DERBYSHIRE WAD AND UMBER

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Abstract: An attempt is made to draw together all that is known of the Derbyshire wad deposits and industry. Wad is an impure maganese deposit with about 50% manganese oxides, whilst umber has about 20% manganese oxides. Both are found mainly in caverns associated with lead mines around Elton, Winster and Brassington where the wad was in layers within sand fills. These probably originated in Pliocene times with the effects of pH changes and permeability barriers being responsible for manganese deposition, though bacteria may have played some part in the process. The source of the manganese is thought to be from dolomitized Carboniferous Limestone. Incomplete production records suggest that some 10,000 tons were raised from the mid 18th century to the early 20th century. A brief review of the uses of wad and umber is presented. Comparisons are made with manganese coated pebbles in cave streams both in the Pennines and in Romania.

INTRODUCTION

Wad is an impure manganese dioxide deposit worked in some two dozen Peak District mines, mainly in the 18th and 19th centuries. Sometimes known as "Bog Manganese", it consisted of black powdery material found in mines chiefly in the Elton - Winster area. The closely related umber was brown in colour and with less manganese oxide and more impurities, mostly iron oxides. Although thousands of tons were produced these two mineral products do not appear to have been the subject of any detailed research. They were referred to by many 18th and 19th century writers (as listed in the bibliography) but these tend to be repetitive and give tantalizingly few details of the deposits. It is hoped that the present account will focus attention on the problems concerning the origin, mode of deposition, mining methods, production and uses of wad and umber.

HISTORY AND OCCURRENCE

"Black Wad", as it was usually known to the miners, was apparently being raised as early as the mid 17th century as the pioneer chemist Robert Boyle is said to have visited a manganese mine in Derbyshire somewhere around 1670. By the mid 18th century it was known as "Black Wadd, or Ochra friabilis nigra-susca" (Mendes Da Costa, 1757, p.102). Wad was best known in mines around Elton "where it occurred in layers a few inches thick . . . or more generally in masses of a dark brown or blackish colour, having a friable earthy appearance not unlike hard balls of soot. It is unctuous to the touch and stains the fingers when handled. It appears as if it had been deposited in layers, for in parts where it forms a bed it has every appearance of being a sedimentary deposit". At Portaway Mine, near Winster, it lay "about 10 fathoms below the Earth's surface . . . strata of it from one inch to ten or twelve inches thick" (Pearson, 1784, quoting Mendes Da Costa, 1757). At the adjacent Heyspots Mine it was found "in layers varying from 6 inches to 2 feet thick, resting upon sand and limestone blocks about 3 ft thick, and below this is a pipe of lead ore " (Stokes, 1878, pp.62-63). These quotations sum up what is generally known about the occurrence of wad.

The use of wad in paint manufacture, and its liability to spontaneous combustion, were briefly described by Roe (1751-2), and enlarged upon by Josiah Wedgwood (1783, pp.284-7) who recorded "black wadd" as a manganese deposit in Derbyshire .

Manganese was known as an additive in glass manufacture in ancient Egyptian times though its exact nature was a mystery. The name first appeared in the writings of Biringuccio (Smith and Gnudi 1942 p.113) about 1541 concerning varieties of glass, who noted that "it colours them a beautiful violet". Agricola (1556; Dover reprint, p.586), however, repeated the confused interpretation of Pliny (c.AD 79) about the meaning of the Roman term *magnes*. Metallic manganese was not extracted and recognized as a distinct element until 1774.

Wedgwood went on to give a simple analysis and recorded the current opinion that wad was used in house and ship painting. He carried out nine experiments on its possible use as a ceramic colouring material, though he did not record in that report whether it was taken into general use. He noted that its use as a pigment had been discovered by Mr Bassano, an artist in Derby about 1752; he also noted that it was found "in a hollow way near Winster" (which may suggest alongside the Portway), but gave no further details of the locality.

A letter to Mr Drewry published in the Derby Mercury on December 4th 1783 gave similar details to Wedgwood's account:-

There is a black earth found about Matlock and Porrige (sic), 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 [?Uppsala in Sweden?]. 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 informed that to produce this effect the Oil must be very rancid.

The letter also briefly mentions the manganese being used in glazing tiles. "Porrige" was referred to as Parwick by Pearson (1784) and evidently meant the area around the village of Parwich, where a few of the silica sand pockets worked out in the 19th century presumably contained wad..

Whitehurst (1786, pp.223-4) also noted "Black Wad" and both his and Wedgwood's comments were repeated by most later writers. Whitehurst noted its occurrence around Winster and Alport. He commented on its friability and repeated the discovery by Richard Roe of Derby that it was liable to spontaneous combustion when mixed with linseed oil (see Roe, 1751). Whitehurst also noted its drying quality, well known to paint manufacturers (see Paulson, 1997). Repeating Whitehurst

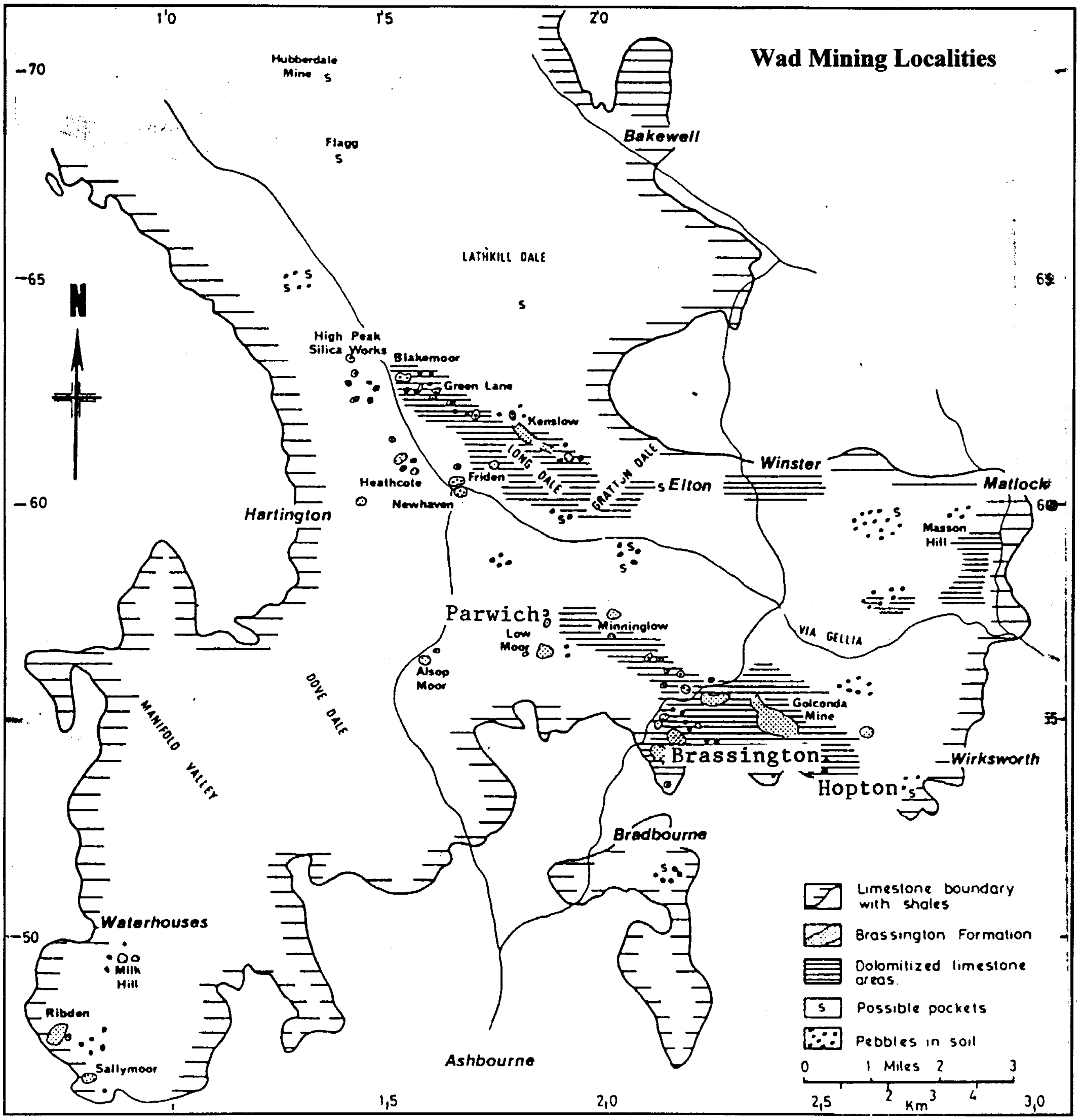

Fig. 1. Wad mining localities in relation to areas of dolomitized limestone and silica sand pockets.

in part, Pilkington (1789, pp.194-5) went on to say that wad was worked at Elton and had lately been found near Parwich. He recorded that it was calcined before use at a works in Wensley. Repeating Wedgwood, Pilkington said that it was "very useful as an oil colour in house and ship painting, and noted that the principal demand had been from the Royal Navy. This use of black wad, I believe, was first found out by Mr Dawson of Winster . . . he made it known to Lord Sandwich, when first Lord of the Admiralty". Farey (1811, p.407) listed mines at Alport, Brushfield, Elton, Great Longstone, Hartington, Hopton, Matlock Bath, Monsal Dale, Parwich, Winster and Youlgrave, but he gave no details and most of the actual locations of those wad workings are unknown today. Adam (1851, p.384) added a little detail: he recorded occurrences at Ball Eye, near Bonsall, and around Elton, where it was "a thin seam in clay beds and yellow ochre . . . pulverized or friable, rarely compact . . . in the shale at Elton, it occurs in compact amorphous masses, sometimes fibrous, associated with zeolite . . . One variety occurs in a mine near Middleton-by-Youlgreave, crystallized in flattish prisms, sometimes radiated or reniform".(Adam may be referring to the black baryte found here). Stokes (1879) noted 40 tons having been raised from Black-Wad Mine, a quarter mile west of Elton, in 1876. Greg and Lettsom (1858, pp.291-2) listed wad from an unspecified mine near "Middleton", but did not say which Middleton - it was probably the one near Youlgreave! They also noted a black variety of barytes, "heavily impregnated with manganese" (see Adam's comments above).

The early Geological Survey *Memoir* (Green *et al.* 1887, p. 159) noted that wad was being worked about a mile south of Middleton-by-Youlgreave; on the Buxton Road about a mile out of Winster, and at Hopton from a hollow in the toadstone on the

Yokecliffe Rake. In the more recent Geological Survey *Memoirs*, manganese ores "collectively known as wad" were recorded as having been extracted at Doglow Wood, Hopton (SK 256 537), and from a shallow working at Foxhole, near Godfreyhole, (SK 274 531) where it was associated with ochre (Frost and Smart, 1979). Wad was noted in "a loose fill of laminated brown clay, dolomitic limestone and fragments of baryte, galena and fluorite" In Wills Founder Mine, near Winster (Aitkenhead *et al.* 1985, p.121). Rieuwerts (1998, p. 164) recorded that wad had been worked at Rath Rake, Elton in 1780-1781 and that nearby Blackwad Grove lead mine was active around the same time.

As most of the wad deposits were worked out long ago, and no accessible deposit is known in any of the Elton-Winster mines today, no definitive description of a wad deposit can be presented, but a speculative hypothesis regarding the wad deposits is given later. The writer has seen black masses of wad up to a metre across and perhaps half a metre thick in the marginal deposits in Kirkham's sand pit near Brassington (NGR SK 218 539), where it was usually associated with patches of the white clay meta-halloysite, known as "snowballs" to the quarrymen - the contrast of black and white was striking (Ford, 1963). Another occurrence was a layer some 30 cms thick in the sand fill of one of the Golconda Mine's caverns. J.H. Rieuwerts has seen similar masses in a spar pit overburden west of the Miners Standard at Winster (NGR. SK 234 598).

Black coatings are well known on pebbles in cave streams. In the Peak District vein calcite gravel in Speedwell Cavern's Whirlpool Passage was coated with black material. Black flowstone below a small inlet in Speedwell's Far Canal contains manganese oxides, and the silt banks close by are enriched in manganese as was revealed by tests following the corrosion of a stainleess steel spade left stuck in the silt for a year. Shelves of black manganese oxides were found in Black Reef Cave at Ribblehead, Yorkshire, analysed as roughly half manganese dioxide and half iron oxide (Crabtree, 1962). Manganese coatings on pebbles are widespread in many Pennine caves (and in Romanian caves: see below). A layer of black wad-like material was found in a gravel of Millstone Grit pebbles in Bradwell Parish Cave, near Bradwell, Derbyshire, but no analyses were done (pers. comm. N.J.D. Butcher).

COMPOSITION

The chemical composition of wad was noted by most 18th and 19th century writers as being about half manganese oxides and half iron oxide. Wedgwood (1783) gave a simple analysis of equal parts of iron and manganese oxides with traces of lead and micaceous insolubles. Greg and Lettsom (1858) gave an analysis with 38.6% "red oxide" of manganese and 52.3% red oxide of iron, regrettably without giving a locality. Others have noted small proportions of barium (usually as barytes), lead and clay or sand in wad. Increasing proportions of iron oxides (limonite) gave brown colouring. The term umber was usually restricted to material with less than 20% manganese oxide, and this graded eventually into ochre with virtually no manganese.

Following Turner (1830), Ford *et al.* (1993) surmised that wad was probably a mixture of pyrolusite [$MnO_2.nH_2O$] with psilomelane, limonite and other impurities, but no analyses have been carried out. Rancieite [$(Ca,Mn_2+) Mn_4.O_9.3H_2O$], has been recorded in several Yorkshire caves (Laverty and Crabtree, 1978) but occurred either within speleothems or as manganese dendrites, and not as layers or lumps of wad. Hill (1983) listed several manganese-bearing minerals in caves - romanechite (a barium-bearing psilomelane) [$BaMn_9O_{16}.(OH_4)$], hollandite [$Ba(Mn,Fe)_8O_{16}$], todorokite [$(Mn_2,Ca,Mg)Mn_3O_7.H_2O$] and birnessite [$Na_4Mn_{14}O_{27}.9H_2O$]: the last-named is regarded as probably the most common manganese mineral found in caves and much so-called pyrolusite may in fact be birnessite (Moore, 1981; Peck, 1986), or todorokite (Hill and Forti, 1997). A full review of the occurrences of several manganese minerals in the cave environment was given by Hill and Forti (1997, pp.124-135) and the microbial contribution to their precipitation is discussed by Northup *et al* (in Hill and Forti, 1997, p.264).

Any or all of these minerals may occur in Derbyshire wad, but no modern mineralogical analyses of Derbyshire material have been traced.

PRODUCTION FIGURES

No production figures have been located for the years before 1876 but wad is known to have been raised from at least the 1780s. Separate figures for umber are rarely recorded. The figures for wad production, often listed simply as manganese ore and including umber, have been extracted from the Mineral Statistics and cover the period 1876-1904 (Burt *et al.* 1981; see also Burt and Waite, 1983 and 1988):

1876	40 tons	1886	364 tons	1896	21 tons
1877	492 tons	1887	456 tons	1897	100 tons
1878	192 tons	1888	125 tons	1898	35 tons
1879	169 tons	1889	34 tons	1899	87 tons
1880	336 tons	1890	67 tons	1900	40 tons
1881	474 tons	1891	71 tons	1901	-
1882	362 tons	1892	119 tons	1902	-
1883	154 tons	1893	376 tons	1903	48 tons
1884	263 tons	1894	36 tons	1904	50 tons
1885	190 tons	1895	102 tons		

The total for Derbyshire was 4803 tons since 1876, about 2% of total British production of manganese ores (most manganese ore came from the Harlech Dome area of North Wales). As wad was raised in Derbyshire for at least a century before the Mineral Statistics records began, it is probable that the overall production was somewhere around 10,000 tons.

The Mineral Statistics (summarized by Burt *et al.* 1981) list individual mines by area, though the details are patchy, incomplete and sometimes plainly inaccurate, with mines placed in the wrong areas. Amendments have been incorporated in the table which follows (next page), and other records have been added from various sources.

Mount Pleasant may be the Umber Pit near Kenslow, Friden. New Venture was the scene of a fatal accident on 2nd October 1884 when Samuel Hodgkinson fell off the ladder.

Presumably the various operators had to pay royalties to the landowners, particularly the Dukes of Devonshire and Rutland, but no details have been found.

With a recorded production of 573 tons of wad, Heyspots Mine, near Winster, was by far the largest producer but, regrettably little is known of the mine as no description has been traced and no plans survive. It was on part of the Portaway Pipe where large caverns are known to have existed, comparable with those known in the Golconda Mine. Explorations were made of Fisher's Portaway Mine in the 1970s but no survey or description has been traced. It was said to contain large caverns full of sand (pers. comm. D. Nash). Presumably the sands were left behind when any wad was extracted.

Table of known black wad producers

AREA	MINE	DATES	PRODUCTION	OPERATORS
Brassington	Coarse Hill	1893-1907	no details	John Gould jr/ J.B.Hodgkinson
	Old Roundlow	1872-1893	no details	J.Gould/John Fearne/J.Gould
Carsington	Carsington Hill	1901-1903	no details	Swan Ratcliffe and Co.
Elton	Black-Wad Grove	1876	40 tons	
	Blakelow Field	1877	150 tons	Marshall, Stone and Taylor
	Blakelow Field	1877	208 tons	J.Marshall (also 5.5 cwts lead).
	Blakelow Field 1	1872-1900	358 tons in 1877	John Marshall
	Blakelow Field 3	1872-1891	no details	Marshall, Stone and Taylor
	Crookacres	1876	40 tons	Geo. Stone and Co.
	Elton	1877-1878	no details	John Boam
	Filbarnes	1880-1898	70 t in 1882	Dan Stone
			30 t in 1883	Jas Bunting
	Inkerman	1877-1883	164 tons	G., W. and H.. Webster
	Inkerman	1877	34 tons	
	Manystones	1892-3	no details	
	Sweep	1877-1888	120 t in 1877-9	Geo. Stone and Co.
Eyam (Elton?)	Blakelow	1881	40 tons	
Friden	Kenslow	?	an umber pit is marked on old maps	
Godfreyhole	Foxhole	?	no details	
Hartington	Meadow Rake	1874-1892	no details	Geo. Johnson
Hopton	Doglow Wood	?	no details	
Middleton-by-Wirks.	Bradwell	1867-1892	20 t in 1881	E.M.Wass and Son
Smerril Grange	Mount Pleasant	1881-1904	18 t in 1881; 35 t in 1882; 40 t in 1900	
Winster	Allotment	1880-1883	210 tons	E.M.Wass and Son
	Brown Edge 1	1880-1913	prod. Mn in 1880-1899	T. and J. Mozeley
	Brown Edge	1914	standing	
	Brown Edge 2	1885-1891	no details	Jos. Toplis
	Dirty Face	1876-1901	115 t in 1881-2	E.M.Wass and Son
	Heyspots	1872-1901	573 tons in 1877-1881	E.M.Wass
	New Venture 1	1872-1906	50t in 1882, 50t in 1883.	E.M.Wass.
	Whitelow	1884-1896	no details	E.M.Wass and Son
Wirksworth	Heward Stone	1879	4.4 tons	J.S. and J.Recton
	Wagstaff Scrin	1880-1892	no details	Wass and Son
Youlgrave	Goodalls Pipe	1872-1902	no details	Geo. and Jos Johnson.

MINING AND PROCESSING WAD

Little is known of the mining methods, but extracting wad layers from unconsolidated sand fills would have been a simple task with a pick and shovel. Sand residues were apparently left in the caverns.

Few details survive of the processing, but it appears that the produce of the Elton and Winster mines was taken for drying and calcining at a mill in Wensley, which no longer exists. Levigation is also mentioned in the 18th century accounts: this was a primitive flotation process to float off the wad and leave the sand and silt impurities behind; levigation would only be necessary if "pure" wad was required, as a bit of sand would not interfere with bleaching processes. Any wad needed for paint was then taken to one or other of the water-powered paint mills described by Paulson (1997). The principal mills were in the Via Gellia (opposite the Ball Eye mines) and at Matlock Bath, below High Tor. The windmill on Carsington Pastures may also have been used to grind wad as some was found on its floor.

THE USES OF WAD

Wad is said to have been used in paint, in bleaching textiles, in glass manufacture and in steel but there are controversies or contradictions concerning all these. As some 5000 tons are known to have been raised from the mid 19th century onwards and probably as much again before then, it was clearly a valued commodity, but no company accounts indicating what quantities were sold and where they went are available for analysis.

The use of wad in paint is the main problem - the 18th century accounts (which tend to be repetetive) refer to its use for painting ships' bottoms, mixed with a carrier such as linseed oil, but the same accounts say that this mixture was liable to catch fire, which would hardly please the ship owners (Roe, 1751, p.70; 1752, p.82).. It is much more likely that wad or umber were mixed with the preservative tar oil (presumably containing creosote) as a siccative, i.e. it accelerated drying. Contemporary accounts of 18th century paint-manufacture make no mention of wad as a pigment, but it is referred to a s a drying agent, e.g. "it is used in Derbyshire as paint, particularly to mix with other colours . . . as chocolate colour, mahogany colour or other colours from priming etc . . . much used by painters on account of it being a quick drier" (Mendes Da Costa, 1757, quoted by Pearson, 1784). The paint makers used various imported pigments for coloured paints and wad was only a small part of their business (Paulson, 1997). Pilkington (1789) mentioned wad being used by the Royal Navy for ships' bottoms, where it was the preservative qualities of "tar oil" which really mattered and wad or umber were just quick-drying additives. What sort of quantities of wad or umber were used this way is unknown. A frustratingly incomplete allusion was made in Lysons' Magna Britannia (1817, p. cxcvii): "It was apparently supplied in a crude form to the government at 70s a ton. When carefully prepared, however, it is said to have been sold as high as £60 or £70 per ton. By 1817, if not some time before, the contract with the government had lapsed and the manufacture was no longer carried on". What the government did with it is not stated, but it is tempting to speculate that it was used on Royal Navy's ships' bottoms during the wars with the French.

There is little doubt that manganese-rich materials like wad were used from prehistoric times onwards, firstly in Palaeolithic cave art, and subsequently by artists in oil paintings, though in these usages it seems that the manganese was incidental and it was just a handy black material.

Other black materials used to make paint included "smut" coals (mainly powdered cannel) from the Derbyshire coalfield, and anthracite powder from near Bideford, Devon Charred bone black was also produced from bone mills (Paulson, 1997).

Wad had several other uses. Mixed with hydrochloric acid it yielded chlorine gas which was used to bleach textiles. The chemist Scheele recognized that pyrolusite contained an unknown element later isolated by the Swedish chemist Gahn in 1774. The bleaching properties of manganese and hydrochloric acid led to the setting up of a chlorine factory in Aberdeen. Within a few years it was found the chlorine could be absorbed by lime to make bleaching powder. By 1790 factories were set up in Widnes (the foundation of today's chemical industry there) and at Basford, Nottingham. Roy Paulson (pers. comm.) speculates that Arkwright, Strutt and local flax industries used considerable amounts of wad from Elton and Winster for bleaching purposes. In the 1840s some 10,000 tons of bleaching powder were manufactured each year and a substantial amount of manganese dioxide went into the mixture, some obtained from Derbyshire wad, though much more probably came from mines in North Wales and a little from around Nuneaton. Later production amounted to 150,000 tons per annum of bleaching powder but much manganese was imported or recycled.

Small quantities of manganese have been used in glass-making since Egyptian times to improve the whiteness of the glass. Manganese reduced the green colour due to the presence of too much iron in the glass sand. However, if Derbyshire wad already had around 50% iron it seems unlikely that wad would have been used to decolourise glass.

Manganese alloyed with iron was found to produce a hard metal patented by J.M. Heath in 1839. By 1863 ferro-manganese was being produced in Glasgow and was sold for £1 per ton percent of manganese. With contents around 25-33% Mn in the alloy, prices were £25-33 per ton. Later it was widely used in armaments etc. Obviously Derbyshire wad could have been used in such alloys but the quantities produced in the Peak District in the late 19th century were trivial by comparison with the amount of manganese steel manufactured. Again, no company records of sales to the steel industry have been located.

If any accounts of the Derbyshire companies supplying wad to the bleaching, steel, glass and paint industries can be located there is obviously room for future research.

MECHANISMS OF DEPOSITION

A consideration of how wad is or was deposited requires a look at present day processes first. Manganese coatings on cave walls and on pebbles in cave streams are widespread (Hill and Forti, 1997). Moore and Nicholas (1964, p.62), Moore, (1981), Hill (1982) and Peck (1986) regarded these coatings as due to the activities of micro-organisms drawing their carbon dioxide from cave waters and causing the precipitation of the oxides. The cave waters draw their manganese content from surface vegetation, which in turn picks it up from the soil and rocks beneath. They suggested that the manganese was held in cave waters in solution as a complex organic molecule. Bacteria such as *Leptothrix* and *Clonothrix* are known to precipitate manganese by utilizing the organic part of complex molecules leaving the manganese to be precipitated as birnessite or psilomelane. Other bacteria have been found in manganese deposits in Romanian caves (Manolache and Onac, 2000) (see below).

As manganese coatings are well-known in both Yorkshire and Derbyshire cave streams, the source can be deduced as almost certainly from the overlying Millstone Grit shales. However, the manganese content of the shales is very low and thinly dispersed; there is much more iron present, mainly as pyrite. Manganese oxides are soluble in more alkaline waters (MnO_2 up to pH 8.5; FeO_2 up to pH 5.5) so that neutralization of acidic waters flowing off the shales on to the limestone would cause some precipitation of iron close to the shale/limestone boundary. With the slight rise of pH further into the limestone manganese tends to be precipitated lower downstream usually with an overlap of iron and manganese deposition Together with bacterial activities, the chemical change in underground streams was responsible for the coatings. How far this process explains the wad deposits around Elton, Winster and Brassington necessitates an assessment of their possible geological history.

The wad deposits of the southern half of the Peak District, enough to account for an estimated 10,000 tons extraction, have come from localized stratiform deposits associated with sands in infilled caverns intersected by lead miners at or close to the dolomite/limestone boundary. As the shales overlying the limestones are not known to be enriched in manganese, the source must be sought elsewhere (manganese is not mentioned in the many analyses of shale given by Plant and Jones, 1989). Whilst the mineral veins carry no manganese minerals, except as occasional films on "dirty" crystals, manganese is widespread as a trace element in the limestones and dolomites. The British Geological Survey's assessment of limestone resources (Harrison and Adlam, 1985) revealed that the manganese content (expressed as MnO) ranged from 20 to 2400 ppm in unaltered limestones, but rather higher, from 620 to 2800 ppm in dolomites, i.e. an average of around 0.1% in the latter. The highest contents were in the dolomitized limestone areas around Brassington and Winster, close to most of the known wad deposits. In addition the altered limestones in the wall-rocks of mineral veins often carry considerable concentrations of manganese (pers. comm. P.R. Ineson). Weathering of the dolomites, as well as wall rocks and unaltered limestones, would release manganese into the soil, where some could be taken up temporarily by vegetation before being carried underground by percolation water and by sinking streams. Changes in pH on meeting varyingly permeable bedded sands and clays in caverns could then cause the precipitation of manganese oxides. Bacteria also cause precipitation of manganese coatings in cave streams, but no equivalent bacteria have yet been recognized in the Derbyshire wad deposits, though none have been sought.

The origin of the manganese being in dolomitized limestones is supported by the distribution of most wad-yielding mines being in or close to the dolomitzed areas. Whether the manganese is carried in the dolomite molecule or not is a matter for future research.

Observations in Golconda Mine and in the Brassington sand pits suggest that the wad and umber were deposited along the boundaries of sand and clay layers with different permeabilities. The wad was therefore later than the sands themselves. The sands in the Elton and Winster mines could have come from four sources - (1) in-washed Millstone Grit sands, (2) residuals from the former cover of Triassic Sherwood Sandstones, (3) inwashed Brassington Formation (Mio-Pliocene) or (4) fluvio-glacial outwash sands as in some of the Masson Hill caverns.

No direct evidence of the in-washed sand being of Millstone Grit age has come to light so possibilty (1) can be excluded. None of the fluvio-glacial sands in the Masson mines has wad layers, so possibility (4) is unlikely. However, the Golconda Mne's sands are close to and probably related to the Brassington Formation seen in the Pocket Deposits. Although the Brassington Formation was laid down in Mio-Pliocene times it comprises much derived Triassic material. However, no deposits of wad or other manganese minerals have been found in the Triassic beds of the Trent Valley area, so a source directly derived from the Trias (2) is unlikely. It is logical from the distribution of the Brassington Formation pockets to deduce that these Mio-Pliocene sands and clays once covered at least the southern half of the White Peak, including the areas of dolomitized limestone, and that some of those sediments were washed down into any available cavities, making possibility (3) the most likely mechanism for the sand fills which then provided the host for wad deposition. Groundwater percolating through the sand cover and into the sand-filled cavities would encounter pH changes along sand/clay interfaces and would meet percolation barriers (grain and pore-size variations) within the fills, and so would be liable to precipitate any iron and manganese as secondary layers therein.

As argued above, the source of the manganese is almost certainly from weathered dolomitized limestone, but as the Brassington Formation sands have clearly been leached, leaving the refractory white quartz sands, the leachate from the Mio-Pliocene sand sheet seems a possible supplementary source. Also some of the Pockets have bleached Millstone Grit shales at their margins and a former sheet of shales sandwiched between the Brassington Formation and the limestone may have been another source, releasing manganese via soil and vegetation before the Brassington Formation was laid down. The manganese in the coatings on pebbles in the stream caves of Castleton, Ribblehead and elsewhere presumably originated from limestones and wall-rocks as there is no dolomite in those areas.

Possible bacterial causes of wad deposition in Derbyshire have not yet been investigated, so their relationship to the stream-pebble coatings around Castleton and the wad deposits of Elton, Winster and Brassington is an avenue for future research.

The extensive workings for lead ore in Old Mill Close Mine were at least partly from sand-filled caverns, but so little of the fill was left by the 17[th] and 18[th] century miners that it is no longer possible to say whether or not they contained wad.

Apart from the above speculations, the problems of the source and the mechanisms of transport and precipitation are unlikely to be solved before further wad deposits are available for study.

A ROMANIAN EXAMPLE

Deposits of manganese and iron oxides coating pebbles in a stream bed in Vantului Cave in Romania have been investigated by Onac (1996) and Manolache and Onac (2000). Whilst the "jelly-like material, which disperses easily under water" does not quite fit the description of wad, it may be a potential future wad deposit. Onac (1996) determined the presence of the minerals birnessite and romanechite, whilst Manolache and Onac (2000) demonstrated that the bacteria *Hypomicrobium* and *Pedomicrobium* and the fungus *Cladosporium* were active in manganese precipitation. The latter authors noted that the inflowing streams carried only small amounts of manganese and argued that the bacteria were the main concentrating factor. They also noted that the deposits showed unusually high concentrations of some Rare Earth Elements.

FUTURE RESEARCH

If any wad deposits become available for study in the as yet unexplored mines and caverns around Elton and Winster, they should be sampled and subjected to full analysis for their mineralogical content, their geochemistry and evidence of bacterial origin.

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