

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 45

MAY-JUNE, 1960

Nos. 5 and 6

MILLISITE IN PHOSPHORITE FROM HOMELAND, FLORIDA*

J. P. OWENS, Z. S. ALTSCHULER, AND ROBERT BERMAN**
U. S. GEOLOGICAL SURVEY, WASHINGTON 25, D. C.

ABSTRACT

Millisite, $(\text{Na,K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}$, and crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$, are major components of the aluminum phosphate zone of the Bone Valley formation of west-central Florida, where they occur as a microcrystalline intergrowth composing the cement in the altered phosphorite. Formerly known only from concretions at Fairfield, Utah, and from the phosphate deposits of Thiès, Sénégal, millisite, like crandallite, is an important phase in the paragenesis of lateritically formed aluminum phosphates.

From optical and *x*-ray study of the Florida mixture and a comparison with phosphates from other localities, it is shown that the Florida material contains millisite rather than the structurally related wardite. It is found that all three known millisites give virtually identical *x*-ray patterns and that their unit-cell parameters are $a_0 = 7.00 \text{ \AA}$ and $c_0 = 19.07 \text{ \AA}$, which differ from those for wardite.

The aggregate index of refraction of millisite, $n = 1.63$, is higher than that reported for type millisite from Fairfield. The aggregate index of refraction of crandallite, $n = 1.59 - 1.61$, is in the lower range of known eucrystalline crandallite.

INTRODUCTION

During the mineralogical investigation of the uraniferous aluminum phosphate zone of the Bone Valley formation of Florida, it was found that millisite, $(\text{Na,K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}$, occurred as a major constituent associated with crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$, and wavelite, $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$. Millisite has previously been known only as a constituent of variscite nodules from Fairfield, Utah, where it was named by Larsen and Shannon (1930), and in phosphorites from Sénégal, French West Africa, where it was recently found by Vissé (1952). The mineralogy and petrology of the Fairfield nodules have been described by Larsen (1942).

The aluminum phosphate zone is principally an alteration of the upper clayey part of the Bone Valley formation and as a result is generally a

* Publication authorized by the Director, U. S. Geological Survey.

** Present address: Westinghouse Bettis Plant, Pittsburgh 30, Pa.

fine-grained intimate mixture of the secondary phosphate minerals, crandallite and wavellite, with kaolinite, and quartz sand (Altschuler, Jaffe, and Cuttitta, 1956). Millisite was first noted as an unidentified phase in *x*-ray diffractometer studies of the phosphatic cement from rocks at several localities in the region.

In the Homeland mine in the Peace River valley of Florida, millisite is the most abundant constituent of the phosphatic portion of the rock, the cement interstitial to the quartz grains. This cement is fine grained, seemingly isotropic, and apparently homogeneous. Therefore on the assumption that a single phase was present, *x*-ray data obtained from it were compared with the ASTM standards and with *x*-ray film patterns of other phosphate minerals, including apatite, crandallite, wavellite, and particularly the two dimorphous series variscite-strengite and metavariscite-metastrengite. Metastrengite (phosphosiderite) had been reported to compose similar material in an adjoining mine in the land-pebble phosphate field by Hill, Armiger, and Gooch (1950). Upon comparison with the minerals known to occur in the Bone Valley formation and secondary phosphate deposits, it became clear that the Homeland material did not contain metastrengite but was a mixture of crandallite and a member of the millisite-wardite group. Wardite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and millisite, $(\text{Na,K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}$, are analogous to crandallite with all or half of the calcium substituted for by sodium and some potassium, and a concomitant decrease in hydroxyl content to balance the charge.

We are concerned, therefore, with demonstrating through *x*-ray studies that the phosphatic cement at Homeland is a mixture containing millisite (not wardite) and crandallite, and with determining the quantitative mineralogy of the Homeland rock.

OCCURRENCE AND PETROGRAPHY

The aluminum phosphate zone is best developed in the Peace River area between Bartow and Fort Meade, Florida. In the Homeland mine, within this area, the zone is 13 feet thick. Homeland is at the northeast corner SW $\frac{1}{4}$ sec. 33, T. 30 S., R. 25 E., Polk County, Florida. The samples studied were taken about 5 feet above the base of the aluminum phosphate zone in an east-west cut of the mine approximately 100 yards east of Florida State Highway 17. This particular cut is now flooded.

The sample of ivory-colored phosphate-cemented quartz sandstone studied is highly leached and coarsely porous. Its porosity is approximately 50 per cent of the volume, and the individual cavities range from microscopic pores to holes 1 cm in diameter. A thin, glazed, greenish coating of secondary phosphate coats most of the cavities, occurs as septa

separating cavities, and is dispersed throughout the rock. In addition, goethite occurs as secondary orange-colored patches and as small nodules in some of the cavities. Due to the secondary phosphatic and ferruginous cements, the rock is indurated, although friable. The bulk specific gravity ranges from 1.5 to 1.7. No apatite pebbles were observed.

Under the microscope the rock is seen to be composed of isolated, medium sand to silt-sized quartz grains in a matrix of brown phosphatic cement (Fig. 1). The phosphatic matrix is optically isotropic or only faintly birefringent, the birefringence being distributed in patches of pin-

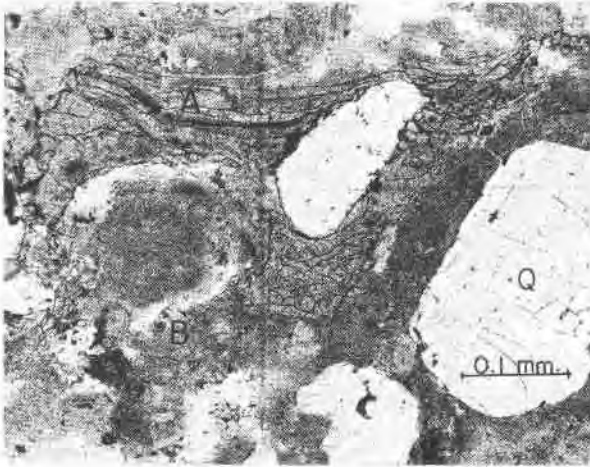


FIG. 1. Photomicrograph of phosphatic quartz (Q) sand containing millisite (A) and crandallite (B). Uncrossed nicols.

point extinction somewhat like that of chert. The index of refraction of the matrix ranges from 1.615 to 1.630. Only an aggregate index is obtainable. Generally the more birefringent material ($B=0.003$) is associated with the secondary cement, that is, with the greenish coatings visible in the hand specimen. In addition, this birefringent material has higher indices of refraction, generally from 1.625 to 1.630. The interstitial matrix is a fine-grained mixture of such birefringent high-index material (1.630) and isotropic low-index material (1.615). All variations of this mixture can be seen under the microscope but only the higher index material can be isolated in an almost pure state. On the basis of x -ray diffraction studies, the material was interpreted to be millisite, as discussed later. (See Figs. 2 and 3.) The lower index material was never successfully separated but is known to be crandallite from the x -ray data.

A birefringent deep-yellow to dark-brown material is present as sec-

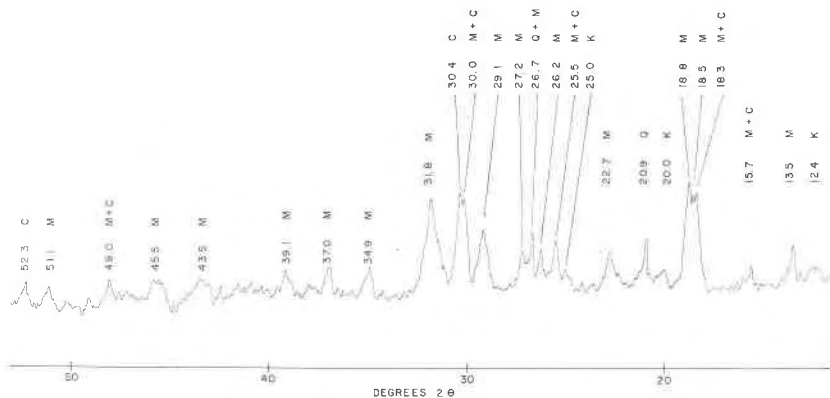


FIG. 2. X-ray diffractometer pattern of phosphatic fraction from Homeland, Florida, phosphorite. $\text{CuK}\alpha$ radiation, Ni filter. M=millisite, C=crandallite, Q=quartz, K=kaolinite.

ondary crusts or nodules. The mass index of the secondary crusts ranges from 1.70 to 1.80; that of the nodules is as high as 1.93. Goethite was found in all of this material by x-ray studies. The lower index material is impure and presumably mixed with secondary phosphate minerals.

IDENTIFICATION OF PHASES PRESENT

The identification of mixtures of crandallite and millisite or wardite in altered phosphorites is complicated by the poorly developed optics and the fact that most x-ray diffraction lines of crandallite coincide with lines of millisite or wardite, and the diffractometer patterns of millisite and wardite differ only slightly from each other. At first, attempts were made to separate the minerals by physical and chemical methods. The rock was dried at 110°C , crushed, split, and stage-ground to -200 mesh, obtaining a fourfold concentration of the phosphatic cement by removal of quartz, which makes up most of the rock but only 20 per cent of the -200 mesh concentrate. Splits of the -200 mesh fraction were then centrifuged in heavy liquids and separated magnetically. All separates were analyzed by x-ray diffractometer for changes in the relative quantities of crandallite and millisite. However, no appreciable concentration occurred. Differential leaching of crandallite from millisite in HNO_3 proved equally futile.

The -200 mesh fraction was then sized by air elutriation into 7 fractions down to $<1\ \mu$. The fraction $10\text{-}1\ \mu$ (measured optically), the finest phosphatic fraction containing little kaolinite, was processed further by

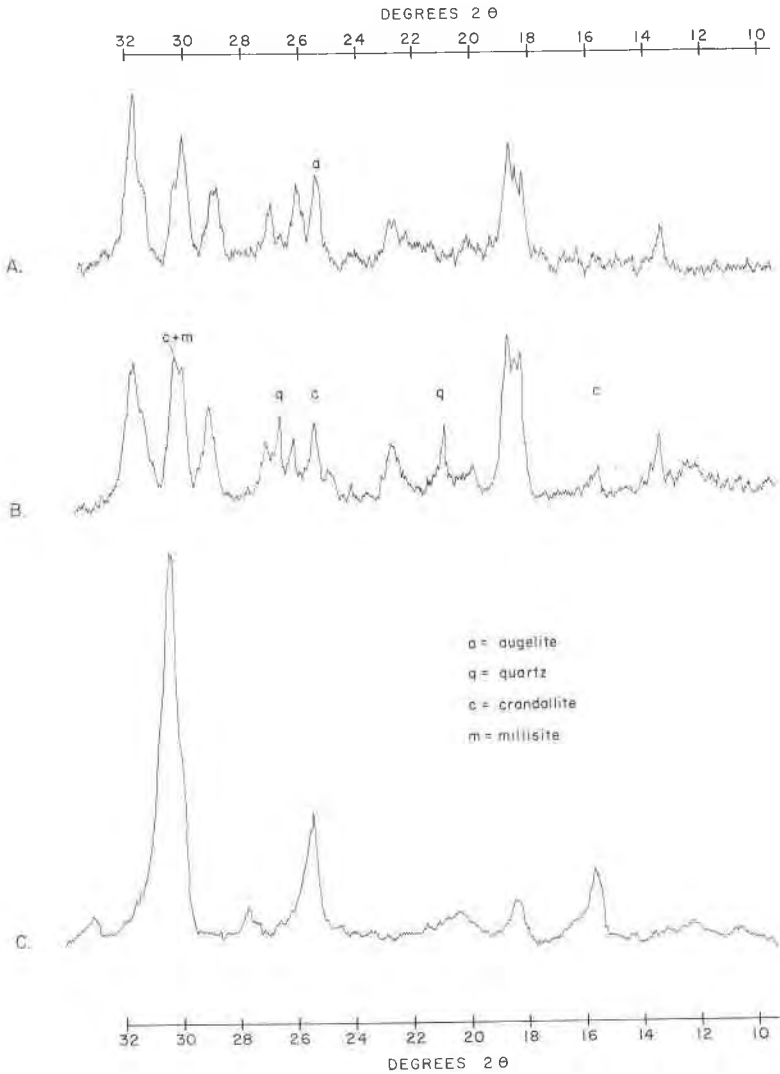


FIG. 3. X-ray diffractometer pattern of millisite, crandallite, and millisite-crandallite mixture.

- A = Millisite plus minor amounts of augelite from Sénégal
 B = Millisite-crandallite mixture from Homeland, Florida
 C = Crandallite from Homeland, Florida

centrifuging in heavy liquids ranging in density from 2.75 to 2.84. The millisite concentration increased progressively, but only slightly, in the heavy fractions, with the highest concentration at 2.83. Figure 2 is an x -ray diffractometer pattern of this concentrate. It was decided at this point that the minerals are mutually interlocked in too fine grained a mixture for complete physical separation, and that the phases would have to be identified from x -ray diffractometer patterns.

X-RAY STUDIES

Nature of Homeland mixture

As is evident from Fig. 3, which is a comparison of diffractometer patterns of the Homeland mixture with ferrian millisite (pallite, from Sénégal) and crandallite (from Florida), almost every peak of crandallite corresponds in position to a millisite peak. This is further illustrated in Fig. 2 which shows that the diffractometer pattern of the mixture contains peaks of unusual height at all positions where the reflections from millisite and crandallite coincide. Among the unique reflections, two strong lines are distinctive of crandallite, one at $d=2.95 \text{ \AA}$, and the other at $d=4.85 \text{ \AA}$. Study of these regions at a slow diffractometer speed and enhanced resolution (Fig. 4) shows both these peaks to be present. The identity of the other phase at Homeland as a member of the wardite-millisite group is further illustrated in Fig. 5, a comparison of the film patterns of the green birefringent material handpicked from the Homeland mixture and the millisite from Fairfield, Utah.

An examination of millisite

Wardite and millisite have similar x -ray patterns. As noted by Larsen (1942) however, they differ in detail, both in d -spacings, and particularly in the presence and absence of certain reflections. On this basis they can be readily distinguished in x -ray diffractometer patterns. However, the determination of which member of this pair is present in the Homeland mixture hinges on a comparison with pure millisite and wardite.

As the millisite from Sénégal, although similar to the Homeland material, is a ferrian variety, inextricably mixed with augelite, and not completely analyzed (Capdecombe and Pulou, 1954), positive identification of the Homeland material must be based primarily on a comparison with Fairfield millisite. Millisite at Fairfield is never separate from wardite with which it is very finely interlaminated. It was therefore necessary to resort to partial segregations of wardite and millisite, obtained by heavy liquid separations of Fairfield material crushed to less than 0.1 mm. The material was handpicked according to color from the interbanded aggregates described by Larsen (1942). The sample was crushed and segre-

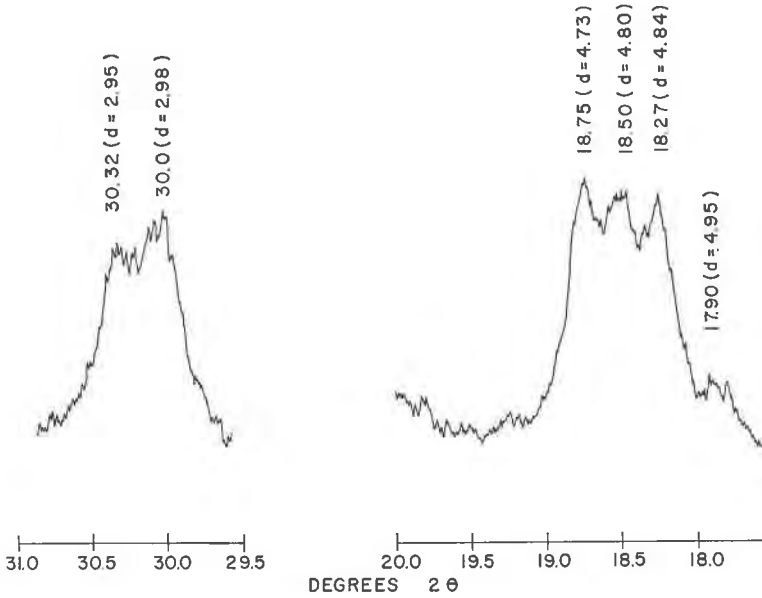


FIG. 4. X-ray diffractometer pattern of phosphatic fraction (Fig. 2) run at $\frac{1}{4}^\circ/\text{min}$. $\text{CuK}\alpha$ radiation, Ni filter.

gated between liquids of densities 2.83 and 2.87 (Fig. 6, pattern A) to guard against minute inclusions of variscite (sp. gr. = 2.57), crandallite (sp. gr. = 2.92), apatite (sp. gr. = 3.18), and quartz. The material was crushed further to pass 230 mesh, and centrifuged, in two successive

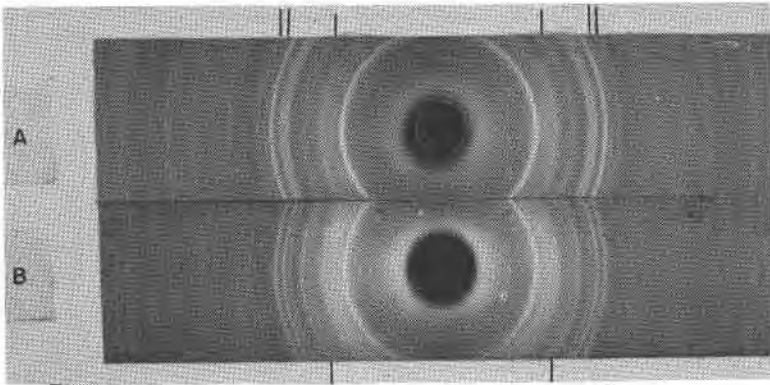


FIG. 5. X-ray powder patterns of millisite. The notches above pattern A indicate apatite lines, those below pattern B indicate quartz lines. A = millisite from Fairfield, Utah. B = unknown from Homeland mine, Florida.

stages, in heavy liquid of 2.83 and density slightly less than 2.83. The first light fraction drawn off is considered to be the purest wardite (Fig. 6, pattern D). The heavy fraction (Fig. 6, pattern B) was again centrifuged in liquid of density 2.83 to yield the best concentrate of millisite (Fig. 6, pattern C) and a light fraction that was discarded.

The x -ray diffractometer patterns of the wardite and millisite concentrates from Fairfield are compared in Fig. 6 with a pattern of pure wardite from Beryl Mountain, New Hampshire (Hurlbut, 1952). It is clear from these patterns that wardite and millisite are indeed different. The wardite from Fairfield is virtually pure and almost identical with the Beryl Mountain wardite. The differences between wardite and millisite from Fairfield are clearly demonstrated in the progressive reduction of the intensities of certain wardite peaks in the millisite concentrates, and by the introduction of peaks in the millisite concentrates which are either absent or weak in the wardite concentrate.

Millisite at Homeland

On the basis of the above observations it is possible to identify the green birefringent mineral at Homeland specifically as millisite. Table 1 lists the measured d -spacings of all materials studied. From either these data or the diffractometer patterns it can be seen that two reflections ($d=3.40$ Å and $d=3.92$ Å; 2θ 26.2° and 2θ 27.1°, CuK α) characterize the Homeland millisite, the Fairfield millisite, and the ferrian millisite (pallite) from Sénégal (Capdecemme and Pulou, 1954). These same reflections are absent in patterns of wardite from Fairfield and from Beryl Mountain (Hurlbut 1952). In addition, three reflections at $d=3.96$ – 3.95 Å, 3.11 – 3.12 Å, and 2.54 – 2.55 Å are present on both wardite patterns but do not appear in patterns of the three millisites.

Besides this, several of the reflections common to both groups differ significantly in d -spacings. This is true for reflections from planes $hkl=101$, 102 , 110 , 004 , and 200 . (See Table 1.)

It has been impossible to index the x -ray patterns of the Florida and Sénégal millisites with the cell parameters for wardite which are given by Larsen (1942) and confirmed by Hurlbut (1952) as $a_0=7.04\pm 0.02$ Å and $c_0=18.88\pm 0.02$ Å. Instead, after numerous trials, the cell parameters $a_0=7.00$ Å and $c_0=19.07$ Å were chosen. Table 1 shows that the computed d -spacings based on the new cell parameters are quite similar to the measured d -spacings for Homeland millisite and Sénégal pallite (ferrian millisite), and also that the reflections distinguishing millisite at $d=3.40$ Å and $d=3.29$ Å fall close to their computed positions, whereas they cannot be indexed on a wardite cell.

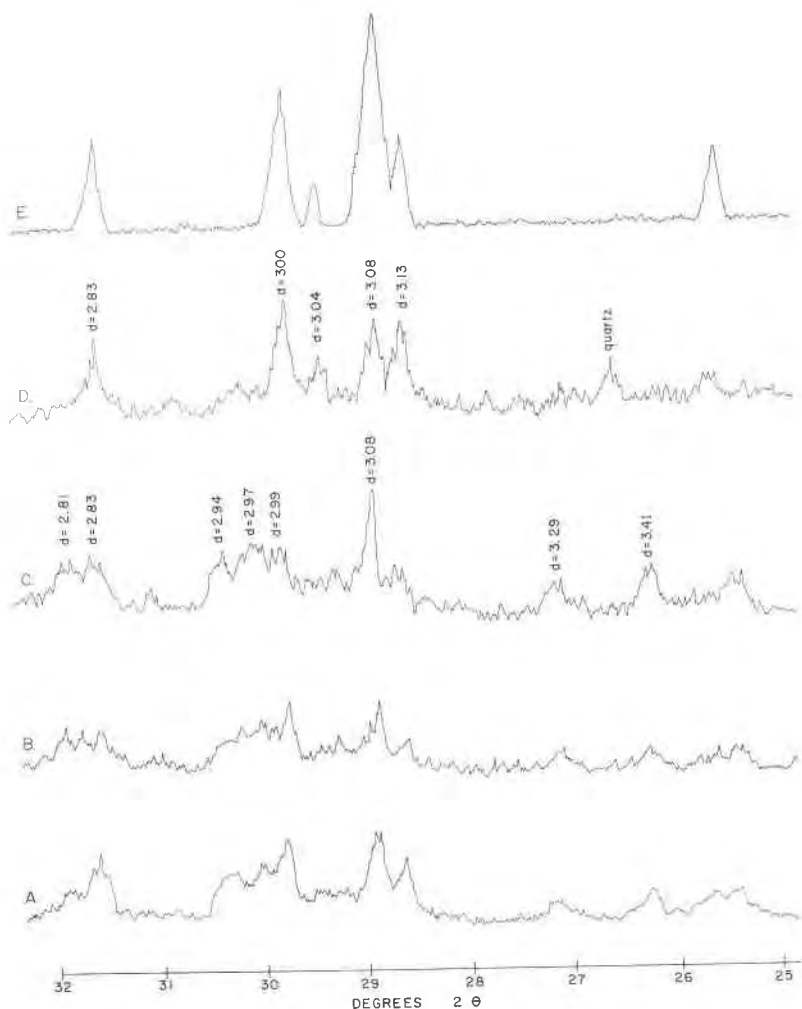


FIG. 6. X-ray diffractometer patterns of wardite-millsite mixture from Fairfield, Utah (A-D), and wardite from Beryl Mountain, New Hampshire (E). $\text{CuK}\alpha$ radiation, Ni filter. A. Initial mixture (sp. gr. 2.83-2.87). B. Heavy fraction from heavy liquid (2.83) separation; millsite rich. D. Light fraction; wardite-rich. C. Heavy fraction, second separation in 2.83 liquid; richest millsite.

MINERAL COMPOSITION

Owing to the impossibility of separating the fine-grained phosphatic mixture in the Homeland rock, and to the uncertainty of optical approximations of composition in replacement mixtures of this type (Fig. 2), it

TABLE 1. INTERPLANAR SPACINGS (Å) OF MILLISITE, WARDITE, PALLITE, AND CRANDALLITE FROM X-RAY POWDER DIFFRACTION PATTERNS (CuK α RADIATION, NI FILTER)

Wardite, Beryl Mountain, N. H. (diffrac- tometer)		Wardite, Utah (diffrac- tometer)		Millisite, Utah (film)		Millisite, Florida (diffractometer)			Pallite, Sénégal (diffrac- tometer)		Crandallite, Florida (diffrac- tometer)		Crandallite, Utah (diffrac- tometer)		
d	I	d	I	d	I	hkl	d (meas.)	d (calc.)	I	d	I	d	I	d	I
6.62	2	6.65	2	6.6	4	101	6.606	6.583	2	6.60	2				
5.72	2	5.68	2	5.68	1	102	5.644	5.646	1	5.64	1	5.68	2	5.72	2
5.01	4	5.04	3	4.98	$\frac{1}{2}$	110	4.950	4.953	1	4.95	1				
4.82	3	4.82	1			111	4.84	4.794	10	4.86	10	4.86	2	4.86	2
4.77	10	4.76	5	4.84	10 VB	004	4.796	4.769	10	4.79	9				
4.73	10	4.72	7			103	4.732	4.708	10	4.73	10				
3.96	3	3.95	4												
3.93	2	3.93	$\frac{1}{2}$	3.93	3 B	113	3.917	3.908	2	3.91	1				
3.47	4	3.48	4	3.48	3	200	3.506	3.499	3	3.50	2	3.49	2	3.51	2
				3.40	3	114	3.414	3.434	2	3.43	2				
		3.36	$\frac{1}{2}$	3.36	$\frac{1}{2}$	105	3.360	3.350	$\frac{1}{2}$	3.35	$\frac{1}{2}$				
				3.29	2	202	3.290	3.290	2	3.29	2				
3.11	5	3.12	5												
3.09	8	3.09	9	3.09	6 B	211	3.099	3.091	4	3.09	4				
3.04	5	3.03	4			203	3.074	3.067	4	3.06	4				
2.99	7	3.00	9	2.98	8 B	212	2.979	2.977	10	2.98	10	2.98	5	2.98	5
2.90	$\frac{1}{2}$											2.95	10	2.95	10
2.83	4	2.83	7			204	2.840	2.822	5	2.82	5				
				2.81	8 B	213	2.813	2.809	8	2.81	8				
2.68	1											2.70	1	2.70	1
2.63	1	2.62	$\frac{1}{2}$												
2.59	7	2.60	1	2.59	3	205	2.578	2.580	2	2.58	2				
2.54	2	2.55	$\frac{1}{2}$												
2.50	$\frac{1}{2}$			2.42	3	215	2.433	2.422	2	2.42	2				
2.39	1	2.39	1											2.37	$\frac{1}{2}$
2.38	1														
2.37	$\frac{1}{2}$														
2.33	$\frac{1}{2}$	2.33	1	2.31	1	223	2.304	2.307	2	2.31	2				
2.30	4														
		2.26	1	2.25	1							2.24	2	2.21	3
2.16	2	2.16	1	2.17	1									2.16	4
2.15	1														
2.115	3	2.115	2	2.11	VB										
2.11	2														
		2.076	$\frac{1}{2}$	2.09	2 VB	225	2.083	2.077	1	2.08	1				
2.06	1														
2.03	$\frac{1}{2}$	2.036	$\frac{1}{2}$												
2.02	$\frac{1}{2}$														
		2.006	$\frac{1}{2}$	1.998	3							1.993	1	1.993	1
1.93	1	1.969	1	1.965	$\frac{1}{2}$	305	1.993		B						
		1.93	$\frac{1}{2}$									1.895	3	1.895	3
		1.87	$\frac{1}{2}$	1.88	2										
		1.84	$\frac{1}{2}$	1.84	1										

B = broad.

VB = very broad.

TABLE 1 (Continued)

Wardite, Beryl Mountain, N. H. (diffrac- tometer)	Wardite, Utah (diffrac- tometer)	Millisite, Utah (film)	Millisite, Florida (diffractometer)	Pallite, Sénégal (diffrac- tometer)	Crandallite, Florida (diffrac- tometer)	Crandallite, Utah (diffrac- tometer)
d I	d I	d I	d d hkl (meas.) (calc.) I	d I	d I	d I
	1.77 3 1.655 1 $\epsilon=1.599$ $\omega=1.590$	1.77 2 1.75 3 $\epsilon=1.584$ $\omega=1.602$	307 1.787 1.772 1 $n=1.63$ $a_0=7.00 \text{ \AA}$ $c_0=19.07 \text{ \AA}$ $a_0:c_0=1:2.7242$		1.755 2 $n=1.59$ -1.61	1.755 2 $\epsilon=1.590$ $\omega=1.631$

Cell dimensions from Lar-
sen (1942) and Hurl-
but (1954)
 $a_0 = 7.04 \pm 0.02 \text{ \AA}$
 $c_0 = 18.88 \pm 0.02 \text{ \AA}$

has been necessary to calculate the mineral composition from the chemical analysis given in Table 2 (column 1). The contributions of insoluble detritals (mainly quartz) and goethite were subtracted from the total analysis to give the essential composition of the phosphatic fraction, calculated to 100 per cent, in the second column of Table 2. Trace constituents determined spectrographically are shown in Table 3.

The quantitative mineral composition was determined in the following manner. The minerals identified optically or by x-ray in the rock are quartz, millisite, crandallite, goethite, kaolinite, and trace quantities of wavellite. Of the constituents present in the chemical analysis, the insoluble residue and the Fe_2O_3 content, and its water equivalent, were subtracted from the total analyses and assigned to quartz and goethite, respectively. This was based on the finding that the insoluble residue consisted entirely of quartz and trace quantities of refractory accessory minerals, and that goethite was present in sufficient quantity to account for all the reported iron. The remainder of the chemical analysis was recalculated to one hundred per cent (Table 2, column 1) and converted to atomic ratios (column 3). Millisite was then subtracted according to the formula $(\text{Na},\text{K})\text{CaAl}_6(\text{PO}_4)(\text{OH})_9 \cdot 3\text{H}_2\text{O}$. In this computation all the Na and K present was assigned to millisite and corresponding amounts of CaO , Al_2O_3 , and P_2O_5 were deducted from the whole. The remaining material must be assigned to crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$, and kaolinite, $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$. This determines that all of the remaining calcium and equivalent amounts of aluminum and P_2O_5 be used in crandallite

TABLE 2. CHEMICAL¹ AND MODAL ANALYSIS OF MILLISITE-CRANDALLITE CONCENTRATE FROM HOMELAND, FLA.

	Weight per cent	Adjusted ² weight per cent	Atomic ratios	Millisite		Crandallite		Remain- ing (Kao- linite)
				Subtrac- tions	Atom ratios	Subtrac- tions	Atom ratios	
Al ₂ O ₃	26.1	37.1	0.729	0.438	6	0.261	3.0	0.030
P ₂ O ₅	21.9	31.0	.436	.292	4	.144	1.7	
CaO	6.4	9.0	.160	.073	1	.087	1.0	
Na ₂ O	1.4	2.0	.065	.073	1			
K ₂ O	0.3	0.4	.008					
Loss on ignition	14.9	20.4						
Acid insoluble (HNO ₃ 1+1)	22.9							
Fe ₂ O ₃	4.9							
U	0.03	0.04						
Total	98.8							

¹ Analysts: S. J. Lundine, M. H. Delevaux, and A. M. Sherwood, U. S. Geological Survey.

² Recalculated to 100 after removal of acid insoluble (quartz and heavies) and goethite (Fe₂O₃+equivalent H₂O).

(Al:P:Ca = 3:2:1) which leaves a proportion of 0.030 atoms of aluminum (in excess) (Table 2, last column) for kaolinite and a deficiency of 0.3 of 2.0 atoms of phosphorus for crandallite. Kaolinite is known to be present in the rock only as a minor constituent. Thus the summations are quite reasonable. The lack of P₂O₅ to fill the theoretical ratio is common in other occurrences of crandallite; material from Sénégal (Capdecombe, 1953); Dehrn (Larsen and Shannon, 1930); Silver City (Loughlin and Schaller, 1917); and Llallagua (Gordon, 1944) are all deficient in phosphate by similar amounts. The missing (PO)₄ is probably compensated

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS, IN PER CENT, OF CRANDALLITE-MILLISITE MIXTURE (AND QUARTZ) COMPOSING CEMENT OF LEACHED-ZONE ROCK

(Analyst: H. W. Worthing, U. S. Geological Survey)

Over 10	10.0-1.0	1.0-0.1	0.1-0.01	0.01-0.001	0.001-0.0001
Al	Si Ca P Fe	Na Ti	Mg Ba Pb Cr Sr Cu B V Zr	Ga Ni Y Mn Sc	Yb Be

TABLE 4. MINERAL COMPOSITION OF ROCK FROM THE ALUMINUM PHOSPHATE ZONE AT HOMELAND, FLORIDA

Mineral	Weight per cent
Quartz and accessories ¹	23
Millisite	41
Crandallite	27
Goethite	6
Kaolinite	3
Wavellite	trace

¹ Accessories identified are zircon, rutile, sillimanite, ilmenite, and tourmaline.

by the presence of $(OH)_4$ as in griphite (McConnell, 1942), a suggestion that is adopted by Palache, Berman, and Frondel (1951) and Van Tassel (1956) for crandallites obviously deficient in phosphate.

Larsen and Shannon (1930) described wardite and millisite as hydrous sodium-calcium alumino-phosphates differing in their relative proportions of sodium and calcium to an extent that millisite had equal atomic amounts of both, and wardite had 1 calcium to 4 sodium atoms. Larsen (1942) noted that potassium was insignificant in wardite but occupied about a third of the sodium positions in millisite, and suggested the Na:K ratio as an additional means of distinguishing between the two minerals chemically. Hurlbut (1952), using a new analysis of Fairfield wardite by Gonyer, has shown that calcium is lacking, as in the Beryl Mountain wardite, and suggests that wardite is essentially hydrated sodium aluminum-phosphate, $Na_4Al_{12}(PO_4)_8(OH)_{16} \cdot 8H_2O$. It is thus readily distinguished from millisite, $Ca_2(Na,K)_2Al_{12}(PO_4)_8(OH)_{18} \cdot 6H_2O$ (Larsen, 1942).

With the information from two new occurrences it can now be seen that the ratio of sodium to potassium in millisite may vary greatly and therefore cannot serve to distinguish millisite from wardite. At Fairfield the deposit is rich in potassium, as seen from the associated dehrnite and lewistonite, and the millisite has an atomic ratio of sodium to potassium of 5:2. In Florida the ratio is 8:1 on the assumption that none of the alkalis derive from crandallite (Table 4). Partial analyses of the augelite-millisite mixture from Sénégal gives $Na_2O = 1.5$ per cent and $K_2O = 0.07$ per cent, yielding an atomic sodium to potassium ratio of 30:1. As augelite contains no alkalis, the Sénégal data are more secure than the Florida data since crandallite, which occurs in the Florida material, may contain some sodium. Apparently K_2O is not essential in millisite but is present in trace to minor amounts.

Capdecemme and Pulou (1954) described pallite as an alkali-free

millisite with substitution of Fe_2O_3 for about 10 per cent of the Al_2O_3 , $\text{Ca}_3(\text{AlFe})_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$. In view of our finding of 1.5 per cent Na_2O in the augelite-"pallite" mixture, and of the identity of the pallite and Homeland millisite x -ray diffractometer patterns, it appears (in the absence of a complete analysis of pure pallite) that the pallite may be a normal millisite in which much of the iron is in associated goethite. This is borne out by several of the analyses of phase "X" in Capdecemme (1953) showing a virtually normal ratio of Al_2O_3 to P_2O_5 .

Based on the computations in Table 2 the phosphatic fraction of the Homeland rock, except for included goethite, is found to consist approximately of the following mixture: millisite 58 per cent, crandallite 38 per cent, and kaolinite 4 per cent. Some error may arise due to the fact that all of the sodium was assumed to reside in millisite. In fact, crandallite may contain some sodium, thus changing the relative proportions of crandallite and millisite. However, the conclusions are supported by the relative prominence of birefringent and isotropic phases in thin-sections of the rock, by the intensities of the crandallite and millisite reflections in the x -ray patterns of the mixture, and by the reasonable summation of the modal analysis.

The total mineral composition of the Homeland rock studied is shown in Table 4.

The mineral composition of the phosphate deposit at Homeland varies considerably, depending on the depth within the alteration zone represented by a particular sample. It has been shown (Altschuler, Jaffe, and Cuttitta, 1956) that the zone as a whole is characterized by progressive replacement of calcium phosphate and clay by aluminum phosphate and quartz. Of the phosphate minerals, apatite characterizes the unaltered and basal part of the zone; the calcium-aluminum phosphates, crandallite and millisite, the middle part of the zone; and wavellite, the pure aluminum phosphate, is the stable and frequently the sole phosphate mineral in the upper, most altered, part of the zone. Although millisite is found in all areas of the land-pebble phosphate field, it is abundant only in the Peace River valley tract between Bartow and Fort Meade, Florida. This second occurrence of millisite in the United States undoubtedly aggregates to hundreds of thousands and possibly millions of tons. The occurrence is geologically interesting as it demonstrates that millisite, in addition to being a rare constituent of concretions, is, like crandallite, an important intermediate phase in the paragenesis of lateritically altered phosphorites, and is probably also a significant host for uranium in such deposits (Capdecemme and Pulou, 1954; Altschuler, Clarke, and Young, 1958).

ACKNOWLEDGMENTS

This work was a part of the U. S. Geological Survey's investigation of radioactive raw materials for the Division of Raw Materials, U. S. Atomic Energy Commission. We are indebted to Prof. Laurent Capdecombe, University of Toulouse, for specimens of "pallite"; to Prof. Clifford Frondel, Harvard University, for wardite from Beryl Mountain, N. H.; and to Dr. George Switzer, U. S. National Museum, for nodules of the Fairfield, Utah, minerals. Marie L. Lindberg kindly supplied x -ray data on Beryl Mountain wardite. We have profited from discussions and reviews of the work with C. L. Christ, M. Fleischer, E. S. Larsen 3d, and Marie L. Lindberg, U. S. Geological Survey.

REFERENCES

- ALTSCHULER, Z. S., CLARKE, R. S., JR., AND YOUNG, E. J. (1958), Geochemistry of uranium in apatite and phosphorite: *U. S. Geol. Survey Prof. Paper* 314-D, 45-90.
- ALTSCHULER, Z. S., JAFFE, E. B., AND CUTTITA, FRANK (1956), The aluminum phosphate zone of the Bone Valley formation, Florida, and its uranium deposits: *Proc. Internat. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1955*, 6, 507-513; *U. S. Geol. Survey Prof. Paper* 300, 495-504.
- CAPDECOMME, LAURENT (1953), Étude minéralogique des gites de phosphates alumineux de la région de Thiès (Sénégal): *Internat. Geol. Cong., 19th, Algiers, Comptes rendus, sec. 11*, fasc. 11, 103-117.
- CAPDECOMME, LAURENT, AND PULOU, R. M. (1954), Sur la radioactivité des phosphates de la région de Thiès (Sénégal): *Acad. Sci. Paris Comptes rendus*, 239, 288-290.
- GORDON, S. G. (1944), The mineralogy of the tin mines of Cerro de Llallagua, Bolivia: *Acad. Nat. Sci. Philadelphia Proc.*, 96, 279-359.
- HURLBUT, C. S., JR. (1952), Wardite from Beryl Mountain, New Hampshire: *Am. Mineral.*, 37, 849-852.
- HILL, W. L., ARMIGER, W. H., AND GOOCH, S. D. (1950), Some properties of pseudowavellite from Florida: *Mining Eng.*, 187, 699-702.
- LARSEN, E. S., JR., AND SHANNON, E. V. (1930), The minerals of the phosphate nodules from near Fairfield, Utah: *Am. Mineral.*, 15, 307-337.
- LARSEN, E. S., 3d, 1942, The mineralogy and paragenesis of the variscite nodules from near Fairfield, Utah: *Am. Mineral.*, 27, 281-300, 350-372, 441-451.
- LOUGHLIN, G. F., AND SCHALLER, W. T. (1917), Crandallite a new mineral: *Am. Jour. Sci.* 43, 69-74.
- MCCONNELL, DUNCAN (1939), Symmetry of phosphosiderite: *Am. Mineral.*, 24, 636-642.
- (1942), Griphite, a hydrophosphate garnetoid: *Am. Mineral.*, 27, 452-461.
- PALACHE, CHARLES, BERMAN, HARRY, AND FRONDEL, CLIFFORD (1951), Dana's system of mineralogy, 2, 7th ed.: New York, John Wiley and Sons, Inc., 1124 p.
- VAN TASSEL, RENÉ (1956), Découverte de crandallite en Belgique: *Institut royal des Sciences naturelles de Belgique*, XXXII, no. 33, 1-10.
- VISSÉ, L. D. (1952), Pseudowavellite et millisite dans les minerais phosphatés dits latéritoides blancs de la région de Thiès (Sénégal): *Acad. Sci. Paris Comptes rendus*, 234, 1377-1378.