REPORT

Manganese mining in the Peak District

The Carboniferous Limestone of the Peak District in Derbyshire is well known as the host rock for numerous mineral veins containing lead, zinc and copper ores, as well as the gangue minerals fluorspar, barytes and calcite. All have been exploited at various times and many hundreds of old mines can be traced along the mineral veins. But there are several other less common minerals which have had economic importance. Most literature on the region either totally ignores them or at best gives them a one-sentence mention. Any applied geologist studying such an area as the Peak District should be aware of these minor mineral deposits and give them due attention. Apart from fluorspar, barytes and calcite, all still produced today, there was once active mining for the zinc ore sphalerite, smithsonite (zinc carbonate, locally known as calamine), iron ore, chert and manganese wad.

The wad is an impure deposit of a mixture of manganese and iron oxides (Ford, 2001). The former is chiefly present as the hydrated manganese oxides pyrolusite and psilomelane whilst the latter are earthy hematite or limonite, but no modern analyses of Derbyshire material could be found in a literature search. Elsewhere wad has been determined as birnessite, a hydrated manganate of sodium, calcium and potassium; this may well be present in Derbyshire wad, but no analyses are known to have been made.

Wad Deposits

Workable wad deposits were at least 50% manganese oxides in layers generally less than half a metre thick found within sand and clay fills of caverns close to the contact of dolomitized and unaltered limestone. These have long been worked out and none of the recorded deposits is accessible for study today. However, open-pit fluorspar mining does occasionally reveal wad deposits, as in Winster Moor Spar Pit (SK234597) where several layers were seen interbedded within coloured clays in April 2005 (Fig. 1).

The formerly mined deposits were in sub-surface phreatic solution caves, mostly with no known natural openings to the surface, though there must have been some fissures for the sand and clay fills to have been washed in later. The fills were probably early Pleistocene glacial outwash but without samples it is difficult to be sure. A thin layer of wad-like material is present in a sand and clay fill in the Golconda Mine, near Brassington (Fig. 2), but it is not thought that it was ever worked there. Small patches of wad, up to about 30 cm across, have occasionally been found around the margins of the silica-sand Pocket Deposits (Mio-Pliocene Brassington Formation) that lie near Brassington. Subsequent collapse of these Brassington Formation sands and clays has resulted in the former horizontal sheet of sediments sagging into hollows, but

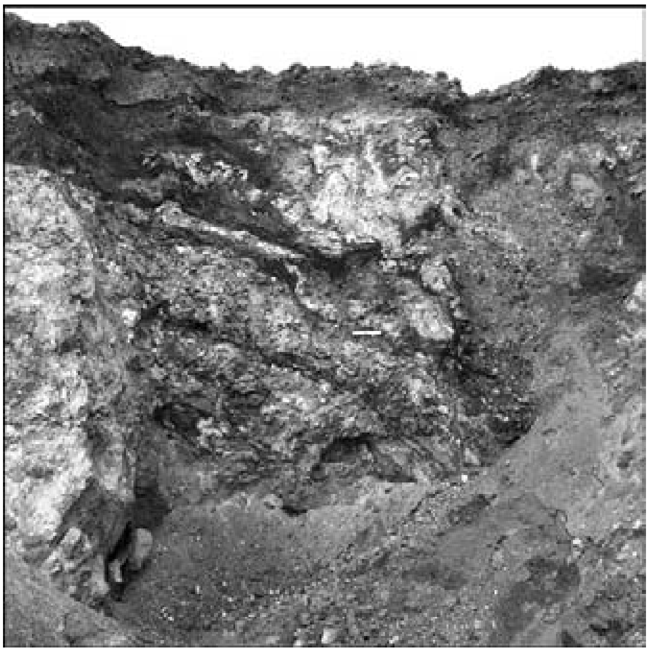


***Figure 1**. Wad deposits in Winster Moor fluorspar open pit.*

no wad deposits are visible at the time of writing. Locally known as pockets, the collapses are thought to have occurred in the early Pleistocene, so both cave and pocket wad deposits can be regarded as having been formed during Pleistocene times.

Manganese coatings are sometimes present on pebbles in stream caves; these are thought to be of bacterial origin, deposited from sinking streams flowing off the Millstone Grit country.

Deposits with considerably less than 50% manganese oxides were brown in colour and known as umber. As with wad, umber was used in paint manufacture but little is known of this aspect of the pigment industry.

The distribution of wad deposits is largely related to the boundaries of the dolomitised areas of the White Peak, with the principal workings being in the Elton and Winster area, west of Matlock (Fig. 3). Between those villages, Heyspots Mine had the largest recorded yield; it lay on part of the important lead ore deposit in the Portaway Pipe vein, but unfortunately its workings have long been inaccessible and no mine plans are known to survive. Other wad deposits were around Brassington, Parwich and Youlgreave. Indeed a field name near Kenslow Knoll (one of the Pocket Deposits southwest of Youlgreave) is Manganese Close.

The source of the manganese and its mode of concentration are problems still requiring research. Whole rock analyses of the Carboniferous Limestone show traces (generally around 100-200 ppm) of MnO in pore-filling cements in some limestones and in a few microfractures in calcite veins, but this trace proportion seems unlikely to be have been enough to account for the wad deposits. Detailed studies of the geochemistry of limestones in Longcliffe Quarry

(Pugh, 1994) revealed around 60 ppm Mn as impure rhodochrosite forming a thin early phase of pore-filling cement. Microfractures in calcite veins occasionally had a few traces of rhodochrosite (Bennett, 2004). However, the amount of manganese present in these cements and fractures is far too small to account for the tonnages of wad that were mined, unless some means of concentration can be found: none is known at present. No records have been found of macroscopic manganese minerals in the lead-zinc-fluorspar-barytes veins.

Analyses of dolomitised limestones (Harrison & Adlam, 1985) generally show much higher manganese figures (mean 1014 ppm) than in the limestones (638 ppm). Weathering of dolomite could release manganese into the soil whence percolating rainwater carried it into sub-surface cavities. Once in the cave environment increased alkalinity of limestone waters presented an environment suitable for manganese oxide precipitation in preference to iron hydroxides, particularly at the permeability changes where clay beds are interlayered with sands. Oxidation from the soluble bivalent ion to the insoluble quadrivalent ion causes precipitation of managanese oxide minerals (Hill & Forti, 1997, 2004) and this mechanism may well have operated in Derbyshire. Elsewhere, bacteria have been shown to precipitate manganese oxides

Figure 2*. A minor wad layer in a sand fill in a cavern in the Golconda Mine, near Brassington.*

(Engel, 2005) so it is possible that bacteria were an active oxidation agent in the Peak District, but without appropriate microbiological analyses it is difficult to confirm their presence.

Mining and processing

Mining wad was simple: a pick and shovel were all that was needed to dig into the sand-and clay fills, taking care not to mix them with the wad.

Once raised to the surface, wad required some processing to remove lumps and to clean away unwanted sand and other rock fragments. There were several local mills, e.g. at Matlock Bath, Wensley and near Bonsall, but none has survived. The little that is known of the processing was summarized by Paulson (1997). It appears that the wad was ground to an even grain and subjected to levigation – an early form of flotation - to separate it from waste sediment. It is not clear how excess iron oxides were removed.

Uses of wad

The use of Derbyshire wad was first recorded by the pioneer chemist Robert Boyle in 1670 but no other details are known. By the mid 18th century artists in Derby such as Richard Roe sought it as a pigment. While its black colour had an obvious attraction, there were other less expensive black materials available, but wad was valued for its property of accelerating drying of paint by oxidation of the oil carrier in the mixture.

A letter contributed to the Derby Mercury on December 4th 1783 (kindly supplied by Roger Flindall) adds a little more:-

As I know you wish to propagate all Kinds of useful Knowledge to your entertaining Paper, I send you the following , viz. "There is a light black earth found about Matlock and Porridge which they call WAD, and which has lately been much used as a Pigment, or Colour to cover Ships with. This Black Earth is an ORE of Manganese, and, when mixed with Lime, will make a Mortar, which will set firmly under Water, as is lately discovered by Professor Bergman, of Upsal**. About 20 years ago, Mr Roe, a Painter of Derby,observed this Black Earth, when mixed with Linseed Oil, spontaneously to take Fire: I am lately informed, that to produce this Effect, the Oil must be very rancid.*

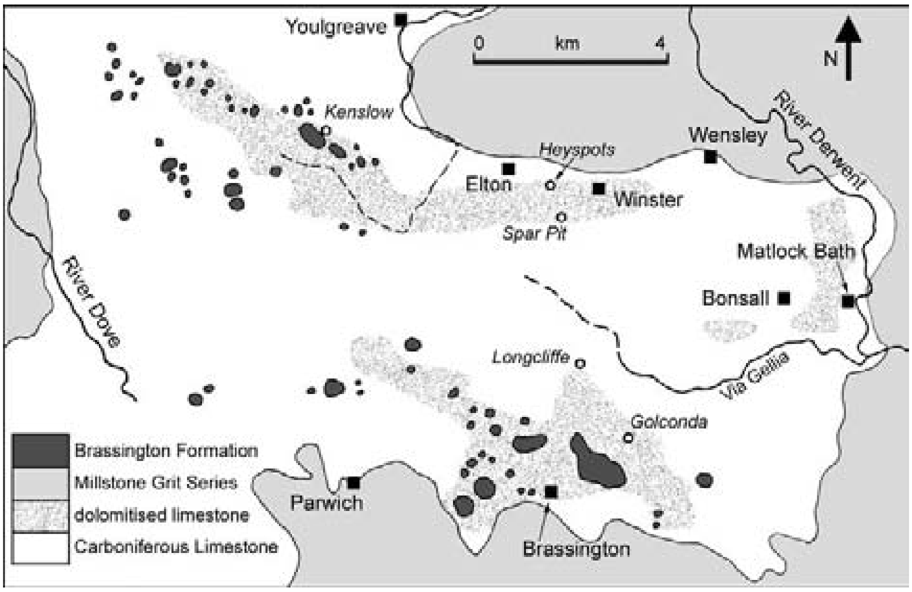
Yours etc X.Y.

** Porridge is now known as Parwich.*
*** Upsal is now known as Uppsala in Sweden*

The letter goes on to mention that manganese was used in glazing blue tiles in Staffordshire, but no details were given.

From the 1780s wad was much in demand for use in treating ships' bottoms, indeed in the Napoleonic wars there was a strong government demand for wad to be used on Royal Navy ships' bottoms. Again, while its

Figure 3. Wad mining localities in relation to dolomitised limestones and silica-sand pockets in the Peak District.



colour was an attraction, it was much more important as a desiccating agent hastening paint drying. Paint in those days was based on either linseed or tar-oil: with a component of creosote as a wood-preservative; it took days if not weeks to dry without the addition of wad, so the drying agent was vital.

Another use for wad was mixing it with hydrochloric acid to yield chlorine gas used in bleaching textiles. Later the chlorine was combined with powdered lime as bleaching powder. In 1790 a factory was set up at Widnes to produce bleaching powder and it became one of the founding factors of that area's chemical industry today.

Small quantities of manganese oxides added to molten glass reduce the colour imparted by too much iron in the glass sand, a phenomenon known in ancient Egypt. It is not known if any Derbyshire wad was used for this purpose.

Manganese metal was not recognized as a separate chemical element until 1774. In 1839, alloying manganese with steel was found to yield a very hard metal which later became important in munitions production and demand grew rapidly. However, no record of Derbyshire wad being sold for metallurgical purposes has been found and the limited quantities of wad available make it unlikely that it was ever used in such alloys. Manganiferous beds in the Cambrian successions of the Harlech Dome were the main British sources of manganese for steel alloy manufacture. Minor quantities were raised from mines in equivalent Cambrian strata near Nuneaton.

Production

Regrettably few production figures for late 18th and early 19th centuries are available, but from 1876 to around 1904 a total of just under 5000 tons was recorded (Burt et al., 1981), and it is reasonable to surmise that at least as much was raised before 1876, making a total yield of around 10,000 tons, perhaps as much as 15,000 tons. Such a figure is much smaller than those for lead ore and fluorspar production, and it is possible that the mining companies concerned regarded it only as a profitable sideline. Heyspots Mine, near Winster, had the highest recorded production yielding 573 tons in four years 1877-1881. With lead ore being the principal product raised from that mine and the adjacent Portaway Pipe, wad on its own would not have made much of a living.

Acknowledgments

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