STUDIES OF RADIOACTIVE COMPOUNDS: VII—PHOSPHURANYLITE AND DEWINDTITE

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ABSTRACT

Phosphuranylite from Urgeirica, Portugal is orthorhombic, *Bmmb* with *a* 15.85, *b* 17.42, *c* 13.76 Å. Dewindtite from Kasolo, Belgian Congo is isostructural as shown by Frondel (1950), with *a* 16.00, *b* 17.62, *c* 13.66 Å. Calculations of unit cell contents do not lead to unique chemical formulas for the minerals. Available chemical analyses suggest that the chemical formulas of phosphuranylite and dewindtite are not analogous.

Recently Frondel (1950) found a remarkable similarity in the *x*-ray powder patterns of phosphuranylite and dewindtite and suggested that the two minerals are isostructural and exhibit at least partial isomorphous replacement between calcium (phosphuranylite) and lead (dewindtite). Three incomplete analyses by Hallowell (in Frondel) on minute quantities however, led to the formula $Ca(UO_2)_7(PO_4)_4(OH)_4 \cdot 10H_2O$ for phosphuranylite in contrast to the accepted formula for dewindtite $Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$ (Dana, 1951).

Frondel's material was unsuitable for single crystal *x*-ray studies and as a result the calculation of unit cell contents which might have explained this discrepancy, could not be made. An opportunity to provide these data came to us when we obtained a small specimen from Urgeirica, Portugal showing numerous tiny laths of phosphuranylite.

The optical properties of this specimen were found to be biaxial negative, $2V$ small, indices of refraction for Na light: nX 1.669 (pale yellow), nY 1.710 (golden yellow), nZ 1.710 (golden yellow). They are in good agreement with the optical constants given by Frondel for phosphuranylite from the Ruggles Mine, New Hampshire and from Carrasca, Portugal. The indices of lead-bearing phosphuranylite are substantially higher. A spectrographic analysis of our specimen showed only a trace of lead. A tiny lath gave the following data from *x*-ray rotation and Weissenberg films: orthorhombic, *Bmmb*; *a* 15.85, *b* 17.42, *c* 13.76 Å. In this orientation the direction of elongation is parallel to [001] and the flattening is parallel to (100) or (110).

The specimen of dewindtite which was available to us proved to be fine-grained and without visible crystal form. Close examination showed that it was interlayered with meta-torbernite. A few small grains of pitchblende were seen as well as a considerable quantity of an orange

mineral of about the same specific gravity as dewindtite. It was practical to separate only enough dewindtite for x-ray powder study.

X-ray powder patterns with copper radiation[1] and using a camera of diameter 114.59 mm. were now prepared of both minerals. The pattern of phosphuranylite was indexed with the aid of the cell constants derived by the Weissenberg study to $d=2.88$ Å. The practically identical dewindtite pattern was then indexed by analogy with phosphuranylite (Table 1). The spacings for three planes ($d_{400}=4.00$, $d_{204}=3.14$, $d_{440}=2.96$

TABLE 1. X-RAY POWDER DATA

PHOSPHURANYLITE			hkl	DEWINDTITE		
I	d(meas.)	d(calc.)		I	d(meas.)	d(calc.)
3	10.34	10.39	101			
10	7.91	7.92	200	10	8.01	8.00
5	5.83	5.86	220	10	5.89	5.92
½	4.92	4.93	301, 212	2	4.99	4.97, 4.98
2	4.73	4.75	311	2	4.77	4.78
3	4.42	4.44, 4.41	032, 103	4	4.37	4.38
1	4.30	4.29	321			
6	3.96	3.96	400	7	4.00	4.00
3	3.88	3.87	232	1	3.90	3.89
3	3.81	3.82	240	1	3.86	3.86
2	3.44	3.44, 3.43	004, 402			
1	3.37	3.38, 3.37	014, 412	5	3.40	3.39
6	3.15	3.16	204	7	3.14	3.14
6	3.10	3.11, 3.10, 3.10, 3.09	052, 214, 143, 501, 511	5	3.07	3.09, 3.07
1	2.93	2.93	440	5	2.96	2.96
6	2.88	2.90, 2.89, 2.85	060, 252, 351	9	2.88	2.87

Å) were used to calculate the cell dimensions: a 16.00, b 17.62, c 13.66 Å. Although care was taken to obtain an undistorted x-ray powder pattern and corrections were made for the personal error in measurement, the values probably have an error of about ± 0.1 Å because only the low

[1] Using Cu $K\alpha=1.5418$ Å.

order reflections could be indexed with assurance and used for the calculations.

The specific gravity of phosphuranylite is not accurately known. Frondel set the value at about 3.2; Branche, Chervet & Guillemin (1951) stated that it sank in methylene iodide of density 3.31. Schoep (1922) determined the specific gravity of dewindtite crystals as 5.03 at 17° C. with a pycnometer.

The chemical composition of phosphuranylite, like the specific gravity, is difficult to determine accurately. This difficulty lies in the problem of obtaining sufficient material free from contamination. Two of the three partial analyses of Hallowell are reproduced in Table 2 (IA, IB) after subtracting insoluble matter and recalculating to 100%. The unit cell

TABLE 2. PHOSPHURANYLITE, ANALYSES AND UNIT CELL CONTENTS

	Analysis A				*Analysis B*			
	I	II	III	IV	I	II	III	IV
CaO	3.43	4.9	5.6	6	2.3	3.3	3.8	4
UO_3	72.94	20.4	23.3	24	77.8	22.3	25.5	24
P_2O_5	10.65	6.0	6.9	6	11.3	6.4	7.3	8
H_2O	[12.98]	57.7	66.0	66	[8.6]	38.2	43.7	44
			calc. S. G.=	4.03				3.94

I. The chemical analyses of Hallowell (nos. 2 & 3 in Frondel, 1950) recalc. to 100% after subtracting insol. II. Calc. unit cell contents for assumed S. G. of 3.5. III. Calc. unit cell contents for assumed S. G. of 4.0. IV. Possible ideal unit cell contents.

contents have been calculated for an assumed specific gravity of 3.5 (IIA, IIB) and 4.0 (IIIA, IIIB). The most probable cell contents for analysis A (IVA) are

$$6CaO \cdot 24UO_3 \cdot 6P_2O_5 \cdot 66H_2O \text{ or } 6[Ca(UO_2)_4(PO_4)_2(OH)_4 \cdot 9H_2O]$$

which have a calculated specific gravity of 4.03. Analysis B (IVB) suggests the cell contents

$$4CaO \cdot 24UO_3 \cdot 8P_2O_5 \cdot 44H_2O \text{ or } 4[Ca(UO_2)_6(PO_4)_4(OH)_2 \cdot 10H_2O]$$

The calculated specific gravity is 3.94.

The analyses of dewindtite by Schoep (1925) are reasonably consistent. The most recent of these analyses is presented in Table 3 (I) and recalculated to 100% (II). The calculated unit cell contents (III) using Schoep's measured specific gravity, 5.03 suggest three alternative ideal cell contents

IV: $4[Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O]$
V: $4[Pb_3(UO_2)_6(PO_4)_4(OH)_6 \cdot 10H_2O]$
VI: $6[Pb_2(UO_2)_4(PO_4)_3(OH)_3 \cdot 7H_2O]$

TABLE 3. DEWINDTITE, ANALYSIS AND UNIT CELL CONTENTS

	I	II	III	IV	V	VI
PbO	24.85	25.43	13.3	12	12	12
UO_3	54.80	56.08	22.9	20	24	24
P_2O_5	10.14	10.38	8.5	8	8	9
H_2O	7.93	8.11	52.6	48	52	51
	97.72	100.00	calc. S.G. = 4.54		5.01	5.06

I. Chemical analysis by Schoep (1925). II. Analysis recalc. to 100%. III. Unit cell contents calculated for analysis. IV. $4[Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O]$, calc. S.G. = 4.54. V. $4[Pb_3(UO_2)_6(PO_4)_4(OH)_6 \cdot 10H_2O]$, calc. S.G. = 5.01. VI. $6[Pb_2(UO_2)_4(PO_4)_3(OH)_3 \cdot 7H_2O]$, calc. S.G. = 5.06.

The first formula is identical with the generally accepted formula. The calculated specific gravity 4.54, is so much lower than the measured value that this formula may be ruled out of consideration. The calculated specific gravities for the remaining two formulas (5.01 and 5.06 respectively) agree closely with the measured gravity. The cell contents are equally compatible with the calculated cell contents for Schoep's analysis. The calculations therefore, do not lead to a unique choice for the cell contents for either phosphuranylite or dewindtite.

Neither dewindtite formula is strictly analogous to either of the possible phosphuranylite formulas although there is some similarity. The main difficulty is with the lead and calcium content. The lead in dewindtite is much higher relative to other constituents than is the calcium of phosphuranylite. At this time it is not possible to say whether the discrepancy in the formulas of the two minerals is real or is due to the difficulty of obtaining accurate chemical data.

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REFERENCES

BRANCHE, G., CHERVET, J. & GUILLEMIN, C. (1951): Nouvelles espèces uranifères françaises, *Soc. franç. minéral., Bull.*, **74**, 457.

DANA, J. D. & E. S. (1951): *System of Mineralogy*, **2**, ed. 7, by C. Palache, H. Berman & C. Frondel, New York.

FRONDEL, C. (1950): Studies of uranium minerals (V): Phosphuranylite, *Am. Mineral.*, **35**, 756.

SCHOEP, A. (1925): Nouvelles recherches sur la dewindtite. *Soc. franç. minéral., Bull.*, **48**, 77.