

Mineralization at Tŷ Coch, Glamorgan (Mid Glamorgan), Wales: the second occurrence of pyrobelonite

A. J. CRIDDLE AND R. F. SYMES B.M.(N.H.)

SUMMARY. The second occurrence of pyrobelonite, $\text{MnPb}(\text{VO}_4)(\text{OH})$, first recorded at Långban, Sweden, is reported. It was found with other manganese and iron minerals at the site of an abandoned 19th-century manganese mine at Tŷ Coch near South Cornelly, Mid Glamorgan, Wales. Reflectance values for pyrobelonite from Tŷ Coch, topotype material from Långban, and for two of the minerals associated with pyrobelonite at Tŷ Coch, vanadinite and hausmannite, are given. Electron-probe analyses of pyrobelonite from both localities give results that are in good agreement with its theoretical composition but disagree with the only previous published analysis.

THE Tŷ Coch pyrobelonite was found during the course of a reflected light study of the manganese and iron ores collected from some small spoil tips at the site of an abandoned and infilled 19th-century manganese mine. A more complete description of the mineralogy of these ore minerals, and of the deposit, is given in Criddle (in press). Watson (1859) provided the only geological record of the deposit: it consisted of an interbedded sequence (sandwich) of 3 ft of 'hematite' (basal), 4 ft of manganese ore, and 1 ft of 'hematite' resting conformably on Carboniferous Limestone and overlain by 6 ft of Keuper conglomerate, all dipping to the south against the prevailing northerly dip of the Limestone. The lateral extent of the deposit was not recorded. From the small size of the spoil tips, from Vivian's (1884, p. 170) comment on the lack of information 'as to the working, or cause of failure', and from Howard's (1893, p. 48) statement that the mine '. . . seems to have disappeared', it can be inferred that the mine was small and not worked for long. Tŷ Coch, or, as it was called by Watson, Gwaer Coch, was the only mine worked for manganese in the south Glamorgan iron-ore field (Gayer and Criddle, 1969). Manganese minerals were found 14 miles E. of Tŷ Coch at one of the major 19th-century iron-ore mines, Trecastell (Vivian, 1884 and 1887), otherwise they have not been found in any abundance in Glamorgan (North, 1917; Sibly and Lloyd, 1927).

The geology of the area was described by Strahan and Cantrill (1904). George (1933) in his detailed stratigraphical study of the area states that the Tŷ Coch limestones are in the S_2 zone of the Carboniferous Limestone, slightly east of the dextral shear of the N by NNW trending, post Triassic, Tŷ Coch fault.

Mineralogy. Watson recorded that the 'massive grey' manganese ore consisted chiefly of psilomelane with minor pyrolusite, carbonates, and quartz and that the 'hematite' was quartz free. North, who did not note the presence of spoil tips at the mine site, found 'manganese ore' and a soft and earthy variety of 'hematite' in a wall near the farmhouse. The drystone walls in the immediate vicinity of the farm house still contain a varied assemblage of ore minerals. However, we were able to collect a more representative suite of ore and gangue minerals from the spoil tips and fields at the farm.

Accepting that these are unlikely to be fully representative of the original mine rocks, and that spatial interpretations are prohibited by lack of exposure, the following five descriptions of the commonest hand specimens and their petrography provide a limited, if incomplete, paragenetic context for the Tŷ Coch pyrobelonite:

A massive, fine grained, compact, very hard, dark grey manganese ore with abundant lenticular masses of varicoloured calcite and baryte (B.M. 1974, 155–158). In some of these specimens strongly sheared, polished, and slickensided surfaces were found. Fibrous (asbestiform) white and grey palygorskite, B.M. 1974, 159 (see addendum), coated many of the shear surfaces. The mineral assemblage consists of equal amounts of euhedral to subhedral braunite and hausmannite with interstitial and vug-filling calcite, manganocalcite, ferroan calcite, dolomite, and baryte; discrete euhedral to anhedral pyrobelonite and vanadinite grains and intergrowths of these phases are minor constituents. Pyrobelonite also occurs as veinlets that are usually less than 0.5 mm thick and can be traced for up to 3 cm. In hand specimens the Tÿ Coch pyrobelonite is identifiable by its adamantine to submetallic lustre, its black to deep red colour and its bright orange powder. Vanadinite associated with pyrobelonite is a pale lemon yellow. Both are brittle and without detectable cleavage.

Interlayered, vuggy, romanèchite and goethite with pure white fibrous calcite lining the cavities, fractured and transected by veins of the same phases (B.M. 1975, 528 and 529). Romanèchite and goethite occur as botryofoms and as compound crystallites. In addition, euhedral crystal clusters of hausmannite occupy layers between the major phases that are otherwise filled with brown calcite. Two optically different phases gave identical romanèchite patterns by X-ray powder photography, and were analysed qualitatively by electron probe. One, barrel-shaped, yellowish and idiomorphic, contained only manganese and may be assumed to be a manganese oxide or hydroxide. The other, much higher reflecting, white cavity-filling mineral, contained Pb in addition to Mn and Ba. The parageneses of the above two groups are consistent with multi-stage cavity deposition from solution and from a colloidal gel.

Massive, wad and psilomelane, infilling cavities and replacing limestone (B.M. 1975, 531). The soft and hard colloform and botryofom layers are amorphous to X-rays. White and varicoloured calcite completely and partially infills lenticles. The other phase present is vanadinite—grey, with a greasy lustre in hand specimen. It occupies cavities up to 5 mm in size in the psilomelane, which displays concentric and radial syneresis.

Massive, alveolate, botryofom goethite with minor hematite in colour bands concordant with the external shape of the botryoids (B.M. 1975, 530). The open botryofom surfaces of the goethite have a coarse velvety to hirsute appearance due to the compound terminations of individual goethite blades. These are overgrown by transparent, colourless, quartz euhedra (up to 1 cm in length). A buff saccharoidal limestone, altered and containing solution cavities, is associated with the goethite. The alteration or metasomatism of the limestone included dolomitization, silicification and iron-oxide mineralization. Extending into the limestone, away from the goethite ore, micro- and equi-granular quartz, intergrown with arborescent goethite, completely replaces the limestone for up to 2 cm. Within 3 cm, however, silicification is partial and goethite ceases to occur. The quartz consists of isolated euhedra, equigranular patches or 'islands', and metasomes after dolomite euhedra. Dolomite replacements (clearly pre-dating the silicification) extend up to 6 cm from the ore contact.

'Breccia ores' of two kinds: goethite, minor hematite, quartz (euhedral, fragmental, and massive), and limestone breccias and microbreccias, in which individual angular fragments, varying from 2 cm to 50 μm are embedded in a fine grained calcareous and ferruginous matrix (B.M. 1975, 532 and 533) and goethite and psilomelane replacement of breccia and microbreccias with minor post-replacement brecciation (B.M. 1975, 534). Small bright yellow encrustations of vanadinite are associated with the first breccia type. Unlike the vanadinite associated with the first and third ore types, it was too fine grained and powdery to enable it to be polished.

These ore textures indicate that mineralization at Tÿ Coch was of the cavity infill and replacement type, that it was episodic, and that it occurred in an environment of periodic tectonic activity.

In the one ore type in which pyrobelonite has so far been found it appears in several different forms in association with all the major constituents: solitary grains and clusters of individual grains and compound grains in calcite, with braunite aggregates, hausmannite euhedra and partial pseudomorphs thereof, and as lamellae between baryte laths. Grain size varies from 20 μm up to 1 cm. Pyrobelonite is sometimes intimately intergrown with vanadinite and often subhedral-euhedral grains of one phase have pellicular overgrowths of the other phase, up to 60 μm wide, upon them.

Optical characteristics of pyrobelonite. Several specimens of Tÿ Coch ore containing pyrobelonite, B.M. 1974, 155, were mounted in a cold-setting epoxy resin, ground with alumina on oil-lubricated cast-iron laps, and polished with diamond abrasives, 6-1/4 μm , on water- and ethanol-lubricated Hypocel Pellon laps. The same procedure was adopted for hand-picked grains from the Långban topotype (Harvard collection 94381). Pyrobelonite from this specimen had been used by Barnes and Qurashi (1952) in obtaining unit-cell and space-group data and by Barnes and Ahmed (1969) for their work on the unit cell of pyrobelonite and its X-ray powder pattern. Identical powder patterns were obtained from fragments of the material analysed in this study (pers. comm. Miss E. E. Fejer).

The reflected-light qualitative optical properties of pyrobelonite from both localities are very similar. In plane polarized light it is grey and bireflectant. Against hausmannite it is slightly darker with a barely perceptible blue tint. Under crossed polars it is strongly anisotropic. The anisotropic rotation colours are greys. Red and orange internal reflections (resembling those of proustite) are common and often mask the rotation colours.

Small < 25 μm inclusions of a gangue phase, probably calcite, occur in all of the Långban grains.

Vanadinite from Tÿ Coch, B.M. 1974, 157, is whiter and slightly higher reflecting than pyrobelonite. Under crossed polars it is colourless to yellow, usually with colourless to white internal reflections. Reflectance measurements were made on pyrobelonite from both localities, and for comparative purposes on vanadinite and hausmannite from Tÿ Coch. Only pyrobelonite grains without internal reflections were measured. Measurements were made from 400 nm to 700 nm at 20 nm intervals and at the four C.O.M.-recommended wavelengths, using Vickers and Zeiss microscopes equipped with photometers and running line-interference filters. Zeiss $\times 8$ air and oil objectives were used on the Vickers microscope and a Zeiss $\times 16$ air objective on the Zeiss microscope. Zeiss silicon carbide standards, numbers 055 and 232, were used. Cargille oil type A was used for oil measurements of pyrobelonite on the Vickers microscope.

As unorientated sections were measured, individual grain values are quoted as R_1 and R_2 for the biaxial mineral pyrobelonite (grains were selected for maximum birefringence). R'_0 for vanadinite could not be established directly from the spectral reflectance curves, obtained from the measurement of different unoriented grains, as the values for the higher and lower reflecting vibration directions showed no significant variation (Table I). As vanadinite is known to be uniaxial negative (Dana, 7th edn, 2, 287), and is translucent in the visible spectrum R'_0 is ascribed to the lower reflectance value. It was because of this translucency that R_0 could not be found directly, since all sections including the basal were masked by internal reflections. R_0 for hausmannite was found from measurement of basal sections. These data are listed in Table I as $R\%$ values. From this table the reason for the occasional higher reflectance of vanadinite when compared with hausmannite, and pyrobelonite when compared

TABLE I. *Reflectivity data*

Pyrobelonite								Vanadinite, Tý Coch			
Tý Coch				Långban							
Air		Oil		Air		Oil		Air			
λ	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_0	R'_0	λ
400 nm	17.0	19.8	4.9	6.7	17.0	19.7	4.8	6.8	21.9 (21.7-22.0)	20.3 (20.0-20.4)	400 nm
420	16.8	19.5	4.8	6.5	16.7	19.3	4.7	6.6	21.0 (20.8-21.2)	19.4 (19.2-19.6)	420
440	16.6	19.1	4.6	6.3	16.5	18.9	4.6	6.3	20.1 (19.9-20.3)	18.6 (18.4-18.8)	440
460	16.4	18.7	4.5	6.0	16.2	18.5	4.5	6.1	19.3 (19.2-19.6)	17.8 (17.6-18.0)	460
470	16.3	18.5	4.5	5.9	16.1	18.3	4.4	6.0	19.0 (18.8-19.2)	17.5 (17.2-17.6)	470
480	16.2	18.2	4.4	5.8	16.0	18.2	4.4	5.8	18.7 (18.5-18.9)	17.2 (17.0-17.4)	480
500	16.0	17.8	4.2	5.6	15.7	17.8	4.3	5.6	18.2 (17.9-18.5)	16.8 (16.7-17.0)	500
520	15.8	17.5	4.1	5.4	15.5	17.4	4.2	5.4	17.7 (17.5-17.9)	16.6 (16.4-16.7)	520
540	15.7	17.0	4.0	5.1	15.2	17.0	4.0	5.1	17.6 (17.4-17.7)	16.5 (16.2-16.6)	540
546	15.6	16.9	4.0	5.0	15.1	16.9	4.0	5.1	17.5 (17.3-17.6)	16.4 (16.1-16.6)	546
560	15.4	16.8	3.9	5.0	15.0	16.7	3.9	5.0	17.4 (17.2-17.6)	16.3 (16.1-16.5)	560
580	15.3	16.6	3.8	4.8	14.8	16.5	3.8	4.8	17.2 (17.1-17.5)	16.2 (16.1-16.4)	580
589	15.2	16.5	3.7	4.8	14.8	16.4	3.8	4.8	17.2 (17.1-17.4)	16.2 (16.1-16.3)	589
600	15.1	16.5	3.7	4.7	14.7	16.3	3.8	4.7	17.1 (17.0-17.3)	16.1 (15.9-16.3)	600
620	14.9	16.3	3.7	4.6	14.6	16.1	3.7	4.6	17.0 (16.9-17.1)	16.0 (15.9-16.2)	620
640	14.8	16.2	3.6	4.5	14.5	16.0	3.7	4.5	16.9 (16.7-17.0)	15.9 (15.7-16.1)	640
650	14.7	16.1	3.6	4.5	14.4	15.9	3.7	4.5	16.8 (16.6-17.0)	15.9 (15.7-16.1)	650
660	14.6	16.0	3.6	4.5	14.3	15.8	3.6	4.5	16.8 (16.6-16.9)	15.9 (15.7-16.0)	660
680	14.3	15.8	3.5	4.4	14.2	15.7	3.6	4.4	16.7 (16.7-16.9)	15.8 (15.6-15.9)	680
700	14.2	15.6	3.5	4.3	14.1	15.6	3.5	4.4	16.7 (16.6-16.9)	15.8 (15.7-16.0)	700

Hausmannite, Tý Coch (Air)					
λ	R_0	R'_0	λ	R_0	R'_0
400 nm	20.9 (20.4-22.1)	18.4 (18.0-18.8)	560 nm	19.1 (18.4-19.9)	16.8 (16.1-17.3)
420	20.7 (20.1-21.8)	18.2 (17.7-18.6)	580	18.9 (18.2-19.7)	16.6 (15.9-17.1)
440	20.5 (19.9-21.6)	18.0 (17.5-18.4)	589	18.8 (18.1-19.6)	16.6 (15.8-17.0)
460	20.3 (19.7-21.4)	17.8 (17.3-18.2)	600	18.7 (17.9-19.4)	16.4 (15.7-16.9)
470	20.1 (19.5-21.2)	17.7 (17.2-18.1)	620	18.5 (17.7-19.1)	16.3 (15.4-16.8)
480	20.0 (19.4-21.0)	17.6 (17.1-18.0)	640	18.3 (17.4-19.0)	16.1 (15.3-16.6)
500	19.9 (19.3-20.8)	17.4 (16.8-17.8)	650	18.2 (17.3-19.0)	16.0 (15.2-16.6)
520	19.6 (18.9-20.5)	17.2 (16.6-17.6)	660	18.1 (17.2-18.9)	15.9 (15.2-16.5)
540	19.4 (18.7-20.2)	17.0 (16.4-17.4)	680	17.9 (16.9-18.8)	15.7 (15.1-16.3)
546	19.4 (18.6-20.1)	17.0 (16.3-17.4)	700	17.7 (16.7-18.8)	15.5 (15.0-16.2)

with vanadinite is clear— R_0 vanadinite $>$ than R_0 hausmannite and R_1 pyrobelonite $>$ R'_0 vanadinite. This also explains the detectable differences in their bireflectances.

Quantitative colour values. Hardy's (1936, pp. 49-51) selected ordinate method was used for the calculation of tristimulus values. The values were calculated for an illuminant (CIE, C) having a colour temperature of approximately 6750 °K. The tristimulus values and the 2-dimensional colour space coordinates derived from them (Table II) reveal that the observed and calculated colour sense (observations were made with unfiltered tungsten halogen sources of 3000-3300 °K) is in general agreement. The excitation purity P_e (expressed as %) of the three species is low, as are the levels of luminance Y . Their dominant wavelengths λ_D are very close; therefore, the observed slight blueness of pyrobelonite and vanadinite against hausmannite is

TABLE II. *Quantitative colour values*

		Air					Oil				
		<i>x</i>	<i>y</i>	λ_D	$P_e\%$	<i>Y</i>	<i>x</i>	<i>y</i>	λ_D	$P_e\%$	<i>Y</i>
Pyrobelonite, Tÿ Coch	{ R_1	0.3021	0.3088	478	3.8	15.46	0.2930	0.2971	475	8.5	3.89
	{ R_2	0.2988	0.3031	474	5.7	16.66	0.2881	0.2927	476	10.8	5.01
Pyrobelonite Långban	{ R_1	0.3008	0.3072	477	4.4	15.09	0.2958	0.2971	475	7.2	3.93
	{ R_2	0.2980	0.3043	477	5.8	16.86	0.2887	0.2927	473	10.8	5.00
Vanadinite Tÿ Coch	{ R_0	0.3000	0.3006	466	5.9	17.42					
	{ R'_0	0.3009	0.3031	468	5.2	16.33					
Hausmannite Tÿ Coch	{ R_0	0.3030	0.3101	479	3.3	19.16					
	{ R'_0	0.3032	0.3100	478	3.3	16.85					

The values are all relative to the CIE illuminant C having a colour temperature of 6750 °K. *Y* is the luminance, *x* and *y* the rectangular chromaticity coordinates. The dominant wave-length λ_D and the excitation purity $P_e\%$ (the 2-dimensional colour-space coordinates) were derived from the *x* and *y* values plotted on Hardy's chromaticity diagram (1936, chart 13, p. 75).

TABLE III. *Chemical analyses*

	Pyrobelonite				Vanadinite			
	1	2	3	4	5	6	6a	7
PbO	57.00	57.86	48.82	56.64	79.37	78.69	78.42	78.80
MnO	17.64	16.40	25.01	18.00	0.05	nil	nil	—
V ₂ O ₅	23.04	22.74	20.03	23.08	18.79	16.76	17.72	19.26
As ₂ O ₅	nil	nil	—	—	nil	0.80	0.99	—
P ₂ O ₅	nil	nil	0.05	—	—	—	0.93	—
Cl	nil	nil	—	—	2.15	2.15	2.50	2.50
Σ less O = Cl	97.68	97.00	99.00*	100.00†	99.87	97.92	100.00	100.00

1. Pyrobelonite, Långban, Sweden (off Harvard 94831); average of 5 probe analyses.
2. Pyrobelonite, Tÿ Coch, S. Wales; average of 5 probe analyses.
3. Pyrobelonite, original analysis, Flink (1919).
4. Theory for PbMnVO₄OH.
5. Vanadinite, Tÿ Coch, S. Wales; average of 2 probe analyses.
6. Vanadinite, Morocco (off BM 1923, 877); average of 2 probe analyses.
- 6a. As 6, wet chemical analysis by Dr. A. A. Moss.
7. Theory for Pb₅(VO₄)₃Cl.

* Includes CaO 0.79, MgO 0.60, FeO 0.47, SiO₂ 0.21, H₂O 3.02 %.

† Including 2.28 % H₂O.

readily explained in terms of their marginally greater purity and slightly lower luminance levels, and not as a result of a change in hue.

Chemistry of Tÿ Coch and Långban pyrobelonite. Grains of pyrobelonite used in the reflectance study were analysed using a Cambridge Instruments 'Geoscan' with an accelerating voltage of 20 kV and a current of 0.6×10^{-7} A. Lead was determined using an analysed anglesite standard from Monteponi, Sardinia. Pure Mn and V metal standards were used for the other elements determined. A vanadinite (B.M. 1923, 877) was analysed by wet chemical and microprobe techniques (Table III, analyses 6 and 6a) and used as a secondary standard and as a check of correction factors. At least 20 spot counts were taken on each grain analysed.

Raw data for those elements determined were corrected using the methods described by Sweatman and Long (1969) and the Mason, Frost, and Reed (1969) microanalysis computer programme.

Areas of pyrobelonite in sections from both localities were checked for homogeneity and analysed qualitatively. In all the grains studied only lead, manganese, and vanadium were detected. Pyrobelonite from Tŷ Coch was found to be associated with vanadinite (Table III, analysis 5) and veins of manganocalcite and dolomite. Other minor elements listed in Mauzelius's original analysis (in Flink, 1919), previously the only published analysis, were sought but not found, although a 0.5 mg fragment of pyrobelonite associated with matrix (essentially manganese oxides) from Tŷ Coch, taken for spectrographic analysis, gave minor concentrations of magnesium, calcium, aluminium, antimony, silicon, and copper as well as the major elements, manganese, lead, vanadium, and iron.

Lead figures for all the analyses were above theoretical values whilst vanadium content appears to be consistent with these values. However, five separate analyses showed Tŷ Coch material to have a lower manganese content than the Långban specimen.

Acknowledgements. We are indebted to Mr. and Mrs. G. Morgan-Joseph for allowing us to collect material from the spoil tips on their farm, and are grateful to Prof. C. Frondel for lending us the topotype specimen from Långban and to Dr. D. A. Bassett for providing us with specimens of palygorskite from Glamorgan.

Addendum. Palygorskite. Mountain leather, synonymous, in part, with palygorskite, was found in unspecified iron-ore mines of the area (Vivian, 1887). North (1916) reported that a specimen in the National Museum of Wales collection was from Mwyndy mine, near Llantrisant, 15 miles east of Tŷ Coch. Three specimens (typical leathery masses) from this area, Nat. Mus. Wales 25.554 GR6, 48.264 GR228, and 90.181 were X-rayed by J. G. Francis and confirmed as palygorskite. The X-ray powder photographs of the Tŷ Coch material differ from these. Miss E. E. Fejer (pers. comm.) identifies them as orthopalygorskite following the recommendation by Gard and Follett (1968) that orthorhombic and monoclinic palygorskite may coexist and be found separately. X-ray powder photographs of topotype specimens of palygorskite and attapulgit (an unnecessary synonym according to Christ *et al.*, 1969) in the BM Collection show measurable differences, which are ascribable to these structural variations.

REFERENCES

- Barnes (W. H.) and Ahmed (F. R.), 1969. *Canad. Mineral.* **10**, 117-23.
 — and Qurashi (M. M.), 1952. *Am. Mineral.* **37**, 407-22.
 Christ (C. L.), Hathaway (J. C.), Hostetler (P. B.), and Shepard (Anna O.), 1969. *Ibid.* **54**, 198-205.
 Dana (J. D.), 1951. *System of Mineralogy*. 7th edn, **2**, 897, London (Chapman and Hall) New York (John Wiley and Sons).
 Flink (G.), 1919. *Geol. Fören. Förh.* **41**, 433-47.
 Gard (J. A.) and Follett (E. A. C.), 1968. *Clay Miner.* **7**, 367-9.
 Gayler (R. A.) and Criddle (A. J.), 1969. *Proc. 9th Commonw. Min. Metall. Congr., London, Min. Pet. Geol. Sect.* 605-26.
 George (T. N.), 1933. *Q. J. Geol. Soc.* **89**, 221-72.
 Hardy (A. C.), 1936. In *Handbook of Colorimetry*. Techn. Press, Mass. Inst. Techn.
 Howard (F. T.), 1893-4. *Trans. Cardiff Nat. Soc.* **26**, 47-54.
 Mason (P. K.), Frost (M. T.), and Reed (S. J. B.), 1969. *Natl. Phys. Lab. I.M.S. Rep.* **1**.
 North (F. J.), 1916. *Trans. Cardiff Nat. Soc.* **49**, 1-34.
 Sibly (T. F.) and Lloyd (W.), 1927. *Spec. Rep. Min. Resour. G.B.* 2nd edn, **10**, 101.
 Strahan (A.) and Cantrill (T. C.), 1904. *Mem. Geol. Surv. G.B.* Part 6, 121.
 Sweatman (T. R.) and Long (J. V. P.), 1969. *J. Petrol.* **10**, 332-76.
 Vivian (S.), 1884. *Proc. S. Wales Inst. Eng.* **14**, 164-75.
 — 1887. *Trans. Cardiff Nat. Soc.* **19**, 48-53.
 Watson (J. J.), 1859. *Geologist*, **2**, 241-56.

[Manuscript received 8 June 1976]