# *Abstract*

*The iron and manganese ores from Paviland cave in the collections of the National Museum of Wales and Oxford University Museum are all rather poorly provenanced, but are believed be from the excavations by Sollas. Of these materials six specimens of iron ores, two of ochres and one specimen of a manganese ore were selected for detailed examination. In addition a specimen of manganese ore in the OUM less certainly derived from those excavations was also examined.*

*The haematitic iron ores are very variable in details of the their petrography, but are consistent with an origin within the Bristol Channel Orefield. They also show some variety in their chemical composition, but there are some features common to most samples, including elevated levels of germanium, vanadium and uranium. This facies of ore geochemistry has only been recognised in samples from around Swansea Bay, and samples from the ores of eastern Gower are particularly close to those from Paviland. The variety of ore textures seen within the major vein cutting the headland from Mumbles to Limeslade Bay parallels the variety seen at Paviland, and represents a likely potential source.*

*The ochres sampled included an indurated particle of ochreous soil, penetrated by fine tubes interpreted as plant roots or burrows. Similar tubes were observed in the ochreous coating on the bones of the “Red Lady”. A small chip of bone within the ochre collection in the NMGW collections had a red ochre on its surface, and this was also sampled. The composition of the ochres was strongly influenced by a large component of a phosphate mineral, which may be the diagenetic phase responsible for the cementation. The chemical composition was compatible with a mixture of sediment with 15-35% iron ore. Modelling of the ochre composition suggests that the added ore might have been of similar composition, and therefore origin, to the lump ores, but in the absence of analysis of unaltered sediment this cannot be tested rigorously.*

*The manganese ore apparently derived from the early excavations proved to be a piece of wad, in which fine-grained manganese minerals are present as a cement to a silt-grade sediment. The provenance of this material is very hard to determine, but an origin as a concretion within superficial sediments is likely. The material might have been derived from a manganese wad deposit in a stream, or as a bog ore deposit. Such deposits are particularly known from upland areas of Wales. Whether the material was collected directly from source, or was picked from a reworked context in a glacial deposit remains unknown. Ochreous sediment adhering to the specimen confirms it as part of the “Red Lady” assemblage.*

*The substantial manganese ore block from the OUM “lithological” collection has a complex internal structure in which zones of replaced euhedral crystals (possibly originally rhodocrosite, now Mn oxides and silicates) are overlain by, and possibly alternate with, laminated coatings of fine-grained manganese minerals (cryptomelane?) with zones of lead-zinc enrichment. Remaining void space is partially occluded by both equant euhedral crystals and fibrous cements. This texture is reminiscent of some lithologies present in the manganese ores of Ty Coch, to the west of Swansea Bay. However, significant differences in the mineralogy and geochemistry cast considerable doubt on a provenance for the ore in this deposit. The most likely source for this ore is suggested to be one of the manganese ore deposits farther north in Wales. If this is the case, then the potential origin lies with the source region for the glacial deposits of Gower, and a natural rather than human agency in bringing the ore to Gower seems likely. Whether the ore came to be in the cave through natural or artificial agency remains unknown.*

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## 1. Material

The most significant concentration of iron minerals associated with the Red Lady is the brownish-red coating on the skeleton itself. This material was not available for detailed investigation during the present project, so the focus of the analytical investigations have been materials less certainly associated with the burial itself. The material is divided between two museum collections, neither of which has a secure provenance.

The Oxford University Museum (OUM) contains some discrete specimens of iron ore, together with collections of both iron and manganese rich materials mounted on boards. These materials all appear to stem from the 19th century excavations. In addition there is a collection of “lithological” specimens which is less securely tied to the old investigations. This collection included a single large block of manganese ore. A box contains a quantity of ochre.

The National Museum of Wales, Cardiff (NMGW) also holds specimens probably derived from the 19th century excavations. These comprise 15 pieces of iron ore and associated materials, totalling approximately 280g. As with the OUM collection, a separate box holds a small quantity of ochre.

Sampling was designed to examine a spectrum of the ore types present. The loose ochreous material was examined using material from the OUM collection, while a small bone fragment within the NMGW ochre collection gave the opportunity of sampling the ochre adhering to the enclosed objects:

| | | |
|---|---|---|
| Ochre: | ochre from OUM | (PAV1) |
| | ochre on bone fragment from NMGW (from boxed ochre sample) | (PAV7) |
| Iron ores: | 1 ore specimen from OUM (S5103) | (PAV4) |
| | 2 ore specimens from OUM (2 out of 7 on larger board labelled *haematite/limonite*) | (PAV5-6) |
| | 3 ore specimens from NMGW (3 out of 17) | (PAV8-10) |
| Manganese ores: | 1 specimen of hard lump ore from OUM (from lithology collection, S5107) | (PAV3) |
| | 1 specimen of wad from OUM (1 out of 8 on board labelled *psilomelane*) | (PAV2) |

There was very little of any of these materials, so samples were small. Most of the ore lumps were of less 25g. These were cut to provide a specimen for mounting in resin and polishing for examination under the scanning electron microscope. The remainder was crushed to provide powder for sample preparation of a fused bead for major element determination by XRF (in many cases there was insufficient material for this) and for dissolution for trace element determination by ICP-MS. The ochre sample PAV1 was a small amount of powder including a larger, slightly more coherent granule. PAV7 was a small amount of ochre mechanically removed from a bone fragment, to which it formed a matrix.

| Sample | XRF | ICP-MS |
|---|---|---|
| PAV1 | | X |
| PAV2 | X | X |
| PAV3 | X | X |
| PAV4 | X | X |
| PAV5 | | X |
| PAV6 | | X |
| PAV7 | | X |
| PAV8 | | X |
| PAV9 | X | X |

Analytical work was undertaken using the Philips PW 1400 X-ray fluorescence spectrometer (XRF), the Perkin-Elmer Elan 5000A inductively coupled plasma - mass spectrometer (ICP-MS) and the Cambridge Instruments S360 scanning electron microscope (with a Link Analytical Ltd. AN10000 energy dispersive X-ray analysis system) of the Earth Sciences Department, Cardiff University.

## 2. Description of the Iron Ores

### 2.1 Petrography

**PAV4 (OUM S5103)**
This specimen represents a corner broken from a larger block of ore. In hand specimen the ore was observed to be quartz-bearing. In polished block the ore proved to a have a relatively coarse micro-botryoidal texture (botryoids up to 200µm across) with pore space filled by coarse-grained quartz (Figure 1a).

**PAV5 (OUM *haematite/limonite*)**
In hand specimen this showed haematite grown on haematised dolomite(?). In polished block a complex replacement texture was revealed, with iron oxides apparently replacing carbonate minerals. The space between the iron oxides was largely filled by quartz, which included islands of surviving Mn-rich calcite (Figure 1b). Some surviving porosity within the haematite showed that the haematite has, at least locally, a texture apparently comprising granules (10-20µm in diameter) formed of haematite platelets (figure 1c).

**PAV6 (OUM *haematite/limonite*)**
In hand specimen this small specimen showed botryoidal haematite over(?) a soft red ochreous haematite. The polished block showed the development of a complex micro-botryoidal texture through the section.

**PAV8 (NMGW)**
This specimen was formed of dense haematite, which was cut by closely spaced parallel fractures. It formed the most abundant lithology of haematite pieces in the NMGW collections. In polished block, the haematite showed a complex structure of branching, bushy growths. These structures were up to several mm in length, with individual branches up to 0.5mm in diameter (Figure 1d). The branches appear to comprise merged spherulites of haematite up to at least 500µm diameter. The cores of the branches are frequently hollow. Both the cores and the voids between the branches are partially or fully occluded by iron oxides with a lower backscatter coefficient that the main generation of haematite (figure 1e). This second generation is probably goethite, but might just include haematite with a less dense packing of crystallites. The second generation shows crystallites with a plate-like form, where seen through surviving porosity (figure 1 f,g). Some areas of the section show a rather simpler iron oxide microstructure of larger scale botryoidal growth (figure 1h).

**PAV9 (NMGW)**
In hand specimen this material appeared as a rather even-textured dense haematite. In polished block the even texture was shown to be due to a microstructure of small spherules, possibly a complex botryoidal growth (Figure 1i). Void space within the haematite was not abundant, but where present locally showed remnants of a quartz cement of corroded appearance (Figure 1j). Where the porosity was not occluded by quartz the granular texture of the haematite was clearly demonstrated, as were the plate-like crystallite terminations (figure 1l).

**PAV10 (NMGW)**
This material in hand specimen appeared as a porous hard red haematite with an open structure, partially occluded by calcite. In polished block the haematite showed a complex botryoidal or spherulitic texture, built into irregular elongate fingers up to several mm long and 0.6mm diameter (figures 1 m,n). The pore space is filled with a cement of calcite, which locally shows iron oxide zones close to the contact with the main generation of haematite (Figures 1 o,p).

### 2.2 Geochemistry

Major element analysis by XRF was possible for only three of the iron ore specimens, because of the small size available for sampling. The totals of all three are a little high (102.1 – 104.3%), reflecting minor problems with calibration at such high iron contents; the relative proportions of other elements are, however, likely to be reasonably accurate. Trace element analysis by ICP-MS was undertaken for all six ores and both ochres.

The major element analysis of the iron ores confirms them as high grade ores, with silica as a significant component in PAV4 and calcium carbonate present in PAV10. Phosphorus contents are uniformly low as is typical for the Bristol Channel Orefield.

The six iron ore specimens show a rather characteristic trace-element composition, with elevated levels of As, Ge, V (4 of 6) and Pb, slightly elevated levels of Zn (4 of 6) and a very low concentration of Ti. The distributions of these elements are illustrated using binary variation diagrams in figure 4. The only samples in our database of approximately 150 analysed ores from the Bristol Channel Orefield which match this pattern of trace element content are those from Gower (Langland and Limeslade Bays).

All the ores show low rare earth element (REE) contents, typical for Bristol Channel Orefield ores, with the total concentration of REEs (ΣREE) ranging from 5 to 16 ppm (i.e. 3% to 11% of average upper crustal concentrations, using the normalising factors of Taylor & McLennan 1981).

The upper crust-normalised REE profiles (Figure 5) for samples PAV4, PAV9 and PAV10 are similar to each other and to that of MUM1. All these profiles show a low concentration of rare earth elements; ΣREE = 8.6ppm, 9.8ppm and 6.0ppm for PAV4,9,10 respectively), a humped profile with the light REE (LREE) more depleted than the heavy REE (HREE) (Paviland samples show $Dy_N/Lu_N$ = 1.25 – 1.38; $Gd_N/La_N$ = 2.11 – 3.19) and a small negative cerium anomaly (Ce/Ce* = 0.50 – 0.61 for Paviland specimens; Ce/Ce* = $Ce_N/[La_N^{0.5} * Pr_N^{0.5}]$ where N refers to an upper crust normalised value). PAV8 has a similar REE profile ($Dy_N/Lu_N$ = 1.41; $Gd_N/La_N$ = 2.35), but has a slightly positive Ce anomaly (Ce/Ce* = 1.20). Sample MUM1, with which these samples compare closely, has a slightly more humped profile ($Dy_N/Lu_N$ = 1.5; $Gd_N/La_N$ = 4.2), a comparable REE content (ΣREE = 6.8 ppm) and a small negative Ce anomaly (Ce/Ce* = 0.51).

Sample PAV5 has an extremely low REE content (ΣREE = 5.1ppm), but shows a slightly flatter upper-crust normalised REE profile (Figure 5) than the group described above ($Dy_N/Lu_N$ = not determined; $Gd_N/La_N$ = 1.94), with a very slightly negative Ce anomaly (Ce/Ce* = 0.83).

Sample PAV6 has a rather different REE profile (Figure 5), with a higher overall REE content (ΣREE = 19.1 ppm; still a very low value in absolute terms), a markedly humped profile with significant LREE depletion ($Dy_N/Lu_N$ = 1.74; $Gd_N/La_N$ = 22.6) and a positive Ce anomaly (Ce/Ce* = 2.69). Extreme values of LREE depletion are commonly seen in the Bristol Channel Orefield in botryoidally textured ores (see Young & Thomas 1999, Figure 5 and compare Figure 6 of this report).

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | LOI | *total* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAV1 | | | ***36.10*** | ***0.40*** | ***0.62*** | ***7.40*** | | | ***0.32*** | ***3.39*** | | |
| PAV7 | | | ***16.90*** | ***0.34*** | ***0.86*** | ***6.86*** | | | ***0.55*** | ***4.95*** | | |
| PAV4 | 12.10 | 0.24 | 89.24 | 0.02 | 0.04 | 0.10 | < | < | 0.00 | 0.04 | 0.33 | 102.12 |
| PAV5 | | | | ***0.01*** | ***0.02*** | ***0.22*** | | | ***0.01*** | ***0.02*** | | |
| PAV6 | | | | ***0.02*** | ***0.05*** | ***0.12*** | | | ***<*** | ***0.10*** | | |
| PAV8 | | | | ***0.16*** | ***0.14*** | ***0.09*** | | | ***0.00*** | ***0.08*** | | |
| PAV9 | 2.69 | 0.14 | 97.82 | 0.16 | 0.11 | 0.09 | < | 0.01 | 0.00 | 0.06 | 2.00 | 103.07 |
| PAV10 | 1.80 | 0.27 | 93.35 | 0.02 | 0.07 | 4.14 | < | < | 0.00 | 0.04 | 4.62 | 104.31 |
| PAV2 | 33.51 | 8.41 | 4.23 | 33.88* | 0.40 | 0.32 | < | 3.82 | 0.61 | 0.12 | 10.12 | 95.42 |
| PAV3 | 1.09 | 0.42 | 0.41 | 57.18* | 0.38 | 0.63 | < | 1.45 | 0.03 | 0.09 | 10.70 | 72.38 |

*Table 1: major element chemistry of samples from Paviland, in wt%, determined by XRF (values for those in bold italics which are based on ICP-MS analysis).*

*< = below detection.* * = Mn calculated as $MnO_2$.

| | Li | Be | Sc | V | Cr | Cu | Zn | Ga | Ge | As | Rb | Sr | Y | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAV1 | < | < | 9.82 | 70.79 | 43.38 | 20.15 | 202.21 | 6.74 | 25.93 | 273.94 | 41.98 | 186.40 | 18.83 | 78.06 |
| PAV7 | 56.69 | 2.01 | 9.58 | 91.75 | 53.81 | 29.91 | 175.94 | 10.07 | 6.49 | 141.57 | 66.83 | 204.80 | 24.53 | 95.80 |
| PAV4 | < | 5.20 | 0.53 | 348.70 | 146.02 | 7.85 | 158.72 | 3.09 | 121.45 | 1223.00 | 1.06 | 24.69 | 3.45 | 2.43 |
| PAV5 | < | < | < | 38.26 | 148.32 | 3.42 | 40.33 | 1.51 | 102.58 | 332.94 | 1.21 | 15.83 | 1.23 | 2.38 |
| PAV6 | < | 9.21 | 7.60 | 35.71 | 10.25 | 2.66 | 18.12 | 1.85 | 199.01 | 2987.20 | 1.12 | 13.04 | 6.09 | 3.66 |
| PAV8 | 5.73 | 17.35 | 0.74 | 418.43 | 12.87 | 15.73 | 172.48 | 5.12 | 103.99 | 922.85 | 1.85 | 17.90 | 3.86 | 1.12 |
| PAV9 | 10.41 | 8.57 | 1.02 | 423.33 | 131.36 | 2.72 | 198.32 | 2.90 | 243.68 | 1832.50 | 2.17 | 42.12 | 3.00 | 2.42 |
| PAV10 | 5.25 | 9.36 | 0.43 | 475.94 | 132.70 | 2.08 | 127.35 | 2.01 | 263.02 | 1516.83 | 1.50 | 28.40 | 4.03 | 0.99 |
| PAV2 | 164.44 | 4.78 | 35.53 | 14.77 | 23.95 | 140.30 | 594.82 | 11.15 | 1.17 | < | 66.63 | 257.29 | 68.05 | 154.99 |
| PAV3 | < | 6.76 | 2.44 | < | < | 570.91 | 3541.49 | 3.21 | 0.53 | 21.92 | 4.62 | 2996.03 | 109.39 | 2.72 |

| | Nb | Mo | Cd | Cs | Sn | Sb | Ba | Hf | Tl | Pb | Bi | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAV1 | 7.00 | 6.88 | 2.41 | nd | nd | 3.46 | 304.60 | nd | 0.52 | 77.12 | 9.88 | 4.77 | 3.37 |
| PAV7 | 10.17 | 3.87 | 0.89 | 2.11 | 239.97 | 4.96 | 501.34 | 2.98 | 0.60 | 78.32 | 0.82 | 8.76 | 3.12 |
| PAV4 | 1.90 | 37.67 | < | nd | nd | 0.96 | 30.36 | nd | 0.07 | 213.92 | < | 0.14 | 34.86 |
| PAV5 | 6.16 | 15.51 | < | nd | nd | 0.84 | 190.36 | nd | 0.16 | 59.75 | < | 0.43 | 13.82 |
| PAV6 | 0.21 | 19.31 | < | nd | nd | 1.72 | 10.70 | nd | 0.05 | 115.97 | 1.11 | 0.26 | 5.50 |
| PAV8 | 0.65 | 157.85 | 0.97 | 0.20 | 66.62 | 1.69 | 50.44 | 0.25 | 0.09 | 1771.60 | 0.83 | 0.14 | 9.03 |
| PAV9 | 2.94 | 32.42 | 0.20 | 0.24 | 211.63 | 1.49 | 560.44 | 0.33 | 0.09 | 241.07 | 0.09 | 0.27 | 21.17 |
| PAV10 | 1.12 | 41.38 | 0.31 | 0.27 | 207.37 | 1.06 | 19.84 | 0.19 | 0.08 | 230.69 | 0.04 | 0.08 | 30.75 |
| PAV2 | 7.26 | 0.43 | 14.14 | nd | nd | 10.17 | 3310.27 | nd | 1.49 | 0.18 | < | 6.89 | 3.97 |
| PAV3 | < | 1.14 | 49.02 | nd | nd | 0.34 | 14000 | nd | 0.23 | 1966.28 | < | 0.13 | 4.15 |

| | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAV1 | 20.01 | 38.34 | 4.88 | 18.88 | 3.95 | 1.05 | 4.06 | 0.64 | 3.56 | 0.69 | 1.80 | 0.25 | 1.68 | 0.23 |
| PAV7 | 33.12 | 63.02 | 8.20 | 30.27 | 6.00 | 1.19 | 5.51 | 0.78 | 4.53 | 0.84 | 2.27 | 0.31 | 2.18 | 0.31 |
| PAV4 | 1.69 | 1.80 | 0.41 | 1.72 | 0.60 | 0.15 | 0.59 | 0.12 | 0.60 | 0.11 | 0.39 | 0.05 | 0.32 | 0.04 |
| PAV5 | 1.07 | 1.94 | 0.24 | 1.02 | 0.24 | 0.09 | 0.26 | 0.04 | 0.26 | < | < | < | < | < |
| PAV6 | 0.53 | 5.25 | 0.37 | 2.32 | 1.15 | 0.46 | 1.53 | 0.31 | 1.86 | 0.32 | 0.82 | 0.12 | 0.63 | 0.10 |
| PAV8 | 2.02 | 5.09 | 0.46 | 1.88 | 0.53 | 0.15 | 0.60 | 0.11 | 0.65 | 0.13 | 0.39 | 0.05 | 0.30 | 0.04 |
| PAV9 | 2.10 | 2.77 | 0.52 | 1.81 | 0.48 | 0.26 | 0.56 | 0.09 | 0.54 | 0.10 | 0.27 | 0.04 | 0.21 | 0.04 |
| PAV10 | 1.16 | 1.31 | 0.31 | 1.26 | 0.37 | 0.10 | 0.47 | 0.07 | 0.39 | 0.09 | 0.27 | 0.02 | 0.18 | 0.03 |
| PAV2 | 51.13 | 329.16 | 20.11 | 80.47 | 26.32 | 6.86 | 25.05 | 4.08 | 20.86 | 3.69 | 9.21 | 1.23 | 7.78 | 0.98 |
| PAV3 | 5.72 | 11.25 | 3.07 | 19.77 | 6.86 | 4.34 | 10.35 | 1.95 | 13.05 | 3.04 | 8.79 | 1.23 | 7.50 | 1.07 |

*Table 2. Trace element chemistry in ppm, for samples from Paviland, determined by ICP-MS (elements also determined by XRF excluded). < = below detection, nd = not determined.*

## 2.3 Discussion

The specimens are all dominated by haematite, and are mainly characterised by a micro-botryoidal, tending towards a micro-spherulitic, structure (PAV5,9,10). These textures are rather atypical of the major Bristol Channel Orefield ore bodies in Glamorgan and the Forest of Dean. In these areas the ores are generally emplaced within pre-existing karstic porosity and demonstrate a range of textures indicating reaction with the wallrock and subsequent stalactitic growth (e.g. the textures illustrated by Young & Thomas 1998, 1999).

The iron ore deposits of eastern Gower, in contrast, are emplaced in a rather different manner, occurring in veins, associated with calcite. The textures seen in these veins are closely comparable with the specimens from Paviland.

Veins on the foreshore east of Langland Bay (Figure 7 (1)) show complex arborescent, botryoidally-textured protrusions from the wall (sample MUM2: Figure 2a), which bear some similarity with the textures seen in PAV8 and PAV10. Where well-developed these protrusions may mimic the “brush” ores of the Forest of Dean, with individual protrusions up to 5cm in length and 3mm in diameter. The protrusions are not perfectly parallel, but do show a preferred vertical orientation within the steeply dipping vein. There are locally identifiable multiple generations of the protrusions, and the inner parts of the vein may comprise their brecciated fragments. This ore texture is clearly closely related to the stalactitic ores of other sectors of the Bristol Channel Orefield.

The larger vein on Mumbles Head (Figure 7 (4)) shows a variety of iron ore textures, even within the comparatively small area of current exposure in Limeslade Bay. Adjacent to the host rock on the east side of the vein are lenticular pods of a massive, to slightly banded, haematitic ore (samples MUM1, MUM5, MUM6; Figure 2 j-m). This is locally overlain by contorted laminated material, probably partially sediment derived from above, which also occurs locally close to the west wall of the vein. The major thickness of the vein is occupied by thick layers of calcite, comprising elongate crystal splays, in several successive generations, growing inwards approximately 0.5m from each wall. The outer (earliest) regions of this calcite show strong wall-parallel zones of haematite (MUM4; Figure 2 c-i) bearing arborescent growths very similar to those of PAV8. These massive haematite near the wall grades into the overlying zoned calcite/haematite facies through an increase in calcite-filled pores, giving rise to lithologies very close to PAV10 (e.g. MUM6; Figure 2m). The innermost (latest) part of the vein comprises a complex of additional calcite, together with brecciated ferruginous material.

To date, only two samples of the ion ores from eastern Gower have been analysed geochemically (MUM1 and MUM2). These show very similar compositions to the Paviland specimens as described above. The table below (Table 3) gives the composition (in ppm) for the Gower ores and the Paviland specimens for those elements which are particularly important for the provenancing evidence.

| | *V* | *Zn* | *Ge* | *Ba* | *Pb* | *U* |
|---|---|---|---|---|---|---|
| PAV1 | 70.8 | 202.2 | 25.9 | 304.6 | 77.1 | 3.4 |
| PAV7 | 91.8 | 175.9 | 6.5 | 501.6 | 78.3 | 3.1 |
| PAV4 | 348.7 | 158.7 | 121.5 | 30.4 | 213.9 | 34.9 |
| PAV5 | 38.3 | 40.3 | 102.6 | 190.4 | 59.8 | 13.8 |
| PAV6 | 35.7 | 18.1 | 199.0 | 10.7 | 116.0 | 5.5 |
| PAV8 | 418.4 | 172.5 | 104.0 | 50.4 | 1772.0 | 9.0 |
| PAV9 | 423.3 | 198.3 | 243.7 | 560.4 | 241.1 | 21.2 |
| PAV10 | 475.9 | 127.1 | 263.0 | 19.8 | 230.7 | 30.8 |
| MUM1 | 426.9 | 116.5 | 134.2 | 25.3 | 244.7 | 33.2 |
| MUM2 | 46.7 | 115.6 | 86.6 | 36.0 | 213.1 | 19.5 |

*Table 3. Extract from table 2, showing the distribution of a selection of elements closely associated with the provenancing evidence in comparison with samples from Eastern Gower.*

Samples PAV4, PAV10 and MUM1 (Limeslade Bay) show a particularly close correlation, within a subgroup characterised by high V and U. When all trace elements are considered PAV9 and PAV6 also show a good correlation with this group. PAV5 and 6 share some features (e.g. high Ge) with the other samples, but differ in having low V, low Zn and (together with PAV8) low U.

## *3. Description of the Ochres*

### 3.1 Petrography

The term ochre is used here for a fine grained material dominated by iron oxides. Buckland used the term reddle for the same material. Both terms carry the implication of a material capable of being employed as a pigment. Two samples of ochre were examined. PAV7 was closely associated with bone, had a pinkish colour and was very fine grained, in contrast sample PAV1 was a brown, slightly concretionary soil of uncertain provenance.

### 3.2 Geochemistry

The major element chemistry of the ochres was not determinable by XRF because of the small sample sizes. Some of the elements normally determined by XRF are also determined by ICP-MS, so these latter values are displayed in table 1. The most significant aspect of these data is the high phosphate content. The levels correspond to a content of an apatite of 8-10% in PAV1 and 12-14% in PAV7. The iron contents were determined as 36.1% and 16.9% expressed as wt% $Fe_2O_3$. The two ochre samples are rather similar in terms of trace element distribution, with the majority of trace elements (including the REE) 1.2-1.8 times more concentrated in PAV7 than PAV1, suggesting a higher clay content. In contrast, calcium, uranium, zinc and manganese were 1.1-1.2 times more concentrated in PAV1 than PAV7, and several metals (Mo, As, Cd, Ge, Bi) were 1.8-12.1 times more concentrated in PAV1 than PAV7. Fe was 2.1 times more concentrated in PAV1.

The upper crust-normalised REE profiles are relatively flat and close to upper crustal average ($\Sigma$REE is at 68% of average upper crust for PAV1 and 108% for PAV7). The profiles are very slightly humped ($Dy_N/Lu_N$ = 1.39, 1.33; $Gd_N/La_N$ = 1.6, 1.31 for PAV1 and PAV7 respectively), with small negative Ce anomalies (Ce/Ce* = 0.88, 0.87 for PAV1 and PAV7 respectively).

The general distribution of the trace elements reflects the more clay-rich nature of PAV7, resulting in enhanced REE and Th concentrations. PAV1 in contrast has lower REE and Th concentrations than typical, for instance, in boulder clay fines elsewhere in S Wales (pers. obs. of samples from Llantrisant and St Fagans). Both ochre samples show enhanced concentrations of metals (As, Mo, Ge, Mn, Cd, Pb, Zn, V, U; in decreasing order of relative enrichment in the Paviland ochres) associated with mineralisation compared with the boulder clays.

### 3.3 Discussion

Unfortunately, since there is no surviving sediment from the appropriate horizon in the cave which is not enriched in iron oxides and phosphate minerals, a sophisticated and rigorous treatment of the mixing of the iron oxides with the host sediment is not possible. The contribution to the cave sediments of metals derived from the intrinsic karstic dissolution of the host limestone in the cave, remains, therefore, unknown. Examination of undisturbed sediments in similar contexts in other caves in the vicinity might provide a course for future investigation. However, if the cave sediments are assumed to have been similar to the fine-grained matrix of the boulder clay of the Vale of Glamorgan, for which a few detailed analyses exist, then a simple mixing model can be constructed. The analytical data suggest that PAV1 can be modelled, rather a crudely, as a mixture of approximately 36% ochre, 9% apatite and 55% detrital minerals, whereas PAV7 comprises 17% ochre, 13% apatite and 70% detrital minerals. Elements associated with the ochre phase are thus more concentrated in PAV1, whereas those associated with the detrital material (especially clay) are more concentrated in PAV7.

Simplistic modelling of this type contains many assumptions, including element immobility during diagenesis. However, it is possible to examine the elements which were important in provenancing the lump iron ores and to calculate tentative compositions. This calculation assumes that the phosphatic phase contains introduced calcium phosphate free from these trace elements. In practice the remobilised phosphate may well contain small proportions of these elements and these estimates given here are accordingly maximum concentrations for ochre mixed with boulder clay. The calculation is presented in Table 4, and the modelled ochre compositions are included in Figure 4. In all cases (except Ti in PAV1) the model compositions plot close to the composition of the lump ore specimens from Paviland. The Pb, V, and As all fall within the range of that determined for the lump ores; Zn and Cd are slightly higher, Ge is slightly lower.

| | Ti | V | Cu | Zn | Ge | Cd | As | Pb | U |
|---|---|---|---|---|---|---|---|---|---|
| **PAV1** | | | | | | | | | |
| *sediment* | 4146 | 61.51 | 14.3 | 110.2 | 1.83 | 0.39 | 12.31 | 34.4 | 2.69 |
| *55% sediment* | 2281 | 33.8 | 7.9 | 60.6 | 1.0 | 0.22 | 6.8 | 18.9 | 1.5 |
| *ochre* | 1927 | 70.8 | 20.2 | 202.2 | 25.9 | 2.41 | 273.9 | 77.1 | 3.4 |
| *difference* | negative | 37.0 | 12.3 | 141.6 | 24.9 | 2.19 | 267.1 | 58.2 | 1.9 |
| *=36% of ore of composition:* | **negative** | **102.8** | **34** | **393** | **69.2** | **6.1** | **742** | **162** | **5.3** |
| **PAV7** | | | | | | | | | |
| *sediment* | 4146 | 61.51 | 14.34 | 110.2 | 1.83 | 0.39 | 12.3 | 34.4 | 2.69 |
| *70% sediment* | 2902 | 43.1 | 10.0 | 77.1 | 1.3 | 0.27 | 8.6 | 24.1 | 1.9 |
| *ochre* | 3290 | 91.8 | 29.9 | 175.9 | 6.5 | 0.89 | 141.6 | 78.3 | 3.1 |
| *difference* | 388 | 48.7 | 19.9 | 98.8 | 5.2 | 0.62 | 133 | 54.2 | 1.2 |
| *=17% of ore of composition:* | **2280** | **286.5** | **117** | **581** | **30.6** | **3.6** | **782** | **319** | **7.1** |

*Table 4. Simplistic calculation of concentration in ochre of Ti, V, Cu, Zn, Ge, Cd, As, Pb and U in ppm, assuming a simple mixture between the ochre and a sediment. The sediment concentrations are the average of three analyses of boulder clay from the Vale of Glamorgan. The resulting models for the ochre composition are shown on Figure 4.*

Despite the errors inherent in the approach, these model compositions permit the tentative conclusion that the ochre is derived from the same, or similar, sources to the lump ores.

The chemical basis for the pigmented layers coating the skeletal remains is problematic, since both the ochre (interpreted to be the source of the iron) and the coatings are red/brown, implying that the iron is in the ferric state. Ferric iron is relatively immobile (unlike reduced, ferrous, iron) and yet the hard pigmented crust suggests the pigment is held by diagenetic mineral phases. The slightly indurated nature of both samples may be related to the development of phosphate minerals. At Pontnewydd, Jenkins (1997) implicated an iron calcium phosphate (possibly calcioferrite) as the major component of red-brown cutans in the pigmented “Intermediate Beds”, which he associated with redistribution of bone phosphate from higher in the stratigraphic section. In the Paviland material, the phosphate phase present is uncertain, but the relative proportions of Ca and P present in the analyses of the ochres are consistent with the phosphate being present as a calcium phosphate (an apatite). It is possible that the iron in this case plays a more passive role in the development of the pigmentation. The source of the phosphate is uncertain, but might be associated with the reworking of phosphate from dissolution of bones or faecal material. Preferential precipitation of the phosphate around and adjacent to bones might be likely, even if the bones were not the immediate source of the phosphate. The role of phosphate in the generation of the characteristic pigmentation of the “Red Lady” might be worthy of further investigation. The implication of a role for phosphate in the generation of the indurated ochres, together with the macroscopic evidence for biological activity in the ochre, suggests an area for the future investigation of ochre-covered skeletal remains.

## *4. Description of the manganese ore and wad*

### 4.1 Petrography

Two specimens of manganese-rich material were examined. One, PAV2, was a specimen from the OUM collection labelled “psilomelane”, and probably from the 19th century excavations. The other, PAV3, was from a poorly provenanced collection of lithological samples in the OUM, and was a large block of dense manganese ore.

Sample PAV2 proved to be a specimen of wad. It comprises a sediment with a silt to fine sand grade, consisting of quartz, feldspar and mica grains, cemented by manganese minerals with a laminar texture (Figure 8 a,b). The specimen still has original matrix adhering to an embay portion. This matrix comprises an iron-rich sediment, supporting the provenance of this ore to the ochre-rich deposits enclosing the “Red Lady”.

PAV3 had a complex texture, involving regions of crystals, frequently euhedral, and typically approximately 20-40µm in length (Figure 8 c-h). These crystals show alteration, with a material of lower backscatter coefficient, apparently replacing a material of higher coefficient, although it is possible both phases represent replacement of the original material (Figure 8 f,h). The crystals show a relict cleavage parallel to their length. The material with the higher backscatter coefficient (interpreted as being earlier) has composition of relatively pure manganese oxide, which gives microanalytical totals close to 100% if it is modelled as an oxide with an overall Mn oxidation state of 3, or as a hydrated oxide (cf. rancieite). The material with the lower backscatter coefficient is rich in silica, and has a composition close to, but slightly less siliceous than, braunite, with Mn:Si of approximately 8. Regions comprising these two phases are abruptly overlain by a zone of very high backscatter coefficient, upon which an acicular phase with lower coefficient has nucleated (Figure 8 h). The material with a high backscatter coefficient has not been positively identified but has Mn:Pb of 6 (i.e. is close to coronadite, which has Mn:Pb =8) and, for most analyses Mn:S of 11. It also bears appreciable vanadium (0.8 wt% oxide). The acicular phase has a composition equivalent to cryptomelane. The basal parts of the needles with a high coefficient are Ba-rich varieties, the distal parts with lower coefficient are K-rich.

| *Spot No.* | **Al** | **Si** | **Mn** | **Ti** | **Mg** | **Ca** | **K** | **S** | **V** | **Ba** | **Cu** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ***cf. Coronadite*** | | | | | | | | | | | | | |
| *10* | 0.22 | | 41.92 | | | | | 2.95 | 0.35 | 0.62 | | 25.99 | |
| *32* | | | 42.25 | | | 0.12 | | 2.94 | 0.35 | 1.36 | | 26.88 | |
| *11* | 0.28 | | 43.35 | | | 0.15 | | 0.15 | 0.29 | 1.12 | | 24.46 | |
| *1* | 0.32 | | 43.97 | | 0.27 | 0.10 | | 2.61 | 0.32 | 0.92 | | 25.91 | |
| ***Cryptomelane*** | | | | | | | | | | | | | |
| *22* | 0.22 | 0.20 | 46.42 | 0.30 | | 0.15 | 0.29 | 0.32 | | 12.25 | | 3.38 | 0.52 |
| *7* | 0.32 | 0.12 | 47.16 | | | 0.16 | 0.87 | 0.38 | | 10.92 | | 4.97 | |
| *26* | 0.24 | | 48.30 | | 0.66 | 0.75 | 0.93 | 0.31 | | 3.02 | | | 0.57 |
| *16* | 0.58 | | 48.35 | | 0.44 | 0.81 | 1.01 | 0.23 | | 2.29 | | 3.47 | 0.62 |
| *24* | | | 53.87 | | | 0.37 | 4.34 | 0.13 | | 1.93 | 0.26 | | 0.40 |
| *29* | 0.85 | | 55.09 | | | 0.14 | 4.44 | 0.10 | | 1.43 | | | 0.35 |
| *8* | | | 55.99 | | | 0.17 | 5.25 | | | 0.93 | 0.35 | | |
| ***cf Braunite*** | | | | | | | | | | | | | |
| *13* | 0.28 | 3.61 | 58.28 | | | 0.63 | 0.51 | | | 0.91 | 0.31 | | |
| *6* | | 3.82 | 58.97 | | | 0.61 | 0.26 | | | 0.32 | | | |
| *3* | | 3.88 | 59.40 | | | 0.66 | 0.08 | 0.11 | | | 0.41 | 0.51 | 1.99 |
| ***Hydrated oxide*** | | | | | | | | | | | | | |
| *14* | | | 65.49 | | | | | 0.44 | | | | 5.72 | |
| *4* | | | 65.51 | | | | | 0.39 | | | | 4.65 | 0.40 |
| *18* | | | 69.57 | | | | | | | 0.36 | | | 0.36 |
| *19* | | 0.12 | 70.04 | | | | | | | | | | |

*Table 5. Representative EDS microanalyses from sample PAV3. Data are wt% element.*

The acicular, probable cryptomelane, phase may be alone in some areas, but generally the zone with the needles contains large (up to 200µm) dispersed rhombic crystals (again probably a hydrate oxide), which also predates the acicular phase and are often extremely altered (to the braunite-like phase), or replaced by secondary porosity (Figure 8 i).

Some regions of the specimen show a complex later history involving botryoidally-textured zones (Figure 8 j), with intimate mixtures of various phases, often showing a fine-grained replacement texture (Figure 8 k,l). The fine-grained replacements are dominated by the possible cryptomelane phase.

The specimen shows ample evidence for strong supergene alteration of the primary ore material. The relict textures of rhombic, cleaved, crystals are suggestive of a primary rhodocrosite mineralogy for much of the specimen.

## 5.2 Geochemistry

The major elemental determination by XRF was problematic for both PAV2 and PAV3 (as well as for the comparative material), having totals of 89.2% and 61.9% respectively when calculated using $Mn^{II}$. Recalculating using $Mn^{IV}$ (which is probably a valid assumption) raises the totals to 95.42% and 72.38% respectively. These results are still very poor, but improvement would require purchase of new high Mn analytical standards. They mean that the major element data can only be employed in a semi-quantitive manner. The trace element data from ICP-MS are not affected by this problem. Comparison of data for Fe, Mg, Ca, Ti, P where they have been determined by both ICP-MS and XRF shows a good correlation (Figure 9), implying that the XRF determinations for Mn probably contain most of the error (since Mn is present in only minor amounts in most geological materials the equipment is only calibrated over a range of correspondingly low values).

The geochemistry of PAV2 shows the influence of the diverse assemblage of detrital minerals present. The loss on ignition is high, suggesting that the manganese is present in a hydrated phase. Some trace metals (notably As, Ba, Pb) are present in much lower concentrations in PAV2 than in the PAV3 and the comparative material from Ty Coch, whereas others (Cu, Zn) are present in similar concentrations (see table 6). PAV2 has a very elevated concentration of REE ($\Sigma$REE = 586.9ppm, $\Sigma$REE excluding Eu = 580.1ppm). The upper crust-normalised profile (Figure 10) is gently humped ($Dy_N/Lu_N = 1.95$; $Gd_N/La_N = 3.87$). There is a marked positive Ce anomaly ($Ce/Ce^* = 2.34$).

PAV3 has a major element chemistry dominated by manganese. The loss on ignition is high, suggesting much of the manganese is present in hydrated mineral phases. The trace element chemistry shows elevated levels of Cu, Zn, Ba and Pb. PAV3 has a $\Sigma$REE value (Eu excluded because of interference with Ba) which is fairly low, at 64% of upper crust average. The upper crust-normalised REE profile (Figure 10) is elevated, with $Er_N$ highest at 3.82, but with depletion of the elements lighter than Er ($Dy_N/Lu_N = 1.12$; $Er_N/La_N = 20.04$; $Gd_N/La_N = 14.28$). Superimposed on the depletion of the LREE is a slight negative Ce anomaly ($Ce/Ce^* = 0.61$).

## 5.3 Discussion

The textures exhibited by sample PAV3 are very similar to those of ore specimens from Ty Coch, near Porthcawl. This former mine is the only significant manganese mineralisation in S Wales, and therefore must be considered as a potential source for manganese ores from Paviland. However, despite the overall similarity in texture, there are some significant differences in detail, and some major differences in geochemistry.

The denser ores (TC1, TC2) from Ty Coch share with PAV3 a texture comprising compact zones of rhombic crystals, which have abrupt junctions (at which there is Pb, Ba, V enrichment) with zones of less dense fibrous material, bearing isolated rhombs, pseudomorphed by material of low backscatter coefficient (Figure 11). As with PAV3 the specimens also bear zones where the fine-grained materials have a botryoidal morphology, with laminae picked-out by elevated Ba content. One subtle difference is that in the Ty Coch specimens the Pb/V enrichment occurs within the outermost rhombs of the compact zone (Figure 11 d); in PAV3 the enrichment occurs as a growth upon those rhombs. A further important mineralogical difference is that the Ty Coch ores examined so far, do not appear to contain the K-rich cryptomelane(?), so characteristic of PAV3. The Ty Coch samples also show a low loss on ignition, suggesting that the manganese minerals are less hydrated than in PAV3, or that the hydrated minerals are balanced by a significant proportion of minerals bearing $Mn^{II}$.

The geochemistry of the specimens examined so far from Ty Coch also appears markedly different from PAV3. The samples suffer from the same poor analytical total for major elements determined by XRF as the PAV3 specimen. The increased silica and very low potassium of the Ty Coch ores is reflected not only by the lack of the K-rich cryptomelane, but also by an increased significance for the braunite-like mineral.

The barium contents of the four Ty Coch specimens are 1.8, 2.0, 2.4 and 2.9%; all higher than the 1.4% of PAV3. PAV3 is much richer in Zn, Rb, Sr, Y and Pb than the Ty Coch specimens. The upper crust-normalised REE profiles of the Ty Coch material are very different from the Paviland specimen. The $\Sigma$REE values are low (41-62% of upper crust average, Eu excluded) and their profiles (Figure 10) are gently humped ($Dy_N/Lu_N = 1.43 – 1.66$; $Gd_N/La_N = 1.09 – 1.56$), with a negative Ce anomaly ($Ce/Ce^* = 0.42 – 0.70$).

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $MnO_2$ | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | LOI | *total* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAV2 | 33.51 | 8.41 | 4.23 | 33.88 | 0.40 | 0.32 | < | 3.82 | 0.61 | 0.12 | 10.12 | 95.42 |
| PAV3 | 1.09 | 0.42 | 0.41 | 57.18 | 0.38 | 0.63 | < | 1.45 | 0.03 | 0.09 | 10.70 | 72.38 |
| TC1 | 9.33 | 1.60 | 0.91 | 60.10 | 1.78 | 1.25 | < | < | 0.19 | 0.05 | 4.12 | 79.33 |
| TC2 | 6.98 | 2.21 | 1.00 | 62.01 | 2.17 | 1.89 | < | 0.18 | 0.14 | 0.06 | 2.79 | 79.43 |
| TC3 | 8.10 | 2.43 | 0.93 | 44.01 | 2.91 | 9.07 | < | 0.05 | 0.17 | 0.09 | 16.98 | 84.75 |

*Table 6. Major element chemistry of Mn ores from Paviland compared with those from Ty Coch. Analyses by XRF quoted in wt%. Low totals probably represent poor calibration at high Mn concentrations. < = below detection*

| | Cu | Zn | As | Ba | Pb |
|---|---|---|---|---|---|
| PAV2 | 140.3 | 594.8 | < | 3310 | 0.2 |
| PAV3 | 570.9 | 3541.5 | 21.9 | 14000 | 1966.3 |
| TC1 | 938.6 | 365.7 | 13.5 | 24400 | 329.3 |
| TC2 | 272.7 | 749.6 | 6.0 | 20060 | > |
| TC3 | 1016.3 | 415.1 | 10.6 | 18030 | 1549.4 |
| TC4 | 425.4 | 2367.7 | 9.1 | 28820 | 1170.1 |

*Table 7. Selected ICP-MS analyses of minor and trace metals from manganese ores from Paviland and comparative samples from Ty Coch. Values in ppm. < = below detection, > = above detection.*

## 6. Conclusions

The iron ores from Paviland show compelling evidence for derivation from a source close to Paviland, and the major vein cutting Mumbles Head is compatible with the available petrographic and geochemical evidence. There is sufficient variability in the mineralisation present within this vein to encompass the variation in the samples from Paviland.

The ochres probably represent a dilute mixture of iron ore with the cave sediment. The ochreous sediment has a composition indicating an admixture of about 35% ochre. In the absence of preserved sediment unaffected by this mixing, certain determination of the ore composition cannot be made, but modelling of the composition by assuming mixing with a sediment of similar trace element composition to a Vale of Glamorgan boulder clay provides model compositions with trace element concentrations close to those of the lump ore specimens. The form of the ochre has not been determined. Natural ochres are known from the Vale of Glamorgan orebodies (Young & Thomas 1998, 1999), and these are interpreted as mainly fine-grained iron oxides released through dissolution of mineralised limestone. No unconsolidated ochres are yet known from Gower, although they may exist. Artificial iron oxide powders produced through crushing the lump ores would be easy to manufacture, for many of the Gower ores (e.g. the massive ore close to the wall of the vein in Limeslade Bay) are particularly soft. The indurated red/brown coating on the bones of the “Red Lady” and other materials is interpreted as having been produced through the precipitation of phosphate minerals during diagenesis.

The manganese ores are much more problematic. The material closely tied to the 19th century excavations is manganese wad, and there are no existing comparative data to permit provenancing. Macroscopically similar material does occur widely as concretionary matter in superficial sediments, particularly in upland areas, but an origin as supergene material associated with a specific manganese ore deposit cannot be ruled out. The unprovenanced manganese lump ore specimen shows textural similarity with the Ty Coch (Porthcawl) manganese ore, but there are striking mineralogical and geochemical differences. Either this specimen derives from a part of the Ty Coch orebody which had a different history of supergene oxidation from the parts of the orebody represented by material surviving on the dump of the former mine, or the textural similarity may be coincidental and the sample derives from a orebody elsewhere (for instance in North Wales). The latter interpretation is favoured, making transport to Gower by ice a likely derivation.

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**Figure 1. Petrography of iron ore specimens from Paviland. All images are backscattered electron photomicrographs, except (k) which is a secondary electron photomicrograph.**

(a) PAV4 (OUM S5103). Botryoidal haematite (white) overlain by quartz (grey). Scale bar 200µm.

(b) - (c) PAV5 (OUM *haematite/limonite*).
(b) low magnification view showing replacement texture with haematite (white) and quartz (pale grey). The quartz bears small inclusions (interpreted as relicts) of manganese-bearing calcite (dark grey). Scale bar 1mm.
(c) detail of void space within haematite (void dark) with haematite display a microbotryoidal or spherulitic structure. The haematite (white) is overgrown by quartz (grey). Scale bar 200µm.

(d) - (h) PAV8 (NMGW)
(d) low magnification view of arborescent structures, commonly with hollow cores surrounded by dense haematite (white), overlain by a phase with a lower back-scatter coefficient, probably goethite (pale grey). Scale bar 2mm.
(e) detail of core of structure to left of centre of (d). The hollow core can be seen to have a concentric structure with porosity generated by dissolution of a phase with a platy form. Scale bar 500µm.
(f) arborescent structures of haematite (white) overlain by ?goethite with a tabular morphology (grey). Dark areas porosity. Scale bar 2mm.
(g) detail showing ?goethite growing into pore space, below centre (f). Scale bar 200µm.
(h) larger scale botryoidal texture in iron oxides. Scale bar 1mm.

(i) – (l) PAV9 (NMGW)
(i) microbotryoidal/spherulitic structure in haematite. Scale bar 1mm.
(j) highly etched quartz cement partially filling pore space. Microbotryoidal texture of haematite visible on pore wall. Scale bar 200µm.
(k) microbotryoidal/spherulitic structure in haematite with tabular crystal terminations visible on walls of porosity. Scale bar 50µm.
(l) detail showing crystal terminations within porosity. Scale bar 20µm.

(m) – (p) PAV10 (NMGW)
(m) Complex botryoidal texture in haematite (white). Porosity filled by calcite (grey). Scale bar 1mm.
(n) Complex botryoidal texture in haematite (white) forming elongate structures. Porosity filled by calcite (grey). Scale bar 2mm.
(o) Complex botryoidal texture in haematite (white), with porosity filled by calcite (grey). Calcite shows dissolution. Scale bar 500µm.
(p) Complex botryoidal texture in haematite (white), with porosity filled by calcite (grey). Calcite shows dissolution. Scale bar 500µm.

**Figure 2. Petrography of comparative iron ore specimens from eastern Gower. All images are backscattered electron photomicrographs.**

(a) – (b) MUM2 (Langland Bay)
(a) stalactite-like protrusions from wall of vein, formed of internally complex botryoidal haematite (white). Porosity filled with calcite (grey). Scale bar 2mm.
(b) detail of botryoidal surface of protrusion, showing zone of small haematite crystals within calcite. Both protrusion and early calcite are truncated (upper left) by calcite veining.

(c) – (i) MUM4 (Limeslade Bay). Zone of haematite banding in calcite vein fill. Very complex succession of mineral replacement involving dolomite, calcite, quartz and haematite.
(c) haematite (very pale grey) overgrowing pointed crystal terminations of early carbonate minerals. This early crystals are now replaced by quartz (pale grey, centre right) and calcite (dark grey). Bright spots in calcite left top are baryte crystals. Scale bar 200µm.
(d) complex replaced carbonate vein, with outlines of early carbonate crystals preserved by haematite rims. Scale bar 2mm.
(e) detail from upper left centre of (d) showing outlines of former carbonate crystals preserved by haematite (white). Replacement of original carbonate mineral includes calcite, dolomite and quartz (all dark grey). Scale bar 200µm.
(f) detail from right centre of (d) showing calcite relict (mid grey lower left centre) rimmed by haematite (white). Central part of view comprises quartz (dark grey) bearing baryte. Lower left and upper right, dolomite is the main phase (dark grey), with calcite on grain boundaries (pale grey). In the upper right a thin haematite layer picks out former carbonate mineral morphology. Scale bar 200µm.
(g) broader area view showing alternating laminae of carbonate crystals and haematite, The original carbonate phase is replaced by a mixture of calcite, dolomite and quartz. Scale bar 2mm.
(h) detail from right centre of (g). Original carbonate material largely replaced by dolomite (dark grey) with calcite (pale grey) on grain boundaries. Grain centre left is quartz (dark grey) with baryte inclusions (white). Haematite lamina (white) shows a variety of morphology, including microbotryoidal protrusions into the vein (lower centre). Scale bar 500µm.
(i) complex area of alternating calcite (pale grey) and haematite (white) fringing cements over early carbonate spar. These alternating fringing cements are relatively well preserved, in contrast to both the post-haematite calcite cements and the earlier spar, which have both been dolomitised. The dolomite forms veins cross-cutting the fringing cements (lower left). Scale bar 2mm.

(j) – (l) MUM5 (Limeslade Bay).
(j) coarse dolomitic (dark grey) wall rock, showing extensive de-dolomitisation, cut by veins of calcite (mid grey). Left of centre the veining shows fringing cements of calcite and haematite. Scale bar 2mm.
(k) detail from left of centre of (j) showing fringing cements of calcite and haematite coating dolomite rhombs. Later calcite in the vein truncates the haematite-rich calcite. Scale bar 200µm.
(l) iron ore in contact with the wall rock is a haematite with a microbotryoidal texture. Porosity (top) filled with calcite.

(m) MUM6 (Limeslade Bay)
Microbotryoidally –textured haematite. Porosity filled with complexly intergrown calcite (pale grey) and dolomite (mid grey). Scale bar 500µm.

**Figure 3. Map of the major ore facies of the Bristol Channel Orefield, showing localities mentioned in the text (*after* Young & Thomas 1999, Figure 1).**

**Figure 4. Binary geochemical variation diagrams of trace metals in the iron ores from Paviland, compared with samples from the Bristol Channel Orefield.**

**Figure 5. Upper crust normalised (Taylor & McLennan 1981) rare earth element profiles for samples of iron ore and ochre from Paviland, together with samples of iron ore from eastern Gower.**

**Figure 6. Plot of $Gd_N/Lu_N$ (HREE depletion compared with upper crust) against $Gd_N/La_N$ (LREE depletion compared with upper crust), for samples of iron ore from Paviland (numbered) and a sample from eastern Gower (MUM1). The fields of analyses from other parts of the Bristol Channel Orefield are after Young & Thomas (1999, Figure 5), with amendments and additional data. Normalisation after Taylor & McLennan, 1981.**

**Figure 7. Map of the Mumbles Head area, showing the locations of faults (heavy lines) and localities where the faults are mineralised (shown by stars, details listed). In set shows the relationship of the area to Paviland and the late Devensian ice front.**

**Figure 8. Petrography of manganese ores from Paviland. All images are backscattered electron photomicrographs.**

(a) – (b) PAV2 (OUM *psilomelane*) Laminar manganese minerals form a cement to a silty sediment.

(c) – (m) PAV3 (OUM lithological collection) Dense manganese ore.
(c) – (f) region in which zone characterised by a spherulitic-like texture of equant to elongate crystals up to 60µm across, comprising phases with compositions close to braunite (darker) and rancieite (brighter), is overlain abruptly by a zone with highly altered equant crystals (dark) in a fine-grained groundmass (bright; probably dominantly cryptomelane).

(c) general view of area. Scale bar 500µm.
(d) detail of left centre of (c). Scale bar 200µm.
(e) detail of boundary between zones, just below centre of (c). Scale bar 100µm.
(f) detail from lower right of (d). Scale bar 50µm.

(g) – (i) region in which spherulitic like texture of equant crystals (dominantly with a composition close to rancieite) is coated both internally and externally by a thin layer of Pb-rich material (close to coronadite in composition) upon which is fine-grained cryptomelane. Externally to the spheroids, the cryptomelane rich zone becomes rich in elongate crystals replaced by the rancieite- and braunite-like phases.

(g) general view of area. Scale bar 200µm.
(h) detail of the abrupt passage into the cryptomelane layer, with the cf. coronadite at the base of the cryptomelane needles.
(i) the altered elongate crystals within the cryptomelane-rich layer.

(j) –(m) region of botryoidal texture, in which replacement of large crystals by fine-grained materials is well demonstrated. In the central part of the area the ghosts of crystals of up to 200µm can be seen within a layer of fine cryptomelane (apparently picked out by varying Ba content). This layer is terminated by a zone of the highly altered crystals seen elsewhere), which in this case appears to be a K-rich cryptomelane. A thin cf. coronadite layer underlies a zone of cryptomelane, which is in turn overlain by a zone of cryptomelane bearing relicts of elongate crystals.

(j) general view of area. Scale bar 200µm.
(k) detail of area upper left of centre of (j). Scale bar 100µm.
(l) detail of cryptomelane needles in area in centre of (k). Scale bar 50µm.
(m) detail of rancieite(?) replaced relicts in cryptomelane, left of centre of (k). Scale bar 50µm.

**Figure 9. Plot of MgO, CaO, $TiO_2$ and $P_2O_5$ in wt% as determined by ICP-MS against the determination by XRF. The good correlation suggests the poor totals in the XRF analyses can be attributed to poor calibration of manganese at high concentrations, and that the error lies within the manganese determination.**

**Figure 10. Upper crust normalised (Taylor & McLennan 1981) rare earth element profiles for samples of manganese ore from Paviland, together with samples of manganese ore from Ty Coch, near Porthcawl.**

**Figure 11. Petrography of manganese ores from Ty Coch. All images are backscattered electron photomicrographs. All images are from sample TC2 which most closely approaches the textures seen in PAV3.**

(a) montage showing a zone of altered crystals showing cleavage and up to 80µm across (compare Figure 8 f.h), which also contains voids up to 100µm across (left of centre), with a similar zone right of centre. The margins of these zones are marked by areas of bright tones, representing elevated levels of Pb, V and locally Ba (compare Figure 8 g,h,l,m). Between the two coarse-grained zones lies a vein of very fine grained material with some residual pore space in its centre. Scale bar 100µm.

(b) montage showing detail from upper left of (a). The pore space can be seen to be fringed with acicular crystals, overlying highly altered equant euhedral forms (compare Figure 8 e,j,k,l). Scale bar 20µm.

(c) zone of large equant crystals, with the surface of the zone enriched in Pb, V, Ba. Scale bar 200µm.

(d) detail from centre of (c). Scale bar 50µm.

(e) area in which the equant phase forms a vein-like feature, with a porous core, within the darker, finer phase. Scale bar 500µm.

(f) detail from right centre of (e)