# Chapter 5 Wales

R.E. Bevins and J. S. Mason

## 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 reestablishment 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 Mineralogy of Wales

## 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, 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 Ll■n. 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 Bowen, 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 ed.,* 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 (MV1) 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).

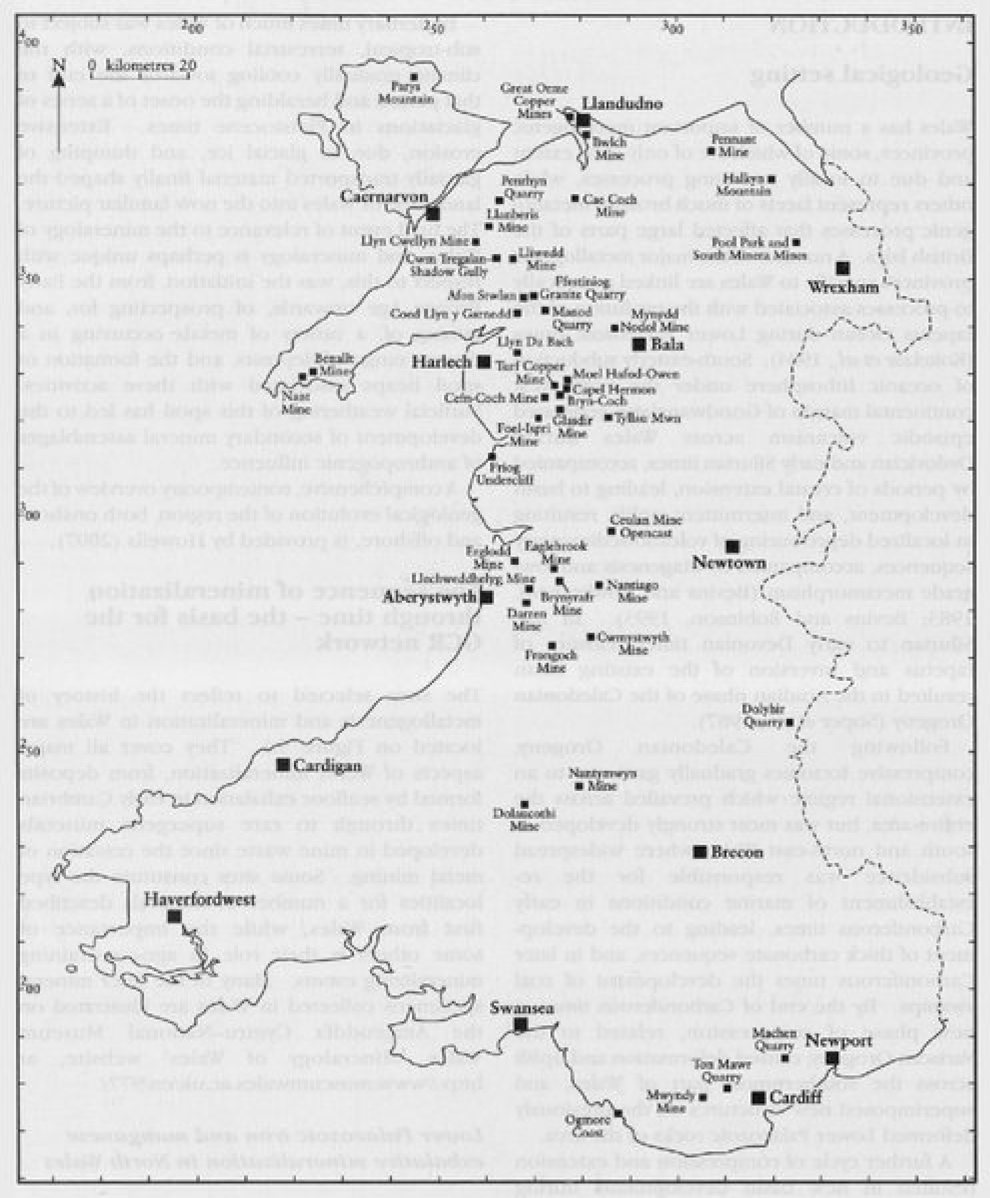
## Lower Palaeozoic iron and manganese exhalative mineralization in North Wales

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 (Figure 5.2) and (Figure 5.3). This mineralization, best 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.

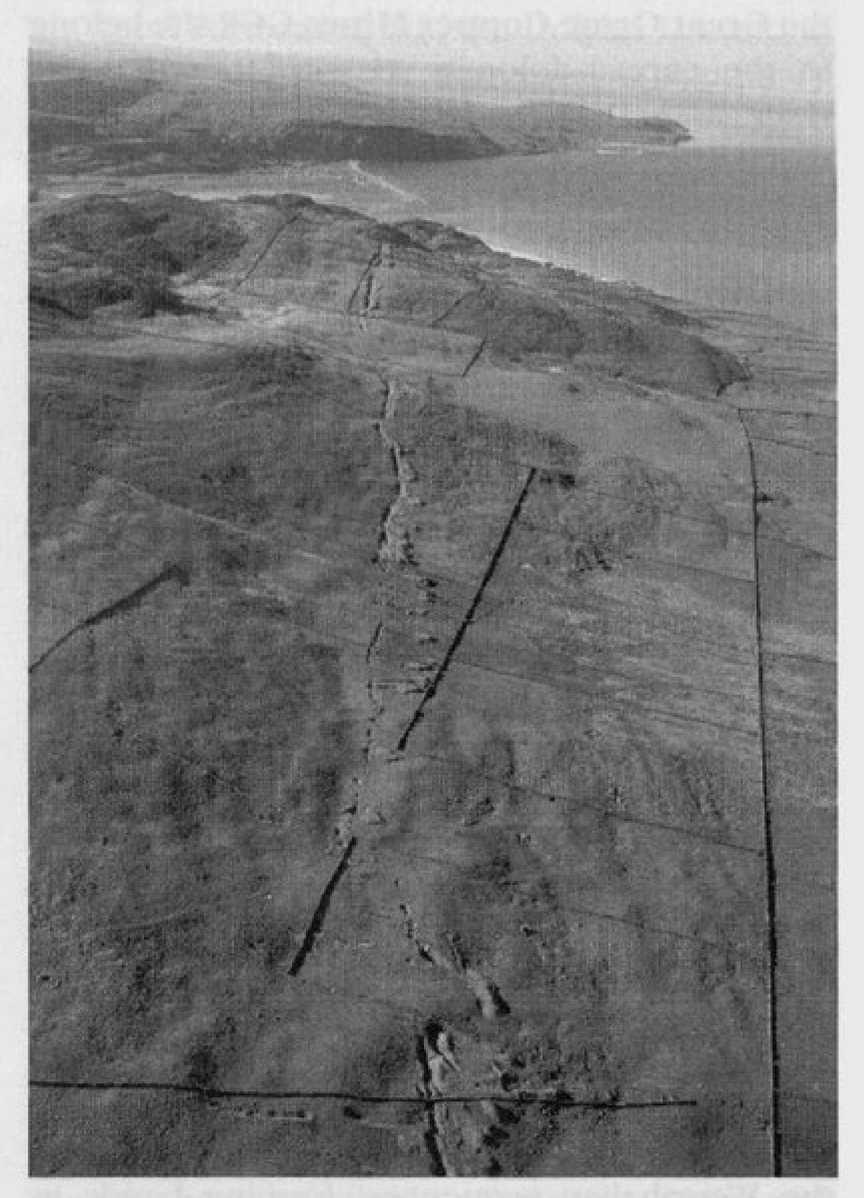
Iron and manganese deposits of Ordovician age are of widespread occurrence across North Wales, where, on Ll■n, they were mined in substantial quantity at the Benallt and Nant Mines GCR site. This site is of considerable scientific importance for the large number of rare, well-crystallized silicate minerals 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 Lyn (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 Tynan Mwn GCR site, on the western flanks of Aran Fawddwy, where, in addition, unusual calcite-apatite-stilpnomelane veins are present (Matthews and Scoon, 1964).

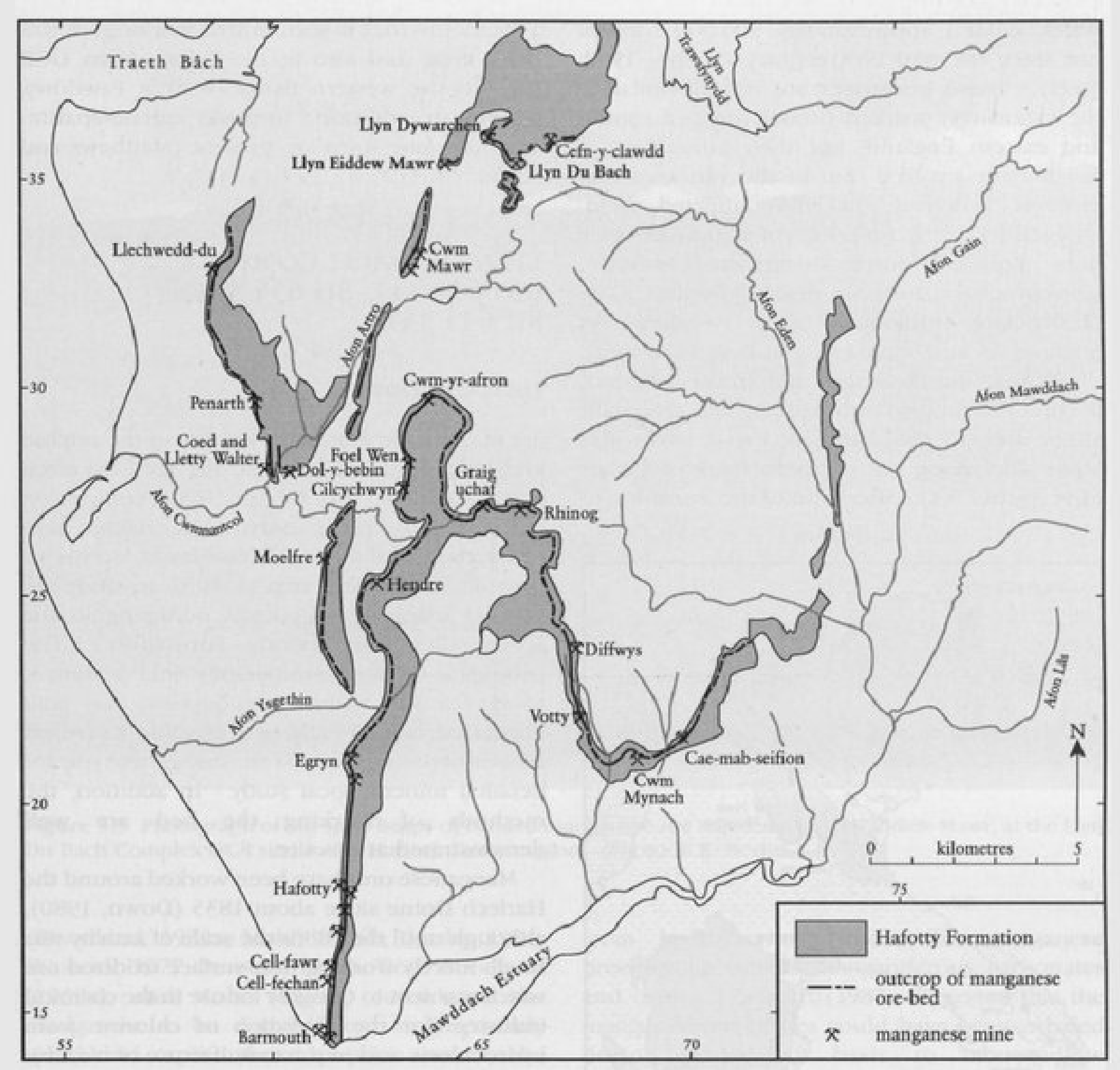
References



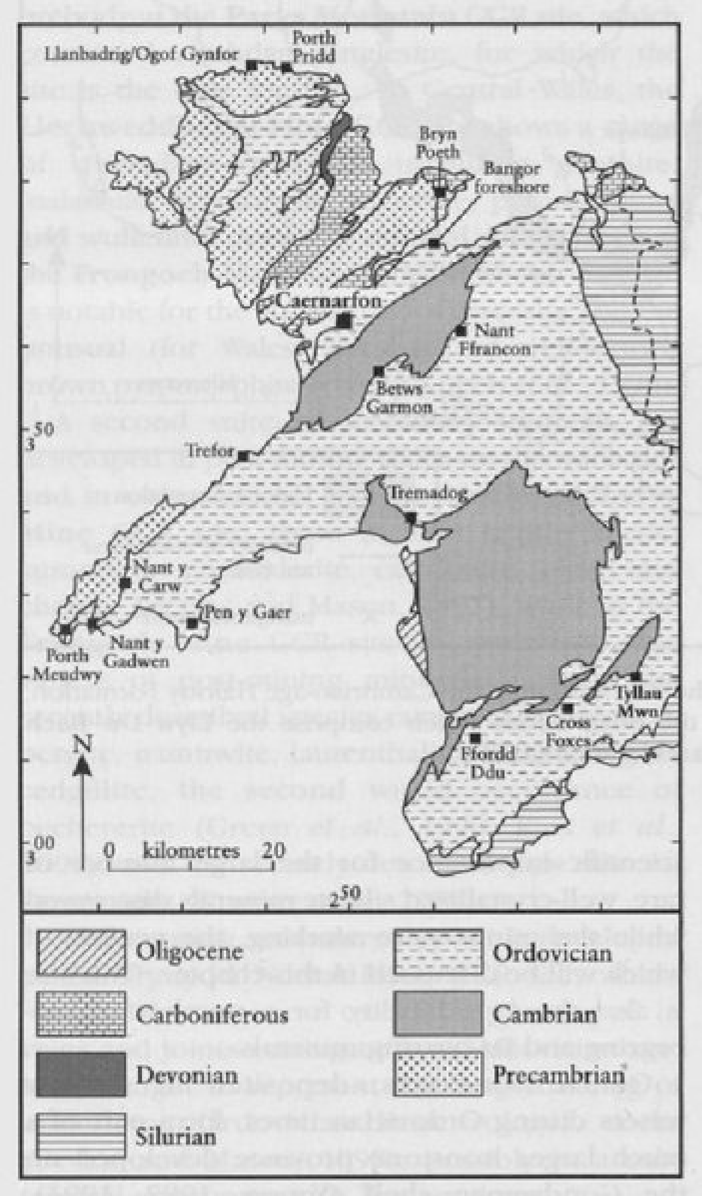

(Figure 5.1) Map of Wales showing the location of the GCR sites described in this chapter.



(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).*




*(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).*