STUDIES OF URANIUM MINERALS (V): PHOSPHURANYLITE*

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ABSTRACT

The ill-defined uranium mineral phosphuranylite, hitherto known only from North Carolina on the basis of the original description by Genth (1879) and a later optical description by Larsen (1921), is redescribed from twelve new localities. Phosphuranylite is isostructural with dewindtite, $Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$, and its ideal formula is presumed to be $Ca_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$. Analyses show much less calcium than required by this formula. It occurs as dense, golden-yellow films composed of microscopic rectangular plates, and is found principally in the weathered zone of pegmatites containing uraninite. Crystallization tetragonal or orthorhombic. Optically biaxial negative with somewhat variable indices: nX=1.660 to 1.690 (colorless to pale yellow), nY=1.696 to 1.724 (golden yellow), nZ=1.698 to 1.724 (golden yellow); 2V=0° to 35°; $r>v$ strong. Lead substitutes for calcium in some varieties with accompanying increase in indices of refraction.

INTRODUCTION

The name phosphuranylite was given by F. A. Genth in 1879 to an ill-defined uranium mineral found in the Flat Rock pegmatite in Mitchell County, North Carolina. The original description stated only that the mineral occurred as microscopic rectangular scales with a deep lemon-yellow color. The formula $(UO_2)_3(PO_4)_2.6H_2O$ was given to the mineral on the basis of an analysis apparently of impure material. These data alone are inadequate to enable the mineral to be recognized with certainty. Fortunately, E. S. Larsen in the first edition of his optical determinative tables (1921, p. 119) cites diagnostic optical data obtained on an authentic specimen borrowed by him. It may be remarked that mineralogists generally are indebted to Professor Larsen for his care in insuring that the voluminous new optical data cited in his Tables were obtained from authentic material.

During the study of an extensive suite of uranium minerals in the Harvard collection, a distinctive and common mineral was recognized which proved to be a hydrated phosphate of uranium and calcium that differed entirely from autunite and meta-autunite, the only other known minerals qualitatively of this composition. This mineral was tentatively identified as phosphuranylite on the basis of Larsen's optical data. *X*-ray study indicated that it was isostructural with dewindtite. Genth's type specimens of phosphuranylite then were borrowed from the part of his personal collection preserved at Pennsylvania State College, and another authentic specimen, labelled as a gift from Genth, was borrowed from

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 316.

Yale University. The latter specimen was that examined by Larsen. The writer wishes to thank Dr. T. F. Bates of Pennsylvania State College and Professor Horace Winchell of Yale University for their courtesy in lending this material for study. Study of this material verified the identification of the mineral at hand as phosphuranylite. A redescription of this species follows.

PHOSPHURANYLITE

Occurrence. Phosphuranylite is a relatively common although inconspicuous mineral that typically occurs in the weathered zone of granite pegmatites. A brief description of the material from the 13 known localities, 12 here described as new, is given in Table 1. It is often associated with autunite or meta-autunite. Less common associates are uranotile, becquerelite, curite, parsonsite and fluorescent hyalite opal. Very commonly the mineral coats irregular cracks in quartz, mica or feldspar in the near vicinity of altered uraninite. In several instances, phosphuranylite was observed as an alteration product of meta-autunite, but it generally is formed earlier than that species. The phosphate content and probably also the calcium content of these species in their pegmatite occurrences appear to be derived principally by the alteration of apatite by meteoric waters in the zone of weathering. The phosphatic solutions thus formed react with uraninite or with intermediate alteration products thereof, such as hydrated oxides, with the formation of the uranium phosphates. Both phosphuranylite and meta-autunite are particularly abundant at the Ruggles pegmatite, Grafton Center, New Hampshire, where apatite occurs in large amounts as a primary mineral immediately associated with uraninite. The uranium silicates uranotile and beta-uranotile, both frequently observed as alteration products or pseudomorphs of uraninite in pegmatites, apparently form when apatite is lacking. The formation of the uranium silicates from uraninite also is preceded by the formation of oxidized-uraninite and of hydrated uranium oxides.

Physical and Optical Properties; Symmetry. Phosphuranylite occurs as thin films or coatings that appear dense, earthy or minutely scaly to the unaided eye, and that are seen to be composed of thin scales with a rectangular outline under the microscope. Macroscopic crystals have not been observed. The color varies from deep golden yellow to rich yellow and is one of the distinctive characters of the substance. The hardness is about 2. The specific gravity, like the hardness difficult to measure because of the mode of aggregation, is about 3.2.

Under the microscope, the mineral appears as irregular or rectangular scales or plates with a perfect cleavage parallel to the flattening. Some

TABLE 1. LOCALITIES FOR PHOSPHURANYLITE

Flat Rock mine, Mitchell County, North Carolina. The Penn State and Yale specimens, and additional specimens from other collections later identified by comparison, consist of smoky or milky quartz, feldspar, muscovite and garnet coated by films of phosphuranylite and meta-autunite. One specimen showed cubical molds of uraninite crystals partly filled with phosphuranylite.

Newry, Oxford County, Maine. A large book of muscovite containing quartz and uraninite along the margins and coated with phosphuranylite along fracture surfaces and in opened cleavages of the mica.

Ruggles mine, Grafton Center, Grafton County, New Hampshire. Films and coatings in fractures and cavities in quartz and feldspar usually near the gummite pseudomorphs after uraninite for which the locality is noted. Found with meta-autunite, parsonsite and a number of other secondary uranium minerals. The indices of refraction vary somewhat in different specimens, with $nZ=1.707$ to 1.716.

Palermo mine, North Groton, Grafton County, New Hampshire. Coatings on aggregates of quartz, muscovite, and kaolinized feldspar containing gummite pseudomorphs. With meta-autunite.

Bedford Hills, Westchester County, New York. Minutely crystalline films on feldspar and quartz, with fluorescent hyalite.

Branchville, Fairfield County, Connecticut. Films and veinlets in altered uraninite. The indices of refraction are relatively high (Table 2) and this material, like that from Urgeirica, may represent a plumbian variety.

Pamplonita, Santander do Norte, Colombia. Earthy films on massive quartz, with meta-autunite. Other specimens from this locality show uraninite altering to curite, schoepite, becquerelite and unidentified minerals.

Carrasca mine, Sabugal, Portugal. Veinlets of flaky phosphuranylite cutting a slab of altered granite whose outer surfaces are thickly incrusted with meta-autunite. The phosphuranylite is admixed with altered (?) meta-autunite of exactly the same specific gravity.

Rosmaneira, Sabugal, Portugal. A slab of deeply altered granite (?) thickly coated with flaky phosphuranylite. The specimen, from the Bello collection, originally was labelled carnotite.

Urgeirica, Cannas de Senhorim, Portugal. A mass of limonitic quartz with drusy cavities containing citron-yellow to brownish yellow microscopic laths and needles mostly clustered in fishbone fashion on crystals of a related mineral. The rectangular laths are beveled by modifying faces. Optically, a zonal growth or mixture of one or several phases with varying indices of refraction. nZ, in part, 1.71–1.72, but mostly 1.72–1.73 and, in part, up to 1.75. All parts of the mixture gave the same x-ray powder pattern. The mixture gave a good test for lead, and probably represents a zoning or intergrowth of plumbian phosphuranylite with dewindtite.

Memoes, near Equador, Rio Grande do Norte, Brazil. Crystalline to earthy films on quartz with meta-autunite and unidentified uranium minerals.

Wölsendorf, Bavaria, Germany. A mass of purple-black fluorite, hematite and quartz with fine-grained crusts of a golden-yellow mineral labelled dewindtite. This represents the dewindtite mentioned by Schoep and Scholz in 1931 as occurring at Wölsendorf. The optical properties, somewhat variable, indicate a mixture or zoning of dewindtite and plumbian phosphuranylite.

TABLE 2. OPTICAL PROPERTIES OF PHOSPHURANYLITE

Pleochroic with X (or E) colorless to pale yellow, Y and Z (or O) golden yellow. Values for $nX \pm .005$, for nY and $nZ \pm .003$.

Locality	Optical Character	2V	*n*X or *n*E	*n*Y	*n*Z or *n*O
Flat Rock mine, North Carolina (Larsen, 1921)	Biaxial—	very small	1.691	1.720	1.720
Flat Rock mine (new data)	Biaxial—	5° to 20°	1.690	1.718	1.718
Mitchell County, North Carolina	Uniaxial—	0°	1.68		1.710
Newry, Maine	Biaxial—, some uniax.—	0° to 5°	1.658	1.699	1.699
Ruggles mine, New Hampshire	Biaxial—	10° to 25°	1.668	1.710	1.710
Palermo mine, New Hampshire			~1.66		1.708
Bedford Hills, New York					1.723
Branchville, Connecticut			1.695		~1.77
Pamplonita, Colombia	Biaxial—	5° to 10°	1.674	~1.724	1.724
Carrasca, Portugal	Biaxial—	5° to 20°	1.669	1.710	1.710
Rosmaneira, Portugal	Biaxial—	15° to 30°	1.660	1.700	1.701
Urgeirica, Portugal	Biaxial—	12° to 22°			1.71 to 1.75
Memoes, Brazil	Biaxial—	10° to 35°	1.660	1.696 to 1.698	1.698
Wölsendorf, Bavaria	Biaxial—	5° to 20°			1.73 to 1.768

material is too fine-grained for satisfactory optical study. The optical character is variable. The mineral rarely is uniaxial negative and ordinarily is biaxial negative with Z always perpendicular to the flattening. 2V is variable, even in material from the same locality, and ranges up to about 35° but usually is small. The biaxial material always shows parallel extinction when crystal outlines are present, and exhibits strong dispersion of the optic axes with $r>v$. The pleochroism is strong, with X (or E) colorless to pale yellow and Y and Z (or O) golden yellow. The indices of refraction are given in Table 2.

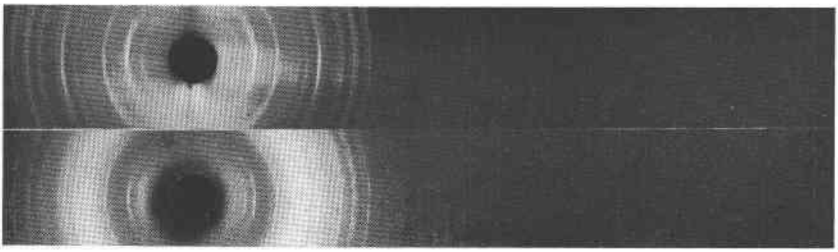

Fig. 1. *X*-ray powder photographs taken in filtered copper radiation of (above) Phosphuranylite from Flat Rock mine, North Carolina, and (below) Dewindtite from Katanga, Belgian Congo.

The occasional uniaxial character and rectangular habit suggests that phosphuranylite may be tetragonal in crystallization. The isostructural mineral dewindtite occurs as microscopic rectangular scales and has been classed as orthorhombic on the basis of the observed biaxial character. The biaxial character of these minerals, however, may be anomalous and is not necessarily indicative of orthorhombic crystallization. This feature may be due to variation in the water content of the crystals. Both autunite and meta-autunite and their analogues are sometimes biaxial with variable 2V due to variation in content of zeolitic water within the limits of stability of the phase, although these species have a tetragonal structure as shown by *x*-ray study (Beintema, 1937, p. 155). The symmetry of phosphuranylite and dewindtite may be tentatively described as tetragonal or orthorhombic, pending *x*-ray study.

The material from Urgeirica, Branchville and Wölsendorf (see Table 2) has relatively high indices of refraction and apparently represents a lead-containing variety in a series toward dewindtite. The latter mineral was described (Schoep, 1925), as biaxial positive with 2E large, $r<v$, and $nX=1.762$, $nY=1.763$. A re-examination here of material from Katanga gave the following results: biaxial negative with moderate 2V and $r>v$; $nX=1.760$ (colorless), $nY=1.768$ (golden yellow), $nZ=1.770$ (golden yellow); Z perpendicular to the plane of flattening.

X-ray Powder Pattern, Systematic Relations. The x-ray powder pattern of phosphuranylite is practically identical with that of dewindtite (Fig. 1) The pattern differs entirely from those of the autunite and meta-autunite groups and from all other uranium phosphates and arsenates with the possible exception of renardite and troegerite. Authentic specimens of the two latter minerals were not available for comparison; most specimens labelled troegerite so far examined in detail have proved to be saléeite, uranospinite or hydrogen-uranospinite. The powder spacing data for phosphuranylite and dewindtite are given in Table 3.

TABLE 3. X-RAY POWDER SPACING DATA FOR PHOSPHURANYLITE AND DEWINDTITE. COPPER RADIATION, NICKEL FILTER (IN Å)

The measured values of d for the two minerals can be taken as identical for all practical purposes. The data here given were measured on phosphuranylite. Different specimens of this mineral show slight differences in detail, notably in a blurring together of lines 11 and 12, 13 and 14, 15 and 16, and in the appearance of very faint, variable extra lines in the region from lines 5 to 18. Line 2 may appear as a doublet due to absorption. Lines beyond no. 49 are omitted.

No.	*d*	*I*	No.	*d*	*I*	No.	*d*	*I*	No.	*d*	*I*
1	10.163	1	13	3.440	1	25	2.156	1	37	1.585	1
2	7.830	10	14	3.363	6	26	2.099	½	38	1.537	2
3	7.196	½	15	3.121	6	27	2.080	2	39	1.506	½
4	6.326	1	16	3.069	4	28	2.040	1	40	1.433	1
5	5.829	8	17	2.940	2	29	2.002	1	41	1.375	1
6	5.372	½	18	2.858	6	30	1.895	5	42	1.358	½
7	4.955	1	19	2.706	1	31	1.852	1	43	1.304	1
8	4.720	2	20	2.585	1	32	1.828	1	44	1.282	1
9	4.332	3	21	2.455	1	33	1.771	1	45	1.252	1
10	4.250	½	22	2.430	2	34	1.719	3	46	1.236	½
11	3.969	9	23	2.243	½	35	1.672	½	47	1.209	½
12	3.834	1	24	2.212	1	36	1.656	1	48	1.197	½
									49	1.179	1

Phosphuranylite contains calcium and ordinarily no lead. Its formula should be analogous to that of dewindtite:

Phosphuranylite	$Ca_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$
Dewindtite	$Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$

Partial analyses of phosphuranylite cited in the following section, however, do not agree with this interpretation.

Chemical Composition. Genth's original analysis of the North Carolina mineral reported 4.40 per cent PbO and CaO apparently was not sought. The lead was deducted by Genth as due to admixture of cerussite, although the actual presence of cerussite was not shown, and the formula of the mineral was derived as $(UO_2)_3(PO_4)_2.6H_2O$. A qualitative chemical re-examination of Genth's material shows that lead is absent and that the mineral is in fact a hydrated phosphate of uranium and calcium. Sufficient material was not available for a quantitative analysis of the type material but partial analyses were obtained of specimens from other localities. The results of these analyses, cited in Table 4, are not very consistent and, further, depart somewhat from the ratios expected on the basis of the isostructural relation to dewindtite. Analysis 3, probably the best of those available, approximates to the formula:

TABLE 4. CHEMICAL ANALYSES OF PHOSPHURANYLITE

	1	2	3	4	5	6	7
CaO		3.40	2.3	2.6	2.19	2.74	8.02
PbO	4.40	tr.	tr.	tr.			
UO_3	71.73	72.25	76.4		78.26	70.72	68.15
P_2O_5	11.30	10.55	11.1	10.0	11.10	14.05	13.53
H_2O	10.48	[12.85]	[8.4]		8.45	12.49	10.30
Insol.		0.95	1.8				
Total	97.91	[100.00]	[100.0]		100.00	100.00	100.00

1. Flat Rock mine, North Carolina. Genth, 1879.
2. Carrasca, Portugal. Hallowell, 1949. Contains about 10 per cent of admixed meta-autunite.
3. Rosmaneira, Portugal. Hallowell, 1949. Analysis on 200 mg.
4. Ruggles mine, New Hampshire. Hallowell, 1949. Analyses on 35 mg.
5. $Ca(UO_2)_7(PO_4)_4(OH)_4 \cdot 10H_2O$.
6. $Ca(UO_2)_5(PO_4)_4(H_2O)_4 \cdot 10H_2O$ or $CaH_4(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$.
7. $Ca_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$.

$$Ca(UO_2)_7(PO_4)_4(OH)_4.10H_2O.$$

The most interesting feature of the analyses is the large deficiency of Ca from that expected on the basis of the relation to dewindtite (column 7, Table 4). Possibly the structure of phosphuranylite is like that of dewindtite but with some of the Ca positions vacant, such as occurs in autunite. The latter substance forms an apparently complete series from the ideal composition $Ca(UO_2)_2(PO_4)_2.10H_2O$ to hydrogen-autunite, $H_2(UO_2)_2(PO_4)_2.10H_2O$, either by base-exchange of crystals immersed in acid solutions or by direct crystallization from Ca-deficient acid solutions. The analyses of phosphuranylite, however, do not support this interpretation (column 6, Table 4) and the exact composition of the mineral remains problematic.

Synthesis. Efforts to synthesize phosphuranylite by reaction of water solutions containing uranyl sulfate or acetate, phosphoric acid or trisodium phosphate, and calcium chloride or acetate have proven unsuccessful. The reactions were carried out both at room temperature and at 90°. The precipitates obtained proved in all instances to be phases that resembled meta-autunite.

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