Chapter 6 The Mendip Hills

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Introduction

Geological setting

This chapter covers the sites located within the Mendip Hills and associated areas (see (Figure 6.1)). The Mendip Hills area consists of a series of ridges of Palaeozoic rocks reaching a maximum height of 300 m and extending WNW from Frome in Somerset to Brean Down, near Weston-super-Mare on the Bristol Channel.

The structure is controlled by four major en-echelon periclinal folds with a dominant east-west axis. The folding is related to the various phases of the Amorican Orogeny. The ridges consist mainly of Carboniferous Limestone which forms the dip-slopes, steeper on the northern limbs, reaching near-vertical in places. Sedimentary rocks of Devonian age form the core of most of the anticlines, as in the Blackdown, North Hill and Pen Hill structures. The Palaeozoic rocks are overlain unconformably by rocks of Triassic and Jurassic age. During the folding of the region a system of faults and joints were developed. Many of these fractures eventually became pathways for fluid movement leading to a varied assemblage of minerals (see (Figure 6.2)).

Mineralization

Mining and quarrying on the Mendip Hills began long before the Roman occupation of Britain. Gough (1967) suggested that Mendip lead was worked as far back as the 2nd and 3rd century BC. However it is the exploitation of the lead ores from the Mendip region by the Romans that made the region famous. Lead from the Mendips area made a major contribution to the plumbing in the villas of Pompeii, and lead ingots stamped with Latin inscriptions are known to have been exported from the Charterhouse area in AD49. Both mining of the lead ores and their smelting took place in the region.

According to the Roman historian Pliny (23–79 AD), Britain became the chief source of lead in the Roman Empire, and much of this came from the Mendip region. After the Romans departed, the industry declined until lead production began to increase in the 15th century, rose to a peak in the 17th century but then declined again, until ceasing altogether in 1908. Green (1958) suggested that some 100 000 tons of metallic lead was obtained from the Mendip region.

Zinc ores were also mined in the Mendips. The ore mineral was normally smithsonite (the zinc carbonate) rather than sphalerite, the primary sulphide. The carbonate ore was first worked in the 16th century, with production ceasing in the 19th century.

Despite the former dominance of galena, the primary lead sulphide ore, the Mendips are recognized importantly as a source of four differing mineralization assemblages. The interplay of fluids associated with the main phases of mineralization led subsequently to an assemblage of secondary minerals unique to the Mendip Hills. The four types of mineralization are: (1) lead and zinc ores; (2) iron and manganese ores; (3) evaporites such as gypsum, halite and celestine; and (4) secondary lead and copper minerals.

Despite the lack of active metalliferous mining, the quarrying industry, which is active in this area, continues to reveal temporary but important sections for study. Most of the original orefield is now overgrown 'gruffy ground', a local term for hummocky ground caused by surface workings for lead ore. Reviews covering aspects of the orefleld are extensive, with important papers being those by Dewey (1921), Green (1958), and Ford (1976). The remarkable suite of secondary minerals has been described by Spencer and Mountain (1923), Symes and Embrey (1977), and Alabaster (1982), while recently several new mineral species and hence type localities have been described (see later).

An authoritative overview of the geological interpretation of many of the important mineral sites in the Mendip Hills region was given by Stanton (1982), while an outline of several of the sites of mineralogical importance in the area was described by Symes (1985).

It is from sites described in Stanton's report, combined with the unpublished work of Haynes (pers. comm.) and the findings of Symes (1985) that the site descriptions in this chapter are based.

Lead and zinc ores

The ancient lead-zinc orefleld of the Mendip Hills was described in detail by Green (1958). The mineral assemblage consists of galena, sphalerite and pyrite, associated with calcite, barite, barytocelestine and rare fluorite, as seen at the Charterhouse Lead Orefield GCR site. Smithsonite ('calamine' or 'dry bone ore') was the main ore of zinc, and although previously it had been believed to be of primary origin it is now considered to be of secondary origin.

The minerals occur in a series of small parallel veins and as fissure-fillings often associated with neptunian dykes. They were once economically important in the Carboniferous Limestone and Triassic Dolomitic Conglomerate, although veins are also found in the younger beds of Jurassic age (Alabaster, 1982). Veins and masses of identical mineralogy occur to the west of the orefield, at Steephohn in the Bristol Channel (Whittaker and Green, 1983), to the north-west at the Clevedon Shore GCR site (Ixer, 1986; her *et al.*, 1993), to the north-east in the Chipping SocIbury Quarries (Rankin and Stanley, unpublished report), and across the Severn Estuary at the Machen Quarry GCR site (see GCR site report, Chapter 5).

Fluorite is only sparingly found associated with the Pb-Zn ores (Smith, 1973). At several localities barite was an important gangue mineral, as for example at the Banwell Caves GCR site, and also occurs along with calcite filling minor veins. Copper minerals are rare in the main Mendip Orefield, although copper minerals were worked previously in the Quantock Hills, to the south-west. Fine specimens of azurite and malachite can be found in mineral collections from the Cannington and Bin Combe areas.

Although not now well-exposed, the Mendip lead-zinc ores have been extensively studied, and recent models make comparisons with other occurrences of carbonate-hosted lead-zinc mineralization, particularly with those of Mississippi Valley-type (MVT), including those of the Northern and Southern Pennines and the Halkyn Mountain–Minera district of north-east Wales, described in chapters 3, 4 and 5 of this volume, and also by her and Vaughan (1993). Models related to this type of mineralization are based on the migration of diagenetically formed metalliferous fluids from adjacent sedimentary basins. It is clearly established that these deposits were formed by the deposition of the minerals from hot (50°–200°C) saline, aqueous solutions some time after the lithification of the host rocks; however this does not preclude important differences in detailed aspects of the genesis of a particular orefield.

The age of mineralization in the Mendip Orefield is still a matter of speculation, few absolute dates having been published. Moorbath (1962) presented lead isotope ages, suggesting a mid-Permian to late Triassic date for the mineralization. However, Ford (1976) and other workers have argued for a Jurassic age. Consensus is that the lead-zinc mineralization began at the end of the Triassic (post the formation of the iron and manganese deposits in mid Triassic times), continued through the Jurassic, and finished in mid- to late Cretaceous times. Haggerty *et al.* (1996) have reviewed lead isotope data for lead ore samples from the Mendip Orefield and concluded that the data infer fluids being derived from three isotopically different sources, considered to be the adjacent Mesozoic sedimentary basins (rather than Carboniferous basins). These included the Wessex Basin, the Central Somerset Basin and the Bristol Channel Basin.

The Harptree Beds, exposed in the central Mendips, are silicified Jurassic limestones (Lias and Inferior Oolite), which contain galena, sphalerite and barite in small amounts, and are best studied at the Wurt Pit GCR site. Green and Welch (1965) commented that the Harptree Beds appear to be the result of metasomatic replacement by chert of late or post-Inferior Oolite age. It was originally thought that this silicification phase was a separate late mineralizing event. However, there is now good reason to assume that on the basis of the fact that the Harptree Beds are always located close to areas of lead-zinc mineralization (Stanton, 1982) they were silicified at about the same time as mineralization.

Iron and manganese ores

Exploitation of the manganese and iron ores in the Mendip Orefield has always been on a small scale because although the sporadic deposits are quite extensive the iron ore tended to be too siliceous for easy smelting, and extraction has centred on those localities where the mineral was found to be useful as a pigment, for example in the Winford area. The manganese ores were primarily worked for use in pottery glazes.

These small supergene iron and manganese deposits are more widespread to the north of the region, around Bristol, and to the east of the orefield. Important localities are the Hartcliff Rocks Quarry and Compton Martin Ochre Mine GCR sites, and Merehead Quarry and I ligher Pitts Farm Quarry (Burr, 1996).

The ores worked were various iron oxides, namely hematite, goethite and limonite, which in many deposits were found to be intimately associated with mixtures of black manganese oxides. The mixtures of black manganese oxides were locally known as 'wad'. Where identifiable the manganese minerals present are shown to be pyrolusite and psilomelane. The iron and manganese minerals occur in pockets within fissures or solution cavities in the Carboniferous Limestones or as patches of metasomatic replacement within the lower beds of the Dolomitic Conglomerate (see (Figure 6.3)). Both iron and manganese oxides often display characteristic banding and botryoidal habit: both may be cavernous, and the manganese oxides commonly occur as pods.

Still exposed in the low adit walls, the iron and manganese minerals of the Higher Pitts Farm Quarry have recently been described by Burr (1996). Iron ores were worked from this locality for some three years in the 1890s, and the manganese pods provided fine examples of the secondary lead-copper oxychloride assemblage. At the Compton Martin Ochre Mine GCR site a hematite-rich conglomerate has been mined for red ochre, providing the largest and best-preserved example of the red ochre deposits of the Mendip area.

In many of the mineralized Triassic fissures in the eastern Mendips region, the Fe-Mn mineralization is truncated by the Inferior Oolite unconformity.

Green and Welch (1965) noted that the emplacement of the hematite pre-dated the lead-zinc mineralization. However, the formation of the ores was probably partially due to descending iron-rich solutions during Triassic times, both the iron and manganese being derived from the leaching of pre-existing sediments by weathering under semi-arid conditions. Spatial distribution of the ore deposits appears to have been controlled by the distribution of suitable replacement environments within the Dolomitic Conglomerate and Carboniferous Limestone, the relative amounts of iron and manganese being determined by the chemical environment at the site of precipitation and the chemistry of the mineralizing solutions themselves. However, Ford (1976) considered the iron ores to be of a gossanous character, derived from weathered pyrite, in late Tertiary times. The manganese ores, although being of limited distribution compared to the iron ores, invariably contain small amounts of secondary lead minerals, commonly cerussite, hydrocerussite and mendipite, as well as a range of rare secondary lead minerals (see below).

Iron minerals are often associated with neptunian dykes and calcite-bearing veins (filled by comb-crystallized calcite); however neptunian dykes of proven Jurassic age commonly transect the Fe-Mn ores, proving an earlier age for the mineralization.

Evaporites

In parts of Somerset and Avon, Triassic sedimentary rocks contain horizons rich in gypsum. Bands of this mineral are particularly well-exposed in the cliff sections of Aust and Blue Anchor Point near Minehead. A considerable salt field of Triassic age has been proven in the Central Somerset Basin from borehole evidence (Whitaker, 1972). As such these occurrences provide information on the varying palaeoenvironment of Triassic times.

However, perhaps most interesting has been the working over the last century of celestine from the Mercia Mudstone Group around Bristol and several localities throughout the Mendips. Most of the workings are now filled in, but traces of gypsum and celestine with green mudstone fragments often occur in surface rubble, as at the Ben Knowle GCR site. The celestine occurred as nodules or irregular masses in the Mercia Mudstone Group rocks. In the past, partially hollow nodules were found containing fine groups of pale-blue crystals. Nickless *et al.* (1976) described the celestine deposits of the Bristol area. They considered the celestine to be diagenetic after gypsum or anhydrite, the primary minerals probably forming in supra-tidal environments. Strontium may have been derived from the conversion of aragonite to calcite in underlying limestones of Carboniferous age.

Nodules and geodes from the Mendip Hills have been known, described and collected for a few hundred years. Such nodules and geodes occur in conglomerates and marls of Triassic age and are found over an area from Bristol to Wells. Here the Triassic sedimentary rocks rest unconformably on the folded and eroded rocks of Silurian, Devonian and Carboniferous age.

Quartz nodules from the Mendips have been given several different names, most commonly 'Potato Stones' or 'Bristol Diamonds'. Perhaps the most prolific locality for such nodules was Dulcote Quarry, near Wells, where the nodules were worked extensively for the lapidary trade (Harding, 1978). The nodules have variable structures but commonly have an exterior shell composed of concentric layers of coloured chalcedonic quartz or agate and a hollow interior lined with well-formed quartz crystals. Tucker (1976) found that the agates contained microscopic inclusions of anhydrite, and so suggested that the nodules were originally formed as anhydrite concretions growing in Triassic desert environments under the influence of warm hypersaline groundwaters. Later many of these nodules were partially or completely replaced by silica, maybe a phase of silicification related to the silicified Harptree Beds exposed at the Wurt Pit GCR site.

Secondary lead and copper oxycbloride minerals and associated mineral assemblages

The oxychloride mineral mendipite was collected from the Mendips long before it was recognized and described as a distinct species. Figured specimens of mendipite survive in old collections; several specimens of mendipite are in the Woodward Collection (1665–1728), now in the Sedgwick Museum, Cambridge. Early specimens were also in the collection of Thomas Pennant (1762–1798), now in the Natural History Museum, and a specimen of mendipite was figured by Rashleigh (1797). Spencer and Mountain (1923) described the new species chloroxiphite, which remains unique to the Mendip Hills, and diaboleite, associated with manganese and iron ores from Higher Pitts Mine, near Priddy. Examples of secondary lead minerals such as cerussite and hydrocerussite have been described from many localities, but it is from the extensive quarrying activity from Merehead Quarry [ST 691 442] that the most extensive vein type-deposits have been described (Symes and Embrey, 1977).

At Merehead Quarry the secondary minerals occur scattered throughout the manganese ores, often intermixed with calcite and, usually, cerussite and hydrocerussite. Associated with this assemblage occurs a further range of rare secondary minerals. This assemblage was first described by Spencer and Mountain (1923), and has been extensively studied and described subsequently by Alabaster (1975), and Symes and Embrey (1977). As quarrying has proceeded in this large Carboniferous Limestone quarry, a series of veins were exposed, most of which were calcite- and breccia-filled, but some being iron- and manganese-rich. These more-or-less continuous structures carry the manganese oxides as a series of swells or pods. Samples collected from these pods and elsewhere in the Mendips consist of an inner core of mendipite, sometimes containing blades of olive-green chloroxiphite and blue diaboleite surrounded by concentric layers of hydrocerussite and cerussite, enclosed by the manganese oxide matrix.

The formation and stability relationships of these rare copper and lead minerals from aqueous solution have been detailed in a series of papers (see Williams, 1990).

Recently three new mineral species have been described from the Merehead Quarry manganese-rich assemblage. Detailed compositional and X-ray crystallographic studies have shown these rare secondary minerals to have most interesting structures (Welch *et al.*, 1996). These three new minerals are:

parkinsonite (Symes et al., 1994)

mereheadite (Welch et al., 1998)

symesite (Welch et al., 2000)

The structures of the layered lead oxychlorides are based on an alternation of litharge PbO layers and sheets of Cl atoms. The main feature of interest is the wide diversity of elements that partially substitute for Pb, namely Si, P, As, V, Mo and W (see Welch *et al.*, 1996). Charge balance is provided by Cl, which forms layers between the PbO-like sheets.

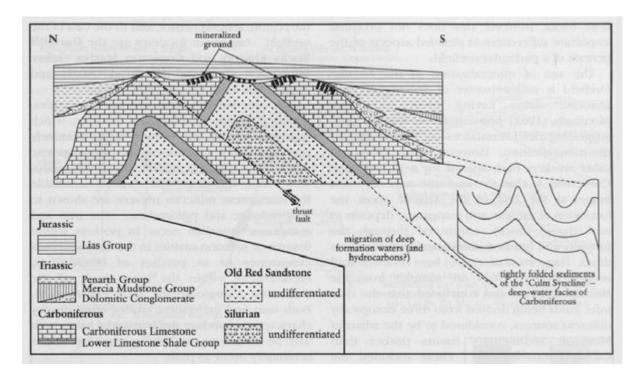
Alabaster (1975, 1982) described the formation of manganese ores at Merehead Quarry. He proposed that Fe and Mn in dilute acid solution, derived from weathering of Coal Measures strata, passed into fissures in the Carboniferous Limestone and Dolomitic Conglomerate during Triassic times. They were precipitated as hydrated oxide gels filling the fissures and replacing the wall-rocks. The Mn oxide gels adsorbed Pb, Cu, Mo, Ba and other cations from ambient solutions, while the Fe oxides adsorbed anions such as Si, As, and P. When gels slowly consolidated and crystallized, the Si remained with the Fe oxides, but other ions were gradually expelled and formed secondary minerals filling cavities. Fe-Mn ores ceased forming in late Triassic times, but in the early Jurassic, following the Rhaetic transgression, the expelled ions were able to react with Cl derived from seawater to produce the rare oxyhalide minerals.

Symes and Embrey (1977) believed prolonged reaction between galena and copper sulphides (or solutions rich in Cu and Pb ions), and manganiferous and saline solutions have produced the oxychloride suite. Brines have often been postulated as mineralizing agents, but in the south-east Mendips area the chloride ion of the brines appears to have been retained as an essential component of the minerals. There are indications that the temperature of the solutions involved was low (Symes and Embrey, 1977). Extensive studies (Williams, 1990) on the chemical stabilities of mendipite, chloroxiphite, diaboleite and other associated phases have been determined in aqueous solution at 282°K (Humphreys *et al.*, 1980; Abdul-Samad *et al.*, 1982), and these studies have shown that small variations in concentration and other chemical parameters of the solutions may determine which members of the assemblage are formed. The Mendip mineral occurrences are critical in providing the natural analogues against which to test these experimental investigations.

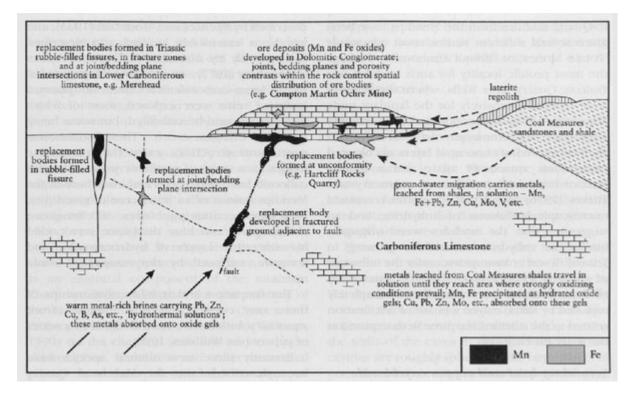
References

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Jurassic	Carboniferous Pennant Sandstone Formation
Liss	Carboniferous Linestone fault
Triassic	Devonian
Mercia Mudstone Group	Devonian
Mercia Mudstone Group with Dolomitic Conglomerate at base	Early Devosian

(Figure 6.1) Map showing the locations of the GCR sites in the Mendips: 1 — Banwell Caves; 2 — Banwell Ochre Caves; 3 — Ben Knowle; 4 — Charterhouse Lead Orefield; 5 — Clevedon Shore; 6 — Wurt Pit; 7 — Compton Martin Ochre Mine; 8 — Hartcliff Rocks Quarry.



(Figure 6.2) Diagrammatic cross-section of the Mendip Hills and the Culm Syncline, showing possible migration route of deep formation waters up-dip. Based on Ford (1976), and Alabaster (1982).



(Figure 6.3) Manganese-iron mineralization in the Mendip Orefield. After Alabaster (1982).