A re-examination of churchite.

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IN the course of a study of certain cerium minerals, a spectrogram of churchite was taken and it was noticed that the cerium lines were barely visible, whereas the yttrium lines were very strong. We therefore decided to re-investigate this species.

Churchite was originally described by A. H. Church in 1865, and named by C. G. Williams in the same year.[1] The specimens were collected by R. Talling from an unnamed locality in Cornwall. It has only been analysed once, by Church, who showed it to be a hydrated phosphate of rare-earths and lime; his quantitative data have been recalculated and included in table I. Church obtained qualitative reactions for the cerium group of rare-earths, and for cerium itself,[2] but made no attempt to determine the ratio of cerium to yttrium earths; he assumed a mean molecular weight for the rare-earths which would correspond to R_2O_3 324, essentially a mixture of cerium earths with but little yttria, but did not adduce any evidence for this assumption. As will be shown below, churchite actually contains very little cerium, and is essentially a phosphate of yttrium with minor amounts of other rare-earths, principally neodymium, erbium, and cerium; but the standard textbooks[3] have listed churchite as 'a phosphate of cerium (didymium)

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[1] A. H. Church, Chem. News, 1865, vol. 12, no. 302 (September 15), p. 121. C. G. Williams, ibid., no. 307 (October 20), p. 183. A. H. Church, Journ. Chem. Soc. London, 1865, ser. 2, vol. 3, p. 259.

[2] A solution of the sulphates of the rare-earths gave a precipitate with potassium sulphate; the oxalate, on ignition, left an orange-brown oxide which dissolved in hydrochloric acid with evolution of chlorine.

[3] For example, Dana, System of mineralogy 6th edit., 1892, p. 820; 7th edit., 1951, p. 773.

and calcium', overlooking the fact that Church only claimed it as a phosphate of the cerium earths and only gave qualitative evidence of the presence of cerium, to which C. G. Williams added qualitative evidence of the presence of neodymium or praseodymium or both.

In 1922, H. Laubmann[1] described a phosphate of yttrium from the Nitzelbuch mine, Auerbach, Bavaria, under the name weinschenkite, a name which unfortunately was used almost simultaneously by G. Murgoci[2] for a variety of hornblende; an analysis by F. Henrich showed that the mean molecular weight of the rare-earths was R_2O_3 251·8, and the formula for the mineral $YtPO_4.2H_2O$, with some Er and probably Tb replacing Yt. In 1935 a new analysis (table I) and re-determination of the mean molecular weight of the rare-earths by F. Henrich[3] gave R_2O_3 248·1; the relative abundances of the rare-earths were determined by optical and X-ray spectrography. In 1942 H. Strunz[4] gave unit-cell dimensions for weinschenkite (from Auerbach) and noted its structural similarity to gypsum.

The only other known occurrence of a rare-earth phosphate of this type is at Kelly Bank mine, Vesuvius, Rockbridge County, Virginia. From here C. Milton, K. J. Murata, and M. M. Knechtel[5] describe material agreeing in optical data and X-ray powder photograph with Bavarian weinschenkite; it was not analysed, but a spectrographic study showed it to be an yttrium phosphate essentially similar to the Bavarian except for a rather higher proportion of Yb; its specific gravity is 3·263 and the mean molecular weight of the rare-earths, 257·0, is practically the same as that for the Bavarian and, as will be seen below, the Cornish material. From a study of the paragenesis,

[1] F. Henrich, Ber. Deutsch. Chem. Gesell., 1922, vol. 55, Abt. B, p. 3013 (October 14). [M.A. 2–12.] H. Laubmann, Geognost. Jahreshefte, Geol. Landesunters. München, 1923, vol. 35 (for 1922), p. 193. [M.A. 2–522.] A preliminary note by F. Henrich appeared in Edel-Erden und -Erze, 1921, vol. 2, p. 181, but the present authors have not been able to see this paper, and it is not clear whether the name weinschenkite appears in it or not.

[2] G. Murgoci, Compt. Rend. Acad. Sci. Paris, 1922, vol. 175, p. 372 (August 21) and p. 426 (September 4). [M.A. 2–221.]

[3] F. Henrich, Journ. Prakt. Chem., 1935, vol. 142, p. 1.

[4] H. Strunz, Naturwiss., 1942, vol. 30, p. 64. [M.A. 8–368.] We adopt the setting with β 113° 24', given in Dana (7th edit., vol. 2, p. 772) for the structure cell, and not the setting with β 129° 24' adopted by Strunz. The transformation matrix from Strunz's to our setting is $\|\bar{1}0\bar{1}/0\bar{1}0/001\|$. This setting corresponds to that adopted by Dana (loc. cit.) for gypsum, brushite, and pharmacolite.

[5] C. Milton, K. J. Murata, and M. M. Knechtel, Amer. Min., 1944, vol. 29, p. 92. [M.A. 9–54.]

Milton, Murata, and Knechtel conclude that the Virginian mineral probably owes its origin to a biochemical concentration of yttrium in chestnut and hickory leaves.

A new analysis (table I) made on 105 mg. of Cornish churchite from the British Museum specimen (B.M. 40636), purchased from R. Talling

TABLE I. Chemical analyses and unit-cell contents of churchite.

	1.	2.	3.	4.		1a.	3a.	4a.
$(Yt,Er)_2O_3$ ...	41·37 ⎫				Yt ...	2·95 ⎫		
$(La,Nd)_2O_3$ ...	7·99 ⎬ 54·6		52·47	52·90	Er ...	0·28 ⎬ 3·92		3·89
Ce_2O_3 ...	1·05 ⎭				(La,Nd)	0·45		
Fe_2O_3 ...	1·43	—	0·24	—	Ce ...	0·06 ⎭		
CaO	1·55	5·4	—	—	Fe ...	0·17	0·03	—
P_2O_5 ...	31·10	28·4	30·20	31·15	Ca ...	0·26	—	—
H_2O	15·29	14·9	16·42	15·96	PO_4 ...	4·08	4	4
insol.	—	—	0·38	0·23	H_2O ...	7·91	8·57	8·08
	99·78	103·3	99·71	100·24	$\Sigma(+)$...	12·24	11·85	11·67
D_4^{20}... ...	3·265	3·14	—	—	$\Sigma(-)$...	12·24	12·0	12·0

1. Churchite, Cornwall (B.M. 40636). Mean mol. wt. of yttria fraction 239·4, corresponding approx. with Yt_2O_3, 35·7, Er_2O_3 5·7 %.
2. Churchite, Cornwall. Anal. A. H. Church, 1865. Re-calculated from Church's weights on the assumption that his ceric oxide was essentially a trioxide, mainly of yttria, and using modern atomic weights.
3. Weinschenkite, Bavaria. F. Henrich, 1922. Mean mol. wt. of total rare-earths 251·8; corresponding approx. with Yt_2O_3 41·3, Er_2O_3 11·2 %.
4. Weinschenkite, Bavaria. F. Henrich, 1935. Mean mol. wt. of total rare-earths 248·1.
1a. Empirical unit-cell contents calculated from the analysis and density of col. 1, together with the unit-cell dimensions determined on the same specimen.
3a.⎫ Atomic ratios, calculated from the analyses of cols. 3 and 4, on a basis of
4a.⎭ $PO_4 = 4$. $\Sigma(+)$, sum of cationic charges; $\Sigma(-)$, sum of anionic charges.

in 1867, showed that this mineral is also essentially an yttrium phosphate, but in this case the principal accompanying element is neodymium, with smaller amounts of erbium and cerium and quite minor amounts of lanthanum and other rare-earths.

The isolated rare-earths (50·41 %) were divided into yttrium and cerium earths through the double sulphates with potassium, in the usual way. The yttria fraction was found (41·37%) to have a mean molecular weight of 239·4, and a solution of its sulphate gave a very distinct erbium absorption band at λ 525 mμ; if it were wholly yttria and erbia, there would be 35·7 % Yt_2O_3 and 5·7 % Er_2O_3. The cerium earths (9·04 %) were found to contain 1·05 % Ce_2O_3, determined volumetrically by the bismuthate method; the remaining 8 % appears to be principally Nd_2O_3, and a sulphate solution gave strong absorption

bands at λ 576 and 523 mμ. The mean molecular weight of the rare-earths as a whole was found to be approximately R_2O_3 252. The specific gravity of this churchite was found to be D_4^{20} 3·265.

X-ray powder photographs (fig. 1) of churchite from this specimen and of weinschenkite from a Bavarian specimen (B.M. 1925,637) are
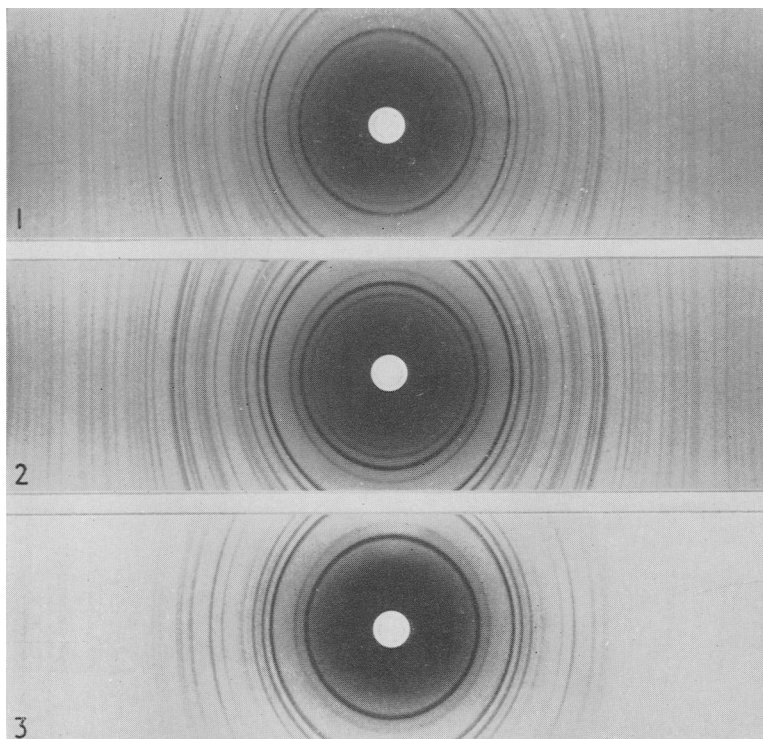

Fig. 1. X-ray powder photographs:
  1. Churchite, Cornwall (B.M. 40635).
  2. Weinschenkite, Auerbach, Bavaria (B.M. 1925,637).
  3. Gypsum, 'Mosul marble'. (British Museum Research Laboratories.) [M.A. 12–190.]

6-cm. diameter camera. Co-$K\alpha$ radiation. Original photographs reduced from 4·5 to 4 inches wide.

an excellent match in spacings and intensities (table II). The empirical unit-cell contents shown in table I are calculated from the new analysis, specific gravity, and unit-cell dimensions (p. 215 and postscript) determined on the same specimen.

Morphologically the Cornish material consists of sub-parallel aggregates of platy crystals, and is quite unsuited for goniometrical study (as Church noted). The Bavarian material is better crystallized, and Laubmann was able to obtain goniometrical measurements; referred to the unit-cell with[1] a 5·60, b 15·11, c 6·18 kX, β 115·3°, the forms observed[2] are a (100), b (010), p (120), R (10$\bar{1}$), and (as a cleavage face)

TABLE II. X-ray powder data (Ångström units) for churchite.

1.		2.		1.		2.	
d.	Int.	d.	Int.	d.	Int.	d.	Int.
7·55	vs	7·50	vs	1·596	mw	1·600	mw
5·22	w	5·22	mw	1·557	vvw	1·560	vw
4·70	mw	4·70	m	1·530	vvw	1·535	vw
4·20	vvs	4·21	vvs	1·503 vw ⎫		1·499	vw b
3·74	ms	3·74	m	1·489 vw ⎭			
3·01	vs	3·02	vs	1·437	w	1·440	w
2·83	m	2·82	ms	1·408	vvw	1·410	vvw
2·61	mw	2·62	m	1·390	vw	1·397	w
2·52	vw	2·51	mw	—	—	1·374	vvw
2·47	vw	2·46	mw	1·344	w	1·438	w
2·44	vw	—	—	1·326 vvw ⎫		1·324	w b
2·37	w	2·39	mw	1·317 vvw ⎭			
2·162	mw	2·17	m	1·301	vw	1·306	w b
2·083	vvw	—	—	—	—	1·286	vvw
2·059 w ⎫		2.05	mw b	—	—	1·270	vvw
2·036 w ⎭				1·249	w	1·253	w
2·005	vvw	2·01	vvw	—	—	1·237	vvw
1·964	w	1·97	mw	1·216	w	1·222	w
1·927	vvw	1·94	vvw	1·197	vvw	1·201	vw
1·855	mw	1·861	m	1·180	vvw	⎧1·186	vw
1·820	w	1·825	mw			⎩1·176	vvw
1·773	m	1·776	m	1·160	vvw b	1·163	vw b
1·755	mw	1·755	w	1·139	vw	1·147	vvw
1·689	vvw	1·692	vvw	1·125 vvw ⎫		1·123	mw b
1·640	mw	1·643	mw	1·118 mw ⎭			

Order of intensities: vvs, vs, s, ms, m, mw, w, vw, vvw. b indicates broad line.
1. Weinschenkite, Nitzelbuch mine, Auerbach, Oberpfalz, Bavaria (B.M. 1925, 637), cobalt-$K\alpha$ radiation.
2. Churchite, Cornwall (B.M. 40635), copper-$K\alpha$ radiation.

c (001); Laubmann measured bp 54° 40′, aR 47°, ac 67°, which, considering the difficult nature of the material, agree reasonably well with the calculated angles bp 56·2°, aR 53·2°, ac 64·7°. The morphological data given in Dana (Syst. Min., 7th edit., p. 771) for weinschenkite are

[1] Re-determined on B.M. 40636. H. Strunz's figures yield by the transformation $||\bar{1}0\bar{1}/0\bar{1}0/001||$, a 5·46, b 15·12, c 6·28 kX, 113° 24′.

[2] Transformation Laubmann to present settings: $||202/0\bar{1}0/00\bar{2}||$.

inaccurate: the β angle cited on p. 771 does not correspond to the adopted setting and axial ratio, but to Strunz's X-ray setting, the correct value being β 113° 24', as given on page 772; the cited ρ-value for u ($\bar{1}$01) is in consequence incorrect, while the prism observed by Laubmann is not (110) but (120) in the adopted setting, corresponding to the common prism of gypsum, which is also (120) in this setting. Laubmann observed an imperfect cleavage parallel to c (001), and a cleavage parallel to [001]; it is probable that this latter was parallel to b (010). It is also possible that some of Laubmann's terminal faces, R ($\bar{1}$01)—his c (001)—were cleavage faces. Church observed three cleavages, a very perfect one parallel to the terminal faces of the prisms, one parallel to the composition planes of the crystal-sheaves, and a third at right angles to the second and inclined to the first. These reports are in good agreement, and indicate that churchite has three cleavages parallel to a (100), b (010), and c (001). Of the isostructural minerals, gypsum has cleavages b (010), a (100), and n (011); brushite b (010) and c (001); and pharmacolite b (010).

The Cornish churchite is not well adapted to optical study owing to the difficulty of isolating single-crystal fragments from the sub-parallel aggregates, but a small single-crystal plate was mounted, orientated by an X-ray oscillation photograph and then examined optically. The crystals prove to be sub-parallel aggregates of plates parallel to a (100), and show an excellent cleavage parallel to b (010), in agreement with Church's observations. On a (100) extinction is straight and the positive acute bisectrix of an optic figure of small angle appears to be just out-side the field of the microscope; on b (010) extinction is at 31° to the trace of (100). The observed refractive indices are included in table III. The optic orientation given by E. S. Larsen[1] is difficult to reconcile with these observations, and has therefore been disregarded.

Churchite and weinschenkite are clearly identical; the small differences in neodymium and yttrium content between material from Cornwall, Bavaria, and Virginia are insufficient to warrant even a varietal distinction. The name churchite has priority, and in our opinion the error in the original description, by which the yttria earths were overlooked, is not a sufficient reason to reject this name in favour of weinschenkite, especially as the latter name has also been used for quite a different mineral.

[1] E. S. Larsen, The microscopic determination of nonopaque minerals. Bull. U.S. Geol. Surv., 1921, no. 679, pp. 58, 168, 217; 2nd edit. by E. S. Larsen and H. Berman, ibid., 1934, no. 848, pp. 72, 113.

Finally, we may note that the interpretation of Church's original analysis presents some difficulties. There are no obvious sources of probable serious error in the analytical methods described, yet the

TABLE III. Optical data for churchite.

	α.	β.	γ.	2V.	Orientation.
1.	>1·58	—	<1·63	Moderate, positive	$\alpha \parallel [010]$, $\gamma : [001] = 28°$ in acute angle β.
2.	1·605	1·612	1·645	— positive	$\alpha \parallel [010]$, $\gamma : [001] = 35°$ strong dispersion of bisectrices.
3.	1·600	1·608	1·645	Medium, positive	$\alpha \parallel [010]$, $\gamma : [001] = 30°$ approx.
4.	1·620	1·620	1·654	Very small, positive	
5.	1·623	1·631	1·657	Small, positive	$\gamma : [001] = 31°$.

1. Weinschenkite, Bavaria. H. Laubmann, 1923.
2. Weinschenkite, Virginia. C. Milton, K. J. Murata, and M. M. Knechtel, 1944.
3. Weinschenkite, Bavaria. E. S. Larsen and H. Berman, Bull. U.S. Geol. Surv., 1934, no. 848, 2nd edit., p. 111.
4. Churchite, Cornwall. E. S. Larsen, 1921.
5. Churchite, Cornwall (B.M. 40636).

phosphate is seriously low compared with the total bases, while the summation is notably high. Even deducting the excess over 100 % from the bases, the ratio of bases to phosphate remains high with any probable mean molecular weight for the rare-earths. The specimens in the British Museum collection agree exactly with Church's description, consisting of a crust of sub-parallel aggregates of minute crystal plates on quartz, and there does not seem to be any more basic mineral present (such as pseudowavellite or an analogue of florencite) that might account for the low phosphate.

Note added in proof.—Because of some remaining uncertainty of the optical orientation of the Cornish crystals the cell dimensions were re-determined by Weissenberg and rotation photographs on morphologically and optically orientated crystals. The cell dimensions (p. 215) differ appreciably from those of Strunz. The X-ray photographs showed the following systematic absences: hkl only with $k+l$ even, $h0l$ only with h even. These lead to the space-group C_{2h}^6 in the orientation A2/a, or C_s^4 in the orientation Aa. The former is the space-group of gypsum.