Reichenbachite from Cornwall and Portugal

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Abstract

Infrared spectroscopy is a rapid method of distinguishing between pseudomalachite and its polymorphs reichenbachite and ludjibaite. This technique, backed by X-ray diffraction has shown that a number of specimens labelled 'pseudomalachite' from Cornwall, in particular from Old Gunnislake mine, are of reichenbachite, thus identified for the first time from the British Isles. Reichenbachite has also been identified with pseudomalachite from Miguel Vacas mine, Vila Viçosa, Evora, Portugal. Identification of pseudomalachite from a number of other localities world-wide has been confirmed, and some specimens have been shown to be arsenatian.

Keywords: reichenbachite, pseudomalachite, ludjibaite, infrared spectroscopy, Cornwall, Portugal.

Introduction

Pseudomalachite (Hausmann, 1813) is the accepted name for the copper phosphate mineral described under a variety of names, including ehlite (Breithaupt, 1832), lunnite (Bernhardi,. 1839), and prasine (Breithaupt, 1841), and assigned various compositions, but now formulated $Cu_5(PO_4)_2(OH)_4$. It has been reported from numerous worldwide localities. British pseudomalachite ('lunnite'), from an unspecified locality in Cornwall, was first analysed by Heddle (1855). Maskelyne and Flight (1872) gave an analysis of 'prasine' which was supplied by the dealer Richard Talling and was associated with white olivenite, and was therefore probably also Cornish, although no locality is given. Church (1873) analysed three Cornish, but not further localized specimens of 'ehlite' and concluded that they were the phosphate analogue of cornwallite and identical with the 'pseudomalachite' 'of Dana' (actually of Hausmann) and the 'ehlite' of Breithaupt. According to Rudler (1905), specimens of 'lunnite or pseudomalachite' from Botallack, Cornwall, were analysed by Professor Church, but the reference given (*J. Chem. Soc.*, 1865, p. 2) is incorrect. No relevant paper by Church other than that mentioned above has been traced, and Botallack as a locality has not been mentioned in the literature again until recently (Bowell, 1992). Kingsbury (1952) specifies five localities for 'pseudomalachite' in Cornwall.

Description

Old Gunnislake mine, Calstock, Cornwall, is one of the best known British localities for 'pseudomalachite' (Kingsbury, 1952), but in 1982 we observed that specimens from here gave infrared spectra similar to but distinctly different from that of authentic pseudomalachite. Moreover, three out of six early 19th century specimens of typical 'pseudomalachite' in the Lady Elizabeth Cornwallis collection in Maidstone Museum, labelled 'compact malachite' or 'malachite' from Cornwall, also gave the abnormal infrared pattern. In 1987 a sample of reichenbachite, the newly described polymorph of pseudomalachite (Sieber *et al.*, 1987), became available to the authors and its infrared spectrum

FIG. 1. Scanning electron photomicrograph of reichenbachite crystals from Cornwall. Off Maidstone Museum specimen 179. Lady E. Cornwallis Collection.

was found to be identical with those of the abnormal 'pseudomalachite' specimens from Old Gunnislake mine. The identification was confirmed by X-ray powder diffraction at the Natural History Museum, London, and is the first of reichenbachite from the British Isles.

Reichenbachite from Old Gunnislake mine was particularly common on Michael's shaft dump (National Grid Reference SX 430 719), formerly a well-known collecting site marked by an ivy-covered chimney, but now built over. It is a supergene mineral, of late generation, typically forming dark green crusts to mammillary coatings, sometimes several mm thick, with compact, indistinctly fibrous radiating structure, and with minutely drusy outer surfaces. Scanning electron photomicrographs (Fig. 1) show the crystal terminations displayed on such drusy surfaces, and may be compared with the SEM photograph of the type material figured in Sieber *et al* (1987). The coatings are usually found as crack fillings and cavity linings on a matrix of milky, somewhat iron-stained, vein quartz with some decomposed feldspar; occasionally they are associated with chrysocolla, fibrous malachite or rectangular plates of metatorbernite. A fine specimen in the Natural History Museum, London (BM 1973,72, from R. W. Barstow) exhibits well-formed emerald green 0.02 mm platy crystals of reichenbachite on the dark green surface of a bluish-green translucent massive crust of reichenbachite 1–2 mm thick.

Seven specimens from Old Gunnislake mine have now been confirmed as reichenbachite by infrared spectroscopy, together with the three Maidstone Museum specimens from Cornwall mentioned above. In addition, a batch of specimens said to have come from Williams' shaft dumps of the same mine (SX 430 7185) in 1986 also proved to be reichenbachite, but another specimen from this dump was of normal pseudomalachite, as was a specimen consisting of a green crust underlying arsenatian libethenite crystals from East Gunnislake mine (SX 433 718). Normal pseudomalachite was also confirmed on three specimens labelled 'Gunnislake mine' or 'Old Gunnislake mine', so it appears that both polymorphs occur at Gunnislake, reichenbachite perhaps being more common, particularly on material known to have come from Michael's shaft (e.g. that collected by the authors). Unfortunately, the two polymorphs appear to be indistinguishable except by X-ray diffraction or infrared spectroscopy.

Reichenbachite has hitherto been reported only from the type locality, Reichenbach, Germany (Sieber *et al.*, 1987) and from Lubietova (= Libethen), Slovakia (Hyrsl, 1991). The discovery of the Gunnislake occurrence prompted us to study 'pseudomalachite' samples from a wide range of localities, though concentrating particularly on SW England, using infrared spectroscopy as a rapid and easy method of distinguishing between the polymorphs. This led to the identification of reichenbachite from Miguel Vacas mine, Vila Viçosa, Evora, Portugal. This mine is a known locality for pseudomalachite (Magalhães *et al.*, 1988), but specimens collected by one of us (RSWB) from the dumps in 1969 were shown to carry reichenbachite. This forms dark green, matt-surfaced mammillary coatings and small spherules, closely associated with libethenite crystals and usually underlying the latter. One specimen displays small globules of reichenbachite dispersed on libethenite crystals and on a somewhat darker green coating of compact fibrous radiating pseudomalachite, on which the libethenite is sprinkled. The matrix of these specimens is of white vein quartz and 'limonite' in a grey slate. The localities at which normal pseudomalachite has been confirmed by our survey are listed in Table 1; note that some are arsenatian, easily distinguished by infrared spectroscopy by the enhanced absorption in the 840 cm^{-1} region (cf. pyromorphite group; see Braithwaite, 1990).

Polymorphs

Studies of synthetic phases formed by hydrothermal techniques in the $CuO-P_2O_5-H_2O$ system revealed the formation of three polymorphs of $Cu_5(PO_4)_2(OH)_4$, which were labelled PM (pseudomalachite), PPM and QPM

TABLE 1. List of localities at which pseudomalachite has been confirmed by infrared spectroscopy (this work)

Locality	Remarks	Specimens examined	Museum specimen numbers[a]
England: Cornwall:			
Wheal Carpenter, Gwinear	Arsenatian, underlying malachite	1	
Penberthy Croft mine, St Hilary	Bright-green minute spherules[b]	1	
South Wheal Frances, Illogan	With libethenite crystals and malachite	1	
Tolcarne mine, Camborne	Arsenatian, with libethenite crystals	1	
United mines, St Day		1	Nev 1985,3530.
Wheal Unity, St Day		1	BM 31243.
Wheal Phoenix, Linkinhorne	One specimen was arsenatian	3	incl. BM 1929,216.
West Wheal Phoenix, Linkinhorne		3	BM 44671, 44672, 44673.
Gunnislake mine, Calstock	Specimen BM 61333[c] is arsenatian	2	MI 1985,12199; BM 61333.
Old Gunnislake mine, Calstock	One specimen was from Williams shaft dump	2	
East Gunnislake mine, Calstock	Underlying libethenite crystals	1	
England: Devon:			
Bampfylde mine, North Molton		3	incl. BM 1968,134 & 1968,135.
England: Cumbria:			
Potts Gill mine, Caldbeck Fells	Arsenatian	1	
Low Pike trial, Caldbeck Fells	Arsenatian, with bayldonite	2	
Short Grain, Caldbeck Fells	Arsenatian	3	
Scotland: Kirkcudbrightshire:			
Auchencairn baryte mine, Rerrick	Translucent drusy crusts on quartz[d]	2	
Portugal: Evora:			
Miguel Vacas mine, Vila Viçosa		3	
Germany: Rheinland-Pfalz:			
Ehl	Arsenatian, sheafy pseudomorphs?	1	BM 42476.
Rheinbreitbach		2	incl. M/C Mus. N3799.
St Josephsberg mine, Virneberg		1	M/C Mus. N3807.
Slovakia:			
Lubietova (= Libethen)		1	M/C Mus. N3816.
Zaire:			
Kambove, Katanga		2	
M'sesa mine, Katanga		2	incl. BM 1968,316.
Zambia:			
N'changa mine, Chingola		4	
Chambishi, between Chingola & Kitwe		1	
Bwana M'kubwa, Ndola		1	BM 1929,1633.
USA: New Jersey:			
Old Schyler mine, North Arlington	'Dihydrite', thin green crust	1	M/C Univ. Geol. Dept. 2847.
Chile(?):			
Tambillos	'Tagilite', with massive libethenite	1	M/C Mus. N3806.
Australia:			
Tottenham, N.S.W.		1	

(a) M/C = Manchester. BM, Nev and MI = Natural History Museum, London. All other specimens from the authors' collections, or submitted to the authors by various collectors.
(b) Infrared result inconclusive; XRD indicates pseudomalachite with broadened bands (J. G. Francis, pers. comm.).
(c) This is the 'erinite' specimen identified as pseudomalachite by Berry (1951).
(d) Confirmed by XRD on one specimen: Livingstone (1993).

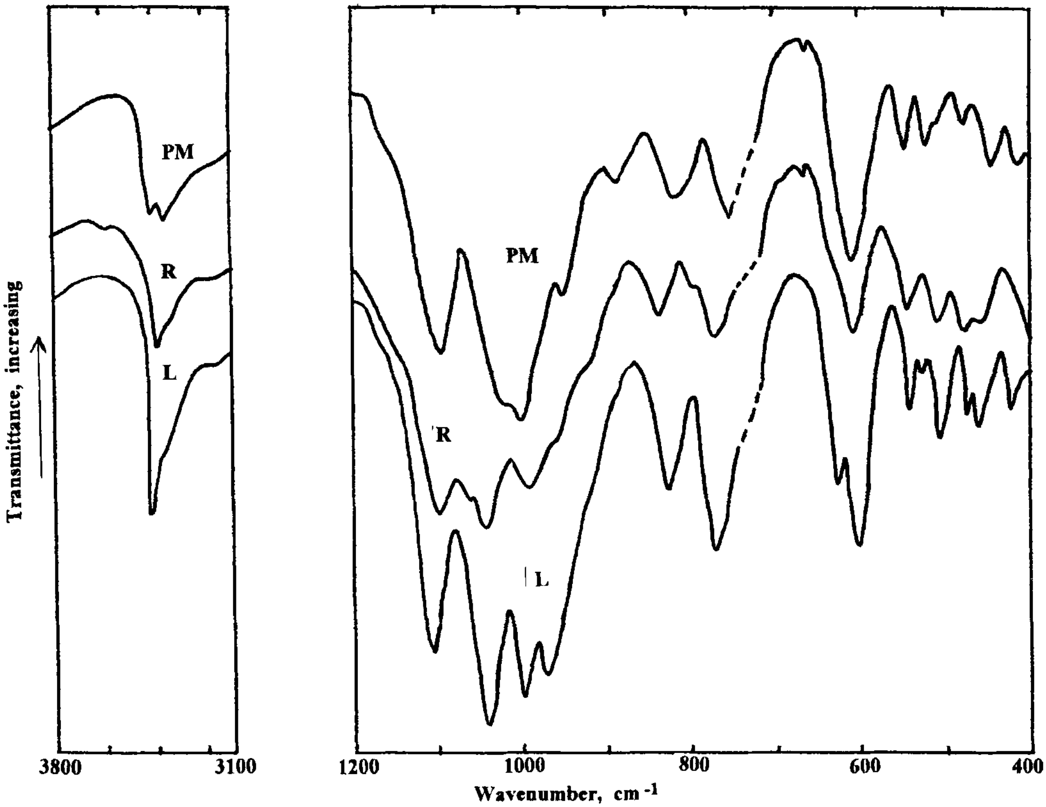

FIG. 2. Fourier Transform infrared spectra of pseudomalachite, reichenbachite and ludjibaite, measured in nujol mulls. No absorption between 3100 and 1200 cm^{-1}. PM = pseudomalachite, N'Changa mine, Zambia; R = reichenbachite, Old Gunnislake mine, Cornwall; L = ludjibaite, Lubietova, Slovakia.

(Shoemaker and Kostiner, 1981). Their crystal structures were determined, indicating space groups $P2_1/c$, $P2_1/a$ and $P\bar{1}$ respectively (Shoemaker *et al.*, 1977; Anderson *et al.*, 1977; Shoemaker *et al.*, 1981). Subsequently PPM was identified in nature as reichenbachite (Sieber *et al.*, 1987), and QPM was found at Ludjiba, Zaire, and described as ludjibaite (Piret and Deliens, 1988). More recent work suggests that other polymorphs might exist in nature and, indeed, the existence of a fourth, triclinic polymorph, 'XPM', has been predicted by Shoemaker and Kostiner (1981).

Infrared spectroscopy

The infrared spectra of a considerable number of samples (Table 1) were measured mostly in nujol mulls between KBr plates, over the 4000–400 cm^{-1} range, using a variety of spectrometers of both grating and Fourier Transform types.

Examples of the spectra obtained of reichenbachite, pseudomalachite and ludjibaite are shown in Fig. 2, and wavenumbers and assignments of absorption maxima are listed in Table 2. Although intergrowths of these species are common, and successive layers of nodules may be composed of different polymorphs, the spectra tend to show one or other of the species rather than mixtures, probably because of careful sampling under the microscope.

Conclusion

Infrared spectroscopy is a rapid method of distinguishing between the polymorphs pseudomalachite, reichenbachite and ludjibaite. Most 'pseudomalachite' specimens studied from Old

TABLE 2. Wavenumbers (cm^{-1}) and probable assignments of infrared absorption maxima of pseudomalachite, reichenbachite and ludjibaite

PM	R	L	Assignments
		3625 vw	
3436 fs	3409 s	3419 s	
3387 fs		3413 s	O–H stretch
	(~3370)	(~3370)	
~3180 vvw,br	3180 vw,br	3180 vw,br	
1098 vs	1098 vs	1107 s	ν_3 of PO_4
(1020) vs	1042 vs	1040 vs	possibly with
999 vs	992 vs	997 vs	CuO–H
953 s	(~955)	970 s	PO_4 ν_1 or ν_3[1]
889 m	(~920) m	(~925)	
		(~890) vw	CuO–H deformation[2]
812 fs	839 m	827 m	
756 fs	770 m	769 fs	
	(~ 620)	627 m	CuO–H deformation
610 s	606 s	601 s	or PO_4 ν_4?[3]
550 m,sp	546 m	546 m	
530 m		530 fw	PO_4 ν_4
510 fw	505 m	504 m	
480 fw	475	474 fw	
446 m	455 fw	459 fw	PO_4 ν_2
417 m	410 fw	419 fw	
360 m	390 w,br	n.d.	
338 m	330 w	n.d.	Cu–O stretch
285 w	258 fw	n.d.	
250 w	(250)	n.d.	

br = broad, f = fairly, m = medium. n.d. = not determined, s = strong, sp = sharp, v = very, w = weak.
Values in brackets are for shoulders:
PM = pseudomalachite, N'Changa mine, Zambia; R = reichenbachite, Old Gunnislake mine, Cornwall; L = ludjibaite, Lubietova, Slovakia.

Notes (Reference: Braithwaite, 1983)
1 Compare band at 950 cm^{-1} in libethenite, unaffected by deuteration.
2 Compare band at 810 cm^{-1} in libethenite, shifted by deuteration.
3 Similar in libethenite, but not in the arsenate olivenite.

Gunnislake mine, Cornwall, consist of the $P1_1/a$ polymorph reichenbachite, identified for the first time from the British Isles. Most of the 'pseudomalachites' studied from other localities consist of the normal $P2_1/c$ polymorph, and some are arsenatian. Specimens from Miguel Vacas mine, Vila Viçosa, Evora, Portugal have proved to contain both reichenbachite and pseudomalachite.

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