SHORT COMMUNICATIONS

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Widenmannite from Cornwall, England: the second world occurrence

WIDENMANNITE, $Pb_2UO_2(CO_3)_3$, is an extremely rare mineral, hitherto known from just one specimen from Michael Mine in Weiler, near Lahr in the Black Forest, Germany (Walenta and Wimmenauer, 1961; Walenta, 1976). During a recent study of supergene uranium mineralization in the St Just district of West Penwith, Cornwall, widenmannite has been identified (by X-ray diffractometry and energy dispersive X-ray analysis) in a coastal exposure at NGR SW 362329, about 0.75 km west of Botallack village.

The widenmannite occurs in a localized patch of Pb–U–Cu mineralization exposed near the base of the cliff, well above high-tide level, at the back of a narrow cove (locally known as a 'zawn'). The cove is nameless on Ordnance Survey maps and mine plans of the area, but for the purpose of this paper will be referred to as 'Loe Warren zawn', Loe Warren being the name of the headland and rocky outcrop forming the southern boundary of the cove.

A NE–SW line of sporadic uraninite mineralization with associated supergene products can be traced for about 5 m across the back of Loe Warren zawn.

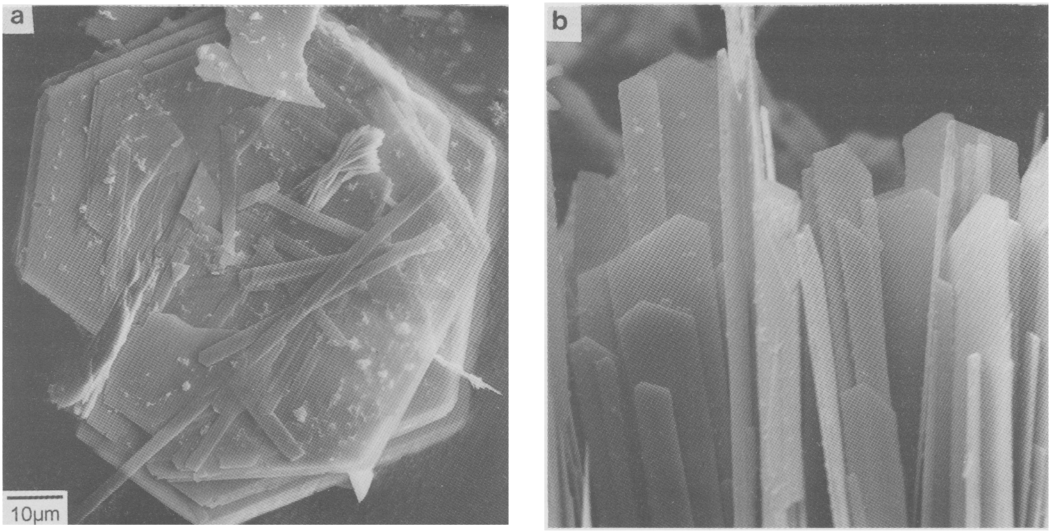


FIG. 1. (*a*) Scanning electron photomicrograph showing laths of widenmannite and a divergent 'bow-tie' group of dewindtite crystals on hexagonal tabular crystals of an unknown basic lead uranyl carbonate from Loe Warren zawn, St Just, Cornwall. (*b*) Free standing crystals of widenmannite are uncommon, but show a similar lath-like habit.

At its SW end, this line intersects an area containing NW-trending swarms of veinlets carrying chalcocite with minor chalcopyrite and pyrite. Surface water draining from rubble at the base of the cliff trickles continuously over this mineralized area and has led to the formation of a rich and interesting assemblage of supergene carbonate and phosphate minerals on exposed surfaces and in joint planes within the rock. The richly mineralized area is very small, about 2–3 m along the NW–SE axis and about 0.5 m wide. Crystals are always microscopic due to the restricted space for growth. The mineralized area at Loe Warren zawn may be related to Hanger Lode, a NW-trending Cu–Sn lode of the Wheal Owles group, formerly worked from the cliff (Dines, 1956). It seems likely that the water trickling over the exposure emanates from a collapsed adit belonging to the Wheal Owles sett.

Widenmannite occurs as transparent, colourless to very pale greenish yellow, lath-like crystals. Most commonly the laths form mats encrusting the matrix, or are arranged in stellate groups; rarely they form free-standing loose spheroidal aggregates (Fig. 1*a*,*b*). White, anhedral flaky masses are also common. In the orientation of Walenta (1976), the crystals are tabular {010}, considerably elongated along the *c*-axis and show the forms {100} and {101}. This habit is identical to that described by Walenta (1976). The laths are rarely more than 10 μm wide, but may reach 100 μm in length.

X-ray diffraction

Indexed diffractometer data for 36 lines are given in Table 1. A sample of anhedral encrusting widenmannite was used, being ground by hand with acetone in an agate pestle and mortar and deposited on a single crystal Si substrate. Fluorophlogopite (NIST SRM 675) was used as an internal standard. Step scans were made in the angular range 6–70° 2θ with 0.02° steps using Cu-$K\alpha$ radiation with a diffracted beam graphite monochromator and 0.1 mm receiving slit. Refinement of the unit cell on the first 23 lines gave a = 8.971(3), b = 9.381(3), c = 5.002(2) Å and V = 421.0 Å^3. Figures of merit for the indexed data are M(20) = 21.7 and F(23) = 20.1 (0.023, 50) This cell has a slightly larger volume than that given by Walenta (1976) who found a = 8.99, b = 9.36, and c = 4.95 Å. Intensities reported in Table 1 differ significantly from those given by Walenta (1976) which were obtained using a 57.3 mm Debye-Scherrer camera and Fe-$K\alpha$ radiation. Some differences may be attributed to differences between the camera and the Bragg-Brentano diffractometer techniques. In particular, preferred orientation on 0*k*0 and poor particle statistics are likely to affect the diffractometer data, while the stronger high-angle intensities in Walenta's Debye-Scherrer data may be due to absorption effects. A few lines reported by Walenta (1976) are missing from the diffractometer data and *vice versa*.

TABLE 1. Powder X-ray diffraction data for widenmannite from Loe Warren zawn

d_{calc} (Å)	d_{obs} (Å)	I/I_o	*hkl*
6.482	6.49	5	110
4.688	4.70	5	020
4.413	4.42	4	011
4.155	4.16	84	120
4.046	4.05	10	210
3.960	3.970	8	111
3.339	3.342	6	201
3.241	3.235	33	220
3.146	3.144	4	211
2.990	2.989	14	300
2.952	2.952	8	130
2.849	2.851	6	310
2.564	2.564	9	230
2.521	2.523	8	320
2.409	2.409	14	102
2.344	2.345	100	040
2.243	2.243	2	400
2.181	2.181	6	202
2.161	2.161	2	330
2.127	2.125	3	212
1.879	1.880	8	312
1.845	1.845	5	340
1.822	1.822	2	430
1.794	1.794	4	500
1.776	1.774	2	322
1.731	1.731	6	341, 250
1.689	1.687	2	501
1.644	1.644	1	412
1.588	1.589	1	521, 350
1.573	1.573	2	422
1.556	1.555	2	530
1.542	1.541	8	441
1.486	1.486	2	531
1.476	1.477	4	610
1.423	1.422	2	252
1.385	1.385	1	360

Infra-red analysis and chemistry

An infra-red transmission spectrum of widenmannite (Fig. 2, Table 2) was obtained using a Nicolet Nic-Plan® Fourier Transform Infra-red microscope. Samples were pressed into freshly prepared KBr discs and examined in transmission. The IR microscope employs a sensitive MCT-A detector which allows analysis of very small amounts of sample, but unfortunately the transmission cut-off is around 600

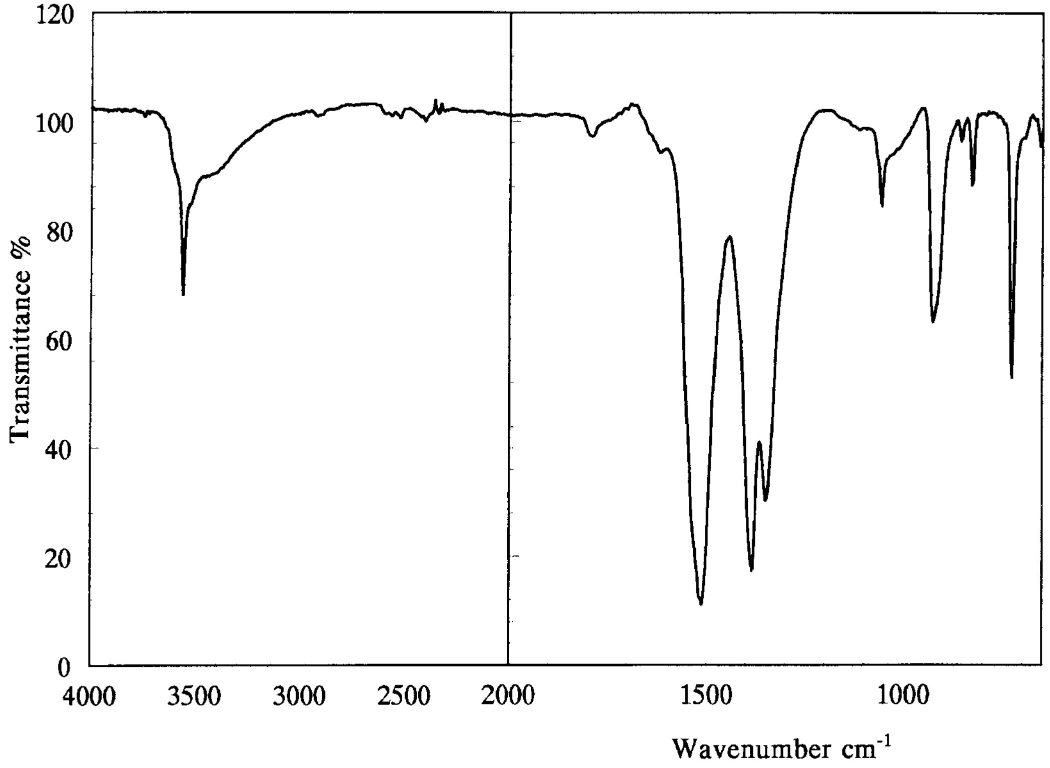


FIG. 2. Fourier transform infra-red transmission spectrum for widenmannite.

cm^{-1}. Several samples were examined and all gave essentially the same result. The infra-red spectrum of widenmannite resembles, in general terms, the spectra of other 1:3 uranyl carbonates (e.g. Jones and Jackson, 1993). The most notable feature of the spectrum is the significant OH absorption at 3561 cm^{-1}, the presence of which conflicts with the published formula for widenmannite. The infra-red spectrum of andersonite, another 1:3 uranyl carbonate, also shows an unexpected OH absorption in the data of Jones and Jackson (1993) and in the authors' unpublished data for andersonite from Geevor mine, St Just.

Semi-quantitative EDX analysis (Table 3) gives a composition in fair agreement with the published formula. Samples were pressed into the surface of an Al disc using a polished steel die. This method is rapid, yet gives a sample with a smooth, flat surface and reasonable homogeneity. Samples were coated with 10 nm thickness of Cu and examined in a JEOL JSM84O SEM with windowless X-ray detector and Oxford Instruments QX2000 analyser. Natural cerussite and synthetic UO_2 were used as standards. Carbon could not be measured directly because of

TABLE 2. Infra-red data for widenmannite

Wavenumber (cm^{-1})	%Transmission
3561	68
3457 *s*	90
1790	97
1620	94
1512	11
1385	17
1350	30
1057	85
925.9	63
856.5	96
829.5	88
725.3	53
655.8	96

s indicates a shoulder

TABLE 3. Semi-quantitative EDX analysis of widenmannite from Loe Warren zawn

Element	1	2
Pb	48.0 ± 0.4	47.92
U	26.4 ± 0.5	27.55
O	21.2 ± 0.2	20.37
C	4.4 ± 0.5	4.16
Total	100.0	100.00

1. Widenmannite from Loe Warren zawn. Average of 9 analyses on 3 grains. C by difference. Beam current, 5×10^{-10} A measured on the Faraday cage; accelerating voltage, 12 kV.
2. Theoretical composition, $Pb_2UO_2(CO_3)_3$.

peak overlap problems, and was determined by difference. The analysis does not account for the presence of OH observed in the infra-red spectrum.

Paragenesis and discussion

Widenmannite is often associated with an unknown basic lead uranyl carbonate (U:Pb ratio *c.* 1:4) which occurs as transparent to translucent hexagonal tabular crystals up to 100 μm across (Fig. 1*a*). The X-ray diffraction pattern of this mineral is distinct from that of widenmannite, although the infra-red spectra of the two minerals are similar. Dewindtite, $Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$, is associated with widenmannite on a number of specimens and occurs as radiated groups and tufts of bright yellow doubly-terminated tapering 'canoe-shaped' crystals (Fig. 3*a*). This is the first reported occurrence of this species in Britain. Dewindtite also occurs as spherules and fans of thin, rather ragged, crystals (Fig. 3*b*), and as pale yellow powdery deposits with chalcocite. Other associated minerals include intermediate members of the torbernite–zeunerite series, kasolite, cerussite, malachite, amorphous copper silicate and rarely cumengeite. Botallackite, atacamite, connellite and lavendulan occur sporadically in the same area.

Widenmannite is commonly found on oxidized surfaces which often have patchy iron oxide or iron silicate coatings. The host rock is predominently hornfels (e.g. Mitropoulos, 1984), but is micaceous or felspathic in places.

Widenmannite was also noted in a small patch of supergene alteration of uraninite about 3 m NE of the main exposure. This area is relatively dry and the widenmannite occurred as white flaky masses on a biotite-rich matrix with kasolite and arsenatian torbernite.

The paragenetic sequence among the supergene species is not particularly well defined (Fig. 4); many appear contemporaneous or to have been deposited sequentially by a retreating front of mineralizing fluid. Widenmannite and dewindtite appear to be the last formed uranium species at Loe Warren zawn. The chlorides cumengeite, connellite and botallackite have formed last of all, presumably by the action of sea spray on pre-existing Pb and Cu species. Their deposition appears to have been episodic, occurring when conditions were appropriate.

Kasolite, dewindtite and torbernite are frequent associates at Shinkolobwe, Zaire (Smith, 1984; Frondel, 1958) and La Faye, Grury, Saône-et-Loire, France (Frondel, 1958). At Michael Mine, Weiler, widenmannite occurred with cerussite, altered galena, kasolite, and the lead uranyl arsenates hügelite and hallimondite (Walenta and

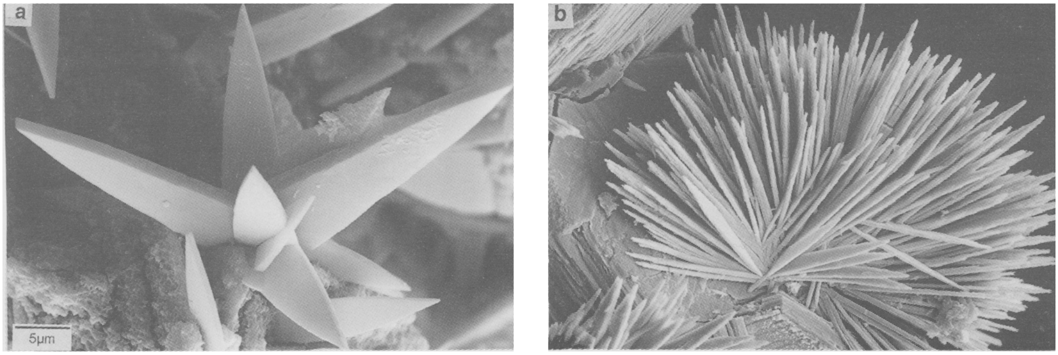
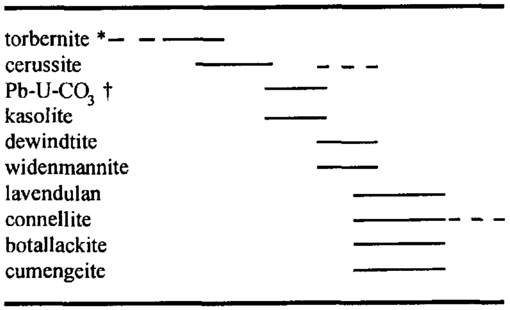


FIG. 3. (*a*) Scanning electron photomicrograph of dewindtite crystals from Loe Warren zawn. The crystals commonly form thick tapering laths, often doubly terminated. (*b*) Fan of ragged dewindtite crystals on chalcocite. Dewindtite is closely associated with chalcocite at Loe Warren zawn.



* includes torbernite/zeunerite intermediates.
† unknown lead uranyl carbonate mineral.

FIG. 4. Approximate paragenetic sequence for widenmannite and associated supergene species at Loe Warren zawn.

Wimmenauer, 1961; Walenta, 1976). Widenmannite formed here by the action of uraniferous waters on galena. The source of uranium was presumed to be wallrock alteration, no primary uranium mineral having been found. By contrast, no galena has been observed in the Loe Warren zawn outcrop. It is possible that the lead is entirely radiogenic as is the case in many other similar assemblages (e.g. Frondel, 1958; Gauthier *et al.*, 1989) or perhaps a small amount of galena formerly present has been completely altered to supergene products.

Water draining from the cliffs would naturally have a relatively high partial pressure of carbonate. The pH of the surface water is close to neutral which is consistent with the known conditions of formation of dewindtite (Ross, 1956). Fluorapatite occurs in an aplite dyke cutting the cliff at the back of the zawn, and as grains in micaceous rocks around the deposit, weathering of which may be responsible for enriching the phosphate content of the groundwater. Precipitation from the mineralizing fluids may have been triggered by the reducing environment produced by the disseminated chalcocite. Chalcocite itself shows little evidence of alteration and frequently occurs as minute, but well formed, crystals.

Samples of widenmannite, dewindtite and other supergene species from Loe Warren zawn have been deposited at the Natural History Museum, London, and the University Museum, Oxford.

Acknowledgements

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