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A mechanism for the formation of the mineralized Mn deposits at Merehead Quarry, Cranmore, Somerset, England

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ABSTRACT

Mississippi Valley type galena deposits emplaced into Carboniferous limestones throughout the Mendip Hills during the late Permian or Triassic period were locally exposed to the action of seawater during the Jurassic period following regional uplift and erosion of the intervening strata. Oxidation of galena initiated the deposition of manganate minerals from the seawater, and these adsorbed heavy metals from both the seawater and local environment. A subsequent hydrothermal event heated the lead-manganate deposits causing decomposition of the galena and creating the conditions which led to the formation of the suite of unusual secondary minerals – including a number of rare oxychlorides – now found at Merehead. Heating of the manganate phases converted them to Mn oxides and released the entrained heavy metals which were then incorporated into unusual mineral phases. The impervious Mn oxide coating which enclosed the cooling Pb-rich areas isolated them chemically, leading to closed-system behaviour. The high-*T* phases at Merehead are similar to those found in the Pb-bearing silicic skarns at Långban, whilst the suite of secondary minerals which evolved in the closed-system environments bears striking similarities to the 'anomalous sequence' of minerals found at the Mammoth-St. Antony Mine. The complexity of these formation processes probably explains the rarity of Mendip-type Pb-Mn deposits. The collective importance of the disconformity, the hydrothermal event, and subsequent sealing of the deposits are recognized for the first time, and the temperature of the hydrothermal event is shown to have been much greater than has heretofore been realized. Silurian volcanic strata underlying the Carboniferous limestones which have previously been assumed to be the source of heavy metals are shown to have been uninvolved in the process.

Keywords: mereheadite, Mn deposits, oxychloride, Somerset, Mendip, Merehead, England.

Introduction

This paper presents a new theory for the formation of the mineralized Mn deposits at Merehead Quarry which accounts for all the features of the deposit that have been observed in the field, including the physical structure of the deposits, the unusual geochemistry and mineral chemistry, the formation of the suite of rare oxychloride minerals for which Merehead is well known, and the gross mineralogical differences between otherwise very similar veins. Previous theories have been unable to account for all of these features.

Carboniferous limestones in the Mendips were regionally mineralized with primary galena-pyrite-fluorite orebodies in the late Permian or Triassic period. The Pb isotope study work of Moorbath (1962) gave a date of 230±30 m.y. for the mineralization. The area was then subjected to regional uplift and subsequent erosion, which removed the Permian and Triassic strata. In the Jurassic period the land surface subsided and the now exposed Carboniferous limestones were submerged below the ocean. The environment must have been one of warm, shallow seawater as reef limestones containing corals were deposited on top of the relict land surface, creating a major disconformity visible in the quarry today. The disconformity represents a gap in stratigraphy of ~130 m.y.

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Submergence allowed seawater to gain ingress to the Pb-bearing veins in the Carboniferous limestone, causing low-*T* (surface) oxidation of the galena. The presence of an oxidizing environment triggered the deposition of manganate minerals (such as birnessite and todorokite) from the seawater by the same process that creates modern marine manganese nodules. Once initiated, this auto-catalytic process continued until the available space was filled. Heavy metals dissolved in the seawater were adsorbed onto the Mn minerals and co-deposited with them. At this stage the vein contents consisted of galena and calcite (or calcite-baryte) veinstuff embedded in manganate mineral layers.

A subsequent hydrothermal event emplaced quartz veins and other silicate minerals, and locally heated the Pb-Mn vein contents, causing decomposition of the galena and initiating a set of mineral-forming reactions. The heating process also converted the manganate minerals to Mn oxides, releasing some of their entrained heavy metal content for participation in mineral-forming reactions. Initially, high-*T* silicate minerals such as kentrolite and melanotekite were formed, and as temperatures fell, these were followed by mesothermal species such as wulfenite and cerussite, then by late-stage minerals such as mimetite and fornacite which scavenged the remaining heavy metals from solution. The last stage of deposition was the formation of the low-*T* minerals including the oxychlorides. The mineral assemblage has been preserved by the calcite lining of the mineralized cavities and their enclosure in a thick coating of Mn oxides. These form an impervious barrier which prevented groundwater from entering. Figure 6 is a schematic diagram showing this sequence of events, and their temporal relations.

This theory provides a credible source for the anomalous quantities of heavy metals present at Merehead. With the exception of V, these were co-deposited from seawater together with the manganate minerals. Thus, neither lithogenic origin nor transport mechanism are required, overcoming what have been the major deficiencies of previous theories which are unable to explain how these metals were emplaced, there being neither a metallogenic source nor a plausible transport mechanism. The Silurian andesitic lavas found close to Merehead had previously been assumed to be the source of the heavy metals, but analysis shows that their chemistry is quite different and they therefore seem to have little relevance to the Mn mineralization.

The theory proves the long-held conjecture that the Mendip Mn deposits are of secondary origin (see for example Green, 1958; Din *et al.*, 1986) and provides a plausible original mineralization, which has previously been unknown. The theory can be extended to other localities which contain mineralized manganese pods, such as Holwell (Coleman's) Quarry, and Higher Pitts, which exhibit many of the same features. However, additional work is needed to determine whether or not this mechanism is generally applicable to all the Mendip Mn deposits.

This paper is based on nearly 40 years of field work by the author in the quarries containing Mn mineralization, plus examination of a large number of specimens held in the Natural History Museum, London, and numerous specimens held in private collections and other museums.

Description

A brief review of Mendip Hills geology

The Mendip Hills are a range of low limestone hills covering ~2500 km^2 to the south and south-east of the city of Bath, in Somerset, England. The Mendips run from Weston-super-Mare on the coast of the Bristol Channel, inland to the town of Frome in the east, a distance of some 70 km (Fig. 1). Much of the region is designated as an 'Area of Outstanding Natural Beauty', and encompasses such well-known features as the Cheddar Gorge and its associated cave systems.

The majority of the Mendip Hills consist of Carboniferous and Jurassic limestones at surface, underlain by shale and Old Red Sandstone of Devonian age. Regional uplift exposed the Carboniferous limestones to erosion, and the erosion surface is now represented by a well developed disconformity, above which lie Jurassic limestones.

Andesitic lavas of Silurian age have been emplaced in the area and underlie parts of the region. These are exposed in the Moon's Hill Quarry some 3 miles to the west of Merehead, where they are quarried for industrial aggregates.

Lead deposits are common and widespread throughout the Mendips, and have been worked for lead since prehistoric times. The deposits have been extensively described in the literature and are generally accepted to be a Mississippian type orebody (Green, 1958; Worley *et al.*, 1977). The Pb isotope study of Moorbath (1962) gave a date

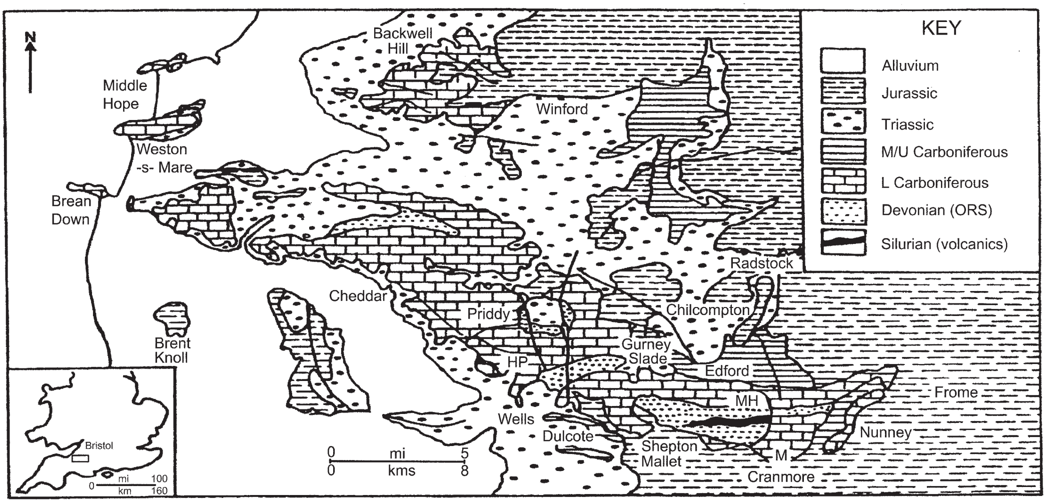

FIG. 1. Simplified regional geological map of the Mendip Hills based on the British Geological Survey 1-inch series, sheets 279–281 and Bristol special sheet. At lower right, M = Merehead, and MH = Moons Hill. HP = Higher Pitts, at bottom centre (after Din *et al*., 1986).

of 230 ± 30 m.y. for the mineralization, thus falling into the late Permian or Triassic periods.

The primary Mendip Pb ore is galena, which occurs as typical small lenses and ore pocket swarms embedded in calcite veins, which in turn occupy fractures and fissure zones in limestones of Carboniferous age. Locally, these are known as 'Black Rock' limestones, due to their colour. Small amounts of chalcopyrite and its oxidation product, malachite, are widespread throughout the area. Sphalerite is unevenly distributed, being relatively common towards the west and absent in the eastern deposits. Consequently, there is no zinc at Merehead, since this locality lies near the eastern edge of the Mendips.

Calcite is the dominant gangue mineral, but baryte and aragonite are sometimes present in considerable quantities. Pyrite and fluorite are common accessory minerals in these veins, although their distribution is very patchy.

The geological setting of Merehead Quarry

Merehead Quarry is located ~8 km west of the town of Frome, in Somerset, England, and has been operated since 1960 by the Foster Yeoman Company. The quarry works limestones of mostly Carboniferous age within the southern limb of the Beacon Hill Pericline, a large plunging anticlinal fold structure. At the southern end of the quarry, the limestones fall into the Clifton Down and Vallis formations, whilst at the northern end, the workings are within the older Black Rock limestone. These beds dip to the south and southeast at moderate angles, typically around 30º. Major fault zones define the southern and western boundaries and the rock within the quarry area is heavily faulted.

The Carboniferous limestones are disconformably overlain by Middle Jurassic oolitic limestone. The intervening Permian and Triassic stratigraphy has been removed by erosion, and the disconformity represents a stratigraphic time gap of ~130 m.y. The disconformity is marked by a dark grey, fine-grained sedimentary layer which is typically between 20 and 30 cm thick and dips gently from north-east to south-west in the quarry. The disconformity is a fossil seafloor; the limestones immediately above contain a suite of marine fossils including a number of unusual corals of interest to palaeontologists. The presence of coral indicates that the water must have been both shallow and warm, and asymmetric ripple marks on the disconformable surface itself shows the presence of a flowing current at the time the surface was preserved (Fig. 2).

An extensive and detailed description of the geological setting of Merehead Quarry can be found in Parkhouse (2004). This document makes the erroneous statement that the 'rare minerals' are completely worked out, however; this is due to the survey being undertaken at a time when the

FIG. 2. A large slab of the fine-grained dark sediment showing ripple marks on the surface of the disconformity. This is the inverted 'top' of the disconformity, so shows a reversed impression of the original ripples. The block is ~1.5 m on each edge.

working areas were in mineralogically barren strata.

The Mendip Mn deposits

Small Mn-Fe deposits are found throughout the Mendip Hills, and although some have been worked in historical times most are sub-economic (Burr, 1996). The deposits consist of small, lenticular areas composed of black Mn oxides, surrounded by brown Fe oxides. These are known locally as 'manganese pods'. Pods are found only in pre-existing calcite (and calcite-baryte) veins which in turn occupy fissures and fracture zones in the Carboniferous limestone. The deposits have long been thought to be of secondary origin, being derived in some unknown way by alteration of an unidentified primary mineralization (Green, 1958; Din *et al.*, 1986).

In Merehead Quarry, individual pods are typically no larger than 2 m along strike and 1 m high (down dip), and 0.2–0.5 m thick, the latter being determined largely by the original width of the host vein. Pods show a gross structural transition spanning four different 'zones' of oxide mineralization: (1) competent and hard black Mn oxides in the core, often well crystallized; (2) a zone of more friable, layered black Mn oxides; (3) a zone composed of powdery black Mn oxide and brown Fe oxides; and (4) an outer zone formed of Fe oxides. Figure 5 shows a schematic cross-section through a typical manganese pod.

The thickness of each zone can vary widely and not all pods contain all four zones. Some lack the outer Fe oxide zone and others lack the competent core zone. Sometimes complete pods composed entirely of Fe oxides are encountered. So far, however, none of these 'iron pods' have contained no mineralization whatsoever.

Cavities in the Mn oxides are frequently filled with secondary Pb and Cu minerals. The predominant secondary Pb mineral in the manganese pods is cerussite, accompanied by significant amounts of aragonite and calcite, and sometimes baryte and celestine. However, the 'Number One' vein exposed in the 1970s was dominated by mendipite, one of the Pb oxychloride minerals for which Merehead is so famous. Most cavities contain a layer of calcite 'lining' the cavity immediately adjacent to the Mn oxides.

In a few places the Mn deposits are extensive enough to entirely fill their host vein systems, forming a 'manganese vein'. Although much larger, these veins have a structure identical to that of a pod. Small mineralized cavities are distributed throughout a much greater quantity of Mn oxides, and the whole is bordered by Fe oxides (see Fig. 3). These veins can in effect be

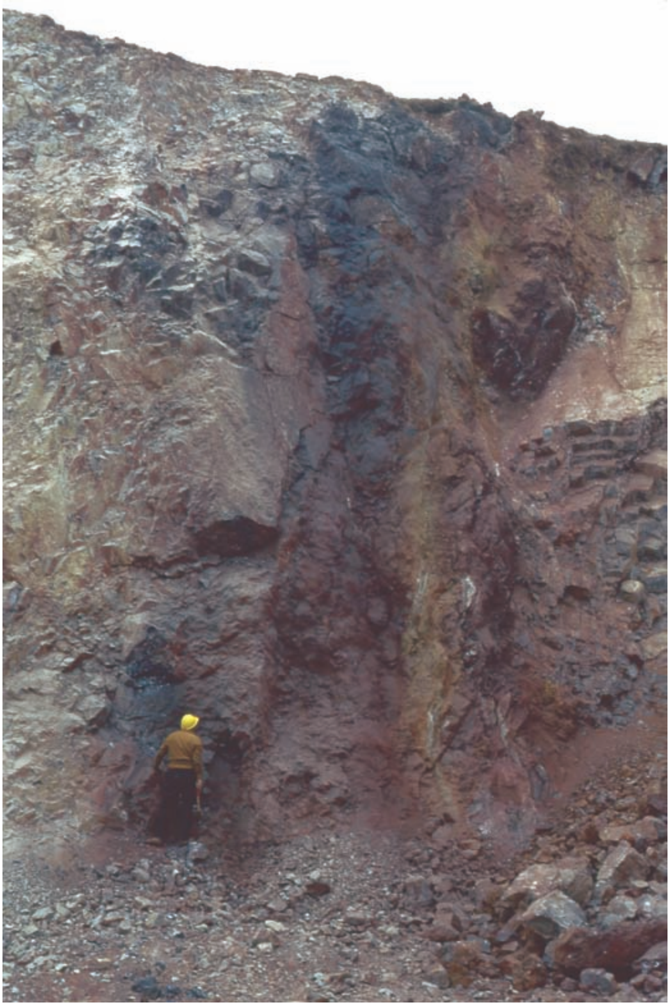

FIG. 3. No. 1 vein exposed in the face of bench A at Merehead in 1974. This was by far the largest individual Mn deposit, yet its structure and macro-chemistry are identical to those of the much smaller manganese pods. Note the brown Fe oxide layers surrounding the black Mn oxides. Picture courtesy of Dr R.F. Symes.

considered very large pods, which have been stretched out along strike.

Adjacent to a pod, the original calcite veins become wider than they are elsewhere. The calcite gangue is often completely missing and in some cases, there has been dissolution and local alteration of the limestone wall rock, occasionally producing minerals such as hydrocerussite. This suggests the dissolution of calcium carbonate, and the occurrence of hydrocerussite further shows that Pb must have been available in solution at the same time. It is not possible to determine whether widening also occurred around No. 1 vein, since this was extremely large and small volumetric variations would be masked.

Mn deposits at Merehead

Field observations show that the Mn deposits are found only in the limestone immediately below the disconformable surface and generally speaking, the Mn-bearing zone is probably no more than perhaps 30 m thick.

During the late 1960s and early 1970s the north-eastern part of the quarry was being worked, and here the disconformable surface

FIG. 4. A manganese pod *in situ* on bench G in July 2006. The hammer is ~60 cm long. Traces of the host calcite vein can be seen running from bottom left to top centre.

outcrops at the current land surface. In this part of the quarry, the famous No. 1 and No. 2 veins also outcropped at surface, extending down through the top two quarry benches, A and B (see Fig. 3). Currently, limestone is being extracted at the south-western section of the quarry. Here, the disconformable surface runs through benches E and F, and manganese pods are now being recovered from benches F and G, immediately below (see Fig. 4).

To date, no Mn deposits have been found in competent limestone. Away from the disconformity, the same Mn-bearing veins carry galena.

Geochemistry

The suite of minerals present at Merehead includes species that contain heavy metals, including Mo (wulfenite), Cr (fornacite), and V (ardennite). Given that there is no local source for these metals, their presence is unexpected.

It has often been suggested that the underlying Silurian andesitic lavas were the source of the heavy metals present in the Mn pods, and that these metals were leached out by groundwater and somehow transported to the Mn deposits. There are two reasons why this is unlikely. Firstly, were these older rocks the source of heavy metals, a mechanism for their mobilization and transportation over considerable distances is required. Although much work has been done over many years, and considerable attention paid to the possible role of groundwater and the water table (Symes *et al.*, 1977; Din *et al.*, 1986), there has been no previous theory which provided satisfactory explanations. Secondly, and perhaps more importantly, the trace element chemistry of lava samples (see Table 1) shows that there are significant differences from that of the Mn

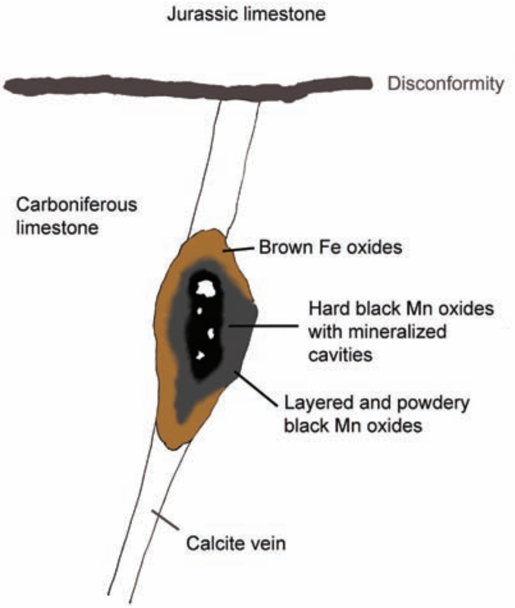

FIG. 5. Schematic section through an *in situ* Mn pod.

deposits (John Wainwright Ltd., pers. comm., August 2006; Din *et al.*, 1986), and these differences are difficult if not impossible to reconcile. Unlike the manganese deposits, the andesites are rich in K and Na, and surprisingly contain a significant amount of Hg.

The present study has found, however, that the Mn oxides themselves contain a significant heavy metal component, and Table 1 shows representative analytical results for a selection of Mn oxide samples from Merehead. It is well known that Mn oxides have a high sorption capacity for heavy metals, and it is in fact the content of such metals that provides the rationale for commercial interest in the mining of deep-sea Mn nodules (Post, 1999) as well as interest in Mn oxides as a means to combat pollution (Matagi *et al.*, 1998) and as a possible component of containment mechanisms for nuclear waste (Dyer *et al.*, 2000; Carlos *et al.*, 1993; Means *et al.*, 1978).

Mineralogy

Merehead is well known for the occurrence of exotic Pb-oxychloride minerals, but these are very rare constituents of a surprisingly diverse suite of secondary minerals. As well as Pb and Cu secondary minerals, species such as wulfenite, mimetite and fornacite occur in the manganese pods. Kentrolite and melanotekite have recently been identified in some quantity, kentrolite in the form of large euhedral crystals and crystal rosettes which closely resemble goethite.

Although there is a suite of arsenate minerals present in the Mn pods, phosphates are absent, despite the presence of collophane (colloidal apatite) in the enclosing limestones.

Carbonates are well represented, as would be expected in a limestone-hosted deposit. Calcite and aragonite are ubiquitous, and the calcite often contains significant amounts of Mn, occasionally

TABLE 1. Chemical composition (analysis by EDX, wt.%) of Mn oxides and Moons Hill andesitic lavas.

	2005-07 pod					2006-06 pod	No. 1 vein	No. 2 vein	No. 2 vein	Moons Hill Andesite		
	Centre		Mid-point		Edge	Centre						
	Black	Grey	Black	Grey-white	Black	Black				1	2	3
Pb	4.74	25.29		21.89	2.45	7.51	2.53	1.28				
Mn	14.32	18.18	11.48	29.08	18.96	3.33	71.33	0.33	48.58		0.12	
O	50.28	39.00	59.20	29.52	46.25	47.78	26.14	55.35	30.24	48.86	59.43	49.28
K										8.63	9.30	5.93
Na												0.94
Ca	30.10	1.46	29.32	17.67	19.63	40.29		22.64	2.70	0.89	1.40	0.84
Mg	0.55	8.54		0.54	1.96				3.38	2.65		3.65
Ba								3.32				
S												0.08
Fe		1.18		0.62	3.73			2.70	1.72	2.21	1.92	2.58
Cu									3.00			
Ti					0.29	1.09			0.56		0.12	0.21
Si		6.36			4.06			2.66	2.95	27.23	28.06	26.81
Al					2.34			7.32	3.99	9.25		9.37
Mo								1.43	2.87			
W				0.68								
As					0.32			2.98				
Hg										0.28	0.58	0.30

The 2005-07 pod contained mereheadite, symesite, kentrolite, fornacite and mimetite.
The 2006-06 pod contained wulfenite, crednerite, kentrolite, melanotekite and mimetite.
EDX cannot detect carbon or lighter elements, so the presence of carbonate is masked; the high result for Pb in column 2 for example is due to the presence of cerussite.

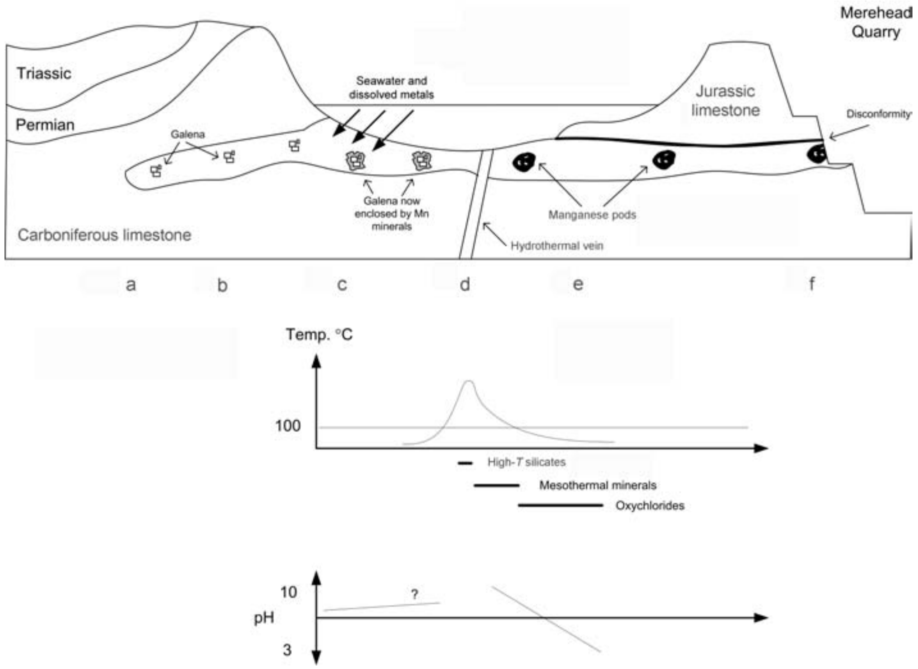

FIG. 6. Important events in the creation of the Merehead Mn deposits: (*a*) calcite-galena veins emplaced; (*b*) regional uplift and erosion; (*c*) seawater and dissolved metals ingress; (*d*) hydrothermal event; (*e*) deposition of Jurassic limestones; and (*f*) disconformity and Mn pods exposed in the quarry wall.

becoming rhodochrosite. Cerussite is the most common Pb secondary mineral and hydrocerussite is locally common, often forming large crystal aggregates. A number of rarer carbonates are present in small quantities.

Quartz veins carry a suite of medium- to high-*T* Na-Ca silicate minerals including datolite and apophyllite (Symes *et al.*, 1977), as well as more unusual silicate minerals such as nasonite and ardennite (R.F. Symes, pers. comm., 2006). These silicates represent primary hydrothermal mineralization and consequently do not occur within the Mn veins and pods. Ardennite is currently the only confirmed V mineral at Merehead, with the exception of a very small number of mimetite crystals which are V-rich; very rarely these have small (<20 μm) areas where the composition has V>As making these regions technically vanadinite.

This mineralogy is broadly similar to that of other Mn deposits in the Mendips, but Merehead contains the widest range of different mineral species.

A volume on the mineralogy of the Mendip Pb-Mn deposits is currently in preparation (Turner and Rumsey).

Mn and Fe oxides

The mineral species present in the Mn and Fe oxides are consistent; black Mn oxide layers are a mixture of manganite and pyrolusite, brownish Mn oxide material, a mixture of manganite and cryptomelane, and Fe oxide zones, a mixture of limonite, goethite and other Fe oxy-hydroxides (J. Post, pers. comm., November, 2006).

Manganite, pyrolusite and goethite frequently occur as euhedral crystals within cavities, usually associated two or three generations of calcite, some of which exhibit a diverse range of crystal habits. In addition, most cavities are lined with a layer of calcite. The co-existence of calcite and Mn oxides is only possible at high pH (T. Bridges, pers. comm., September, 2006).

Other Mn-bearing oxide minerals such as coronadite, romanechite and hausmannite have previously been reported (Morse, 2004) but these were not seen during the present study and no positively identified specimens exist in the Natural History Museum collections. These species may occur in localized areas but are not widespread.

Hydrothermal activity and silicification

There have been one or more pulses of hydrothermal activity throughout the Mendips generally, as is shown elsewhere by the silica-impregnated clays and limestones at Wurt Pit to the north of Wells, and at Dulcote Quarry, where 'potato stones' – agate geodes containing crystalline quartz, calcite and baryte – are quite common. The source of the hydrothermal material is not known, and there is no evidence of either regional metamorphism or magmatic activity.

One such hydrothermal event occurred at Merehead and emplaced quartz veins carrying silicate minerals. The hydrothermal veins occupy a separate set of structures to the Mn-bearing veins and their sidewalls are altered by silicification. Significant amounts of quartz are found within the limestone. The quartz is occasionally an attractive light purple colour, presumably due to the presence of Mn, and smoky quartz has been found at nearby Holwell Quarry. Quartz crystals as large as 5 cm are known, but crystals of this size are rare.

Where the quartz veins intersect Mn-bearing veins, these are altered. Any nearby Mn pod is silicified producing compound silicates of Pb and Mn or Fe such as kentrolite and melanotekite. These are embedded on and in the calcite-aragonite-cerussite cavity infill. Where there are voids, euhedral crystals can occur, and these minerals clearly developed *in situ*. Quartz may be present within the altered Mn pod.

Paragenetic sequences

The paragenetic sequences given in Figs 7–10 have been reconstructed from field observations and from detailed study of specimens from the various pods and veins. Given that each pod and vein was entirely isolated from its neighbours and therefore carries a different suite of minerals, it is in general difficult if not impossible to correlate across deposits. There are, therefore, different diagrams for different parts of the deposit.

Some species – particularly calcite and aragonite, and to a lesser extent manganite, baryte, cerussite and mendipite – have been deposited more than once and it can be very difficult to separate these deposition events. Finally, not all parts of a sequence are present in all cases, and any given sequence can also be incomplete, which further complicates the picture.

Consequently, the sequences are composites of many observations, and must be regarded as indicative generalizations rather than as definitive.

Discussion

New marine deposition theory

It is reasonable to suggest that galena was once present at Merehead, as in other parts of the Mendip Hills, and that these galena lenses were the original mineralization now being replaced by the Mn deposits. There is considerable – if circumstantial – evidence at Merehead to support this suggestion. Firstly, there is little or no

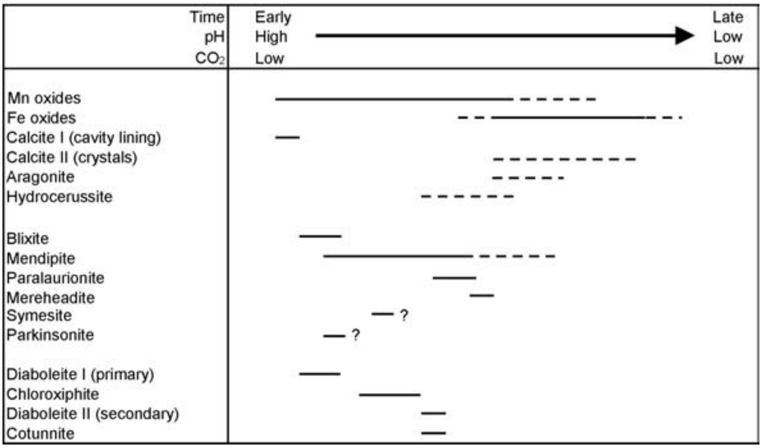

FIG. 7. Paragenetic sequence for No. 1 vein. This vein is mineralogically consistent and therefore this sequence is likely to hold true for all samples.

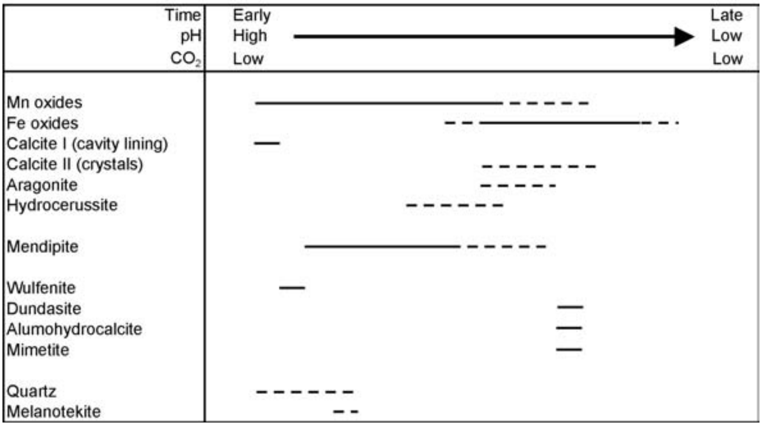

FIG. 8. Paragenetic sequence for No. 2 vein. This is very incomplete as No. 2 vein had extremely complex and variable mineralogy, and relatively few specimens have been preserved.

primary galena in the immediate vicinity of Mn deposits, both at Merehead and other nearby Mn mineral localities. However, away from the Mn-bearing areas, typical galena and galena-pyrite-fluorite mineralization can be found in the same vein systems. For example, at Holwell Quarry (~3 km east of Merehead) there are three adjacent working areas. Manganese pods were found in one of these – the 'big pit' – in the period from 1994 to ~2000, and there was no galena in this area. However, just 250 m away in the 'middle pit', there is normal galena-pyrite-fluorite mineralization within the same vein systems. These veins can often be traced through the wall separating the two working areas, so there is no doubt that they are continuous features. The mechanism which changed the original galena was clearly very localized. Secondly, the overall shape, size and spatial distribution of Mn pods (and pod swarms) closely match the distribution of galena lenses elsewhere in the Mendips. Like the galena lenses, the pods are only found within a few of the calcite-filled veins that occur within the area – the majority being barren of any minerals except calcite. Manganese-bearing veins are typically persistent and where exposures can be observed, veins can be traced for distances of up to several hundred metres. These veins have the same characteristics as Pb-bearing veins elsewhere in the Mendips. Thirdly, most Mn pods

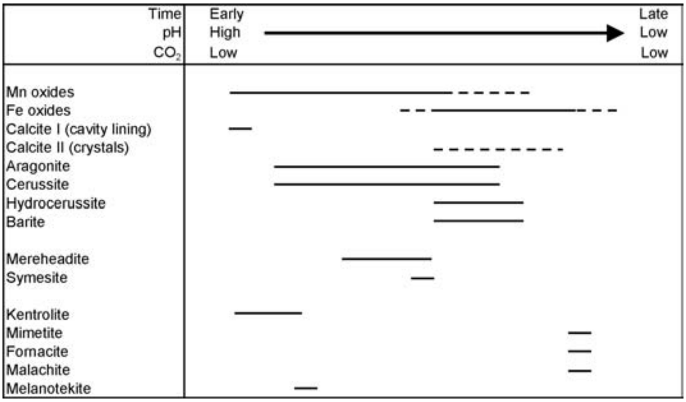

FIG. 9. Paragenetic sequence for the mereheadite-bearing pod found in July 2005. This is a cerussite-dominated environment, rich in heavy metals.

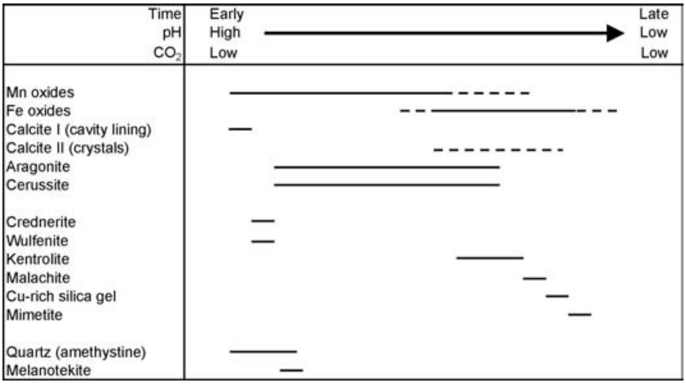

FIG. 10. Paragenetic sequence for the wulfenite and crednerite bearing pod found in June 2006; another cerussite dominated, heavy-metal-rich environment.

contain cavities filled with secondary Pb minerals, usually cerussite, which is a common end-state mineral for galena oxidation under aqueous conditions, as reported by Dermatas *et al* (2004) who also found that hydrocerussite and paralaurionite were formed by the same mechanisms. Historically, however, the dominant Pb secondary mineral in the old No. 1 vein at Merehead was mendipite. This is discussed below.

Small amounts of sulphide minerals are known from Merehead, although they are extremely rare. Relict galena is present on a sample in the Natural History Museum collection (BM1988,164). The theory presented here would predict that any surviving galena specimens would have highly corroded surfaces indicating post-depositional dissolution, and this is indeed the case. The surfaces are coated with cerussite in places but show bare galena in other areas. The mixture of bare and coated surfaces is what would be expected from material science research, which found that galena alters by pitting, producing 'pillars' which eventually spall off. Chalcopyrite has previously been found at Merehead (Symes *et al.*, 1977), and a single grain of chalcopyrite preserved in calcite was found by the author in the Mn pod extracted in July 2005. This specimen has now been placed in the NHM collection.

There is no reason to attribute any special properties to the original galena deposits, and it seems sensible to suppose that there was nothing unusual about them at the time they were emplaced.

When seawater entered the vein systems, the galena immediately began to oxidize. Work on the dissolution of galena in water, mostly performed by materials scientists in the semiconductor world where it is used to manufacture infrared sensor chips, has shown that the main decomposition products are varied. Moses and Ilton (1998) found that PbO (litharge) and PbS_2O_3 (Pb thiosulphate) were the main intermediate compounds formed by dissolution under a wide range of conditions, with $PbCO_3$ (cerussite) and $PbSO_4$ (anglesite) forming under some circumstances. They also found that the production of PbO was an essential precursor to the formation of $PbCO_3$. Kim *et al.* (1995) added $Pb(OH)_2$ to the list of decomposition products, and Prince *et al.* (2002) discovered that Pb_3O_4 as well as $Pb(OH)_2$ were produced in preference to PbO near defects in the crystal structure. A number of studies found that H_2S was produced (Cama *et al.*, 2005; Nava and Gonzalez, 2005). This would have oxidized immediately, leading to the production of hydrosulphuric acid and ultimately, sulphate.

The overall galena dissolution mechanism is not well understood, but is generally accepted to involve atomic substitution with *n*-type PbS gradually becoming *p*-type before oxidizing (Moses *et al.*, 1998). This process appears to involve adsorption of oxygen, first removing free electrons and thus bonding oxygen to donor Pb atoms, forming PbO, litharge. This is a surface reaction rather than a bulk process and the rate of reaction is obviously sensitive to the amount of dissolved oxygen in the water, and thus to pH and temperature as well. The dissolution process is expounded in Kim *et al.* (1995). As dissolution progresses, larger donor defects are formed which provide additional reaction sites, whilst areas which become depleted in Pb are in effect coated with passivated sulphur (another intermediate) which slows down reactions at that point. The surface thus becomes covered with pits and protrusions on a nanometre scale (Mikhlin *et al.*, 2006). Since dissolution seems to preferentially occur around defects in the galena crystal lattice, it proceeds at varying rates and along different reaction paths from point to point, and therefore it is reasonable to suppose that all the intermediate dissolution products listed above (and perhaps others such as sulphites) were produced in varying amounts.

The oxidation of galena in this way occurs spontaneously and can be very rapid given the right conditions of humidity and pH (there is a large body of literature on this topic, see for example Cama *et al.*, 2005; Kim *et al.*, 1995; Mikhlin *et al.*, 2006).

The high-pH requirement for the co-existence of calcite and Mn oxides can be met in this environment. One method of driving pH up to the levels required is to mix litharge and calcium sulphate (both of which would have been present at the time). However, oxidation of other species by oxygen will consume protons (as in $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) and this would have had a similar effect on pH. Modern seawater has a pH of about 8.3, and it is therefore likely that conditions were already somewhat alkaline to begin with.

Deposition of Mn minerals

Field observations clearly show that the area containing Mn deposits lies immediately below the disconformity. This is a fossil sea-floor, and the pre-existing faults and fractures which hosted the Pb veins would have allowed easy entry and circulation of seawater. Being so close to the ocean, there would have been an essentially unlimited supply of seawater.

When seawater entered the Pb-bearing vein systems, the surfaces of the galena began to oxidize and the presence of an oxidizing environment caused Mn^{2+} ions present in the seawater to be oxidized, producing (insoluble) Mn^{4+} compounds, which condensed around the nuclei provided by heavy minerals such as the decomposing galena. This is the mechanism that initiates the formation of marine Mn nodules (Post, 1999). Once initiated, autocatalytic precipitation of Mn and Fe oxides takes place on the pod surface and the deposition process becomes self-sustaining.

The structure of a Mn pod shows – on a larger scale – a structure very similar to that of marine Mn nodules, both being composed of concentric layers of brown to black Mn and Fe oxides. It is known that marine Mn nodules can grow at rates of up to 1 m per year in near-shore environments (Post, 1999) and these rates of growth make it entirely feasible that even the larger Mn veins were deposited in this way.

There is one significant difference between Mn pods and marine Mn nodules, however. Marine nodules usually contain a mixture of birnessite (7 Å manganate) and todorokite (10 Å manganate), but these are no longer present at Merehead. Post-depositional heating caused by the hydrothermal event caused their replacement by manganite and/or pyrolusite (J. Post, pers. comm., December, 2006). This change requires complete breakdown and replacement of the crystal structure and one would expect the material that resulted to be very disordered. Perhaps this is the source of the powdery black mixture of manganite and pyrolusite that is now found so widely in Merehead Mn pods. No fluvial structures have been observed within the Mn deposits, suggesting that any evidence of these was also destroyed during the heating process.

The observed chemical and physical zonation in the Mn pods must reflect changes in depositional environment. There seems to be no relevant research on this topic, but it seems reasonable to suggest that thermal gradient was one key factor. As at Långban, Mn oxide precipitation seems to have dominated in the (hotter) core regions, being gradually replaced by Fe oxides towards the outside of the pod at the edge of the vein. The Mn-free 'iron pods' could thus be attributed to formation at a lower temperature. This would perhaps also explain their lack of mineralization – presumably, temperatures were not high enough to initiate precursor reactions.

The presence of cryptomelane in the brownish Mn oxides material suggests that these layers might have formed from an original mixture of manganite and pyrolusite by a process akin to lateritic weathering (Parc *et al.*, 1989).

Deposition of heavy metals

The marine formation hypothesis leads to the contingent suggestion that the heavy metals present also largely originated from seawater, and were concentrated in the pods by co-precipitation with, or sorption by, the Mn minerals. The consequence of this co-deposition was that heavy metals were already present at the time the secondary minerals began forming, and thus neither lithogenic source nor transport mechanism is required.

Table 1 shows some representative analyses of Mn oxides from Merehead. As would be expected, the analyses show significant amounts of Pb and Ca, the former presumably from the galena and the latter from either the calcite gangue or the limestone. The As present almost certainly originated in the galena, and perhaps also Mo (Takahashi, 1960). Traces of chalcopyrite (and its oxidation product, malachite) are not uncommon in galena-bearing veins in the Mendips, and since the EDX analyses show that little Cu is contained in the Mn oxides, Cu too must have originated from *in situ* sulphide mineralization, but the remaining elements – including the chloride ions necessary for the formation of halides and oxyhalides – were probably of marine origin.

Since the only significant V mineralization seems to be confined to the hydrothermal phase, and given the scarcity of V in the EDX results, it appears that V was largely of hydrothermal origin. Lighter elements such as Si, Al and possibly also Ti could have originated in the silica-rich hydrothermal fluids too.

It is interesting to note the heavy metal distribution in the pod recovered in July 2005; quantities are highest at the outside of the pod and decrease markedly towards the centre. This presumably represents depletion of these elements as minerals such as mimetite and fornacite formed, and also suggests that there was a time dependency on deposition as would be expected.

The chemical simplicity of No. 1 vein is discussed below. The observation that the chemistry of No. 2 vein appears to be significantly more complicated than that of No. 1 vein bears out field observations made in the 1970–1985 period, when these veins were exposed for examination and sampling.

Was groundwater important?

It can be argued that the deposition of Mn oxides was due to the reaction of seawater with groundwater brines, the latter being loaded with heavy metals and acidic due to weathering of pyrite and galena mineralization. There are, however, field observations and experimental results that tend to disprove this suggestion.

Firstly, field observations show that the galena and pyrite in nearby quarries are unaltered. The simplest explanation for this is that there has been no significant groundwater weathering. To suggest otherwise would mean that there would have to be special conditions present only where there are now Mn deposits, and it is not clear what type of mechanism could operate on such a selectively local basis; there are no observations to indicate that something unusual happened locally. Secondly, the lack of a suitable metal transport mechanism has already been mentioned, and is one of the chief failings of earlier theories. Unlike the mineralogically similar deposits at Långban and Tiger, Merehead did not have a large-scale thermal source to drive groundwater recirculation (the hydrothermal event was of too short a duration to have been important in this sense). Finally, if a seawater-groundwater reaction was the source of the Mn deposits, one would expect there to be a uniform distribution of Mn deposits within any given vein, and no differences between veins since any fracture or fissure which intersected the disconformity would allow seawater and groundwater to meet and mix. Field observations however show that pods are very irregularly distributed, and exist only in a few veins. Most veins are entirely barren, and even Mn-bearing veins are mostly empty. The distribution is therefore highly irregular, and as noted previously, the distribution pattern of Mn pods is very similar to that of galena lenses elsewhere in the Mendips.

Experimentally, Brugger and Meisser (2006) discuss the use and significance of various heavy metal ratios as diagnostic tools for determining the origin of Mn deposits. These measures are capable of discriminating Mn deposits formed by groundwater-seawater interaction from those of hydrothermal and marine origins. Using their methods, EDX results such as those in Table 1 suggest that the Merehead deposit contains material of both 'detrital-diagenetic' and hydrothermal origin, but none fall into the groundwater-seawater interaction region, strengthening the argument that this mechanism was not present. The high As contents and As/V ratios imply a hydrothermal origin, as do the small amounts of Co and Ni present. Al_2O_3/SiO_2 ratios are scattered but it is suggested in the paper that this measure may be unreliable in the case of carbonate-hosted deposits. The presence of large quantities of Mg is often indicative of marine origin, but this element may have been derived from dolomitic bands in the limestone. Marine sources should also provide high levels of Na but this element is not present in significant quantities.

Components of detrital origin may well have supplied the small amounts of relatively insoluble metals such as Ti present. The evidence provided by heavy metal ratio measures is therefore inconclusive, and the results should be interpreted with caution, particularly as the original sulphides would have supplied Pb, Cu, As and possibly other elements in quantities sufficient to distort the measurements.

Hydrothermal event

The hydrothermal event which emplaced quartz and silicates must have been of short duration as there are no signs of thermal metamorphism beyond sidewall alteration, and even here, silicification rarely extends beyond 15–20 cm from the vein. This implies that there was a short 'pulse' of hydrothermal activity, which is consistent with field evidence in other parts of the Mendips.

Before the hydrothermal event commenced, the veins must have contained patches of galena, calcite gangue, and possibly fragments of limestone wallrock all embedded within a fine-grained matrix of Mn-bearing minerals such as birnessite and todorokite. This mixture was heated by the hydrothermal event, causing the galena and calcite to decompose and converting the manganate minerals to the Mn oxides found today. The presence of Mn-Fe-Pb silicates in the Mn pods shows that the Mn and Fe minerals must have been deposited before the hydrothermal event. The late Permian to Triassic emplacement date for galena and the constraint that this must have preceded hydrothermal activity suggest that both deposition and hydrothermal event may have been associated with the very late stages of the Variscan orogeny.

The Mn pods extracted in July 2005 and June 2006 contained large amounts of kentrolite in their cores, as large euhedral crystals embedded in (and on) calcite and cerussite. It is clear that these crystals must have formed *in situ*. The work of Lindqvist and Charalampides (1987) at Långban showed that the presence of kentrolite places a lower limit on the mineralization temperature of ~325ºC and an upper limit on the crystallization temperature of ~525ºC due to the kentrolite-melanotekite solvus point. The occurrence of melanotekite near the outside of Mn pods shows that the lower temperatures must have been present near the vein margins at Merehead and that the central regions must therefore have been hotter.

This evidence suggests that the temperature of the hydrothermal event was considerably greater than has previously been suggested for the Mendips generally, and further research is needed to resolve this question. Lindqvist and Charalampides (1987) showed that it is possible to use the composition of kentrolite and melanotekite as a geothermometer to determine the temperature of deposition. This method may be extensible to Merehead but no work has been done on this topic.

Despite the temperatures reached, there are no skarn minerals or simple Mn silicates such as rhodonite. Being close to the surface, pressures were not high, and therefore there are no high-pressure metamorphic artefacts or minerals.

The hydrothermal event must have ended before the oxychloride minerals formed, as they are only stable at low temperatures.

Mineral chemistry

At the maximum hydrothermal temperatures present, galena would have decomposed rapidly, releasing Pb ions. The S present would have gone into solution and been removed, some forming the baryte and celestine that now occur. Calcite and limestone would have released CO_2 creating both carbonate and hydroxide ions, although gaseous CO_2 was probably removed when the gas escaped into the seawater, and eventually the atmosphere.

This complicated set of dissolution reactions created the initial starting conditions for subsequent mineral-forming reactions. At the highest temperatures, the silicate minerals formed and were deposited. As temperatures fell, a range of other materials crystallized, starting with mesothermal minerals such as wulfenite and cerussite, completing with the deposition of late-stage minerals such as fornacite and mimetite which scavenged residual metals from solution and formed the last generation of cavity minerals. Deposition ultimately ended with the formation of the oxychlorides and other very low-T minerals. This gradual cooling explains how cavities can contain kentrolite crystals in association with mereheadite – a field observation that is otherwise impossible to explain.

One means of producing the high pH necessary for calcite and Mn oxides to co-exist at hydrothermal temperatures can be achieved by reacting galena with Mn oxides (Holtstam and Langhof, 1999). The necessary equation is:

$$PbS + 3Mn_3O_4 + 8H_2O \rightarrow Pb + 9Mn^{2+} + SO_4^{2-} + 16\ OH^- \quad (1)$$

All the intermediate compounds formed by the dissolution of galena are thermodynamically unstable, and will eventually end up as Pb sulphate (anglesite), or where CO_2 is present, as Pb carbonate (cerussite). Cerussite is less soluble than anglesite at moderate temperatures with comparable sulphate and carbonate activities (Scheckel *et al.*, 2001) and will therefore tend to be preferentially preserved. This fact may explain the absence of anglesite at Merehead (where cerussite is common).

The decomposition of galena created an environment where there was a free supply of Pb and sulphate ions, together with an abundant supply of carbonate ions (from calcite and limestone). We can therefore derive a set of reactions which will produce cerussite:

$$Pb^{2+} + CO_3^{2-} \rightarrow PbCO_3 \quad (2)$$
$$PbO + CO_2 \rightarrow PbCO_3 \quad (3)$$
$$PbSO_4 + CO_3^{2-} \rightarrow PbCO_3 + SO_4^{2-} \quad (4)$$

As cerussite is the dominant secondary Pb mineral in No. 2 vein and in the more recently discovered pod deposits, this reaction pathway appears to be the important one.

In the absence of available CO_2, the cerussite-producing pathway in equations 2 to 4 cannot occur and things proceed along a different route, leading to the deposition of oxychlorides, including mendipite.

The juxtaposition of calcite and Mn oxides shows that the pH must initially have been high and the sequence of deposition of oxychlorides as pH falls is blixite → mendipite → (para)laurionite (Edwards *et al.*, 1992). The transformations between phases relate to the varying pH and chloride activities prevailing at any one time.

In all the following equations, the chloride ions come from seawater.

Blixite

Reaction paths leading to the formation of blixite include:

$$2Pb^{2+} + 3H_2O + Cl^- \rightarrow Pb_2(OH)_3Cl + 3H^+ \quad (5)$$
$$2Pb^{2+} + 2H_2O + Cl^- \rightarrow Pb_2O(OH)Cl + 3H^+ \quad (6)$$

Note that there is some dispute in the literature as to the exact chemical formula of blixite; the idealized chemical formula is used in equation 5 and the commonly quoted one in equation 6. Since the only difference between these two equations is the amount of water required, it is probable that there is no difference in the conditions required.

Mendipite

Possible transformations producing mendipite from blixite are:

$$3Pb_2Cl(OH)_3 + Cl^- + H^+ \rightarrow 2Pb_3O_2Cl_2 + 5H_2O \quad (7)$$
$$3Pb_2ClO(OH) + Cl^- + H^+ \rightarrow 2Pb_3O_2Cl_2 + 2H_2O \quad (8)$$

Equation 7 is that for the idealized blixite formula, and equation 8 for the commonly quoted one.

Paralaurionite

Paralaurionite can be produced from mendipite by the following transformation:

$$Pb_3O_2Cl_2 + Cl^- + H^+ + H_2O \rightarrow 3PbOHCl \quad (9)$$

The co-occurrence of cerussite and oxychlorides

Cavities that contain both cerussite and oxychlorides suggest that the mineral deposition process switched between the two different pathways outlined above. Where CO_2 was originally present, but became depleted before the end of the mineral deposition process, cerussite production would have switched to oxychlorides. Most specimens from Merehead that contain both show the oxychloride as the later phase, so this would seem to be the common transition although this evidence is inevitably skewed by the overall falling temperatures and the lower formation-temperature range of the oxychlorides. The converse is also true however; if CO_2 suddenly became available, cerussite production would have preferentially occurred depositing cerussite on older oxychlorides.

All the halide and oxy-halide minerals are unstable with respect to cerussite in the presence of CO_2. Being limestone hosted, the groundwater at Merehead is carbonated and if this penetrated mineralized cavities would rapidly have destroyed these minerals, replacing them with cerussite. It can therefore be argued that all the mineralization initially went down the mendipite pathway, that all cavities were originally mendipite-bearing, and that those now containing cerussite do so because of alteration. Whilst this is a plausible scenario, it must be borne in mind that much of the cerussite is highly crystalline, and shows the characteristics of being a primary mineral, not an alteration product. Specimens that show a rind of granular cerussite around mendipite may indicate alteration, however.

Where mineralized cavities contain mendipite this can be taken as showing that groundwater did not penetrate. In this respect, it may be notable that the most prolific mendipite source, the No. 1 vein, was much larger than all the others and therefore provided more of a barrier to the entry of water.

The formation of sulphates

Neither the cerussite nor oxychloride-producing reaction paths consume the sulphate produced by the dissolution of galena. However, baryte is locally common at Merehead and it seems likely that the excess sulphate reacted with Ba from the seawater to produce this species. Celestine also occurs in locally abundant quantities, and this would result from a similar reaction involving Sr. The amount of baryte and celestine present is relatively small and cannot account for all the sulphate produced, however. This shows that other sulphate-consuming reactions also occurred and many of these would have resulted in water-soluble products that would have been carried away where the system was still open to circulation.

However, in a closed environment where the sulphates were trapped *in situ*, later reactions would have resulted in deposition of sulphate-bearing compounds. That this happened is indicated by the occasional presence of minute amounts of what appear to be unusual sulphate phases, possibly including complex sulphates of Na, Ca and Mg. It also seems likely that the sulphate essential to the oxychloride symesite ($Pb_{10}[O_7|SO_4|Cl_4].H_2O$) originated by this mechanism. This may explain the extreme rarity of symesite, if it could only have formed in the small proportion of cavities that became sealed before reactions had completed.

The abundance of arsenate minerals

One unusual facet of Mn pod mineralization is the dominance of arsenate phases and the complete absence of phosphate minerals, despite the presence of collophane (a colloidal form of apatite, or calcium phosphate) in some of the limestones themselves. Even mineral species such as mimetite which normally contain significant amounts of PO_4 do not do so here and Merehead mimetite invariably has a nearly pure arsenate end-member composition.

It is likely that much of the As originally came from the galena itself, as Mendip galena is high in this element (high enough, in fact, that Pb from the Mendips was once favoured for producing musket balls, due both to its greater hardness and its tendency to form perfectly spherical droplets when balls were 'cast' by the long drop method).

Manganese oxides are well known for their ready participation in redox and cation exchange reactions and are known in particular to oxidize soluble As^{3+} anions to an insoluble form (Post, 1999). This would also have caused arsenic to co-precipitate from seawater with the Mn oxides, thereby selectively enriching the pods with arsenic. Whilst Mn oxides are also effective in concentrating phosphates, their concentration must have been low, and this is probably due to the difficulty of releasing phosphate from apatite group minerals (e.g. collophane) at the pH conditions that existed whilst the seawater was circulating.

In passing, the general restriction of V to the hydrothermal event means that vanadate minerals do not occur in the Mn pod cores. Crystals appearing to be vanadinite are in fact mimetite, even where they are red or orange in colour. The only 'true' vanadinite that has been confirmed from Merehead occurs as minute (<20 μm) spots within V-rich mimetite, where there happens to be a local area with V > As. Every V-rich mimetite crystal that has been found has been observed to lie either immediately adjacent to or within the Mn oxides themselves (Mike Rumsey, pers. comm., December 2006). Mimetite crystals in the same cavity but not in contact with the Mn oxides are V-poor. This suggests that the minute amounts of V involved here originated from seawater adsorption into the Mn oxides, and not from the hydrothermal event.

Chemical microenvironments and their consequences for mineral formation

The marine hypothesis indicates that Mn minerals began to precipitate around existing nuclei containing decomposing galena. As soon as a continuous layer formed around the nucleus it became isolated from external chemical conditions and influences. The contents of what would eventually become a mineral-filled cavity were now fixed, and from this point on the system became an isolated and closed environment.

Since different nuclei would have been enclosed at different times, it seems reasonable to suppose that each nucleus – and subsequent mineralized cavity – contained a slightly different mix of chemical components giving rise to a unique chemical microenvironment. The initial conditions for subsequent mineral formation would have been slightly different in each case and mineral forming reactions would have proceeded down differing paths, ultimately resulting in each cavity having its own distinct mineralogy, as is observed in the field.

On the whole, individual pods tend to have reasonably consistent mineralogy, but from pod to pod there is considerable variation. For example, the mineral finds in June 2006 seem to have come from two pods, one immediately above the other. The upper pod contained calcite, wulfenite, crednerite, and other Cu-rich minerals together with the Pb-silicate mineral kentrolite, and the lower pod contained aragonite, cerussite, wulfenite and mimetite. Despite being adjacent and no more than 2 m apart, the mineralogy in each pod was distinct and there was no 'crossover' mineralization.

Field observations show that individual cavities within a single pod can contain unique mineralogy when they are isolated from their neighbours by Mn oxides. The degree of variability exhibited within a single pod is demonstrated by the July 2005 find, which contained the mineral fornacite. We therefore know that Cr must have been present, yet this metal does not appear in the EDX analyses of the Mn oxides from the same pod. The fornacite occurrence was limited to one small cavity, and neighbouring cavities no more than a few centimetres away contained a different suite of minerals including the oxychlorides mereheadite and symesite, together with mimetite and kentrolite.

The type of closed chemical system proposed here for the Merehead Mn deposits is identical to that considered to have operated at the Mammoth-St. Antony mine in Tiger, where the mineralogy is very similar in many respects (see, for example Abdul-Samad *et al.*, 1982; Bideaux *et al.*, 1997).

Although in some cases the rate of deposition of Mn oxides was high, leading to rapid sealing of cavities, the mineral-forming reactions within would still have taken place over a much longer period. The process is analogous to placing a handful of chemicals into a flask; putting a cork in the top does not stop the reactions taking place within.

Chemistry of the large vein systems

These same observations on chemistry appear to be true of the larger vein systems exposed in the 1970 to 1985 period. EDX analyses seem to bear out field observations that No. 2 vein was chemically much more complex than No. 1 vein. Whilst No. 1 vein cavities consistently contained a suite of minerals dominated by mendipite, No. 2 vein had a much more variable mineralogy.

No. 1 Vein

The sheer size of the No. 1 vein in particular (see Fig. 3), which was up to 5 m thick in places and extending over a vertical distance of up to 30 m, suggests that deposition of Mn minerals must have occurred very rapidly in this vein. Since deposition rates of up to 1 m per year are observed in present-day marine Mn nodule formation, even this size is not unreasonable in terms of a marine origin theory.

A second indication of a high rate of deposition comes from the EDX results, which show that No. 1 vein Mn oxides have very little heavy metal content. If the rate of deposition was high there, would be insufficient time for the surface layer to adsorb heavy metals before it was covered. Once the Mn oxides were in a solid state, cation exchange would become diffusion limited and there would be little subsequent spatial migration of heavy metals.

A third factor suggesting a high rate of deposition in No. 1 vein is the homogeneity of the mineralogy in the vein. The dominant Pb secondary mineral filling cavities was the rare oxychloride mineral mendipite, together with occasional and much smaller amounts of diaboleite, chloroxiphite, and sometimes the other oxychloride species symesite and parkinsonite. The formation of mendipite only happens under a narrow range of conditions (Edwards *et al.*, 1992) and the widespread nature of this mineral would appear to indicate that all the cavities must have had similar starting conditions, which suggests that all the nuclei that formed the cavities were sealed off from outside influences within a short period of time. This could only have happened if the rate of deposition was high.

Finally, a fourth factor suggests that the rate of Mn deposition in the No. 1 vein was high. The formation of mendipite in preference to cerussite requires that CO_2 be absent, as has been discussed above. Given that these deposits are hosted in calcite veins in limestone, there could only have been an absence of CO_2 if the cavity contents were quickly shielded from access to the $CaCO_3$ host rocks.

No. 2 Vein

No. 2 vein is known from field observations and from extant specimens to have had a much more complex mineralogical suite than its larger cousin. Both mendipite-dominated cavities and cerussite cavities occurred in this vein, indicating that some portions were free of CO_2 whilst others were not. Presumably, this represents local differences in the rate of deposition of Mn, but why this variation in rate happened is unknown.

Manganese oxides from those areas of No. 2 vein which contain cerussite – and therefore deposited slowly – contain a complex mixture of heavy metals, as can be seen in Table 1. This complexity appears to be diagnostic and may thus represent a useful way of distinguishing the origin of specimens housed in collections which do not have this information in their provenance data.

The formation of calcite-only and empty cavities

Although this paper concentrates on the mechanisms leading to the formation of the suite of secondary Pb minerals, it should be noted that a significant number of cavities within Mn pods are either empty, or contain only $CaCO_3$ in the form of calcite and/or aragonite.

Whilst Mn deposition requires a triggering nucleus, once begun the process is autocatalytic and therefore does not need further initiation. The spreading deposition event would thus envelop any loose blocks of material around, including fragments of vein calcite and spalled off chunks of limestone wall rock. When heated, these would have broken down and recrystallized as the deposit cooled, leading to the creation of a cavity filled with (only) calcite and aragonite.

Since many cavities contain voids, some of the material originally filling the cavity must have escaped, which would have occurred if the material decomposed into components which were gaseous or were water-soluble compounds. An entirely empty cavity must have lost all its original contents, or perhaps was formed from a trapped gas bubble.

The depletion of heavy metals in the Mn oxides layers close to a cavity show that water was circulating during Mn oxide deposition, and these metals now appear in-core as minerals such as mimetite and fornacite for example. There are relict traces of soluble compounds still present. Finally, in some of the cavities we have altered or corroded calcite, cerussite and baryte, so here there was clearly some form of resorption process happening post-deposition.

Observations on mineral-formation conditions

It is not possible to fully reconstruct detailed conditions of mineral formation from the available data. However, some general observations are possible.

Overall conditions

It is clear that the overall formation environment at Merehead was a highly oxidizing one as all the Mn minerals found contain Mn^{3+} (with the sole exception of pyrolusite, which contains Mn^{4+}). pH was initially high, as shown by the co-location of calcite and Mn oxides, and fell over time, indicated by the depositional sequence of the oxychlorides. The final pH stopped somewhere between 3 and 4, as shown by the absence of primary cotunnite.

Temperatures during the hydrothermal event probably reached between 325ºC and 525ºC as shown by the presence of kentrolite, and then fell, as shown by the deposition first of mesothermal minerals and finally by the deposition of the oxychlorides, which form at <100ºC.

Cerussite and hydrocerussite

Cerussite and hydrocerussite often form together, with the relative proportions being controlled predominantly by the amount of free carbon dioxide available. Hydrocerussite is stable with respect to cerussite at ambient temperatures and atmospheric CO_2 levels, which represent the very low pCO_2 conditions necessary (Mercy *et al.*, 1998).

The key reaction here is:

$$3PbCO_3 + H_2O \rightarrow Pb(OH)_2{\cdot}(PbCO_3)_2 + CO_2 \quad (10)$$

Most commonly, cerussite coats hydrocerussite and was therefore formed later. However, hydrocerussite crystals sometime occur in cavities with cerussite, having formed after the cerussite, and in such cases a CO_2 depletion mechanism must have been at work. Both can occur if CO_2 partial pressures fluctuate around the equilibrium value for equation 9 ($p\mathrm{CO}_2 = 10^{-2.24}$ at 298.2 K).

One unusual feature of the mineralogy at Merehead is that hydrocerussite is often found occurring in cavities in the limestone wall rocks immediately adjacent to a Mn pod. This too can be explained by the removal of gaseous CO_2 by circulating water (either seawater or hydrothermal) creating conditions suitable for hydrocerussite to be deposited as a stable phase.

'Plumbonacrite' [$Pb_5O(OH)_2(CO_3)_3$] and shannonite [$Pb_2O(CO_3)$]

It is possible that the related species 'plumbonacrite' and shannonite will be found to occur at Merehead, as these species are both produced by the decomposition of cerussite (Krivovichev *et al.*, 2000*a*,*b*).

Plumbonacrite forms under similar conditions to hydrocerussite in aqueous oxidation environments, the species produced being controlled by pH. Plumbonacrite forms in more acid conditions, but is thought to be metastable and therefore transforms into hydrocerussite easily (Krivovichev *et al.*, 2000*a*).

Given this, plumbonacrite would be most likely to occur in cavities in the core of a pod, if the pH in that cavity fell to a suitable level and if there was a mechanism to absorb or remove any carbon dioxide formed. Plumbonacrite crystallizes as small, transparent hexagonal plates.

Shannonite is normally found as a white powdery coating consisting of minute anhedral to platy white crystals, with a distinctive waxy lustre and if present, would be most likely to occur in the same way as plumbonacrite.

Crednerite [$CuMnO_2$] and related species

Crednerite is occasionally found in Mn pods, usually as bladed masses embedded in calcite or aragonite. The blades are often altered to malachite to a greater or lesser extent (see Turner, 2005, for example).

The mode of formation of this mineral does not appear to have been studied in detail, but as crednerite invariably occurs embedded in calcite, it must have formed very early in the sequence of deposition, and at high pH and mesothermal temperatures when the calcite was being deposited. Enclosure by calcite would then have protected the crednerite from subsequent changes (the malachite surface coatings invariably present on crednerite most likely have come from reaction with the enclosing calcite).

To date, there has been no recorded occurrence of the closely related mineral, delafossite (the Fe analogue, $CuFeO_2$) at Merehead. The two species seem to occur under very similar environmental conditions and therefore it is possible that delafossite may occur in the more Fe-rich portions of the Mn deposits.

Kentrolite [$Pb_2Mn_2[O_2/Si_2O_7]$] and melanotekite [$Pb_2Fe_2[O_2/Si_2O_7]$]

Kentrolite has been known from Merehead for some years, but in minute quantities. Two or three tiny pieces were originally identified in material from No. 2 vein in the 1970s (R.F. Symes, pers. comm., 2006) and the species had not been seen since then.

Recently, however, large quantities of kentrolite have been found to occur in the pods recovered in July 2005 and June 2006. Exceptional large jet black euhedral crystals up to 5 mm long have been found lining cavities and embedded in calcite. These crystals were originally mistaken for goethite (which species they resemble very closely indeed) and it is highly likely that kentrolite has occurred before but was simply misidentified. Kentrolite is a high-T mineral but here was found intimately associated with oxychlorides, which are destroyed by even moderate temperatures. The kentrolite crystals must therefore have formed early in the sequence of deposition, and the necessary $Si_2O_7^{6-}$ ions must have originated from the hydrothermal event.

A third kentrolite mode of occurrence was discovered at the same time, and this is somewhat puzzling. In this mode of occurrence, kentrolite occurs as a brownish black bladed material, replacing crednerite blades. Under the microscope, the replacement can be seen to be composed of minute rosettes of kentrolite crystals. It is currently not possible to define the conditions which caused this to happen.

The Fe analogue, melanotekite, also occurs sparingly at Merehead as thin, greenish yellow crusts made up of powdery material. However, its mode of formation is entirely different; it was produced when the outer Fe oxide layers of a pod were silicified by the hydrothermal event.

Lead halides and oxyhalides

Blixite [$Pb_2O(OH)Cl$], mendipite [$Pb_3O_2Cl_2$] and paralaurionite [$PbOHCl$]

Both low-*T* and hydrothermal dissolution of galena can increase pH to the point where Mn oxides are stable alongside calcite. The initial deposition of the minerals that were beginning to infill cavities thus took place in an alkaline environment.

The oxychloride deposition sequence blixite → mendipite → paralaurionite is observed, showing that the pH must initially have been ~8 but fell over time to ~4, perhaps from the depletion of hydroxide ions or from the production of sulphuric acid. Temperatures must already have been <~100ºC but >30ºC, as below this temperature mendipite is not stable (Edwards *et al.*, 1992).

Since field observations show that both paralaurionite and blixite always occur embedded in mendipite, it is possible that these reflect local variations of pH within a cavity, the blixite being relict, and the paralaurionite representing a region of locally increased acidity.

Edwards *et al.* show that deposition of the blixite → mendipite → paralaurionite sequence does not occur when CO_2 is present. In the case of No. 1 vein, the rapid deposition of Mn minerals isolated pod contents from the wall rocks very quickly, limiting the supply of $CaCO_3$ and thus CO_2, favouring the formation of mendipite which became the dominant Pb secondary mineral in this vein. However, cerussite does occur locally, which suggests that fragments of calcite or limestone wall rock were trapped in some cavities creating CO_2-rich chemical microenvironments.

Paralaurionite is produced directly by precipitation from Pb-rich solutions when the aqueous environment is poor in SO_4^{2-} ions and the pH is >~6 (Abdul-Samad *et al.*, 1982). The stability field for this species does not overlap those of cerussite and hydrocerussite, and therefore it cannot be found in any assemblage that includes either of these two minerals. Since cerussite is common at Merehead, it follows that paralaurionite will be rare. Field observations show that the only valid occurrences of paralaurionite are patches of massive material embedded in mendipite, and in the cavities containing paralaurionite cerussite is absent or nearly so.

However, the pH does not seem to have fallen enough to produce primary cotunnite ($PbCl_2$) so presumably did not go below about ~3 (Edwards *et al.*, 1992).

Chloroxiphite [$Pb_3CuCl_2(OH)_2O_2$]

Chloroxiphite occurs as bladed crystals embedded entirely in mendipite. These crystals are never found touching other species such as calcite or Mn oxides. It is therefore clear that the formation conditions for chloroxiphite must be identical to those for mendipite, in other words a pH of ~6–8, and the absence of CO_2.

Obviously, a source of Cu must have been present, and this was probably chalcopyrite.

Diaboleite [$Pb_2CuCl_2(OH)_4$]

Primary (early stage) diaboleite occurs as roughly formed euhedral crystals which are now found embedded in mendipite and cerussite, and occasionally in calcite. From this mode of occurrence, it would seem that this type of diaboleite crystallized as a mesothermal species that was later trapped by the enveloping mineral.

The presence of this primary diaboleite (in cerussite) indicates that there must have been a period of low carbonate activity, even where cerussite is now abundant (Abdul-Samad *et al.*, 1982). This is evidence for the environment switching between cerussite and oxychloride pathways. Primary diaboleite crystals tend to be reasonably well formed (if crude) which suggests that the crystals had room to grow freely and therefore formed relatively early on.

Diaboleite is produced by a second mechanism, which is the decomposition of chloroxiphite. Crystals of the latter are often surrounded by a light blue alteration halo, consisting mostly of diaboleite. On one specimen, cotunnite ($PbCl_2$) is also present, admixed with the diaboleite. Presumably this represents highly acidic local conditions with pH <3 and increasing $p\mathrm{Cl}^-$ (Edwards *et al.*, 1992).

Mereheadite [$Pb_2O(OH)Cl$]

Merehead is the type locality for mereheadite (Welch *et al.*, 1998) and even here, it is not abundant. Since mereheadite occurs both in mendipite from No. 1 vein as well as in cerussite/aragonite-filled cavities in recent finds, its stability field must overlap those of both mendipite and cerussite. The stability fields for mendipite and cerussite in Edwards *et al.* (1992) would therefore suggest that formation of mereheadite probably occurred in the pH range of 4 to 6. However, there appears to have been no formal studies of the stability of this species.

It is possible that mereheadite is produced by a reaction similar to that in equation 5 above:

$$2Pb^{2+} + 2H_2O + Cl^- \rightarrow Pb_2O(OH)Cl + 3H^+ \quad (11)$$

This would account for the presence of mereheadite in No. 1 vein. However, although chemically almost identical to blixite, it is clear that the formation of mereheadite cannot be as sensitive to pCO_2 levels, since mereheadite occurs intimately associated with cerussite in specimens recovered in July 2005. The reaction pathway leading to the formation of mereheadite in cerussite-rich environments is not clear, and this relationship and its implications require further investigation.

The chemical similarity to blixite suggests that there may well be a polymorphous relationship between the two species, although the work of Welch *et al.* suggests that boron is an essential chemical component in mereheadite.

Symesite [$Pb_{10}[O_7/SO_4/Cl_4].H_2O$] and parkinsonite [$Pb_7MoO_9Cl_2$]

Symesite and parkinsonite are two extremely rare oxychlorides which at the present time are only confirmed to occur in the Mendip Mn deposits.

Symesite (Welch *et al.*, 2000) is a complex, sulphate-rich oxychloride originally found in No. 1 vein, where it occurs completely enclosed by mendipite. This indicates that the stability fields and formation mechanisms of both species must be similar. As symesite does not form distinct crystals it is unclear whether it formed before mendipite, or is contemporaneous. More recently – in July 2005 – symesite was found together with mereheadite in cerussite-filled cavities. As with mereheadite, the implication of the presence of symesite in both environments requires further investigation.

To date, the Mo-bearing oxychloride, parkinsonite, has only been found to occur as minute crystals embedded in mendipite from No. 1 vein (Symes *et al.*, 1994; Welch *et al.*, 1996). These crystals must have formed before the enclosing mendipite. Parkinsonite is extremely rare, which is understandable if it represents a product of a chemical microenvironment rich in Mo, all the more so because Mn oxides in No. 1 vein were deposited rapidly and therefore tend to be poor in heavy metals.

The formation mechanism of parkinsonite is not clear, though some inferences can be drawn. In their treatment of the mineral deposits at Tiger, Abdul-Samad *et al.* (1982) found that all Pb^{2+} chlorides, carbonates and sulphates are thermodynamically unstable with respect to wulfenite. Since wulfenite is found at Merehead, clearly the conditions were appropriate for its formation, and the survival of parkinsonite can only be due the cavities where it occurs being rapidly enclosed in a protective sheath of impervious Mn oxides and/or calcite. This may explain why parkinsonite only occurs in the No. 1 vein, where there was rapid deposition of Mn minerals.

The correct chemical formula for parkinsonite is that given by Welch *et al.* (1996). The structure of parkinsonite is analogous to pinalite (Grice *et al.*, 2000) in that the Mo^{6+} is in square-pyramidal coordination (as W^{6+} is in pinalite), the ninth oxygen forming the apex of the MoO_5 pyramid. There are no vacant Pb sites as implied by the formula in Symes *et al.* (1994).

Other lead halides and oxyhalides

Stability fields indicate that there is a possibility that the compound $Pb_7O_6Cl_2.2H_2O$ could exist at Merehead. This compound is known synthetically but not as a valid mineral species; although the name 'lorettoite' was assigned to the anhydrous compound, this has been discredited as man-made material. However, if present at Merehead it will be probably be associated with blixite since it would be a precursor phase formed at higher pH, being stable under even more alkaline conditions (Edwards *et al.*, 1992).

Baryte and celestine

Baryte is a relatively common gangue material in the Mendip Hills, and therefore could be expected to occur in the Mn-bearing veins, and it is indeed often present at Merehead. Unusually however, celestine is sometimes present locally in abundant quantities despite relatively low levels of Sr in the limestone.

Since seawater contains both Ba and Sr in some quantities, it is probable that both species formed either directly using the excess sulphate ions or by exchange reaction with the Pb sulphate produced by the dissolution of galena, giving rise to the following set of equations:

Baryte

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \quad (12)$$

$$PbSO_4 + Ba^{2+} \rightarrow BaSO_4 + Pb^{2+} \quad (13)$$

Celestine

$$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4 \quad (14)$$

$$PbSO_4 + Sr^{2+} \rightarrow SrSO_4 + Pb^{2+} \quad (15)$$

Comparisons with Långban and Tiger

There are partial parallels between the mineralogy of Merehead and the deposits at Långban, Sweden, and at the Mammoth-St. Antony Mine in Tiger, Arizona.

It is noteworthy that the two most similar deposits are hydrothermal in origin, which suggests that the hydrothermal event at Merehead had an importance that has not previously been recognized. The remarkable mineralogy would seem to be due to the fortuitous combination of unusual starting conditions and heat, and its preservation due to enclosure in an equally unusual and impervious sheath of Mn oxides.

Långban

At Långban, differentiated Mn-Fe mineralization was hydrothermally emplaced into dolomite layers interbedded with siliceous volcanics, which have now been extensively metamorphosed by a series of granitic intrusions.

Here the hydrothermal mechanism was one of regional-scale groundwater circulation driven by magmatic heat. As might be expected, therefore, the parallels with Långban mostly occur in the high-temperature silicates, although there was no comparable large-scale hydrothermal mechanism at Merehead.

The silicates shared between the two localities are kentrolite, melanotekite, nasonite, apophyllite, datolite and quartz (the latter being an oxide, strictly speaking). At Långban, these are limited to a small subset of the environments present, suggesting that conditions at Merehead were similar. Långban is the type locality for kentrolite, where the mineral occurs as a constituent of Pb-bearing silicate skarns that are known to have crystallized at >500ºC (Bollmark, in Holtstam *et al*., 1999). These skarns form in the contact zone between siliceous Mn ores and bedded carbonate rocks, and contain a suite of minerals that also includes ganomalite (in the case of Merehead, the closely related species, nasonite, occurs).

The Mn minerals at Långban show little similarity, being dominated by hausmannite and braunite, representing primary mineralogy and metamorphosed primary deposits respectively.

Being carbonate-hosted, Långban also contains a range of carbonates which is similar to that at Merehead, including cerussite, hydrocerussite, rhodochrosite, malachite, azurite, calcite and aragonite. The more unusual secondary minerals in common at both localities include crednerite, mendipite and blixite. Clearly, therefore, both deposits followed similar trajectories on cooling, despite their different origins.

Tiger

The mineralogically similar deposits at the Mammoth-St. Antony mine in Tiger, Arizona are considered to have been formed within a closed system, such as the one suggested here for Merehead (Abdul-Samad *et al*., 1982).

At Tiger, the mineralization was emplaced in connection with the intrusion of a porphyritic rhyolite facies, which deposited Pb-Zn-Ag sulphides into a fault-controlled orebody. The deposit is adjacent to an older, large scale Cu-Mo porphyry (the San Manuel deposit) which probably contributed these metals. The seminal paper on the geology of the deposit is that of Creasey (1952). Post-deposition, the Tiger orebody was oxidized to a considerable depth and the mineralogy is therefore very complex and highly variable (see Bideaux, 1980, for example).

The parallels between Merehead and Tiger exist in the 'anomalous suite' of secondary minerals at the latter locality. This suite consists of oxy- and hydroxy-chlorides, sulphates and carbonates, including minerals such as paralaurionite, diaboleite, mendipite and chloroxiphite which occur at both localities. However, the Mammoth-St. Antony deposit is polymetallic and considerably more complex than simple Mendip Pb veins, and therefore the range of chemistry occurring there was considerably more diverse, leading to a far wider range of mineral species than at Merehead.

The Mammoth-St. Antony deposit is clearly of purely hydrothermal origin with the alteration taking place post-emplacement. This sequence of events is mimicked at Merehead; although the original galena deposits were already in place, they were subjected to hydrothermal heating, followed by a phase of alteration.

At Tiger, large quantities of wulfenite are found – enough that the mine was worked for Mo in the early 20th century. Wulfenite there is a very late-stage mineral, often found well crystallized. Abdul-Samad *et al*. (1982) attribute this to Pb^{2+} chlorides, sulphates and carbonates being thermodynamically unstable with respect to wulfenite, meaning that the existing minerals in any cavity which was open to later solution activity were dissolved and replaced by wulfenite. Similar arguments are made for vanadinite and pyromorphite, amongst other minerals. The areas containing the anomalous suite of minerals at Tiger therefore only survived because they were protected by enclosure within silicified horizons, which prevented water from entering. A similar argument can be made for Merehead, although obviously the protection mechanism (enclosure in Mn oxides and calcite) is different. One implication is that the surviving mineralized cavities at least were sealed and protected from subsequent water incursion. Wulfenite has, however, been found in a few localized places, and usually occurs with (only) cerussite and calcite/aragonite. It is therefore tempting to suggest that these cavities were open and that the original mineralization has been replaced, but there is no firm evidence for this.

Further research

Further research is needed into a number of questions posed by this new theory, including the temperatures attained by hydrothermal event. It is possible that kentrolite may be viable as a geothermometer, and fluid inclusion studies could be performed on the quartz.

Stability fields and modes of formation are needed for the species: mereheadite, symesite, parkinsonite, crednerite and kentrolite.

Mereheadite and symesite occur in both CO_2-rich and CO_2-poor environments, and this needs explanation in relation to their formation mechanisms.

The conditions which cause the alteration of chloroxiphite to diaboleite, chloroxiphite to diaboleite plus cotunnite, and the alteration/replacement of crednerite to kentrolite are all unknown, and require further investigation.

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References

Abdul-Samad, F., Thomas, J.H., Williams, P.A., Bideaux, R.A. and Symes, R.F. (1982) Mode of formation of some rare copper (II) and lead (II) minerals from aqueous solution, with particular reference to deposits at Tiger, Arizona. *Transition Metal Chemistry*, **7**, 32–37.

Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols M.C. (1997) *Handbook of Mineralogy*, vol. III, p. 143. Mineral Data Publishing, Tucson, Arizona.

Bideaux, R.A. (1980) Famous Mineral Localities – Tiger, Arizona. *Mineralogical Record*, **11**, 155–181.

Brugger, J. and Meisser, N. (2006) Manganese-rich assemblages in the Barrhorn Unit, Turtmanntal, Central Alps. Switzerland. *The Canadian Mineralogist*, **44**, 229–248.

Burr, P.S. (1996) Famous mineral localities: The Higher Pitts Mine, Mendip Hills, Somerset, England. *Mineralogical Record*, **27**, 245–262.

Cama, J., Acero, P., Ayora, C., and Lobo, A. (2005) Galena surface reactivity at acidic pH and 25ºC based on flow-through and in situ AFM experiments. *Chemical Geology*, **214**, 309–330.

Carlos, B.A., Chipera, S.J., Bish, D.L. and Craven, S.J. (1993) Fracture-lining manganese oxide minerals in silicic tuff, Yucca Mountain, Nevada, U.S.A. *Chemical Geology*, **107**, 47–69.

Creasey, S.C. (1950) *Arizona Zinc and Lead Deposits*. Arizona Bureau of Mines Bulletin **156**, pp. 63–84.

Dermatas, D., Dadachov, M., Dutko, P., Menounou, N., Arienti, P. and Shen, G. (2004) Weathering of lead in Fort Irwin firing range soils. *Global Nest*, **6**, 167–175.

Din, V.K., Symes, R.F. and Williams, C.T. (1986) Lithogeochemical study of some Mendip county rocks with particular reference to boron. *Bulletin of* *the British Museum (Natural History)*, Geological Series Miscellania II, **40**, 247–258.

Dyer, A., Pillinger, M., Harjula, R. and Amin, S. (2000) Sorption characteristics of radionuclides on synthetic birnessite-type layered manganese oxides. *Journal of Materials Chemistry*, **12**, 1381–1386.

Edwards, R., Gillard, R.D. and Williams, P.A. (1992) Studies of secondary mineral formation in the PbO-H_2O-HCl system. *Mineralogical Magazine*, **56**, 53–65.

Green, G.W. (1958) The central Mendip lead-zinc orefield. *Bulletin of the Geological Survey of Great Britain*, **14**, pp. 70–90.

Grice, J.D. and Dunn, P.J. (2000) Crystal-structure determination of pinalite. *American Mineralogist*, **85**, 806–809.

Holtstam, D. and Langhof, J. (editors) (1999) *Långban, the Mines, their Minerals, Geology and Explorers*. Christian Weise Verlag, München, Germany.

Kim, B.S., Hayes, R.A., Prestidge, C.A., Ralston, J. and Smart, R. (1995) Scanning tunnelling microscopy studies of galena: The mechanisms of oxidation in aqueous solution. *Langmuir*, **11**, 2554–2562.

Krivovichev, S.V. and Burns, P.C. (2000*a*) Crystal chemistry of basic lead carbonates. Part 1, crystal structure of synthetic shannonite. *Mineralogical Magazine*, **64**, 1063–1068.

Krivovichev, S.V. and Burns, P.C. (2000*b*) Crystal chemistry of basic lead carbonates. Part 2, crystal structure of synthetic 'plumbonacrite'. *Mineralogical Magazine*, **64**, 1069–1075.

Lindqvist, B. and Charalampides, G. (1987) Stability and kinetic studies of synthetic solid solutions in the kentrolite-melanotekite series. *Geologiska Foreningens i Stockholm foerhandlingar*, **109**, 73–82.

Matagi, S.V., Swai, D. and Mugabe, R. (1998) A review of heavy metal removal mechanisms in wetlands. *African Journal of Tropical Hydrobiology*, **8**, 23–35.

Means, J.L., Crerar, D.A., Borcsik, M.P. and Duguid, J.O. (1978) Radionuclide adsorption by manganese oxides and implications for radioactive waste disposal. *Nature*, **274**, 44–47.

Mercy, M.A., Rock, P.A., Casey, W.H. and Mokarram, M.H. (1998) Gibbs energies of formation for hydrocerussite and hydrozincite. *American Mineralogist*, **83**, 739–745.

Mikhlin, Y.L., Romanchenko, A.S. and Shagaev, A.A. (2006) Scanning probe microscopy studies of PbS surfaces oxidized in air and etched in aqueous acid solutions. *Applied Surface Science*, **252**, 5645–5658.

Moorbath, S. (1962) Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance. *Philosophical Transactions of the Royal Society of London, Series A, Mathematical and Physical Sciences*, **254**, 295–360.

Morse, G. (editor) (2004) *Minerals of the Mendips*. Published by the Southern Branch of the Russell Society.

Moses, C.O. and Ilton, E.S. (1998) *Surface and solution-interface geochemistry of PbS and PbSe minerals.* Office of Science and Technology Investigation final report DE-FG02-93ER14373, 13 pp.

Nava, J.L. and Gonzalez, I. (2005) Los electrodos de pasta de carbono en el estudio electroquímico de minerales metálicos. *Química Nova*, **28**, 5.

Parc, S., Nahon, D., Tardy, Y. and Veillard, P. (1989) Estimated solubility products and fields of stability for cryptomelane, nsutite, birnessite, and lithiophorite based on natural lateritic weathering sequences. *American Mineralogist*, **74**, 466–475.

Parkhouse, S.J. (2004) *Geodiversity Audit of Active Aggregate Quarries - Torr Works, Cranmore, Somerset, England*. www.somerset.gov.uk/.

Post, J.E. (1999) Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proceedings of the National Academy of Sciences of the USA,* **96**, 3447–3454.

Prince, K.C., Heun, S., Gregoratti, L., Barinov, A., and Kisinova, M. (2002) *Long Term Oxidation Behaviour of Lead Sulfide Surfaces*. Lecture Notes in Physics, vol. **588**, pp. 111–120. Springer, Berlin, Heidelberg.

Scheckel, K.G., Impellitari, C.K. and Ryan, J.A. (2001) *Assessment of a sequential extraction procedure for perturbed lead contaminated samples with and without phosphorus amendments*. UK Environmental Protection Agency Risk Management Research Laboratory.

Symes, R.F. and Embrey, P.G. (1977) Mendipite and other rare oxychloride minerals from the Mendip Hills, Somerset, England. *Mineralogical Record*, **8**, 298–303.

Symes, R.F., Cressey, G., Criddle, A.J., Stanley, C.J., Francis, J.G. and Jones, G.C. (1994) Parkinsonite, $(Pb,Mo,\square)_8O_8Cl_2$, a new mineral from Merehead Quarry, Somerset. *Mineralogical Magazine*, **58**, 59–68.

Takahashi, T. (1960) Supergene alteration of lead and zinc deposits in limestone. *Economic Geology*, **55**, 1083–1115.

Turner, R.W. (2005) A note on crednerite from Merehead Quarry. *Newsletter of the Russell Society*, p. 47.

Turner, R.W. and Rumsey, M. (2007) The Manganese-Hosted Mineral Deposits of the Mendip Hills (in prep.).

Welch, M.D., Schofield, P.F., Cressey, G. and Stanley, C.J. (1996) Cation ordering in lead-molybdenum-vanadium oxychlorides. *American Mineralogist*, **81**, 1350–1359.

Welch, M.D., Criddle, A.J. and Symes, R.F. (1998) Mereheadite, $Pb_2O(OH)Cl$: a new litharge-related oxychloride from Merehead Quarry, Cranmore, Somerset. *Mineralogical Magazine*, **62**, 387–393.

Welch, M.D., Cooper, M.A., Hawthorne, F.C. and Criddle, A.J. (2000) Symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, a new PbO-related sheet mineral. *American Mineralogist*, **85**, 1526–1533.

Worley, N.E. and Ford, T.D. (1977) Mississippi Valley type orefields in Britain. *Bulletin of the Peak District Mines Historical Society*, **6**, 201–208.

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