

STUDIES OF URANIUM MINERALS (XXII): SYNTHETIC CALCIUM AND LEAD URANYL PHOSPHATE MINERALS*

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ABSTRACT

The uranium minerals phosphuranylite, renardite, "dewindtite," dumontite, parsonsite and the phase lead-autunite have been investigated synthetically to establish identity and the conditions of deposition. In the acid range, autunite and parsonsite predominate. Under neutral and alkaline conditions, there exist a number of renardite-type phases of variable lead content with closely related x -ray spectra and properties. It is suggested that "dewindtite" be discredited as a distinct mineral species. A phase has been prepared that corresponds chemically but is not identical to dumontite on the basis of limited, existing data on the mineral. The methods of synthesis and resultant phases in the systems calcium- and lead-uranyl-phosphate-water are described. Chemical, optical and x -ray data are included.

I. PRE-EXISTING PHASE DATA

(a) *System: Calcium-Uranyl-Phosphate-Water.* The mineral phases that have been described earlier in the system are: autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12 \text{H}_2\text{O}$; meta-autunite-I, containing $2.5\text{--}6.5 \text{H}_2\text{O}$; meta-autunite-II, with $0\text{--}6 \text{H}_2\text{O}$ (1, 6, 11) and phosphuranylite, $\text{Ca}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ (2, 5, 8, 10). Blinkoff (4) described the preparation of a yellow, tetragonal phase that may be chemically analogous to "dewindtite."

(b) *System: Lead-Uranyl-Phosphate-Water.* The minerals encountered in the system are: renardite, $\text{Pb}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot 7 \text{H}_2\text{O}$ (isostructural with phosphuranylite) (3, 9, 15); "dewindtite" (8, 10, 14); dumontite (14, 15); and parsonsite $\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (3, 5, 13, 15).

The chemical analysis of "dewindtite" (14) implies a phase that is chemically distinct from renardite, but the x -ray data (8, 9, 10) indicate that they are isostructural. Bignand (2) compared specimens of the two minerals and inferred that they are identical, but suggested further studies. Lead-autunite, never previously described as a mineral occurrence, was prepared by Fairchild (6).

II. DISCUSSION OF PHASE RELATIONS

The systems calcium- and lead-uranyl-phosphate-water were surveyed for mineral relationships. The phase relations are closely similar in the two systems and may be generalized in the same diagram, Fig. 1. At high concentrations of uranyl-ion, calcium and lead may be considered

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synonymous. The phases observed in both systems tend to be isostructural. Due to the complexity of a four-component system, the phase relations in Fig. 1 have been reduced for simplicity to express the relative acidity, alkalinity and cation (uranyl to calcium or lead) concentrations. The numerical values refer to the concentrations of the entire system. In this respect, the compositions of the lead phases bear a linear relation to the compositions of the system as a whole; while proportionately less calcium is found in the solid phases of the system calcium-uranyl-phosphate owing to the greater solubility of the latter ion. All solid phases

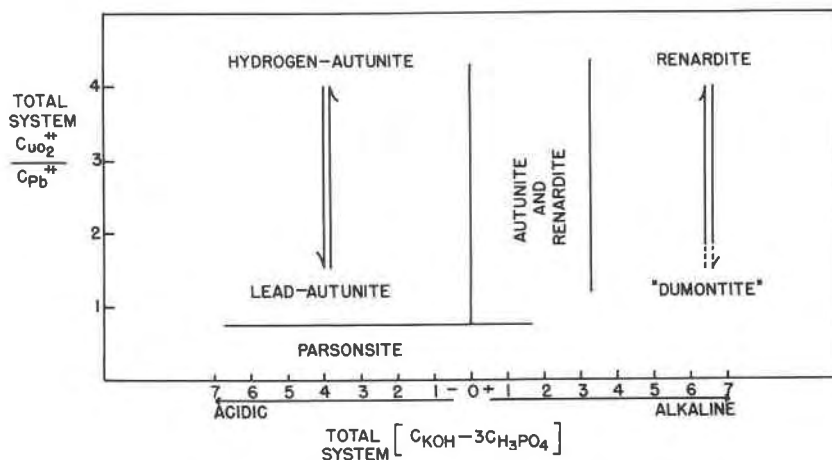


FIG. 1. Phase relations in the system: lead-uranyl-phosphate-water, as functions of the acidity, alkalinity and relative cation concentrations.

have been referred to the general formula, $\text{Pb}_x(\text{UO}_2)_y(\text{PO}_4)_z(\text{OH})_z \cdot n\text{H}_2\text{O}$. The methods of synthesis and resultant phases and the chemical, optical and *x*-ray data are included in section III.

(a) *System: Calcium-Uranyl-Phosphate-Water.* The phases of mineralogical importance that have been observed are hydrogen-autunite, calcium-autunite, phosphuranylite and a calcium-derivative of parsonsite. The stable acid phases are hydrogen-autunite (12), which is formed at high concentrations of uranyl ion; calcium-autunite at intermediate concentrations of calcium- and uranyl-ion; and a calcium derivative of parsonsite at greater calcium concentration. In the alkaline region, only phosphuranylite was observed to form.

(b) *System: Lead-Uranyl-Phosphate-Water.* The phases studied in this system, depicted in Fig. 1, are hydrogen-autunite, lead-autunite, renardite ("dewindtite"), *D-I* (a new phase with similarities to dumontite) and parsonsite. At high concentrations of uranyl ion (UO_2/Pb ratio of approximately 4.0), the stable phase is hydrogen-autunite under acid

conditions. Renardite is formed in the absence of free acid over a wide alkaline range and coexists with hydrogen-autunite in the neutral region. At higher lead concentrations, lead-autunite is observed to form and appears to crystallize in a partial series with hydrogen-autunite. (Inter-layering rather than isomorphism is more probable in view of the cation differences.) The pure lead phase is formed when the ratio of UO_2/Pb is 2.0 in the acid range of pH 1.5 to 4.0. Parsonsite is stable in acid to neutral solutions (pH 2 to 6) at high lead concentrations (UO_2/Pb ratio less than or equal to one-half). In the weakly alkaline region, renardite has been found to coexist with hydrogen- or lead-autunite at compositions similar to that of "dewindtite." The latter name should probably be discredited as representative of a single mineral species.

Approaching higher lead concentrations, a series of renardite-like phases of variable lead content have been observed to form. This series of structurally related phases, from chemical analyses, x-ray and optical evidence (Section III) appears to extend from renardite $\text{Pb}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot n\text{H}_2\text{O}$ to the phase, $\text{Pb}_3(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$, which is chemically and optically related to dumontite. The remaining portions of these systems have not been investigated since they do not include important minerals. It appears that most of the complex calcium and lead-uranyl phosphates are deposited under acid or neutral conditions, and that extremely low phosphoric acid concentrations are sufficient.

III. PREPARATION AND DESCRIPTION OF SYNTHETIC PHASES

(a) *System: Calcium-Uranyl-Phosphate-Water.* The syntheses and chemical analyses* of phases observed in this system are arranged in Table 1.

1. *Phosphuranylite.* Phosphuranylite was prepared from mildly acid to strongly alkaline solutions using relatively high concentrations of uranyl ion. Optically it is orthorhombic, biaxial negative, $\alpha = 1.656 \pm .001$

I/I_0	$d_{\text{meas.}}$	hkl	I/I_0	$d_{\text{meas.}}$	hkl
1	10.34	101	3	3.427	004, 402*
10 b.	7.90	200*	3	3.153	204
1—	6.33	012	5	3.058	501, 511
3	5.83	220	1	2.942	432, 440
$\frac{1}{2}$	4.93	301, 212	4	2.863	351, 060, 252
3	4.38	032, 103, 040*	1 b.—	2.49	602
5 b.	3.97	400	1 b.	2.43	612
3 b.	3.83	410			

b—broad line.

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TABLE 1. ARTIFICIAL SYNTHESIS IN THE SYSTEM: CALCIUM-URANYL-PHOSPHATE-WATER

Synthesis	Components of aqueous system, mols per liter	Procedure	Resultant Phase(s) and Final Solution pH	Partial Chemical Analysis*	Equivalent Formula
1. Phosphuranylite	0.01 $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ 0.04 $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ 0.02 $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ 0.04 KOH	Colloidal precipitate digested 40 hrs. at 100° C. Base-exchanged in dil. $\text{Ca}(\text{NO}_3)_2$ solution, two weeks.	Phosphuranylite, finely crystalline, light yellow. pH = 5	% Ca— 3.14 U—61.6 P— 4.10	$\text{Ca}_4(\text{UO}_2)_4(\text{PO}_4)_4(\text{OH})_4 \cdot 8 \text{H}_2\text{O}$
2. Blinkoff's compound—I	CaHPO_4 (super-saturated) $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Ref. Section I)	Precipitated at 60° C.	Hydrogen-calcium derivative of parsonite, light greenish-yellow crystalline. pH = 1	% Ca— 7.92 U—43.0 P— 9.59	$\text{Ca}_3\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10 \text{H}_2\text{O}$
3. Blinkoff's compound—II	$\text{Ca}_3(\text{PO}_4)_2$ (1) HNO_3 $\text{UO}_2(\text{NO}_3)_2$ (6) (Ref. Section I)	Sealed hydrothermal at 200°.	Hydrogen-autumite. pH = 1	% Ca— 0.00 U—51.4 P— 6.43	$\text{HUO}_2\text{PO}_4 \cdot 6 \text{H}_2\text{O}$
SYSTEM: BARIUM-URANYL-PHOSPHATE-WATER					
4. Barium-Phosphuranylite	0.01 $\text{Ba}(\text{NO}_3)_2$ 0.04 $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ 0.02 $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ 0.04 KOH	Digestion 40 hrs. at 100° C. Base exchange in dil. $\text{Ba}(\text{NO}_3)_2$ solution.	Barium-phosphuranylite, coarsely crystalline, lemon yellow.	—	$\text{Ba}_2(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ (postulated)

* Water, calculated by difference.

(pale yellow), $\beta = 1.689$ (golden yellow), $\gamma = 1.691$ (golden yellow). $2V$ is approximately 20° . X-ray powder data obtained in $\text{CuK}\alpha$ radiation on the recording diffractometer are given below. The phase is orthorhombic with cell dimensions $a = 15.8 \text{ \AA}$, $b = 17.5 \text{ \AA}$, $c = 13.7 \text{ \AA} \pm 0.1 \text{ \AA}$, calculated from the starred reflections for space group $Bmmb$.

2. *Blinkoff's Compound I.* (Hydrogen-calcium parsonsite derivative?). An attempt was made to repeat Blinkoff's original synthesis, incompletely described in the literature (4). The resulting acidic phase was found to be structurally similar to parsonsite, having the same relative uranyl-phosphate ratio. The original phase may have been formed under more alkaline conditions as indicated by the reported composition $-3\text{Ca}0.5\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$. Optically, it is uniaxial negative. $n = 1.559 \pm .001$, $\omega = 1.561$ (elongation). X-ray powder data obtained in $\text{CuK}\alpha$ radiation on the recording diffractometer are as follows:

I/I_0	$d_{\text{meas.}}$	I/I_0	$d_{\text{meas.}}$
6	11.79	8	2.191
4	7.25	1	1.765
10	6.862	4	1.707
2	4.54	5	1.647
2	3.85	1	1.530
1	3.66	1	1.512
9	3.378	3	1.365
2	2.73	2	1.316
4	2.270		

3. *Blinkoff's Compound II.* (Hydrogen-autunite). A hydrothermal synthesis of the previous phase was also described. (4). "Quadratic platelets" of the latter were formed at 200°C . from a nitric acid solution of calcium and uranyl nitrates. In the present interpretation, the phase obtained was hydrogen-autunite (12), as might be anticipated from the concentrations of the reagents and the high acidity.

Analogues. Attempts were made to synthesize the calcium-analogues of the lead-minerals "dewindtite" (Blinkoff's Phase?) and dumontite under the same conditions of acidity and concentration that were used to form the corresponding lead phases. The phases formed were autunite and phosphuranylite, respectively.

Barium-Phosphuranylite. A barium-analogue of phosphuranylite (and renardite) was prepared in a similar manner (Table 1). The renardite samples analyzed by Cuttitta in Frondel (11) contained slightly less than one per cent barium oxide. Optically, barium-phosphuranylite is ortho-

rhombic, biaxial negative, $\alpha = 1.660 \pm .001$, $\beta = 1.690$, $\gamma = 1.695$. X-ray powder data were obtained in $\text{CuK}\alpha$ radiation on the recording diffractometer. The phase is orthorhombic, with probable space group $Bmmb$ and the calculated elements $-a = 16.2 \text{ \AA}$, $b = 17.7 \text{ \AA}$, $c = 13.9 \text{ \AA}$.

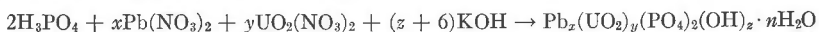
I/I_0	d_{meas}
5 b.	8.0
3 b.	5.9
2 d.	6.46
4	4.412*
7	3.83
5	3.47*
4 d.	3.18
10	3.08
7	2.88
5	2.13

(b) System: *Lead-Uranyl-Phosphate-Water*. To simplify the stoichiometry, all member phases were reduced to the general formula: $\text{H}_w(\text{Pb}_x(\text{UO}_2)_y(\text{PO}_4)_z(\text{OH})_z \cdot n\text{H}_2\text{O})$. To prepare the above phases, the

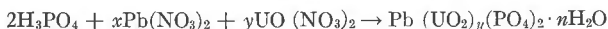
Ratio	Phase	
UO_2/Pb	Acid range	Alkaline range
4.00	—	Renardite (9) $\text{Pb}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot 7 \text{ H}_2\text{O}$
2.00	Lead-autunite (6) $\text{Pb}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 \text{ H}_2\text{O}$	"Dewindtite" (10) $\text{Pb}_{1.5}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5 \text{ H}_2\text{O}$
2.00	—	"Dewindtite" (10) $\text{Pb}_{1.33}(\text{UO}_2)_{2.66}(\text{PO}_4)_2(\text{OH})_2 \cdot 4.6 \text{ H}_2\text{O}$
1.67	—	"Dewindtite" (14) $\text{Pb}_{1.5}(\text{UO}_2)_{2.5}(\text{PO}_4)_2(\text{OH})_2 \cdot 5 \text{ H}_2\text{O}$
1.50	—	Dumontite (14, 15) $\text{Pb}_2(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_4 \cdot 3 \text{ H}_2\text{O}$
0.50	Parsonsite (3, 7) $\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2 \cdot 2 \text{ H}_2\text{O}$	—

stoichiometric equivalent amounts of phosphoric acid, lead and uranyl nitrates and potassium hydroxide were combined in aqueous solution.

The existence of free acid in solution appeared to prevent the formation of the hydroxylated phases. Synthesis were carried out with just enough base to neutralize the free acid, assuming that phosphoric acid completely dissociated as a tribasic acid. The formation of the hydroxylated phases is expressed by the equation:



and for the acid members, by the methathesis:



The various synthetic phases and partial chemical analyses are listed in Table 2.

1. *Renardite*. The synthesis of renardite proceeded in the manner described for hydroxylated members (Table 2). The crystallinity was improved by the presence of potassium hydroxide and a trace amount of hydrochloric acid. On adding larger amounts of acid, hydrogen-autunite was observed to form. Optically, renardite is orthorhombic, biaxial negative, $\alpha = 1.715$ (pale yellow), $\beta = 1.735$ (yellow), $\gamma = 1.738$ (yellow), $2V$ large. X-ray powder data were obtained in $\text{CuK}\alpha$ radiation on the recording diffractometer. The calculated elements are $a = 15.9 \text{ \AA}$, $b = 17.6 \text{ \AA}$, $c = 13.8 \text{ \AA}$.

I/I_0	d_{meas}
$\frac{1}{2}$	9.94
7 b.	7.76-7.95†
2	6.42
6 b.	5.79
8	4.39*
9 b.	3.87
7	3.453*
8	3.153
10	3.069
8	2.858
3	2.137

† Dependent upon hydration.

2. "*Dewindtite*." The validity of "dewindtite" as a separate species is in doubt, as it appears to be structurally identical to renardite, but chemically different. Using the initial compositions listed in Table 2, one commonly observes the two phases lead-autunite and renardite which coexist at equilibrium at the composition attributed to "dewindtite" by Schoep.

3. *Dumontite*. Precise chemical and crystallographic specifications on dumontite were lacking. An examination of a minute sample of the

TABLE 2. ARTIFICIAL SYNTHESIS IN THE SYSTEM: LEAD-URANYL-PHOSPHATE-WATER

Synthesis	Components of aqueous system, mols per liter	Procedure	Resultant Phase(s) and final solution pH	Partial Chemical Analysis*	Equivalent Formula
1a. Renardite I.	0.01 Pb(NO ₃) ₂ 0.04 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.02 Na ₃ PO ₄ · 12 H ₂ O 0.04 KOH	Digestion 48 hrs. at 100° C. Base-exchanged 1:1 dil. Pb(NO ₃) ₂ solution two weeks.	Renardite, finely crystalline, yellow-orange, pH = 5	% Pb—10.9 U—57.1 P—4.00	Pb(UO ₂) ₂ (PO ₄) ₂ (OH) ₁ · 8 H ₂ O
1b. Renardite II.	As above, with additional: 0.005 Pb(NO ₃) ₂ and hydrochloric acid	*	Renardite and hydrogen-autunite, pH = 3	% Pb—6.50 U—57.7 P—4.67	Pb(UO ₂) ₂ (PO ₄) ₂ (OH) ₁ · n H ₂ O and (2) UO ₂ HPO ₄ · (16-n) H ₂ O
2a. "Dewindrite" I.	0.01 Pb(NO ₃) ₂ 0.03 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.02 Na ₃ PO ₄ · 12 H ₂ O 0.04 KOH	*	Renardite—type, pH = 4+	—	—
2b. "Dewindrite" II.	0.01 Pb(NO ₃) ₂ 0.02 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.02 Na ₃ PO ₄ · 12 H ₂ O 0.04 KOH	*	Dumonite-type, pH = 7+	—	—
2c. "Dewindrite" III.	0.01 Pb(NO ₃) ₂ 0.04 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.02 Na ₃ PO ₄ · 12 H ₂ O 0.02 KOH	*	Autunite, trace of renardite, pH = 4—	—	—
2d. "Dewindrite" IV. (Hogarth and Nuffield Formula)	0.0133 Pb(NO ₃) ₂ 0.0266 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.0200 Na ₃ PO ₄ · 12 H ₂ O 0.0200 KOH	*	Lead-autunite and renardite, pH = 4+	% Pb—15.3 U—48.3 P—4.05	Pb(UO ₂) ₂ (PO ₄) ₂ (OH) ₁ · n H ₂ O and Pb(UO ₂) ₂ (PO ₄) ₂ · (12-n) H ₂ O
2e. "Dewindrite" V. (Schoep Formula)	0.015 Pb(NO ₃) ₂ 0.025 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.020 Na ₃ PO ₄ · 12 H ₂ O 0.020 KOH	*	Lead-autunite and renardite, pH = 5—	—	—
3a. Dumonite I. (D-I)	0.020 Pb(NO ₃) ₂ 0.030 UO ₂ Cl ₂ 0.020 Na ₃ PO ₄ · 12 H ₂ O 0.040 KOH	*	Dumonite-type, fine powder, light orange, pH = 4—5	% Pb—22.9 U—47.3 P—4.14	Approaching Pb ₂ (UO ₂) ₂ (PO ₄) ₂ (OH) ₁ · 5 H ₂ O
3b. Dumonite II. (D-II)	0.020 Pb(NO ₃) ₂ 0.030 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.020 K ₂ PO ₄ 0.040 KOH	*	Renardite-type, fine powder, light orange, pH = 4	% Pb—16.6 U—56.9 P—4.08	Approaching Pb(UO ₂) ₂ (PO ₄) ₂ (OH) ₁ · 2 H ₂ O
4. Lead-meta-autunite	0.010 Pb(NO ₃) ₂ 0.030 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.020 H ₂ PO ₄	Precipitation at 50° C. Precipitation at room temperature (refer to text)	Lead-meta-autunite, micro-square, yellow crystals, pH = 1	% Pb—19.9 U—46.0 P—5.58	Pb(UO ₂) ₂ (PO ₄) ₂ · 6.5 H ₂ O and Pb(UO ₂) ₂ (PO ₄) ₂ · 8 H ₂ O (Room Temperature)
5. Parsonite	0.020 Pb(NO ₃) ₂ 0.010 UO ₂ (NO ₃) ₂ · 6 H ₂ O 0.020 H ₂ PO ₄	*	Parsonite, pale yellow finely crystalline, pH = 1—2	—	—

* Water, calculated by difference.

mineral from Katanga revealed the presence of green torbernite and a colloidal orange phase. From the matrix, a microscopic, yellow prismatic crystal was separated for x -ray analysis. Optically, it was found to be orthorhombic, biaxial positive. Prismatic [001] elongated. $\alpha = a = 1.88$ (pale yellow), $\beta = c = 1.89$, $\gamma = b = 1.90$ (deep yellow) (14), (15). X -ray data for the mineral were obtained from Weissenberg photographs using $\text{CuK}\alpha$ radiation. It was found to be orthorhombic with the Laue symmetry: $mmmC\cdots$, $a = 8.57 \text{ \AA}$, $b = 11.01 \text{ \AA}$, $c = 6.93 \text{ \AA} \pm 0.01 \text{ \AA}$. The calculated specific gravity = 3.86 for $Z = 1[\text{Pb}_3(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}]$. The measured specific gravity was variable: 3.82 (most homogeneous sample). On the basis of this unit cell, some of the x -ray powder reflections were not indexable, but could be attributed to the orange component if it were a renardite-type phase. The synthetic phases obtained in the compositional range of dumontite were orange colored, poorly crystalline (Table 2) and structurally similar to renardite. Phase D-1 was observed to be chemically and optically similar to dumontite; phase D-2 chemically and optically comparable to renardite. The x -ray data are given beyond.

In general, the alkaline syntheses at various lead concentrations yielded a series of renardite-type phases of variable composition. These alkaline phases are orthorhombic, biaxial negative, with the exception of D-1, which is positive. The mean refractive index has been observed to increase with increasing lead content.

Relative Concentration	Mean Index*
1. $[\text{UO}_2/\text{Pb}] = 4.0$ $[\text{OH}] = 4.0$	~ 1.73 (Renardite)
2. $[\text{UO}_2/\text{Pb}] = 2.0$ $[\text{OH}] = 4.0$	~ 1.76 (Corresponding to natural "dewindtite")
3. $[\text{UO}_2/\text{Pb}] < 2.0$ $[\text{OH}] = 4.0$	~ 1.78
(D-1)	1.775 (Positive)
(D-2)	1.76-1.78

* Indices of 1.8 and greater have been found on partially dehydrated samples.

X -ray powder data for phases obtained during the dumontite syntheses were obtained on the recording diffractometer in $\text{CuK}\alpha$ radiation.

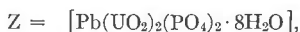
D-1		D-2.	
I/I_0	$d_{meas.}$	I/I_0	$d_{meas.}$
4	7.63 (poorly crystalline)	5 b.	7.69
7 b.	6.81	7	6.97
4	4.58	1	6.41
3	4.10	5 b.	5.68
10	3.460	4	4.44
9	3.10	9	3.850
8	2.98	10	3.520
7	2.95	8 b.	3.10
6	2.87		

Regarding the cell parameters of the variable renardite-type phases, two trends were noted:

1. The d_{200} spacing for the cation ratio $[\text{UO}_2/\text{Pb}] = 4.0$ decreases from 7.95 Å. in the less alkaline region (Fig. 1) to 7.56 Å at higher basicity. (Net $[\text{OH}]$ concentrations: 3.0–8.0).

2. The d_{200} spacings for the net $[\text{OH}]$ concentration = 4.0 and different cation concentrations vary from 7.95 Å to 7.01 Å, decreasing with increasing lead content.

4. *Lead meta-autunite.* In the acid range, dark yellow, tetragonal crystals of lead meta-autunite, measuring about 1.5 millimeters wide, were grown at room temperature over a period of several months. A super-saturated solution of tribasic lead phosphate and uranyl nitrate in the ratio 1:2 was prepared with just enough nitric acid to dissolve the former salt. The thin quadratic platelets formed rosettes of composite crystals with $\{001\}$ predominating. The phase fluoresces light greenish-yellow in ultra-violet light. It is probably isostructural with meta-torbernite and related minerals. Optically, lead meta-autunite is tetragonal, uniaxial negative, $\omega = 1.655$ (yellow), $\epsilon = 1.635$ (light yellow). From Weissenberg data obtained in $\text{CuK}\alpha$ radiation, the phase was determined to be tetragonal, space group: $P 4/nmm$, $a = 6.93$ Å, $c = 17.13$ Å ± 0.01 Å, $c/a = 2.472$. With prolonged exposure to x -radiation, very weak reflections become apparent midway between the layer lines about $[001]$. The tetragonal pseudo-cell has the dimensions $a = 6.93$ Å, $c = 8.57$ Å, $c/a = 1.237$. The calculated specific gravity is 4.367 for



and the measured value was 4.31. At 110° C. 13.7 per cent water was lost.

Powder diffraction data. Film. $\text{CuK}\alpha$ radiation.

I/I_0	$d_{\text{meas.}}$	hkl	$d_{\text{calc.}}$	I/I_0	$d_{\text{meas.}}$	hkl	$d_{\text{calc.}}$
10	8.59	002	8.57	4	2.110	312, 216	2.123, 2.099
4	5.40	012	5.39	5	2.045	108, 304	2.045, 2.033
2	4.93	110	4.90	2	1.963	314	1.951
8	4.28	004, 112	4.28, 4.28	3	1.881	322	1.876
9	3.648	104	3.642	2	1.824	208	1.821
4	3.50	200	3.465	1	1.766	324	1.782
4	3.226	114, 022	3.224, 3.212	1	1.713	402	1.698
3	2.931	122	2.915	5	1.618	1.1.10, 404	1.617, 1.606
6	2.644	106	2.640	3	1.537	318, 422	1.531, 1.525
4	2.475	116, 220	2.466, 2.450	1	1.429	328	1.430
1 b.	2.36	222	2.355	2	1.400	1.0.12	1.398
2	2.206	310	2.192	1	1.372	1.1.12	1.370
8	2.141	008	2.141	1	1.352	3.1.10	1.349
				1	1.323	2.0.12	1.320

5. *Parsonsite*. Parsonsite was prepared from both acid and neutral solutions. The pale yellow phase appeared dense and relatively anhydrous in comparison to the other phases. The x-ray powder data include low angle reflections which were omitted in some earlier descriptions. Anhydrous parsonsite is optically monoclinic with mean index greater than 2.00. X-ray powder data given below were obtained on the recording diffractometer in $\text{CuK}\alpha$ radiation.

I/I_0	$d_{\text{meas.}}$	I/I_0	$d_{\text{meas.}}$	I/I_0	$d_{\text{meas.}}$	I/I_0	$d_{\text{meas.}}$
1	10.05	2	3.083	2	2.222	1	1.714
1	6.73	2	2.994	2	2.191	2	1.649
2	5.99	3	2.914	3	2.118	1	1.616
1	5.71	4	2.778	1	2.091	1	1.595
2	5.04	2	2.691	2	2.032	1	1.563
1—	4.85	3	2.600	1	2.002	1	1.530
10	4.175	2	2.547	1	1.974	1	1.514
2	3.934	2	2.515	1	1.938	1	1.501
2	3.873	1	2.423	$\frac{1}{2}$	1.904	1	1.492
9	3.381	2	2.350	2	1.873	1	1.480
8	3.267	2	2.305	2	1.841	1	1.421
9	3.222	2	2.246	1	1.771	1	1.336
8	3.147			1	1.755		

ACKNOWLEDGMENTS

The author is grateful to Professor C. Frondel for suggesting this problem and for his continued assistance and advice. Support for the

research from the Division of Raw Materials of the U. S. Atomic Energy Commission on Contract No. AT(30-1)1403 is acknowledged.

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Manuscript received April 23, 1956