploration commenced in 1948, and almost continually since that date a number of international mining companies have carried out extensive exploration programmes, involving not only drilling 150 holes, producing some 60 km of core, but also the sinking of 130 shafts. The most recent phase of exploration led to the sinking of the 300 m-deep Morris Shaft undertaken by Anglesey Mining plc.

Until comparatively recently, there was little literature describing the Parys Mountain mineral deposit, and detailed accounts of the nature of the orebody before large-scale extraction are not available. In addition, few mineral specimens are preserved from the early phase of mining. From the early description of Pennant (1783), there was undoubtedly a gossan capping to the Great Lode, and it was this gossan which hosted abundant anglesite, which was first described as a new species from Parys Mountain in 1832 (Beudant, 1832). However, as early as 1783, Withering (quoted in Dana, 1868) had described immense quantities of 'lead mineralized by sulphuric acid and iron' from the 'Island of Anglesea'. Probably the most important early account of Parys Mountain was that by Lentin (1800), a German technical specialist from the University of Leipzig who spent six years at Parys Mountain towards the end of the 18th century. In a series of 10 'letters', Lentin (1800) provided, amongst other things, an account of the mineralogy of the deposit, including a description of the form and occurrence of 'bleiglas', the old German term for anglesite.

Parys Mountain was later discussed by Ramsay (1866), who reported on the distribution of the principal lithologies present. It was Greenly (1919), however, who provided the first detailed geological synthesis. He concluded that the mineralization was epigenetic in origin, considering the deposit to be a series of mineral veins or 'lodes' hosted by rocks of Ordovician age related to 'mineral changes that took place during, but chiefly after, the great Post-Silurian earth-movements' Importantly, Greenly (1919) presented the first interpretation of the geological structure of the area. Further reports on the structure and stratigraphy were provided by Manning (1959), and Hawkins (1966), while Bates (1966) refined earlier models for the Parys Mountain deposit on the basis of faunas in adjacent sedimentary rocks, and on field mapping, work which he subsequently expanded (Bates, 1972, 1974).

From the early 1970s through to the present day, a series of PhD and MSc studies have investigated the mineralogy and genesis of the Parys Mountain deposit. In addition, there have been numerous unpublished reports from mining exploration companies. Wheatley (1971b) provided the first paragenetic interpretation of Parys Mountain, and concluded that the mineralization had both syngenetic and epigenetic characteristics, but that it was certainly pre-deformation. Thanasuthipitak (1974) investigated the petrology and geochemical character of the associated volcanic rocks, and suggested that the mineralization was syngenetic, and related to the volcanism. Ixer and Gaskarth (1975) compared the mineralization to the Kuroko deposits of Japan, and linked it to Ordovician plate tectonics. Nutt *et al.* (1979) questioned this notion and, on the basis of K-Ar age determinations, suggested that the mineralization was of late Caledonian age. However, Pointon (1979), and Pointon and Ixer (1980) convincingly re-instated the idea that the Parys Mountain deposit was linked to volcanism, arguing that the deposit was related to the exhalation of mineral-rich fluids into seawater contemporaneous with submarine volcanism. They went on to argue that the mineral deposit was later deformed, which was accompanied by deformation and remobilization of sulphides, with the generation also of quartz and chlorite.

Southwood (1982, 1984) established the presence of basic volcanic rocks at Parys Mountain, overturning the previously held notion that the volcanic sequence was solely silicic in character; critically, the potential for equating magmatism at Parys Mountain with that in central Snowdonia was advanced considerably. The most recent doctoral studies include those by Westhead (1993), and Tennant (1999); the former study conformed to the previously held view that the overall structure at Parys Mountain was that of an overturned syncline; in contrast the latter study suggested that the dominant structure represents a N-dipping homoclinal sequence. Tennant and Steed (1997) presented the results of an investigation into the lithogeochemistry of the various volcanic rocks at Parys Mountain and presented a new model which suggested that the volcanism was in part of early Silurian (Aeronian) age, in contrast to most earlier accounts which had considered the volcanism to be entirely of Ordovician (Caradoc) age. Finally, Barrett *et al.* (1998, 1999) have reviewed the findings of research undertaken by Anglesey Mining plc since 1995, which has focused on re-logging of available core, remapping of surface geology, and undertaking a lithogeochemical investigation. Their principal conclusion is that mineralization is controlled by the distribution of silicic eruptive centres and related volcanic facies.

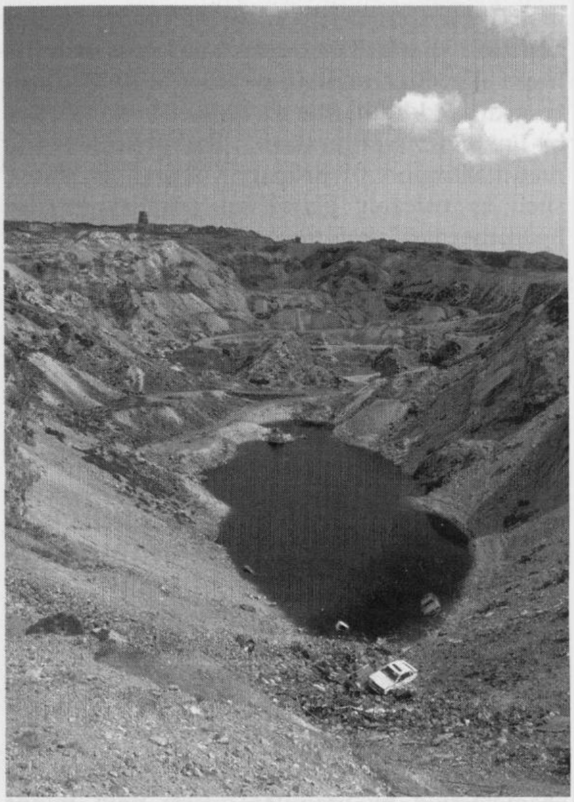


Figure 5.36 Photograph of the Parys Mountain GCR site. (Photo: S. Campbell.)

Description

Parys Mountain forms a prominent whaleback hill which rises to 147 m OD, located 3 km south of Amlwch, in north-east Anglesey. The hill is orientated ENE–WSW and is approximately 2.5 km in length. The legacy of mining manifests itself in a devastated landscape over some 3 m^2, dominated by two large open-pits (Figure 5.36).

Greenly (1919) described the geology of Parys Mountain as being dominated by a central zone of shales of Silurian age flanked by intrusive 'felsite' and shales both to the north and south and overstepped to the north of the mine by Precambrian rocks forming the hangingwall of the Carmel Head Thrust. The overall disposition of these strata and the identification of graptolites of supposed Silurian age in the southern shales led Greenly (1919) to infer the presence of a roughly E–W-trending antiformal structure through the area. He also identified the importance of a later phase of approximately N–S-trending oblique-slip faulting, the so-called 'cross-courses'. Bates (1966, 1972, 1974) reviewed the field evidence and faunas, and concluded that in fact the southern shales were of Ordovician age and hence the structure across Parys Mountain was actually synformal, with the northern limb being overturned to the south. This is a view that has until recently been widely accepted, for example by Pointon and Ixer (1980), and Westhead (1991, 1993). The latter author also noted the importance of thrusting at Parys Mountain, particularly at depth. More recently, however, the structure of the Parys Mountain area has been re-appraised and the area is now considered to be underlain by a homoclinal structure with the sequences dipping more-or-less uniformly to the north (Tennant and Steed, 1997).

The volcanic rocks which host the mineralization are predominantly silicic, and were described initially as 'felsite' (Greenly, 1919). A range of volcanic and pyroclastic rocks has now been identified at Parys Mountain, although many descriptions are from drill-core samples and only a relatively restricted range of lithologies is recognizable in weathered surface outcrops. In addition, the rocks have been affected by extensive alteration, comprising early recrystallization of primary volcanic products, such as volcanic glass and pumice, intense hydrothermal alteration, and later low-grade regional metamorphism. Consequently, the nomenclature of the primary character of the volcanic rocks has been both variable and controversial.

Pointon and Ixer (1980) described the presence of rhyolitic and dacitic lavas, intrusive rhyolite, siliceous sinter, chert, chloritic chert and shale, tuffs and volcaniclastic rocks. They recorded rhyolitic flows and flow breccias from the western and eastern ends of Parys Mountain, occurring as slabs several metres long and averaging 1 m in thickness, with breccias containing blocks 0.1–1.0 m across set in a fine-grained matrix. The lavas show well-developed spherulitic and perlitic recrystallization textures after primary volcanic glass. The rhyolites are dominated by recrystallization textures characterized by granular quartz with minor chlorite and white mica. Phenocrysts are rare, being typically quartz and less commonly feldspar. Dacitic lavas, described by Thanasuthipitak (1974), are both porphyritic and non-porphyritic, the former containing plagioclase feldspar phenocrysts up to 10 mm in length. The aphyric rocks show plagioclase feldspar laths in a fine-grained matrix dominated by quartz aggregates showing a primary perlitic texture.

One of the most interesting units described by Pointon and Ixer (1980) is the so-called siliceous sinter, a unit established originally by Thanasuthipitak (1974). This unit occurs in the Carreg-y-doll Lode zone (at SH 445 905) and at the western extremity of the outcrop, at Morfa-du (at SH 433 903). It is essentially stratiform and comprises a rock showing fine-scale, colour-dominated layering, with evidence of repeated brecciation. The rock is composed of very fine-grained aggregates of quartz, clay and white mica, with chalcedony or recrystallized quartz-filled voids, although recrystallization is extensive. Locally, as at Morfa-du, the rock shows polyphase brecciation.

Interestingly, Pointon and Ixer (1980) recorded only minor tuff horizons within the Parys Mountain volcanic succession, noting that Thanasuthipitak (1974) had recorded pyroclastic rocks from the western end of the outcrop. Pointon and Ixer (1980) also described the presence of various volcaniclastic rocks, derived from the volcanic horizons of the Parys Mountain area. Basic volcanic rocks were later identified from the western end of Parys Mountain (Southwood, 1982, 1984).

The most recent investigations of Parys Mountain, by Tennant and Steed (1997), adopted a different approach to previous studies. Accepting the problems posed by secondary alteration in interpretation of primary mineralogy, textures and chemistry, they utilized concentrations of those trace elements typically considered to be immobile during such alteration events in order to establish a chemostratigraphy. On this basis, they identified a tri-partite compositional structure for the Parys Mountain volcanic rocks, comprising comendite/pantellerite-rhyolite, rhyolite-dacite, and sub-alkaline basalt-andesite. More significantly, critical immobile element plots have identified five discrete rhyolite units at Parys Mountain (A, B, C-1, C-2, and D), along with two thin mafic units (Barrett *et al.*, 1998).

Rhyolite A shows both pyroclastic, fiammé-bearing rhyolitic tuffs, exposed to the south-west of the Great Open Pit, and a flow-banded facies with overlying rubble, which is exposed at the western end of the Great Open Pit. Pyroclastic facies of C-2 rhyolite are also seen in the Great Open Pit, for example forming the small knoll at the western end of the pit and also forming parts of the northern wall. Flow-banded rhyolites of Rhyolite D are exposed in the vicinity of Ty'n-y-mynydd, this rhyolite being interpreted as a dome facies. This same facies is also seen in the east of the area, at Pensarn, occurring in association with pyroclastic blocky breccias and lapilli tuffs. Significantly, Barrett *et al.* (1998) interpreted the 'White Rock', considered by Pointon and Ixer (1980) to be siliceous sinter, to be in fact mainly silicified mudstone, with a small percentage representing silicified rhyolitic rocks.

Early records of the mineralogy of the Parys Mountain deposit are patchy, concentrating upon particularly unusual discoveries, such as the formerly abundant anglesite (Lentin, 1800; Beudant, 1832). The first attempt to systematically describe the nature of the primary mineralization was made much later, by Greenly (1919). The importance of this account is that it was based not only on field observations but also on contemporary local knowledge and mine reports. Greenly (1919) noted that the chief sulphide minerals present are pyrite, chalcopyrite, chalcocite, sphalerite and galena. He distinguished between a pyrite-chalcopyrite-quartz assemblage and a dense rock, called 'bluestone', consisting of galena and sphalerite with minor pyrite and chalcopyrite. Note was also made of the 'accumulations' of silica, including the 'quartz rock' of the Carreg-y-doll Lode, the siliceous sinter of Pointon and Ixer (1980).

Importantly, Greenly (1919) noted the 12 'lodes' that he described to dip a little west of north at around 45°, and, critically, depicted them as concordant features. He considered the Great Lode to be the most economically important of the ore deposits, describing it to be an enormous 'aggregate' or 'bunch', with a broad zonation of sulphides comprising pyrite to the north, chalcopyrite in the central zone and bluestone to the south.

Later studies revealed a hitherto greater complexity to the sulphide mineralogy at Parys Mountain. Wheatley (1971b), and Sivaprakash (1977) reported electron microprobe analyses on polished sections of Parys Mountain ores, which confirmed the presence of both tetrahedrite and tennantite, accompanied by minor bournonite. In addition, a suite of bismuth-bearing minerals was identified by Sivaprakash (1977), including native bismuth, bismuthinite, kobellite and galenobismuthite.

Pointon and Ixer (1980) did not recognize either the broad classification of ores or their zonation as proposed by Greenly (1919). Instead, they established a paragenetic sequence based on the textural relationships of the ore minerals observed in numerous polished sections. Four generations of pyrite (A–D) were recognized, each with or without a diagnostic suite of associated minerals. Pyrite A is a minor phase comprising often euhedral crystals in altered volcanic and sedimentary rocks. Pyrite B, the main pyrite generation, is ubiquitous in its occurrence as euhedral crystals, and contains an inclusion assemblage of pyrrhotite, hematite and rutile. Pyrite B is frequently zoned, and has also been abundantly replaced by later sulphides comprising chalcopyrite, galena and sphalerite. Pyrite C is framboidal, occurring as a surround to pyrite B, and is frequently replaced or cemented along fractures by galena and chalcopyrite, accompanied in places by tetrahedrite, sphalerite, arsenopyrite and bismuth minerals. Pyrite D is directly associated with the polymetallic mineralization and is both unzoned and inclusion-free, occurring as subhedral to anhedral grains intimately intergrown with chalcopyrite and marcasite.

Clearly, the pyrite generations A–C pre-dated the polymetallic mineralization, and Pointon and Ixer (1980) recognized that both types of mineralization have been extensively modified, possibly by regional metamorphism. Late quartz-chlorite and quartz-carbonate-barite veins, which cross-cut the pyritic and polymetallic mineralization and which carry pyrite, arsenopyrite, marcasite, chalcopyrite, galena, sphalerite and hematite, are interpreted by these authors to indicate a post-depositional remobilization process. Other features which may be attributed to later deformation are polygonal grain boundaries in recrystallized galena and extensively developed twinning in chalcopyrite.

More recently, exploration work by Anglesey Mining plc has focused on the western part of the site, and, through a combination of diamond drilling and underground development, two significant zones of stratiform mineralization have been investigated, known as the 'Engine Zone' and the 'White Rock Zone'. The Engine Zone consists of a series of massive sulphide-rich debris-flows dominated by sphalerite (Tennant and Steed, 1997), resting mainly on shales and silicic pyroclastic rocks. It is much disturbed by the later cross-course faulting. Within the White Rock Zone, a series of massive, Zn-Pb-Cu-dominated sulphide lenses occurs within a larger zone of quartzose breccia, extending to surface as the Morfa-du siliceous sinter. The mineralization intersected during this exploration also contains 78 g/t silver and 0.66 g/t gold (Charter, 1995).

At surface, the complexity of the mineralization can be readily appreciated. Although the common lead, copper and zinc minerals are seen, accompanied by ubiquitous pyrite, the rarer primary phases require ore microscopy for their determination, many occurring as grains only a few microns across. The presence of much 'gossan' is also evident, although since the 19th century searches by many mineralogists have failed to re-discover the large (> 10 mm) gemmy, yellow to colourless anglesite crystals, discovered in the 18th century, for which the site is now justly famous (Southwood and Bevins, 1995). In addition to anglesite, accounts by Pennant (1783), and Lentin (1800) strongly suggest the presence of pyromorphite, native copper, 'melaconite' (presumably tenorite) and native sulphur as components of the gossan. More recently, Pointon and Ixer (1980) recorded, from polished section investigations, chalcopyrite being replaced by bornite, chalcocite, covellite and cuprite.

Within the underground workings at Parys Mountain, an extensive suite of post-mining secondary minerals, formed primarily by bacteriogenic pyrite decay in a highly acidic environment (pH as low as 2), is the subject of an ongoing investigation (Jenkins and Johnson, 1993; Jenkins, 1999). The post-mining mineralogy is dominated by a variety of rare sulphate minerals in addition to ferrous hydrous oxides. The sulphates are dominated by yellow jarosite and possibly hydronium jarosite, accompanied by an extensive range of other species including chalcanthite, halotrichite, cuprian melanterite (Bor, 1950), antlerite, basaluminite, copiapite, coquimbite, fibroferrite, jarosite, gunningite, römerite(?), siderotil and rozenite (Jenkins, 1999; Jenkins *et al.*, 2000). Jenkins *et al.* (2000) provided a description of the occurrence of these various post-mining sulphate minerals, in both surface and underground environments. They noted that underground the commonest alteration product of chalcopyrite is the bright-green hydroxysulphate antlerite, which often overlies blue-green brochantite, reflecting a drop in pH. Basaluminite, a rare aluminium hydroxysulphate, also occurs as an efflorescence on the mine walls, along with allophane. Above ground the rare species fibroferrite, coquimbite and copiapite occur in overhangs and recesses in the open-pit walls. Unfortunately, a unique occurrence of the rare hydrated zinc sulphate gunningite coating sphalerite has been destroyed in recent years.

Interpretation

A critical discussion relating to the Parys Mountain ore deposit has focused on whether the primary mineralization is of epigenetic or syngenetic origin. Probably the first interpretation was forwarded by Greenly (1919), who proposed that the orebody was principally epigenetic in origin. However, on a key structural cross-section in Greenly (1919), he clearly showed the Carreg-y-doll and Charlotte's lodes as being concordant with their host shales and 'felsite'. Manning (1959) also supported a syngenetic origin for the mineralization, while Wheatley (1971b) suggested that the deposit included both epigenetic and syngenetic elements, but that it certainly preceded deformation.

Thanasuthipitak (1974) was the first to propose that the Parys Mountain mineralization is entirely of syngenetic origin, and linked to rhyolitic volcanism. Ixer and Gaskarth (1975) later suggested that it was similar to the Kuroko-type deposits of Japan, and related to the exhalation of metal-rich brines into the sea in Ordovician times. This theory was re-inforced by the studies of Pointon (1979), and Pointon and Ixer (1980).

Nutt *et al.* (1979) challenged the syngenetic origin and, on the basis of K-Ar age determinations, argued that the mineralization was epigenetic, being of late Caledonian (Acadian) age. Bearing in mind the degree of metamorphic remobilization, it is highly likely that the K-Ar ages are in fact reset ages, and hence do not reflect the true age of mineralization.

The Parys Mountain deposit, comprising a series of massive layers, lenses and disseminations of sulphide mineralization, has many features which are most compatible with a syn-sedimentary origin, contemporaneous with submarine volcanism in mid-Ordovician to early Silurian times. The strongest evidence comes from the occurrence of syn-sedimentary disturbances within the sulphide bodies, such as slump structures and debris flows. The difficulty in recognizing the syngenetic nature of the deposit has been due to the fact that the mineralization has not only been modified by regional low-grade metamorphism, but also it has been tilted 45° to the NNW and much disturbed by faulting.

In their genetic model, Pointon and Ixer (1980) envisaged mineralization both contemporaneous with volcanism, in which slumped masses of sulphide were mixed in debris flows with clastic and pyroclastic material, and continuing with fumarolic activity as volcanism waned, resulting in the massive sulphides of the Great Lode and Carreg-y-doll Lode, occurring with cherts and shales in the upper part of the sequence. Fumarolic activity finally ceased in early Silurian times, with a return to fine-grained clastic sedimentation.

In their conclusions, Tennant and Steed (1997) indicated that minor volcanism continued into early Silurian (Aeronian) times, and also that the degree of structural modification during Acadian deformation was much less than had previously been thought. They concluded that when the Parys Mountain succession was tilted to the NNW, the shale units took up much of the strain, with reversed shearing along lithological contacts and the development of localized and, importantly, disharmonic drag-folding. These conclusions may go a long way towards explaining why anomalous bedding-cleavage relationships are so frequently observed within the shales at Parys Mountain.

There has been much debate regarding the age of the sedimentary rocks to the north of the mine; whether they are Ordovician (as previously believed) or Silurian (as suggested by Tennant and Steed, 1997) is clearly a critical factor in determining which structural model is correct. The Ordovician age of these reportedly structureless sedimentary rocks, in which macrofossils have been found, is based on micropalaeontological data, obtained by the former Institute of Geological Sciences and summarized in Bates (1972). However, the micropalaeontological evidence is based entirely on poorly preserved acritarchs, which Tennant and Steed (1997) suggest may have been reworked during Silurian sedimentation. Although this could feasibly be the case, it would be extremely difficult to prove, and further detailed examination of the northern shales is required in order to fully assess their age, and thereby confirm which structural model is most reliable.

Whichever structural model proves to be correct, the evidence for a major centre of exhalative seafloor hydrothermal activity being established in conjunction with volcanism in mid- to late Ordovician (and probably early Silurian) times is compelling. Continuation of volcanism into early Silurian times (Tennant and Steed, 1997) is a particularly important hypothesis given that in the remainder of North Wales volcanic activity, although widespread, had ceased by the end of Caradoc times. It may be the case (Barrett *et al.*, 1998) that basement-related structures in northern Anglesey acted as particularly influential conduits both to ascending magmas and to circulating hydrothermal fluids. A basement connection is in fact supported by the findings of Fletcher *et al.* (1993), in which the lead isotope ratios in galena from Wales were determined and interpreted. For Parys Mountain, the galenas have variable and radiogenic $^{206}Pb/^{204}Pb$ ratios, and consistently high $^{207}Pb/^{204}Pb$ compared both to other galenas from Wales and to global model growth-curves, leading to the inference that the lead may have been sourced, at least in part, from the Monian basement which underlies Anglesey.

Conclusions

The Cu-Pb-Zn mineralization at Parys Mountain, in north-east Anglesey, worked since Bronze-Age times, represents, in its currently favoured interpretation, one of the finest examples of a volcanic-related submarine exhalative 'Kuroko-type' deposit in the British Caledonides. Becoming Europe's largest copper producer with the development of the Great Lode in the late 1700s, the origin of the deposit has been, and remains, the subject of much debate. Current evidence strongly points away from a model of epigenetic 'lodes' emplaced into the strata in fractures, and more towards mineral deposition taking place during the eruption and accumulation of the associated Lower Palaeozoic volcanic and sedimentary succession. Of additional interest, not least because the site is the type locality for the lead sulphate anglesite, is the former presence of a considerable gossan capping to the deposit containing a variety of secondary copper and lead minerals. Formerly present in abundance, anglesite specimens are now rarely found. The microbiological-biochemical systems involved in the post-mining oxidation of pyrite in the old underground workings are also of considerable importance and are still under investigation.

CAE COCH MINE (SH 775 654)

Introduction

The Cae Coch massive pyrite deposit is of controversial origin and has been variably interpreted as an altered ooidal ironstone, an epigenetic fracture-fill, and a kuroko-type volcanogenic exhalative deposit, while the most recent examination has classed it as a syn-diagenetic inhalative body. Clearly, the deposit is of major metallogenic interest, but it is also internationally famous for the microbial ecosystem developed within the old underground workings, where acidophile autotrophic and heterotrophic bacteria form an estimated 100 m^3 of gelatinous streamer-growths (Jenkins and Johnson, 1993).

Cae Coch Mine (Figure 5.37) was worked for pyrite for sulphuric acid manufacture. It was worked intermittently between 1817 and 1895, and later from 1917 to 1919, and produced 107 650 tons of ore grading in excess of 30% sulphur in that time. Further reserves of 86 000 tons have been proven (Dunham *et al.*, 1978; Ball and Bland, 1985) but the fine-grained pyrite is difficult to separate effectively from waste, which has deterred any further working.

An early account of the site was presented by Sherlock (1919), who concluded that the

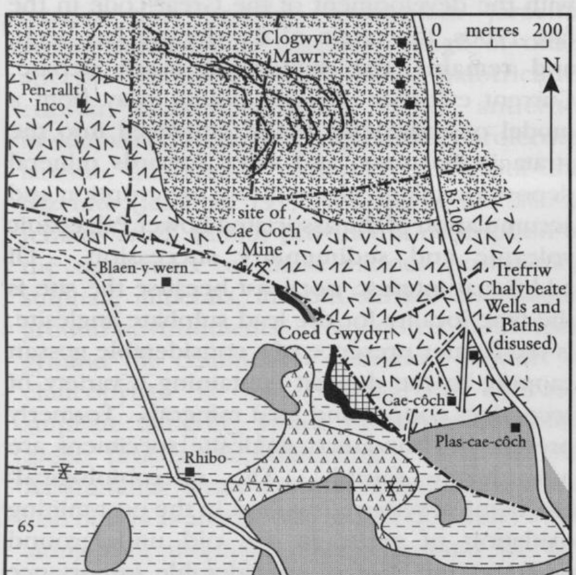


Figure 5.37 Map of the Cae Coch Mine GCR site. After Ball and Bland (1985).

mineralization was of sedimentary origin and represented a pyritized ooidal iron ore-bed, with pyritization due to intrusion of a 'diabase' body beneath the bed. According to Ball and Bland (1985), an unpublished mining consultant's report had re-interpreted the orebody as being epigenetic and fault-controlled.

Ball and Bland (1985) presented the results of a detailed study into the geology, mineralogy and major- and trace-element geochemistry of the deposit. Their conclusion was that Cae Coch represented a Kuroko-style volcanogenic submarine exhalative deposit. Important evidence was described, in the form of tubular growths of pyrite, 5–10 mm in diameter, in the upper part of the ore-bed, interpreted as being fossilized 'black-smokers' or possibly 'chemical garden' growths of pyrite from a precursor gel.

The site was re-interpreted later by Bottrell and Morton (1992), who investigated the deposit using a combination of isotope and elemental geochemistry. They found little or no evidence for the existing volcanogenic massive sulphide classification, suggesting instead that the sulphides had been produced by bacterial sulphate-reduction within anoxic sediments, which produced excess H_2S; ascendant iron-rich waters then reacted with the H_2S within 5 m of the sedimentary surface to form pyrite.

Description

The Cae Coch deposit (Figure 5.38) is hosted by a package of sedimentary and volcanic rocks of Caradoc age. It is underlain by the 300 m-thick Dolgarrog Volcanic Formation, which includes pillowed basalts, basaltic tuffs and hyaloclastites; below this unit is the Crafnant Volcanic Formation, comprising acidic ash-flow tuffs. Rhyolite domes, one of which occurs close to the deposit, locally intrude the sequence. These strata correlate with the Bedded Pyroclastic and Upper Rhyolitic Tuff formations (Reedman *et al.*, 1985) of the Snowdon volcanic centre to the south-west, described at the **Lliwedd Mine** GCR site. The change from dominantly volcanic to sedimentary conditions is marked at the horizon at which the deposit occurs, and the pyrite body is overlain by a thick (450 m) sequence of pyritic mudstones, with only occasional thin tuffaceous bands. These mudstones, belonging to the Nod Glas Formation, are intruded by small dolerite bodies, and the entire sequence has been affected by lower-greenschist-facies regional metamor-

Figure 5.38 Photograph of the Cae Coch Mine GCR site, showing the top open-pit. (Photo: T. Colman.)

phism and Acadian deformation, which has produced a strong cleavage in the pyritic mudstones.

The pyrite deposit is up to 2.2 m in thickness, is thickest in the axial zones of folds (Ball and Bland, 1985), and extends along strike for *c*. 200 m. It consists predominantly of pyrite with minor pyrrhotite, in a gangue of minor quartz and calcite. The pyrite, which is locally framboidal, occurs in two modes, one massive and compact, and the other porous and intergrown with the gangue minerals. The commonest ore-type is the 'rubbly ore', which tends to occur in the lower part of the deposit, and its resemblance to the Kuroko ores of Japan was commented upon by Ball and Bland (1985). Above the 'rubbly ore' the pyrite becomes more laminated, and in the upper 0.5 m of the deposit, hollow tubes of pyrite, 5–10 mm wide, and filled with radiating quartz, occur. Ball and Bland (1985), citing examples from the Carboniferous exhalative mineralization of Ireland, suggested that these tubes may be fossilized 'black smokers', sites of hydrothermal exhalation onto the seafloor. Further pyrite tubes were recorded projecting from the top of the bed into the overlying mudstones.

Geochemically, the deposit shows minor enrichment of other metals, with up to 450 ppm Cu, 50 ppm Ag, 100 ppm Sn, 140 ppm As and 0.1 ppm Au. Molybdenum is present in more elevated quantities (up to 7400 ppm), and molybdenite has been identified in electron microprobe studies of the ore (Ball and Bland, 1985). Cobalt and nickel values in the pyrite are low, Ni not exceeding 100 ppm, a factor of relevance in interpretation of the deposit by Bottrell and Morton (1992). Wall-rock alteration is most intense in the underlying basic volcanic rocks of the Dolgarrog Volcanic Formation and accompanying rhyolites, which are enriched in K, Ba and S and are slightly silicified (Ball and Bland, 1985). Within these rocks, veinlets and disseminations of pyrite and pyrrhotite are common, and immediately below the pyrite deposit occur a number of lenses of calcite-rich rock.

Secondary mineralization, which has locally oxidized the ore to a ferruginous clay close to the outcrop, is more important in the post-mining context. Large-scale post-mining oxidation of the pyrite has produced copious quantities of sulphate minerals, dominated by the basic hydrated iron sulphate fibroferrite, accompanied by melanterite and copiapite (Johnson *et al.*, 1979). Gypsum is widespread, as indeed it invariably is in post-mining environments wherever pyritic rocks are exposed.

It is the fact that the post-mining oxidation of pyrite is largely bacteriogenic that has brought Cae Coch to international attention (Johnson *et al.*, 1979; Jenkins and Johnson, 1993). The most significant bacteria involved in the process are autotrophic species, which obtain carbon from CO_2 and have minimal nutritional requirements. These bacteria thrive to the exclusion of others in acidic environments, and many obtain their energy from the oxidization of reduced sulphur compounds. The best-known species flourishing in such environments are *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, but heterotrophic bacteria, moulds, yeasts, rotifers and protozoans are also present in what constitutes an intricate microbial ecosystem, thriving in conditions which would appear at first sight to be hostile to life.

The microbial ecosystem in Cae Coch Mine manifests itself as gelatinous, stalactite-like growths hanging from moist surfaces underground, and as 'acid-streamer' growths which inhabit the mine drainage system. These growths, which may be up to 0.5 m in thickness, are pale cream to pinkish in colour and occur in extraordinary quantities; Jenkins and Johnson (1993) have estimated that Cae Coch contains more than 100 m^3 of microbial biomass. Why these growths, which are not uncommon in abandoned metal mines, are so prolific in Cae Coch Mine is not fully understood, but a major reason may lie in the almost exclusively pyritic nature of the mineralization, with relatively low contents of other metals. Interestingly, once the mine drainage exits to surface, the 'acid-streamers' disappear, a fact which Jenkins and Johnson (1993) took to infer that the bacteria may have an intolerance of light.

Interpretation

The interpretation of the Cae Coch mineral deposit has been controversial, commencing with the assertion that it was a sulphidized ooidal ironstone (Sherlock, 1919), the sulphidization being a metasomatic effect due to the underlying 'diabase'. The 'diabase' has since been remapped as a sequence of basic volcanic rocks belonging to the Dolgarrog Volcanic Formation. Although the Ordovician ooidal ironstones do contain minor pyrite (see **Tyllau Mwn** GCR site report, this chapter), the interpretation of Sherlock (1919) is clearly no longer valid, and neither is the other early interpretation that it is an epigenetic fracture-hosted deposit. The Cae Coch mineralization is without doubt a stratabound deposit; the problem now lies chiefly in finding the mechanism for its deposition.

Ball and Bland (1985) advocated a Kuroko-type model for the Cae Coch deposit, suggesting that the laminated ore in the upper part of the deposit represented pyrite precipitation within a brine-pool on the seafloor, with hydrothermal fluids escaping via 'black-smokers' represented by the pyrite tubes. The lower, rubbly ore, they suggested, had been disturbed during debris-flow movements. In addition, they argued that alteration patterns in the basic rocks of the Dolgarrog Volcanic Formation and in the rhyolites are closely comparable to those in the Uchinotai and Uwamuki deposits in Japan, involving, particularly, an increase in overall potassium content. Ball and Bland (1985) also briefly compared Cae Coch with other Ordovician stratabound sulphide deposits, such as at the **Parys Mountain** GCR site, on Anglesey, and Avoca in south-east Ireland, noting the similarity of these stratabound sulphide deposits all occurring within a mudstone succession, associated with bimodal acid-basic volcanism. In conclusion, Ball and Bland (1985) suggested that the Cae Coch mineral deposit was generated from brines enriched in potassium (leached from underlying acidic volcanic rocks) and carbonates, which were discharged into an euxinic seafloor environment.

Bottrell and Morton (1992), in contrast, adopted a different approach to investigating the Cae Coch mineralization, concentrating upon sulphur isotope ratios and Co/Ni ratios in pyrite. Most of the orebody pyrite samples gave $\delta^{34}S$ ratios in the –20‰ to –24‰ range, with occasional samples giving heavier signatures. These values are much lighter than would normally be expected had the deposit been of volcanogenic origin (they are in fact much lighter than 'sedimentary' pyrite values from the host rocks) and were interpreted by Bottrell and Morton (1992) as being the signature of bacterial sulphate reduction. For such light $\delta^{34}S$ ratios, either the site of deposition had to be open to permit re-supply of seawater sulphate, or the bacterial reduction involved sulphate derived from both seawater and from the underlying, and still warm, volcanic succession. The latter alternative, involving fluids leaching the volcanic succession, could also have supplied the requisite iron to the system.

The ratio of Co:Ni in the pyrite was found to be < 0.5, a value typical for sedimentary pyrite (Bralia *et al.*, 1979), but not characteristic of volcanogenic deposits, where values of 5 to 50 would be expected. Taking all the available data into account, Bottrell and Morton (1992) proposed a new genetic model for the Cae Coch deposit, in which bacterial sulphate reduction within anoxic muds generated H_2S and Fe, which combined as early framboidal pyrite. In time, H_2S production exceeded Fe availability, so that the sediment porewaters were H_2S-rich. Iron, in solutions generated from porewaters in the underlying Dolgarrog Volcanic Formation, interacted with the H_2S when the solutions were expelled upwards into the still unlithified, H_2S-rich muds, producing the ore pyrite. This process, operating over a prolonged timescale, resulted in the eventual pyritization of the mud, preserving sedimentary structures in its upper part. Eventual isolation of the system from further sulphate availability resulted in an end to the bacterial reduction: at this time any sulphate migrating up into the deposit from the underlying igneous rocks would have combined with iron to form pyrite with a much heavier isotopic composition ($\delta^{34}S$ = > 0‰).

Such an inhalative replacement model is clearly supported by the data of Bottrell and Morton (1992), and the textures described by Ball and Bland (1985), namely laminated ore and pyrite tubes, could represent pyritized original sedimentary structures. It is possible that the pyritized tubes are mineralized burrows. The leaching and upward migration of fluids from the underlying bimodal volcanic succession could also have supplied molybdenum to the system, together with the other low-level metal concentrations. In this model, the formation of an ore deposit has depended largely on two factors: firstly the sedimentary environment, namely a euxinic seafloor but with a continuing supply of seawater; and secondly the nature of the underlying succession, being a still warm acid/basic volcanic sequence capable of driving a hydrothermal leaching/migration system.

The extraordinary post-mining acidophilic bacterial community developed underground is the subject of ongoing research. The decomposition of pyrite through microbiological activity is a phenomenon which has many implications in biotechnology, in particular the treatment of pyritic ores containing fine-grained gold and other metals. Bio-leaching technology is now being used in many parts of the world as an agent in ore beneficiation. Conversely, the bacterial oxidation of pyrite is responsible for major environmental problems due to acid mine drainage.

Conclusions

The Cae Coch Mine massive stratabound pyrite deposit is of controversial origin. The most recent model for the genesis of the Cae Coch deposit involves the large-scale bacterial reduction of sulphate to sulphide, in the presence of an iron-rich flux leached from the underlying volcanic rocks, while the post-mining, large-scale bacterial oxidation of sulphide to sulphate, resulting in an acidic iron-rich mine drainage, constitutes the second principal point of scientific interest at this site.

FFESTINIOG GRANITE QUARRY (SH 695 453)

Introduction

The Ffestiniog Granite Quarry in the Tan y Grisiau Microgranite intrusion (Figure 5.39) exposes a rare occurrence of allanite mineralization, present both as an accessory phase in the granite itself, and more interestingly in veins and cavities in the roof zone of the intrusion.

The Tan y Grisiau Microgranite is one of a small number of silicic intrusions exposed in Snowdonia which lie outside of the main area of Snowdon Caldera subsidence which developed during the 2nd Eruptive Cycle in Ordovician (Caradoc) times (Howells *et al.*, 1991). The intrusion invades Lower Ordovician (Tremadoc) strata comprising well-bedded, medium- to fine-grained sandstones and siltstones of the Upper Sandstone Member of the Dol-cyn-afon Formation (Howells and Smith, 1997), which show clearly the effects of contact metamorphism.

The age of the Tan y Grisiau intrusion has long been a subject of debate, being variably assigned a Caradoc or late-stage 'Caledonian' (i.e. late Silurian to early Devonian) age (see, for

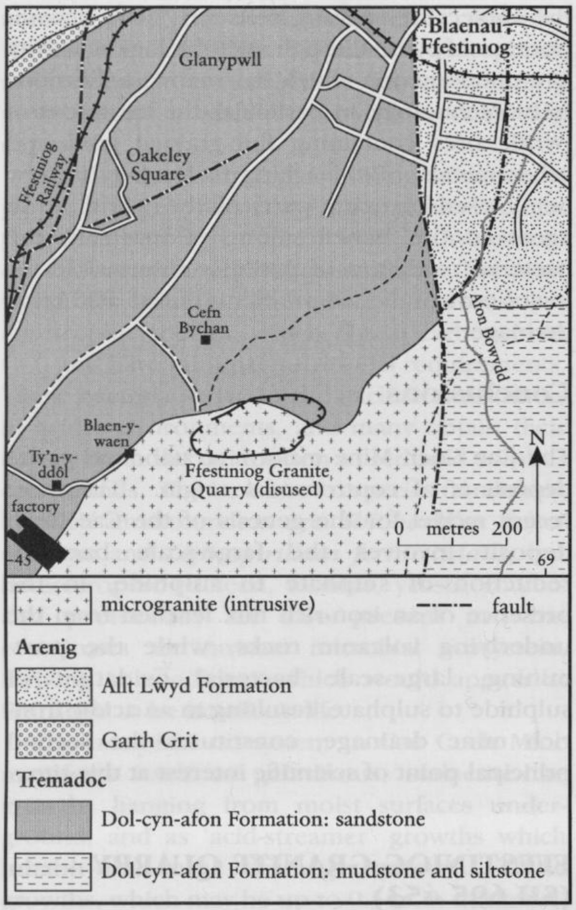


Figure 5.39 Map of the Ffestiniog Granite Quarry GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

example, Read, 1961; Fitch *et al.*, 1963; Thomas *et al.*, 1966). However, recent studies have helped to constrain its Caradoc age. To the south-west of Tan y Grisiau, granophyric apophyses and veins cut strata of Arenig age, and transgress both the mid-Caradoc unconformity (Smith *et al.*, 1995) and the disrupted strata within the Rhyd mélange (Bromley, 1969; Smith, 1988; Howells and Smith, 1997). Most important, however, is the fact that hornfelsing effects of the intrusion are found in rocks of the Moelwyn Volcanic Formation, of Costonian–Harnagian (Caradoc) age (Bromley, 1963, 1969), while younger strata are not affected. Thus the intrusion is constrained to the Caradoc, and is thought to be a sub-volcanic intrusion linked to the Snowdon Volcanic Group activity. Additional support for this correlation is provided by the geochemistry of the intrusion. Compositionally, taking account of trace-element concentrations, the intrusion has rhyolitic to rhyodacitic affinities, and a comparison has been drawn between the chemistry of the Tan y Grisiau Microgranite and rhyolitic lavas and tuffs of the Lower Rhyolitic Tuff Formation of central Snowdonia (Howells *et al.*, 1991). In contrast, K-Ar and Rb-Sr isotopic determinations have indicated a younger age, but these dates have almost certainly been affected by low-grade metamorphism during the Acadian Orogeny (Evans, 1991).

The Tan y Grisiau intrusion has an exposed surface area of *c.* 4 km^2, with the outcrop pattern of a truncated ellipsoid. However, the broad area of rocks showing the effects of contact metamorphism, combined with geophysical evidence, suggests that the intrusion is in fact a much larger body at depth (Howells and Smith, 1997). Available geophysical data have been interpreted as demonstrating a steep-sided, sub-vertical body, stretching some 10 km to the north-east and 5 km to the south-west of the main exposed area, with a roof that dips to the NNW (Cornwell *et al.*, 1980; Campbell *et al.*, 1985).

The intrusion is best exposed in the Ffestiniog Granite Quarry at Cefn Bychan, where its roof zone is exposed, along with its contact with the overlying Tremadoc sedimentary rocks (Figure 5.40). The contact dips to the north-west at 40°.

The presence of allanite mineralization at the quarry was first noted as early as 1908, by W.G. Fearnsides during a Geologists' Association field excursion to North Wales (Fearnsides, 1910). However, he could not identify the mineral that he had found in a narrow pegmatite-like vein in the north-west face of the quarry, and forwarded the 'peculiar mineral' to H.H. Thomas, of the Geological Survey. Thomas (1909) reported that the mineral was in fact 'orthite' (now called 'allanite'). Little further attention was paid to this occurrence until the area around Blaenau Ffestiniog was investigated by Bromley (1963). As part of a broad investigation into the Ordovician geology of the area, and in particular of its igneous history, he noted that not only does allanite occur in the veins and pods of the roof zone of the Tan y Grisiau intrusion, but that also it is an important accessory mineral in the microgranite itself (Bromley, 1964). Subsequently, Roberts (1979) made a brief reference to the allanite mineralization in the Ffestiniog Granite Quarry.

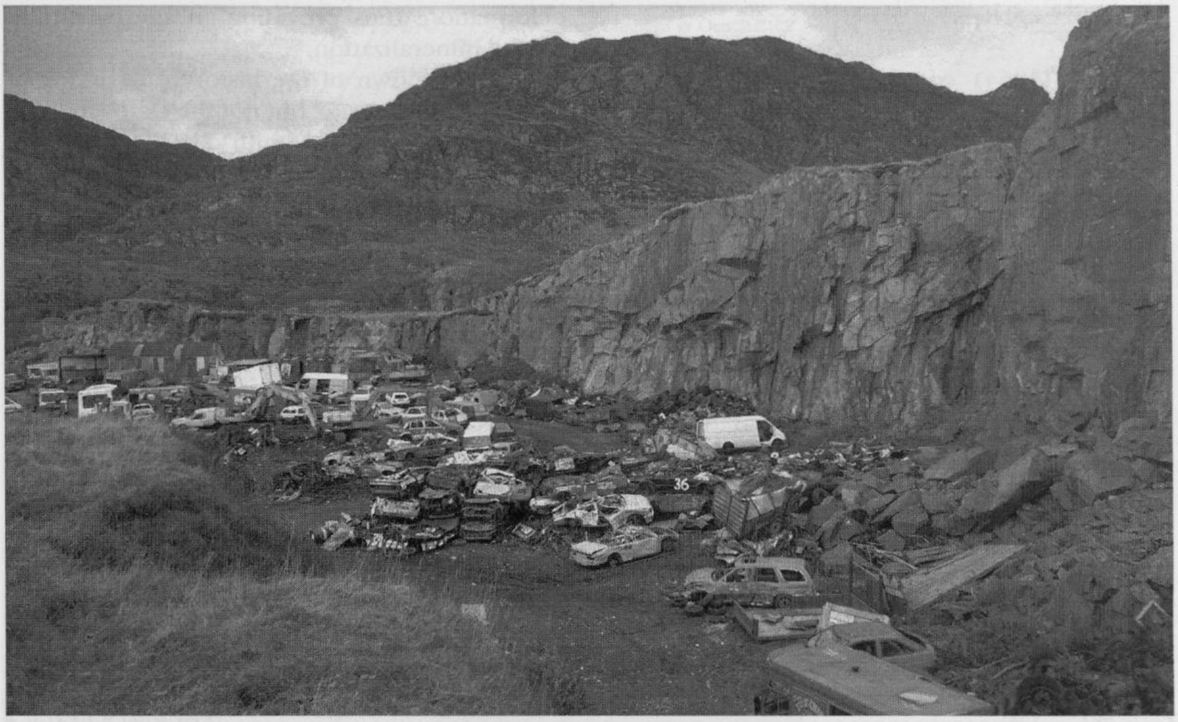


Figure 5.40 Photograph of the Ffestiniog Granite Quarry GCR site, exposing the roof zone of the intrusion. (Photo: R. Mathews.)

Description

The Tan y Grisiau Microgranite chiefly comprises a homogenous, equigranular, grey-green rock, with an average grain-size of between 2 mm and 4 mm. It is composed mainly of plagioclase (albite-oligoclase), microperthitic alkali feldspar, quartz, dark clots of chloritized biotite and rare ferrohastingsite (Bromley, 1964, 1969). Accessory minerals include magnetite, zircon and allanite, along with minor titanite, monazite and fluorite. Bromley (1964) noted two occurrences of allanite in the body of the granite. Firstly, it is present as small, euhedral crystals up to 1 mm in length, partly or completely surrounded by chlorite, which apparently crystallized at a late stage, and secondly replacing the orthoclase component of microperthite crystals, resulting in intergrowths of plagioclase and allanite.

The roof zone of the intrusion shows particular characteristics. Exposed in the northern face of the Ffestiniog Granite Quarry, the granite here is fine grained, and highly vesicular. The original mineralogy has mostly been replaced, with the orthoclase component of the microperthite converted to muscovite and the plagioclase component replaced by albite, granular calcite and quartz. All mafic phases are pseudomorphed by chlorite. This zone is also characterized by veins with graphic pegmatites and granite apophyses, and contains rounded metasomatized xenoliths. It is in this zone that the richest allanite mineralization occurs.

In the roof zone of the intrusion, allanite is also present in narrow (up to 3 cm wide) veins and broad (30 cm diameter) cavities which have a drusy character. Allanite crystals are prismatic to tabular in character, are orientated parallel to the *b* crystallographic axis, and reach up to 10 mm in length. The crystals are typically compositionally zoned and are usually twinned. Epidote, occurring as crystallographic overgrowths, is common. The mineral assemblage also contains quartz, chlorite, pyrite, molybdenite, pyrophyllite (Roberts, 1979) and calcite. Bromley (1964) also noted the presence of strong pleochroic haloes in chlorite surrounding allanite crystals, as well as possible alpha particle tracks as dark lines in surrounding calcite crystals, suggesting that the allanite crystals may contain significant radiogenic element concentrations.

Interpretation

Bromley (1964) considered that the allanite (and presumably the other minerals present in the veins and cavities) crystallized during a period of post-magmatic hydrothermal activity, in which volatiles were concentrated preferentially in the roof zone of the intrusion, a contention supported by Roberts (1979).

Campbell *et al.* (1987) identified five geochemically distinct groups of high-level rhyolites associated with the (Ordovician) Snowdon Caldera. Contents of certain trace elements vary markedly between the two groups, including the rare earth elements (REE), with the highest REE concentrations being in the B1 rhyolites, exposed for example at Bylchau Teyrn (SH 6170 5076), and it is possible that the Tan y Grisiau Microgranite intrusion represents a deeper-level representative of the Group B1 rhyolites. Unfortunately, there are no published REE analyses for the Tan y Grisiau intrusion.

Conclusions

Allanite, a comparatively uncommon rare-earth-element-bearing hydrous silicate mineral, is found in the Tan y Grisiau Microgranite intrusion, exposed at the Ffestiniog Granite Quarry. It occurs not only in the body of the granite, replacing K-feldspar and as small, well-formed crystals in chlorite, but also in veins and cavities cutting the intrusion. It is thought to have been generated at a late stage in the history of magma cooling, when volatiles were trapped in the roof zone of the intrusion.

AFON STWLAN (SH 671 446)

Introduction

Metalliferous quartz veins are widely developed throughout the Ffestiniog–Porthmadog belt, and largely unsuccessful attempts have been made to exploit them. A mineral vein striking across the Afon Stwlan GCR site (Figure 5.41), which was tried but not extensively worked, has since been superbly exposed by the construction of the service road to the Llyn Stwlan hydro-electric feeder reservoir. Not only does the exposure reveal very rich sulphide mineralization, but also critically it shows the effects of Acadian deformation, thus providing an age constraint for the mineralization.

Little is known of the history of working at Afon Stwlan. The site, but not the exposure, was mentioned by Foster-Smith (1977). It was, however, apparently part of a sett of workings known as 'Moelwyn', which in 1919 was being worked by the Union Zinc Mining Co. (Dewey and Smith, 1922). At this time, the site was producing sphalerite, of which there were apparently 1700 tons lying in stock. The workings referred to by Dewey and Smith (1922), however, lie farther down the hillside, towards Tan y Grisiau Reservoir, where extensive spoil-heaps and opencuts reveal abundant sulphide mineralization, dominated, as stated by Dewey and Smith (1922), by sphalerite. The Afon Stwlan exposure, although smaller in extent, is more informative geologically.

Description

The NE–SW-trending vein is exposed at approximately 390 m OD on the upslope side of the first hairpin bend on the service road, in a position high above the Tan y Grisiau Reservoir (Figure 5.42). Here the vein is hosted by dark-grey mudstones of the Nant Ffrancon Subgroup of Arenig to Caradoc age, clasts of which within the vein reveal thermal spotting, a contact metamorphic effect of the nearby Tan y Grisiau Microgranite. The vein consists of a rib, up to 0.3 m in width, of almost solid sphalerite and galena in quartz, with several parallel quartz-sulphide stringers and clay-gouge planes. The sulphide is largely fresh, apart from a little superficial hydrozincite replacement of sphalerite in the upper, near-surface part of the exposure.

In polished section, the mineralization can be seen to consist of sphalerite and galena, both of which contain inclusions of other sulphides. The galena carries pyrite and chalcopyrite inclusions, while the sphalerite contains pyrrhotite blebs, and also shows the development of chalcopyrite-disease. Quartz and chlorite are the gangue minerals, but are less abundant than the sulphides, a common feature in the better-developed metalliferous veins of this district.

Deformation is well displayed in the outcrop, particularly on the northern (hangingwall) side, where a thin (2–4 cm) quartz vein displays well-developed boudinage. The vein sulphides are

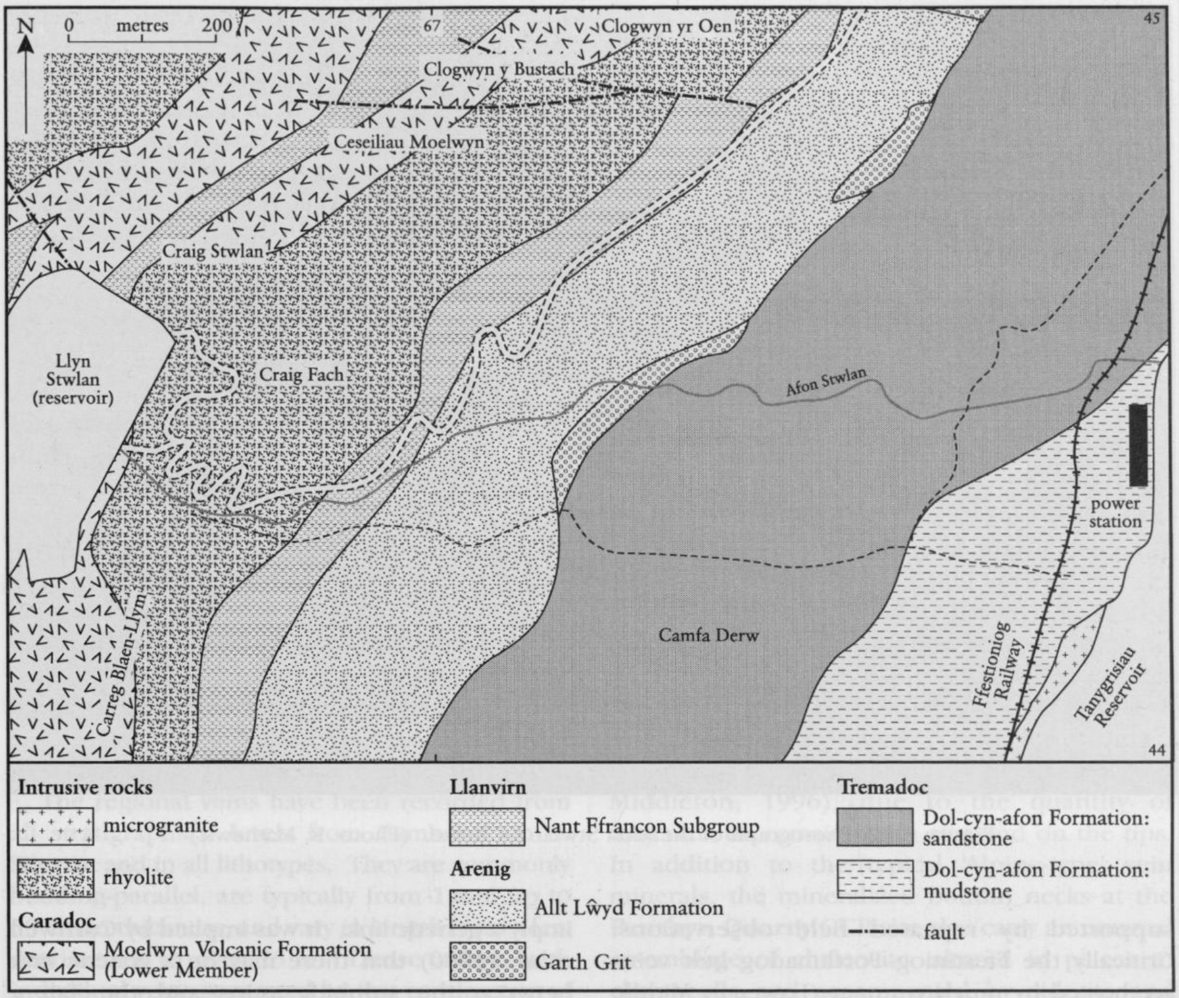


Figure 5.41 Map of the Afon Stwlan GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

also deformed, showing textures in hand specimen indicative of recrystallization; for example the galena has a 'steel-ore' texture. A large polished block, made from a loose block of sulphide found below the track, reveals boudins of quartz and the flowage of galena in between the relatively competent quartz bodies. Polished sections reveal that sphalerite and chalcopyrite have undergone cataclastic shattering within the relatively ductile galena matrix.

Interpretation

This exposure is critical in that it provides clear evidence for constraining the age of the quartz-sulphide veins of the Ffestiniog–Porthmadog belt, proving them to be pre-tectonic with respect to the Acadian compressional deformation (Mason *et al.*, 1999). This places them within the group of pre-tectonic metalliferous veins of North Wales, along with the Dolgellau Gold-belt veins and the copper-rich veins of the Snowdon Caldera (Mason *et al.*, 1999).

The Ffestiniog–Porthmadog belt lies to the north of the gold-belt and to the south of the Snowdon Caldera. The northernmost occurrences of worked gold mineralization, in the Cwm Prysor–Prince Edward mining district, lie *c.* 9 km to the south-east of this site, while the Sygun Copper Mine, within the south-eastern perimeter of the Snowdon Caldera, is *c.* 6.5 km to the north-west.

It has been reported (Lynas, 1973; Mason *et al.*, 1999) that the Gold-belt veins are restricted to Cambrian strata below the top of the Ffestiniog Flags Formation, a contention

Figure 5.42 Photograph of the Afon Stwlan GCR site. (Photo: R. Mathews.)

supported by repeated field observations. Critically the Ffestiniog–Porthmadog belt veins are hosted by much younger (Lower to Middle Ordovician) rocks, and additionally they cut the Tan y Grisiau Microgranite, both at the **Coed Llyn y Garnedd** GCR site and in roadside exposures to the south-west of Tan y Grisiau, at SH 6925 4409. This would suggest that the Ffestiniog–Porthmadog belt veins could be co-eval with those of the Snowdon Caldera. In fact, the Ffestiniog–Porthmadog belt veins bear a much greater textural resemblance to the Snowdon Caldera veins than to the Gold-belt veins. The latter group of veins is quartz-rich and tends to occur as composite ribbon-rock zones, a feature not evident in the Ffestiniog–Porthmadog belt. Also, the larger Ffestiniog–Porthmadog belt veins tend to have high sulphide:quartz ratios, as do the Snowdon Caldera veins, whereas in the gold-belt the inverse is generally the rule.

Consequently, available evidence suggests that the Ffestiniog–Porthmadog belt veins more closely resemble those of the Snowdon Caldera, although this does not necessarily imply a genetic link. It was implied by Cornwell *et al.* (1980) that there may be a genetic link between the sulphide veins and the Tan y Grisiau Microgranite. However, the fact that the Ffestiniog–Porthmadog belt veins contain clasts of thermally spotted mudstone, as at this site, shows that they post-date the intrusion and its metamorphic effects. Further investigations into the genesis of the pre-tectonic metalliferous veins of the Ffestiniog–Porthmadog belt are needed before any further conclusions may be drawn.

Conclusions

Sulphide-rich Pb-Zn-Cu vein mineralization, of widespread distribution in the Ffestiniog–Porthmadog belt, is particularly well-developed in a cutting on the service road to the Llyn Stwlan hydro-electric feeder reservoir. The exposure at Afon Stwlan provides critical evidence which indicates that the veins are pre-tectonic in relation to Acadian deformation. The genesis of the veins, however, is more problematic; field evidence suggests that they are more likely to be linked genetically to the mineralization in and around the Snowdon Caldera to the north-west, rather than to the Dolgellau Gold-belt to the south-east. They are geographically close to the Tan y Grisiau Microgranite; however they post-date the metamorphic effects of that intrusion.

'ALPINE-TYPE' VEINS CUTTING CARADOC AND OLDER SEDIMENTARY AND IGNEOUS ROCKS

In addition to the diverse range of metalliferous veins present in the Welsh Caledonides, non-metalliferous veins, dominated by quartz, occur commonly. These fall into two broad groups: firstly there are the 'Regional veins' (Fitches, 1987) which typically manifest themselves as the flat-lying arrays of massive milky quartz veining that are often conspicuous on rocky mountainsides in Snowdonia; and secondly there are what have become known by mineralogists as 'Alpine-type veins', which contain a diverse range of well-crystallized and often rare minerals.

The regional veins have been recorded from all stratigraphical levels from Cambrian up to Silurian and in all lithotypes. They are commonly bedding-parallel, are typically from 1 mm up to 50 cm in thickness, and vary in length from a few centimetres to over 25 m. Dense arrays, with individual veins separated by just centimetres of strata, are commonly observed, with rarer bedding-normal veins linking them. As well as quartz, they may contain carbonates, chlorite, occasional pyrite, stilpnomelane and feldspar: their composition broadly reflects that of the host rock so that pyrite is most likely to occur in veins hosted by dark, pyritic mudstones, while siderite and stilpnomelane are both known from veins hosted by sedimentary ironstones. The veins are locally seen to be folded, cleaved and boudinaged, all indications of their pre-tectonic development with respect to the Acadian deformation. Exposures of such veins are a common sight, especially in rocky areas such as the mountains of Snowdonia; the **Coed Llyn y Garnedd** GCR site features numerous examples. The veins are considered to be products of hydraulic jacking by overpressurized pore-fluids during burial-related metamorphism (Fitches, 1987), and as they formed during progressive burial of the various lithologies of various ages, they are clearly diachronous.

The 'Alpine-type' veins are widespread but more localized in occurrence. They are partially open, vuggy fissures formed in competent and brittle lithologies as a response to Acadian deformation: thus, they occur in boudin necks in slate-hosted dykes at the **Penrhyn Quarry** GCR site, in larger igneous intrusions at numerous sites across Snowdonia including the **Manod Quarry** GCR site, and in boudin necks in the lodes of the Dolgellau Gold-belt, as seen at the **Friog Undercliff** GCR site. They are dominated by quartz and albite, often finely crystallized, but they contain a variable and diverse suite of accessory minerals, comprising anatase, brookite, rutile, titantite, hematite, chlorite, epidote, clinozoisite, monazite-(Ce), xenotime-(Y), synchysite-(Ce) and apatite, all of which are typically well-crystallized. One locality, Prenteg, near Tremadog, where 'Alpine-type' veins are hosted by a dolerite sill, formerly produced brookite specimens that are still regarded as world-class (Starkey and Robinson, 1992). However, as a scientific study site for this suite of veins, the **Manod Quarry** GCR site near Blaenau Ffestiniog is of particular note (Green and Middleton, 1996), due to the quantity of material still remaining *in situ* and on the tips. In addition to the typical 'Alpine-type' vein minerals, the mineralized boudin necks at the **Penrhyn Quarry** GCR site also carry an unusual assemblage of chalcocite, altered in places to chrysocolla and accompanied by siderite and calcite.

MANOD QUARRY (SH 708 448)

Introduction

Manod Quarry, a large disused working on the hillside overlooking the road between Ffestiniog and Blaenau Ffestiniog (Figure 5.43), provides an excellent site for the study of 'Alpine-type' veins which occur regionally in the Ffestiniog–Porthmadog belt. The quarry worked a large intrusion of quartz-latite which was emplaced into the Allt Lŵyd Formation of Arenig age, and the overlying Nant Ffrancon Subgroup of Arenig to Caradoc age (British Geological Survey, 1997).

The intrusion is host to a series of veins, several of which are exposed at the northern end of the quarry. In addition, numerous boulders

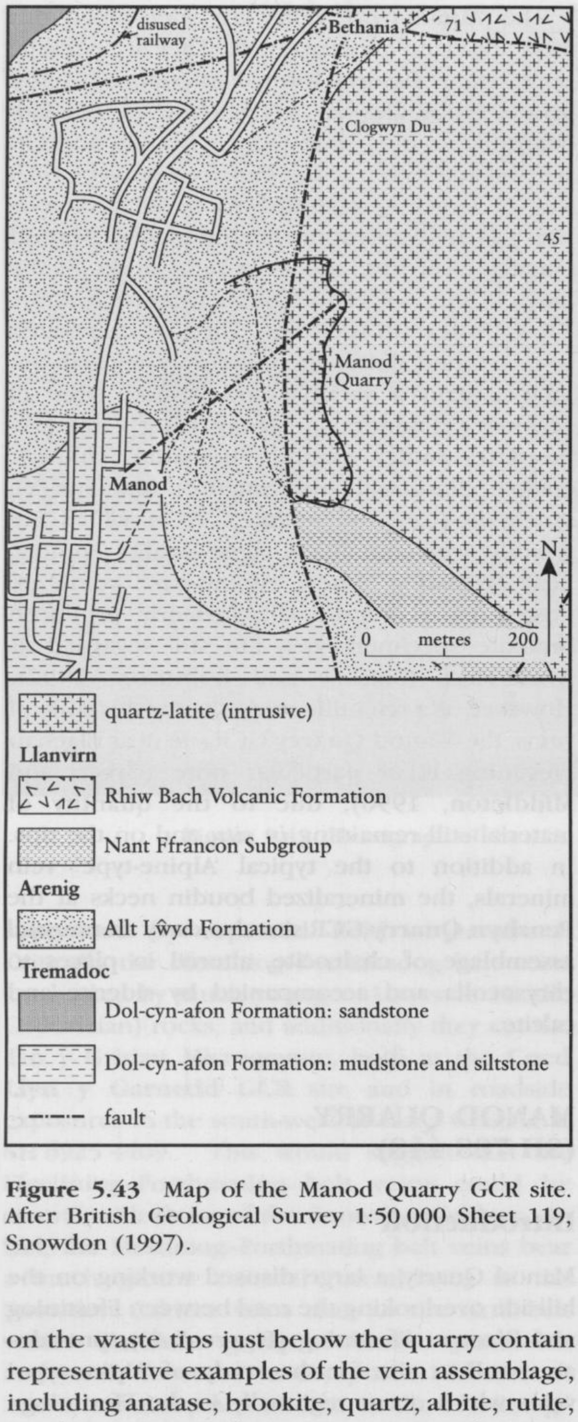


Figure 5.43 Map of the Manod Quarry GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

on the waste tips just below the quarry contain representative examples of the vein assemblage, including anatase, brookite, quartz, albite, rutile, synchysite-(Ce) and titanite (Bevins and Mason, 1998). The relationships between the three TiO_2 polymorphs are of particular interest.

Little work has yet been undertaken on this group of veins, despite the fact that such mineralization was amongst the earliest to be described in detail from Wales. Sowerby (1809) wrote the first account of the occurrence of brookite in the area, the specimen almost certainly having been collected from the now famous locality at Prenteg, near Tremadog, to the west of Manod (Starkey and Robinson, 1992). This 'oxide of titanium' was systematically described by Lévy (1825), based on specimens both from Prenteg and the Dauphiné region of France; hence Prenteg, along with the Dauphiné occurrence, is a joint type locality for brookite.

Since that time, the only attention given to this style of mineralization has largely been that by specimen collectors. At Prenteg, the renowned mineralogist Sir Arthur Russell collected specimens as early as 1905, while some years later, quarrying for roadstone at the same locality produced many fine samples (Starkey and Robinson, 1992).

Manod Quarry itself has been almost totally neglected by researchers, despite the many fine specimens collected by amateurs over the years. Occurrences of the various mineral species present were noted by Bevins (1994), while Green and Middleton (1996) compared a similar assemblage at the nearby Tan y Grisiau Station locality to that at Manod. In reality, the site has for many years been overshadowed by Prenteg; however, in view of access problems which have affected the latter site, not least accessibility in both safety and legal terms, Manod was considered by Bevins and Mason (1998) to be the most practical site for the study of both the geological features and the mineralogy of this important class of mineralization.

Description

Quartz-dominated mineral veins occur frequently within the large, competent quartz-latite body at Manod Quarry (Figure 5.44). The veins tend to occur in sub-parallel bunches of limited strike length and often occupy joint fractures in the quartz-latite. They typically strike east–west and are steeply dipping to vertical, forming open fissures, bridged across in places by quartz but often revealing extensive plates of freely grown crystals. Mineralogically, the most complex veins tend to be thin (< 15 mm wide), while thicker veins, up to 8 cm, have a simpler mineralogy, usually being filled solely with quartz.

In the open cavities, quartz forms crusts of water-clear crystals occasionally reaching 1–2 cm in length. Associated with the quartz is abundant chlorite, the latter being an early phase and often included in quartz, giving the crystals a greenish tint. A very rare pink phase,

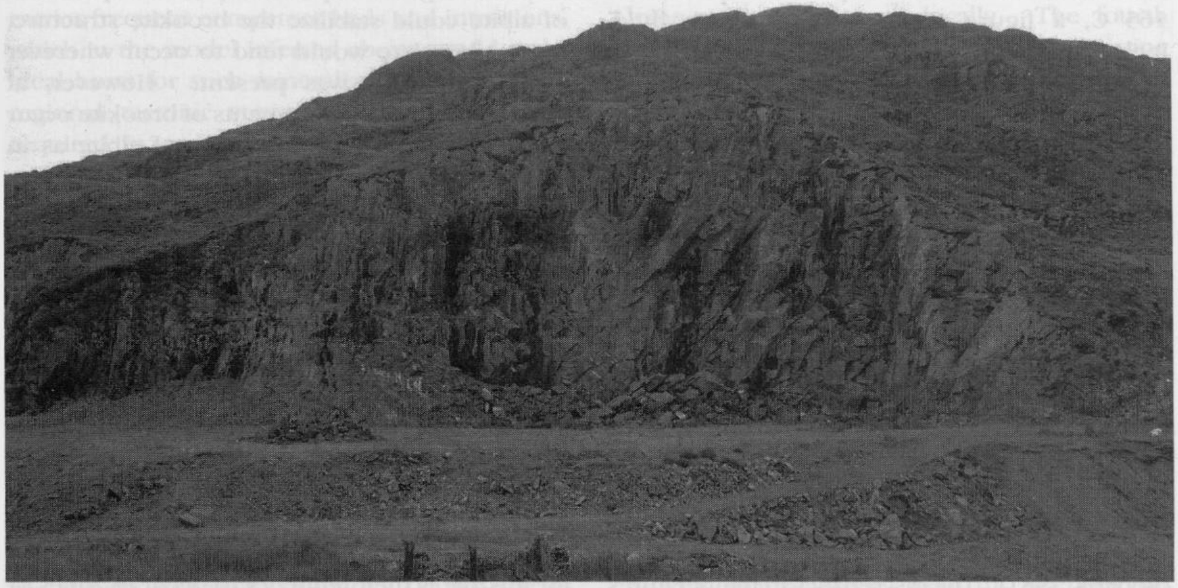


Figure 5.44 Photograph of the Manod Quarry GCR site. (Photo: R. Mathews.)

forming small (1–2 mm) grains in quartz and therefore an early component of the paragenesis, has recently been identified as titanite (authors' unpublished data).

All three TiO_2 polymorphs occur in the Manod Quarry veins. Anatase occurs most noticeably on quartz, as aggregates of twinned tabular crystals, stepped parallel to the c-axis and exceptionally up to 4 mm in size. These stepped crystal groups are sapphire-blue in colour, but broken sections reveal brown internal cores. Thin, tabular, yellowish-brown anatase crystals, often in confused groups and reaching 1 mm across, are also common. Brookite is earlier in the paragenesis than anatase, forming characteristic striated blades exceptionally up to 10 mm, associated with quartz and chlorite but also occurring alone as striking orange coatings on thin joints in the adjacent quartz-latite. Brookite crystals have invariably been shattered and healed, with numerous, small, new crystal terminations developed along fractured surfaces. Both anatase and brookite have locally been altered to rutile, which forms sub-metallic golden needles, often aggregated together into 1–2 mm reticulated masses.

All three TiO_2 polymorphs are overgrown by albite, which is abundant and typically forms striated tabular, white to colourless crystals up to 10 mm. Synchysite occurs rarely as minute (1 mm) rosettes and is a late-stage development, while a single tabular apatite crystal, of uncertain paragenetic position, has been noted. The assemblage has been overgrown to varying degrees by late-stage, coarsely crystalline calcite, a feature common to many 'Alpine-type' mineral veins in this area.

Interpretation

Much of the published information regarding the 'Alpine-type' veins in North Wales has been of a descriptive nature and presented little interpretation of the genesis of the mineralization. Green and Middleton (1996) merely stated that the 'Alpine-type' vein assemblage formed as a result of low-grade regional metamorphism. However, Starkey and Robinson (1992) investigated the analogous mineralization at Prenteg in some detail, including analysis of fluid inclusions present in quartz and brookite crystals. They determined a minimum temperature for vein emplacement of 160°–170° C, the fluids involved being of moderately low salinity. The lack of a suitable geobarometer, such as an equilibrium assemblage of metamorphic minerals, however, precluded a pressure correction for the fluid-inclusion data; hence they represent a minimum temperature of crystallization. According to Starkey and Robinson (1992), illite crystallinity (IC) values obtained from the mudstones hosting the dolerite sill at Prenteg indicate a formation temperature of around 165° C, a figure compatible with the fluid-inclusion data. Therefore, Starkey and Robinson (1992) concluded that the actual temperature of vein emplacement was not significantly higher than the minimum value obtained from fluid inclusions. However, it is by no means certain that the illite crystallinity values are directly related to, and of the same age as, the process of 'Alpine-type' vein generation. Indeed, the temperature estimate appears to be low when IC data from Roberts and Merriman (1985) are considered. According to these authors, IC values at Prenteg are $< 0.25\Delta°2\theta$, indicative of epizonal conditions, implying temperatures perhaps as high as 250°–300° C. This is in accordance with secondary mineral assemblages in metabasites in this part of North Wales, which are indicative of greenschist-facies conditions (Roberts, 1981). The discrepancy in temperatures between the 'Alpine-type' veins and the low-grade metamorphic indicators in the host rocks can be interpreted as either indicating that the events are not directly related (although the veins may represent a late-stage event during thermal decline, perhaps consistent with their suggested syn-Acadian age) or that the two events may be related but that the fluid-inclusion data are of little relevance because of the lack of application of a pressure correction.

Starkey and Robinson (1992) stated that the mineral assemblage at Prenteg was deposited in the order apatite, rutile, anatase, monazite, chamosite, quartz, brookite and albite. This contrasts with the Manod assemblage, where the TiO_2 sequence is brookite-anatase-rutile, with the rutile clearly replacing brookite (Bevins and Mason, 1998). Moreover, the habit and colour of anatase at both Manod and other adjacent localities (tabular, brown-cored, sapphire-blue) contrasts with the dark-brown tetragonal bipyramids from Prenteg.

At Tan y Grisiau Station it is recorded that the TiO_2 sequence is rutile-brookite-anatase (Green and Middleton, 1996). Here, the rutile occurs as typical hair-like inclusions in quartz and other minerals, whereas at Manod it forms reticulated sheaves of crystals which replace brookite. Thus, each of the three studied 'Alpine-type' vein localities in the Ffestiniog–Porthmadog belt has its own unique sequence of TiO_2 polymorph crystallization.

Starkey and Robinson (1992) discussed the relative stabilities of the three TiO_2 minerals, commenting on the possibility that the presence of albite could stabilize the brookite structure, so that brookite would tend to occur wherever significant albite was present. However, at Manod the rutile replacements of brookite occur just as regularly in the absence of albite as in close proximity to it. Therefore, the paragenetic relationships between these three minerals and their associates in the Ffestiniog–Porthmadog belt remains to be qualified.

The maximum age of the 'Alpine-type' veins of the Manod Quarry GCR site is clearly constrained by the strata that host them, which are of Llanvirn to Caradoc age. The minimum age is more problematic, but two lines of evidence support the hypothesis that they are syn-tectonic with respect to the Acadian deformation, which would give them a Lower Devonian age. The most compelling evidence for this age is their tendency to occur in zones of extension and brittle fracture that have clearly developed as a response to regional Acadian strain, such as boudin necks and tension cracks in competent units. Secondly, all pre-Acadian quartz veins in North Wales are strongly deformed and recrystallized. In contrast, within the 'Alpine-type' veins, groups of crystals of great delicacy are invariably well-preserved, the only signs of disturbance being occasionally observed fracturing and healing of crystals. This observation applies whether the veins are hosted by large intrusive bodies or by thinner beds such as tuffs. These observations combine to suggest: (a) formation in localized extensional environments occurred during compressive deformation; and (b) because of formation in such 'protected' structural locations, the mineralization was preserved in its original state, in contrast to the effects observed in the clearly pre-tectonic veins.

Similar veins are known from other parts of the Welsh Caledonides, for example on Mynydd Ysgyfarnod, in the northern Harlech Dome region (T.F. Cotterell, pers. comm.), and in dolerite at Hendre Quarry in the Berwyns (Starkey *et al.*, 1991), and in parts of Central Wales, where they occur in sandstone units. In the latter case the mineralization is limited to quartz, although texturally it is identical. However, the tract of country from the Migneint through the Ffestiniog district westward towards Porthmadog contains the best-known and most frequent occurrences. The stratigraphy through this tract, the southern slate-belt of Snowdonia, is dominated by ductile mudstones, but also carries frequent competent beds and intrusions, which in the model inferred above would make ideal hosts for such mineralization during high regional tectonic strain. Further research is required in order to test the viability of this genetic model.

Conclusions

Quartz-chlorite-dominated mineral veins at Manod Quarry contain albite and minor amounts of a range of comparatively rare minerals, including anatase, brookite, rutile, synchysite-(Ce) and titanite. These veins have been compared with the Alpine cleft veins of the central Alps. These so-called 'Alpine-type' veins of the Ffestiniog–Porthmadog belt present an interesting enigma: they contain concentrations of typically immobile elements, particularly in the form of the three TiO_2 polymorphs anatase, rutile and brookite, and are particularly common in this belt, which features a mudstone-dominated sequence but within which a variety of competent beds and intrusions are present. The detailed paragenetic sequences, particularly of the TiO_2 minerals, vary from site to site, and to date little detailed work has been undertaken with regard to their genesis. In addition, although a likely syn-Acadian age has been proposed for these veins, the model requires further research to test its validity.

COED LLYN Y GARNEDD (SH 650 420)

Introduction

Forest roads that were extended in the late 1990s on the wooded hillside at Coed Llyn y Garnedd (Figure 5.45) provide an almost continuous section through sedimentary, volcanic and intrusive rocks of Tremadoc through to Caradoc age. Mineralization exposed in the roadside cuttings falls into four distinct categories and the section offers some valuable age-constraining relationships when examined in conjunction with the **Ffestiniog Granite Quarry**, **Manod Quarry** and **Afon Stwlan** GCR sites. Two generations of veining, the 'Regional veins' (Fitches, 1987), and the Ffestiniog–Porthmadog Belt quartz-sulphide veins, are pre-tectonic with respect to Acadian deformation, while apparently syn-tectonic veins of the 'Alpine-type' suite occur locally. The fourth generation of veining is post-tectonic, consisting of coarsely crystalline marcasite associated with quartz, an assemblage which occurs regionally across North Wales.

Description

The track section described here commences from the B4410 Garreg-Maentwrog road at a forest car-park, and passes up through Tremadoc-age sedimentary rocks (intruded by a dyke-like body of microgranite) into Arenig–Llanvirn sandsones and mudstones, including, at the top, laharic flow-breccias, and finally rocks of the Moelwyn Volcanic Formation of Caradoc age. The section is described in an anticlockwise manner.

In the first kilometre from the car-park, the geology comprises sandstones and siltstones of the Dol-cyn-afon Formation of Tremadoc age, intruded at one point by a wall-like body of microgranite, related genetically to and probably part of the Tan y Grisiau Microgranite. The sedimentary rocks reveal thermal spotting to a considerable distance from the microgranite outcrop, indicating that the intrusion is of much wider extent at depth than its surface exposure suggests. The microgranite varies in colour from mottled grey to pink, and is cut by two types of veins. Firstly there are quartz veins with pyrite and sphalerite, belonging to the Ffestiniog–Porthmadog belt group, as exposed at the **Afon Stwlan** GCR site. Secondly, there are vuggy veins carrying quartz, chlorite, pink albite and rare anatase, belonging to the 'Alpine-type' group. Both types of veins are thin and irregular, but they usefully demonstrate their age relationship with the microgranite.

Further along the track, a prominent outcrop on its eastern side is dominated by a massive, NW–SE-striking steeply dipping quartz vein hosted by spotted grey siltstones belonging to the Dol-cyn-afon Formation. The surface of the vein has been smoothed by glacial action but broken debris occurs immediately to its south. Much of this consists of siltstone clasts and quartz, derived from the vein margins, and where the quartz-clast interface has ruptured, a crystalline vug-lining assemblage has developed which consists of further quartz, pink to white albite and deep sapphire-blue tabular anatase. Many of the anatase crystals, which reach 1–2 mm,

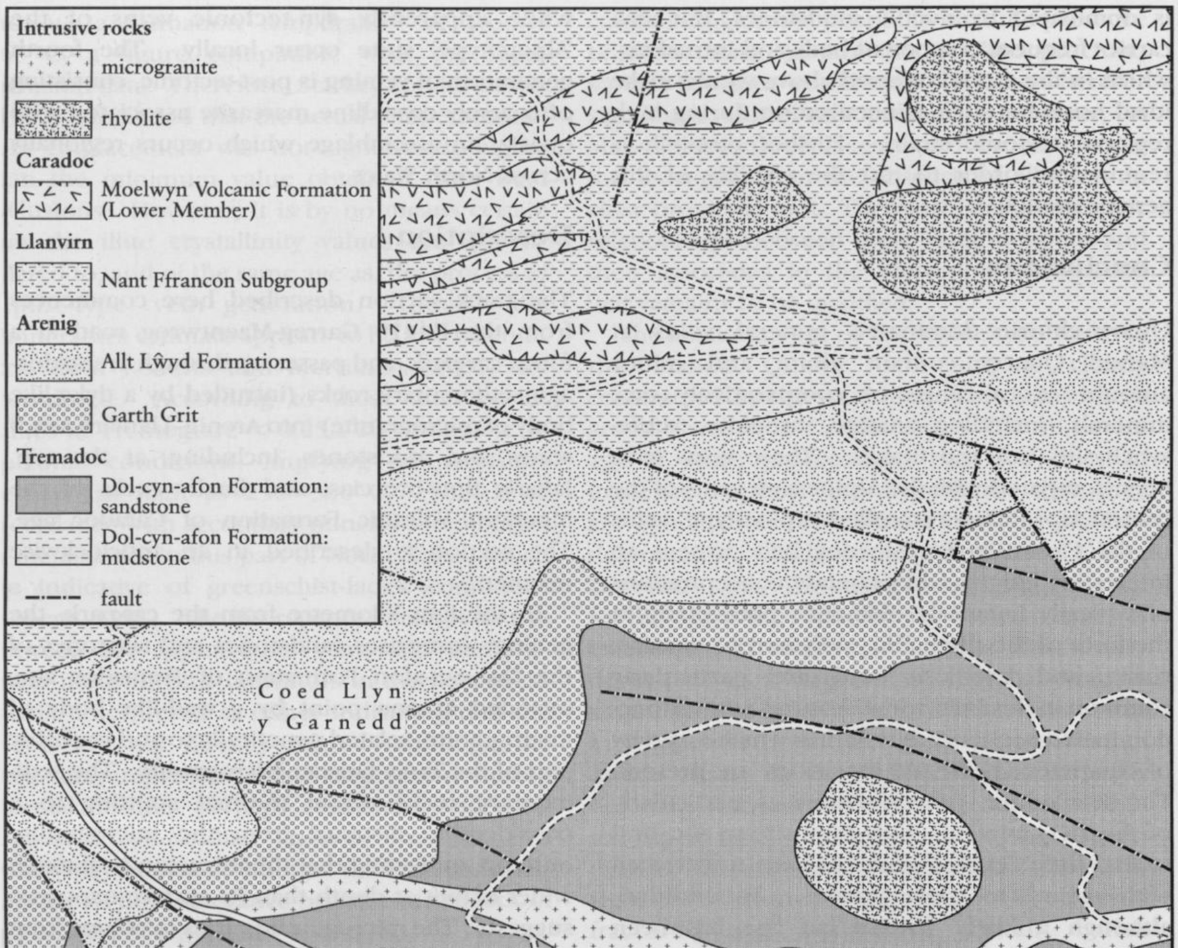


Figure 5.45 Map of the Coed Llyn y Garnedd GCR site. After British Geological Survey 1:50 000 Sheet 119, Snowdon (1997).

have been broken and healed, giving them a slightly curved appearance. The massive quartz vein is thought to belong to the 'Regional veins' noted in the 'Introduction', whilst the anatase-bearing vug-filling mineralization, belonging to the 'Alpine-type' suite, is thought to represent localized extensional fracturing along the interface between the massive quartz and sedimentary rock clasts during Acadian deformation.

The track climbs for a few hundred metres, passes two minor turn-offs on the right and then turns sharply back left. Here, lying unconformably above the Dol-cyn-afon Formation is the Garth Grit, belonging to the Allt Lŵyd Formation. The grit is a coarse, quartzose sandstone of Arenig age, which contains numerous milky quartz veins. Along the descending track section from this locality, grey, spotted mudstones belonging to the main part of the Allt Lŵyd Formation are particularly intensely veined. One set of veins (set 1), belonging to the Ffestiniog–Porthmadog belt suite, consists of milky quartz with sphalerite and occasional pyrite and chalcopyrite. These veins form two well-defined subsets (sets 1a and 1b) at this locality: firstly, there are numerous, low-angle 2–3 cm-wide veins, dipping NNW at 25°–30° with the bedding; and secondly there are steep to vertical link-veins, generally striking in a north-east–to south-west to ENE–WSW direction. The other set of veins (set 2) strikes ENE–WSW to east–west and slightly displaces the quartz-sphalerite veins where it cuts them. The set 2 veins consist of open fracture-linings of cockscomb marcasite, now rather weathered, accompanied by clear to greyish stumpy quartz crystals. Pyritic haloes up to 0.3 m in width have formed in the wall-rock adjacent to the set 2 veins.

The track climbs slightly and reaches a T-junction. To the right, a short distance on, a small roadside quarry has been worked in thick scree derived from Nant Ffrancon Subgroup rocks, and has exposed the underlying glacially smoothed bedrock. A short distance up the exposure, there crops out an irregular, strongly jointed quartz vein belonging to the 'Regional veins', and blocks lying beneath reveal small extensional fractures at its margins, forming vugs containing green crystalline rosettes of chlorite up to about 2 mm and hair-like crystals of rutile, this belonging to the 'Alpine-type' suite.

Leftwards from the T-junction, the track steadily descends back towards the road. Along its western side there are numerous exposures of mudstones belonging to the Nant Ffrancon Subgroup with strong developments of veining in places, especially those belonging to the 'Regional veins'. These occur in locally dense arrays of flat-lying quartz veins separated by a few centimetres of strata. The veins are typically 3–30 cm in thickness and are buckled and weakly boudinaged in places; cleavage in the mudstone between the veins has been strongly disturbed in places (Figure 5.46). Thinner steeply inclined veins join the flat-lying veins in places and are occasionally seen to extend above the vein arrays only to pinch out after a few tens of centimetres. Broken vein sections reveal intra-vein partings deformed into strongly stylolitic surfaces marked by chlorite. The other veining along this section belongs to the Ffestiniog–Porthmadog suite and consists of narrow (2–3 cm) quartz-sphalerite-chalcopyrite-pyrite veins which are almost concordant with bedding, dipping into the hillside at 20°–30°. Well-exposed intersections with the 'Regional veins' are hard to find today: in 1997, when the exposures were fresher and less vegetated, it was noted that the Ffestiniog–Porthmadog belt veins were very occasionally seen to cut the 'Regional veins' without displacing them.

Interpretation

This section has demonstrated the age relationships of the various types of mineralization and the sedimentary rocks and a major intrusion within the Ffestiniog–Porthmadog slate-belt, and complements other GCR sites in the area, where their detailed mineralogy is displayed to better effect. It reveals the important time sequence of intrusion and mineralization which is as follows:

1. Post-burial development of the 'Regional veins' of predominantly flat-lying quartz vein-arrays;
2. Intrusion of the Tan y Grisiau Microgranite into strata of Lower Ordovician age;
3. Fracturing and emplacement of the Ffestiniog–Porthmadog belt quartz-sulphide veins;
4. Acadian deformation and local extensional fracturing; formation of 'Alpine-type' veins; and
5. Emplacement of regional crustiform quartz-marcasite-dominated veins.

The 'Regional veins', recorded across the Welsh Basin from all stratigraphical levels from Cambrian up to Silurian and in all lithotypes, are

Figure 5.46 Arrays of flat-lying regional pre-tectonic quartz veins hosted by mudstones of the Nant Ffrancon Subgroup. Note disturbance of the cleavage of the mudstone adjacent to the veins. (Photo: J.S. Mason.)

considered to be products of hydraulic jacking by overpressurized pore-fluids during burial-related metamorphism (Fitches, 1987), and as they formed during progressive burial of the various lithologies of various ages, they are clearly diachronous. However, the burial depth at which they started to form is uncertain. The hydraulic jacking mechanism, explained by Fitches (1987), involved porewaters migrating upwards through the sedimentary pile and regularly getting trapped beneath layers of argillite whose permeability had been reduced by compaction and diagenesis. High fluid pressures in such instances would have led to failure along the lines of weakness represented by bedding surfaces, resulting in bedding-parallel cavities opening up with minerals being deposited on cavity surfaces. The veins at a steep angle to bedding formed due either to hydraulic fracturing of cavity ceilings or, possibly, where the strata were slightly inclined, with assistance from extra horizontal tensile stresses due to downslope extension. By these processes, a stack of bedding-parallel veins, linked by steeper veins, would propagate upwards through the sedimentary pile, and would continue to form while there was sufficient availability of fluids. The hydrothermal systems involved seem to have been rather localized in extent, in the order, perhaps, of just hundreds of metres, and the fluids would probably have been a mixture of buried seawater and water released via dehydration reactions during diagenesis. The limited extent and lack of circulation of the fluids is the likely explanation for the veins being: (a) dominated by quartz; and (b) having accessory minerals that reflect host-rock composition.

The pre-Acadian Ffestiniog–Porthmadog belt mineralization has been discussed in detail elsewhere in this chapter (see the **Afon Stwlan** GCR site report). That the veins cut both the 'Regional veins' and the Tan y Grisiau Microgranite, yet are themselves deformed, as seen at Afon Stwlan, constrains their age to a point between the Caradoc, when the microgranite was intruded, and the early Devonian. In the immediate vicinity, the only other identified metallogenic episode during the above time-frame was the Snowdon Caldera Cu-Zn-Fe-Pb-As mineralization, seen for example at the **Lliwedd Mine** GCR site. Snowdon is less than 10 km away from this site, and it is possible that these quartz-sulphide veins represent a distal facies to the caldera mineralization, which, it is already known, extended beyond the caldera margin, as seen at the **Llanberis Mine** GCR site.

The 'Alpine-type' veins are only weakly represented at this site. However, one interesting feature is well-demonstrated here in that they can develop along the margins of existing 'Regional veins', a feature also well known in the Alps where they have been worked for specimens for centuries. Under high-strain situations, the strong rheology-contrast across the often irregular interface between the margin of a favourably orientated massive quartz vein and its wall-rocks can become a locus for shear movements and consequent localized extensional fracturing, creating small cavities that any available fluids would enter, depressurize and deposit minerals on the cavity sides. In such a scenario, the sources for the fluids would be extremely localized, as would be the elements dissolved in them. Widespread circulation of fluids is less favoured in high-strain situations.

The quartz-marcasite veining is representative of a regional group of post-Acadian crustiform veins which is developed throughout the Welsh Caledonides. Closely similar veins are common in the Dolgellau Gold-belt, where they cut, but rarely displace, the gold-belt veins (Mason *et al.*, 1999). Within the Snowdon Caldera and environs, crustiform-banded calcite-marcasite-dominated mineralization is widespread in small amounts (Bevins and Mason, 1998) and is Assemblage 4 of Reedman *et al.* (1985). To the north-east of the Snowdon Caldera, such mineralization is more intensively developed within the Llanrwst mining district, where it was extensively worked for lead and zinc (Haggerty, 1995), while to the south of Snowdonia, the late (A2) assemblages of the Central Wales Orefield (Mason, 1994, 1997) frequently exhibit mineralogical and textural features which suggest that they may also be assigned, at least in part, to this regional suite of veins.

The regional, post-Acadian crustiform fissure-fill veins are expressions of periodic regional crustal extension and hydrothermal fluid-flow at various times from Upper Palaeozoic times onwards. Such tectonic regimes and associated hydrothermal activity were a feature of the Welsh Caledonides in pre- and particularly post-Variscan times, when the area was surrounded by a series of subsiding basins from which connate brines were driven, either into uplifted Lower Palaeozoic rocks or into Carboniferous carbonate-dominated sequences, as in the North-east Wales Orefield. If anything, the information that can be gained by studying their extent, in terms of size and distribution, may serve to indicate crudely the intensity of regional extension in any given area.

Conclusions

Roadside exposures in Coed Llyn y Garnedd, exposing strata of Tremadoc to Caradoc age, reveal structural evidence which provides age constraints for the various suites of mineral veins occurring within the Ffestiniog–Porthmadog belt, an area of considerable geological controversy, particularly in relation to its structural evolution.

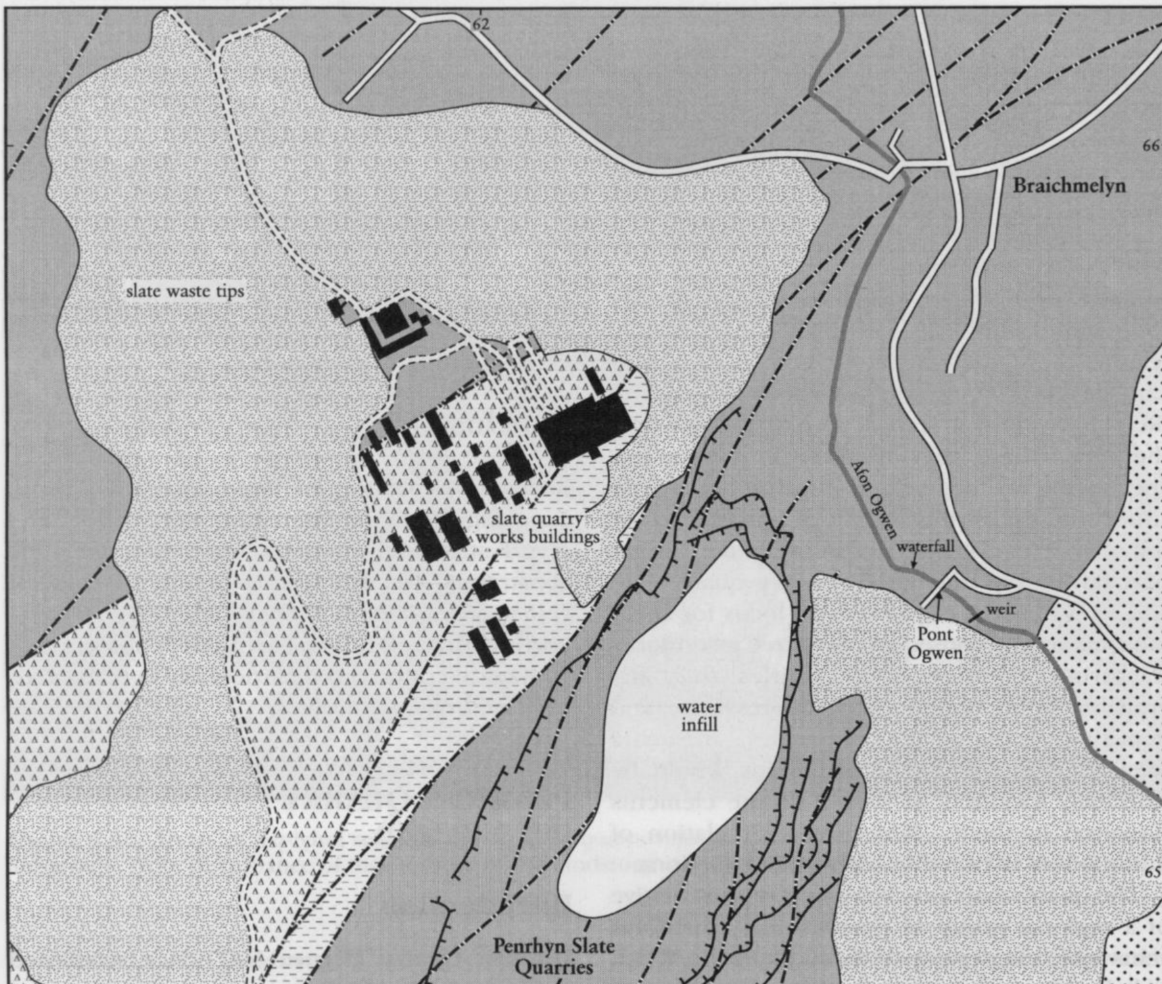
PENRHYN QUARRY (SH 620 650)

Introduction

Penrhyn Quarry (Figure 5.47) is a renowned geological site for the famous boudinaged dolerite dykes which traverse the Cambrian slates. These dykes are strongly mineralized, particularly in the neck zones of the boudins, and an 'Alpine-type' vein assemblage, notable for large, specular hematite crystals, is overprinted by chalcocite mineralization with associated chrysocolla. The origin of the chalcocite is equivocal, as chalcocite is typically a supergene copper mineral.

Description

Penrhyn Quarry (Figure 5.48) works slates of Lower Cambrian age, which have been intruded by a series of basic dykes of mainly Lower Palaeozoic age, although cross-cutting Tertiary dykes have also been reported (Williams and Ramsay, 1968). The Lower Palaeozoic dykes have been altered during regional metamorphism and were strongly boudinaged during Acadian compressive deformation, which was particularly intense in this area, lying within the


62
66
Braichmelyn
slate waste tips
slate quarry
works buildings
Afon Ogwen
waterfall
weir
Pont
Ogwen
water
infill
65
Penrhyn Slate
Quarries
slate waste tips
N
0 metres 200
64
Fronllwydd
Upper Cambrian
Marchlyn Formation
Bronllwyd Grit Formation
Lower Cambrian
Llanberis Slates Formation
Fachwen Formation
?Lower Cambrian/Precambrian
Padarn Tuff Formation
fault

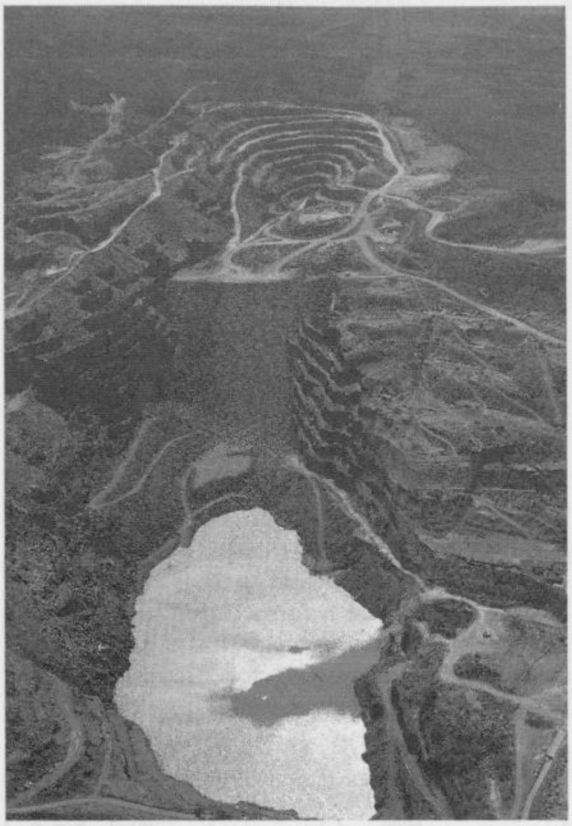


Figure 5.48 Photograph of the Penrhyn Quarry GCR site. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

so-called 'Cambrian Slate-belt' of Wales (Scott, 1992). The dykes are pervasively mineralized with the development of ladder-vein systems, which represent syn-deformational, infilled fractures at the neck zones of the boudins. These veins are restricted to the dykes; the slates are generally non-mineralized, apart from occasional bands of well-formed pyrite cubes of diagenetic to low-grade metamorphic origin.

Within the veins, four mineral assemblages may be discerned, namely: rock-forming minerals; calcite and ferroan carbonates; chalcocite mineralization; and supergene mineralization. Initial veining, showing certain resemblances to the 'Alpine-type' veining seen elsewhere in North Wales (e.g. the **Manod Quarry** GCR site), consists of quartz accompanied by abundant chlorite, with lesser amounts of pink

◂**Figure 5.47** Map of the Penrhyn Quarry GCR site. After British Geological Survey 1:50 000 Sheet 106, Bangor (1985a).

albite and platy, specular hematite which forms crystal rosettes up to 30 mm across (Bevins, 1994). The dolerite dykes are strongly chloritized adjacent to these veins. At the nearby Dinorwic slate quarry, similar mineralization is accompanied by abundant epidote, and the dyke rocks are epidotized (Bevins and Mason, 1998). In places, these veins have undergone post-emplacement deformation. Subsequent carbonate mineralization resulted in the crystallization of siderite, which forms brown, rhombohedral crystals and is overgrown by scalenohedral calcite. This assemblage shows no evidence for deformation.

Copper mineralization occurs in analogous settings at other slate quarries in the Dinorwic area, but is particularly well-developed at Penrhyn Quarry. It comprises massive chalcocite (up to several centimetres across), which fills voids and cracks in both earlier assemblages. Bornite has also been reported as a component of the copper mineralization (Bevins, 1994), but is extremely rare. In polished section, alteration along cracks in the chalcocite to covellite is a frequent feature, but the most obvious alteration product is chrysocolla. This forms typically sky-blue to greenish-blue, massive replacements of chalcocite, with occasional botryoidal developments lining fractures. Malachite is also present, but in much lesser amounts. There is also a report of the vanadium-copper supergene mineral calciovolborthite from this area (Bevins, 1994), but the occurrence, represented by a single specimen in a private mineral collection, requires verification.

Interpretation

The varied mineral assemblages hosted by fractures within the boudinaged basic dykes at Penrhyn Quarry are indicative of a multi-phase history of localized fracturing associated with fluid migration. The earliest assemblage, comprising quartz-chlorite-albite-specular hematite (with, additionally, epidote at similar localities nearby), represents the initial, syn-deformational, ladder-vein development as those dykes aligned at a high angle to the maximum (north-west–south-east) compressive stress field were boudinaged. Deformation of this early assemblage clearly indicates that it formed during incremental deformation, so that those phases which crystallized earliest were subsequently deformed as the compressive process continued.

This early assemblage bears some resemblances to the 'Alpine-type' vein mineralization which is particularly common in the Ffestiniog–Porthmadog belt. The key difference is the presence of specular hematite, although hematite of a similar habit is of frequent occurrence in the analogous Alpine Fissures of the Alps. However, the Penrhyn veins were formed in different lithologies and at a deeper structural level to those of the Ffestiniog–Porthmadog area, so such a difference is perhaps not particularly significant in genetic terms. What both occurrences share is that the mineral assemblages are interpreted as having been derived locally with relatively restricted circulation of mineralizing fluids.

The carbonate mineralization is of uncertain origin and is again restricted to the dykes. The delicate, undamaged calcite scalenohedra overgrowing siderite are perhaps suggestive that this assemblage post-dates the Acadian compression. However, there is nothing similar in the immediate district to compare with this phase of mineralization; hence its exact genesis remains unclear.

The abundant chalcocite mineralization is of particular metallogenic interest. Chalcocite, the only major species present, is generally regarded as a secondary alteration product of primary chalcopyrite. However, detailed examination of mineralization at Penrhyn Quarry has failed to detect any chalcopyrite, both in hand specimen and polished section, while bornite is present only in trace amounts. Typically, as at the **Dolyhir Quarry** and **Llechweddhelyg Mine** GCR sites, supergene chalcocite contains numerous patches of bornite surrounding the remnant hypogene chalcopyrite. No such texture has been observed at Penrhyn Quarry, which raises the likelihood that the chalcocite may have an unusual primary genesis. This is re-inforced by the observation that supergene conversion of chalcopyrite to chalcocite in the nearby, pre-Acadian, Snowdonia copper veins is at most only superficial in nature.

Alteration of primary chalcopyrite to malachite, chrysocolla and other minerals is of frequent occurrence through the Welsh Caledonides (e.g. at the **Llechweddhelyg Mine** GCR site). At Penrhyn Quarry, this type of supergene alteration has affected the chalcocite. The sequence of veining by covellite and replacement by chrysocolla and malachite is interpreted as being the product of prolonged oxidation of sulphides by groundwaters during deep weathering which affected the area in Tertiary times (Mason, 2004). The supergene alteration occurs at all levels of the quarry, over a considerable vertical distance, reflecting the fact that the pervasively fractured basic dykes acted as particularly permeable zones relative to the impermeable slates, and thus provided access for oxidizing groundwaters to the chalcocite. If this oxidation process took place during Tertiary times, then the implication is that the chalcocite had been deposited some time prior to this but after the Acadian deformation.

There appears to be no direct analogy to this occurrence of dyke-hosted chalcocite mineralization elsewhere in Great Britain. In other areas in or around the Welsh Caledonides where significant chalcocite is present, such as in south-west Shropshire (Smith, 1922), and the **Dolyhir Quarry** GCR site, there is almost always clear evidence that it formed due to the in-situ alteration of chalcopyrite. This is not the case at Penrhyn Quarry, and for the present, the genesis of the chalcocite mineralization remains unresolved.

Conclusions

Mineralization associated with basic intrusions cutting slates at Penrhyn Quarry is multi-phase and was controlled by the dominant geological structures. Quartz-chlorite-specular hematite-albite veins were deposited in the neck-zones of boudins as the dykes were subjected to compressive deformation. This was followed by carbonate mineralization, precipitating siderite and calcite, which was overprinted in turn by locally intense chalcocite mineralization, the genesis of which remains uncertain. The chalcocite has commonly been altered to chrysocolla.

STRATABOUND GOLD-ARSENIC MINERALIZATION ASSOCIATED WITH LOWER PALAEOZOIC PYRITIC MUDSTONES

DOLAUCOTHI MINE (SN 663 403)

Introduction

Dolaucothi Mine (Figure 5.49) is unique in the metallogenesis of Wales. In an area otherwise mineralized only by Pb-Zn-Cu-Ag veins typical

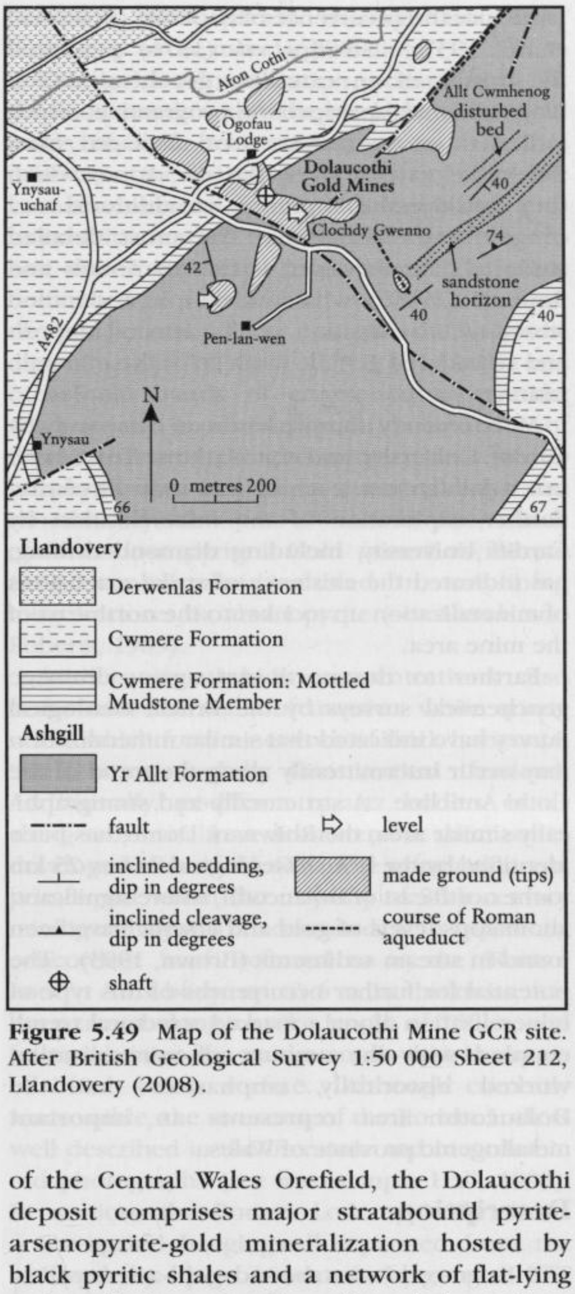


Figure 5.49 Map of the Dolaucothi Mine GCR site. After British Geological Survey 1:50 000 Sheet 212, Llandovery (2008).

of the Central Wales Orefield, the Dolaucothi deposit comprises major stratabound pyrite-arsenopyrite-gold mineralization hosted by black pyritic shales and a network of flat-lying and vertical quartz veins, the whole package deformed into a series of tight isoclinal folds. The deposit is situated along the axis of the dome-shaped Cothi Anticline, a parasitic fold on the north-western flank of the major Tywi Anticline (Annels and Roberts, 1989). Exposures in and around the old open-pits and the accessible underground workings graphically illustrate the complexity of this enigmatic ore deposit.

At surface, the Dolaucothi workings consist of a system of open pits occupying an ovate area extending over 1 km in length (Figure 5.50). These are now accepted as largely being the work of the Romans, a number of ancient features being supportive of this assertion. For example, a long leat from the Afon Cothi runs over 10 km to arrive at a series of holding tanks above the open pits on Allt Cwmhenog (Hall, 1993; Annels and Burnham, 1995). It has been estimated that this was capable of providing the opencast workings with around 2.5 million gallons of water per day. This water demand has led many authors (for example Hall, 1993) to conclude that it must have been brought in for sluicing away the oxidized part of the deposit, in which pyrite and arsenopyrite would have been weathered to a gossanous clay, the gold previously locked up within their crystals thus being liberated and freely extracted by a system of sluices and gold catchers, such as turves or fleeces. This is re-inforced by the existence of the two 'Roman Adits', two hand-driven tunnels running into the lower parts of the main opencast, and through which it is suggested the debris was sluiced and the gold was caught. Such mining methods were used by

Figure 5.50 Aerial photograph of the Dolaucothi Mine GCR site. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

the Romans and were described, in fact, by Pliny, in his '*Natural History*', published in AD 77. The Roman age of the workings has been further indicated by a radiocarbon age obtained on a part of a wooden drainage wheel found preserved in mud when old workings were broken into during the 1930s. Analysis gave a calibrated age of 90 ± 70 BC (see Annels and Burnham, 1995).

The open pits are substantial in scale. An estimated 4 million tons of rock, of which 0.5 million were auriferous, were extracted, according to James Mitchell (see Hall, 1993), who worked the mine from 1905 to 1910. Mitchell also estimated that these operations had previously yielded 1 million oz of gold. A more conservative but still impressive estimate, given by Annels and Burnham (1995), was that from the Ogofau surface pit alone, 0.5 million tons of rock had been extracted, a third of which was ore, yielding 830 kg of gold (assuming a bulk gold grade of 5 g/t).

Serious interest in the mine revived in the 19th century, perhaps prompted by the discovery of a particle of gold in quartz by an officer of the British Geological Survey in 1844 (see Smyth, 1846). The mine was then intermittently worked through to 1939. Particular interest was taken in the site when Britain abandoned the Gold Standard in the early 1930s. However, the biggest problem that the operators had was that nobody in Britain would smelt the auriferous concentrates produced at the mine because of their high arsenic content. They therefore had to be shipped overseas. Initially, test batches went to Hamburg, but as the political climate in Europe changed during the late 1930s this became impossible and the ore had to be sent to Seattle at an intolerable cost. This alone would have brought about the mine's closure if the outbreak of war had not. Despite all the difficulties, the mine still yielded 1388 oz of gold from 16 862 tons of ore in 1938, the high tonnage of ore reportedly including much peripheral material fed through the mill between batches of ore-grade rock (Hall, 1993). During these later years of activity, the mine, which was romantically worked under the name 'Roman Deep', reached a depth of 140 m below surface (Annels and Burnham, 1995).

There is very little detailed published work on the Dolaucothi deposit. Early studies considered aspects of the mineralogy of the deposit, in particular the occurrence of cookeite (Brammall *et al.*, 1937). Steed *et al.* (1976) presented the results of an extensive geochemical and biogeochemical prospecting programme, which indicated an anomalous area displaced from the strike extension of the ore zone, which they considered to represent an additional area of gold mineralization. The most detailed study to date, however, is that by Annels and Roberts (1989), who undertook a detailed structural investigation of the mineral deposit and considered genetic models for the mineralization.

More recently, the site has been run jointly by Cardiff University and the National Trust, who use it jointly as a teaching and tourism centre. Further exploration of the mineralization by Cardiff University, including diamond drilling, has indicated the existence of strike extensions of mineralization up to 1 km to the north-east of the mine area.

Farther to the north-east again, drainage geochemical surveys by the British Geological Survey have indicated that similar mineralization may occur intermittently along the trend of the Cothi Anticline. A structurally and stratigraphically similar area, the Rhiwnant Dome, has been identified by the British Geological Survey 25 km to the north-east of Dolaucothi, where significant, anomalous levels of gold and arsenic have been found in stream sediments (Brown, 1993). The potential for further occurrences of this type of mineralization along a marked structural trend, coupled with the amount of mineralization worked historically, emphasizes that the Dolaucothi area represents an important metallogenic province of Wales.

Description

The Dolaucothi stratabound gold-arsenopyrite-pyrite deposit is hosted by Ashgill-age black-shales and grey siltstones belonging to the Yr Allt Formation which outcrop in the core of the dome-shaped Cothi Anticline, parasitic on the north-western flank of the major, probably basement-controlled, Tywi Anticline (Annels and Roberts, 1989). The host strata are overlain by turbidites of the Cwmere Formation (Llandovery), which include a prominent massive conglomeratic horizon. In the vicinity of the mine, the strata are deformed by a complex series of tight to isoclinal folds, often sheared and overthrust along their axes. A pervasive axial planar cleavage has been developed in the more argillic units.

The gold mineralization occurs both in sulphidic bands within the black shales and in a series of shale-hosted quartz veins. In the mine area, the shales carry a series of sulphidic formations up to 1.5 m in thickness, which tend to exhibit a marked thinning both to the north-east and south-west of the mine. These are dominated by pyrite, which occurs in a number of modes, comprising clusters of framboids, disseminations of small euhedral crystals, and occasional bands of coarse cubic crystals. Arsenopyrite is an important component of the shale-hosted mineralization. It occurs as porphyroblasts and forms euhedral laths and rhombic crystals up to 20 mm in size, which often enclose pyrite. Gold occurs as minute (<< 1 mm) grains included in, or lining microfractures in, arsenopyrite (see Annels and Roberts, 1989).

Auriferous sulphide concentrations also occur near the walls of massive, white quartz veins, which form a network of thick horizontal 'reefs' connected by thin vertical 'feeders'. Additionally, podiform quartz bodies occur along subvertical reverse-movement shear zones developed above fold axes. The principal quartz vein, upon which the majority of 20th century mining activity was concentrated, is an apparently concordant 'reef' referred to as the 'Roman Lode'. This body, up to 6 m in thickness, has been traced along a strike length of 250 m, and followed down-dip to the south-west in excess of 140 m below surface. Although currently inaccessible, the structure of the Roman Lode is well described in the literature and recorded in old photographs (see for example Hall, 1993). In section, the Roman Lode typically shows a corrugated hangingwall separated from the wall-rock by up to 10 cm of clay-gouge. The footwall consists of shale impregnated with pyrite and arsenopyrite, both of which are auriferous. Steeply discordant 'leader' veins descend from the Roman Lode footwall into the wall-rocks.

The lode and associated veins both consist of locally vuggy milky quartz, with subordinate amounts of ferroan dolomite and 'hydro-muscovite', more recently characterized as 2M1 illite (Annels and Roberts, 1989). The Li-bearing chlorite-group mineral cookeite is locally common, and its presence has been cited by Brammall *et al*. (1937) as evidence for a magmatic input to the fluids responsible for the mineralization. In the Roman Lode and associated veins, gold is present within patches of auriferous pyrite (with associated arsenopyrite), which in the case of the Roman Lode occur with increasing frequency towards the footwall.

The Au-As mineralization in all modes is cut locally by small Pb-Zn-Cu-bearing quartz-carbonate-sulphide veins with minor remobilization of gold (Annels and Roberts, 1989), which resemble those of the Central Wales A1- and A2-type mineralization. Further Central Wales-style Pb-Zn-Cu mineralization occurs at Dolaucothi along two transverse normal faults, known as the 'Clochdy Gwenno Fault' and the 'Lead Lode Fault'.

Although secondary minerals are not obvious at the site, both pyrite and arsenopyrite have weathered in places to yellow ochres. Greenish scorodite locally forms thin coatings on arsenopyrite. Gypsum is common as a post-mining crystalline efflorescence on the mine walls, a common feature in almost all underground driveages where pyrite occurs.

Interpretation

The origin of the Dolaucothi pyrite-arsenopyrite-gold deposit is controversial. It was initially assumed to be a classic saddle-reef system, and in the 1930s a magmatic source for the mineralization was considered most likely (Brammall *et al*., 1937). More recently, the possibility that Dolaucothi was formed by exhalative activity on the early Silurian seafloor was considered by Annels and Roberts (1989). In the same paper, the authors cited sulphur isotope data that consistently favour an epigenetic (though not necessarily direct magmatic) hydrothermal origin, thereby, in their view, ruling out the exhalative hypothesis. The preferred model favours a mineralized thrust (the Roman Lode) and associated extensional shear-gash veins (the steeply discordant footwall 'leaders'). In this model, the pyrite- and arsenopyrite-bearing shales represent alteration by replacement of receptive lithologies. The model places the hydrothermal fluid migration and mineralization within the context of the Acadian deformation, suggesting that it occurred at an early stage of this compressive event. During this early stage, prograde metamorphism of the basement rocks below the area resulted in the leaching, by circulating fluids, of gold, arsenic and other elements from intrusive and extrusive igneous rocks. The resultant overpressured hydrothermal fluids then escaped to higher crustal levels during successive phases of uplift and accompanying tectonism.

While several lines of evidence provide support for this model, this is a complex deposit. Therefore, it is anticipated that as further information is generated by ongoing research, the genetic model will continue to be modified, as has indeed been the case over the years at the even more complex **Parys Mountain** GCR site.

The relationship of the Dolaucothi Au-As mineralization to the more regionally widespread Central Wales-type base-metal vein mineralization (well developed at the nearby **Nantymwyn** GCR site) is well defined. Late cross-cutting normal faults, such as the Lead Lode, show clearly that the pyrite-arsenopyrite-gold mineralization was relatively early in the sequence of events.

Conclusions

The pyrite-arsenopyrite-gold mineralization occurring on a substantial scale at Dolaucothi Mine is unique in Wales. It clearly pre-dates the Central Wales Pb-Zn-Cu vein mineralization and, according to current models, was developed as a result of basement-derived hydrothermal fluids migrating up deep-seated fractures during the uplift which occurred at the onset of the Acadian deformation. Research continues actively at the site and it is anticipated that the models advocated for the genesis of this complex deposit will continue to be refined as more data are obtained.

QUARTZ-SULPHIDE VEIN MINERALIZATION OF DEVONIAN AND VARISCAN AGE IN CENTRAL WALES

Mining for a variety of minerals, principally the ores of lead, zinc, copper and silver, but also the minerals marcasite, barite and witherite, has taken place intermittently in the Central Wales Orefield over a considerable length of time. Copper was sought during the Early Bronze Age at a number of sites (Timberlake, 1988, 1989, 1992). The Romans were active militarily in the area and mined gold to the south, at the **Dolaucothi Mine** GCR site. Until recently, it was not known whether they had mined lead in Central Wales. However, excavations in 2004–2005 between Llancynfelyn and Talybont, on the western side of the orefield, revealed a Roman smelting site beneath a medieval trackway. Lead mining was certainly active during Monastic times (Hughes, 1981a), although details of operations in the Middle Ages are only fragmentary.

The first major documented boom of activity was during the 17th century, when silver was the main target, sought particularly at a group of mines between Talybont and Goginan, where the ordinarily argentiferous galena is accompanied by richly argentiferous tetrahedrite. However, the most intensive phase in the mining history of Central Wales came in the mid-19th century, when hundreds of workings, ranging from short trial adits through to full-scale mines, were prosecuted in search of lead and, particularly later in the century, for zinc, with silver and copper as by-products. Locally intense marcasite mineralization, which in places contaminated the lead and zinc ores sufficiently to render them unsaleable, was occasionally sold as 'pyrites' (Jones, 1922) for sulphuric acid manufacture, while small amounts of barite and witherite were mined in the eastern part of the orefield.

Mining had declined considerably by the early 20th century, the industry finally fading away after the First World War, when the release of Government metal stocks (particularly zinc), coinciding as it did with the dramatic rise of Broken Hill in Australia, caused a major slump in prices. Apart from very minor trials and a number of exploration projects, the post-Second World War years have seen the industry in this area dormant.

Mineral production figures were only compulsorily recorded in the United Kingdom after 1845, so that the produce of the intensive 17th century years remains unknown. Therefore the preserved figures represent an unknown percentage of the total (Mason, 1997). From 1845 onwards, the Central Wales Orefield produced more than 450 000 tons of lead ore concentrates containing in excess of 2.5 million oz of recovered silver, more than 140 000 tons of zinc ore concentrates and more than 8000 tons of copper ore concentrates. Most of the production came from a small number of major mines, such as Van, which exceeded

125 000 tons of lead- and zinc-ore concentrates between 1866 and 1917 alone (Burt *et al.*, 1990).

Geologically, the Central Wales Orefield occurs in the deformed remnants of a structurally controlled marginal basin (the Welsh Basin), which developed on the south-eastern continental margin of the Iapetus Ocean during Lower Palaeozoic times (see Dewey, 1969). Turbidite-dominated sequences of Ashgill to Upper Llandovery age comprise the host rocks to the mineralization, the range of basinal facies present varying from coarse conglomeratic sandstones developed in proximal channels, to hemipelagic graptolitic black-shales deposited on the basin plain. Periodic facies variations were controlled by sediment availability, which was in turn related to transgressive and regressive phases of the Welsh Basin seas.

The Acadian deformation, responsible for inverting the Welsh Basin, occurred in early Devonian times (Soper *et al.*, 1987), with the development of a series of major open NNE–SSW-trending periclinal folds, the most important being represented by the Plynlimon, Machynlleth and Van inliers (Cave and Hains, 1986). Between these key structures, smaller parasitic folds occur on all scales. NNE–SSW-trending strike faults and thrusts commonly developed as compression accommodation structures, while cleavage, approximately axial planar to folds, is only pervasive in the more argillic units, some of which have been worked for poor-quality slate.

Mineralization in Central Wales falls into two broad categories, namely minor but widespread pre-tectonic mineralization, and major, post-tectonic fracture-hosted vein mineralization. The pre-tectonic mineralization is partly diagenetic, comprising locally common framboidal, nodular or cubic pyrite, nodular apatite, silica, carbonate and monazite (see for example Read *et al.*, 1987; Milodowski and Zalasiewicz, 1991; Smith *et al.*, 1994). Additionally, pre-tectonic veins are widespread in all lithotypes and contain abundant quartz accompanied by variable amounts of chlorite, pyrite and ferroan dolomite (Fitches, 1987). Vein compositions directly reflect host-rock lithology, implying the localized derivation of fluids during an early stage of sediment dewatering. The veins are characteristically limited in extent, with strike lengths rarely exceeding 10 m, and are usually flat-lying and irregular in shape, due partly to later deformation. The post-tectonic metalliferous veins cut the pre-tectonic veins (Mason, 1994, 1997).

The post-tectonic metalliferous veins (or lodes) are hosted by a swarm of transverse fractures, which vary in magnitude from mineralized joints to major normal fault-zones with displacements of over 200 m (Figure 5.51). The predominant strike of the fractures is ENE–WSW, although localized north-west–south-east and north-east–south-west trends also occur. Transverse fracturing and mineralization were effectively synchronous, and fracture propagation and the accompanying brecciation were both assisted by the hydraulic properties of the mineralizing fluids. Indeed, the role of hydraulic fracturing in the formation of mineralized vein-breccias was first proposed by Phillips (1972), using the Central Wales Orefield as a model. The breccias consist of angular fragments of wall-rock cemented by the various ore and gangue minerals. Radial growths of minerals cementing matrix-supported rock clasts indicate that mineral nucleation on the rock fragments took place rapidly after brecciation. In addition to the mineralized breccias, some demonstrably late-stage veins consist of crustiform open fissure-fillings.

Prior to the 1970s, the detailed paragenesis of the metalliferous mineralization in the Central Wales Orefield had received little attention. The probable late Caledonian age of the mineralization was postulated by Jones (1922), although earlier Finlayson (1910b) had suggested that the Lower Palaeozoic sedimentary-hosted metalliferous veining occurring throughout Wales was of Hercynian age.

The first major paragenetic study of the Central Wales Orefield was by Raybould (1973, 1974), who reached the conclusion that the mineralization involved a single, generalized paragenetic sequence, showing a gradual change in mineralogy through successive cross-cutting and re-brecciation episodes. The sequence identified comprises sustained quartz deposition with associated minerals being precipitated in the order pyrite (first), ankerite, chalcopyrite, sphalerite, and galena (last). In addition, occurrences of marcasite, arsenopyrite and, at one locality, minor cobaltite were described. Raybould (1973, 1974) also perceived a zonation pattern, in which the proportion of galena in the ore-bodies increases while that of chalcopyrite decreases as the lodes on the western flank of the Plynlimon Inlier are traced westwards.

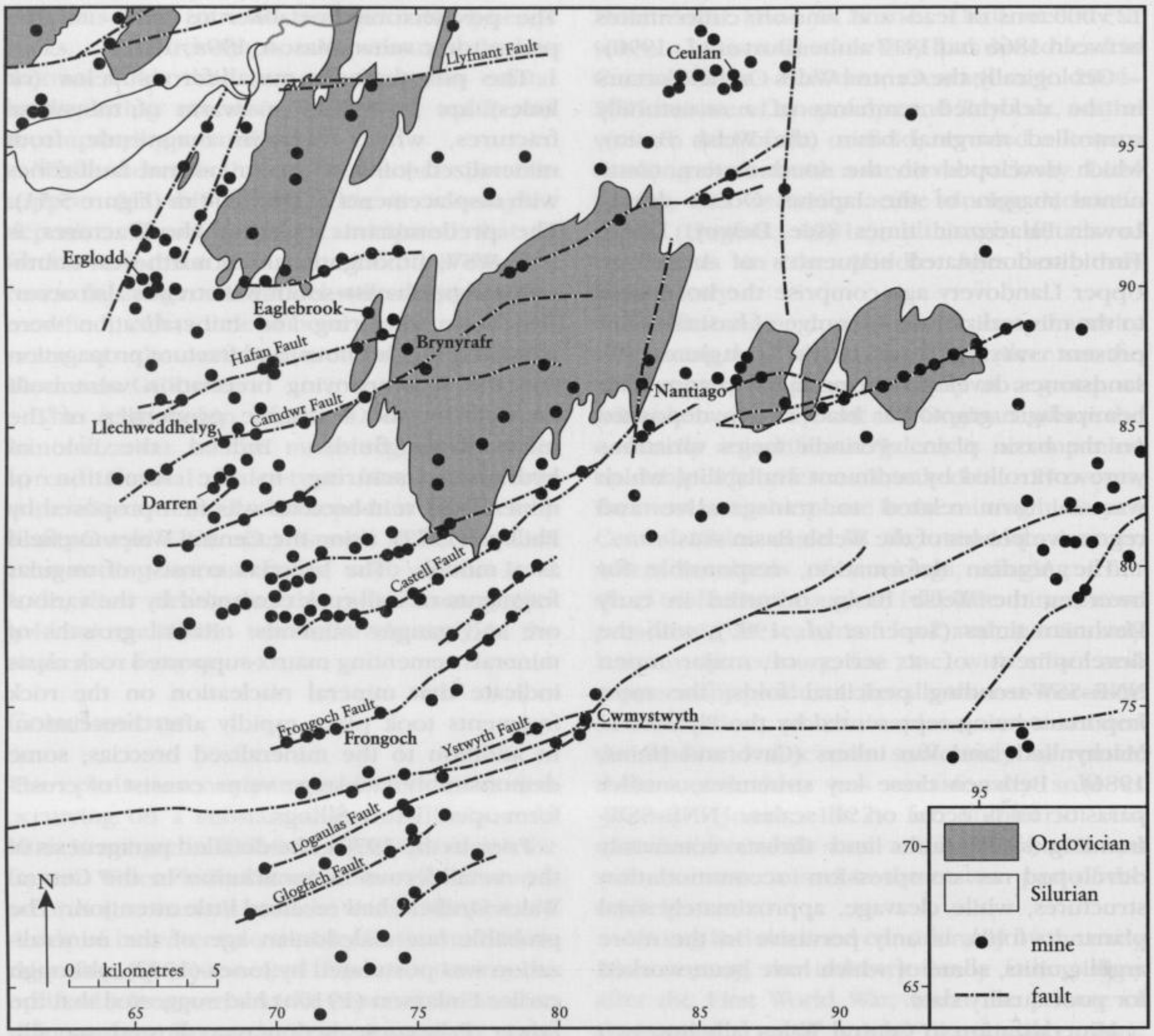


Figure 5.51 Map showing the distribution of old metal mines in the Central Wales Orefield. The location of the GCR sites are highlighted. After Ball and Nutt (1976).

The area was re-investigated in the late 1980s and early 1990s by Mason (1994, 1997). Preliminary fieldwork had led to the recognition that the mineralization of Central Wales is in fact polyphase and is mineralogically far more complex than had hitherto been believed. The subsequent detailed investigations, which resulted in the discovery of a number of rare ore minerals, such as the third worldwide occurrence of tucekite [$Ni_9Sb_2S_8$], also resulted in a re-appraisal of the paragenesis of the Central Wales Orefield. Mason (1994, 1997) identified that the post-tectonic metalliferous veining of Central Wales may be divided into two groups of assemblages, termed 'A1' and 'A2' (see Table 5.1), which were referred to as the 'Early Complex' and 'Late Simple' groups. In fact, many of the mineralized fractures of the Central Wales Orefield contain assemblages belonging to both groups, since they have been subjected to repeated episodes of tectonic activity, re-brecciation and mineralization. Spatially, the distribution of the two groups of assemblages is erratic, although in some areas one group is prevalent over the other.

Veins carrying assemblages belonging to the early or A1 group, which are commonly 'welded' to their walls, are compact and consist of numerous angular clasts of shattered sedimentary rock cemented by sulphide-bearing quartz (Mason, 1994, 1997). The quartz of the A1 group of assemblages is milky-white, close-

Table 5.1 Classification of Central Wales Orefield mineralization into the 'Early Complex' A1 and 'Late Simple' A2 groups. Minor/trace species are in italics; major phases are underlined. After Mason (1994, 1997).

A1 ('Early Complex') assemblages	**A2 ('Late Simple') assemblages**
Early Devonian isotopic age Post-Caledonian relaxation?	Early Carboniferous to Permian isotopic ages Mainly Variscan extension?
WEAK BRECCIATION	MAJOR BRECCIATION
A1-a Minor early Cu qtz + chalcopyrite + ferroan dolomite	**A2-a Pb-Zn assemblage** qtz + sphalerite + chalcopyrite + galena
BRECCIATION	MAJOR BRECCIATION
A1-b Early sphalerite assemblage qtz + pyrite + sphalerite (with chalcopyrite disease) + ferroan dolomite + chlorite	**A2-b Ullmannite-bearing Pb-Cu assemblage** qtz + chalcopyrite + ullmannite + galena
MAJOR BRECCIATION	CRUSTIFORM OVERGROWTH
A1-c Polymetallic assemblage qtz + pyrite + siegenite + cobalt pentlandite + millerite + chalcopyrite + *pyrrhotite* + tucekite + ullmannite + *gersdorffite* + *electrum* + tetrahedrite + bournonite + *boulangerite* + galena	**A2-c Calcite-dominated assemblage** qtz + galena + sphalerite + calcite + *chalcopyrite* + *pyrite*
SHEARING OF SULPHIDES	CRUSTIFORM OVERGROWTH
A1-d Minor late veining chalcopyrite + galena + "honey-blende" sphalerite	**A2-d Coarsely crystalline quartz** qtz + *chalcopyrite* + *pyrite*
LOCALLY MAJOR BRECCIATION	RELATIONSHIP UNKNOWN
A1-e Ferroan dolomite influx qtz + ferroan dolomite	**A2-e Barium minerals assemblage** *qtz* + sphalerite + galena + calcite + barite + witherite
LOCAL FRACTURING	MAJOR BRECCIATION AND TECTONISM
A1-f Late cavity-filling qtz + *siegenite* + *cobalt pentlandite* + millerite + chalcopyrite + galena	**A2-f Iron sulphides assemblage** qtz + sphalerite + pyrite + marcasite
Important economic assemblages: A1-b (moderate Zn); A1-c (major Pb-Ag, moderate Cu); A1-f (minor Pb-Cu)	**Important economic assemblages: A2-a (major Pb-Zn, minor Ag); A2-b (moderate Pb, Ag, Cu); A2-c (locally major Pb-Zn); A2-e (locally major Pb, barite)**

grained and tough; occasional vugs contain slender prismatic crystals with water-clear terminations. The diverse sulphide minerals are usually fine-grained and complexly intergrown. Economically, Pb, Cu and Ag were the prime metals mined from the A1 group of assemblages. Other elements present in minor amounts comprise Zn, Sb, Fe, Ni, Co, As, and Au, in estimated order of abundance. Varying facets of the A1 style of mineralization are best seen at the **Darren Mine**, **Erglodd Mine**, and **Eaglebrook Mine** GCR sites.

The A2 or later group of assemblages contrasts strongly with the A1 group, with a simple mineralogy of generally less than five mineral species in each assemblage being characteristic (Mason, 1994, 1997). The A2 assemblages have a much coarser grain-size compared to A1 assemblages. The sulphides are optically 'clean', under high-powered magnification, in striking contrast to the complex, microscopic intergrowths of the A1 assemblages. The A2 assemblages occur in both previously unmineralized and re-activated A1 mineralized fractures, and form breccia cements, banded fissure-fill and composite vein deposits, often separated from their wall-rocks by bands of clay-gouge. The coarsely crustiform textures exhibited in many cases are reminiscent of some of the 'Pennine-type' deposits. The chief gangue mineral is, again, quartz, but it is relatively friable compared to the A1-type quartz; colourless to greyish-white in colour, it forms common, squat, stumpy crystals. Calcite is widespread and locally occurs in large amounts, but ferroan dolomite is very rare. Contrasting features of the A2 style of mineralization are best seen at the **Ceulan Mine Opencast** and **Nantiago Mine** GCR sites.

The **Cwmystwyth Mine** and **Brynyrafr Mine** GCR sites provide classic sites where the textural features of the mineralization belonging to both the A1 and A2 episodes are clearly demonstrated, while the **Nantymwyn** GCR site emphasizes the highly regional nature of the mineralization.

Secondary mineralization, the detailed paragenesis of which is as complex as that of the primary mineralization, is widespread throughout the Central Wales Orefield, and there has been considerable research on the subject (see, for example, Rust, 1990a,b, 1992; Mason, 1992, 2004; Mason and Rust, 1995; Green *et al.*, 1996). Many rare secondary minerals have been reported from Central Wales in recent years, often occurring in complex, post-mining assemblages formed within dumps of sulphide-rich material. The suite of minerals which formed *in situ* is simpler. In common with many base-metal mining districts, cerussite, pyromorphite, wulfenite, bindheimite, hemimorphite, malachite, cuprite, native copper, chalcocite, goethite and limonite are of frequent occurrence, although typically only in small quantities. Nevertheless, field evidence suggests that both malachite and cerussite were locally worked at vein outcrops. The **Frongoch Mine**, **Llechweddhelyg Mine** and **Eaglebrook Mine** GCR sites reflect aspects of this secondary paragenesis.

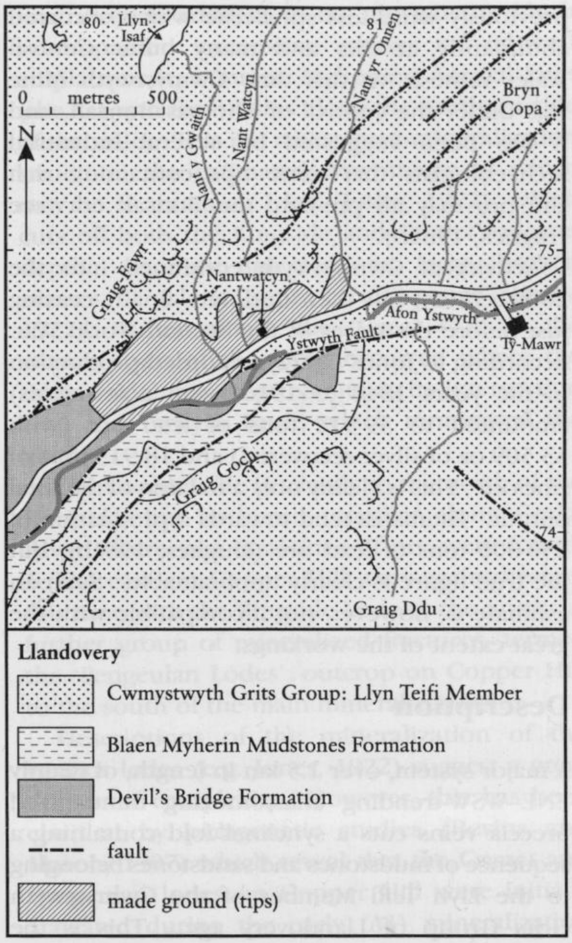
In summary, two major episodes of mineralization resulted in the emplacement of the A1 and A2 groups of assemblages, a point reinforced by both tectonic (Mason, 1994) and isotopic evidence (Fletcher *et al.*, 1993). Post-orogenic relaxation has been proposed as the mechanism for the development of fractures carrying the A1 assemblages in early Devonian times, while fractures carrying the A2 assemblages are believed to have formed in response to regional Variscan extension from early Carboniferous times onwards (Mason, 1997). There is also isotopic evidence for further mineralization during Permian times (Swainbank *et al.*, 1992), when the area was once again under extension as basin development took place in the Irish Sea area, to the west of the orefield. It may therefore be suggested that the A2 vein mineralization in Central Wales includes components reflecting both the major early Carboniferous metallogenic epoch, when the Irish Pb-Zn deposits were formed, and the Permo–Triassic phase of activity, when Mississippi Valley-type (MVT) vein mineralization was emplaced in many areas, generating the so-called 'Pennine-type' orefields of Britain. Clearly, the Central Wales Orefield offers much potential for further research into its relationship to other major Upper Palaeozoic Pb-Zn orefields in the UK.

CWMYSTWYTH MINE (SN 802 746)

Introduction

Cwmystwyth Mine (Figure 5.52) is a classic locality for the study of mining geology, mineralogy and industrial archaeology, as well as providing an excellent introduction to the mineralization of the Central Wales Orefield. Although no element of the primary or secondary paragenesis exhibited here is unique, several paragenetic stages belonging to the early A1 and late A2 phases of metallogenesis (Mason, 1994, 1997) are well represented.

The Cwmystwyth Mine site comprises two areas. Adjacent to the mountain road to Rhayader, and on the lower slopes of Graig-Fawr and Copper Hill (Bryn Copa), large amounts of study material ensure that Cwmystwyth is an ideal teaching and demonstration site (Figure 5.53). The more remote parts of the site high on Graig-Fawr and Copper Hill include, in addition to primary minerals, significant secondary mineralization (Bevins and Mason, 1997) and spectacular mining geology. Additional interest is provided by ancient opencast workings on Copper Hill, which have been excavated by mining archaeologists. Charcoal, deer antler implements and wood unearthed during these excavations have been dated by radiocarbon



◄**Figure 5.52** Map of the Cwmystwyth Mine GCR site. Based on British Geological Survey 1:50 000 sheets 179, Rhayader (1993a), and 178, Llanilar (1994).

techniques to Early Bronze-Age times (Timberlake, 1989), making this one of the most important early mining sites in Europe (Figure 5.54).

Whether the Romans worked lead at Cwmystwyth has long been a subject of speculation, since hard evidence for any Roman activity at the site itself has yet to be found. It is likely, however, that some mining took place under the administration of the Cistercian Monks responsible for the construction of the nearby Strata Florida abbey, which was completed in 1201 (see Hughes, 1981b, for a detailed historical account). However, specific records of mining in Central Wales are generally scarce prior to the middle of the 16th century. An interesting account of the site during the reign of Henry VIII was given by Leland in his '*Itinerary in Wales 1536–39*', where he describes approaching the mine from the direction of Rhayader:

'About the middle of this Wstwith (*sic.*) valley that I ride in, being as I guess three miles in length, I saw on the right hand of the hill Cloth

Figure 5.53 Photograph of the Cwmystwyth Mine GCR site. (Photo: J.S. Mason, © National Museum of Wales.)

Figure 5.54 Oblique aerial photograph of the Cwmystwyth Mine GCR site, showing complex sets of hushes and leats. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

Moyne (= Clodd Mwyn, translating as 'Mine of Lead Ore'), where hath been a great digging for Leade, the smelting whereof hath destroid the woodes that sometimes grew plentifully thereabout' (see Hughes, 1981b).

The description shows that, by this time, the workings were already sizeable. From then onwards, the mine was rarely inactive. Leases for its working passed through the hands of many great 17th century mining figures, including Sir Hugh Myddleton and Thomas Bushell, each with strong connections to the Society of Mines Royal, but both of whom, however, were more concerned with the much more argentiferous ores at the Goginan and Darren mines, to the north-west (see **Darren Mine** GCR site report, this chapter). By the mid-1700s the Champion Process had been set up to extract metallic zinc from the previously worthless sphalerite which occurred abundantly at this and many other Central Wales mines. At this time Cwmystwyth Mine was under the control of Thomas Bonsall, and it has been suggested by several industrial archaeologists that mine tips containing rich zinc-ore may all pre-date the Bonsall era (see Hughes, 1981b).

Activity at Cwmystwyth continued into the 20th century, but then declined, finally ceasing just before the onset of the Second World War. According to Jones (1922), recorded production in the years 1848 to 1916 (with a few gaps) amounted to 39 912 tons of lead ore (with 33 509 oz of silver recovered) and 18 913 tons of zinc ore. This is clearly only a fraction of the total output. Estimates tend towards a production of 250 000 tons of lead ore (Hughes, 1981b), but the true figure is clearly unobtainable. Such an estimate is, however, not incompatible with the great extent of the workings.

Description

A major system, over 1.5 km in length, of mainly ENE–WSW-trending anastomozing mineralized breccia veins cuts a synclinal fold containing a sequence of mudstones and sandstones belonging to the Llyn Teifi Member of the Cwmystwyth Grits Group of Llandovery age. This is the highest stratigraphical horizon intersected by significant vein mineralization in the Central Wales Orefield. Many individual veins are noted on old mine plans, but three principal mineralized fractures can be identified. These comprise the S-dipping Comet and Kingside lodes and the less-important, N-dipping Mitchell's Lode (Jones, 1922; Davies *et al.*, 1997). In the western part of the mine, the Kingside Lode was generally referred to as 'Main Lode'. Both the Kingside and Comet lodes dip to the south at 50°–65°. In the western part of the mine, however, the dip of the 'Main Lode', flattened out between the 15-fathom and 30-fathom levels, where, 'for an area of at least 150 sq. yds. a mass of galena, lying almost horizontally with a constant thickness of 6 ft 2 in. between its roof and its floor, was worked' (Jones, 1922). This area was known as 'The Great Flat' (Jones, 1922).

Mitchell's Lode is of interest as it displaces the Comet Lode at their point of intersection, downthrowing the Comet Lode to the north. Indeed, this tract of ground has been subject to repeated fracturing; in addition to the movements which accompanied successive phases of mineral emplacement, a major, N-dipping normal fault (the Ystwyth Fault) runs along the northern side of the valley. This is a major, post-mineralization structure, the estimated downthrow of which may be as much as 1 km (Jones, 1922), which cuts off both the Kingside and Comet lodes at depth. At these intersections, large, broken masses of galena occur in clay-gouge (Jones, 1922). Interestingly, the 'Great Flat' in the western part of the mine occurred where the 'Main Lode' was in proximity to its intersection with the Ystwyth Fault, which terminated the 'Flat'.

The Comet Lode is usually to the north of the Kingside, but both run together along Graig-Fawr, where vast quantities of ore were found. To the east, on Copper Hill, they again diverge, this time with the Kingside Lode to the north. A further group of mineralized fractures, termed the 'Pengeulan Lodes', outcrop on Copper Hill to the south of the main mineralized belt.

Descriptions of the mineralization of the various lodes (e.g. Jones, 1922) suggest a great degree of complexity. However, this has been clarified by paragenetic studies (Bevins and Mason, 1997) which reveal that the Comet and Pengeulan lodes on Copper Hill were initially activated during the early (A1) mineralization (Mason, 1994, 1997). This period of mineralization is represented by breccias cemented by quartz and sphalerite (A1-b assemblage) and by breccias cemented by quartz, galena (with ullmannite inclusions), chalcopyrite (hence the name, 'Copper Hill') and minor late sphalerite (A1-c/d assemblages). Abundant ferroan dolomite with quartz, belonging to the A1-e assemblage, cements clasts of both rock and earlier mineral assemblages.

The early breccias typically consist of angular rock-fragments evenly distributed throughout a mineral cement, predominantly consisting of quartz. The quartz cementing these early breccias is typically milky-white and tough; it forms radial growths around clasts and contains vugs lined with long prismatic crystals (< 15 mm) which have water-clear terminations. The aforementioned sulphides tend to occupy quartz vugs, although well-formed crystals are rare.

The remainder of the mineralization at Cwmystwyth belongs to the late (A2) phase (Mason, 1994, 1997). This is far more widespread, being abundant on all mine tips, and provided most of the lead- and zinc-ores mined. Typically the A2 mineralization has a more open texture and comprises vuggy breccia cements and local crustiform-banded veins. Coarsely crystalline sphalerite, followed by galena with quartz, represents the A2-a assemblage and is followed by fibrous sphalerite with quartz, calcite and late pyrite (A2-c assemblage). The latest mineralization at Cwmystwyth comprises pyrite-marcasite (A2-f assemblage). Contamination of earlier Pb-Zn ores by marcasite net-veining is particularly noticeable in the western workings, where some sphalerite was so contaminated with iron sulphides as to be worthless (Jones, 1922). Old reports also indicate some vertical mineral zonation, particularly citing Mitchell's Lode, where galena in the upper workings gradually gave way to sphalerite at depth (see Davies *et al.*, 1997).

Post-mineralization tectonic movement along some of the mineralized fractures is indicated by the presence of foliated galena, containing bands of cataclastic sphalerite debris on some of the tips. The major, post-mineralization Ystwyth Fault is not exposed, since it runs along the valley bottom and is buried under alluvium, which extends in places to a considerable depth below the present valley floor. Indeed, 'gravel of glacial origin' was encountered in underground drivages in the vicinity of the fault zone at depths approaching 30 m from surface (Jones, 1922). The footwall of the Ystwyth Fault may at times be discerned by a line of rising springs along the side of Afon Ystwyth, some of which represent mine waters escaping to surface and are thus a potential source of pollution.

Secondary mineralization is widespread at Cwmystwyth Mine, particularly in the upper workings on Copper Hill, where the tips from surface workings on the Kingside Lode locally contain coarsely crystalline, yellow-green pyromorphite and cerussite. Good specimens are, however, rare due to centuries of weathering. Underground, crystalline hemimorphite on quartz has been collected from the Level Fawr section of the mine (Bevins, 1994), while workings on the Comet Lode in the Copper Hill area have yielded post-mining basic copper sulphates including brochantite and posnjakite, a rare member of the langite group. Minor amounts of micro-crystalline post-mining hydrozincite, malachite and linarite are widespread throughout the site.

Interpretation

The paragenetic sequences within the various mineral assemblages at Cwmystwyth Mine are typical of the Central Wales Orefield, with its complicated history of repeated phases of mineralizing activity extending from Devonian through into Carboniferous (and possibly even later) times (Mason, 1994, 1997). With the exception of Brynyrafr Mine, the other Central Wales Orefield GCR sites are paragenesis specific, showing the relationships of the constituent minerals of the specific assemblages.

The wide belt of mineralized tensile fractures at Cwmystwyth, accompanied by a major post-mineralization normal fault, is suggestive of the presence of a deep-seated crustal weakness underlying the area, which has focused repeated fracturing along this line. The numerous lodes described in old reports are interpreted as anastomozing mineralized tensile fractures developed within an ENE–WSW-trending zone of tensile failure which was re-activated at a later stage, when the Ystwyth Fault was formed. Furthermore, the mineralized fractures themselves may have been re-activated during development of the Ystwyth Fault. Mitchell's Lode has a similar dip to the Ystwyth Fault and has displaced the Comet Lode in a normal sense. The mineralization within Mitchell's Lode belongs to the A2-a assemblage, which is widespread within both the Kingside and Comet lodes, and is therefore likely to be cogenetic with them. It is not unreasonable, therefore, to suggest that the displacement focused along Mitchell's Lode was post-mineralization, occurring in response to the much greater movement on the Ystwyth Fault.

More speculatively, it is possible that another feature, the change in attitude of the 'Main Lode', from 50° to near-horizontal in the immediate vicinity of the Ystwyth Fault, can be explained by the effects of post-mineralization drag-folding along the hangingwall of the fault.

Mineral-cemented breccias occurring along large, generally ENE–WSW-trending tensional fractures, characteristic of the Central Wales Orefield, are particularly well-developed at Cwmystwyth. The mechanism for their development was initially described by Phillips (1972). In this now widely accepted model, fracture propagation was assisted directly by the presence of hydrothermal fluids which had migrated into the fracture plane. Fracturing propagated upwards in a series of pulses, each brittle failure occurring when the coupled forces of regional tensional stresses and the hydraulic effect of the highly pressurized hydrothermal fluid, which literally jacked the fracture walls apart, overcame the tensile strength of the rock. Following each hydraulic fracturing episode, a relatively low-pressure void, filled with hydrothermal fluid, was created, setting the scene for the next stage of the hydraulic brecciation process.

Several factors probably combined to trigger the next step of the process, amongst which the sudden drop in fluid pressure and the seeding effect generated by the introduction of millions of small rock clasts, are important. The outcome would be that the hydrothermal fluid is destabilized, so that elements previously held in solution are rapidly precipitated as quartz, carbonates and the base-metal sulphides. The minerals would nucleate on the surfaces of the angular rock-clasts, crystallizing into radial growths around the clasts and eventually locking them into a mineralized, matrix-supported breccia.

Many specimens of vein material at Cwmystwyth and other Central Wales Orefield mines reveal more than one phase of brecciation; it is not uncommon to see, for example, angular fragments of quartz-chalcopyrite mineralization cemented in a matrix of ferroan dolomite. Again, it is likely that hydraulic brecciation was the agent responsible for such textures: sudden depressuring of quartz would be likely to cause it to shatter through the hydraulic pressure of inclusion fluids. Provided a sufficient pressure differential is established rapidly enough, hydraulic brecciation is likely to occur.

This process, from hydraulic fracturing through hydraulic brecciation to mineral deposition, is likely to have been extremely rapid, otherwise the rock clasts would sink and coalesce together. Instead, they occur evenly spaced throughout the breccia, locked fast in their mineral cement.

Conclusions

The mineral veins at Cwmystwyth Mine form a branching network which trends ENE–WSW and is cut off to the south by the post-mineralization Ystwyth Fault. The veins consist of breccias, cemented by quartz and other minerals. The breccias were formed by hydraulic fracturing caused by the response of pressurized mineralizing fluids to sudden and sharp pressure changes as crustal fractures extended upwards through the strata. The most important ore minerals at Cwmystwyth are galena and sphalerite. Chalcopyrite, pyrite and marcasite are less common. The mineralization was emplaced through repeated phases of tensile fracturing which began in Devonian times and continued through into Carboniferous and, possibly, later times. Major upper crustal tensile failure subsequently occurred along the same structural trend, resulting in the formation of the universalized Ystwyth Fault, with a downthrow to the north of up to 1 km.

BRYNYRAFR MINE (SN 745 879)

Introduction

Brynyrafr Mine is a key site for the study of the Central Wales Orefield mineralization. It is the largest working on the ENE–WSW-striking Hafan Lode, a major, multi-phase mineralized fracture with a strike length of some 9 km (Figure 5.55). The mine was developed relatively late in comparison with other Central Wales mines, only beginning production in 1881. It then operated continuously for 31 years (Jones, 1922), during which time almost 5000 tons of galena concentrates and over 8000 tons of sphalerite concentrates were sold (Burt *et al*., 1986).

Brynyrafr Mine (Figure 5.56) provides one of the best sites for the textural study of both early (A1) and late (A2) generations of metalliferous vein mineralization in the Central Wales Orefield. The extensive dumps are rich in boulders which reveal a variety of brecciation, re-brecciation and cross-cutting textures, particularly when cut and polished. The demonstration of such repeated sequences of re-brecciation and cross-cutting vein relationships is an essential element in the interpretation of the mineralization of the Central Wales Orefield. Additionally, fine specimens of the rare nickel sulphide millerite occur locally.

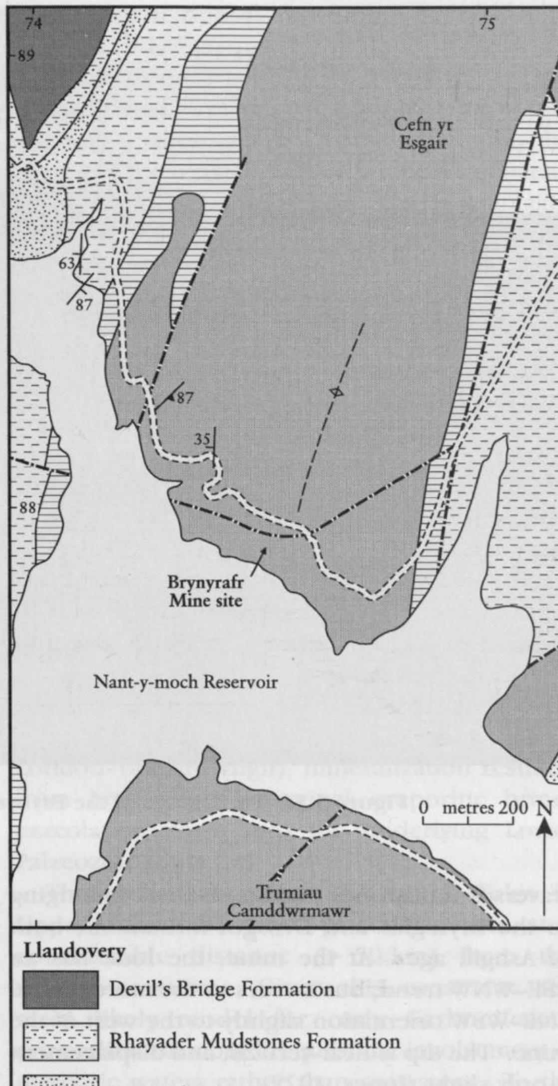


Figure 5.55 Map of the Brynyrafr Mine GCR site. After British Geological Survey 1:50 000 Sheet 163, Aberystwyth (1984).

Description

Mineralization at Brynyrafr Mine occurs in association with the fracture known as the 'Hafan Lode', one of a number of predominantly ENE–WSW-trending mineralized fractures cutting Upper Ordovician to Lower Silurian clastic rocks on the western flank of the Plynlimon Inlier (Cave and Hains, 1986). At Brynyrafr, the lode

Figure 5.56 Photograph of the Brynyrafr Mine GCR site. (Photo: T. Cotterell.)

traverses mudstones and sandstones belonging to the Bryn-glâs and Drosgol formations, both of Ashgill age. At the mine, the lode has an ESE–WNW trend, but it veers to the more typical ENE–WSW orientation slightly to the west of the mine. The dip is near-vertical, and displacement is only slight (Jones, 1922).

The mineralization was emplaced in two main episodes, represented by a total of five mineral assemblages (Mason, 1994, 1997). The early (A1) mineralization consists of breccias cemented by milky quartz with a range of sulphides. A feature of the breccias which is of particular interest is the presence of small, open fissures crossing intra-breccia rock-clasts. These are lined with an 'Alpine-type' mineral assemblage comprising micro-crystalline quartz, albite, rutile and apatite. Their genesis is as yet poorly understood. The main A1 assemblages represented comprise the A1-b quartz-sphalerite association, followed by the A1-c assemblage, here featuring quartz with chalcopyrite, abundant millerite and rare galena. Excellent specimens, by Central Wales standards, of acicular millerite up to 20 mm, associated with chalcopyrite, have been found in quartz cavities. The A1-e 'ferroan dolomite influx' is only weakly represented at this site (although it is abundant at Henfwlch Mine, only 1 km to the west) and comprises rare ferroan dolomite filling cavities in earlier breccias.

The later (A2) mineralization, consisting of glassy quartz-cemented breccias and crustiform fracture-linings, comprises two assemblages. Firstly, quartz with coarse-grained galena and sphalerite, some of the latter showing a fibrous, banded texture (A2-a), is common and appears to have been the main economic assemblage at the mine. Secondly, abundant quartz-pyrite-marcasite intergrowths (A2-f) occur, including finely crystallized, bladed marcasite and attractive crusts of quartz crystals up to 3 cm. As at other Central Wales Orefield mines, the A2-f assemblage appears to represent the final phase of primary mineralization.

Brynyrafr Mine is not particularly noteworthy as a locality for secondary minerals. Minor micro-crystalline hemimorphite occurs as an alteration product of sphalerite, while traces of post-mining linarite, malachite and brochantite have been found coating oxidized chalcopyrite of the A1-c assemblage.

Interpretation

Re-brecciation and cross-cutting vein textures clearly demonstrate that the primary mineralization at Brynyrafr Mine is polyphase and equates to the regional paragenetic assemblages of the Central Wales Orefield, as proposed by Mason (1994, 1997). In Central Wales, the vast majority of mineralized fractures of both A1 and A2 groups have an ENE–WSW trend. The production and subsequent re-activation of a regional set of open fractures of this orientation would require extensional stresses operating on an approximately NNW–SSE alignment, essentially normal to the Caledonian compressive trend.

The early (A1) phase of mineralization is believed to be of early Devonian age, based both on lead isotope data (Fletcher *et al.*, 1993) and on the postulated tectonic regime at that time, when post-compressional relaxation would have allowed the liberation of intra-formational waters. These would have been formed earlier, during metamorphic dewatering of the underlying sedimentary pile, but would have been largely trapped under the Caledonian compressive stresses prevailing. Under the conditions of post-folding relaxation, such fluids would have become mobilized. Upward migration, accompanied by leaching of metals, would then ensue; as relaxation progressed, the metalliferous fluids would logically migrate into the low-pressure zones created by relaxation joints. Given sufficient fluid availability, the process of upward fracture propagation by hydraulic action would commence (Philips, 1972), resulting in the development of mineralized breccia-zones.

The later (A2) mineralization of the Central Wales Orefield has given a variety of lead isotope ages (Swainbank *et al.*, 1992; Fletcher *et al.*, 1993), ranging from early Carboniferous (A2-a) to Permian (A2-b + c). The A2-f marcasite-bearing assemblage clearly post-dates all assemblages for which lead isotope data have been obtainable. In regional tectonic terms, the emplacement of the A2 assemblages clearly marked the re-establishment of a similar extensional stress regime to that which led to the development of the A1 mineralization. Regional stresses of this type were again operative during the extensional phase of the Variscan orogenic cycle in late Devonian and early Carboniferous times. As with the early phase of mineralization, brecciation has played an important role in the formation of the A2 deposits, although in addition some fluids simply rose up open fractures to produce coarse-grained crustiform deposits reminiscent of the Mississippi Valley-type (MVT) mineralization of the 'Pennine-type' orefields. As with the A1 mineralization, the pattern is of the younger assemblages either cutting or re-brecciating older ones.

Mineralization similar to the Central Wales Orefield A2 assemblages is widespread in several areas of Lower Palaeozoic strata in Wales and the Welsh Borderland. The Llanengan Orefield on Llŷn, the Llanrwst Orefield in eastern Snowdonia, and the West Shropshire Orefield in south-west Shropshire are all examples. Recent work on the West Shropshire Orefield, at the **Snailbeach Mine** GCR site (see GCR site report, Chapter 4; Pattrick and Bowell, 1991), has highlighted the role of early Carboniferous seawater as a potential fluid source. In their genetic model for the West Shropshire Orefield, Pattrick and Bowell (1991) inferred that during early Carboniferous times, when much of Wales and the Midlands comprised a landmass (the London–Brabant High), mineralization resulted from high-salinity marginal evaporitic brines percolating down into the underlying Lower Palaeozoic strata.

The palaeogeography of Central Wales in Upper Palaeozoic times places the area at a considerable distance (> 50 km) from the nearest seawater. Given this constraint, the most likely model for early Carboniferous mineralization would require the involvement of meteoric waters rather than seawaters. To the west of the Central Wales Orefield, however, lies the Permian to Tertiary basin of Cardigan Bay, containing approximately 6 km of sedimentary fill and a ready source of connate brines migrating up and eastward into the Central Wales area. Therefore, the inferred Permian mineralizing event, suggested by lead isotope data, is more compatible with a model involving connate brines migrating from the Cardigan Bay Basin (Mason, 1997).

Conclusions

Brynyrafr Mine provides one of the best sites for the study of textural features of mineralization in the Central Wales Orefield. The large dumps are rich in vein material from both the early (A1) and late (A2) phases of mineralization. Superb textures in breccias and cross-cutting crustiform veins are present in abundance. The site is of un-paralleled quality for demonstrating the repeated sequence of re-brecciation and cross-cutting which characterizes the primary paragenesis of the Central Wales Orefield. The A1 mineralization is thought to be early Devonian in age and linked to post-Caledonian relaxation, while the A2 mineralization is considered to have developed in early Carboniferous times and, on a smaller scale, in Permian times.

DARREN MINE (SN 680 832)

Introduction

Darren Mine (Figure 5.57) is a critical site in the interpretation of the early (A1) assemblages of the Central Wales Orefield primary paragenesis, situated as it is within a cluster of mines all historically famed for the silver content of their lead ores. Galena concentrates sold from Darren and neighbouring mines in the latter half of the 19th century contained up to 30 oz of silver per ton, whereas many Central Wales mines yielded grades of only 3–5 oz per ton. Research at this site in the 1980s (Mason and Hughes, 1990; Mason, 1998) clarified why the silver content of ores raised at these mines was significantly greater than at other mines. The galena of the A1-c assemblage, which dominated the orebodies worked at Darren and its neighbouring mines, was found to contain common and richly argentiferous (up to 18 wt% Ag) inclusions of tetrahedrite, a feature absent from mines with low silver grades, which worked tetrahedrite-free galena belonging to later (A2) assemblages.

In the Central Wales Orefield, outcrop workings on several chalcopyrite-bearing mineral lodes have been reliably dated by radiocarbon methods back to the Early Bronze Age (Timberlake, 1988). Although such research has yet to be carried out at Darren, it is widely believed that the original workings are of great antiquity. The lode crosses a hill-top, and at the summit, a hill-fort of probable Iron Age origin lies close to old opencut workings. A boulder containing galena was discovered in the ramparts of the hill-fort in 1985 (Hughes, 1990), re-inforcing the suspicion that the lode had already been excavated by the time the fort was constructed.

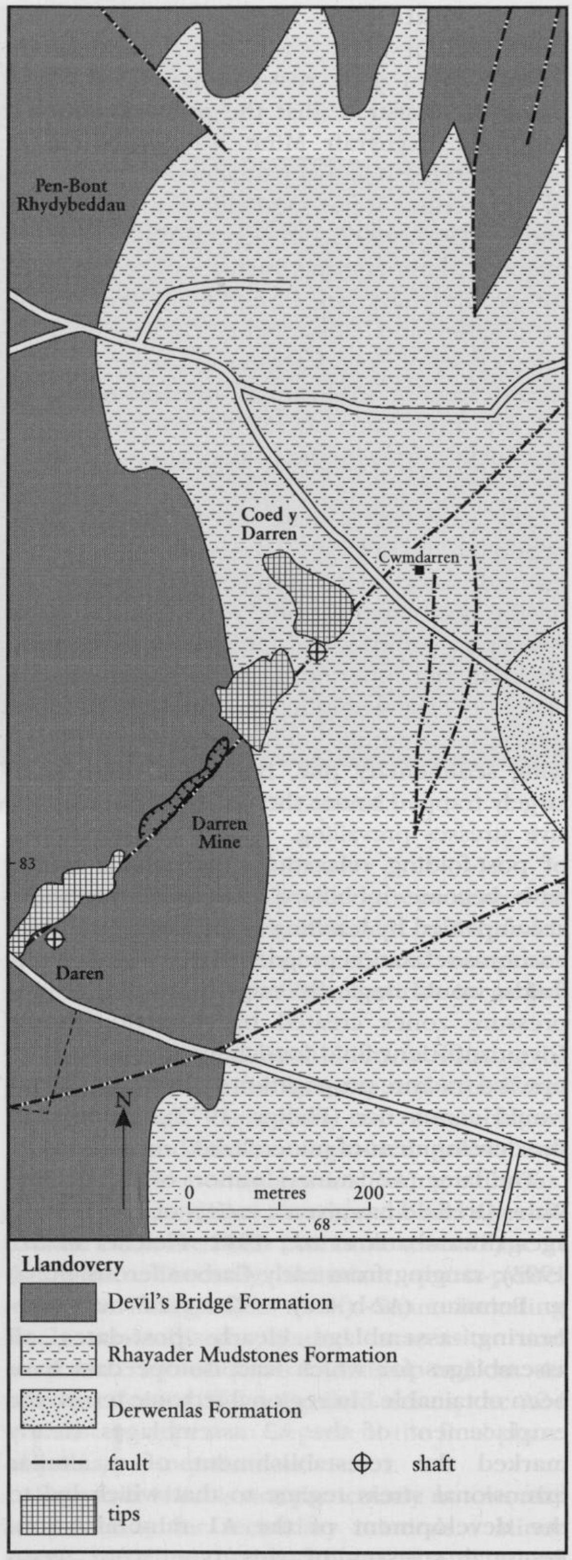


Figure 5.57 Map of the Darren Mine GCR site. After British Geological Survey 1:50 000 Sheet 163, Aberystwyth (1984).

The working of Darren Mine from Elizabethan times onwards is well documented (Hughes, 1990). By the end of the 18th century, the mineralization had been extensively stoped away, 19th century operations being little more than reworking over what was left, with a few exceptions. The mine finally closed in the 1880s.

Description

The mineralized fracture known as the 'Darren Lode' trends almost north-east–south-west across the hill and cuts greenish-grey, banded mudstones of the Rhayader Mudstones Formation, passing up into grey mudstones and thin sandstones of the Devil's Bridge Formation, both of Llandovery age (Cave and Hains, 1986). The lode is filled with brecciated sedimentary rock clasts in a cement of quartz and sulphides. The lode is not currently well-exposed but its width (> 5 m in places) may be appreciated where it crosses the hill-top, a short distance to the north-west of the Iron Age hill-fort.

The primary mineralization at Darren Mine (Figure 5.58) is dominated by the A1-c assemblage, an important member of the early phase of mineralization in the Central Wales Orefield. The ore consists of quartz with (in order of crystallization) chalcopyrite, ullmannite and gersdorffite, tetrahedrite, bournonite, and galena. Chalcopyrite, tetrahedrite, bournonite, and galena occur as coarse, intergrown aggregates lining cavities in milky quartz, while tetrahedrite and bournonite also occasionally occur in easily visible masses up to 3 cm in diameter. In contrast, ullmannite and gersdorffite are only visible in polished section, where they may be observed as inclusions in galena (accompanied by numerous small tetrahedrite and bournonite grains). Cavities in the quartz also contain rare traces of late-stage (A1-d), red to orange, translucent sphalerite. Other gangue minerals present comprise chlorite, commonest around breccia clasts, traces of albite, and rutile, all occurring, as at the **Brynyrafr Mine** GCR site, within intra-clast fissures. In addition, ferroan dolomite and calcite occur as fillings to quartz cavities. A2 mineralization is represented by very minor late calcite and marcasite.

Secondary mineralization is widespread at Darren Mine, although the minerals occur in small amounts and are generally micro-

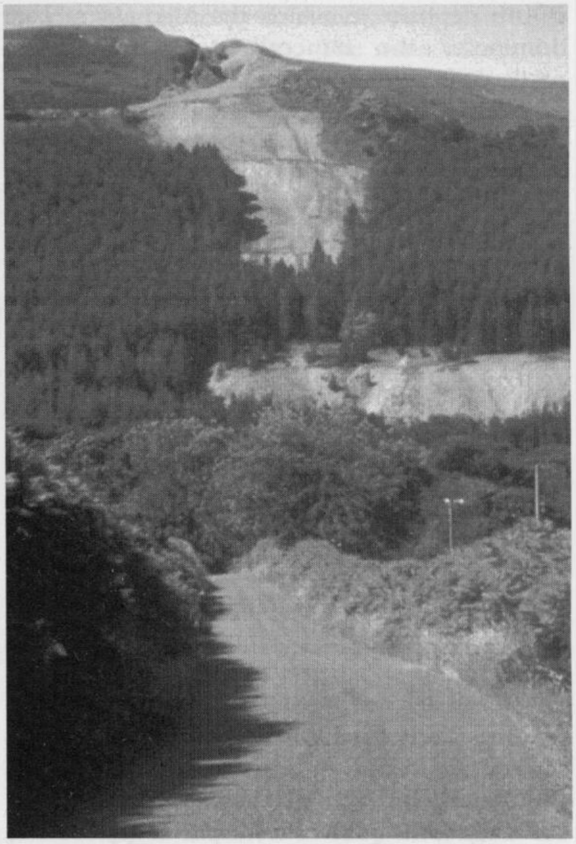


Figure 5.58 Photograph of the Darren Mine GCR site. (Photo: J.S. Mason.)

crystalline. Joints in the breccias are lined with thin coatings of a variety of species, including cerussite, hydrocerussite, wulfenite, beaverite, mattheddleite, leadhillite, anglesite, caledonite, linarite, brochantite, langite, malachite and native sulphur. Arsenates such as beudantite and mimetite are also locally present. An interesting feature is the occurrence of erythrite as thin, pink coatings derived by the weathering of cobalt-bearing gersdorffite. A temporary exposure of the lode created during stope capping activities in 1992 revealed, unusually, hydrocerussite, leadhillite and other minerals *in situ*; this exposure is now buried. More recently redgillite has been recorded from Darren Mine (Pluth *et al.*, 2005).

Interpretation

The localized group of richly argentiferous lodes in the Darren–Goginan area, typified by the Darren Mine, represents a particular cluster of ore deposits in which the A1-c assemblage dominates the mineralization and carries particularly abundant argentiferous tetrahedrite, accompanied by bournonite. Both minerals occur in this assemblage at most of its localities, but not in the concentrations encountered at the Darren and neighbouring mines. This, however, is a feature of the A1-c assemblage, which is noteworthy because certain constituent minerals occur in greater proportions in certain areas (Mason, 1994, 1997, 1998). Thus, there is the concentration of siegenite-rich mineralization in the area north of Talybont, typified by the **Erglodd Mine** GCR site, the concentration of tucekite occurrences in the area to the north-west of Plynlimon, represented by the **Eaglebrook Mine** GCR site, and the cluster of particularly tetrahedrite-rich deposits of the Darren–Goginan area.

Such variations in the mineralogy of a single assemblage, hosted by similar strata across the orefield, tend to suggest that there were subtle variations in the geochemistry of the ore-forming fluids from place to place within the orefield as a whole. Given that the models postulated for the Central Wales Orefield mineralization (Fletcher *et al.*, 1993; Mason, 1994, 1997) involve a single crustal source of lead and other metals which was repeatedly tapped as successive phases of mineralization took place, it is possibly the case that the spatial variations in mineralogy reflect a similar source terrain within which geological features, for example the distribution of acid or basic volcanic rocks, had an influence on the geochemistry of the fluids derived from their leaching and therefore the mineralogy of the resultant regional assemblages.

Darren Mine also provides an interesting demonstration of the value of mineral production statistics. The mine is officially credited with producing just over 1650 tons of lead ore concentrates (containing just over 21 000 oz of silver) and 50 tons of copper concentrates, between the years of 1849 and 1879 (Jones, 1922). These figures give the impression that this was a relatively modest working. However, a visit to the site immediately conveys the picture of an old and extensive mine, and a study of the mine's history (Hughes, 1990) shows that it was intensively worked during the 17th and 18th centuries, during which much of the richest mineralization was worked away. Official compilation of mineral production statistics was only commenced in 1845, however, and Darren provides an excellent illustration of the fact that the official returns represent an unknown percentage of the total. The geological relevance of this is that, when examining a pre-19th century mine, post-1845 production figures are not a reliable tool to use in estimating the true size of the mineral deposit worked.

Conclusions

Darren Mine is a key site for studying the early (A1) assemblages of the Central Wales Orefield paragenesis. The A1-c assemblage in the Darren–Goginan area is characterized by a relative abundance of richly argentiferous tetrahedrite, containing up to 18 wt% Ag. This factor alone attracted the Elizabethan miners, whose quarry was principally silver. Until the presence of tetrahedrite inclusions in galena was discovered during the 1980s, the mineralogical reason for the relatively argentiferous character of the ores of the Darren–Goginan area was not known. In addition to the tetrahedrite, the galena also contains bournonite, ullmannite, and gersdorffite, while a range of secondary minerals, including a number of rare arsenates, is present.

ERGLODD MINE (SN 657 903)

Introduction

Erglodd Mine (Figure 5.59) is one of a small number of key sites in the interpretation of the early (A1) phase of the Central Wales Orefield primary paragenesis, as identified by Mason (1994, 1997). The site exhibits an important development of the early polymetallic (A1-c) assemblage, here containing an exceptional quantity of Co-Ni minerals, principally siegenite. A number of samples of veinstone have assayed in excess of 3 wt% combined Co + Ni; in these samples the pale-pink to white siegenite is clearly visible in hand specimen. Additionally, the assemblage contains cobalt pentlandite, millerite, ullmannite, and pyrrhotite (not reported elsewhere from the A1-c assemblage), and is auriferous; minute gold grains have been identified in polished section and gold grades locally exceed 0.5 g/t.

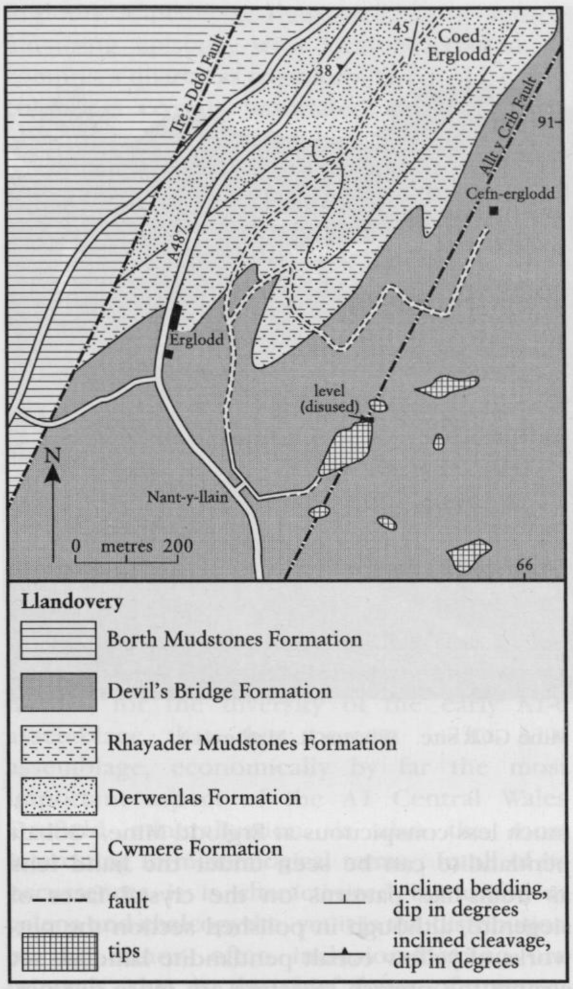


Figure 5.59 Map of the Erglodd Mine GCR site. After British Geological Survey 1:50 000 Sheet 163, Aberystwyth (1984).

Description

Erglodd Mine (Figure 5.60) worked an ENE–WSW-trending vein of mineralized breccia cutting grey mudstones and sandstones of the Devil's Bridge Formation of Llandovery age. It is undoubtedly an old working and the abundance of stone hammers amongst the debris from outcrop workings may even point to it being one of a number of Early Bronze-Age copper workings in the area (S. Timberlake, pers. comm.). The Roman road, Sarn Helen, runs nearby, and in 1976 a Roman fortlet was discovered nearby, while in 2004–2005 an extensive Roman smelting site was discovered during archaeological excavations close to the edge of Borth Bog, at the foot of the slope below the mine. However, the recorded history commences in the late 18th century (Hughes, 1981a). The mine was in the hands of John Taylor and Sons in the 1840s, when a deep adit cross-cut was driven to drain the old workings. However, when this holed through it was still well above the lowest workings: the assumption that ancient miners were unable to work to any great depth was disproved in Central Wales many times in the 19th century, at some considerable expense to the then operators.

The mine fell into disuse in about 1883, by which time a recorded total of 16 tons of lead and 12 tons of zinc sulphide concentrates had been sold. Production prior to the advent of statistical collation in 1845 is unknown but is unlikely to have been very large. The current site layout is partly the result of much dump removal for hardcore in the 1970s; above the remnant tips lies a deep and dangerous open-cast working. The deep adit portal is situated at the top of the area of disturbed tips, but is now collapsed.

The sulphide mineralogy of Erglodd Mine is of particular interest and as such it was selected as one of the key sites in the Central Wales Orefield by Mason (1994). Although ore microscopy is required to fully investigate the assemblages, the presence of cobalt and nickel minerals, in highly elevated levels compared to other Central Wales Orefield sites, may be appreciated in hand specimens of veinstone. Most of the cobalt and nickel occurs in the rare mineral siegenite, one of the thiospinel group of minerals with the formula $(Co,Ni,Fe)_3S_4$.

Early (A1) mineralization, which consistently gives a Lower Devonian isotopic age (Fletcher *et al.*, 1993), dominates the vein worked at Erglodd Mine. Initial mineralization resulted in the formation of breccia cements of quartz, with abundant dark-brown sphalerite accompanied by minor pyrite, ferroan dolomite and chlorite (A1-b assemblage). However, the majority of this material occurs as clasts, brecciated and cemented by later mineralization of the subsequent A1-c assemblage. This, the most polymetallic assemblage of the Central Wales Orefield, has here developed in two sub-stages with brecciation in between, a feature not recognized elsewhere in the orefield. The first sub-stage consists of quartz and fine-grained sulphides, which give the quartz a bluish colour. The fine grain-size makes paragenetic determinations impossible without resorting to ore microscopy. The depositional sequence of sulphides in this

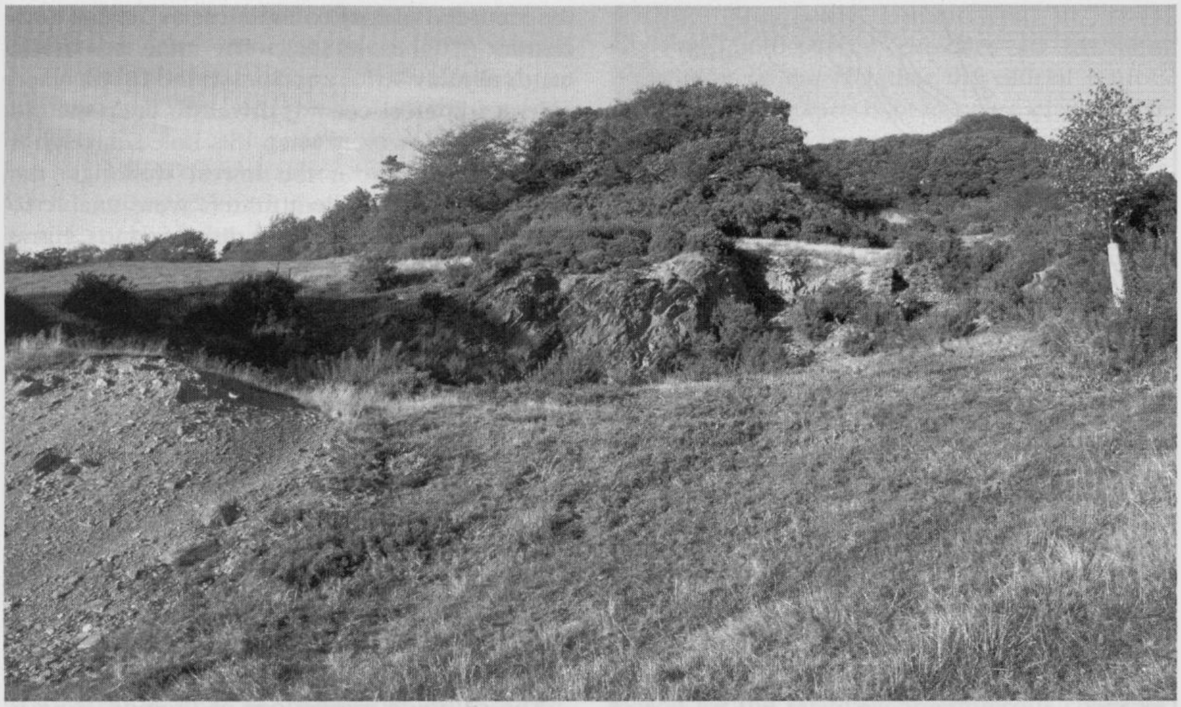


Figure 5.60 Photograph of the Erglodd Mine GCR site. (Photo: R. Mathews.)

quartz is trace pyrite, trace marcasite, siegenite, cobalt pentlandite, chalcopyrite, trace pyrrhotite and galena. Brecciated fragments of enclosed A1-b sphalerite have been spectacularly affected by chalcopyrite disease, particularly where in proximity to later deposits of chalcopyrite.

The second A1-c sub-stage has a cyclic paragenetic sequence, with repetition of several minerals being observed in layered overgrowths around clasts. It comprises, in order of crystallization, chalcopyrite, minor ullmannite, minor bournonite, galena, quartz, trace gold, siegenite, cobalt pentlandite, trace millerite, chalcopyrite and trace galena. Tetrahedrite, although not noted in the samples studied to date, occurs in minor amounts in this assemblage at several neighbouring mines, the inference being that it can be expected to be found at Erglodd Mine with further study.

Although many phases can only be observed under the microscope, siegenite is conspicuous in hand specimen, forming euhedral crystals typically up to 1 mm across, aggregated into pale-pink to white, metallic patches dispersed throughout the quartz matrix. Indeed, Jones (1922) noted its presence on the dumps, but mis-identified it, stating that '...some pyritous lode-matter occurs on the tip.'. Pyrite is, in fact, much less conspicuous at Erglodd Mine. Cobalt pentlandite can be seen under the hand lens as trellis-like patterns on the crystal faces of siegenite, although in polished section the networks of yellow cobalt pentlandite lamellae set against the pinkish siegenite are more distinct. Apart from galena, chalcopyrite and millerite, all other sulphide phases occur as microscopic inclusions in galena, with ullmannite being the most frequently observed. Gold occurs as minute (10 μm) crystals associated with siegenite, and assays performed on samples from this mine (Mason, 1998) show a close positive correlation between levels of gold, cobalt and nickel.

Later cavity filling, a common feature of the A1 mineralization in the Central Wales Orefield, involved the crystallization of minor, typically yellow to orange, translucent sphalerite ('honey-blende') overgrown by minor calcite. Polished sections reveal that this sphalerite generation has locally replaced A1-c galena, with the development of caries texture along sphalerite-galena contacts. Curiously, inclusions of ullmannite within the galena have remained unaffected by this process.

Late (A2) mineralization, which in the Central Wales Orefield is often found along re-activated A1 fractures, occurs in only trace quantities at

Erglodd Mine. Accompanied by a minor fracturing episode, with local brecciation, it comprises quartz, as crustiform layers of stumpy colourless crystals, associated in places with granular-textured, reddish-brown sphalerite and later intergrown pyrite and marcasite.

Secondary mineralization is limited at Erglodd Mine to thin brochantite and linarite, occurring as thin, dump-formed coatings on chalcopyrite fragments. Covellite often replaces chalcopyrite superficially. Cerussite and pyromorphite occur as insipid, filmy coatings on quartz. Siegenite often shows alteration to oxides, via an intermediate phase petrologically resembling violarite. The alteration of siegenite-cobalt pentlandite composite crystals always commences along the cobalt pentlandite lamellae.

Interpretation

Erglodd Mine is one of three GCR sites in the Central Wales Orefield selected, amongst other factors, for the diversity of the early A1-c assemblage that they portray. The A1-c assemblage, economically by far the most important aspect of the A1 Central Wales Orefield mineralization, is also the most interesting in mineralogical terms. In all of its occurrences it is characterized by abundant galena and chalcopyrite, yet it is the distribution of the minor, often inclusion-forming ore minerals, that is the chief focus of interest. Certain of these phases, particularly tetrahedrite, siegenite, millerite and tucekite, occur more abundantly in some areas than in others, and it is the clustered nature of these occurrences that is of note. Thus, there is the concentration of siegenite-rich mineralization in the area north of Talybont, typified by the Erglodd Mine GCR site, the concentration of tucekite occurrences in the area to the north-west of Plynlimon, represented by the **Eaglebrook Mine** GCR site, and the cluster of particularly tetrahedrite-rich deposits of the Darren–Goginan area, as seen at the **Darren Mine** GCR site.

Siegenite is in fact widespread throughout the Central Wales Orefield, but outside of the area immediately to the north of Talybont it occurs only as a trace phase, detected only by ore microscopy. Cobalt and nickel levels are likewise lower outside of this one area. The nickel sulphantimonide mineral ullmannite is present at widely scattered localities as a component of the much later A2-b assemblage, where it occurs as macroscopic crystals in a crustiform layered assemblage, as occasionally seen at the **Frongoch Mine** GCR site.

Marked, well-constrained variations in the mineralogy of a single assemblage, hosted by similar strata across the Central Wales Orefield, tend to suggest that there were variations in the geochemistry of ore-forming fluids from place to place within the area as a whole. The isotopic model proposed for the Central Wales Orefield mineralization (Fletcher *et al.*, 1993) involves a single crustal source of lead (and other metals), repeatedly tapped as successive phases of mineralization took place. In this context, it is likely that the spatial variations in the mineralogy and geochemistry of a single assemblage reflect a source terrain within which key geological horizons have influenced the geochemistry of the fluids derived as a result of their leaching.

It is therefore possible, as suggested by Mason (1994, 1997), that the A1-c assemblage was formed by the action of a series of co-existing hydrothermal cells, each leaching metals from broadly similar crustal levels, but each encountering a variety of strata acting as metal reservoirs. Within the Lower Palaeozoic sequences of the Welsh Basin, even if the Cambrian sequences are discounted, there remains a wide range of sedimentary rocks from pyritic shales through sedimentary ironstones to greywackes, and notably in the Ordovician sequences both acid and basic volcanic and intrusive rocks. These all outcrop just to the north of the Central Wales Orefield, in the area between Machynlleth and Dolgellau (Pratt *et al.*, 1995), and it is quite likely that similar sequences underlie the orefield itself, thereby providing a geochemically diverse source terrain, particularly in terms of minor element variations. In the case of the Erglodd Mine area, a source terrain relatively rich in Co and Ni is required to explain the abundance of siegenite if the overall model of Fletcher *et al.* (1993) is appropriate.

Conclusions

Erglodd Mine is the most significant example of one of a number of localities to the north of Talybont where the early, A1-c polymetallic assemblage (see Table 5.1) is particularly rich in cobalt and nickel minerals, to the extent that they may be observed in hand specimen. This clustering together of localities, where particular minerals or metals are unusually abundant, is characteristic of the A1-c assemblage, the most widely developed facet of the early mineralizing episode. The occurrence of such clusters suggests that the A1-c mineralization was emplaced across the Central Wales Orefield by a series of co-existing convective hydrothermal cells, each tapping similar, but subtly different, source rocks at depth.

EAGLEBROOK (NANTYCAGL) MINE (SN 736 892)

Introduction

Perhaps the most renowned locality in Central Wales for secondary copper, lead and zinc minerals, Eaglebrook Mine, or Nantycagl Mine (Figure 5.61) has been recognized also as a key site for the study of the primary paragenesis of the Central Wales Orefield. The mineralization spans several assemblages emplaced during both the early (A1) and late (A2) metallogenic episodes, as described by Mason (1994, 1997). Prime features of the A1 mineralization are the cobalt-nickel minerals and electrum occurring in the A1-c assemblage, and the well-demonstrated post-ore ferroan dolomite influx (A1-e assemblage). Of particular interest is the presence, in the Co-Ni minerals, of the rare sulphantimonide tucekite, $Ni_9Sb_2S_8$, which occurs here in significant quantities. This is the first British and only the third occurrence worldwide of the mineral, and additionally its first description from a hydrothermal vein. Secondary mineralization, formed both prior to and post-mining, has resulted in a diverse assemblage, including many rare species which occur as well-developed micro-crystals. The suite includes rare species such as wroewolfeite, lautenthalite, ramsbeckite, laurionite, and cesàrolite, and for specimens of these and other species the site is justifiably famous.

Eaglebrook Mine (Figure 5.62) is an extensive site and gives the impression of much greater activity having taken place than the rather sketchy historical references imply. The mine was originally known as 'Dolrhuddlan', and later also 'Nantycagl', and was being worked by the Company of Mine Adventurers prior to 1708 (Bick, 1976). However, their lease was relinquished in 1722 and the mine remained unworked from then until the mid-1850s, when the Francis brothers, under the new name Eaglebrook, promoted as the forgotten Welsh Potosi, relaunched it as a speculative venture. Such changes of name were not uncommon in the 19th century, their function being to give the impression of completely new discoveries in the

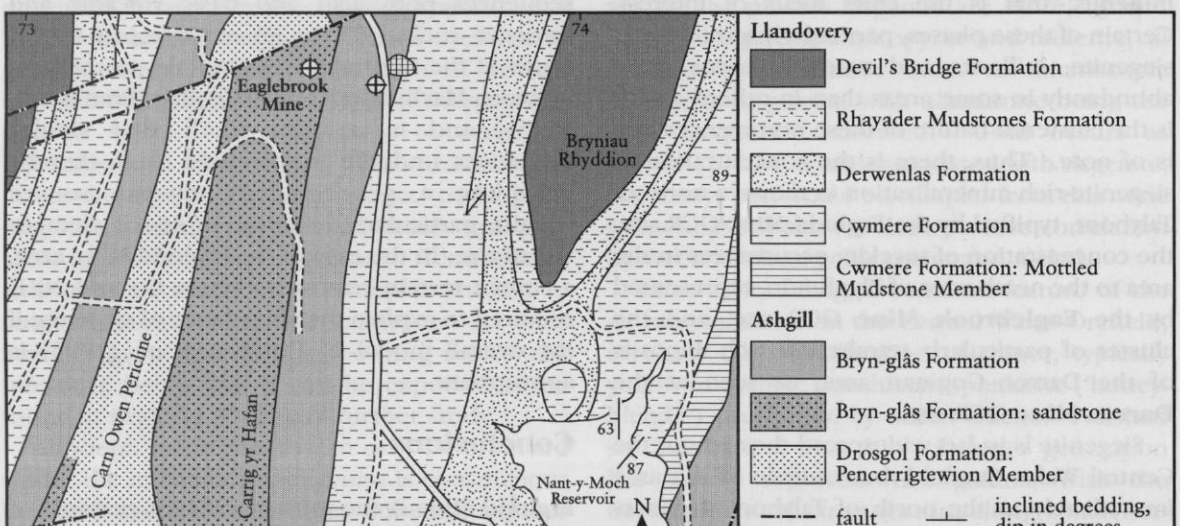


Figure 5.61 Map of the Eaglebrook Mine GCR site. After British Geological Survey 1:50 000 Sheet 163, Aberystwyth (1984).

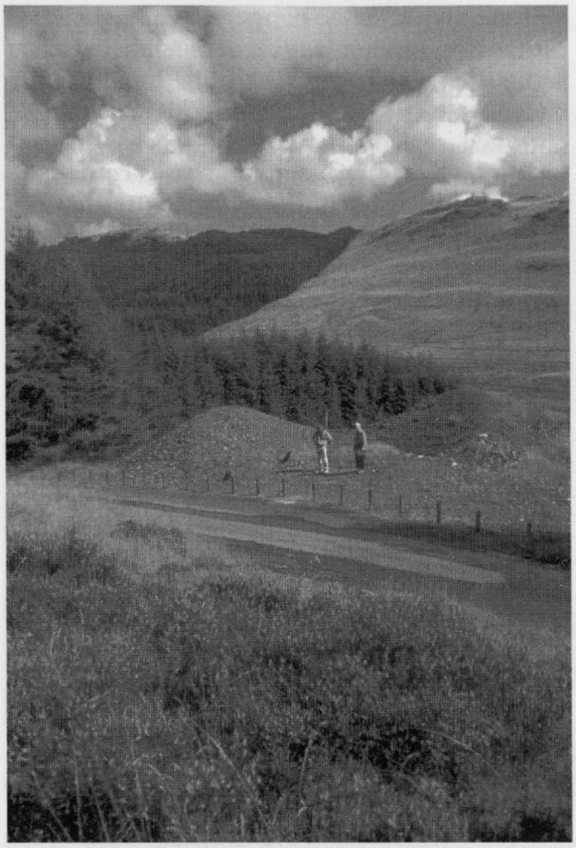


Figure 5.62 Photograph of the Eaglebrook Mine GCR site. (Photo: S. Campbell.)

drive to inflate share prices. The mine closed, however, in the mid-1870s, having reached a depth of 50 fathoms (109 m) from surface.

In post-1855 times the mine produced 598 tons of galena concentrates and 71 tons of chalcopyrite concentrates (Jones, 1922); production figures presented by Burt *et al.* (1986) give higher yields for certain years, but this is because the mine's output was at times returned in conjunction with that of other nearby sites. The true production, clearly much greater than this, remains unknown.

Description

The mineralization at Eaglebrook Mine occupies an E–W-trending fracture with a small northerly downthrow that crosses the axis of the Carn Owen Pericline. Close to the core of the fold, sandstones and massive, poorly cleaved mudstones of the Drosgol and Bryn-glâs formations, of Ashgill age, host the mineralization, but to the east the fracture passes into pyritic mudstones of the Cwmere Formation (Lower Llandovery) and the mineralization weakens. Due to favourable bedding-cleavage intersections, bedding-parallel slabs of graptolitic mudstone from the *Glyptograptus persculptus* Biozone of the Cwmere Formation occur among the tips of the eastern workings and contain well-preserved, three-dimensional pyritized graptolites and occasional orthocones.

Both early and late elements of the Central Wales Orefield paragenesis (Mason, 1994, 1997) are present on the extensive tips. Early (A1) mineralization comprises three assemblages. The A1-c polymetallic assemblage provided most of the lead and copper ores mined and comprises, in order of crystallization, quartz, pyrite, siegenite, cobalt pentlandite, millerite, chalcopyrite, electrum, tucekite, ullmannite and galena. Siegenite occurs in a similar mode to that occurring far more abundantly at the **Erglodd Mine** GCR site, although in this case it is locally replaced by millerite as well as the ubiquitous cobalt pentlandite. Tucekite, first described as a British mineral from this site (Mason, 1994, 1997, 1998), forms distinctive, highly anisotropic tetragonal crystals up to 0.5 mm in galena. It is difficult to observe with the naked eye, but in polished section it can be seen in conspicuous amounts, where it is occasionally associated with electrum. The electrum, which electron microprobe analysis shows to be a 60:40 Au-Ag alloy, forms rare, ragged grains (< 0.1 mm) either in tucekite or adjacent to it in galena. Ullmannite inclusions also occur in the same generation of galena. Again, ore petrology and, in this case, repeated sectioning of anomalous material, are required in order to detect the electrum grains. The gold grade of the mineralization, while quite consistently above background, does not exceed 0.5 g/t, and is therefore of no economic interest. The A1-c assemblage at Eaglebrook Mine is best studied in comparison with that occurring at the **Darren Mine** and **Erglodd Mine** GCR sites.

The A1-e ferroan dolomite influx was a major event at Eaglebrook Mine and large blocks of the mineral are abundant on the tips, often clearly enclosing brecciated fragments of the A1-c assemblage. Ferroan dolomite is veined and locally brecciated by the A1-f assemblage, which comprises white, prismatic, crystalline quartz and minor sulphides (siegenite, cobalt-pentlandite, millerite, chalcopyrite and galena); millerite needles up to 15 mm in length are the most interesting feature of this assemblage.

Late (A2) mineralization is less abundant, but distinctive veinstone consisting of abundant calcite with galena and sphalerite, accompanied in places by minor quartz and chalcopyrite, has been interpreted by Mason (1994) to represent the A2-c assemblage. This material may be seen cross-cutting ferroan dolomite and other A1 material, thus demonstrating the age relationship. The latest mineralization at Eaglebrook Mine belongs to the A2-f 'iron sulphides' assemblage. As at other localities, this assemblage cross-cuts all others, often net-veining sphalerite, calcite and ferroan dolomite. Marcasite is the dominant mineral, accompanied by pyrite, quartz and minor calcite. The pyrite is noteworthy since it is strongly zoned, containing nickeliferous bands (R.A. Ixer, pers. comm.), and is often spectacular when viewed in polished section.

Prior to the discovery of rare primary minerals at Eaglebrook Mine, the site's reputation lay in the great diversity of secondary species present (Jones and Moreton, 1977; Jones, 1983). These fall into two genetic groups, namely pre- and post-mining minerals. The pre-mining, entirely natural generation of secondary minerals was clearly strongly developed at Eaglebrook Mine and comprises: massive and crystalline cerussite, rare pyromorphite and traces of wulfenite, all derived from galena; abundant malachite, with minor chrysocolla, chalcocite, covellite, cuprite and native copper, derived from chalcopyrite; and manganese oxides, goethite, smithsonite and hemimorphite. Hand-cobbed fragments of cerussite, malachite and occasionally cuprite occur around old ore-dressing areas, suggesting that both minerals were worked as ores in the past.

Post-mining mineralization has developed in the dumps, and is particularly significant in the Eastern Shaft dump. It is difficult in some cases, however, to determine whether a mineral is definitely pre- or post-mining in origin, and some species, such as linarite and anglesite, may have formed in both supergene environments. The post-mining minerals tend to occur as small (< 2 mm) groups of micro-crystals which are, however, impressive when viewed microscopically. The presence of post-mining minerals is often indicated by the coating of the outer surfaces of sulphide-rich rock fragments by linarite and brochantite. The paragenesis of the post-mining mineralization is variable according to the host in which the mineralization is developed. Thus in a ferroan dolomite or calcite matrix, basic zinc-copper sulphates and carbonates predominate, comprising common serpierite accompanied locally by devilline, aurichalcite and, rarely, ramsbeckite. Lumps of corroded chalcopyrite contain brochantite and linarite. Gossanous goethite masses containing pre-mining malachite, smithsonite, hemimorphite, cerussite, cuprite and native copper carry a diverse range of copper-lead-zinc basic sulphates. These include brochantite pseudomorphs after octahedral cuprite and well-crystallized linarite, langite and wroewolfeite. Less frequently, leadhillite and very rare lautenthalite, the latter often grown epitaxially on wroewolfeite, have been found. Corroded galena again contains linarite and leadhillite, with frequent cerussite and micro-crystals of anglesite. Rarer species found recently comprise caledonite, laurionite (Rust, 1995b) and dundasite, as well as the recently described mineral redgillite (Pluth *et al.*, 2005), and the rare supergene manganese mineral cesàrolite (Cotterell, 2006b).

Interpretation

The primary mineralization at Eaglebrook Mine has as its prime interest the occurrences of tucekite and electrum within the A1-c assemblage. The extremely rare mineral tucekite is the antimony analogue of hauchecornite (Ni_9BiSbS_8), and was first described as a mineral species (Just and Feather, 1978) from a mineralized Archean chlorite schist at Kanowa, western Australia, and from auriferous concentrates produced from the Vaal, Carbon Leader and Ventersdorp Contact Reefs in the Witwatersrand, South Africa. As well as its occurrence at Eaglebrook Mine, it has been found in lesser amounts at a cluster of nearby mines, namely Henfwlch, Esgairhir, Esgairfraith and Hyddgen. It has not been found elsewhere in Wales, or indeed Great Britain, however, outside of this very restricted area.

These tightly clustered occurrences of a rare mineral again emphasize a characteristic feature of the A1-c assemblage, namely that it tends to exhibit strong local mineralogical features from area to area. Gold is rather more widespread within the A1-c assemblage but seems, from the data acquired to date, to be particularly conspicuous, occurring in electrum, at Eaglebrook Mine. The occurrences at the Eaglebrook Mine and **Erglodd Mine** GCR sites are the first to have been authenticated in the orefield, though many claims were made to its presence in Central Wales during the 19th century. For example, in 1854, at Caegynon Mine in the Rheidol Valley, which worked A2 Pb-Zn mineralization, a 'gossan' was supposed to be under investigation which, it was claimed, contained over 2 oz of gold per ton. However, nothing came of this and, as Bick (1975) commented, it was more likely to be a sure sign that lead ore reserves were at that time running low. Later, similar claims were made, reported by Jones (1922), that the Kingside Lode on Copper Hill at the **Cwmystwyth Mine** GCR site contained 'three pennyweights of gold to the ton'. While gold does appear to be widespread in the Central Wales Orefield, particularly, and perhaps entirely, within the A1-c assemblage, the grades so far recorded are, however, of academic interest only.

Of particular interest, however, is the strong positive correlation, reported by Mason (1998), between gold levels and occurrences of cobalt-nickel minerals in the Central Wales Orefield. Siegenite and tucekite, in particular, are important associates. The reason for this feature is currently not known: it may lie in the nature of the source terrain from which the fluids responsible for the A1-c mineralization were derived.

The diverse secondary mineralization at Eaglebrook Mine is composed of common Central Wales Orefield species that may be expected in the oxidation zones of mixed base-metal veins, and rare species which have formed in localized geochemical environments within mine tips. The post-mining phases, such as lautenthalite, ramsbeckite and wroewolfeite, may be regarded as thermodynamically unstable minerals which are generally absent from geologically mature deposits (Mason and Green, 1996). The formation of such a diverse assemblage of basic sulphate minerals may be attributed initially to mining processes which have resulted in the juxtaposition of blocks of unstable primary minerals, such as marcasite, with rocks containing carbonates and Cu-Pb-Zn sulphides in essentially a surface environment. The decomposition of marcasite, as a result of reaction with rainwater percolating through a tip, releases sulphuric acid which then reacts with other sulphides; the resultant solutions then precipitate secondary sulphates on carbonate blocks or when permeating masses of gossan containing pre-mining secondary mineralization (Mason and Green, 1995). Although the exact mechanisms involved for each localized secondary assemblage have yet to be evaluated, there appears, from data collected at Eaglebrook and other mines (e.g. Mason and Green, 1995), to be a strong correlation between the nature of the matrix containing the post-mining minerals and the species present in the assemblage. A common problem in the investigation of such assemblages, however, is the lack of thermodynamic and other stability data for mineral species which have only been described as such within the last decade or so.

Conclusions

Eaglebrook Mine is a diverse GCR site where the primary mineralization includes occurrences of the extremely rare mineral tucekite and also of electrum; the association of gold with Co-Ni mineralization is noteworthy. The secondary mineralization was partly developed *in situ* and partly within the tips after mining had placed fresh, unstable iron sulphide debris close to carbonate and base-metal sulphide-bearing rock, and gossan with pre-existing secondary mineralization. Mechanisms for the development of the post-mining assemblage are poorly understood because stability data for some of the minerals present are lacking, the minerals only having been recently described as species. In addition, at least two crystalline phases occur which have yet to be fully described.

CEULAN MINE OPENCAST (SN 853 978)

Introduction

Situated in the north-eastern extremity of the Central Wales Orefield, Ceulan (Figure 5.63) is one of a group of workings developed on Pb-Zn-bearing veins belonging to the later (A2) phase of epigenetic mineralization in this complex and polyphase orefield (Mason, 1994, 1997). The opencast at Ceulan Mine (Figure 5.64) provides the finest surface exposure of an A2 Pb-Zn sulphide-bearing vein in the Central Wales Orefield, being a more complete section than is visible on Graig-Fawr at the **Cwmystwyth Mine** GCR site. Both important geological and textural features are clearly visible.

The opencast lies at the westernmost end of the Ceulan sett, close to the boundary with the Rhoswydol Mine. Both mines are of consider-

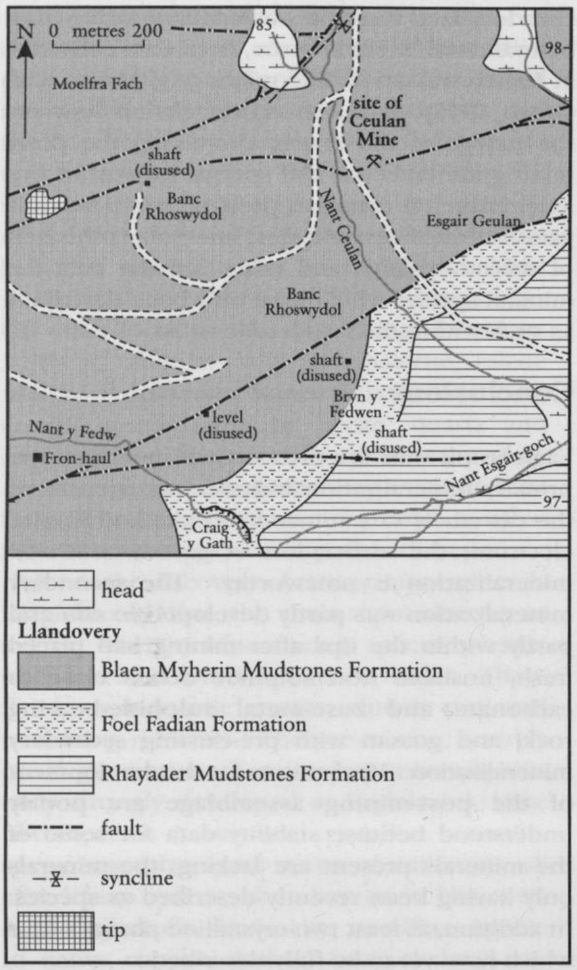


Figure 5.63 Map of the Ceulan Mine Opencast GCR site. Based on unpublished British Geological Survey 1:25 000 Sheet SN89, and Bick (1977).

able antiquity (Bick, 1977), perhaps not surprising as the veins outcrop on both flanks of the steep-sided ridge of Esgair Geulan, and would have been noticed by early prospectors passing through the district.

Ceulan was a relatively small mine by Central Wales Orefield standards. The production figures are fragmentary, being partly entered under Cardiganshire figures and for 1870 being split as North and South Ceulan. Hence the figures given by Jones (1922) are slightly lower than the true total given by Burt *et al.* (1986, 1990). These figures show intermittent production from 1857 to 1888, the total being 268.2 tons of galena concentrates yielding 814 oz of silver. The latter metal was only produced in certain years, the grade, typically for this mineral assemblage, rarely exceeding 5 oz of silver per ton of galena concentrate. The extent of pre-19th century workings, and production therefrom, is not clear.

Description

The vein mineralization at Ceulan Mine is hosted by a fault traversing mudstones and siltstones of Llandovery age. The opencut lies just above a forest road and runs up the hillside with a ENE–WSW orientation, narrowing as it is traced eastwards. The lode is exposed about a third of the way up the opencut, in an unworked pillar, where it is nearly 1 m wide. The exposure clearly reveals brecciated mudstone cemented by quartz, galena and sphalerite with an open-space, locally crustiform texture typical of the late or A2 mineralization. The amount of sulphide, in particular galena, left unworked is unusual and provides a valuable example of the A2-a (low-Ag galena, sphalerite and quartz) assemblage (Mason, 1997), which was exploited

Figure 5.64 Photograph of the Ceulan Mine Opencast GCR site. (Photo: R. Mathews.)

at many Central Wales Orefield mines. On the well-defined footwall of the vein, which dips to the SSE at 60°, strong, W-plunging (60°) quartz slickencryst development indicates an element of dextral wrench movement. As is often the case with the Central Wales Orefield veins, the hangingwall is relatively ill-defined.

Samples of the mineralization are not abundant but may be found among the debris below the forest road. They reveal traces of early (A1) mineralization, forming very weakly quartz-veined breccia, and showing that, as is the case with many Central Wales Orefield mineralized fractures, there is a history of polyphase fracturing and mineral deposition. More abundant later (A2-a) mineralization, corresponding to that exposed in the pillar, comprises thin quartz coatings on rock clasts overgrown by galena (both with rare micro-scopic chalcopyrite inclusions), followed by sphalerite and crystalline quartz. This assemblage is widespread in the mines of the north-eastern part of the Central Wales Orefield, where the early or A1 phase of mineralization tends, in general, to be poorly developed. Some of the mineralized fractures in this part of the orefield also carry a late sphalerite-pyrite-marcasite assemblage which overprints the more typical Pb-Zn mineralization. Secondary mineralization at Ceulan is developed only on a superficial basis, as demonstrated by the fresh sulphide exposed only a few metres from surface in the opencut. Traces of cerussite, malachite and hemimorphite have been noted among the spoil.

Interpretation

The Pb-Zn mineralization exposed at Ceulan Mine opencut was deposited during a phase of transtensional movement which resulted in the formation of a mineralized, S-dipping normal fault with an element of dextral wrench movement. While the indication of transcurrent movement is of significance, the dip of the fault plane is less so. This is but one of a group of sub-parallel mineralized fractures which were all active during the A2 phase of mineralization, so that remarkably similar vein assemblages are developed throughout this part of the Central Wales Orefield. The fractures generally strike ENE–WSW, but may dip either to the south or north (Jones, 1922), and the best interpretation of the Ceulan area is to view the various sub-parallel lodes as planes of movement within a larger zone of focused transtensional stress. Such features are not uncommon within the Central Wales Orefield, where zones containing numerous sub-parallel mineralized fractures are frequently separated by tracts of apparently unaffected ground.

The structure of the mineralized fracture, with its well-defined, slickencryst-marked footwall and poorly defined hangingwall, is characteristic of the Central Wales Orefield. The process of hydraulic brecciation, which was critical in the formation of the mineralized fracture exposed here, is more fully discussed elsewhere (see **Cwmystwyth Mine** GCR site report, this chapter); in the exposure at Ceulan it is possible, however, to study the features created by the process closely and *in situ*. On the hangingwall, mineral-cemented breccia grades through fractured rock into relatively undisturbed mudstone. Such features indicate that it was the hangingwall that was the focus of hydraulic brecciation. This may be explained by examining the mechanism by which hydraulic brecciation occurs (Phillips, 1972).

During the formation of a normal fault, such as that exposed at Ceulan, the maximum principal stress is effectively vertical and equates to the lithostatic pressure (P), defined by $P = p \times g \times d$, where 'p' is the average saturated bulk density of the rock, 'g' is the gravitational acceleration and 'd' is the depth. During normal faulting, the horizontal principal stresses, caused by crustal extension, are reduced, leading to the creation of shear stresses on the fault plane. In the case of the mineralized faults of the Central Wales Orefield, fracture propagation was also assisted by hydraulic fracturing caused by ascending hydrothermal fluids. If the pressure exerted by such fluids exceeds the effective stress normal to the fault plane, hydraulic fracturing will take place, extending the fault plane. In the model of Phillips (1972), these pressurized hydrothermal fluids also penetrated the pore spaces of the wall-rocks, and particularly, since they were rising, those of the hangingwall. Following each phase of fracture extension, an abrupt drop in hydrothermal fluid pressure would then cause the adjacent rock, into which the hydrothermal fluid had permeated, to burst apart, forming an angular breccia.

An alternative interpretation, considered by Mason (1994), is that hydraulic brecciation occurs when strata and their contained pore-fluids, both under the lithostatic pressure of the overlying stratigraphical pile, are suddenly subjected to a drop in pressure, such as the formation of an open, fluid-filled fracture. The result of creating such a pressure differential causes a rockburst effect in the fracture walls, driven entirely by compressed pore-fluids.

Whichever model is correct, be it hydrothermal fluids being able to permeate metamorphosed and deformed sedimentary rocks, or the original sediments still containing sufficient trapped porewater to cause explosive rupture, the brecciation effect in inclined fracture planes is much greater within the hangingwall. In the model of Phillips (1972) this was explained by the tendency for vertically ascending hydrothermal fluids to preferentially permeate the hangingwall. However, in discussion of that paper, it was commented by Knill (Phillips, 1972, pp. 355–6) that a large back-pressure in the hangingwall rocks was essential to allow for the downward collapse and consequent brecciation effects, following a rapid drop in pressure in the vein itself.

The model of Phillips (1972) also needs to explain why, in many Central Wales Orefield veins, massive mineral phases such as quartz, galena and sphalerite have undergone re-brecciation, showing development of the same textures as those developed in the brecciated sedimentary rocks. Perhaps these minerals had undergone explosive brecciation as a result of being permeated, like the sedimentary rocks in the model of Phillips (1972), by rising pressurized hydrothermal fluids. Clearly, there remains considerable scope for further research into the origin of these breccias.

Conclusions

The lode exposure at Ceulan Mine opencut clearly displays the geological features typical of the Central Wales Orefield mineralized fractures: a normal fault, with an element of dextral wrench movement, and a well-defined slickencryst-marked footwall; a central zone of angular rock breccia cemented together by sulphides and quartz; and a poorly defined hangingwall in which brecciation grades into shattering and finally into unaffected rock.

NANTIAGO MINE (SN 826 863)

Introduction

The extensive tips at Nantiago Mine (Figure 5.65) provide the finest demonstration in the Central Wales Orefield of the resemblance of certain late (A2) mineralization to that of the 'Pennine-type' orefields. Textures at Nantiago show clearly that the mineralization developed as crustiform, banded fissure-fillings deposited on the walls of open fractures. The result is that the ore worked at Nantiago consists of repeated layers of galena and sphalerite, with late cubic pyrite, all in a very coarsely crystalline calcite gangue.

The site has suffered much less damage than most Central Wales Orefield mines and is still of great interest also to the industrial archaeologist (Figure 5.66). A Pelton-wheel still remains on site, a reminder that this mine was one of the last Central Wales operations to close, operating up to and through the First World War. Indeed, a major factor in its closure was the fall in metal prices brought about by the sale of Government stocks after the Armistice (Bick, 1990), coupled as it was with the fact that Nantiago is a remote site, with consequent high costs for haulage to and from the mine. Nevertheless, the mine was eventually sunk to a depth of 70 fathoms (128 m) below adit-level. Between 1846, when mining in earnest was commenced at the site, and 1917, the mine produced a recorded output of 1709 tons of galena (from which desilvering, only in certain years, yielded 1651 oz Ag) and 1929 tons of sphalerite concentrates (Jones, 1922). In more-recent years, the property was considered as a potential source of white calcite, but was rejected because of the calcite's sulphide content (S.J.S. Hughes, pers. comm.).

Description

The vein worked at Nantiago Mine varies from a vertical to steep, S-dipping mineralized fissure. It trends virtually east–west and is hosted by dark-grey mudstones of the Bryn-glâs Formation and, at depth, by sandstones of the Drosgol Formation, both of Ashgill age. These outcrop in the core of an anticline of Caledonoid trend; hence both to the east and west of the mine the vein at surface runs into the pyritic shales of the Cwmere Formation of Lower Llandovery age. According to Jones (1922), the vein varied

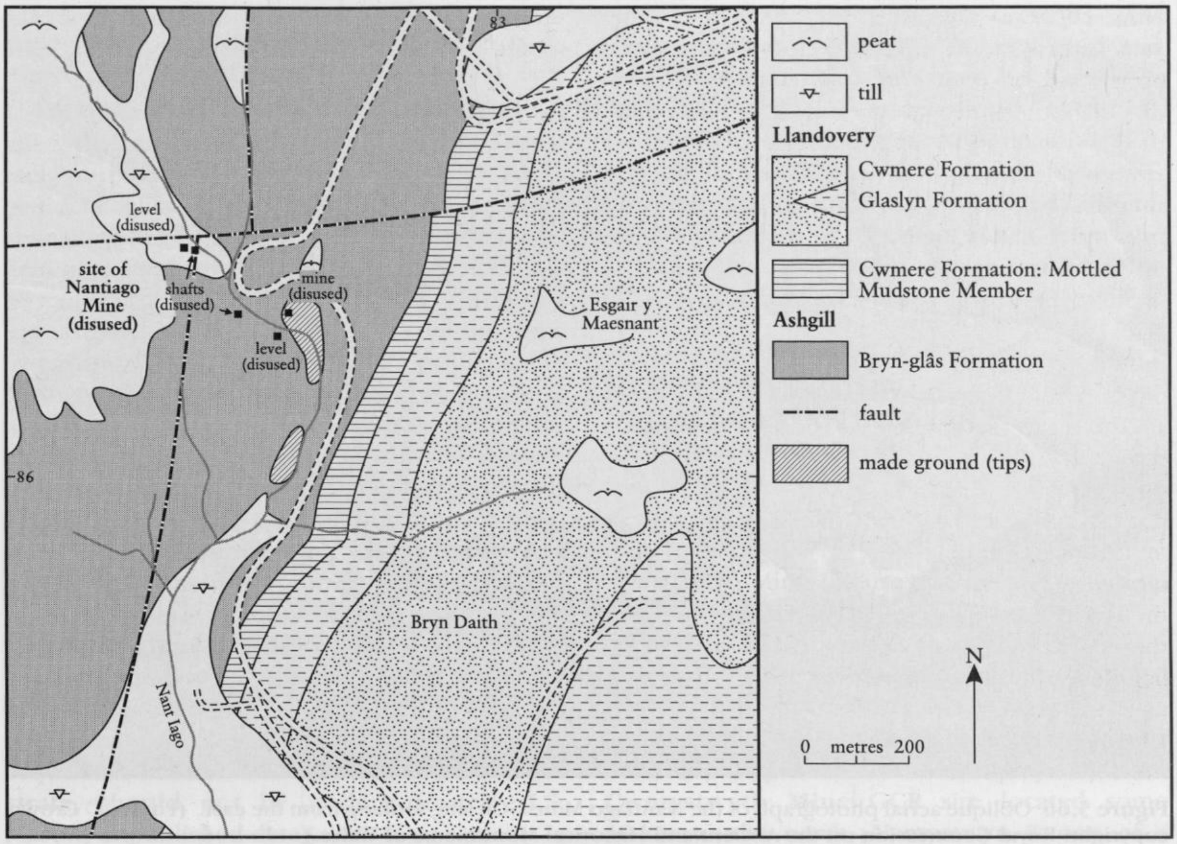


Figure 5.65 Map of the Nantiago Mine GCR site. Based on unpublished British Geological Survey 1:25 000 Sheet SN88, and Jones *et al.* (2004).

between 1–2 m in width, with a tendency to split into branches at the western end of the mine. Jones (1922) also commented upon the frequent vugs, lined with elaborately branched masses of calcite rhombs, which were encountered underground. Economic quantities of ore were said to be largely restricted to the Bryn-glâs Formation mudstones; the sandstones proved to be a poor host-rock, so that the orebody, following the favoured mudstone beds over the crest of the anticline, took the form of a broad arch (Jones, 1922).

The mineralization has been assigned to the A2-c assemblage of Mason (1994, 1997), and this is its strongest development in the Central Wales Orefield, although it is actually of widespread occurrence. The mineralization comprises abundant octahedral galena (with minute chalcopyrite inclusions) and chocolate to dark-brown sphalerite, which occur in multiple, repeated bands in a calcite matrix. Some attractive galena specimens, consisting of crusts of octahedral crystals 1–1.5 cm across, have been collected from the site in the past. Quartz is minor and early in the sequence, forming thin coatings to rock clasts. Large, unfortunately bruised and weathered calcite crystal groups on the tips show low rhombohedral crystals aggregated together into sub-parallel, often stalactitic masses up to approximately 15 cm in length. Minor, late pyrite occurs both as a dark dust included in the outer layers of calcite crystals, as well as cubic crystals up to 5 mm scattered over calcite crystal faces.

Secondary mineralization is of little significance at Nantiago Mine, being limited to traces of malachite, cerussite and hydrozincite, occurring in thin, probably post-mining, coatings on weathered sulphides.

Interpretation

Although the minerals occurring at Nantiago Mine are all common species, the site is nevertheless important in metallogenic terms as it demonstrates textural features which can be

Figure 5.66 Oblique aerial photograph of the Nantiago Mine GCR site, looking from the east. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

linked to a specific type of mineralizing event, namely the filling of an open-space fissure. While much of the Central Wales Orefield mineralization occurs as cements to breccias formed by hydraulic fracturing, some assemblages belonging to the later or A2 group frequently, and in some cases predominantly, occur as banded fissure-fills. Typically an open-space fissure-fill consists of ribs of clean, relatively (and often entirely) clast-free gangue (in this case calcite) containing sulphides and other primary minerals in repeated, often continuous layers, thus demonstrating that the vein was built up through time as repeated injections of hydrothermal fluid passed through an open fracture system.

Such vein textures are more typical of the 'Pennine-type' orefields of Britain, but in fact occur throughout the Welsh Caledonides. The Llanrwst Orefield, in northern Snowdonia, is another example, where the Parc Mine was a rich source of banded veinstuff, until the site was largely reclaimed (Bevins and Mason, 1998). Late calcite-marcasite veins are also of frequent occurrence throughout the Snowdonia copper-mining district and are widespread in the Dolgellau Gold-belt, where particularly attractive banded sphalerite-marcasite-galena-calcite ore occurs at the West Cwmheisian Mine, although at this site representative material is now much more sparse at surface than at Nantiago Mine. Similar textures are commonly also seen in the mineralization of the West Shropshire Orefield, and, to the south of the Central Wales Orefield, at the Llanfyrnach Mine, in Pembrokeshire. The fact that such crustiform-banded veins, with a simple calcite-galena-sphalerite-iron sulphides-dominated mineralogy, are a regional feature of the Welsh Caledonides in turn suggests that they may represent the products of a metallogenic process operating on a regional scale.

Because of the resemblance of the mineralization at Nantiago Mine to that of the 'Pennine-type' orefields, the mine was one of a number of sites selected for Pb-Pb isotopic studies by Swainbank *et al.* (1992). Pb-Pb isotopic ratios of galena from Nantiago Mine plot outside the main cluster of A2-a galenas, which give a Lower Carboniferous model age, but fall within a wide field populated by A2-b and other A2-c galenas, all of which are relatively radiogenic and imply deposition in Permian times (270–240 Ma).

The high ^{206}Pb component of these galenas led Swainbank *et al.* (1992) to conclude that a metamorphic fluid source from the Welsh Basin could be eliminated. Given that the isotopic characteristics of these galenas falls within the field of galenas from the 'Pennine-type' orefields of central and northern Britain, it is not unreasonable to infer that these late-stage veins in Central Wales are the products of the same, regionally extensive, mineralizing episode, albeit in older strata than those which host the typical 'Pennine-type' mineralization. However, it is not unknown for 'Pennine-type' veins to be traced through their usual Dinantian carbonate host-rocks and into underlying Lower Palaeozoic strata. This was indeed the case at some mines in the North-east Wales Orefield (see **Pool Park and South Minera Mines** and **Pennant Mine** GCR site reports, this chapter). The ability for Mississippi Valley-type (MVT) fluids to migrate, not just into Carboniferous carbonate sequences, but also into uplifted blocks of older strata, should not be underestimated (J.S. Mason, unpublished data).

Several features, therefore, combine to suggest that the later (A2-b and A2-c) vein assemblages of the Central Wales Orefield were deposited during the same broad episode of mineralization that was responsible for the development of the 'Pennine-type' orefields. In terms of fluid sources, the 'Pennine-type' orefields are believed to have been formed from evolved brines expelled from adjacent Permian to Jurassic sedimentary basins (Ixer and Vaughan, 1993). The current hypothesis for the evolution of such brines is contentious (Ixer and Vaughan, 1993), but their ability to transport metals in solution over distances of hundreds of kilometres (Garven and Freeze, 1984) is accepted widely. It was therefore advocated by Mason (1994) that the fluid source for the late veins of the Central Wales Orefield could feasibly be the Upper Palaeozoic to Mesozoic sequences of the Cardigan Bay Basin, less than 40 km to the west of Nantiago Mine.

Conclusions

In the Central Wales Orefield, the later stages of mineralization are probably related to the metallogenic episode responsible for the development of the British MVT 'Pennine-type' orefields. This is supported on geological, mineralogical and textural grounds, and is backed up further by the results of a lead isotope study. Therefore, the crustiform-banded, calcite-dominated Pb-Zn-bearing mineralization at Nantiago Mine was probably deposited from modified basinal brines expelled in Permian times from the Cardigan Bay Basin, lying approximately 40 km to the west of the area.

NANTYMWYN MINE (SN 791 443, SN 789 448, SN 782 447)

Introduction

Nantymwyn Mine (Figure 5.67) is the largest of the old base-metal mines in the southern part of the Welsh Caledonides, a key feature being the spectacular lode exposure along the crest of Pen Cerrig-mwyn (SN 791 443). Although it is apparently set apart from the main Central Wales Orefield, typified, for example, by the **Cwmystwyth Mine** GCR site located some 30 km to the north, Nantymwyn is one of a number of scattered, mainly small, mines and trials which occur throughout the southern Cambrian Mountains. Mineralization at Nantymwyn is remarkably similar to that of the Central Wales Orefield, and the site offers an excellent opportunity to compare the mineralization in this, the southern outlier of the Central Wales Orefield, with that of the main part of the orefield.

Production figures for Nantymwyn are, as with all pre-19th century mines, incomplete. However, in the periods 1775 to 1797 and 1824 to 1900, recorded sales of galena concentrates amounted to 80 000 tons (Hall, 1993). These figures alone place the mine in the same category of lead producers as the celebrated mines of Van, in Powys, and the **Snailbeach Mine** GCR site (see GCR site report, Chapter 4), in south-west Shropshire. The absolute age of the workings is unclear; peoples passing through the area, including the Romans, who actively extracted gold at the nearby **Dolaucothi Mine** GCR site, must have noticed the spectacular lode outcrop. According to local tradition, the mine was being worked during the reign of King Charles I, and it is well documented that the mine was being worked intensively by the last quarter of the

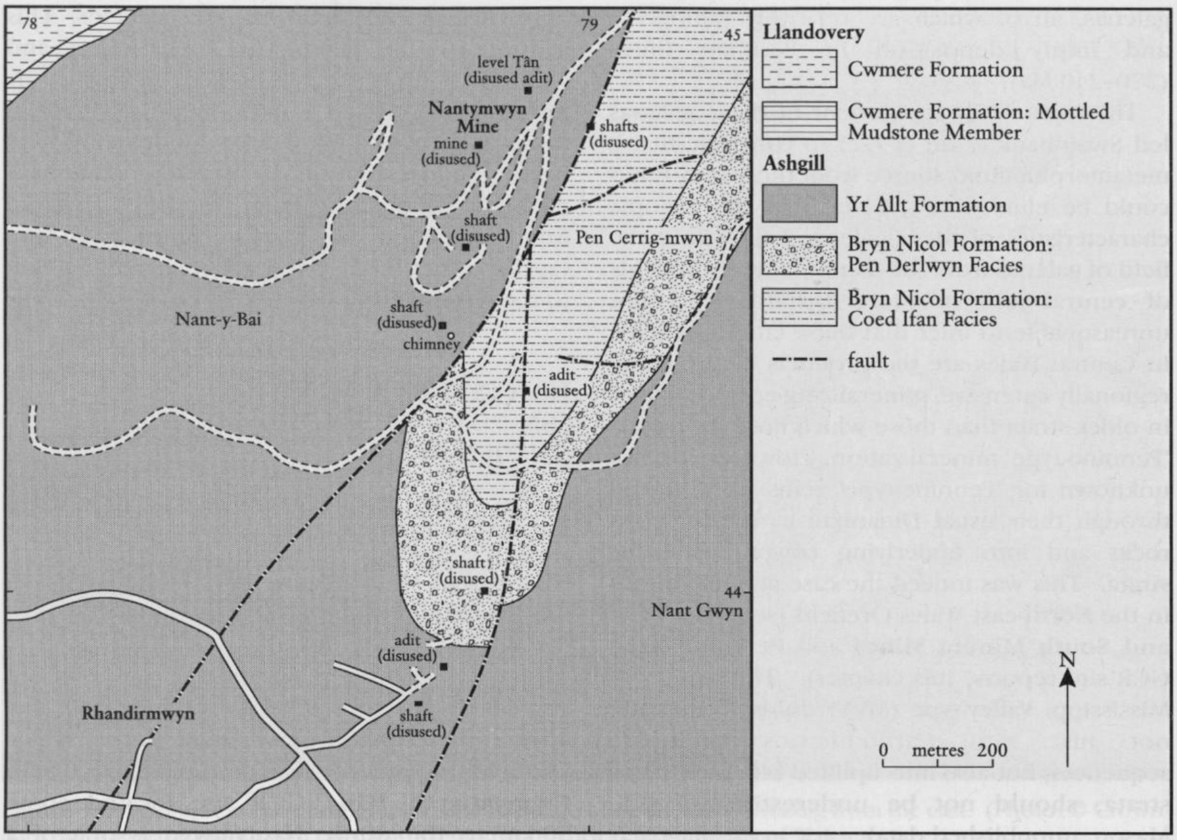


Figure 5.67 Map of the Nantymwyn Mine GCR site. After British Geological Survey 1:50 000 Sheet 195, Lampeter (2006).

18th century (Hall, 1993). Unusually, the mine was serviced by two large 'boat levels', along which the lead ore was brought out on barges for milling. The Deep Boat Level, the blocked portal of which is situated in Rhandirmwyn village, was commenced in 1785; the Upper Boat Level had been in service long before this time. The Deep Boat Level holed through to the main part of the mine in 1798, a drivage of nearly 800 m being completed.

Parts of the mine were extraordinarily rich. For example, in 1779 an orebody was being worked '6ft wide in solid galena, with another 12ft of rich ground alongside' (Hall, 1993). Well before the mid-19th century, the mine had reached its deepest level, some 30 fathoms (nearly 55 m) below the Deep Boat Level. Working continued throughout the remainder of the 19th century, but tailed off as mineral reserves diminished; in the early years of the 20th century the mine was also producing 'sandstone', a sign of difficult times. In 1925, a new phase of activity began when the Sulphide Corporation, proprietors of the famed Broken Hill mines in Australia, took on Nantymwyn in a search for zinc ore reserves. Much development followed, but results were disappointing. Test-milling was discontinued after 1930 and, despite the delineation of mineral reserves totalling 209 000 tons, the low prices of lead and zinc, coupled with the depressed state of the economy, dictated against the operation being profitable. The mine finally closed in 1932.

Description

The extensive tips at Nantymwyn (Figure 5.68) are rich in quartz-sulphide mineralization which has a multi-phase paragenesis, with elements resembling both the Central Wales Orefield early and late (A1 and A2) phases of metallogenesis (Mason, 1994, 1997). As in Central Wales, the transition from early fine-grained polymineralic breccia cements to late simple mineralogies in coarse-grained crustiform deposits is notable. The site is also of interest for the large growth-

Figure 5.68 Photograph of the Nantymwyn Mine GCR site, showing the wall-like lode exposure on Pen Cerrig-mwyn. (Photo: J.S. Mason, © National Museum of Wales.)

zoned quartz crystals developed during the later mineralization, which reach up to 15 cm in length.

The mineralization is emplaced in a N–S- to NNE–SSW-trending fracture-system, in contrast with the dominant ENE–WSW trend in the main part of the Central Wales Orefield. The fractures, which dip steeply to the west or WNW, form a broad mineralized zone 50–60 m in width, within which individual lodes were recognized. The deposit is hosted by turbiditic rocks of Ashgill age; the richest orebodies, as described above, occurred where the fractures intersected thick packages of massive, gritty sandstones, locally known as the 'Lead Mine Grits'. In the underlying mudstones and shales the degree of mineralization rapidly deteriorated. The mineralization is well exposed on Pen Cerrig-mwyn and reveals a great width of quartz veining enclosing rock clasts in places. The quartz contains numerous crystal-lined cavities.

The paragenetic sequence of the mineralization at Nantymwyn is remarkably similar to that within the main part of the Central Wales Orefield. Early sulphide mineralization is hosted by quartz-cemented breccias; the ore minerals, locally in rich masses, are finely intergrown. Galena is dominant, with accessory chalcopyrite and pyrite. A second distinctive assemblage comprises sphalerite scattered through quartz. In both cases the quartz is compact, with occasional prismatic crystals and is locally accompanied by minor, late ferroan dolomite.

Later mineralization is particularly distinctive, particularly due to the almost chalcedonic banding of the quartz in breccia cements, which is also represented by growth zoning in quartz crystals. The quartz sometimes contains inclusions of chalcopyrite, while outer zones of the crystals are often darkened by the occurrence of numerous small dendritic masses of iron sulphide. This coarsely crystalline quartz is strikingly similar in appearance and accessory mineralogy to that of the A2-d assemblage of the Central Wales Orefield, developed for example at the **Frongoch Mine** GCR site. However, the size of the crystals at Nantymwyn is exceptional. These all occur as single crystals with fractured bases, often heavily coated in goethite and it is possible that they were dislodged from their growth positions by earthquakes. Unfortunately, undamaged crystals are very rare, although zoned fragments are common.

Secondary mineralization is well developed around the lode outcrop on Pen Cerrig-mwyn and is present in small tips immediately to the west of the outcrop (SN 791 443). Pyromorphite is conspicuous as green coatings and rare small solid masses. It is arsenic-bearing, with a PO_4:AsO_4 ratio of 90:10 (G. Ryback, pers. comm.). Cerussite is also present as tabular and acicular crystal masses. Linarite and brochantite, post-mining in origin, occur all over the site, although well-formed micro-crystals are rare. Traces of a yellowish-white acicular phase, possibly mimetite, and thin localized erythrite coatings have also been observed. The primary source of the arsenic has yet to be determined.

Interpretation

The mineralized fractures at Nantymwyn, although seemingly anomalous in their NNE–SSW trend, otherwise bear such a strong paragenetic resemblance to those in the main part of the Central Wales Orefield that they are interpreted as representatives of the same, regional phase of mineralization. The structural trend at Nantymwyn is rare in the main part of the Central Wales Orefield, although examples are known, such as at the Snowbrook (Nantyreira) mine (Jones, 1922). This interpretation would date the mineralization at Nantymwyn as having been emplaced episodically between the Devonian and Permian periods. As in the Central Wales Orefield, the inferred mineralizing processes (Mason, 1994, 1997) would comprise initial, post-Caledonian relaxation, allowing the migration of fluids liberated by sediment dewatering during deformation. Later phases of mineralization would have occurred as a result of connate waters being expelled from adjacent Carboniferous to Permian sedimentary basins during extensional phases of the Variscan Orogenic Cycle.

The reason for the rarer NNE–SSW trend of mineralized fractures in the Nantymwyn area may lie in the basement geology. This area was marginal to the Welsh Basin in Lower Palaeozoic times, and extensional fracturing on a north-east–south-west trend in part controlled basin development. Re-activation of such basement fractures during subsequent episodic extensional regimes, during which times the mineralization was emplaced, may have influenced fracture trends in the overlying Lower Palaeozoic strata. Undoubtedly the rheology of the host rocks had a direct influence on the development of rich ore-shoots at Nantymwyn, the more brittle sandstones fracturing with greater ease and creating larger openings than the thinner fractures developed in the relatively plastic argillitic rocks.

Extensional fracture-hosted multi-phase vein-breccia mineralization occurs abundantly within the area traditionally defined as the Central Wales Orefield (Jones, 1922). Nantymwyn, 30 km to the south of the main orefield, is one of a number of scattered workings within the southern Cambrian Mountains where Central Wales-style mineralization was mined. The reason for the relatively low frequency of such mineral deposits in this southern area is unclear. However, within the southern Cambrian Mountains, there are substantial tracts of ground that are, in comparison to the main part of the Central Wales Orefield, heavily masked by a thick glacial-drift cover. This would have precluded successful prospecting activity during the 18th and 19th centuries. The same criteria apply to the area between Llanfyrnach and the southern Cambrian Mountains, where prospecting would have been hampered by a thick soil cover leading to prime agricultural land in an area of relatively subdued topography. Indeed, the apparent low frequency of productive mines does not necessarily imply a relative scarcity of mineral deposits, as there are recognized geochemical anomalies in southern Cardiganshire in areas with no record of metal extraction (Ball and Nutt, 1975; S.J.S. Hughes, pers. comm.).

Furthermore, within the main Central Wales Orefield, scrutiny of the distribution of productive mines reveals that these tend also to occur in clusters in certain areas with sizeable, apparently unmineralized tracts of ground in between. It can thus be argued that it is the nature of Central Wales-type ore deposits to occur in specific areas characterized by clusters of mineralized fractures within a much larger area than was defined in the memoir by Jones (1922). The definition of the precise boundaries of the Central Wales Orefield is, therefore, difficult. If based on style and paragenesis of mineralization alone, it would readily comprise the vast tract of Upper Ordovician and Silurian strata in the area bounded by Tywyn, Machynlleth and Newtown in the north and by Fishguard, Carmarthen, Llandeilo and Llandrinidod Wells in the south.

The difficulty in defining the precise boundaries of the Central Wales Orefield serves to emphasize the regional nature of the Central Wales-type mineralization. This is particularly the case with the later (A2) assemblages, which are characterized by their simple mineralogy, coarse grain-size, and frequently crustiform-banded nature. In fact, quartz + calcite + Pb/Zn/Cu/Fe/Ba vein mineralization of a broadly similar nature to the Central Wales A2 assemblages occurs throughout the Lower Palaeozoic strata of Wales and reflects mineralizing processes which affected large areas at certain times.

Conclusions

The major Pb-Zn mineralization at Nantymwyn bears critical resemblance to that of the main part of the Central Wales Orefield, such that, together with other scattered deposits throughout the southern Cambrian Mountains, it is interpreted as a peripheral representative of the Central Wales Orefield mineralization. This conclusion strongly emphasizes the regional nature of post-Caledonian Pb-Zn-dominated vein mineralization occurring along extensional fracture systems cutting the Lower Palaeozoic strata of Wales.

COPPER-LEAD-ARSENIC-BARIUM VEIN MINERALIZATION IN THE WELSH BORDERLAND

DOLYHIR QUARRY (SO 245 579)

Introduction

Quarrying at Dolyhir (Figure 5.69) dates back over many years, the chief products being road aggregates, produced mainly from Precambrian rocks, and agricultural lime, produced from limestones of Wenlock age. Mineralization in this area has been documented in the past. Murchison (1839) noted occurrences of copper ores at Stanner and Old Radnor, while Lewis (1967) referred to small-scale mining for lead at Hanter Hill, to the south-east of Dolyhir. According to Hall (1993), no sign can now be seen of old workings in the district. Malachite specimens have long been known from the nearby Old Radnor Quarry (Bevins and Sharpe, 1982; Bevins, 1994), while Parnell and Eakin (1989) reported minor tennantite-barite-chalcopyrite mineralization in the Old Radnor district.

The significance of the mineralization described here was first noted in the early to mid-1990s (D.I. Green, pers. comm.) and was sampled intensively and studied in the period 1996 to 1997 (D.I. Green, unpublished data; Bevins and Mason, 1997). Since that time, quarrying has removed the most sulphide-rich exposures. However, it is likely that further mineralized outcrops will be exposed during future quarrying activities.

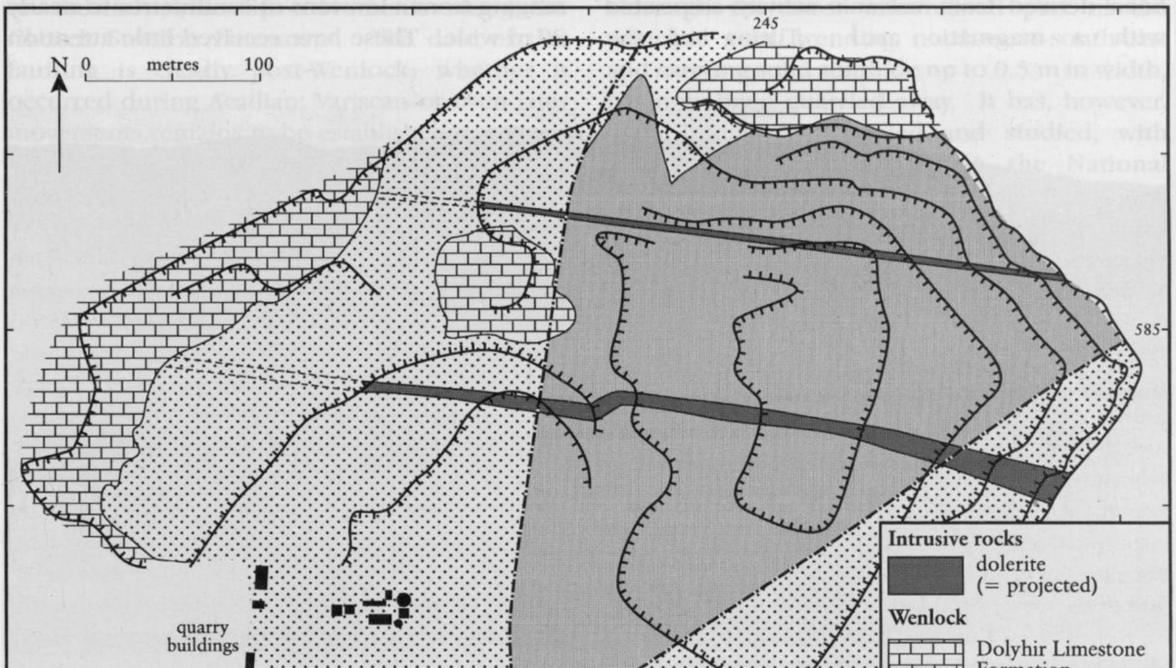


Figure 5.69 Map of the Dolyhir Quarry GCR site. Based on Woodcock (1988), and unpublished mapping by T. Cotterell.

Description

At Dolyhir Quarry, clastic and volcaniclastic rocks of Neoproterozoic age, belonging to the Longmyndian Supergroup (Pauley, 1990), are unconformably overlain by algal-reef limestones of Wenlock age (Figure 5.70). The Neoproterozoic rocks constitute part of the Old Radnor Inlier, and outcrop within the major lineament of the Church Stretton Fault System. The inlier is approximately 3 × 1 km in extent and is aligned, as is the fault system, in a north-east–south-west direction.

Rocks belonging to the Longmyndian Supergroup exposed in Dolyhir Quarry comprise the Yat Wood Formation and the Strinds Formation. The Yat Wood Formation comprises at least 90 m of greenish-grey to grey laminated siltstones and mudstones with interbedded fine-grained sandstones. The Strinds Formation, at least 600 m thick, comprises sandstones and occasional conglomerates. Both formations are predominantly volcaniclastic (Pauley, 1990) and are interpreted as having been derived from volcanic activity associated with a magmatic arc. Tilting of the Neoproterozoic rocks, largely to the north-west, and the occurrence of metamorphic segregation quartz veins, themselves heavily fractured, within the sequence, represents pre-Silurian deformation and metamorphism.

Quartz pebbles, probably derived from the metamorphic veins, accompany numerous clasts of Longmyndian rocks within the basal conglomerate developed at the Precambrian–Wenlock unconformity. The overlying Dolyhir Limestone Formation was a localized development which formed on an elevated tract of the Silurian seabed (see Woodcock, 1993). The Dolyhir Limestone Formation is an algal-reef deposit with an abundant calcareous algal, coral and shelly fauna. The reef limestones pass upwards into brown and grey nodular shales; the top of the limestone is highly irregular, with shale-filled hollows in between dome-like reef structures. The nodules in the shales are commonly septarian, containing cracks lined with quartz, calcite and, rarely, barite.

The Precambrian basement is cut by a number of igneous dykes, post-dating the folding, and ranging from a few tens of centimetres to nearly 20 m wide. These have received little attention

Figure 5.70 Photograph of the Dolyhir Quarry GCR site. (Photo: T. Cotterell.)

from previous authors, although one of them is likely to be the 'trap' referred to by Murchison (1839) as a 'dyke about 16 ft in width'. The main dykes have been observed cutting through both the Yat Wood and Strinds formations in a roughly east–west direction, and are doleritic in composition but with pervasive and locally intense late magmatic hydrothermal alteration (epidotization and chloritization). The largest dyke, which is 15–20 m wide, is the freshest and has been traced for over 400 m across the quarry. The thinner dykes are more altered, so much so that most of the original constituents have been replaced. The pre-Wenlock erosion surface affects dykes and sediments alike: the absolute age of the dykes is, however, unknown.

The pattern of fracturing exposed in the quarry is complex. Both Longmyndian and Wenlock strata are cut by faults which are predominantly strike-slip in nature, and trend north–south to NNE–SSW and north-west–south-east to NNW–SSE. The whole structure of the Old Radnor Inlier has been described as a strike-slip duplex (Pauley, 1990). This has been attributed to sinistral strike-slip movements along the Church Stretton Lineament. The date of this faulting is clearly post-Wenlock; whether it occurred during Acadian, Variscan or even later movements remains to be established.

A number of the strike-slip fractures are mineralized with calcite and traces of chalcopyrite. However, a few fractures show a much more complex history of mineralization. The Longmyndian strata, exposed in the lower, northern parts of the quarry, are cut by thin (< 15 m) veins locally carrying white to yellow (rarely blue) crystalline barite, barytocalcite, witherite and chalcopyrite. Also present are rare proustite and luzonite (T.F. Cotterell, pers. comm.). Recently, Green *et al*. (2005c) have reported the occurrence of the rare carbonate mineral ewaldite from Dolyhir Quarry, forming yellow-brown hexagonal pyramidal crystals with pinacoid terminations, associated with core-bit twins of harmotome. This represents the first British occurrence of ewaldite, and only the fourth worldwide. Recently the occurrence of paralstonite, associated with alstonite and barytocalcite has been determined, forming chalky, finely crystalline, white coatings on harmotome in fractures in Longmyndian strata in the northern face on the upper level of the quarry (Cotterell and Dean, 2007). Inclusions of tennantite and galena occur within massive barite, whilst nodular luzonite with covellite and chalcocite form within massive calcite with coarse, crystalline barite overgrowths. Rare proustite and enargite have also been recorded (T.F. Cotterell, pers. comm.).

In the northern and eastern parts of the quarry, exposures of realgar mineralization have been uncovered at times: these consist of thin films of scarlet realgar occupying narrow fractures in dark-grey Yat Wood Formation mudstone, with very occasional millimetre-sized euhedral crystals occurring in rare wider veinlets, the crystals overgrowing euhedral chalcopyrite (T.F. Cotterell, pers. comm.). Finally, in an area in the upper, south-western part of the quarry, now worked away, veins in grits belonging to the Strinds Formation carried chalcopyrite, accompanied by quartz and hydrocarbon and altered to massive chalcocite and bornite, these both coated in places with fibrous malachite and well-crystallized azurite.

Mineralization is also strongly developed in the limestones of Wenlock age which are exposed in the western part of the quarry, although the most mineralized part of the principal vein, trending north-west–south-east and carrying solid sulphide up to 0.5 m in width, has now been quarried away. It has, however, been intensively sampled and studied, with reference material lodged in the National Museum of Wales and Manchester Museum. This vein was thickest at the top of the limestone; in the overlying shales it pinched out dramatically. The vein assemblage consists of tennantite, intergrown with galena, chalcopyrite and an undetermined member of the enargite group, associated with bladed, white barite plus scalenohedral calcite. Primary greenockite occurs as bright-yellow cleavage sections within the other intergrown sulphides and is locally altered to the rare cadmium carbonate otavite (D.I. Green, pers. comm.). The generally fine-grained sulphide intergrowths also contain pyrite and sphalerite, the latter species being very rare (R.A. Ixer, pers. comm.).

Secondary alteration of the complex sulphide assemblage described above has resulted in the formation of a diverse, arsenate-sulphate-carbonate-dominated suite of supergene minerals which includes some minerals as yet to be characterized. The assemblage is dominated by malachite and azurite, with rarer tyrolite, which all form extensive crystalline coatings on the limestone vein walls. Associated with these minerals, cuprite, olivenite, dundasite and chrysocolla have been recorded (D.I. Green, pers. comm.). The massive sulphide contains cavities lined with oxidation products, including well-crystallized anglesite, azurite, cerussite, mimetite and beudantite, associated with a number of as yet undetermined species (D.I. Green, pers. comm.). Near the top of the vein exposure, and close to the overburden, heavily oxidized sulphidic material, collected in the early to mid-1990s, has been shown to contain a suite of micro-crystalline minerals including lanarkite, elyite, linarite, caledonite, beudantite and leadhillite (D.I. Green, pers. comm.). Wulfenite has also been recorded (D.I. Green, pers. comm.) but is extremely rare.

Further supergene mineralization occurs on minor joint-planes within the overlying shales, and comprises fibrous malachite and azurite, which often replaces fossil debris. Within this setting, azurite also occurs as daisy-like, radiating aggregates on joints, and as relatively massive developments, associated with gossanous limonite.

Interpretation

It is clear that the vein mineralization at Dolyhir Quarry, with the exception of metamorphic quartz in the Longmyndian rocks, is closely related to tectonic activity within the north-west–south-east part of the strike-slip duplex described above. The mineralization is only locally intense, but the apparent confinement of the richest sulphide-barite body to the upper part of the limestone sequence suggests that the ascending hydrothermal fluids were ponded at that point due to the presence of the overlying, relatively impermeable shales. The shales would not only act as a cap due to their impermeability but their relatively plastic nature, in comparison to the underlying brittle limestone, would also inhibit the formation of large open fractures during faulting.

In other mineralized areas of the quarry, the mineralization is weak but persistent. This also supports the contention that fluids, passing through the Old Radnor Inlier, only deposited significant amounts of ore minerals where they were ponded in open fractures. It also implies that further Pb-Cu-As-dominated sulphide bodies might be expected in fractures near the top of the Dolyhir Limestone elsewhere in the inlier.

The dominant sulphide minerals within the Dolyhir Quarry assemblage are tennantite, galena and chalcopyrite. While none of these are rare species worldwide, the paucity of sphalerite is an unusual feature, particularly with regard to Wales and the Welsh Borderland where, both in the Central Wales Orefield (see GCR site reports, this chapter), and south-west Shropshire (see **Snailbeach Mine** GCR site report, Chapter 4), sphalerite accompanies galena in abundance. However, in both of the latter areas, arsenic is rare or absent from epigenetic vein deposits. The lack of sphalerite at Dolyhir Quarry may explain why, very unusually, primary greenockite occurs as a component of the sulphide assemblage. In most Pb-Zn ore deposits, cadmium is present as a significant minor element in sphalerite.

Nickel is present at low (100–150 ppm) levels, as is silver (75–125 ppm) and mercury (up to 12 ppm), whilst bismuth was not detected. Most of the zinc present in the Dolyhir Quarry mineralization must occur in another sulphide phase, the likely candidate being tennantite, a mineral known for its tendency to have a variable composition incorporating a number of metals.

The level of 0.95 wt% Zn in a sample in which sphalerite had not been detected implies that most of the zinc present in the Dolyhir Quarry mineralization must occur in another sulphide phase, which in this case is tennantite.

The primary mineralization at Dolyhir Quarry is highly anomalous in regional terms, and it is difficult to identify any comparable deposit in Great Britain. Perhaps one of the most similar deposits is at the **Clevedon Shore** GCR site, on the southern side of the Bristol Channel, 15 km to the north-west of the Mendip Orefield (Ixer *et al.*, 1993). Here, tennantite- and enargite-group minerals accompany the typical MVT assemblage of the Mendip Orefield, dominated by galena, sphalerite, barite and calcite. Furthermore, cadmium levels in sphalerite are markedly elevated, reaching 8.46 wt% in some samples.

Despite the unusual mineralogy, however, the geological setting of the mineralization at Dolyhir Quarry has some characteristics with Mississippi Valley-type affinities, namely that the mineralization was deposited from fluids which rose through an uplifted block of Precambrian basement capped by Palaeozoic reef carbonate sedimentary rocks, and that weak mineralization in the Precambrian strata contrasts with locally important sulphide deposits at the top of the limestone sequence, where the overlying shales acted as a barrier to the hydrothermal fluids and effectively capped the mineral deposit. The nature and source of the mineralizing fluids currently remains undetermined; the Mesozoic Severn Basin, with a thick sedimentary fill, including Triassic evaporites, has been suggested as a source area (D.I. Green, pers. comm.).

Supergene alteration at Dolyhir Quarry is widespread and occurs in several modes, which are comparable to other well-documented occurrences of secondary mineralization. Alteration of chalcopyrite, occurring in veins in Longmyndian rocks, to massive bornite and chalcocite overgrown by malachite and azurite, is remarkably similar to the pattern of mineralization observed in the Longmyndian succession in south-west Shropshire, for example at the Huglith (see **Huglith Mine** GCR site report, Chapter 4) and Westcott mines (Smith, 1922). In contrast, however, the supergene alteration of the mineralization occurring at the top of the Dolyhir Limestone Formation is far more complex. Near-surface alteration has resulted in the development of a suite of micro-crystalline minerals similar to the post-mining suite developed at many Central Wales Orefield sites, such as at the **Frongoch Mine** GCR site (Green *et al.*, 1996). At greater depths, patchy but locally intense alteration has produced azurite accompanied by an arsenate-sulphate assemblage, which is in some respects similar to that present at certain sites in South-west England, such as the **Penberthy Croft** GCR site (Camm and Merry, 1991). However, in view of the predominance of tyrolite at Dolyhir Quarry, a more reasonable comparison might be made with the localized underground tyrolite-dominated supergene assemblage at the Gwaithyrafon Mine in the Central Wales Orefield (Mason and Rust, 1995).

The abundance of azurite at Dolyhir Quarry is significant, since in both the Central Wales Orefield (see this chapter) and the Pb-Zn zone of south-west Shropshire (see Chapter 4), wherever chalcopyrite occurs in association with galena it is the secondary basic sulphate, linarite, which tends to form. At Dolyhir Quarry, however, the calcareous host lithologies would presumably have created a relatively alkaline geochemical environment in which secondary copper carbonates would be relatively stable. At Dolyhir Quarry, azurite is more abundant than malachite, which it overgrows. Stability data for malachite and azurite (Vink, 1986) show that malachite is stable at higher pH levels than azurite, and tends to form when acidic solutions, produced by oxidizing sulphides, are buffered by carbonate lithologies to well above pH 7. Discussing the restricted occurrence of azurite relative to malachite at the **Great Orme Copper Mines** GCR site, Ixer and Davies (1996), using the results of Vink (1986), suggested that azurite was the main copper secondary mineral to develop where there was insufficient carbonate available to create this buffering effect. The paragenetic sequence of minor malachite followed by major azurite at Dolyhir Quarry appears to reflect such a situation.

Conclusions

Mineralization intermittently exposed in Dolyhir Quarry is unique in Wales; the primary mineralization, of probable Mississippi Valley-type affinities, appears to have no equivalent elsewhere in Great Britain, while the secondary mineralization includes a number of minerals which are either of extreme rarity or, in a few cases, remain to be described as new mineral species. The research potential, both on-site and with the extensive sample suites collected recently, is considerable.

MISSISSIPPI VALLEY-TYPE LEAD-ZINC-FLUORITE AND COPPER-DOLOMITE ASSOCIATIONS IN NORTH-EAST WALES

The North-east Wales Mississippi Valley-type (MVT) Orefield is one of five major 'Pennine-type' orefields in Great Britain in which epigenetic Pb-Zn-Ba-F mineralization occurs within Lower and Middle Carboniferous carbonate-dominated sedimentary sequences. The four other orefields, described in chapters 3, 4 and 6 of this volume, comprise the Alston and the Askrigg blocks of the Northern Pennines, the Peak District, and the Mendip Orefield, the latter extending across the Bristol Channel into . All of these latter orefields have been far more intensively studied than the North-east Wales Orefield (Ixer and Vaughan, 1993), and in some cases well-defined patterns of mineral zonation have been demonstrated.

Mineralization in the North-east Wales Orefield comprises four principal types of deposit. Firstly, there are localized occurrences of Pb-Zn-Ba vein mineralization within the Lower Palaeozoic sedimentary rocks (see **Pennant Mine** GCR site report, this chapter). Secondly, along the margins of the Permo–Triassic sequences of the Vale of Clwyd occur a number of oxide-facies iron deposits, comprising fault zones impregnated with mainly earthy hematite, accompanied in places by earthy, black Co-Ni oxides (Bevins and Mason, 1999). Cobalt and nickel, as well as iron, were formerly mined from such deposits in the Prestatyn area (Burt *et al.*, 1992), while at the Great Orme, copper-rich black oxide deposits occurred. Thirdly, there is the major epigenetic fracture-hosted MVT Pb-Zn mineralization of the Halkyn and Minera blocks, represented by the **Halkyn Mountain** and the **Pool Park and South Minera Mines** GCR sites. To the west of this area, the **Great Orme Copper Mines** GCR site, hosted again by a carbonate-dominated Lower Carboniferous sequence, is the first example of the copper-dolomite class of mineral deposit to be recognized in Great Britain (Ixer and Davies, 1996).

In comparison to the other 'Pennine-type' orefields of Great Britain, the North-east Wales Orefield is geologically simple. A sandstone–shale turbidite succession of Silurian age, folded during Acadian deformation, crops out to the west of the Clwydian Range, and dips eastwards beneath a Carboniferous cover. The unconformity at the base of the Carboniferous succession is marked locally by a basal conglomerate which passes rapidly up into a shallow-water sequence of impure, bituminous to arenitic limestones with minor horizons of chert, shale and rare thin coals (Smith, 1921). Above this succession, and extensively quarried, lie the massive Loggerheads Limestone Formation (previously the 'Middle White Limestone') and the overlying Cefn Mawr Limestone Formation (previously the 'Upper Grey Limestone') of Asbian to Brigantian age. This facies change indicates a palaeo-environmental transition to clear, offshore waters in which coral reefs developed and an abundant benthic fauna flourished, dominated by crinoids and brachiopods. In the Halkyn Mountain area, the Cefn Mawr Limestone Formation is represented in its upper parts by a banded chert-dominated sequence.

In the upper part of the Dinantian succession, a transition to shallow-water, probably estuarine, conditions is marked by an increasing sandy component to the limestones. In the overlying Cefn-y-Fedw Sandstone Formation, of Namurian age, there is again a marked facies variation, while in the southern part of the orefield the formation consists of coarse sandstones. In the Halkyn Mountain area bedded cherts are a major component. The Cefn-y-Fedw Sandstone Formation is overlain by Westphalian coal-bearing strata, worked for coal in places around the periphery of the orefield and marking the final transition from estuarine to coastal swamp conditions and implying a long history of gradual uplift of the landscape. Relatively major uplift then occurred in post-Westphalian times, which was probably related to the Variscan Orogeny, although the area lies well to the north of the Variscan Front. The entire Carboniferous sequence was tilted eastwards, so that presently it dips beneath the Permian and Triassic sequences of the Cheshire Basin.

The epigenetic Pb-Zn mineralization, emplaced chiefly along N–S- and E–W-striking Variscan tensional dip-faults, is mainly developed within a > 750 m-thick succession between the Loggerheads Limestone Formation and the upper part of the Cefn-y-Fedw Sandstone Formation, although extensions into the overlying Coal Measures have been reported (Smith, 1921). The E–W-trending fractures are the most richly mineralized, while those running north–south tend to carry only calcite and rarely show any appreciable sulphide content. In addition to steeply dipping veins, the mineralization manifests itself as metasomatic replacement flats and pipes, and also as fillings to pre-existing palaeokarstic voids. The distribution of the larger mineral deposits is controlled strongly by lithological variations in the host rock. Particularly intense mineralization tends to occur in thinly bedded limestone sequences overlain by shale bands; clearly the shales presented a barrier to brittle fracture propagation, acting as cap-rocks, ponding hydrothermal fluids which then migrated laterally along bedding planes of the underlying limestones to form 'flats'. In textural terms, the mineralization tends to be of a coarse (i.e. centimetre, not millimetre) crystal size, and exhibits features indicative of open fracture filling, such as crustiform banding.

In comparison to the other 'Pennine-type' orefields of Great Britain, the mineralogy of the North-east Wales Orefield is relatively simple. It is dominated by calcite, galena and sphalerite, with quartz becoming an important gangue mineral in the south, around Minera. Fluorite is present at a number of localities in the orefield's central and northern sectors, although rarely in large quantities, in contrast to the Pennine orefields where it has been mined in large tonnages; the same applies to barite, which at many localities (with the exception of the **Pennant Mine** GCR site) is little more than a trace mineral. Minor sulphides comprise chalcopyrite, pyrite, marcasite and enargite, while uraninite-bearing bituminous hydrocarbons are present at several sites.

GCR sites illustrating the character of the North-east Wales Orefield Mississippi Valley-type deposits (Figure 5.71) show contrasting mineral assemblages; the **Halkyn Mountain** GCR site, in which quartz is rare, contrasts with the quartz-rich mineralization of the Minera Block, in the southern part of the orefield, represented by the

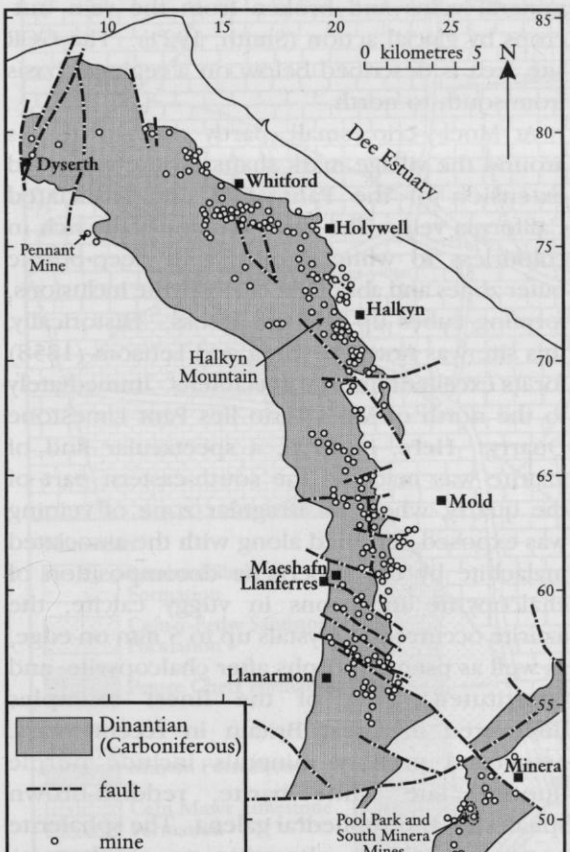


Figure 5.71 Map showing the distribution of old lead mines in the North-east Wales Orefield, showing the locations of the **Halkyn Mountain**, **Pool Park and South Minera Mines**, and **Pennant Mine** GCR sites. After Lewis (1976).

Pool Park and South Minera Mines GCR site. In addition to the primary mineralization, in the **Halkyn Mountain** GCR site area, supergene alteration has resulted in the formation of cerussite, pyromorphite, smithsonite, cinnabar, malachite, chrysocolla and azurite. Additionally, some of the finest known specimens of azurite from Wales have been discovered very recently at the **Halkyn Mountain** GCR site (Bevins and Mason, 1999). Finally, a possible extension of the orefield, at the **Pennant Mine** GCR site, shows the additional presence of barium mineralization.

HALKYN MOUNTAIN (SJ 195 705)

Introduction

The Halkyn Block area includes many old, and often grassed-over, mines and trials, as well as several disused and two working limestone quarries in which mineralization is intermittently exposed. In terms of industrial archaeology, the area is of great importance as an ancient mining landscape, with mining dating back to Roman and possibly older times (Williams, 1995). The detailed history of mining is, prior to the 17th century, poorly documented, although scattered references imply that the veins of the area may have yielded lead, with associated silver, virtually continuously from Roman times to the late 20th century.

By the mid-17th century, the Grosvenor family effectively controlled mining in the area, although the political upheavals associated with the Civil War brought disruption to mining operations from time to time. However, activity increased throughout the 18th century, with a series of major discoveries, including, in 1770, the opening up of the Pant-y-Pwll-dŵr vein, which, over the succeeding 30 years, yielded in excess of £1 million worth of ore (Smith, 1921). Such discoveries served to promote the area as a mining centre, with the consequent expansion of local towns and villages such as Holywell and Pentre Halkyn.

By 1850, problems were being encountered at Halkyn due to the difficulty of keeping the workings water-free, and output consequently declined. However, this trend was reversed in 1875, by which time the Halkyn deep drainage tunnel, commenced in 1818, had been driven under the area, draining several mines; the drainage system was thereafter extended by the Halkyn District Mines Drainage Company, who, having secured the drainage of a number of significant workings, went on to charge a levy on ores raised from them. At the same time, the demand for sphalerite was increasing and, as it became more abundant at depth, production increased accordingly.

A much more ambitious drainage scheme was commenced in 1897, when the Milwr (or Sealevel) Tunnel was started at Bagillt, on the Dee Estuary. While this was being driven southwards towards the mines, the onset of the First World War resulted in an increase in the demand for both lead and zinc ores, to the extent that a Government-funded pumping scheme was implemented (Smith, 1921). The Milwr Tunnel was eventually extended as far south as Loggerheads, just to the west of Mold and 16 km from the portal, although there had been plans to drive it even farther to the south, in order to drain rich ore deposits in the Llanarmon-yn-Ial district.

The many miles of drivages from this tunnel eventually drained as many as 50 separate veins (Williams, 1995), and guaranteed continued, water-free production on a large scale through to the late 1950s, and smaller-scale working thereafter, although nothing has been undertaken in recent years. During this period, limestone, as well as lead and zinc ores, was worked underground.

The total production from the Halkyn mines is impossible to estimate, as they were clearly highly productive for centuries prior to the advent of accurately compiled mineral statistics. Despite this, it is not unreasonable to suggest that the Halkyn Mountain district has yielded in excess of 1 million tons of galena since Roman times. Some idea of the productivity of these mines may be gleaned from the figures for Halkyn Mine which, between only 1883 and 1913, produced a total of 73 328 tons of galena concentrates, yielding 459 019 oz Ag, and 18 529 tons of sphalerite concentrates (Burt *et al.*, 1992).

Description

On Halkyn Mountain, Carboniferous-hosted MVT mineralization is developed along a conjugate set of east–west and north–south fault-fractures (Figure 5.72). The mineralization is developed chiefly in a sequence of thin limestones and intercalated shales of Dinantian age, passing up into banded cherts of Namurian age, the whole sequence overlying the economically important Loggerheads Limestone Formation. Features typical of this type of open fissure-fill mineralization include joint veins, flats (particularly developed below impermeable shale caps), metasomatic replacement veins, and infilled palaeokarstic features.

Lines of shafts and bell-pits mark the course of numerous mineralized faults, while in some areas the ground is literally pockmarked with bell-pits (Figure 5.73). The latter groups of workings often appear to have no structural alignment and are reminiscent of bomb-craters, the result of diggings for the so-called 'Gravel-Ore', a form of lead ore which was locally important in the northern part of the orefield. This consisted of blocks of superficially oxidized galena, occurring in trains in the vicinity of mineral veins and broken from the vein outcrops by glacial action (Smith, 1921). The GCR site area is described below on a regional basis from south to north.

At Moel-y-crio, small, partly overgrown tips around the village mark shafts on the westward extension of the Pant-y-Gof and associated California vein. The veins are unusually rich in colourless to white fluorite with deep-purple outer zones and abundant chalcopyrite inclusions, forming cubes up to 5 cm across. Historically, this site was noted by Greg and Lettsom (1858) for its excellent fluorite specimens. Immediately to the north of Moel-y-crio lies Pant Limestone Quarry. Here, in 1998, a spectacular find of azurite was made in the south-eastern part of the quarry, where an irregular zone of veining was exposed. Formed along with the associated malachite by the supergene decomposition of chalcopyrite inclusions in vuggy calcite, the azurite occurred as crystals up to 5 mm on edge, as well as pseudomorphs after chalcopyrite, and constituted some of the finest examples discovered in Great Britain in recent years. Associated primary minerals include purple fluorite, late white barite, reddish-brown sphalerite, and subhedral galena. The sphalerite commonly shows alteration to smithsonite ('calamine'), and traces of cinnabar have been identified recently (D.I. Green, pers. comm.). The primary assemblage also includes bituminous vein hydrocarbon, forming black lustrous masses in calcite up to several centimetres

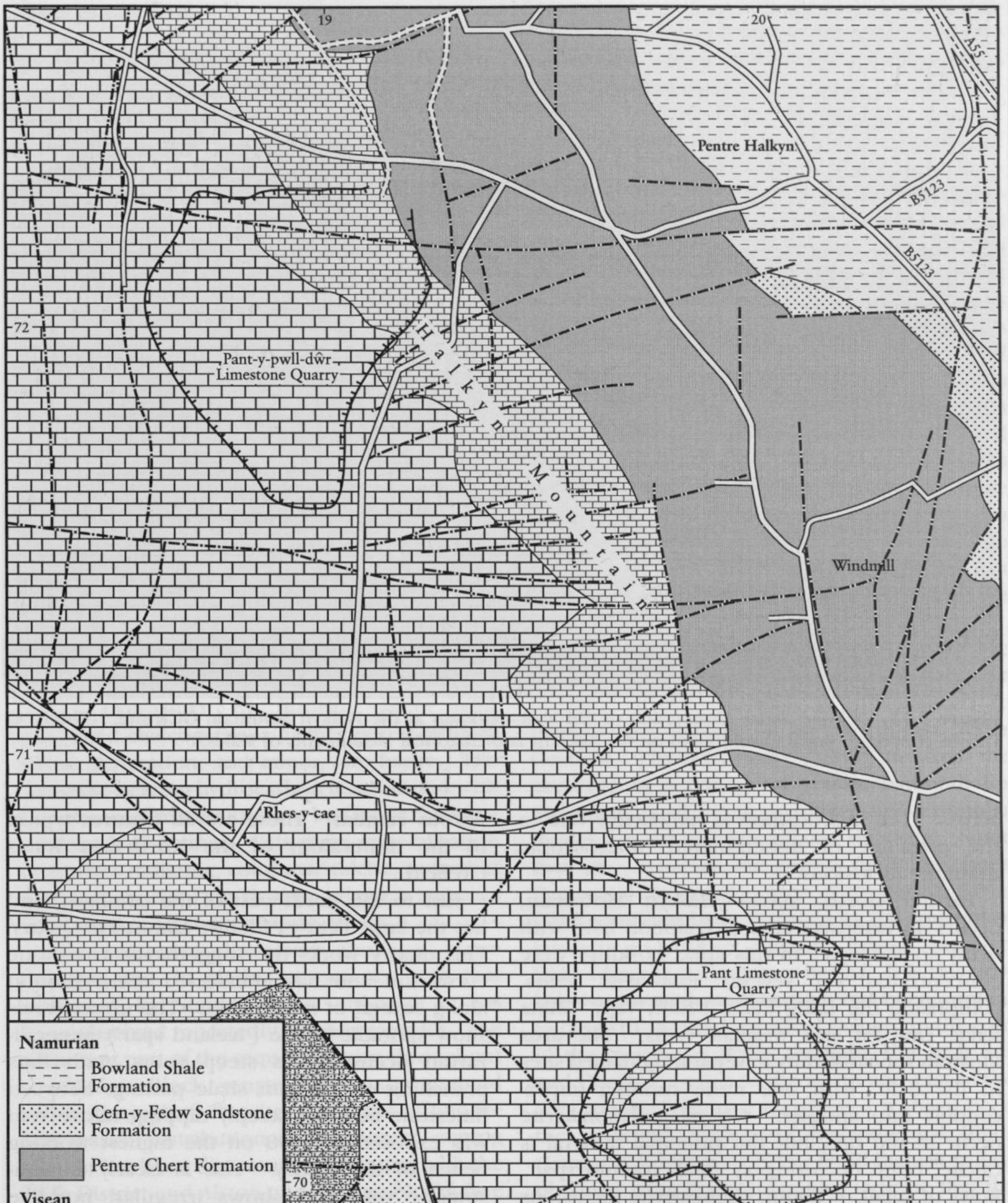


Figure 5.72 Map of the Halkyn Mountain GCR site. After British Geological Survey 1:50 000 Sheet 108, Flint (1999).

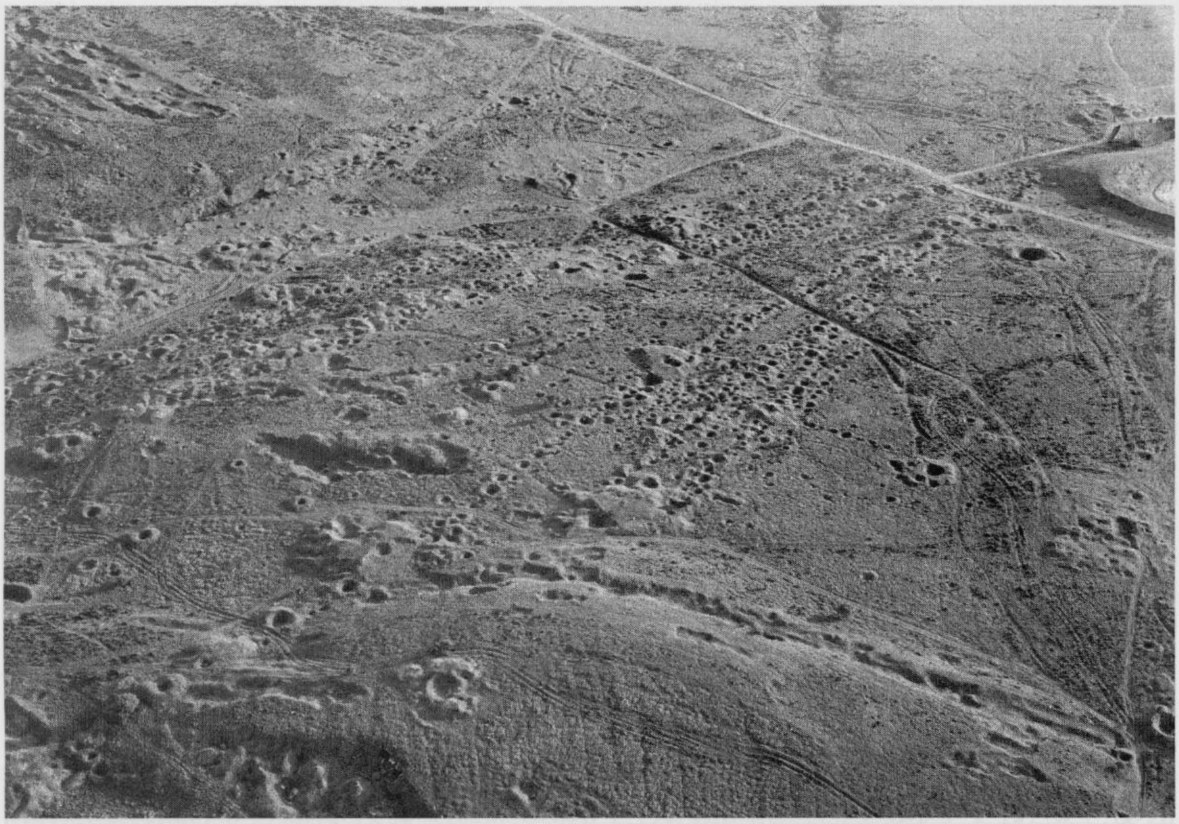


Figure 5.73 Oblique aerial photograph of old lead workings at the Halkyn Mountain GCR site. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

across. The hydrocarbon is radioactive due to the presence of disseminated, microscopic uraninite inclusions.

Farther north, across Halkyn Mountain, occurs an extensive area of common land with many spoil-heaps. In this area, workings were concentrated on several east–west veins, comprising the Long Rake, Union Vein, China Rake, Dog Pit and Wagstaff veins. The area illustrates the difficulty in separating named sites in the field, with one mine running imperceptibly into another. Galena and sphalerite occur in the tips, but the principal mineral is calcite, often occurring as clear 'Iceland spar'. Rows of small, < 2 mm, chalcopyrite inclusions occur within the calcite and are often oxidized to malachite, with minor chrysocolla. Secondary lead-zinc minerals occur in modest quantities; cerussite and smithsonite are the chief species, but pyromorphite locally occurred in workable quantities (Traill, 1821). Some specimens show two generations of calcite; in addition to the 'Iceland spar' variety, a coarse-grained white generation occurs brecciated in a mottled, locally fibrous cement. These are all features typical of the mineralogy of the North-east Wales Orefield.

Just to the north-west of the common land lies the large Pant-y-Pwll-dŵr Limestone Quarry. This quarry works the Loggerheads Limestone Formation and has intersected mineralization along several of its benches. The upper levels show sporadic calcite ('Iceland spar') mineralization occurring as steep veins, with flats branching off beneath shale partings between limestone beds. A steeply dipping calcite vein was exposed in 1998 on the highest working bench of the quarry. This is clearly a metasomatic vein and shows irregular, pod-like replacements of the limestone. In the lower levels of the quarry, a series of fractures was recently intersected which are either mineralized with galena and calcite or alternatively with an assemblage comprising white calcite, veined by orange, crystalline sphalerite overgrown by pale-purple fluorite. Associated with some of the calcite veins are spots of black, pitch-like hydrocarbon up to 10 mm across.

Interpretation

In comparison with the other orefields of Wales (e.g. the Central Wales Orefield), the North-east Wales Orefield has a simple paragenesis. Field observations suggest that there was a single, if somewhat protracted, period of fracture initiation, fracture movement, and hydrothermal primary mineralization, followed by lengthy and highly variable supergene remobilization and re-deposition of the metals, largely as carbonates.

Studies of the mineralization at Halkyn and elsewhere in the northern part of the North-east Wales Orefield (Bevins and Mason, 1999) have indicated that the mineralization displays a well-defined paragenetic sequence, comprising an early phase of minor hematite (not observed at Halkyn), minor pyrite and/or marcasite, and fine-grained buff calcite. Quartz occurs as doubly terminated micro-crystals which have metasomatically replaced the limestones in places. The main, ore-bearing mineralization consists of abundant coarse-grained calcite intergrown with coarse-grained sphalerite followed by galena, the calcite containing rows of chalcopyrite inclusions; these minerals are in places overgrown by fluorite, again with associated chalcopyrite, a further coarse-grained calcite generation, and minor, late barite. The uraninite-bearing hydrocarbon is associated with this phase of mineralization, but its paragenetic position is ill-defined. Late-stage mineralization comprises radiating, columnar calcite, as seen at workings on the Dog Pit Vein, where it cements brecciated coarsely crystalline calcite.

The sequence described above is more complex and, in places, at variance with that presented by Smith (1921), although it has been observed repeatedly in many samples. The dominant part of the sequence, seen throughout the Halkyn Block, ranges from coarse-grained calcite through to fluorite. In terms of fluorite and barite distribution, no apparent zoning pattern has been discerned, contrasting with the Peak District and Alston and Askrigg blocks (see chapters 3 and 4). The fact that some veins carry fluorite+/–barite, or neither of these minerals, is interpreted as being controlled by the chronology of fracturing and fluid migration. If a fracture was either filled with minerals or tectonically sealed after deposition of the main generation of coarse-grained, lead-zinc-bearing calcite, access by the later fluorite- and final barite-depositing fluids would be prevented. If, however, the fracture remained open throughout the mineralizing episode then it would be more likely to admit further fluids and the resultant vein would then carry both fluorite and barite.

The observation by Smith (1921) that sphalerite tends to persist at depth while galena decreases in amount, is borne out by examination of the distribution of these minerals in the two working quarries. In the lower levels of both the Pant and Pant-y-Pwll-dŵr quarries, sphalerite is much more abundant than galena. However, it is also worth noting that above these levels sphalerite tends to be increasingly oxidized to a skeletal boxwork of smithsonite, while much of the galena remains relatively unaltered. This implies that supergene processes may, in certain areas, result in an apparent pattern of vertical zonation. However, in the North-east Wales Orefield, the tendency for galena to become scarce at depth was well documented at a number of mines (Smith, 1921), particularly to the north of Halkyn Mountain, and also at Minera, so that some vertical zonation within the orefield appears to be present.

Although less intensively studied than the other 'Pennine-type' orefields of Great Britain, a number of theories have been advanced to explain the genesis of the North-east Wales Orefield. Initially, Earp (1958) invoked the presence of a concealed granite batholith for the existence of a vein province, then a popular model for the genesis of ore deposits. Since that time, however, the granite model has been disproved in many cases throughout Great Britain and has been replaced by the concept of laterally migrating, connate brines expelled from adjacent sedimentary basins. It is this now largely accepted model which has been applied to the MVT orefields of Great Britain; in the case of the North-east Wales Orefield, the Irish Sea and Cheshire basins to the north and east of the area, respectively, are considered to have been the principal sources of hydrothermal fluids (Ixer and Vaughan, 1993). Fluid-inclusion data obtained from fluorite samples indicate that the mineralization was derived from fluids with temperatures of 105°–130° C and salinities of *c.* 24 wt% NaCl equivalent (Smith, 1973), features typical of sedimentary basin oilfield brines, and hence consistent with the above model.

The age of the mineralization is slightly more problematic. The only available isotopic date is a Pb-Pb date (Moorbath, 1962) that indicates an early Jurassic age, but this may not be reliable

(Ixer and Vaughan, 1993). However, it seems reasonable, given the field evidence that the mineralized fractures cut strata as young as Westphalian (Smith, 1921), to infer that the mineralization is post-Carboniferous in age and was probably related to the development of sedimentary basins in adjacent areas in Upper Palaeozoic to Mesozoic times. Subsidence associated with this period of basinal development would also have caused regional crustal extension across Wales, creating favourable conditions for the development of tensional fractures, ideal for access by hydrothermal fluids.

Secondary mineralization is widespread but rather limited in the number of species present. Not surprisingly, in an area dominated by carbonate sedimentary sequences, the pattern of sulphide alteration is principally linked to the generation of secondary carbonate species. Although limited in diversity, the quantity of alteration products is greater than in most other Welsh mining areas. Most notably, the alteration of sphalerite produced historically workable deposits of smithsonite ('calamine') at several localities (Smith, 1921). Secondary lead minerals, however, are of relatively limited abundance: cerussite tends to form thin, earthy external rinds on otherwise fresh galena, and only locally has significant pyromorphite been found, indicative of the relative stability of galena in comparison to sphalerite. Although occasionally occurring as aesthetically pleasing specimens, the copper carbonates azurite and malachite are only present in minor quantities, reflecting the relative paucity of the primary source copper mineral chalcopyrite. The extent of sulphide oxidation is interpreted as being related to the relatively high permeability of the Carboniferous carbonate-dominated host-rocks, allowing an enhanced amount of interaction between the primary assemblage minerals and groundwaters. Such processes continue to the present day, and extensive cementation of peri-glacial sands and gravels by aragonite discharged from a karstic spring has been reported at the Hendre Gravel Quarry, to the south of Halkyn Mountain (Bevins and Mason, 1999).

Conclusions

The Halkyn Block of the North-east Wales Orefield, typified by the **Halkyn Mountain** GCR site, is, compared to the other orefields of Wales, paragenetically simple. Mineralization, developed within a conjugate set of east–west and north–south extensional fractures, is dominated by calcite, with associated galena, sphalerite, chalcopyrite, fluorite and barite. The geological setting and fluid-inclusion characteristics of the mineralization are consistent with emplacement by connate brines expelled from adjacent sedimentary basins in late Palaeozoic to Mesozoic times. This genetic model is also consistent with the overall model for the development of the other major 'Pennine-type' lead-zinc orefields in Great Britain.

POOL PARK AND SOUTH MINERA MINES (SJ 249 506, SJ 253 501)

Introduction

These two closely adjacent sets of workings provide the opportunity to study mineralization in the southern part, or Minera Block, of the North-east Wales Orefield (Figure 5.74). Mineralization in this district differs significantly from that of the Halkyn Block (see **Halkyn Mountain** GCR site report, this chapter) in that quartz is a major gangue phase, accompanying, in large amounts, the more typical calcite. The textural and mineralogical resemblance of the mineralization to that in various Lower Palaeozoic-hosted lead-zinc orefields around Wales and the Welsh Borderland is a striking feature, and suggests that there may be strong genetic links, both in terms of the timing of the mineralization, as well as mode of emplacement.

Minera was formerly one of the most intensively mined districts of Wales. However, as in other old mining districts, many of the features seen on contemporary photographs have now disappeared. Reclamation works have removed a substantial amount of the mining waste at Minera itself, and many of the tips have been grassed over and planted with trees. The whole Minera district is still, however, of interest to the industrial archaeologist, and much excavation and restoration has been undertaken, including the conversion of the area around Meadow Shaft into a mining museum.

During the last four decades much underground exploration has taken place at Minera, both in the old mines themselves and in the cave systems, many of which were intersected during

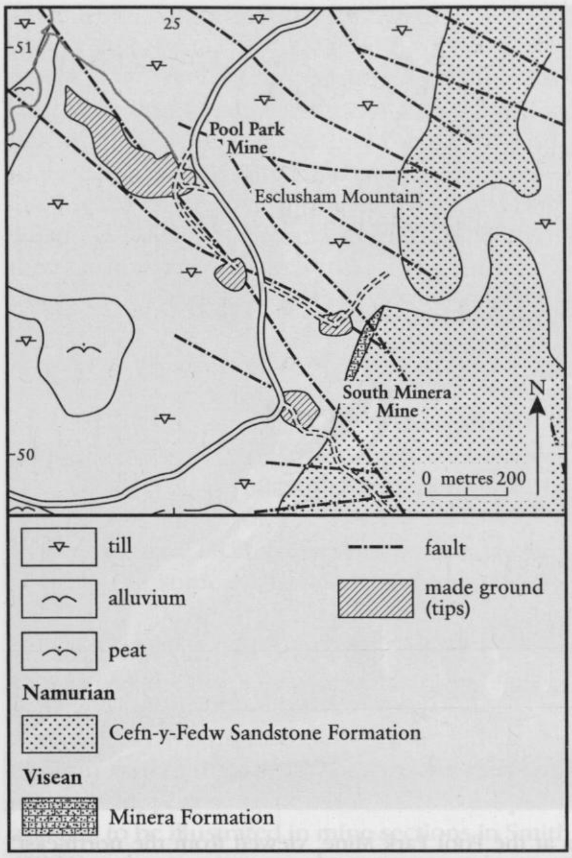


Figure 5.74 Map of the Pool Park and South Minera Mines GCR site. After British Geological Survey 1:50 000 Sheet 121, Wrexham (1993b).

mining operations (Appleton, 1995). The range of passage forms, flowstone and dripstone formations and other features have led to the cave systems being given SSSI status. However, in view of current circumstances, the surface interest at Minera lies not in the main area, but to the south, on the high moorlands of Esclusham Mountain, which are crossed by a narrow mountain road from Minera to Llangollen. Here, extensive unvegetated mine tips remain essentially undisturbed, and vein material, strongly representative of the district as a whole and often in a fresh and unweathered state, occurs in great abundance.

Although there is evidence of Roman lead-mining elsewhere in north-east Wales, in the Minera district the first documented information dates from Medieval times. The Esclusham Mountain workings described here appear to be a relatively recent development; detailed production figures commence in 1860 (Burt *et al.*, 1992) and indicate that these mines were worked from that time through to the close of the 19th century.

Ore production from the South Minera and Pool Park mines was small in comparison to the Minera Mine itself, which produced, in the period between 1852 and 1913, when full records were kept, 134 630 tons of galena concentrates alone, and regularly returned over 5000 tons per year during the years 1861 to 1871 (Burt *et al.*, 1992). Minera was, however, one of the great British lead-zinc mines, comparable in status with Van Mine in central Wales, the **Snailbeach Mine** GCR site in south-west Shropshire, and Millclose Mine in Derbyshire. The mines on Esclusham Mountain were more typical of the area in productivity terms. South Minera produced, prior to amalgamation with Pool Park, 6 tons of galena concentrates in 1867 (yielding 30 oz of silver); between 1860 and 1874 Pool Park produced 1780 tons of galena (yielding 7276 oz of silver) and 128 tons of sphalerite. After the mines were amalgamated in 1877 they were worked as Minera Mountain until 1897, producing 301 tons of galena concentrates (yielding 1457 oz of silver) and 1098 tons of sphalerite (Burt *et al.*, 1992).

Description

The Pool Park (Figure 5.75) and South Minera mines worked two steeply dipping epigenetic fissure-veins, hosted at Pool Park entirely by limestones of the Minera Formation, of Dinantian age; and at South Minera by Minera Formation limestones, and sandstones of the overlying Cefn-y-Fedw Sandstone Formation, the latter being responsible for the relatively acidic soils that support the boggy heather moors of the uplands of Esclusham Mountain. Productive mineralization was confined to the limestones (Smith, 1921). The veins cross each other obliquely at Pool Park Mine. The Pool Park vein trends 125° and downthrows to the south-west, while the South Minera vein trends 145° and downthrows to the north-east (Smith, 1921). This is in contrast to the veins in the remainder of the North-east Wales Orefield, where the predominant trend of the productive veins is approximately east–west (Smith, 1921).

Primary mineralization, examples of which are abundant in the mine tips, occurs as breccia cements and as crustiform-banded fissure-fills. The mineralization consists of coarse-grained, reddish sphalerite with galena, set in a matrix of

Figure 5.75 Oblique aerial photograph of old workings at the Pool Park Mine, viewed from the north-east, showing old lead shafts, natural sink-holes, and a prominent leat system. (Photo: © Crown copyright: Royal Commission on the Ancient and Historical Monuments of Wales.)

'stumpy' crystalline quartz, calcite and minor dolomite. Traces of chalcopyrite and fluorite have also been recorded from the Minera district (Smith, 1921). In paragenetic terms the mineralization is simple, with a well-defined depositional sequence. Early, clear, 'stumpy', crystalline quartz, locally associated with dolomite, coats rock fragments and partly encloses abundant euhedral, translucent, orange-red sphalerite. Later galena is also abundant, and is associated with still later abundant overgrowing calcite. This paragenesis is typical of the Minera district, from where many fine crystallized specimens of both the ore and gangue minerals are known, including a number of fine samples, collected around the turn of the century by the then Mines Inspector for North Wales, G.J. Williams, and passed to the National Museum of Wales in 1927.

Secondary minerals occur commonly, although they tend to be micro-crystalline. Smithsonite commonly forms partial, boxwork-like replacements of sphalerite crystals, and is accompanied by rarer hemimorphite. Hydrozincite stains on blocks of tip material are a conspicuous post-mining weathering product. These secondary minerals are all common throughout the North-east Wales Orefield.

Interpretation

The Minera district is of particular interest within the overall context of the Carboniferous-hosted North-east Wales Orefield as the mineralization bears a distinct resemblance, both mineralogically and texturally, to some of the Lower Palaeozoic-hosted, late-stage mineralization worked in adjacent areas such as south-west Shropshire (Pattrick and Bowell, 1991; see Chapter 4), Central Wales (Mason, 1994, 1997; see this chapter), Llanrwst (Haggerty, 1995; Bevins and Mason, 1998), and Llangynog (Bevins and Mason, 1997).

These late-stage, Lower Palaeozoic-hosted vein assemblages are ascribed by the above authors as representatives of Variscan metallogenic processes operating on a regional scale. They have been cited by these authors variably as being either of Lower Carboniferous age, and possibly related to the episode of mineralization that resulted in the deposition of the Irish stratiform lead-zinc mineralization, or to the post-Carboniferous phase of mineralization during which the 'Pennine-type' orefields, including the North-east Wales Orefield, were formed. Importantly, certain of the late-stage Lower Palaeozoic-hosted vein assemblages have yielded Pb-Pb model isotopic ages which places them within the 'Pennine-type' orefield spread (Swainbank *et al.*, 1992). These include particular assemblages from the Central Wales Orefield, some of which are strikingly similar to the mineralization of the Minera district (see **Nantiago Mine** GCR site report, this chapter).

Although some of the shafts at Minera did penetrate the underlying Lower Palaeozoic strata, it appears, from available literature, that the economic mineralization died out at that interface. For example, Hall (1995) quoted an unidentified writer thus: '...when reaching the Silurian rocks, the vein closes up wedge-form, and to all appearances dies out'. The same point appears to be illustrated in mine sections in Smith (1921), where veins are shown to terminate at the base of the Carboniferous succession. Recent examination of a limited exposure of Lower Palaeozoic rocks deep underground at Minera confirmed that they contained only minor mineralization, despite being situated directly below a rich system of veins and replacement flats.

Although there thus appears to be no significant mineralization below the basal Carboniferous rocks, there are occurrences of fissure-vein mineralization in Lower Palaeozoic rocks in close proximity to the North-east Wales Orefield, of which the best example is the **Pennant Mine** GCR site. However, such occurrences are isolated. The most likely reasons for the relative lack of mineralization in sub-Carboniferous strata lie in the differing characteristics, in terms of geochemistry, rheology and permeability, of the Carboniferous succession compared to the underlying folded Lower Palaeozoic rocks, coupled with the greater effects of extensional tectonics on the relatively near-surface Carboniferous strata.

Some of the mineralogical features at Minera contrast strongly with those of the Halkyn Block. Fluorite and barite. frequent in the Halkyn Block, are virtually absent, with one or two very minor exceptions, at the Minera mines. In addition, dolomite is present at Minera in small but conspicuous amounts, yet has not been observed within the veins of the Halkyn Block. Finally, quartz is present at Minera, although its abundance here is not readily explained. Possibly, the Cefn-y-Fedw Sandstone Formation, which is particularly thick and markedly quartzitic in this area, contributed silica to the hydrothermal system through remobilization of detrital quartz. In the Halkyn Block, in contrast, the reverse is the case, and metasomatic quartz only locally replaces vein-wall carbonate rocks.

Conclusions

The Minera Block of the North-east Wales Orefield, typified by the Pool Park and South Minera Mines GCR site, exhibits notable mineralogical differences to the main part of the orefield in the Halkyn Block, exemplified by the **Halkyn Mountain** GCR site. Mineralization at the Pool Park and South Minera Mines GCR site consists of a simple galena-sphalerite sulphide assemblage in a gangue of quartz, calcite and minor dolomite. The abundance of quartz at Minera, a relatively scarce mineral in the Halkyn Block, is a key feature, while the striking resemblance of the mineralization to that occurring in some of the Lower Palaeozoic-hosted orefields of the Welsh Caledonides is particularly notable. A detailed comparison of the mineralization at this site with that present in Lower Palaeozoic-hosted settings elsewhere in Wales is worthy of further study.

PENNANT MINE (SJ 085 754)

Introduction

Located only *c.* 5 km from the western margin of the intensively worked Halkyn Block of the North-east Wales Orefield, and closely adjacent to the Carboniferous–Lower Palaeozoic unconformity, Pennant Mine worked two near E–W-trending fissure-veins emplaced into mudstones and shales of Wenlock to Ludlow age, belonging to the Nantglyn Flags Formation. As in the North-east Wales Orefield, the chief metalliferous minerals are galena and sphalerite, with minor chalcopyrite. Here, however, barite is the principal gangue species, accompanied not only by calcite but also by significant quantities of witherite. Despite the similarity (in terms of sulphide mineralogy and textures) of the mineralization and its close proximity to the Carboniferous-hosted North-east Wales Orefield, barium minerals are rare in the latter orefield.

Pennant Mine was developed initially for lead in the 1700s (Vernon, 1993), and there are records of intermittent subsequent workings during the early 19th century (Foster-Smith, 1974). However, the main period of mining was during the latter half of the 19th century, when, in the period 1858 to 1891, 850.7 tons of galena concentrates were produced, yielding, in 1874, 35 oz of silver from 7.8 tons of ore (Burt *et al.*, 1992). Barite was produced between 1874 and 1891, and in 1913 the total recorded production was 2924 tons (Burt *et al.*, 1992), although some of these figures relate, in fact, to extraction of witherite (Carruthers *et al.*, 1915). Between 1913 and 1920, several hundred tons of witherite, with some barite and galena, were produced, partly by reworking of the extensive waste dumps (Wilson *et al.*, 1922).

Although sphalerite is a common mineral at Pennant Mine, there was no recorded zinc production, and the fact that the sphalerite proved difficult to separate from the associated barite (Dewey and Smith, 1922) may have been the reason for this. In 1919, a plant was established at the mine in an attempt to achieve this separation by heating the mixed barite/sphalerite concentrates to *c.* 400° C on an iron plate, which caused the barite to decrepitate to a fine powder, supposedly making it easier to remove. Apparently, it was not successful (Wilson *et al.*, 1922).

Description

At Pennant Mine (Figure 5.76), shales and mudstones, of Wenlock to Ludlow age, belonging to the Nantglyn Flags Formation, are cut by a major, near E–W-trending vein (the Main Vein), a less-important sub-parallel vein (the South Vein), and a number of branch veins. The Main Vein, exceeding 3 m in width in places, has been worked over a 500 m strike length, and has been traced for a distance of approximately 1500 m (Carruthers *et al.*, 1915). Contemporary reports describe the Main Vein as having a central band rich in galena, with smaller quantities dispersed through the surrounding gangue, accompanied

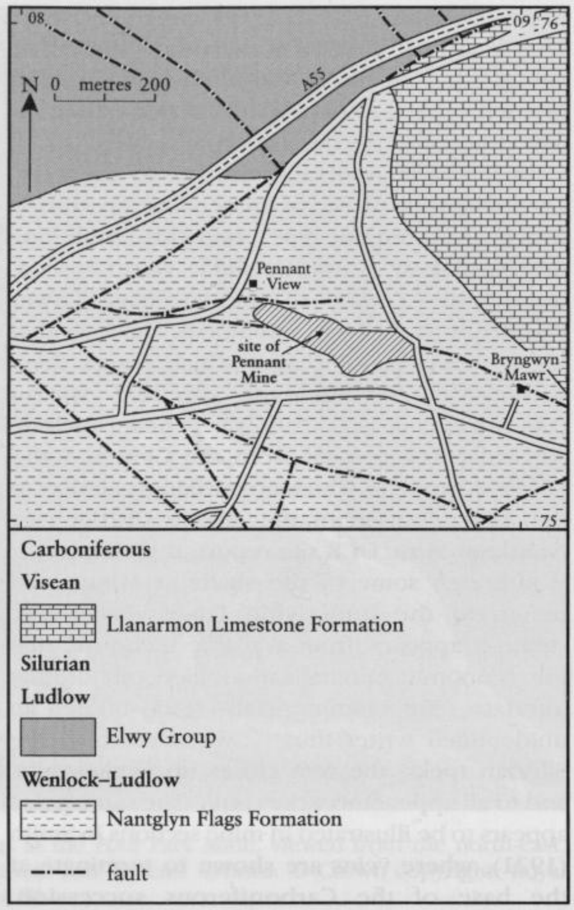


Figure 5.76 Map of the Pennant Mine GCR site. Based on Institute of Geological Sciences 1:50 000 Sheet 95, Rhyl (1970), and British Geological Survey 1:50 000 sheets 107, Denbigh (1985b), and 108, Flint (1999).

by 'zinc blende in aggregates of all sizes' (Dewey and Smith, 1922). The barite was described as forming a solid rib, up to 2 m in width, and was 'clearest' at the eastern end of the mine, where it was 'in proximity to the Carboniferous Limestone' (Carruthers *et al.*, 1915). Witherite was described as occurring in discrete pockets with a radial, crystalline structure.

The site (Figure 5.77) has been in a dilapidated, highly overgrown condition for many years, but recently extensive remedial works, including shaft capping and building restoration, have been undertaken in a project which will in due course see the mine open to the public as an interpretative centre. However, the amount of spoil visible at surface is now limited, although that uncovered during the restoration project has been saved and should be available for study (P. Selley, pers. comm.).

Figure 5.77 Photograph of the restored engine-house at the Pennant Mine GCR site. (Photo: T. Cotterell.)

Material examined during the restoration works showed that sphalerite was the most abundant sulphide in the tips, perhaps not surprising given the difficulties experienced in separating it from barite. The coarse-grained sphalerite, of a pale yellowish-brown colour, is associated with minor chalcopyrite and occurs close to rock clasts, suggesting that it is early in the depositional sequence. Overgrowing barite, and intergrown with galena, are witherite and subordinate calcite. Strontianite has been recorded, while a report of alstonite is thought to refer to a mis-provenanced sample (see Bevins, 1994). Secondary minerals are not common, although hydrozincite, probably post-mining in origin, occurs in trace amounts.

Interpretation

At Pennant Mine, an east–west fracture, of similar trend to those carrying Pb-Zn mineralization in the Carboniferous strata of the North-east Wales Orefield, carries a simple Pb-Zn-minor Cu ore assemblage, accompanied by calcite and barium minerals. It is possible that the mineralization worked at Pennant Mine represents a development of the North-east Wales Orefield mineralization within the subjacent Lower Palaeozoic succession. If this were proven, it would challenge the currently held view that the MVT mineralization occurring within the 'Pennine-type' orefields of Britain is confined to Carboniferous and younger carbonate-dominated, shallow-water sedimentary sequences.

Vein deposits with strong similarities in gross mineralogy and texture to those of the North-east Wales Orefield (i.e. simple mineral assemblages occurring as generally coarse crustiform growths) are abundant throughout the Lower Palaeozoic rocks of the Welsh Caledonides. These include the A2 or late-simple Central Wales veins (Bevins and Mason, 1997; Mason, 1997), the Llangynog Orefield (Bevins and Mason, 1997), the late-stage crustiform veins of the Dolgellau Gold-belt (Mason *et al.*, 1999), the Llanengan veins on Llŷn, and the Llanrwst Orefield, in northern Snowdonia (Haggerty, 1995; Bevins and Mason, 1998). Similar veins occur on a small scale, cutting the Lower Palaeozoic strata of the Denbigh Moors and

Clwydian Range (Bevins and Mason, 1999). The possibility exists, albeit unproven, that all of these post-Caledonian vein deposits may represent facets of a broad province of MVT vein mineralization formed during extensional phases of the Variscan cycle and linked with connate brine expulsion from adjacent sedimentary basins. Such basins developed around the Welsh Caledonide region in a piecemeal pattern over a protracted period of geological time from the Dinantian through to the early Jurassic, and were responsible for generating the fluids which so pervasively mineralized the carbonate sequences of the Carboniferous outcrops (Ixer and Vaughan, 1993).

A problem in linking the mineralization at Pennant Mine to that of the Halkyn Block lies in the quantity of barium minerals occurring in the Pennant Mine mineralization. Barite is, in quantitative terms, a rare mineral within the Halkyn Block, only occurring as a late-stage phase overgrowing fluorite (which has not been reported from Pennant Mine). Witherite is virtually unknown from the Halkyn Block, the only reported occurrence being a specimen in the mineral collection of the National Museum of Wales (formerly from the R.J. King Mineral Collection), labelled as from Halkyn Mines (Bevins, 1994). Barite does occur, however, in Carboniferous rocks in other outlying areas of the North-east Wales Orefield, for example at the Bron-Eyarth Mine, to the south of Ruthin, and at Llangynhafal, to the north of Ruthin (Carruthers *et al.*, 1915). However, both of these occurrences are, compared to the Pennant Mine, relatively minor. The reason, therefore, for this localized major concentration of barium minerals remains to be established. Otherwise, the sulphide mineralization at the Pennant Mine is, in terms of textures and paragenetic sequence, remarkably similar to that of the Halkyn Block.

The mineralization at Pennant Mine warrants more detailed comparison with that of the Halkyn Block, involving a study of sulphur isotopes (using barite, galena and sphalerite) and Pb-Pb isotope analyses of galena from both areas.

Conclusions

The mineralization worked at the Pennant Mine carries a simple Pb-Zn-minor Cu ore assemblage accompanied by calcite, barite, witherite and rare strontianite. It possibly represents an extension of the Carboniferous-hosted MVT North-east Wales Orefield, but emplaced into the subjacent Lower Palaeozoic strata. The possibility that MVT mineralization can develop in older, non-carbonate sequences as well as its more usual host is worthy of further detailed investigation, as many vein deposits in the Welsh Caledonides have mineralogical and textural similarities to the limestone-hosted MVT 'Pennine-type' deposits. The direct comparison of the Pennant Mine with the closely neighbouring Halkyn Mountain area warrants further research.

GREAT ORME COPPER MINES (SH 770 830)

Introduction

Mining for copper on the Great Orme (Figures 5.78 and 5.79), a prominent headland overlooking Llandudno and Colwyn Bay, goes back to Bronze-Age times, and the mine is well renowned as an archaeological site of international importance. In addition, the style of mineralization worked here, belonging to the copper-dolomite class of deposits, is of considerable metallogenic importance.

Bronze-Age mining features are well preserved at the Great Orme due to the sealing in of many artefacts by aragonite flowstone. Stone hammers and antler picks have been recovered and the early mining dates have been confirmed by ^{14}C dating (Lewis, 1990). Mining since that time has continued intermittently until the late 19th century (Bick, 1985), and in 1842 a new drainage adit, driven in at sea level, broke through into the workings. The high-grade ore obtained at the Great Orme was often sent to Amlwch, on Anglesey, for smelting with lower-grade produce mined at Parys Mountain. According to Hunt (1884), the mine was abandoned when unexpectedly the sea broke into the workings along hidden fissures which could not be sealed off. Between 1804 and 1881, the mines (initially worked as the two separate ventures known as 'New Llandudno' and 'Old Llandudno') produced a total of 26 506 tons of copper ore concentrates, of an unknown copper content. Production prior to 1804 remains unknown but was clearly substantial.

The metallogenesis and mineralogy of the site have received considerable attention. William

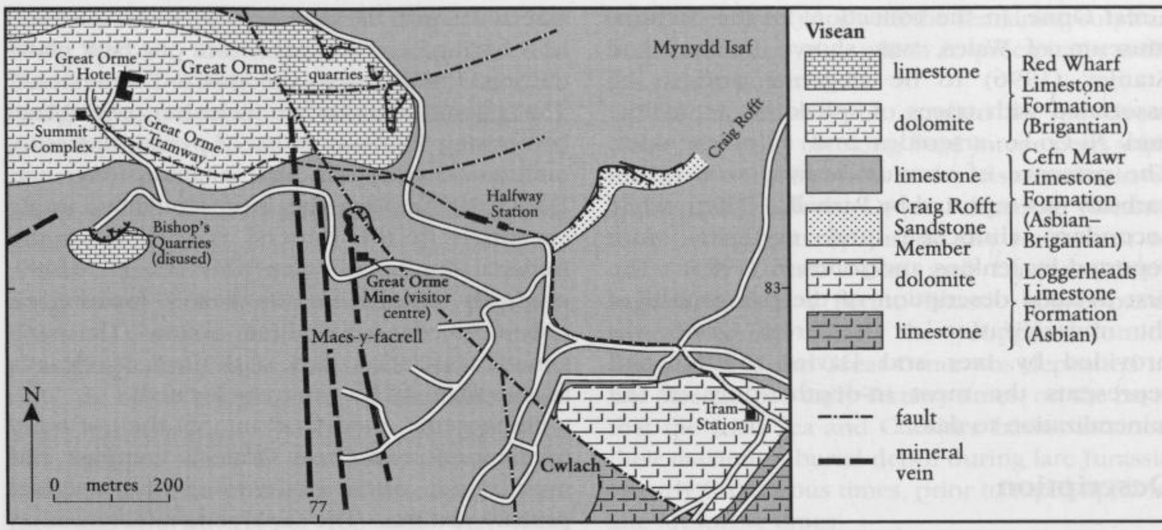


Figure 5.78 Map of the Great Orme Copper Mines GCR site. After British Geological Survey 1:50 000 Sheet 94, Llandudno (1989a).

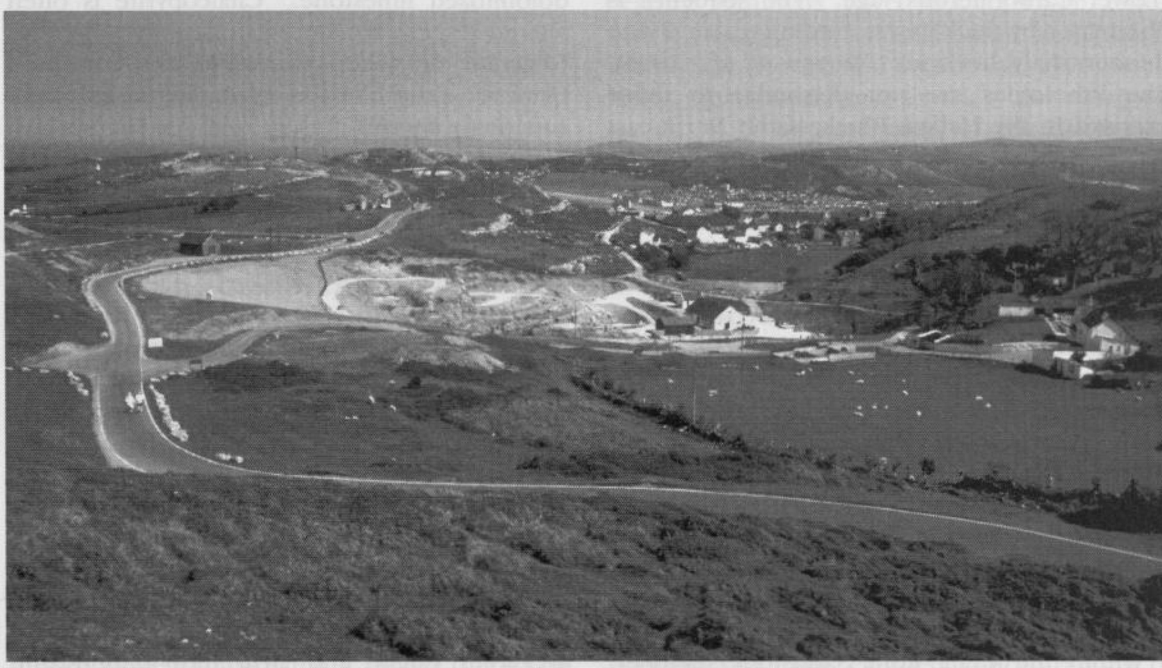


Figure 5.79 Photograph of the Great Orme Copper Mines GCR site. (Photo: S. Campbell.)

Vivian, working as Mine Captain for John Taylor & Sons, reported in 1859 the presence of arborescent native copper in the workings (Vivian, 1859). Hunt (1884) gave a full description of the mine, abstracted by Dewey and Eastwood (1925). In Hunt's account, four sub-parallel N–S-trending lodes were described, plus a number of minor cross-veins. Workable ores were said to occur where these lodes traversed certain beds of crystalline limestone, and particularly in the vicinity of junctions of the lodes with the cross veins. Hunt (1884) also referred to the presence of an extensive oxidized zone in the upper part of the mine, below which chalcopyrite was the main ore mined.

More recently, studies into the mineralization have revealed the presence of a number of rare minerals. A specimen of 'linnaeite' from the

Great Orme, in the collections of the National Museum of Wales, was shown by Ixer and Stanley (1996) to be siegenite and to be associated with traces of sphalerite, tennantite and Ni-Co-Fe arsenides and sulpharsenides. The presence of uranium-bearing vein hydrocarbons was reported by Parnell (1988b), while secondary clinoclase and erythrite were reported by Jenkins and Johnson (1993). The first detailed description of the paragenesis of the mineralization at the Great Orme was provided by Ixer and Davies (1996), and represents the most in-depth study of the mineralization to date.

Description

The strata hosting the copper-dolomite deposit at the Great Orme comprise a shallow-water carbonate-dominated sequence of Dinantian (Lower Carboniferous) age. The sequence is dominated by thick limestones intercalated with thinner shaly horizons (Warren *et al.*, 1984). The lithologies are not dissimilar to those exposed in the Halkyn Block of the North-east Wales Orefield, except that the limestones at the Great Orme have been heavily dolomitized.

The mineralization is developed in the Craig Rofft Sandstone Member of the Cefn Mawr Limestone Formation and the overlying Red Wharf Limestone Formation. It occurs within a zone in which numerous sub-parallel N–S-trending high-angle faults cut the succession (Ixer and Davies, 1996). The faults show slight displacement (0.5–1.5 m) and are all mineralized, although the most intense mineralization, now worked out, was developed along four particularly large fractures. The mineralization is strongly controlled by the host lithology, being best developed in the thickest beds of dolomitized limestone.

Within the Craig Rofft Sandstone Member, primary mineralization is restricted to joint planes and faults, and consists of minor chalcopyrite accompanied by saddle dolomite and calcite (Ixer and Davies, 1996). The overlying dolomitized limestones are intensively mineralized along the faults, on joints, in void infillings and along bedding planes. Typical primary ore consists of saddle dolomite, forming crusts of typically curved crystals, upon which sphenoidal chalcopyrite crystals, typically 3–5 mm across, are scattered, accompanied by minor, and later, pyrite and marcasite. Traces of sphalerite are associated with the chalcopyrite. Galena is rare, only having been recorded from one fault plane cutting fine-grained dolomitized limestone. The galena contains an inclusion assemblage comprising 5–60 μm grains of pyrite, marcasite, millerite, chalcopyrite and sphalerite (Ixer and Davies, 1996). Siegenite, represented by a single specimen in the mineral collection of the National Museum of Wales (NMW 83.41G.M1489, originally labelled as 'linnaeite') forms grey, cubo-octahedra up to 4 mm across. The paragenetic association of the siegenite is not clear as further material has yet to be located.

Supergene modification of the primary mineralization at Great Orme is complex and multi-stage, often obliterating the original primary textures. The supergene mineralization is essentially void-filling, but is associated with limited wall-rock alteration, comprising the de-dolomitization of saddle dolomite and the dolomitized limestone. Chalcopyrite is often altered directly to supergene copper sulphides (digenite, djurleite, spionkopite and covellite). However, malachite and calcite are the principal supergene species present.

Three principal generations of supergene calcite have been determined (Ixer and Davies, 1996). The first generation is of a dull orange-red colour and is luminescent. It is associated with malachite and overgrows altered chalcopyrite. The chalcopyrite is pseudomorphed by limonite, and the pseudomorphs contain patches and veinlets of cuprite, malachite, native copper and tenorite, all of which are fine grained. The second, and principal, calcite generation forms euhedral crystals up to 10 mm, which are strongly zoned, luminescent and vary in colour from dull to bright orange-red. Malachite and limonite crusts have been deposited in between stages of calcite crystal growth. The third calcite generation consists of fine-grained infills of voids in earlier calcite and clear, non-luminescent, coarse-grained crystals, again with included malachite and iron oxides.

Malachite, which occurred at the Great Orme in sufficient amounts to be mined in its own right, tends to form botryoidal crusts, and also pseudomorphs after chalcopyrite, as illustrated by Bevins (1994). Rarely, azurite forms cores to the malachite botryoids. Azurite also forms rare crystalline aggregates on saddle dolomite (Bevins, 1994). A further occurrence of azurite, described by Ixer and Davies (1996), consists of small, spheroidal nodules up to 2 cm in diameter developed within a non-calcareous shale horizon, the 'Azurite-bearing Shale' of Warren *et al.* (1984). In these shales, there are two generations of azurite, an early, fine-grained, greenish-blue phase, sometimes enclosing chalcopyrite, and a later, deep-blue, crystalline phase which lines fractures within the fine-grained material.

The galena-bearing assemblage shows alteration to cerussite, accompanied by digenite, djurleite, covellite and spionkopite. A further alteration assemblage comprises the 'copper dhu' or black copper ore, which infills veins lined with dolomite, malachite and goethite. The 'copper dhu' is extremely fine-grained and fails to give a clear X-ray diffraction pattern. Ixer and Davies (1996) reported that X-ray fluorescence analysis of the 'copper dhu' revealed the presence of major Fe, Cu and Ni, with minor Co, As, Pb, Mn and Cr.

Interpretation

With the exception of the galena-bearing fracture, which has been assigned (Ixer and Davies, 1996) to the North-east Wales Orefield mineralization, and the isolated siegenite specimen, the primary mineralization at the Great Orme consists of saddle dolomite, chalcopyrite, minor iron sulphides, and calcite filling veins and voids within dolomitized limestones. This assemblage has been assigned to the copper-dolomite association (Ixer and Stanley, 1996), a worldwide class of mineralization, which is genetically associated with exhalative lead-zinc or MVT deposits. Typically, such associations are deposited at temperatures of 60°–150°C (Radke and Mathis, 1980), often in positions marginal to MVT orefields.

Using the mineralization at Tynagh, in Ireland, and Mount Isa, in Australia, as case studies, Russell (1983) constructed a model to explain the connection between the copper-dolomite associations and sedimentary exhalative Pb-Zn deposits. The exhalative deposits are produced by deepening hydrothermal cells developed during episodes of crustal extension. Towards the end of the depositional cycle, the hydrothermal fluids become magnesium-rich and sulphur-poor, and deposit saddle dolomite as they pass through carbonate sequences at high crustal levels. Should the fluids circulate through either deeply buried red-beds or volcanic rocks, they take copper into solution, which then combines with the remaining sulphur to form chalcopyrite, which co-precipitates with the saddle dolomite.

This model may be applied to the Great Orme, either by invoking fluid interactions with the Permo–Triassic rocks of the Irish Sea Basin or alternatively with the Lower Palaeozoic volcanic rocks which outcrop just to the south-west of the Great Orme. Ixer and Davies (1996) suggested that a Permo–Triassic source-basin would imply that the copper-dolomite association at the Great Orme was deposited in late Mesozoic to early Tertiary times, on the basis that the Irish Sea and Cheshire basins attained their maximum burial depth during late Jurassic to early Cretaceous times, prior to rapid uplift in late Mesozoic times.

This age for the mineralization is, however, at odds with isotopic dates obtained from this and adjacent sites. Both galena samples and uranium-bearing bitumens have yielded Pb-Pb dates which suggest the mineralization is of early Triassic age (Parnell and Swainbank, 1990; Rohl, 1995). This model age is similar to that obtained for the MVT mineralization of the North-east Wales Orefield (Fletcher *et al.*, 1993). However, Ixer and Davies (1996) considered that the dates obtained from the bitumens merely represent the age of migration of the bitumen, as opposed to the age of the copper mineralization.

Ixer and Davies (1996) argued, albeit on limited evidence, that the galena-bearing vein, which they associated with the North-east Wales MVT mineralization, is earlier than the copper-dolomite mineralization. Both types of mineralization clearly post-date Variscan faulting, but it is clear from the above discussion that the precise post-Variscan age remains to be clearly established. However, there is further evidence to consider. The 'copper dhu' ore, which is a wad-like, fine-grained, amorphous, post-dolomite deposit containing elevated concentrations of Fe, Cu, Ni, Co and Mn, amongst other elements, bears a close resemblance to the earthy Fe-Ni-Co-Mn oxide mineralization which was mined in now largely overgrown workings in the Prestatyn area, on the eastern margin of the Permo–Triassic-filled Vale of Clwyd (Warren *et al.*, 1984; Bevins and Mason, 1999). This has been interpreted (Bevins and Mason, 1999) as being formed by the circulation of oxidizing groundwaters in Triassic times. This would suggest that the copper-dolomite mineralization was formed prior to that time.

An alternative interpretation of the 'copper-dhu' and Vale of Clwyd-type mineralization, however, could relate it to a widespread oxide-facies mineralization event, which has been noted at several sites in the Welsh Caledonides, such as the **Mynydd Nodol Mine** GCR site. This mineralization, with associated pervasive bleaching of the volcanic or sedimentary host-rocks, is poorly understood but consists of botryoidal Fe-Mn oxides filling available fracture spaces, and may have formed during Tertiary sub-tropical deep weathering. If this were the case, the late Mesozoic to early Tertiary age for the Great Orme mineralization, suggested by Ixer and Davies (1996), may be more realistic.

The supergene alteration of chalcopyrite at the Great Orme, comprising initial conversion to copper sulphides and limonite followed by multiple generations of calcite and malachite, is interpreted as being related to an increase in oxidation potential through time (Ixer and Davies, 1996). This is supported by cathodoluminescence of the supergene calcite, which is restricted to the first two generations. Cathodoluminscence in calcite. is activated by the incorporation of divalent manganese into the mineral, where it substitutes for calcium. Divalent iron counters the effect. Hence, the phenomenon is a good indicator of prevailing oxidation-reduction conditions, since both Mn and Fe are common in groundwaters. With increasing oxidation potential, Mn may remain divalent while Fe precipitates as trivalent oxides. At still higher oxidation potentials, both metals are deposited as trivalent oxides, hence the final, non-luminescent calcite generation is associated with Fe-Mn oxides.

The relative scarcity and early paragenetic position of azurite relative to malachite was explained by Ixer and Davies (1996) as being related to pH. Malachite is stable at much higher pH values than azurite. Within the dolomitic rocks of the Great Orme, the mine groundwaters, with a pH of 7–10, are within the malachite stability field but only marginal with respect to azurite. However, the predominance of azurite in the shale unit is explained by the non-calcareous nature of the shales; acidic fluids produced by the oxidation of pyrite and chalcopyrite would lack the necessary carbonate input to buffer the groundwaters to pH values in excess of 7. Under these conditions, azurite would be the more stable phase.

Conclusions

The simple primary copper-dolomite association at the Great Orme represents the first deposit of this class to be recognized in the UK. The mineralization is believed to have been deposited from magnesium-rich, sulphur-poor, copper-bearing hydrothermal fluids towards the end of a major hydrothermal episode, probably during Mesozoic times. The secondary alteration of the deposit is extremely complex and reflects alteration of the primary copper-bearing mineralization in an increasingly oxidizing environment by circulating groundwaters which were, except very locally, of a highly alkaline nature. The relationship of the mineralization and its alteration to that within the adjacent North-east Wales Orefield, with its Mississippi Valley-type mineralization, warrants further investigation.

UPPER PALAEOZOIC MILLERITE-BEARING IRONSTONES OF THE SOUTH WALES COALFIELD

Introduction

Sedimentary ironstones are widely developed in the Westphalian (Upper Carboniferous) 'Coal Measures') of South Wales, and provided the majority of ore for Welsh iron production. Under this group of iron ores there are two sub-types: blackband ironstone, and brownband or claystone–ironstone. Claystone–ironstone nodules (Figure 5.80) occur throughout the 'Coal Measures', forming bands in the dark-grey mudstones adjacent to coal seams, while blackband ironstones are relatively restricted in occurrence. They are concentrated stratigraphically in the lower Westphalian C strata, particularly in the Margam area, close to the postulated coal basin depocentre (Young, 1993). They were mined for their iron content, but in comparison to some areas, such as the Midlands, where they formed the backbone of the iron industry, production in South Wales was relatively limited in comparison to the brownband or claystone–ironstones.

Between 1855 and 1917, a total of 17.1 million tons of iron ore were produced from the brownband ironstone beds (Young, 1993). The industry closed in the 1930s. Since the ironstones often occurred intercalated with coal seams, it was often the case that both coal and iron ore were

Figure 5.80 Photograph of claystone–ironstone nodules exposed in Cwm Gwrelych, Glyn Neath. (Photo: R.E. Bevins.)

worked from the same pit. Common throughout the British coalfields, the South Wales claystone–ironstone are of particular importance in mineralogical terms for the well-crystallized sulphide assemblage developed in septarian cracks within the claystone–ironstone nodules. This assemblage, accompanied by siderite, dolomite, calcite, quartz, barite, carbonate-fluorapatite, waxy hydrocarbons and clay minerals, comprises millerite, galena, chalcopyrite, sphalerite, pyrite, marcasite and siegenite. It is, however, the excellent acicular groups of millerite crystals, reaching several centimetres in length on occasion, that have chiefly made the South Wales ironstones internationally famous in mineralogical terms.

Recently, similar, and clearly structurally controlled mineralization, has been observed *in situ* encrusting open joint-surfaces in 'Coal Measures' sandstones in the north-western part of the coalfield (Bevins and Mason, 2000). Together with recent fluid-inclusion and isotopic studies (Alderton and Bevins, 1996; Alderton *et al.*, 2004), the new discoveries throw a considerable amount of light on the genesis of the mineralization, and may have connotations with regard to the overall evolution of the coalfield.

In the South Wales Coalfield the selection of a single representative site for conservation purposes is not practical. The reason for this is that exposures of the productive strata are transient, as they are essentially limited to opencast coal mines, which tend to be short-lived and are covered by rigorous planning conditions, including their complete restoration upon cessation of mining. However, as one opencast closes, another opens, so that opportunities to study this internationally important mineralization *in situ* should continue to be available for the foreseeable future.

The ironstone-hosted sulphide mineralization of South Wales is also present in the once numerous coal tips of the area, albeit to varying degrees. However, due to the grassed over nature of these tips, good opportunities to sample and study the mineralization occur only when the tips are being landscaped, a process which ultimately removes the mineralogical resource. Nevertheless, a comprehensive suite of material is preserved in the Mineral Collection of the National Museum of Wales, where it is available for study.

For the above reasons, the millerite-bearing claystone–ironstone mineralization has not been allocated a specific GCR site, although it is of GCR importance. As such, the paragenesis of the mineralization is described here in detail because of its relevance to the overall metallogenic framework of Wales. In field terms, it is recommended that visits should be arranged to whichever opencast workings are in operation at any given time.

Description

The claystone–ironstones sometimes occur as continuous layers but are more commonly observed as concretionary bands, the concretions varying in size from a few centimetres to over 1 m. The concretions tend to have a flattened appearance, and are often 'bun-shaped', with a convex top and flat base. The ironstone is a hard, splintery micritic siderite-dominated rock, of a dark-grey colour, weathering to brown. The concretions are hardest internally, with relatively soft outer zones.

Most of the concretions contain thin siderite-lined cracks, but a considerable number host networks of open, septarian fissures. These form interconnecting mosaics of principally vertical, often slightly curved, fractures, extending from the centres of concretions to the outer zones, where they die out before reaching the concretion surface. The cracks are lined with crystalline siderite, sometimes in sharp contact with the micritic siderite of the fracture walls, but more often appearing to pass gradationally from micrite through dark-brown, increasingly sparry siderite to the yellowish-white crystalline variety, in a texture suggestive of wall-rock metasomatism. The presence of carbonate-fluorapatite as a late-stage mineral crystallized on siderite and millerite has been described recently by Plant and Evans (2005).

The sulphide minerals occur on the siderite and have clearly grown in an open-space environment. Many fine specimens have been recovered over the years (Bevins, 1994), including some of the world's finest examples of millerite, with sprays of lustrous, sometimes twisted, acicular crystals reaching over 4 cm on occasion, and water-clear quartz crystals 3–4 cm in size, locally referred to as 'Merthyr Diamonds'. Of particular note, and still not uncommon today, are small sprays of millerite upon which are threaded bright cubo-octahedra of galena. Sphalerite also overgrows millerite, while chalcopyrite is so infrequently observed in actual contact with millerite that a strict paragenetic relationship has yet to be determined. Siegenite is relatively minor and forms usually microscopic (< 1 mm) octahedra scattered about on the siderite. Pyrite and marcasite are relatively rare within the septarian cracks, although a few fine specimens have been reported (Bevins, 1994). Barite is also rare and is a late-stage mineral. The various waxy long-chain hydrocarbons, such as hatchettite ($C_{38}H_{78}$), occur as orange to yellowish spheroids (Firth, 1971).

The distribution of the claystone–ironstone sulphide minerals has been debated by various authors (see North and Howarth, 1928; Firth, 1971). It has long been suggested that millerite tends to be confined to the part of the coalfield in which high volatile bituminous coals occur, and is apparently absent from the north-western anthracite zone. However, millerite has recently been identified from the anthracite zone, occurring on joints in sandstones associated with quartz, ankerite and chalcopyrite (Bevins and Mason, 2000). This sandstone-hosted mineralization is in fact also widespread throughout the South Wales Coalfield, and at the time of writing was well exposed at the Nant Helen Opencast site, Abercraf (Bevins and Mason, 2000).

At Nant Helen, the sandstones carry a strong set of open, mineralized joints orientated approximately north–south. In some sections, conjugate joint-sets striking north-east–south-west and north-west–south-east, are also mineralized in a broadly north–south obtuse zigzag pattern. East–west joints are unmineralized. The joints are most heavily mineralized above the hanging-wall of a significant N–S-trending, E-dipping normal fault plane (with evidence for a separate phase of strike-slip movement). Away from the fault, the amount of mineralization decreases steadily until, at about 50 m distant, only traces are present. The fault appears to post-date the mineralization, as heavily slickensided quartz and ankerite, in both normal and strike-slip orientations, can be seen on the fault plane.

The mineralization is crustiform in nature, consisting generally of simple, fissure-wall-coatings with a well-defined paragenetic sequence. Initial mineralization consisted of the development of thin (< 1 cm) fibre-quartz spanning slowly opening fissures. However, this eventually gave way to more expansive opening of the joints, with the result that the fibre-quartz crystals developed well-formed terminations where detached from the wall-rock. The second generation of quartz, nucleating upon some of the terminated fibre-quartz crystals, occurs as large (up to 4 cm × 3 cm) crystals of the 'Merthyr Diamond' habit, some occurring as sceptres upon the fibre-quartz and others as flat-lying doubly terminated forms.

Both generations of quartz are overgrown, abundantly in places, by rhombic ankerite (typically 10–20 mm), which is yellowish when fresh but a rich tan-brown where weathered. Additionally, further fracturing accompanied the ankerite deposition, so that in places the ankerite coats otherwise unmineralized rock surfaces, or cements cracked quartz. Sulphides occur sporadically on both ankerite and quartz and are most abundant in the widest, most intensively mineralized, sections of the joints. Chalcopyrite is abundant as scattered 1–3 mm sphenoidal crystals. Millerite is more restricted in occurrence, and seems to occur commonly along joints in certain sandstone beds but is absent from others. Millerite forms characteristic sheaves of acicular crystals up to 3.5 cm, the larger crystals completely spanning the open joints.

Finally, unusual mineralization has recently been recorded from bedding-normal micro-fractures ('cleats') in anthracitic coals in the north-western part of the coalfield (Gayer and Rickard, 1993). As well as a variety of sulphides, lead-selenium minerals and microscopic, collomorphic gold occur within this assemblage.

Interpretation

The blackband ironstones have been interpreted as having been formed as the result of the diagenesis of a 'bog iron-ore'-type precursor, although direct siderite precipitation from iron-enriched tropical swamp waters is also thought to be possible (Young, 1993). The genesis of the brown claystone–ironstone beds and nodules has been the subject of considerable debate (summarized in Young, 1993). They may occur close to marine bands, or within totally non-marine parts of the Westphalian sequence. Typically, the largest ironstone beds were generated within fine-grained sediments which were deposited in a lacustrine swamp environment. Within these sediments, concretions nucleated around organic debris and other 'seeding' agents.

The source of the iron (and minor manganese) could have been soil sesquioxides or unstable silicates (Young, 1993). Microbial oxidation of adjacent organic matter, resulting in the reduction of Fe(III) to Fe(II), also released HCO_3^-, the consequent rise in alkalinity favouring carbonate precipitation. Thus, concretion growth involved the deposition of micritic siderite within the pore spaces of relatively unconsolidated sediments, so that the central part of any concretion has the highest micritic siderite content. These early, and probably rapid, stages of growth may have been initiated under as little as 1 m of sedimentary cover (Curtis *et al.*, 1986). As burial depths increased, concretion growth continued, the final stages, under perhaps a burial depth of several hundred metres (Curtis *et al.*, 1986), producing, in the case of the South Wales ironstones, the characteristic relatively siderite-poor rim.

The formation of the septarian cracks has been the subject of many theories. A popular and long-standing theory, discussed by Astin (1986), involved the existence of an initially soft concretion interior which subsequently dehydrated, leading to formation of shrinkage cracks. However, as Astin (1986) pointed out, the specific nature of the postulated clay-rich centre or precursor gel has not been explained. Furthermore, it is hard to explain the nature of a suitable chemical environment during diagenesis capable of dehydrating clay-rich concretion centres.

Using examples occurring in Jurassic and Eocene strata, Astin (1986) concluded that the septarian cracks developed as stress-induced tensile fractures during progressively deeper concretion burial. Under these conditions, the principal stress involved is the load pressure, related directly to depth of burial. As a consequence of the load pressure, horizontal tensile stresses arise and, for a rock of given tensile strength, tensile fractures will form instantaneously when the effective minimum tensile stress equals the tensile strength.

This theory is attractive, since it explains certain features, in particular the failure of the septarian cracks to reach concretion surfaces. These outer layers, transitional to the mudstone host-rocks, with a much lower micritic siderite content, would have a much lower tensile strength than the intensely cemented inner zones. Under high load pressures, this contrasting rheology would result in progressive plastic deformation of the weak outer zones about the rigid interior, until the effective minimum tensile stress reached the tensile strength of the interior, resulting in the brittle failure of the inner zone.

The mineralization of the septarian cracks within the nodules has yielded important data regarding the P–T conditions under which the assemblages were formed. Alderton and Bevins (1996) examined fluid inclusions in quartz crystals from nodules collected at the landscaped Wyndham Colliery, near the centre of the South Wales Coalfield. Fluids were found to be of low salinity but highly methanoic. The study led to the conclusion that the quartz occurring within the nodules formed at a temperature of around 150° C under a pressure of around 500 bar. More recently, Alderton *et al.* (2004) have compared fluid-inclusion data for samples from the ironstone nodules and from fracture fillings in sandstones (see below), and concluded that the carbonates probably crystallized at relatively low temperatures (< 100° C), whilst the quartz formed at a later stage and at higher temperatures (between 150° C and 200° C). Their evidence of variations in the temperature and composition of the mineralizing fluids which correlate with coal rank variation across the coalfield indicates a probable causal link. Their data also confirmed a geothermal gradient of *c.* 45° C km^{-1} at maximum burial. Such figures suggested a much higher palaeogeothermal gradient in the area than was previously considered. This, combined with other evidence, implies a much higher degree of heat flow than one would expect for a foreland basin setting to the South Wales Coalfield (Kelling, 1988; Frodsham and Gayer, 1997), and the possibilities of other basin development mechanisms, for example lithospheric extension, require further examination (Bevins *et al.*, 1996b).

The recently discovered sandstone joint-hosted mineralization at the Nant Helen Opencast is important because the assemblage in many aspects resembles that of the septarian cracks, suggesting the likelihood that the two styles of mineralization are cogenetic. Additionally, the clearly defined structural trend of the sandstone joint mineralization relates the mineralization to a specific structural regime operating at a specific stage of basin development.

The paragenetic features of the Nant Helen mineralization indicate that it developed over a N–S-trending structural weakness along which tensile stress was focused during regional extension associated with basin deepening. This was relieved initially by the opening of joints, with fibre-quartz development, in the sandstones and by ductile deformation in the mudstones and coals. Increasing tensile stress opened the joints out into small veins and was finally relieved by much larger-scale normal faulting.

Faulting similar to that exposed at Nant Helen is abundant across the whole of the South Wales Coalfield, trending north-west–south-east in the eastern part of the coalfield and NNW–SSE or north–south in the western sector. This intensive fault pattern is consistent with east–west to north-east–south-west extension across the coalfield during basin development. If the fault at Nant Helen is typical, the faulting post-dates the mineralization on the sandstone joints, and the common orientations of both fault and joints suggests that they both developed as part of the same overall process (J.S. Mason, unpublished interpretation).

Similar quartz-bearing sandstone joint assemblages occur in the western extension of the coalfield, for example in coastal exposures in the Saundersfoot district of Pembrokeshire. However, in this area, which lies to the south on the Variscan Front, tectonism has resulted in the shattering of the mineralization, leaving the open joints crammed with the broken shards of the quartz crystals (Bevins and Mason, 2000), indicating that such mineralization clearly pre-dates the Variscan compressive deformation.

Evidence therefore suggests that the mineralization of the South Wales Coalfield is a pre-Variscan, burial metamorphism-/extension-related event within a rapidly subsiding extensional basin (Bevins *et al.*, 1996b; Bevins and Mason, 2000). The age constraints are demonstrable: the mineralization was clearly developed at some point between sediment deposition in early to mid-Westphalian times, and late Westphalian times, when intense deformation occurred which shattered the mineralization at sites south of the Variscan Front.

Methanoic, low-salinity mineralizing fluids (Alderton and Bevins, 1996) were generated from sedimentary porewaters during burial-related low-grade metamorphism under a high geothermal gradient. The fluids remobilized Ni, Co, Cu, Pb and Zn from the sediments (including the ironstones) and re-deposited them upon accessing nearby low-pressure zones, such as tensile fractures, as small amounts of their sulphides, accompanied by quartz, clay minerals and abundant, metasomatically recrystallized siderite (in ironstones) and ankerite (in sandstones). Traces of Au and Se were also deposited, particularly on fracture surfaces within anthracitic coals (Gayer and Rickard, 1993).

As subsidence waned, so did the mineralizing activity, so that the Upper Coal Measures (Pennant Sandstone Formation; Westphalian C-D) is, so far as has been observed, unmineralized. At the end of Carboniferous times the area underwent a period of uplift, folding and thrusting along the east–west Variscan trend. To the south of the Variscan Front, in southern Pembrokeshire, the basin sequence was intensely folded, and in this area the majority of the delicate crystal growths developed during the mineralization event were destroyed.

Conclusions

An important form of mineralization occurs in strata of the South Wales Coalfield, principally within septarian cracks in claystone–ironstone nodules but also on open joints in sandstone beds of Lower to Middle Westphalian (A–C) age. These were deposited in a rapidly subsiding coal swamp basin and rapidly subjected to a steep geothermal gradient and overpressuring as a result of deep burial. Horizontal tensile stresses increased as a consequence of the increasing load pressure and deformed the coals, mudstones and ironstone concretion exteriors plastically, while units of higher tensile strength, such as sandstones and the interior zones of ironstone concretions, underwent brittle failure as the minimum effective tensile stress eventually exceeded their tensile strength. Metals, liberated from the ironstones and associated sediments during porewater migration, were re-deposited as minor amounts of well-crystallized sulphides within the septarian ironstone concretions and on sandstone joints.

MESOZOIC IRON-MANGANESE AND LEAD-ZINC-COPPER-BARIUM MINERALIZATION IN SOUTH WALES

Four discrete types of mineralization characterize the Mesozoic to Recent mineral deposits of South Wales. Three of the mineralization events are of epigenetic origin with respect to their host rocks, whilst the fourth involved the supergene alteration of the earlier events. The epigenetic mineralization comprises oxide-facies iron and manganese ores (represented by the **Mwyndy Mine** GCR site) with superimposed, and often spectacular, metasomatic cavity-fill assemblages, well exposed at the **Ton Mawr Quarry** GCR site. Mississippi Valley-type (MVT) veins carry lead, zinc and minor copper sulphides with associated calcite, fluorite and barium- and strontium-bearing minerals, the age of which is constrained at the **Ogmore Coast** GCR site. The locally intense supergene weathering, which is particularly evident in the MVT veins, has produced mostly common secondary minerals, but locally some unusual assemblages have been recorded, the most complex of which is seen at the **Machen Quarry** GCR site.

MWYNDY MINE (ST 056 819)

Introduction

Iron ores have been extracted from the Dinantian limestones of South Wales since Roman times (Rankin and Criddle, 1985), with activity peaking during the 1500s and again in the 19th and 20th centuries, the last mine to close being Llanharry, in 1974. The ore averaged 48% Fe and total production is estimated to have been in the order of 9.5 million tons (Shepherd and Goldring, 1993). Ore production was strictly related to global demand and availability, as well as to the availability of smelting fuel, both in the form of wood charcoal and coal; hence the rather erratic working pattern through the ages (T.P. Young, pers. comm.).

There are now few obvious remains of this once extensive iron ore industry which formerly dominated the Llantrisant district. However, at Mwyndy Mine (Figure 5.81) a considerable area of tips still remains. Although these are overgrown, small excavations readily reveal representative samples of the style of mineralization worked in these mines, namely oxide-facies iron (and less-frequent manganese) ores.

The ores consist of goethite, hematite, quartz and a range of late accessory phases. Originally, they were believed to be of supergene origin (Sibly and Lloyd, 1927). Williams (1958), however, challenged that theory, suggesting that the ores had been emplaced by ascending

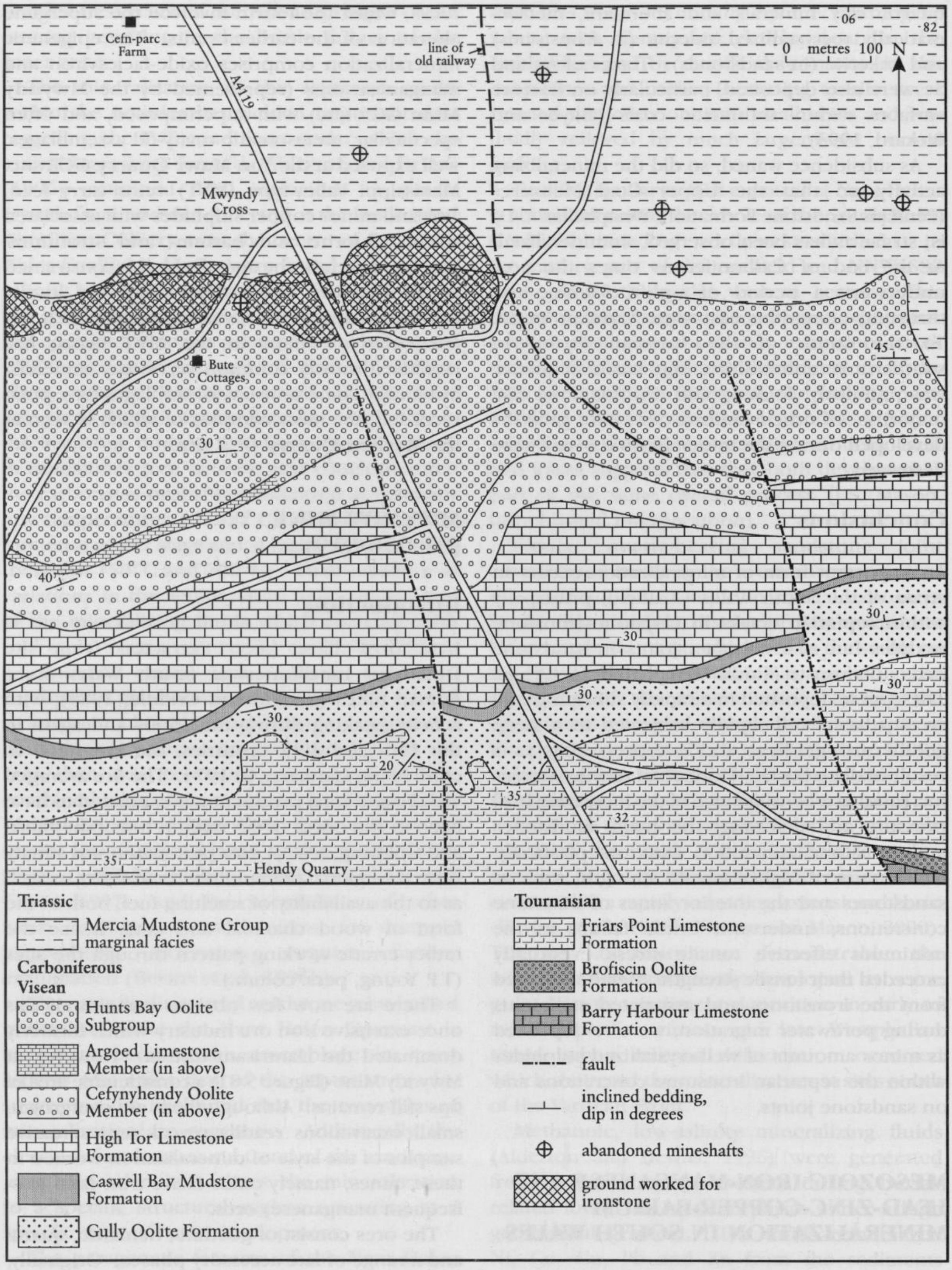


Figure 5.81 Map of the Mwyndy Mine GCR site. Based on British Geological Survey 1:50 000 sheets 261 and 262, Bridgend (1989b), and Institute of Geological Sciences 1:10 000 Sheet ST08SE (1984).

hydrothermal fluids during Miocene times, thus linking the mineralization to tectonic disturbances during the Alpine Orogeny. Conversely, Gayer and Criddle (1969) were able to demonstrate that the ore distribution was controlled in fact by Variscan fracture patterns, and that the mineralization was itself cut by faults of probable Alpine age.

Evidence, in the form of detrital hematite and fragmented quartz crystals, within strata of Rhaetian age from the Bridgend area, led Gayer and Criddle (1969) to conclude that the ores were most probably of late 'Keuper' (Triassic) age. Rankin and Criddle (1985) also concluded that the ores were pre-Jurassic in age, citing the Mendips as an analogy, where unmineralized Jurassic sedimentary rocks lie directly upon Dinantian limestones containing Fe-Mn oxide ores.

Fluid-inclusion studies, carried out by Rankin and Criddle (1985) on calcite and quartz samples from Llanharry Mine, yielded homogenization temperatures and salinity data indicating that the mineralization was deposited from alkaline fluids of relatively low temperatures (30°–98° C) and bimodal salinity (2–10 wt% and 10–24 wt% equivalent NaCl). They suggested that the mineralization was emplaced in late Triassic times, involving groundwaters that leached Fe (and Mn) as they passed downwards through the Triassic strata. Such groundwaters, derived from the extremely saline sabhka environments that existed in this part of South Wales during late Triassic times, would have also been capable of dolomitizing the limestones which they passed through, a feature widespread in the vicinity of these iron deposits. Rankin and Criddle (1985) suggested that these descendant, iron-rich fluids had probably interacted with hotter fluids rising up the Variscan fracture systems within the Dinantian strata, to create a fluctuating hydrothermal system which deposited the iron mineralization in a rhythmic manner, leading to banded mineral deposits.

Rankin and Criddle (1985) observed also that the fluid-inclusion data from Llanharry Mine were not incompatible with results which would be expected for MVT Pb-Zn mineralization, and they noted that there were showings of such mineralization in the Llantrisant area. The lack of significant Pb-Zn mineralization in the vicinity of the Mwyndy iron deposits was interpreted, albeit speculatively, as being due to the low brine fluid temperatures (< 100° C), MVT fluids typically being between 80°–200° C.

Shepherd and Goldring (1993) suggested that an alternative interpretation of similar fluid-inclusion data from both the west Cumbria and South Wales iron ore deposits was for initial, low-temperature fluid descendant iron mineralization, followed by higher-temperature mineralization along pathways through the iron ore. This is in accordance with newly described evidence seen at both the **Mwyndy Mine** and the **Ogmore Coast** GCR sites (Bevins and Mason, 2000) which indicates that the cavity-fill quartz, calcite and barite mineralization of the South Wales iron mines could have been deposited by rising MVT fluids percolating through pre-existing iron oxide deposits.

Description

All of the South Wales goethite-hematite ore deposits occur to the south of the South Wales Coalfield and are hosted by carbonate sequences of Dinantian age, overlain to the north by Namurian shales, in the 'south crop' of the coalfield. The limestones were tilted to the north or NNW by Variscan deformation and subsequently eroded in an arid climate during Permo–Triassic times. Progressive subsidence in late Triassic times, prior to the Rhaetic marine transgression, led to the gradual burial of much of this eroded Carboniferous surface by mudstones of the Mercia Mudstone Group. In topographically high areas, flash floods led to the deposition of breccias and clast-supported conglomerates (previously called the 'Dolomitic Conglomerate'), consisting chiefly of subangular fragments of Carboniferous-age limestone, filling hollows in the erosion surface.

The iron ore deposits at Mwyndy, and elsewhere in the immediate vicinity, usually occur within 150 m of the eroded surface of the tilted Carboniferous strata. Typically, limestones are pervasively dolomitized and hematized in wide zones around the orebodies. Hematization and dolomitization of Dinantian limestones is in fact common throughout its outcrop to the south of the coalfield and is much more widespread than are the actual orebodies, giving the soils in the vicinity of the orebodies a characteristic deep-red colour. The overlying

Triassic conglomerates are also hematitic, but to a lesser extent, and the conglomerates appear to have formed a cap to the high-grade iron mineralization, as at Llanharry, described by Rankin and Criddle (1985).

At the iron mines of the south crop area, including Mwyndy, good exposures of the mineralization are lacking, due to most of the open workings having been backfilled. Those that remain reveal little information regarding the structural character of the mineral deposits, except that they formed irregular, but broadly linear, massive fracture-fills and replacements (possibly palaeokarstic in part) of the limestones along WSW–ESE-trending lineaments.

Hand specimens of iron ores from the tips at Mwyndy Mine show the ore to consist typically either of earthy to massive, often banded goethite or hematite. Goethite-dominated ore, which is certainly the commonest material seen on the tips at present, comprises massive to banded goethite, the latter variety containing intergrown quartz along some bands. Vugs in this ore are lined with goethite stalactites and quartz, calcite and barite. Crystalline goethite may coat, and form inclusions in, the quartz and calcite, imparting a smoky colour to them.

Massive, siliceous hematite ore was known traditionally by the miners as 'blue-ore', due to its steel-grey colour. Cavities within the 'blue-ore' hematite contain both crystalline quartz and specular hematite, which, by analogy with the goethite ore, occur in several superimposed generations. Calcite and barite are again associated phases.

Pyrite is not uncommon on the tips at Mwyndy Mine, where nodular aggregates of modified pyrite cubes up to 15 mm in diameter occur as fist-sized lumps in the tips nearest the Barn public house. These pyrite aggregates, overgrown by traces of barite, have been pseudomorphed by mid-brown goethite, although locally fresh pyrite remains in the inner parts of the nodules. Such pseudomorphs are widespread throughout this part of South Wales but the replacement is usually total. Chalcopyrite was reported from this site by North (1916), but its paragenetic position is unclear; in polished section the pyrite is free of other inclusion-forming sulphides.

Calcite is an abundant mineral in these iron ore deposits and formerly occurred as well-developed nailhead and scalenohedral crystals (Rankin and Criddle, 1985; Bevins, 1994). It is common at Mwyndy Mine as cavity-fills, and particularly as veins cutting hematized limestone. Barite occurs as well-formed, euhedral, tabular crystals, and some fine specimens were preserved when the mine was working, including an exceptional, doubly terminated 50 mm, yellow-brown barite crystal (Figure 5.82) in the National Museum of Wales collection (Bevins, 1994). Barite is clearly a late-stage mineral; in addition to occurring on pyrite pseudomorphs and in cavities in hematite and goethite, it is present within massive iron ore, as thin, cross-cutting veinlets. Barytocalcite, again a late-stage mineral, is present as rare, yellowish, bladed crystals up to a few millimetres in length.

The iron ores of South Wales thus have a straightforward paragenetic sequence in general terms, comprising initial goethite-hematite-quartz-pyrite deposition, followed by cavity infilling and cross-veining by euhedral quartz, calcite, barite and barytocalcite, the quartz and calcite being overgrown by goethite and specular hematite in places.

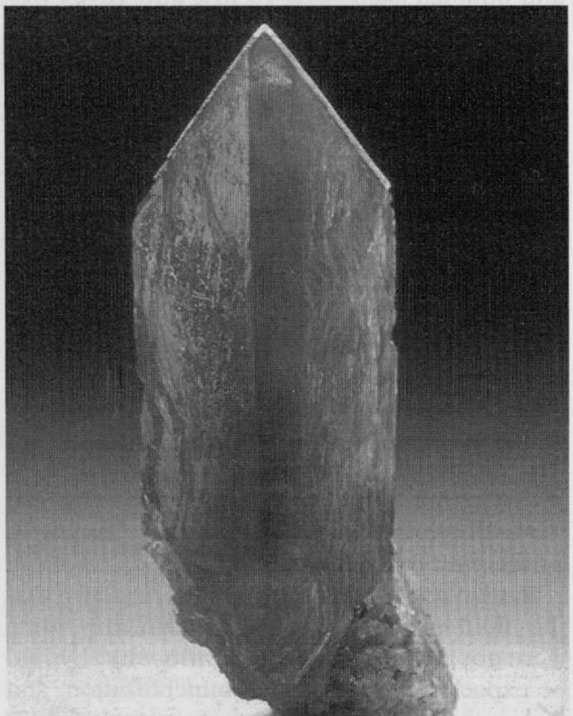


Figure 5.82 Photograph of barite from the Mwyndy Mine GCR site. (Photo: M.P. Cooper, © National Museum of Wales.)

Interpretation

This oxide-facies class of iron and manganese ore deposit is unusual in global terms (Shepherd and Goldring, 1993), being represented in Great Britain by significant orefields in west Cumbria, the Forest of Dean and the South Wales–Mendip area. In each case the ores occur in near-surface Dinantian limestone sequences overstepped by red-bed-type sedimentary rocks of Permo–Triassic age; the host limestones are hematized and dolomitized and the ores tend to occur along pre-existing Variscan fracture systems. The genesis of the deposits has been successively re-interpreted, but a central theme is that the iron must have been supplied from the overlying red-beds by downward migration of hypersaline brines.

Paragenetic studies of the mineralization all point to early, colloform-banded iron oxides and silica being overprinted by crystalline quartz, iron oxides, calcite and finally barite. It has recently been suggested (J.S. Mason, unpublished interpretation) that the late-stage, cavity-filling minerals may have been formed during a transition from descending, iron-rich groundwaters in late Triassic times to ascending, MVT fluids in early Jurassic times. That such fluids were active then is readily demonstrated at, for example, the **Ogmore Coast** GCR site, where intense Pb-Ba mineralization cuts and impregnates sedimentary rocks belonging to the Lower Lias, of Hettangian age (Fletcher, 1988).

This hypothesis is in accordance with the alternative interpretation of the West Cumbria Orefield proposed by Shepherd and Goldring (1993), and is further supported by relationships at the **Ogmore Coast** GCR site, where calcite-barite-galena veins cut and brecciate hematized limestone. This would suggest that, since the hematization is believed to be cogenetic with ore formation, that the MVT Pb-Ba mineralization post-dated the oxide-facies iron mineralization.

Mason's new interpretation, reported by Bevins and Mason (2000), may be summarized thus: warm, hypersaline, alkaline, Mg-rich brines percolated through the Keuper marls during late Triassic times to access Variscan fracture-controlled pathways (and perhaps palaeokarstic fissures) in the Dinantian limestones, after passing first through the relatively permeable conglomerates, breccias and sandstones of the Mercia Mudstone Group. They leached metals, in particular Fe and Mn, and their subsequent reaction with the Dinantian limestones resulted in dolomitization and hematization. Due either to metasomatic reactions with the Dinantian limestones, or the mixing of ascendant and descendant fluids, layers of iron and manganese oxides, with quartz, were deposited in the upper part of the limestone sequence and, locally, in the Mercia Mudstone Group. Conditions at times permitted the iron to precipitate as pyrite. During Rhaetian times, as crustal subsidence increased, basin development in the Bristol Channel began to generate deep-seated, hot, MVT fluids which, in their circulation, found their way back up the same fracture systems. These deposited calcite, quartz, and finally barite, percolating through the vuggy iron ores to fill cavities, or in some cases lining new fractures, which cut the hematized limestones and iron ores. Initially, mixing of fluids from above and below continued, with the deposition of the oxide facies (i.e. goethite and specular hematite) within developing quartz and calcite. However, this was relatively minor compared to the bulk of the iron ore which had already been emplaced by this time, and may have been due to iron-oxide recrystallization. Evidence from the **Ogmore Coast** GCR site suggests that this phase of mineralization was followed by more typical MVT calcite-barite-galena-sphalerite-dominated mineralization.

Fluid-inclusion data for the West Cumbria and South Wales iron deposits, taken from quartz, calcite and fluorite in the West Cumbria Orefield (Shepherd and Goldring, 1993), and quartz and calcite from South Wales (Rankin and Criddle, 1985) are remarkably similar. Both data-sets show that these minerals were deposited from highly saline (up to 24 wt% NaCl equivalent) calcium- and magnesium-rich alkaline brines at temperatures of 84°–121° C (West Cumbria) and up to 98° C (South Wales). These temperatures are rather high for simple descendant brines originating in a sabhka environment, as recognized by both sets of authors. However, if these minerals had been deposited in cavities in pre-existing hematite-goethite by rising fluids, then the fluid-inclusion data would merely refer to the fluids which deposited the late cavity-fill minerals and not the banded hematite and goethite, which could then have been deposited at a much lower temperature, a possibility recognized by Shepherd and Goldring (1993).

Conclusions

The iron oxide mineralization at Mwyndy Mine is controlled by the juxtaposition of Dinantian limestones, with attendant Variscan fractures and Triassic red-beds. The iron was probably sourced by sabhka brines leaching Mercia Mudstone Group rocks and then entering the Variscan fractures via the more permeable conglomerate, breccias and sandstones. Later, cavity-fill minerals, upon which the fluid-inclusion data are based, were deposited from hot, hypersaline brines of MVT affinity, as the style of mineralization transferred from oxide-facies Fe (and Mn) to MVT Pb-Zn-Ba.

TON MAWR QUARRY (ST 115 823)

Introduction

This relatively small quarry, situated near Taff's Well to the north of Cardiff (Figure 5.83), exposes an excellent example of the Dinantian-hosted, metasomatic cavity-fill mineralization which is developed to varying degrees throughout the Dinantian outcrop in South Wales. Fresh exposures of this type of mineralization are limited to the few working quarries in the area, and, in both mineralogical and practical terms, Ton Mawr Quarry provides an excellent representative example (Bevins and Mason, 2000).

The metasomatic cavity-fill type of mineralization has long been known from the Taff's Well area. Greg and Lettsom (1858) referred to the large calcite crystals once found in quarries at Castell Coch, in the rock-faces which now overlook the A470 near to its junction with the M4. More recently, specimens of calcite and barite from the neighbouring, much larger, Taff's Well Quarry were illustrated by Bevins (1994). However, the paragenesis of the cavity-fill mineralization, as seen at the Ton Mawr Quarry GCR site, has not been studied in any detail, in comparison to the oxide-facies iron ores and the MVT lead-zinc vein mineralization, and their relationship merits examination.

Figure 5.83 Map of the Ton Mawr Quarry GCR site. After Institute of Geological Sciences 1:10 000 Sheet ST18SW (1979).

Description

Ton Mawr Quarry (Figure 5.84) exploits Dinantian-age limestones which dip regularly northwards at up to 30°, due to Variscan tilting. The abundant mineralization falls into two categories. Firstly, there are iron oxide deposits, which take the form of limestones reddened due to hematite impregnation, with occasional pod-like masses of more massive goethite (iron ore), overgrown by quartz, often of a smoky to amethystine colour. These are, however, relatively minor examples of the major iron ore deposits which were formerly worked along the Dinantian outcrop from Rudry westwards to Llanharry, and are described in the **Mwyndy Mine** GCR site report (this chapter).

Secondly, there are the crystalline, metasomatic cavity-fill deposits, which are the focus of interest at this site. Two generations of calcite are present; firstly there are large, irregular cavities, which have previously been noted in the area reaching up to several metres in diameter, and which are filled with massive to crystalline calcite. The calcite varies from white through to yellowish in colour; the coloured varieties contain small goethite inclusions. Crystals, which have a typically scalenohedral habit, exceed 15 cm in length, and are almost invariably covered in a second generation of rhombic calcite, giving the crystals a 'stepped' appearance; although impressive in size terms, they are generally, in the words of North (1916), to be 'of such a nature as to be looked at rather than collected'.

The second generation of calcite, already referred to as coating the large scalenohedra, occurs abundantly in complex, multiply stacked groups of planar solution-voids, typically 200–300 cm^2 in area and 10–40 mm in depth. In orientation terms, they are virtually flat-lying and appear to have propagated upwards through the hematized and dolomitized limestone via open joint-fractures. The ubiquitous calcite-fill manifests itself as coatings of sharp, lustrous rhombic crystals, often of a reddish colour, and reaching 15 mm in size. Less frequently, attractive pink to white, bladed barite is present; specimens indicate that the barite is early in this

Figure 5.84 Photograph of the Ton Mawr GCR site showing well-bedded limestones dipping to the NNW. (Photo: L. Garfield.)

paragenesis as it is overgrown by the rhombic calcite generation.

Interpretation

The formation of the metasomatic features seen in Ton Mawr Quarry is of considerable scientific importance, for the dissolution of the limestone in this manner indicates that it was attacked by particularly aggressive groundwaters. The development of the mineralization is constrained at Ton Mawr by two important observations. Firstly, the flat-lying, stacked, planar cavities are discordant to bedding, which dips regularly to the north as a result of Variscan tilting. The cavities appear to have formed by the horizontal migration of aggressive fluids outwards from conduits such as joint fractures: therefore, the stacked metasomatic cavities probably post-date the Variscan tilting. Secondly, the fluids have metasomatically attacked dolomitized and hematized limestone, carrying scattered iron ore pods. Extensive replacement of hematized limestone appears to have been the mechanism by which the calcite crystals lining these cavities have taken on a reddish colouration in places, due to included fine-grained residual hematite. It can therefore be surmized (J.S. Mason, unpublished interpretation) that the formation of the stacked, planar cavities also post-dates the oxide-facies iron mineralization.

The more irregular, large cavities lined with the 'giant calcite' crystals strongly resemble those described from the underground workings of the Llanharry iron mine, near Llantrisant, by Rankin and Criddle (1985). At Llanharry, cavities up to 3 m in section were noted to be lined with scalenohedral calcite crystals up to 0.6 m in length. Rankin and Criddle (1985) also reported that the calcite crystals contained goethite inclusions and were coated by a final generation of rhombic crystals. The highly irregular shape of many of the coarse, calcite-lined cavities at Ton Mawr Quarry is suggestive of filling of pre-existing, possibly palaeokarstic voids.

Barite was apparently the earliest 'spar' mineral to crystallize during this metasomatic episode, as it is overgrown by the rhombic calcite and, in addition, has been seen in the neighbouring Taff's Well Quarry to be overgrown by the coarse, scalenohedral calcite. The generalized paragenetic sequence of the mineralization at Ton Mawr Quarry is, therefore, iron oxides-quartz-barite-coarse calcite-rhombic calcite, the mineralizing process involving metasomatic replacement of host-rock carbonate throughout.

The fact that such parageneses, and various modifications thereof, have been reported throughout the iron-oxide mining district (Rankin and Criddle, 1985) is suggestive of an extensive, open system in which the introduced fluids superimposed successive generations of mineralization as they attacked the carbonate host-rocks; the more the host rocks were attacked, the more permeable pathways were created through them. It is perhaps surprising, therefore, that the cavity-fill assemblage of the iron-oxide mining district nowhere contains base-metal mineralization (Bevins and Mason, 2000). Such mineralization, of Mississippi Valley-type (MVT) affinities, is widespread in the Dinantian rocks that crop out to the south of the South Wales Coalfield. However, it is apparently restricted in its occurrence within the Dinantian strata to linear, re-activated Variscan fractures, only spreading out laterally to fill cavities where developed in the overlying marginal conglomeratic facies of the Triassic Mercia Mudstone Group and the marginal shelly limestones of the succeeding Lower Lias, as described at the **Ogmore Coast** GCR site.

Conclusions

The occasionally spectacular, vuggy mineralization exposed in the working Ton Mawr Quarry was formed by the reaction between dolomitized and hematized Carboniferous limestones of Dinantian age and aggressive hydrothermal fluids migrating through the tilted strata. The sequence of deposition indicates a transition from barite deposition through to calcite, although the lack of base-metal ores in the cavity-fill assemblage is a curious feature. It is inferred that the cavity-fill assemblage represents a mineralizing event developed after the oxide-facies iron mineralization event and before the later Mississippi Valley-type base-metal-bearing mineralization event in this part of Wales.

OGMORE COAST (SS 871 741, SS 885 727)

Introduction

This critical site comprises a coastal section between Ogmore-by-Sea and the headland of Trwyn y Witch, near Southerndown (Figure 5.85), and is fully accessible only at low tide. It is of major metallogenic importance for three reasons; firstly, it is of relevance with respect to the timing of the MVT Pb-Zn-Cu-Ba mineralization of the South Wales–Mendip Orefield; secondly, the relationship of the oxide-facies Fe-Mn mineralization sporadically developed throughout the district, to the MVT mineralization is clarified; and thirdly, evidence is seen for a further, post-early Jurassic phase of metalliferous vein mineralization.

Neither lead nor iron have been worked at the Ogmore Coast GCR site: the exposure is entirely natural, occurring along a series of wave-cut platforms and cliff sections. Inland, there are a number of largely obliterated, small, trial workings for lead in the area between the Ogmore Coast site and Bridgend, and Fe-Mn ores have been extracted at the Tŷ Coch Mine, near Porthcawl (SS 828 795). The latter site is of considerable mineralogical importance due to the occurrence of the Pb and Pb-Mn vanadate minerals vanadinite and pyrobelonite (Criddle and Symes, 1977). Wulfenite has also been reported (Braithwaite and Lamb, 1986). However, there are only scattered samples of the manganese and iron ore in small remnants of tips and in farm tracks, and the site now yields little information regarding the geology of the deposit.

The importance of the Ogmore Coast GCR site was determined only recently, following mapping of the Bridgend sheet (British Geological Survey, 1990). Its importance relates to the fact that it categorically demonstrates that Pb-Ba-dominated mineralization post-dated the initial marine transgression which occurred in the area during late Triassic to early Jurassic times. Moreover, the evidence, superbly exposed in these wave-cut platforms, indicates that the mineralization occurred during the ongoing transgression, and is considered to have been exhalative into the marine environment (Fletcher, 1988).

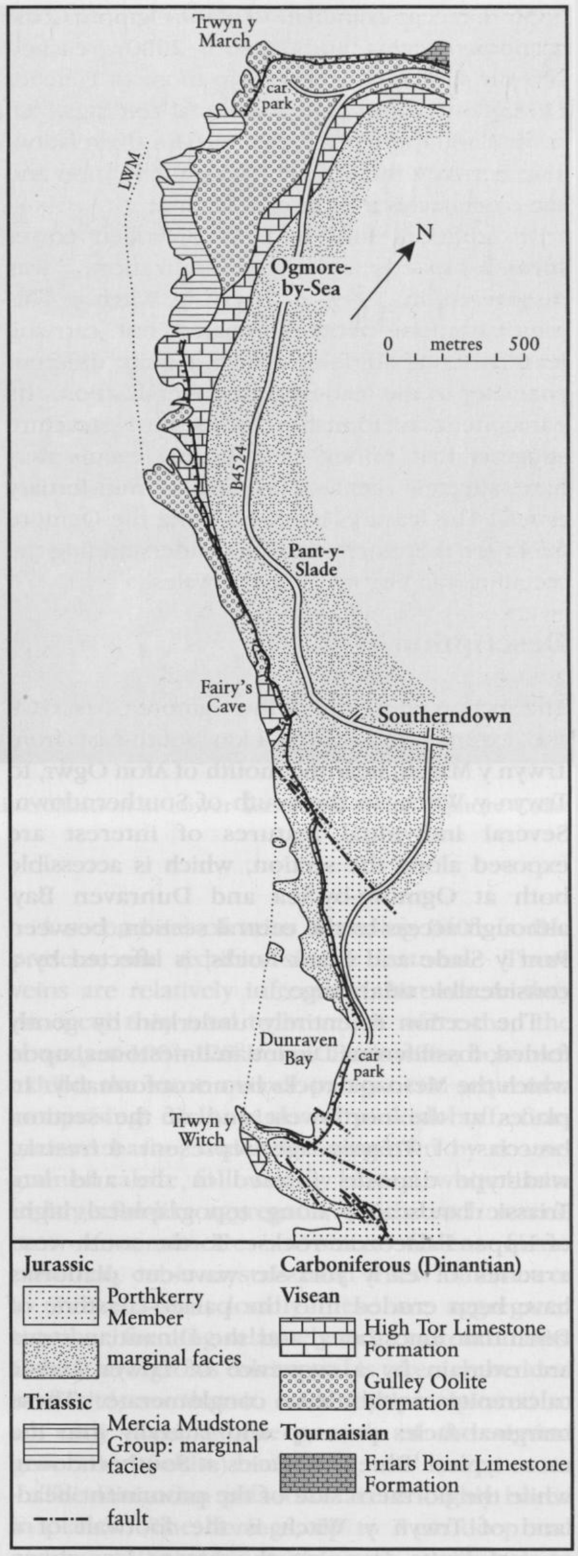


Figure 5.85 Map of the Ogmore Coast GCR site. After Wilson *et al.* (1990).

More-recent examination of the Ogmore Coast sections (Bevins and Mason, 2000) reached broadly similar conclusions to those of Fletcher (1988) but with some additional findings. Of particular importance is evidence for the relationship between the MVT Pb-Ba mineralization and the oxide-facies iron mineralization.

In addition, further, fault-controlled Lower Jurassic-hosted vein mineralization, was discovered in 1999 at Trwyn y Witch. This mineralization, pyrite-dominated but carrying lead and zinc sulphides, is of a quite different character to the lead-barium mineralization. Its paragenetic relationship to its host structure suggests that minor metallogenic events may have affected the area as late as mid-Tertiary times. The features exposed along the Ogmore Coast are therefore critical to understanding the metallogenic history of South Wales.

Description

The section of interest at the Ogmore Coast GCR site extends for nearly 4 km south-east from Trwyn y March, near the mouth of Afon Ogwr, to Trwyn y Witch, to the south of Southerndown. Several individual features of interest are exposed along the section, which is accessible both at Ogmore-by-Sea and Dunraven Bay, although access to the central section, between Pant y Slade and Black Rocks, is affected by a considerable tidal range.

The section is entirely underlain by gently folded, fossiliferous Dinantian limestones, upon which the Mesozoic rocks lie unconformably. In places at the north-west end of the section, breccias of Triassic age represent terrestrial wadi-type deposits formed in the arid late Triassic landscape, along topographical highs of Upper Palaeozoic rocks. To the south-west, a series of early Jurassic wave-cut platforms have been eroded into the palaeo-coastline of Dinantian limestones, and the Dinantian strata are overlain by a sequence of Lower Liassic calcarenites, with a basal conglomerate. These marginal facies pass up and laterally into the more typical 'Blue Lias' facies at Southerndown, while the northern side of the prominent headland of Trwyn y Witch is the footwall of a normal fault, dropping the Lower Lias down against the Dinantian rocks, which constitute the headland.

Mineralization along the section takes a variety of forms, from what might be considered typical, Dinantian carbonate-hosted MVT veins to complex, and perhaps syn-sedimentary deposits, occurring at and just above the unconformity (Figure 5.86), and finally fault-hosted vein mineralization occurring at even higher stratigraphical levels. The mineralization is described from north-west to south-east along the section.

Along parts of the north-western end of the section, the eroded surface of the Dinantian strata is seen to be impregnated with earthy red hematite. This hematization extends down into the limestone to varying degrees but is particularly marked where it has followed Variscan joints and also where it has partially replaced calcite occurring in tension-gash sets, again interpreted as being related to Variscan deformation. In both cases, this has resulted in the formation of thin (< 1 cm), red hematite veins. In the vicinity, upper surfaces of affected limestone beds often have a bleached appearance.

The Dinantian limestones of South Wales host a number of significant hematite deposits, particularly in the Llantrisant area (see **Mwyndy Mine** GCR site report, this chapter), but in many exposures, both adjacent to the orebodies and in areas where no orebodies are known, their hematization, particularly along joint systems, is a notable feature. At the Ogmore Coast site, the hematized limestones and thin joint-veins of hematite are cut by clean, MVT calcite-barite-galena veins. This important relationship is discussed below in more detail.

The wadi-type deposits at the north-western end of the exposure form a chaotic ridge, approximately 60 m in width and 10–15 m in thickness, extending from the top of the low cliffs seaward across the extensive platform. The clast-supported breccia deposits consist of angular fragments of Dinantian limestone, randomly arranged and largest in the upper part, where they reach several metres across. They occupy a shallow channel, cut into the Dinantian strata, and are both cemented and veined by calcite and barite, with galena present locally. Several generations of cement minerals are discernable by careful examination (Lee, 1991). The veins cut both the breccia matrix and, in places, the clasts.

To the south-west, where Jurassic marine sedimentary rocks overlie eroded platforms of Dinantian limestones, MVT epigenetic veins, carrying calcite with barite and galena,

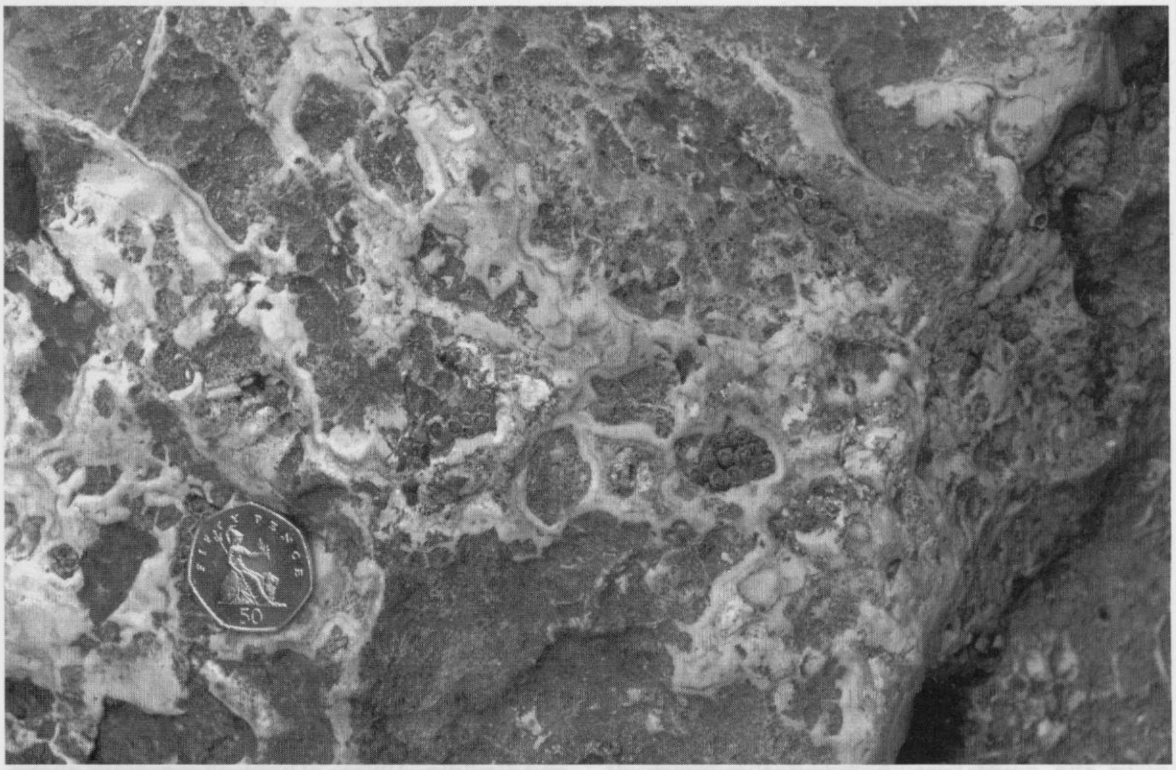


Figure 5.86 Photograph of calcite, barite and galena mineralization in Lower Lias strata at the Ogmore Coast GCR site. (Photo: S.R. Howe.)

are of frequent occurrence within the Dinantian rocks. These pass upwards into the basal Jurassic conglomerates and overlying sandstones, where the mineralization takes on a number of forms. At the unconformity, palaeokarstic fissures are common in the Dinantian limestones. They are particularly prevalent on a 100°–120° trend, along which the limestones have been dolomitized, prior to the development and infill of solution cavities. The dolomitization manifests itself as brownish zones, usually a few tens of centimetres in width. The fissures have been filled with rounded to subangular clasts of both limestone and dolomitized limestone, to depths of over 1 m in places. The same fractures have then opened up, so that veins within the Dinantian rocks pass up into mineralization occurring as cements to these palaeokarstic fissure-fills. However, the fissure-fills are not affected in their entirety, so that while some zones are severely impregnated by calcite, barite and accompanying galena, others nearby are almost devoid of minerals. Where present, the minerals occur typically as rims about the clasts.

A second set of veins, trending 040°, is also present, and exhibits similar features. These veins are relatively infrequent, but where they do occur they tend to be much wider than the abundant 100°–120° veins. Both veins, however, exhibit the same overall paragenetic sequence, comprising early, pink to pinkish-buff, fine-grained barite, which is overgrown by coarse-grained calcite, followed by bladed, white barite in large fan-like aggregates which reach several tens of centimetres in size. Galena forms euhedral, cubic crystals from a few millimetres to 3 cm in size; locally these are aggregated together, forming relatively rich concentrations. Galena overgrows calcite and is often embedded in barite, so that it evidently precipitated at an early stage in the growth of the second generation (white) barite.

The Dinantian palaeosurface is highly bored in places. The borings, up to 7 cm deep and a few millimetres wide, are attributed to *Trypanites* and the lamellibranch *Lithophaga* sp. (Fletcher, 1988), and where not completely filled by Liassic sediment have been mineralized by coarse-grained calcite.

Further mineralization extends upward into the basal Lias, where solution cavities have formed both in the basal breccias and in the overlying strata. These features are most prevalent along the Slade Trough, between Ogmore-by-Sea and Southerndown. This feature, described by Fletcher (1988), is a dip in the unconformity, up to 10 m deep and 200 m wide, so that the basal Lias is exposed at the present-day sea-level. Here, the basal breccias are relatively thick (up to 2 m) and are overlain by calcarenites and coquinoid limestones. Mineralization occurs in flat-lying cavities, 10–40 cm in length and width and 5–15 cm in depth. The floors of these cavities are highly embayed, while the roofs are relatively bedding-parallel. The cavity-fill consists of a lower layer of fine-grained, banded, geopetal sediment, which is capped by up to 6 cm of coarse calcite. Barite occurs firstly as a fine-grained buff-coloured cement to the geopetal sediments, and secondly as white to pink, crystalline deposits both overlying the calcite and in veinlets cutting the geopetal sediments.

To the south-east, between the beach at Dunraven Bay and the headland of Trwyn y Witch, the Lower Lias consists of the 'normal' facies of alternating limestones and dark-grey shales. Mineralization in the Lias is limited to thin, calcite-bearing joint-veins within the limestones. However, the south-eastern end of Dunraven Bay is marked by a major fault which juxtaposes 'normal' Lower Lias against the basal facies and, towards the tip of the headland, the underlying Dinantian limestones. Along the length of the fault plane, which dips steeply to the SSE, is sporadically developed vein mineralization.

The veining is up to 0.5 m in width and consists of calcite, with up to 70% pyrite. Both minerals have a shattered and re-cemented appearance, and the vein is devoid of open vugs. Galena and sphalerite both occur in trace amounts, forming thin (1 mm), but often persistent, veinlets cutting the deformed pyrite and calcite. The mineralization does not occur as a single continuous vein, but as a number of elongate boudin-like pods within the fault-gouge comprising sheared Liassic shale and limestone. In polished section, a depositional sequence of galena overgrown by pale, banded sphalerite is seen. Both galena and sphalerite enclose pyrite, but it is uncertain whether this pyrite represents a second generation or merely represents cataclastic pyrite debris overgrown by the lead-zinc sulphides.

Interpretation

The fact that MVT calcite-barite-galena veins cut hematized Dinantian limestones and also thin joint-veins of hematite is of critical importance in understanding the pattern of metallogenesis in South Wales. It is highly likely that this hematization represents the regional oxide-facies iron mineralization present in the Dinantian limestones in the Bridgend–Porthcawl district, and that therefore the oxide-facies mineralization pre-dates the MVT Pb-Ba mineralization of the South Wales Orefield. The age of hematization is constrained by the fact that it is cut by MVT veins which are of early Jurassic age, based on the relationship between the MVT mineralization and the lowermost Jurassic strata. This suggests that the hematization is of Triassic age, an inference in accordance with the postulated late Triassic age for the oxide-facies iron mineralization (Rankin and Criddle, 1985). These observations therefore are of importance in the interpretation of the genesis of the iron ores, as discussed in the **Mwyndy Mine** GCR site report, and serve to support the conclusions presented.

The age of the MVT mineralization itself is constrained by the fact that it is restricted to the marginal facies of the basal Lias, and is certainly not seen in the 'normal' Lias at Southerndown. The textures of the mineralization led Fletcher (1988) to conclude that it was deposited from fluids exhaled into the marginal Liassic sediments near to surface, the cooling of the fluids causing galena and barite to precipitate from solution. The exact timing is unclear, but the fact that this mineralization is restricted to the basal Lias around topographical highs of Dinantian limestone and is not present in higher beds is supportive of an early Jurassic age. As a rule, exhalative mineralization is developed when hydrothermal fluids discharge onto the seafloor, forming stratiform, often bedded, mineral deposits. However, evidence for this type of mineralization in the Upper Triassic–Lower Jurassic strata of South Wales is scant; the only documented occurrence is in Rhaetian black-shales exposed along the disused railway cutting, *c*. 1 km to the south-east of Cowbridge, where galena crystals (or cerussite-bearing cavities thereafter) have been recorded scattered through the rock

(Willey, 1970). Given the amount of galena and barite exposed along the Ogmore Coast section, one might expect true sedimentary exhalative Pb-Ba mineralization to be of more widespread occurrence in the South Wales area. Perhaps the rate of sedimentation was too great to permit the concentration of these minerals in recognizable amounts, except during occasional periods when euxinic environments with low sediment input prevailed, resulting in lithologies like the Rhaetian black-shales described by Willey (1970).

The Pb-Ba mineralization occurring in karstic fissures in the Dinantian limestones, which are filled by Lower Jurassic conglomerates, is epigenetic with respect to the conglomerates, since the fissures have clearly re-opened to an extent in places. Furthermore, in some fissures only a part of the conglomerates have been mineralized along a clear line of pervasive microfracturing, which has permitted the fluids to deposit minerals around the conglomerate clasts. Wider zones of mineralization in the same fissures reveal crustiform deposition of calcite, barite and galena in open zones between walls of re-cemented conglomerate.

The cavity-fill structures of early Lower Jurassic age were formed when hydrothermal solutions entered solution cavities floored with geopetal sediment, the replacement of the latter by barite possibly being of metasomatic origin. Again, there are epigenetic features present, such as the development of crystalline barite in thin, cross-cutting veins that traversed the geopetal sediment.

Exposures in the north-western part of the section show that the mineralization was at least partly epigenetic with respect to the Triassic breccias, for some veins cut straight through clasts in the breccias. However, the cement-like calcite-barite developed locally could either be very early (diagenetic) or alternatively be an epigenetic filling of voids within these highly permeable, clast-supported deposits.

The veining along the fault at Trwyn y Witch is clearly younger than the unconformity-related deposits at the Ogmore Coast site, since it occurs at much higher horizons in the Lower Lias. Additionally, it is wholly different in character, not only since it occurs on a major fault-fracture but also since it consists largely of pyrite-calcite; barite is absent, while galena and sphalerite occur only in minor cross-cutting veinlets.

The deformation of this mineralization into a series of pods within the gouge of the fault zone suggests that it pre-dates the main movement on the fault, which is a re-activated Variscan fracture (Perkins *et al.*, 1979). The deformation is intense and includes the cataclasis of pyrite and recrystallization of calcite; the minor Pb-Zn sulphide veinlets cut the deformed minerals. The fault has an apparent polyphase history of activity; its SSE dip, but with older rocks in the hangingwall, shows that the final movement was reverse in nature, a movement consistent with compressive stresses acting from south to north and probably connected to the Alpine Orogeny of Miocene age. Such reversed movement would better explain the intensity of the pyrite-calcite deformation, and would suggest that the pyrite-calcite mineralization is post-Liassic/pre-Miocene in age, while the cross-cutting galena and sphalerite veinlets represent a still younger, if minor, phase of metallic mineralization.

Fault-controlled rifting along ENE–WSW-trending fractures was associated with the development of the Mesozoic Bristol Channel Basin (Nemcock and Gayer, 1996). The basin was initiated during Permo–Triassic times and rifting then occurred episodically through to early Cretaceous times, with the accumulation of 1–2 km of shallow-water calcareous marine sediments (Nemcock *et al.*, 1995). Inversion of the basin occurred in early Tertiary times, and much of the Mesozoic sequence was then eroded away onshore, leaving only Triassic and Lower Jurassic rocks exposed.

The fault at Trwyn y Witch is interpreted as being active during the extensional phase of basin development (Nemcock and Gayer, 1995), and was probably active then as a normal fault, the later reverse movements being due to Alpine compressive-related re-activation. Nemcock and Gayer (1995) modelled palaeostresses within this basin, and concluded that the main post-Triassic rifting phase commenced towards the end of the Pliensbachian (Middle Liassic), after 600 m of Liassic sediments had been deposited. This conclusion tends to suggest that the pyrite-calcite vein was emplaced at some point between the end of the Pliensbachian and the Aptian (Lower Cretaceous), when rifting ceased.

MVT mineralization is a potential effect of any sedimentary basin development, particularly where such development is controlled by extensional tectonics and marginal normal faulting. The pyrite and calcite were probably sourced from the pyritic shales and limestones which constitute the Lower Jurassic sequence in this area, away from marginal zones. The source of the minor galena and sphalerite veinlets is, however, more enigmatic.

Conclusions

The excellent exposures in the Ogmore-by-Sea to Trwyn y Witch coastal section present documentary evidence for the sequence of metallogenesis in South Wales. Initially, Triassic subaerial weathering and leaching of iron from red-beds resulted in minor amounts of hematite, occurring as joint veins and as hematized zones in Dinantian limestones. Later, as basin development progressed in the Bristol Channel area, MVT fluids invaded the Dinantian limestones, Triassic breccias and the overlying marginal Liassic sediments, to deposit abundant calcite, barite and galena in veins and cavity-fillings. Basin-related extension caused the re-activation of Variscan fractures in early Jurassic times, with the emplacement of vein pyrite-calcite at Trwyn y Witch. This fault was re-activated once again during Alpine Earth movements in Tertiary times, moving in a reverse sense and deforming the calcite and pyrite, which were later cross-cut by minor galena and sphalerite veinlets.

MACHEN QUARRY (ST 223 886)

Introduction

The large, working quarry at Machen (Figure 5.87), set prominently on a steep hillside overlooking the Newport to Caerphilly A468 road, exploits dolomitized Dinantian limestones of the Pembroke Limestone Group. It is of mineralogical importance chiefly because of the species range and quantitative extent of supergene mineralization, which has formed by the alteration of Pb, Zn, Cu and Fe sulphides within Mississippi Valley-type (MVT) veins. , The supergene minerals include some of the finest examples of anglesite recorded in Great Britain and also the presence of a number of rare species, including scotlandite and fraipontite.

Quarrying has taken place in the Machen–Ochrwyth area for many years, as was, formerly, lead mining, although historical records of such activities are fragmented and contradictory (see Tucker and Tucker, 1975; Foster-Smith, 1981). Lead mining was a locally important industry along the south crop of the South Wales Coalfield, exploiting veins in limestones of Dinantian age and in the overlying Mercia Mudstone Group (Triassic) rocks, with old workings scattered along a line from Machen, through Draethen and Rudry, westwards towards Llantrisant and the Bridgend district. It has been suggested (Hall, 1993) that the workings were active as far back as Medieval times, but the only well-documented lead-mining activity was in the mid-19th century, by which time mine operators were required to furnish mineral production data on an annual basis.

The mines in the area in and around Machen Quarry are not well-documented and were generally small-scale pittings. Voids occasionally broken into during quarrying may to an extent represent old workings, although some are undoubtedly karstic. However, an ENE–WSW-striking vein, which crosses the northern part of the quarry, contains sufficient galena that, had its presence been known in the 19th century, it would without doubt have been regarded as an attractive mining proposition.

The MVT Pb-Zn-Ba-dominated vein mineralization occurring in the Dinantian sequences of South Wales has received little academic attention, in comparison to the studies of deposits worked or exposed in higher horizons, such as the Mercia Mudstone Group of the Llantrisant area (see Bevins and Mason, 2000), and the marginal Lias at the **Ogmore Coast** GCR site. The essential features of the Dinantian-hosted veins are that: they occur along re-activated ENE–WSW-striking faults of Variscan origin; their primary mineralogy is dominated by barite, calcite, galena and sphalerite; and that texturally they are very different to the irregular iron oxide deposits and the associated and superimposed calcite-barite-dominated cavity-fill assemblages, as seen at the **Ton Mawr Quarry** GCR site. Machen Quarry provides an excellent opportunity to examine this important aspect of the metallogenesis of South Wales.

The MVT vein sulphides of South Wales are frequently seen to be extensively oxidized, with the development of a wide range of secondary minerals, dominated by anglesite and cerussite after galena, and smithsonite and hemimorphite after sphalerite. Machen Quarry is of particular note for a suite of specimens collected in the mid-1980s

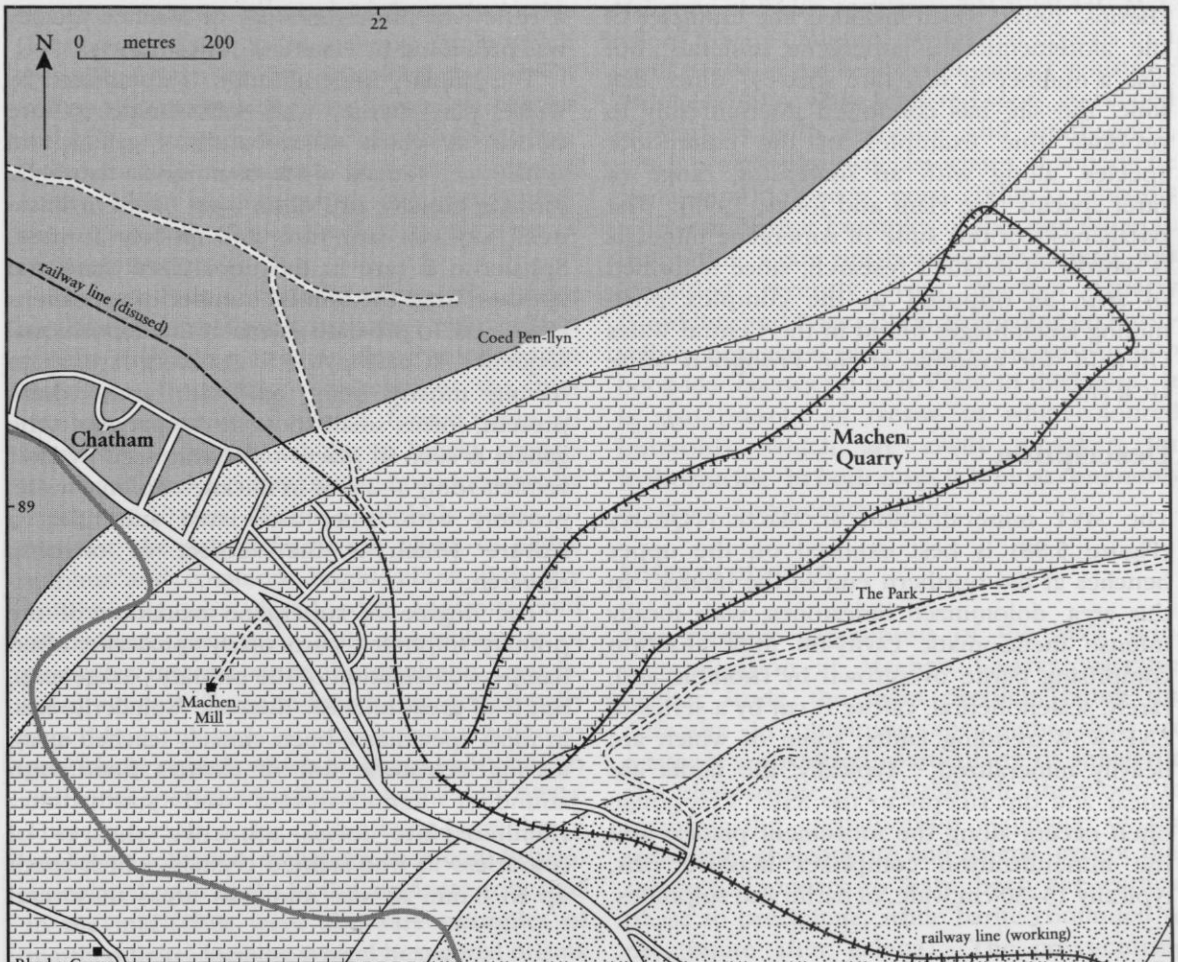


Figure 5.87 Map of the Machen Quarry GCR site. After Institute of Geological Sciences 1:50 000 Sheet 249, Newport (1975).

(Bevins, 1994), which included fine examples of the aforementioned supergene minerals, but also a number of very rare species. Since that time, the site has continued intermittently to produce fine examples of the commoner species, along with an increasing range of rarer species (see Plant and Jones, 1995). The paragenesis of this suite of supergene minerals is worthy of detailed research, since it formed *in situ*, as opposed to the complex post-mining assemblages found in the Central Wales Orefield, for example at the **Frongoch Mine** GCR site.

Description

The MVT mineralization at Machen Quarry (Figure 5.88) is best exposed on the upper benches at the northern end of the quarry. In this area, dolomitized limestones, with locally intense metasomatic cavity-fill mineralization comprising barite overgrown by rhombic and, rarely, scalenohedral, calcite is cut by a series of ENE–WSW-trending faults, some of which are heavily mineralized. Typically, the faults are linear and dip steeply to the SSE. Clay-gouge often occurs along the movement planes, and the mineralization comprises massive ribs, typically 15–30 cm wide, of barite and sulphides. A review of the mineralogy of Machen Quarry was presented by Plant and Jones (1995).

The primary mineralization is dominated by white, platy barite, with subordinate to rare calcite, in which occur bands of galena and sphalerite. Galena is the commonest sulphide, forming massive ribs often over 10 cm in thickness; crystals are rare and poorly formed. Sphalerite is rare in the unoxidized state and appears, from the limited number of specimens examined, to pre-date galena in the depositional sequence. Chalcopyrite is also very rare, again having mostly been oxidized, and, where present, forms small spots in the gangue. The galena is seen in places to be traversed by later veinlets, only 1–2 mm in thickness, of marcasite, possibly with other associated sulphides, a feature which is the subject of ongoing research.

The degree of supergene oxidation of the primary sulphides, particularly sphalerite, often hampers elucidation of the primary paragenesis, but is of great intrinsic interest. Sphalerite has, in most specimens, been entirely leached away, leaving veinstone full of cavities lined with abundant hemimorphite and smithsonite. Hemimorphite forms attractive sheaves of colourless to iron-stained crystals, which reach up to 8 mm in size and coat areas to several

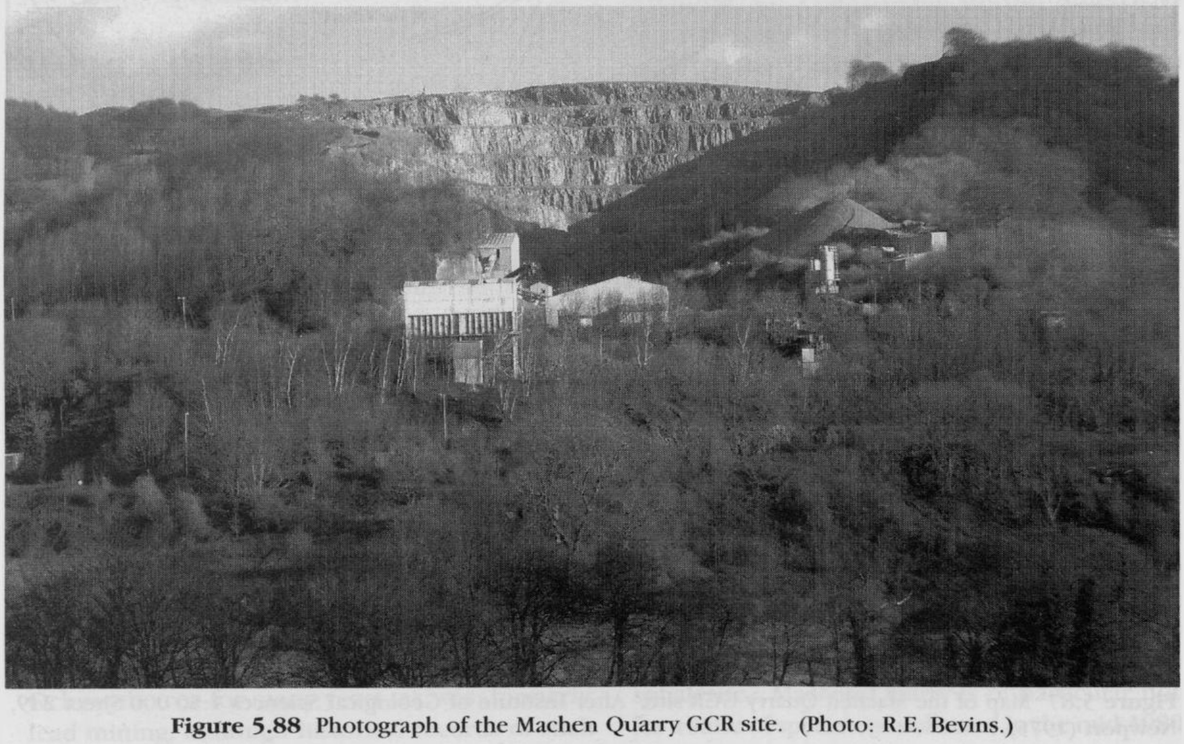


Figure 5.88 Photograph of the Machen Quarry GCR site. (Photo: R.E. Bevins.)

square centimetres. Smithsonite forms distinctive globular aggregates to up to 3 mm across which are toffee-brown to white in colour, and which, under the microscope, are seen to exhibit multiple, stepped, rhomb-face terminations. Hydrozincite is a common late phase, forming earthy, white coatings which are iron-stained, and occasionally display small (*c.* 1 mm) areas of pink colouration.

The oxidation pattern of galena varies according to whether it has taken place within a pure sulphide matrix or along galena-barite interfaces. In the latter environment, the chief product is cerussite, which forms white to brownish or greyish, tabular to blocky crystals usually in the 3–5 mm range but occasionally exceeding 10 mm. Within a sulphide matrix, in contrast, the galena frequently alters to native sulphur and common, bright-yellow, powdery bindheimite, associated with anglesite and subordinate cerussite. This assemblage is of particular interest since the anglesite crystals, usually only 1–2 mm in length, are occasionally superbly developed, forming lustrous, white to grey, sharp crystals which reach up to 30 mm on particular specimens collected in the mid-1980s. These represent some of the finest examples of anglesite collected anywhere in Great Britain. Associated with some of the anglesite collected in the mid-1980s were also rare examples of mattheddleite, forming typical hexagonal prisms with pointed terminations reaching up to 0.5 mm in length, and also scotlandite, which allegedly formed adamantine, colourless, tabular crystals up to 2 mm. This latter occurrence, however, has yet to be verified.

The minor amounts of chalcopyrite oxidized along with the other sulphides have influenced the secondary assemblage in places. The most frequently observed copper-bearing supergene mineral is aurichalcite, which typically forms small, turquoise spots, but also occurs as acicular crystals forming a sky-blue, felty coating to cavities. Malachite and rosasite are much rarer associates, as is linarite, which has been recorded as small (1 mm), bladed crystals. The linarite was originally identified as schmiederite (Bevins, 1994) but has since been shown by electron microprobe analysis to be selenium-free (Plant and Jones, 1995).

Two further supergene minerals occurring at Machen Quarry are particularly worthy of note, namely cinnabar and fraipontite. Cinnabar has been confirmed qualitatively on National Museum of Wales specimen NMW 89.43G.M.7, where it forms minute, orange-red crystals in a small cavity in oxidized barite-galena veinstone (Bridges, 1990), while brick-red spots, associated particularly with cerussite and smithsonite, which are characteristic associates of supergene cinnabar (D.I. Green, pers. comm.), probably represent further examples of this rare mineral. Fraipontite, a rare zinc-bearing clay mineral, was identified recently from Machen Quarry (Goulding and Price, 1995) as forming greenish-yellow, hexagonal plates, often intergrown into book-like masses up to 0.5 mm in thickness. It is also present as cream- to white-coloured botryoids, which are easily mistaken for hydrozincite. In both cases it is most commonly developed on hemimorphite.

Interpretation

The primary paragenesis of the MVT vein-mineralization at Machen Quarry warrants further study, the main problem being the difficulty in obtaining specimens that are relatively unoxidized, particularly of sphalerite and chalcopyrite. It is difficult, therefore, to establish the crystallization sequence of the sphalerite, chalcopyrite and galena, except that sphalerite appears to have been the earliest phase to precipitate, while barite continued to precipitate after galena. The cross-cutting marcasite veinlets in the galena also require further detailed examination, but they clearly represent a post-Pb-Zn phase of epigenetic mineralization.

The primary MVT mineralization may be equated with similar Pb-Zn-Ba vein-hosted deposits occurring in Dinantian limestones, the Mercia Mudstone Group and marginal Lias rocks across South Wales. Evidence exposed at the **Ogmore Coast** GCR site constrains this mineralization as being early Jurassic in age, and it is not unreasonable to assign all of the vein-hosted MVT Pb-Zn-Ba mineralization in South Wales to a regional metallogenic episode occurring at this time.

Trace elements present in the primary assemblage are represented by the supergene minerals cinnabar, bindheimite and the pink-tinted hydrozincite. The source for the mercury and antimony is uncertain: antimonial galena is well known from Wales (see **Frongoch Mine** GCR site report, this chapter), but another possibility, given the geographical location of

Machen, is that both elements have been derived from a minor, associated tetrahedrite-group mineral. Tennantite, with substantial antimony content, is a component of MVT barite-galena-dominated vein mineralization occurring in the marginal facies of the Mercia Mudstone Group on the southern side of the Bristol Channel, at Clevedon (Ixer *et al*., 1993; see **Clevedon Shore** GCR site report, Chapter 6). Both the Clevedon and Machen Quarry MVT mineralization falls within the South Wales–Mendip Orefield, and the possibility of further occurrences of tetrahedrite-group minerals within the South Wales sector of the orefield cannot be discounted. The rare, pink spots in hydrozincite (and possibly similar-looking fraipontite) have so far failed to provide distinctive X-ray diffraction patterns (S.L. Chambers, pers. comm.). It is probable that they represent contamination of zinc compounds by another transition metal cation (e.g. Co^{2+} or Mn^{2+}). Further work is required to establish the nature of these small but conspicuous features.

Typically, oxidation of sphalerite follows a well-defined sequence, in which initial smithsonite is overgrown by hemimorphite, which in turn is coated by hydrozincite and fraipontite. Generally, however, smithsonite and hemimorphite tend to be mutually exclusive, so that in a typical specimen, adjacent cavities may be lined with only smithsonite or only hemimorphite. Only rarely is hemimorphite observed directly overgrowing smithsonite. Hemimorphite is by far the commonest supergene zinc mineral at Machen Quarry, suggesting that, despite the veins being hosted by carbonate sediments, little free carbonate was available during the supergene process, silica being predominant.

Another interesting feature of the supergene mineralization at Machen Quarry is the rare occurrence of cerussite overgrown by smithsonite, suggesting that the oxidation of galena was proceeding at the same time as that of sphalerite. The latter sulphide is normally regarded as being less stable than galena, and therefore usually reacts first in the supergene environment. However, the almost total oxidation of sphalerite indicates that such relationships are relatively localized. The association of bindheimite with anglesite plus cerussite and minor native sulphur is well known from other Welsh localities (see **Frongoch Mine** GCR site report, this chapter), and is usually encountered in cavities within massive galena with little connection to the outside environment. Detailed paragenetic information regarding the associations of scotlandite and mattheddleite is, unfortunately, currently lacking.

Conclusions

Fine examples of supergene mineralization which developed *in situ* are well exposed at Machen Quarry. Both the primary and supergene mineralization exposed at Machen Quarry are worthy of further research. The primary paragenetic sequence requires clarification, as does the possibility of the occurrence of minor sulphide phases carrying trace elements such as Sb and Hg, both of which form compounds within the supergene assemblage. Secondary mineralization is diverse, and it is anticipated that further field and laboratory work will increase both the number of species present, and, more importantly, the understanding of the mechanisms responsible for its genesis.

SECONDARY MINERALIZATION

Supergene minerals feature strongly at a number of the GCR sites in Wales described above. Some, such as the **Machen Quarry**, **Dolyhir Quarry** and **Eaglebrook Mine** GCR sites, are as important for their secondary as for their primary mineralization. The **Turf Copper Mine** GCR site, with a dominantly supergene context, has been described as part of the Coed y Brenin network, for it is best considered in that context.

Three further GCR sites are, however, of prime importance for the understanding of the genetic processes responsible for the supergene mineral deposits in Wales. At the **Llechweddhelyg Mine** GCR site, the deep leaching of both ore deposits and their host rocks has produced an assemblage of base-metal supergene minerals in quantity. At the **Mynydd Nodol Mine** GCR site, leaching of Ordovician volcanic rocks was accompanied by the deposition of complex botryoidal manganese oxides in joints and fault-fractures. At both of these sites the intensity of the supergene leaching and mineralization is interpreted as being due to Tertiary sub-tropical weathering.

At the **Frongoch Mine** GCR site, a deep leaching-related supergene assemblage is accompanied by complex, post-mining mineralization of great diversity. Interestingly, secondary mineralization at Frongoch contributes to the ongoing debate, in the mineralogical world, as to what defines a true mineral; at Frongoch and elsewhere, certain crystalline solids have been generated by weathering processes affecting material with a significant anthropogenic input.

LLECHWEDDHELYG MINE (SN 683 848)

Introduction

The small working at Llechweddhelyg (Figure 5.89), which was centred on a shaft sunk in the 1850s on a section of a major fracture-belt referred to as the 'Camdwr Lode' (Jones, 1922), encountered, by Welsh standards, an unusually substantial zone of supergene enrichment formed by the alteration of a primary Cu-Pb-dominated vein sulphide deposit. The site has produced many fine specimens of the secondary species malachite, chrysocolla, cerussite, pyromorphite and wulfenite, which are widespread in the Central Wales Orefield. In addition, a number of extremely rare micro-crystalline supergene species have been recorded, including the first Welsh occurrence of the rare Cu-Pb sulphate mineral chenite (Rust, 1994). The importance of the Llechweddhelyg site lies in the pervasive nature of the supergene alteration, in contrast with most other Central Wales Orefield sites where fresh sulphides occur in surface exposures. The suggestion has been made (Mason, 1994, 2004) that the supergene zone at Llechweddhelyg represents one of only a few preserved examples of a remnant of widespread Tertiary alteration of hypogene mineralization, most other occurrences having subsequently been eroded away by Pleistocene glaciation.

Little has been published on the history of Llechweddhelyg, except that it was active in the 1850s and produced, in 1853, 3.4 tons of lead ore (Burt *et al.*, 1986). However, it must have been active prior to this, as there are also two short trial adits, the cramped dimensions of which are diagnostic of pre-19th century drivages. During the 19th century it was at times part of the Vaughan sett, along with the neighbouring Lletty Evan–Hen Mine, which was somewhat more productive (Jones, 1987).

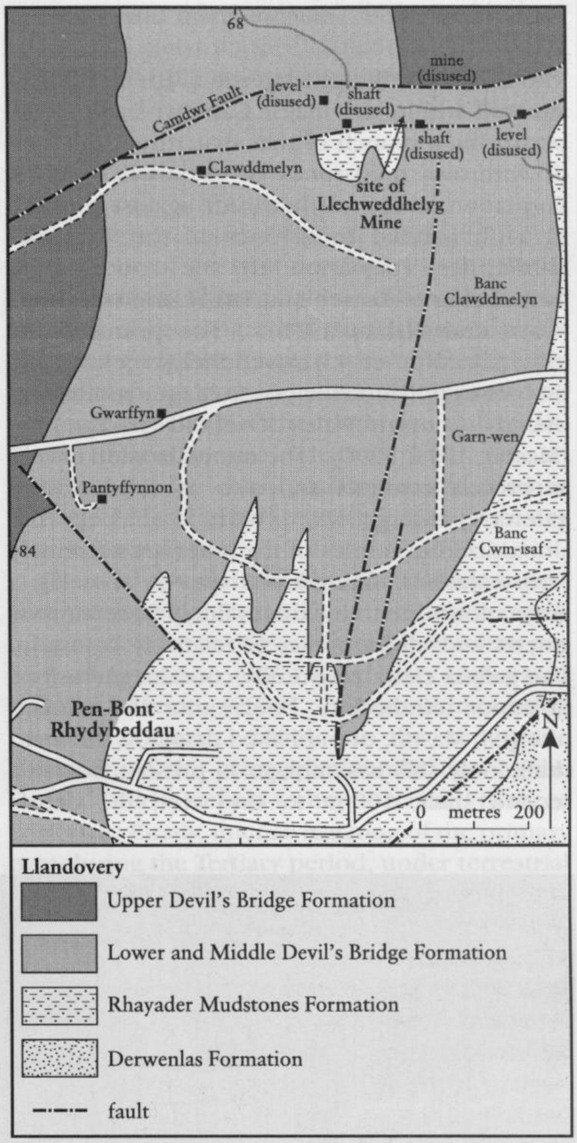


Figure 5.89 Map of the Llechweddhelyg Mine GCR site. After British Geological Survey 1:50 000 Sheet 163, Aberystwyth (1984).

Llechweddhelyg has long been known to mineral collectors, and is consequently well picked-over. The mineralogy was first described by Jones (1987), and subsequent discoveries have been recorded by Bevins (1994), and Rust (1990b, 1994). Although spectacular specimens are now unlikely, the site still provides worthwhile research material. The following description is based on the above accounts, along with the results of fieldwork and subsequent research undertaken in the late 1980s (J.S. Mason, unpublished data).

Description

The Llechweddhelyg deposit (Figure 5.90) is situated within the major Camdwr Fault Zone, occupying a branch of that structure. The fault downthrows mudstones of the Devil's Bridge Formation on the northern side against greenish to buff, banded mudstones of the Rhayader Mudstones Formation to the south, both units being of Lower Silurian (Llandovery) age (Cave and Hains, 1985). The primary vein mineralization at Llechweddhelyg belongs to the A1-c polymetallic assemblage within the overall Central Wales Orefield paragenesis (Mason, 1994, 1997). The mineralization occurs as breccia cements and also as solid ribs of galena intergrown with chalcopyrite. Unoxidized examples of the latter are extremely rare. Massive, fine-grained quartz, showing a grey colour due to included, finely disseminated galena and chalcopyrite, is relatively common. The galena characteristically contains inclusions of minor tetrahedrite, bournonite and ullmannite (J.S. Mason, unpublished data). At the main shaft, only this assemblage is present but at a second shaft, 100 m to the west, the debris indicates that calcite-marcasite mineralization, belonging to the A2 or late Central Wales Orefield paragenesis (Mason, 1994, 1997), was intersected.

Supergene processes have resulted in the pervasive alteration of the massive sulphides to a carbonate-dominated assemblage, occurring in a massive, vuggy matrix of iron oxides. Within the massive, fine-grained quartz, alteration has resulted in the deposition of secondary minerals along the numerous open joints that cross-cut it. Within the breccias, quartz-hosted sulphide veinlets have been partially oxidized to a wide variety of secondary minerals.

Within the iron oxides matrix, massive cerussite and fibrous malachite, accompanied in places by chrysocolla, are the chief secondary species, with pods of solid cerussite up to 5 cm having been recorded (J.S. Mason, unpublished data). Linarite occasionally replaces marginal areas of the cerussite. Malachite is abundant, and replaces chalcopyrite as massive, fibrous aggregates, which sometimes form attractive crystal sprays up to 40 mm across in part-filled cavities. Malachite is replaced in some samples by chrysocolla, and is overgrown by cerussite or,

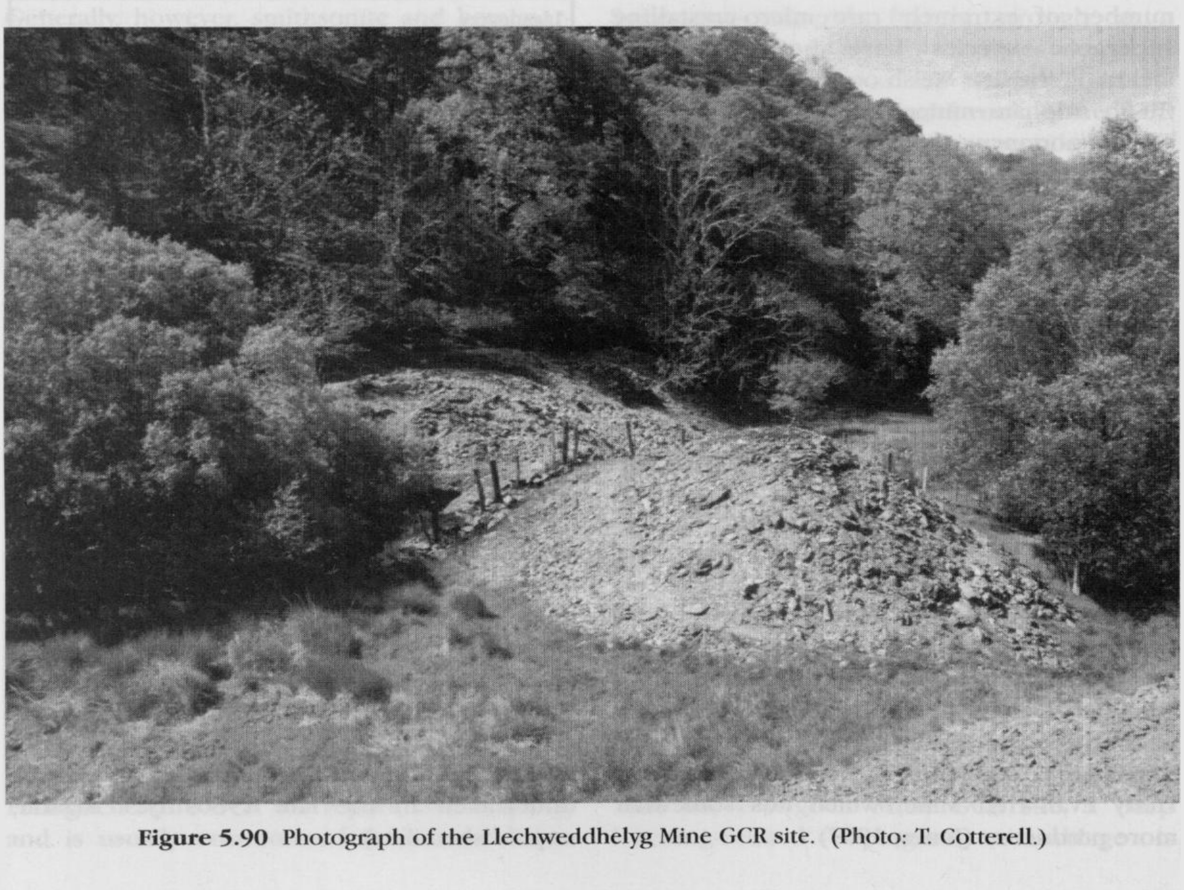


Figure 5.90 Photograph of the Llechweddhelyg Mine GCR site. (Photo: T. Cotterell.)

less frequently, by equant pyromorphite up to 3 mm. Coarse-grained cerussite and equant pyromorphite never occur on the same sample (Mason, 2004), although wulfenite, forming tabular crystals up to 2 mm (exceptionally up to 5 mm) is invariably associated with pyromorphite, which it overgrows. A minor, subsequent generation of micro-crystalline pyromorphite occasionally coats, and partially replaces, cerussite.

In polished section, the alteration of the sulphide ore is of particular interest as it reveals the process by which chalcopyrite is incrementally converted to chalcocite. Both bornite and covellite are intermediate products of this process: while bornite forms rare flame-like, chalcopyrite-cored inclusions in chalcocite, covellite is common and pervasively net-veins both chalcopyrite and galena (J.S. Mason, unpublished data). Small (10–20 μm), bright-yellow grains, embedded in iron oxides adjacent to the alteration products described above, have been identified optically as native gold (J.S. Mason, unpublished data), an identification supported by assays of this material which frequently show gold levels of *c.* 0.75 g/t (S.J.S. Hughes, pers. comm.).

Within the open joints traversing the massive quartz, cerussite or pyromorphite + wulfenite are the chief secondary species present; locally, spheroidal fibrous malachite (< 10 mm) accompanies the tabular cerussite crystals. These species also occur within the part-oxidized sulphide veinlets within the breccias, but are accompanied there by a much wider range of minerals which form a suite similar to that developed at the **Eaglebrook Mine** GCR site. Within the breccias, bleaching of mudstone clasts, with strong development of manganese oxide dendrites, is not uncommon. The supergene assemblage is sulphate-dominated, with subordinate carbonates, and comprises, in order of abundance, linarite, caledonite, hydrocerussite, susannite, anglesite, brochantite, langite, wroewolfeite, schmiederite, steverustite, mattheddleite, elyite and chenite. Recently, redgillite has been determined from Llechweddhelyg Mine (Pluth *et al.*, 2005). All of the above mentioned species are micro-crystalline (<< 1 mm) but they tend to be well formed. The rarer species are only represented by a few samples, so that definitive associations are unclear. However, a particularly consistent association is observed between caledonite, susannite and mattheddleite. Small veinlets of intergrown native copper, chalcocite and cuprite also occur within brecciated mudstones, but are rare.

Interpretation

The supergene assemblage at Llechweddhelyg Mine is one of the best developed in the Welsh Caledonides. This is evident from the sheer quantity of coarse-grained supergene minerals and the pervasive replacement of normally stable sulphides such as galena, accompanied by the local bleaching of the mudstone wall-rocks. These features are characteristic of an environment in which prolonged and intense secondary leaching and reprecipitation processes have been acting.

The concept that the Llechweddhelyg supergene assemblage actually constitutes a well-preserved survivor of glacial erosion was first put forward by Mason (1994), and later elaborated upon by Mason (2004). There is mounting evidence (Mason, 2004) for the supergene alteration of the primary mineralization in the Central Wales Orefield to have occurred in three episodes. Firstly, intense leaching of the primary ores during the Tertiary period, under terrestrial (Cope *et al.*, 1992), protracted sub-tropical conditions, produced the coarsely crystalline supergene assemblage as seen at Llechweddhelyg Mine. Prior to the Pleistocene glaciation, such supergene zones may have existed in the near-surface parts of most if not all sulphide-bearing veins in the orefield. However, glacial erosion removed most of these zones, leaving behind only localized remnants.

Secondly, and following the Pleistocene glaciation, groundwaters began once again to attack newly exposed surfaces and, over the geologically short period of time since the end of the last glaciation, relatively modest alteration has resulted in the development of mainly micro-crystalline secondary minerals. The breccia-hosted micro-crystalline secondary assemblage at Llechweddhelyg Mine is likely to have at least partly formed in this manner.

Thirdly, the activity of mining the various deposits caused fresh sulphide surfaces to be exposed to surface conditions, so that very recent, anthropogenic secondary minerals were formed, again with a tendency to be micro-crystalline. These post-mining assemblages tend to contain metastable minerals, with often-complex parageneses (Mason and Green, 1996). At Llechweddhelyg Mine, it is uncertain whether any of the secondary minerals are of post-mining origin. However, by analogy with other sites, for example the **Frongoch Mine** GCR site (Green *et al.*, 1996), it may be surmized that elyite, hydrocerussite, langite and wroewolfeite, which all occur on part-oxidized sulphide, are likely to be of post-mining origin.

At Llechweddhelyg Mine, substantial supergene mineralization clearly extends to a considerable distance below surface. However, there are other mines in the Central Wales Orefield where the reverse is the case. This is revealed at the **Ceulan Mine Opencast** GCR site, where fresh galena and sphalerite occur close to surface. Furthermore, an opencut at Tynyfron Mine (SN 724 785), on the side of the glacially carved Rheidol Valley, reveals fresh marcasite exposed at surface (Mason, 2004). Marcasite is particularly unstable in the near-surface environment and it is most unlikely that it would withstand millions of years of sub-tropical weathering: therefore it follows that glacial erosion must have stripped off any oxidized zone to reveal the mineral in its fresh state at surface.

The preservation of the major supergene zone at Llechweddhelyg Mine suggests that it extended to a relatively great depth, so that only part of it was eroded away. Such deep oxidation of the primary sulphide assemblage would be facilitated by the shattered nature of the broad tract of ground affected by the Camdwr Fault, permitting relatively easy and deep circulation of oxidizing groundwaters.

The pre-glacial theory for the origin of the supergene mineralization at Llechweddhelyg Mine is also supported by comparing the Welsh Caledonides with other mineralized areas of the British Isles. Only one area of the British Isles, namely South-west England, has been relatively unaffected by the erosional effects of glacial ice (see Campbell and Bowen, 1989). In this area, major supergene zones composed of coarse-grained secondary minerals are present within most, if not all, metalliferous veins. The quantity of coarsely crystalline supergene minerals in areas which have been intensively eroded by glaciation, such as the Caldbeck Fells, in the English Lake District (Cooper and Stanley, 1990), can be explained by particularly permeable ground conditions allowing unusually deep and extensive supergene alteration to occur, as at Llechweddhelyg Mine.

The source of the phosphate necessary for the genesis of the coarse-grained pyromorphite may be explained by the spatial link between such mineralization and bleached mudstone wall-rocks. In turbidite-dominated areas, phosphatic concretions and phosphate-rich hemipelagites are common, and the Central Wales region is no exception (Cave and Hains, 1986). Both apatite and monazite (Read *et al.*, 1987) occur in these circumstances throughout Central Wales, providing a ready source of phosphorus to aggressively leaching groundwaters. Similarly, the molybdenum required for wulfenite formation could have been provided by the wall-rocks. Only low levels of molybdenum would be necessary for wall-rock leaching to provide the small amounts of molybdenum necessary for formation of wulfenite which, although conspicuous in this assemblage, occurs in only trace amounts in quantitative terms.

Conclusions

Supergene mineralization is particularly well-developed at Llechweddhelyg Mine. Evidence from Llechweddhelyg Mine supports the notion that more than one episode of supergene alteration has affected the metalliferous veins of the Central Wales Orefield. Deep, sub-tropical weathering in Tertiary times resulted in the formation of large quantities of oxidation products occurring as coarsely crystalline masses with well-defined parageneses in extensive zones. Glacial erosion stripped these from many veins, while exposing further fresh sulphides, which supergene processes once again began to affect, producing relatively limited amounts of secondary minerals. Finally, the creation of new, fresh sulphide exposures by mining activities again renewed the process, resulting in the post-mining suite of minerals.

FRONGOCH MINE (SN 722 744)

Introduction

Frongoch (Figure 5.91) is one of the largest old mines in the Central Wales Orefield and is as important in mineralogical terms as it is historically. The mine worked lead-zinc-dominated mineralization belonging to the late (A2) group of assemblages of the Central Wales

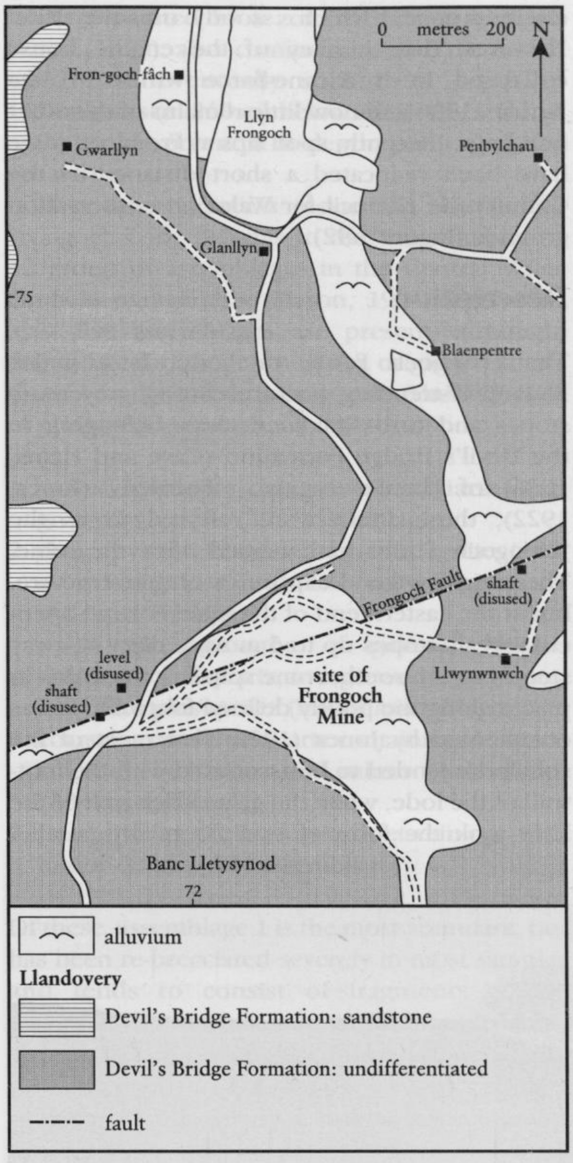


Figure 5.91 Map of the Frongoch Mine GCR site. After British Geological Survey 1:50 000 Sheet 178, Llanilar (1994).

regional paragenesis (Mason, 1994, 1997; Green *et al*., 1996), occurring along a major fracture system, the Frongoch Fault (Davies *et al*., 1997). In addition to a number of interesting features revealed by the primary mineralization, Frongoch Mine is of particular note for its complex suite of secondary minerals, produced both by pervasive deep weathering of the mineralization *in situ* and also by post-mining geochemical processes operating within old mine tips. A number of extremely rare secondary minerals occur within this post-mining suite, including the second reported world occurrence of the new mineral bechererite, a complex zinc-copper basic sulphate-silicate (Green *et al*., 1996; Rust *et al*., 2004), the rare zinc-bearing supergene mineral brianyoungite (Cotterell *et al*., 2003), redgillite, and the new lead-bearing thiosulphate mineral steverustite (Cooper *et al*., 2009).

Frongoch Mine was a noteworthy site early in its history, being one of very few Central Wales mines to receive a mention by Greg and Lettsom (1858). At the time, it was merely known as 'a mine near Devil's Bridge', but the 'brilliant hair-brown' pyromorphite crystals, for which the mine was mentioned by Greg and Lettsom (1858), are diagnostic. Brown pyromorphite is rare in Britain compared to the commonplace green variety, and Frongoch is the only Welsh locality where it has been found in anything exceeding trace amounts. Thus, the site has long attracted amateur mineralogists seeking the occasionally fine pyromorphite (and cerussite) specimens.

In more-recent years, hard-core extraction operations have resulted in the excavation of the old dumps along and below the lode outcrop, revealing intensely altered sulphide-rich material. Within these deep excavations, many fine, albeit micro-crystalline, specimens of caledonite, susannite and a large variety of other rare supergene species have been recovered (Green *et al*., 1996). Comprehensive suites of this material are preserved in the collections of the National Museum of Wales and the Natural History Museum.

Frongoch was known as a lead mine by the mid-18th century (Bick *et al*., 1986), although production was relatively small until the 19th century, when the mine eventually became one of the greatest producers of lead and zinc in the Central Wales Orefield. The mine, as one of the Lisburne mines, controlled and leased by the eponymous Lord, attracted several major 19th-century operators. Between 1825 and 1834, it was controlled by the Williams family of Scorrier, who were followed between 1834 and 1878 by John Taylor and Sons, who were extremely successful in their development and exploitation of the deposit, frequently producing in excess of 1500 tons of galena concentrates per annum, an impressive figure considering that a large number of Central Wales mines never exceeded this figure in their entire working life. In the period 1834 to 1903, sales of 50 669 tons of galena concentrates, yielding 38 071 tons of lead and 19 014 oz of silver, were recorded (Jones, 1922). Galena was only desilvered intermittently, the yield never exceeding 5 oz per ton of lead ore (Burt *et al.*, 1986).

By the latter quarter of the 19th century, the increasing importance of zinc resulted in reworking of the walls of Taylors' lead stopes under the management of John Kitto; this, coupled with previous sphalerite production, resulted in a total of 50 856 tons of sphalerite concentrates being sold up to 1903. Subsequently, further tonnages of sphalerite and minor galena were recovered in an ambitious project which involved transporting the mine waste, by aerial ropeway, a distance of *c.* 2.5 km to a new mill which was installed on the banks of Afon Ystwyth. Further intermittent exploration, but without any major production, took place in both pre- and post-Second World War years: the last major venture involved the drilling of a deep borehole in 1971. Since then, many of the remaining tips have gradually been removed for hard-core, although remnant areas are still surprisingly rich in massive sphalerite.

Frongoch Mine is a Scheduled Ancient Monument on the basis of the fine collection of buildings, including a 19th century Cornish engine-house, which stood on the site. However, the chimney of the engine house collapsed in hurricane-force winds in late January 1990 and now little remains of the other buildings. Recently, spoil tips at Frongoch Mine have been re-located a short distance by the Countryside Council for Wales on conservation grounds (Figure 5.92).

Description

The Frongoch Fault, or Lode, is a major ENE–WSW-trending fracture cutting grey mudstones and turbiditic sandstones belonging to the Devil's Bridge Formation (Cave and Hains, 1986) of Llandovery age. Formerly (Jones, 1922), these strata were referred to as the 'Frongoch Formation', named after the mine. There are few good exposures of this structure, but at the eastern end of the mine, a large opencut reveals stopes up to 5 m wide dipping away steeply to the south; some sphalerite remains in places along the poorly defined footwall. It was commented by Jones (1922) that most of the sphalerite tended to be associated with the footwall of the lode, while the galena-rich part of the lode took the form of two essentially parallel

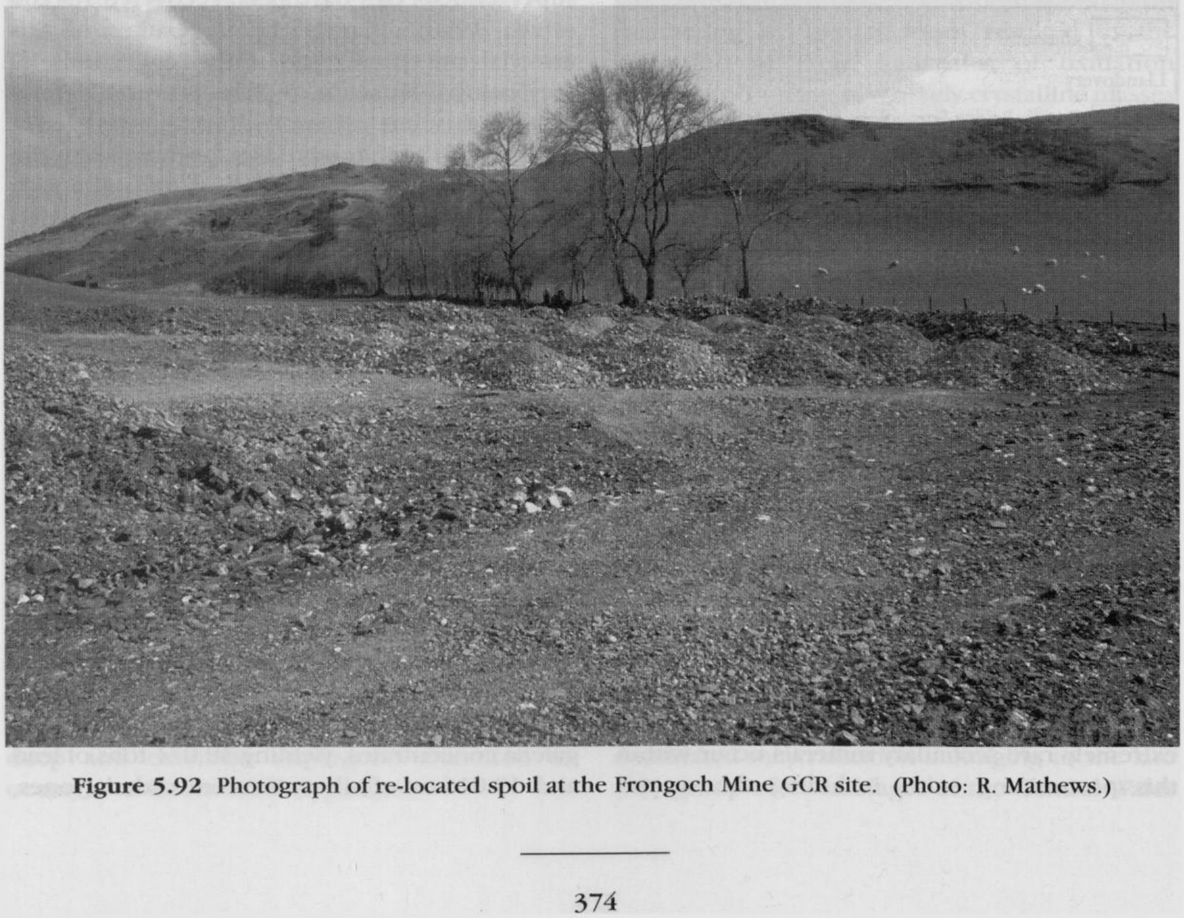


Figure 5.92 Photograph of re-located spoil at the Frongoch Mine GCR site. (Photo: R. Mathews.)

bands separated by a zone of barren ground. Jones (1922) also commented that the mine, which was eventually sunk to a depth of 142 fathoms (*c*. 260 m) below adit-level, still had considerable potential at depth, particularly for sphalerite.

The mineralization occurring along the Frongoch Lode belongs to the 'Late Simple' or A2 group of assemblages in the Central Wales Orefield paragenesis (Mason, 1994, 1997). At least five assemblages are present, although, due to later brittle deformation, original textures have been obscured to an extent. The sequence of primary mineral assemblages is:

1. coarse sphalerite overgrown by quartz overgrown by galena (A2-a assemblage)
2 chalcopyrite overgrown by ullmannite overgrown by galena in a silicic fault-gouge matrix (A2-b assemblage)
3 open-space growths of galena, fibrous sphalerite and quartz, overgrown by pyrite and marcasite plus quartz (?A2-c/f assemblages)
4 coarsely crystalline quartz containing dendritic sulphide inclusions and minor chalcopyrite (A2-d assemblage)
5 pervasive pyrite-marcasite net-veining with minor quartz (A2-f assemblage)

Of these, assemblage 1 is the most abundant, but has been re-brecciated severely in most samples and tends to consist of fragments of the constituent minerals in a 'muddy' sphalerite/quartz matrix, this material commonly occurring in large blocks on the dumps. Assemblage 2 is relatively minor, and where unoxidized consists of < 5 mm spots of chalcopyrite, 2–4 mm twinned ullmannite cubes, and < 10 mm cubo-octahedra of galena in a quartz or silicic gouge matrix. The fibrous sphalerite of assemblage 3 is present as part-spheroids up to 10 cm in radius. The coarsely crystalline quartz of assemblage 4 is characteristic of this generation of Central Wales Orefield mineralization, with growth-zoned crystals, often with dark dendritic sulphide inclusions, exceptionally reaching 8 cm on edge. Pyrite-marcasite net-veining of earlier assemblages is relatively rare, in comparison to sites such as Cwmystwyth (see **Cwmystwyth Mine** GCR site report, this chapter), where it contaminated Pb-Zn ores to the extent that they were unsaleable in the worst cases.

The Frongoch Lode runs sub-parallel to the major, post-metallogenic Ystwyth Fault (Jones, 1922), which crops out *c*. 2 km to the south of the mine. The two structures dip toward one another and it is probable that, at great depth, the Frongoch Lode is 'faulted out' in an analogous situation to that affecting the Comet Lode at Cwmystwyth (see **Cwmystwyth Mine** GCR site report, this chapter). It also appears that some of the movements along the Ystwyth Fault affected the Frongoch structure, as large blocks of loose, uncemented crush-rock, consisting of cataclastic quartz and sulphides, are common on the dumps at Frongoch.

Secondary mineralization is most pervasively manifested in the tips along the outcrop of the lode, where the host grey shales have been deeply leached to yellowish and pinkish shades. Goethite and bright-red, earthy hematite commonly coat fracture surfaces in this leached mudrock, and are accompanied by abundant cerussite and locally by brown pyromorphite. Cerussite forms massive veins up to 2 cm in thickness, twinned crystals up to 3 cm, and has also been observed as reticulated 'snowflake' groups covering large hand specimens (Green *et al*., 1996). It is sufficiently abundant that it was probably worked as a lead ore.

Pyromorphite, locally overgrown by cerussite, occurs most commonly as prismatic crystals with pinacoidal terminations which exceptionally reach up to 2.5 cm in length. Rarely, crystals show strong development of the hexagonal pyramid, and sub-parallel sheaves of acicular crystals have been recorded (Green *et al*., 1996). Pyromorphite varies in colour from rare colourless crystals to the more usual brown and occasionally purple-brown; two specimens in the collection at the National Museum of Wales feature pyromorphite crystals which have thin green outer zones and brown cores. More characteristic (for the Central Wales Orefield) green micro-crystalline pyromorphite crusts, overgrowing cerrusite, also occur especially towards the western end of the sett near to the boundary with Wemyss Mine. The crusts occasionally feature small tabular crystals of wulfenite, notably showing hopper structure in some specimens.

Associated with cerussite, where oxidation of galena is less pervasive, is a mineral belonging to the bindheimite group of lead-antimony oxides. This occurs commonly as pale- to canary-yellow crusts, which are typically less than 1 mm thick but cover large areas of veinstone. It is often found in cavities in quartz containing relict masses of corroded galena, and additionally forms resinous cubic pseudomorphs after ullmannite.

Cerussite, pyromorphite and the bindheimite-group mineral, plus small amounts of malachite, aurichalcite, rosasite and hemimorphite, constitute the in-situ formed supergene assemblage. The remainder of the supergene minerals reported from Frongoch Mine belong to the post-mining, basic sulphate-dominated supergene suite. In this suite of minerals occur a number of assemblages whose mineralogy has been directly influenced by local geochemical conditions. Galena alters firstly to micro-crystalline anglesite, which occurs quite commonly as small (< 1.5 mm) transparent crystals, of a tabular or blocky morphology. Anglesite is commonly associated with secondary covellite, which forms thin micro-crystalline films on the galena, and occasionally with native sulphur, which occurs as yellow-green, rounded crystals up to 3 mm, with a typically resinous lustre. Galena is also replaced by cerussite, which is commonly black due to numerous relict galena inclusions, and very rarely contains small dendritic masses of native silver (Green *et al.*, 1996).

Further oxidation of the galena, particularly in the presence of minor chalcopyrite, has resulted in the development of what has been termed a 'Leadhills-type suite' of secondary minerals (see Green *et al.*, 1996). This assemblage comprises susannite (which is unusually common at Frongoch), linarite, caledonite, hydrocerussite, lanarkite and mattheddleite. Previous unconfirmed reports of leadhillite (Bevins, 1994) probably refer to susannite, the only mineral of the leadhillite-group confirmed by X-ray diffraction investigations (Green *et al.*, 1996). All of the species present occur as micro-crystals less than 2.5 mm across or smaller (in the case of mattheddleite). Susannite tends to form pseudohexagonal, tabular to blocky crystals varying from colourless to yellowish, brownish and bluish shades. Caledonite forms characteristic bright sky-blue sprays of acicular to prismatic crystals with well-developed terminations. The limited paragenetic information obtained from this suite indicates that the sequence linarite–susannite–caledonite–mattheddleite is typical; lanarkite is only known from two specimens (in the S.A. Rust private collection), while hydrocerussite appears to occur in a number of positions in the paragenetic sequence.

Linarite is also present as a decomposition product of chalcopyrite, occurring as blue, bladed crystals up to 2 mm, and as fine-grained external coatings, with brochantite, on small sulphide fragments within deeper parts of the dumps. Recent analyses (Green *et al.*, 1996) have shown that some linarite specimens show significant substitution of selenium for sulphur, placing them within the linarite-schmiederite solid solution series. Recently, a new lead-bearing thiosulphate mineral, steverustite, has been described from the dumps at Frongoch Mine (Cooper *et al.*, 2009).

Within the assemblage produced by chalcopyrite decomposition, native copper is occasionally observed as dull, pointed crystals up to 1 mm, associated with cuprite, and superficially replaced by basic copper sulphates. These comprise langite, as euhedral pseudo-hexagonal and blocky, blue-green crystals up to 1 mm, and wroewolfeite, as blue-green, acicular to prismatic crystals up to 0.5 mm. The extremely rare mineral lautenthalite occurs very rarely as emerald-green, tabular to bladed crystals up to 0.7 mm, often forming epitaxial overgrowths on prismatic wroewolfeite. Both langite and wroewolfeite are replaced locally by brochantite. Associated with these copper sulphates is the 'undescribed mineral' recorded also from Esgairhir Mine (Rust and Mason, 1988) and Eaglebrook Mine (see **Eaglebrook Mine** GCR site report, this chapter), now determined to be the new mineral redgillite (Pluth *et al.*, 2005). At Frongoch Mine, as at other localities, it forms minute groups of intense, light-green, divergent, lath-like crystals.

Given the amount of sphalerite occurring at Frongoch Mine, it is perhaps surprising that supergene zinc minerals are only superficially developed and, with the exception of minor amounts of hemimorphite, are largely confined to the post-mining suite. Most Central Wales Orefield sphalerites contain trace amounts of cadmium (Khan Kakar, 1971), and its presence at Frongoch is belied by the occurrence of an as yet undifferentiated cadmium sulphide, which is occasionally conspicuous on freshly broken, part-weathered sphalerite as typical canary-yellow coatings. Recently, however, the rare zinc-bearing supergene mineral brianyoungite related to hydrozincite, first described by Livingstone and Champness (1993) from Brownley Hill Mine in Cumbria, has been reported from Frongoch Mine, occurring as spherulitic aggregates of pearly white lath-like crystals up to 0.5 mm across (Cotterell *et al.*, 2003).

Post-mining hemimorphite occurs as individual grey-white botryoids and thin botryoidal crusts, often-overgrowing susannite, and is one of the latest minerals in this assemblage. Hydrozincite also occurs as part of the post-mining mineral assemblage, as crusts of white, lath-like crystals, which are commonly associated with hemimorphite.

Where sphalerite has oxidized in the presence of copper cations, a variety of minerals, some extremely rare, have formed. Namuwite occurs very rarely as pale blue-green, pseudohexagonal platy crystals and rosettes up to 0.5 mm. Ramsbeckite occurs rarely as typically emerald-green, pseudo-orthorhombic crystals up to 0.7 mm, on schulenbergite, which itself forms light blue-green rosettes of thin platy crystals up to 0.7 mm, and which are easily confused with namuwite. All three species may occur on altered sphalerite, or with the other post-mining species on quartz-dominated veinstone.

The newly described mineral bechererite (Geister and Rieck, 1996) occurs as morphologically striking but characteristic colourless to pale-green or ice-blue, inverted cone-like crystals. It is associated with namuwite, susannite, hemimorphite and corroded cerussite. The distinctive crystals exceptionally approach 1 mm in length but are usually, like the type material, no more than 0.25 mm in size. Frongoch Mine is one of a number of Central Wales Orefield localities where this mineral has been noted as a component of the post-mining supergene assemblage (Green *et al.*, 1996; Rust *et al.*, 2004).

Recent important discoveries include the second British occurrence of cesàrolite (Cotterell, 2007), and the first Welsh occurrences of corkite and himsdalite (Cotterell and Todhunter, 2007).

In such post-mining assemblages, highly local influences on geochemistry can produce particularly unusual minerals. Frongoch Mine is no exception to this general observation, and a small area of dump overlain by collapsed masonry, which was partly removed in the early 1990s, produced specimens of two minerals whose development appears to have been affected by the juxtaposition of lime mortar debris with sulphide-rich dump material. In this area, elyite was found rarely as minute, pale-violet masses of lath-like crystals in small cavities in galena with hydrocerussite and cerussite. Nearby blocks contained cerussite, which had been corroded, with the development of amorphous masses and equant octahedra of bright-red litharge up to 0.5 mm. Rarer, minute areas of a powdery yellow phase associated with the litharge have been tentatively identified as massicot (Green *et al.*, 1996).

Interpretation

The primary mineralization at Frongoch Mine is not unusual in the overall Central Wales Orefield context, having many features similar to that seen to better advantage at the **Cwmystwyth Mine** GCR site. However, the development of abundant, uncemented (and therefore post-mineralization) crush-rock, derived from the Pb-Zn-rich lode-filling, is of particular interest as it is strongly indicative of considerable tectonic activity along the Frongoch Fault, which is probably related to movement along the parallel and major tectonic lineament, the Ystwyth Fault. The fact that the Frongoch and Ystwyth faults dip towards one another would tend to preclude normal movements along both faults simultaneously, and it is possible that such severe cataclasis of part of the mineralization along the Frongoch Fault could have been caused by wrench movements along the Ystwyth Fault, which would be more likely to have caused concurrent movement at Frongoch. Curiously, however, there is little evidence for such severe mechanical deformation within the mineralized fractures at Cwmystwyth Mine, 7.5 km to the east of Frongoch Mine and in close proximity to the Ystwyth Fault.

The secondary mineralization at Frongoch may be divided logically into pre- and post-mining assemblages. The pre-mining assemblage, occurring in considerable quantity and associated with severely leached mudstone wall-rocks, was probably formed over a protracted period of intense deep weathering (see **Llechweddhelyg Mine** GCR site report, this chapter; Mason, 2004), but is chiefly remarkable for the occurrence of brown pyromorphite. Few other occurrences of brown pyromorphite are documented in Britain, two notable examples being at the Barrow and Force Crag mines in Cumbria (Green *et al.*, 1997), specimens from the latter site strongly resembling those from Frongoch Mine. The reason for the colour is unknown: Green *et al.* (1996) commented on two similarities between the Force Crag and Frongoch pyromorphites, specifically that both occurrences are often developed on a siliceous matrix and that both orebodies carry abundant ferroan sphalerite.

The origin of colour variation in pyromorphite is not entirely understood and cannot be explained merely by arsenate substitution for phosphate, or calcium substitution for lead, although in the latter case, greyish pyromorphites from Broken Hill, New South Wales, were shown by Inegbenebor *et al*. (1992) to contain enhanced levels of calcium. At Broken Hill, brown pyromorphites were commonly found by Inegbenebor *et al*. (1992) to be of near-phosphate end-member composition, a feature reflected by IR spectrography of Frongoch pyromorphite, which shows no arsenate present, regardless of whether it is green or brown (G. Ryback, pers. comm.). The colour variation of Frongoch pyromorphite remains, therefore, to be explained.

The post-mining supergene mineralization at Frongoch Mine is the result of removal of sulphide-rich rock from deep mine-workings and its transfer to the surface environment, where the sulphides are relatively unstable; as such, it is a partly anthropogenic process, although the weathering of such material to produce the post-mining assemblage is an entirely natural process. Mineral assemblages with an anthropogenic element in their origin have recently been the subject of controversy, a situation complicated by the fact that minerals such as susannite may occur in entirely natural, part- and wholly-anthropogenic situations. Thus, the 'Leadhills-type' mineral association present in the post-mining assemblage at Frongoch Mine, occurs *in situ* and in quantity at Leadhills (Livingstone and Sarp, 1984), in the Caldbeck Fells, Cumbria (Cooper and Stanley, 1990), and also in weathered slags (Green, 1987). Recently, it has been decided (Nickel, 1995) that supergene compounds occurring as a result of the weathering of metalliferous slags are not, strictly speaking, minerals, as they have formed by the weathering of a totally anthropogenic substance. At present, although fresh sulphide material brought to surface by mining activity has an anthropogenic component, compounds formed by its weathering are accepted as minerals. However, it is anticipated that the debate as to what constitutes a mineral will continue, perhaps citing sites such as Frongoch Mine.

Conclusions

Frongoch Mine is famous as one of the few localities in Great Britain where well-crystallized, brown pyromorphite, the coloration of which remains poorly understood, is well exposed. As well as the secondary mineralization which formed *in situ*, due to deep weathering of sulphides, there also exists an extensive suite of post-mining minerals, including some extremely rare mineral species, whose genesis and status are at present contentious.

MYNYDD NODOL MINE (SH 860 393)

Introduction

Ores of manganese have been worked in the Arenig district of North Wales since the 19th century (Dewey and Bromehead, 1915). In contrast to the extensive, bedded silicate-carbonate-dominated manganese ore deposits of the Harlech Dome, to the west (see **Llyn Du Bach Complex** GCR site report, this chapter), the Arenig ores are vein-hosted black oxides, the genesis of which is of relevance when considering the history of deep weathering and supergene mineralization in Tertiary Britain.

Little has been published regarding these mines. Dewey and Bromehead (1915) described the manganese ores as being hosted by 'a feldspathic ash, generally of a greenish-yellow colour', and that there were 'no true veins, but the ore fills joints and irregular fissures'. The ore was described as mainly consisting of psilomelane, with occasional pyrolusite, derived by leaching of the rocks and re-deposition by surface waters. The ore was said to contain in the range 43–54% manganese, the highest grades being obtained from 'kidney-ore'. The best ore was worth £11/ton in the late 1860s.

More recently, Lynas (1973), in an account of the geology of the Migneint district to the north-west of the Arenigs, described minor manganese mineralization occupying mainly N–S-orientated faults in yellowish tuff of the Aran Fawddy Formation of Ordovician (Caradoc) age. Significantly, X-ray diffraction of the 'psilomelane' present proved it in fact to be hollandite, a Ba-bearing Mn oxide. This represented the first record of hollandite in the British Isles.

The Mynydd Nodol Mine GCR site was selected not only because it is representative but also because small-scale quarrying has revealed a fine exposure of the manganese mineralization (Bevins and Mason, 1998).

Description

A number of slumped adit portals are scattered along the open hillside at Mynydd Nodol, along the outcrop of important manganese mineralization (Figure 5.93). This suggests that the deposits were extensively prospected although only worked to a limited extent. The exposure is visible from the minor unfenced mountain road running across the undulating moorland between Arenig Fawr and Llyn Celyn, as a buff patch on the hillside. Closer examination reveals that the tips from small trial workings have been partially removed, exposing the rocks below.

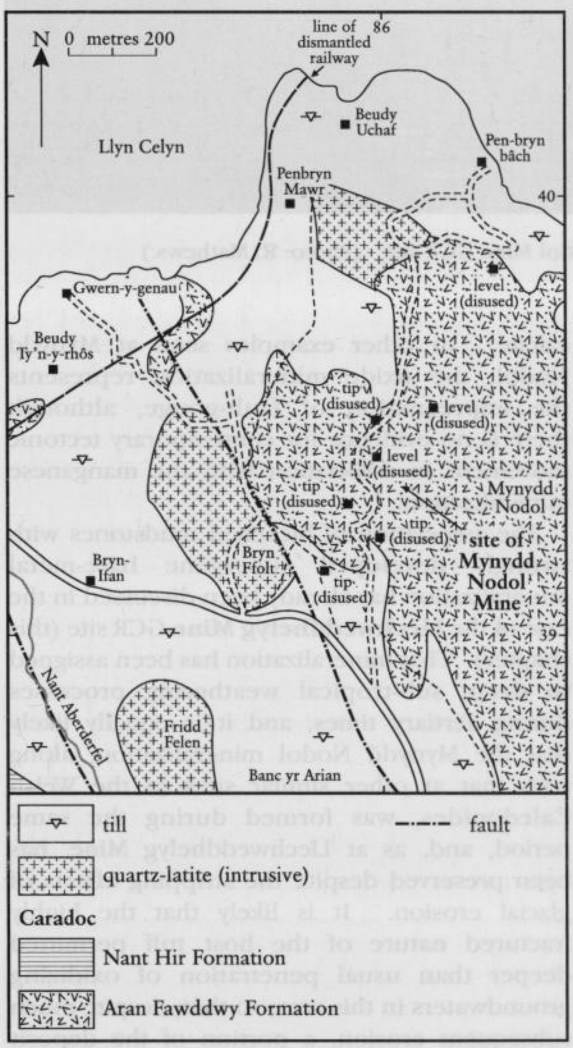


Figure 5.93 Map of the Mynydd Nodol Mine GCR site. After British Geological Survey 1:50 000 Sheet 137, Corwen (1993c).

The exposure (Figure 5.94) reveals numerous strings of black manganese oxide cutting intensely bleached, yellowish to iron-stained reddish acidic tuffs of the Aran Fawddwy Formation, belonging to the Aran Volcanic Group of Ordovician age (British Geological Survey, 1993c), which range in thickness from less than 1 mm to several centimetres. These occupy not only minor N–S-orientated fractures, as described by Lynas (1973), but also joints and irregular cracks of variable orientations in the tuffs. Some of the mineralized fractures also contain the remnants of thin quartz veins. In hand specimen, the ore forms massive, botryoidal coatings to the fracture walls. In polished sections the finely banded nature of the manganese oxide botryoids is evident.

Interpretation

Banded, botryoidal manganese oxide ores occur at several sites within the Welsh Caledonides. For example, in the Central Wales Orefield, a trial on the Camdwr Fault at Drosgol (SN 762 882), over 450 m above sea-level, yielded small amounts of manganese ore (Bevins and Mason, 1997). The ore occurred in a high-level setting in a fracture more usually known for carrying base-metal sulphides in a quartz/brecciated grey mudstone gangue. At Drosgol, as at Mynydd Nodol, extensive and pervasive bleaching and reddening of the mudstones is a striking feature. Similar mineralization occurs farther north, in iron trials near the Sygun Copper Mine (SH 604 483), where tuffs of the Lower Rhyolitic Tuff Formation, of Caradoc age, are intensely bleached and traversed by botryoidal goethite veinlets, and at Sychnant (SH 758 768), where attractive botryoidal goethite has been collected (D. Jenkins, pers. comm.).

In both South and north-east Wales, oxide-facies Fe-Mn (+/– Cu, Pb, V, Co and Ni) mineralization is widespread in fractured and hematized Carboniferous strata. Examples in South Wales include Tŷ-Coch (Criddle and Symes, 1977) and the Llanharry orefield (Rankin and Criddle,

Figure 5.94 Photograph of the Mynydd Nodol Mine GCR site. (Photo: R. Mathews.)

1985), both of which, from evidence at the **Ogmore Coast** GCR site, were formed in pre-Jurassic times in a Triassic continental-arid environment. In North-east Wales, soft, nodular, botryoidal, complex oxides occur at Moel Hiraddug and are represented at the **Great Orme Copper Mines** GCR site by the 'Copper Dhu' ore.

The Carboniferous-hosted oxide mineralization, in both South and north-east Wales, is complex in mineralogical terms and additionally often has characteristics of epigenetic mineralization, with intergrown quartz, calcite and, in places, barite. The oxide deposits of the Welsh Caledonides, such as Mynydd Nodol, on the other hand, are simple impregnations of voids in severely bleached mudrocks and volcanics. The quartz occurring at Mynydd Nodol is interpreted as representing much older quartz veinlets, which are extremely common throughout the Arenig region (authors' unpublished data). The fact that manganese oxides are now present in the same fractures most probably represents re-activation of pre-existing weaknesses, perhaps with the spaces for oxide deposition having been created by the dissolution of metastable vein minerals such as calcite. In other examples seen at Mynydd Nodol, the oxide mineralization represents the impregnation of fault-gouge, although there is no evidence for contemporary tectonic movement in association with the manganese mineralization.

The association of bleached mudstones with strongly developed supergene base-metal mineralization has already been discussed in the case of the **Llechweddhelyg Mine** GCR site (this chapter). That mineralization has been assigned to deep, sub-tropical weathering processes during Tertiary times, and it is equally likely that the Mynydd Nodol mineralization, along with that at other similar sites in the Welsh Caledonides, was formed during the same period, and, as at Llechweddhelyg Mine, has been preserved despite the stripping effects of glacial erosion. It is likely that the highly fractured nature of the host tuff permitted deeper than usual penetration of oxidizing groundwaters in this area, so that, despite much subsequent erosion, a portion of the deposit remained.

The survival of just a small number of sites where severe bleaching and oxide mineralization is present bears testimony to the extent of erosion that occurred during the Pleistocene glaciations. These sites, typified by Mynydd Nodol Mine, therefore represent a rare example of what much of the surface exposure, especially in fractured areas, would have looked like prior to the glacial epoch.

Conclusions

The Mynydd Nodol Mine GCR site represents a rare, well-exposed example of a sporadically distributed class of mineral deposit within the Welsh Caledonides, namely the association of black Mn-Fe oxides with severely bleached, highly permeable host-rocks. Such deposits formed during protracted and deep, tropical to sub-tropical weathering, most probably during Tertiary times. Most of the weathered material was subsequently stripped away by glacial erosion, leaving only scattered remnants, of which Mynydd Nodol Mine is the best-known example in Wales.