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DEPARTMENT OF THE INTERIOR
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Dr. Phillip L. Merritt, Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
P. O. Box 30, Ansonia Station
New York 23, New York

Dear Phil:

Transmitted herewith are six copies of TEI-316, "The occurrence of millisite and pseudowavellite in the leached zone at Homeland, Florida," by J. P. Owens, R. Berman, and Z. S. Altschuler, March 1953.

We are asking Mr. Hosted to approve our plan to publish this report in the American Mineralogist.

Sincerely yours,

Dwight M. Lemmon
for W. H. Bradley
Chief Geologist

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Geology and Mineralogy

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE OCCURRENCE OF MILLISITE AND PSEUDOWAVELLITE IN THE LEACHED ZONE AT HOMELAND, FLORIDA*

By

J. P. Owens, R. Berman, and Z. S. Altschuler

March 1953

Trace Elements Investigations Report 316

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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THE OCCURRENCE OF MILLISITE AND PSEUDOWAVELLITE IN THE LEACHED ZONE AT HOMELAND, FLORIDA

By J. P. Owens, R. Berman, and Z. S Altschuler

ABSTRACT

Millisite and pseudowavellite are locally abundant in the leached zone of the highly phosphatic Bone Valley formation in west-central Florida.

A sample of a phosphate-cemented quartz sand from Homeland, Fla., was found to contain millisite $\left[(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O\right]$ and pseudowavellite $\left[CaAl_3(PO_4)_2(OH)_5 \cdot H_2O\right]$ as the principal cementing agents. These minerals are similar in their physical properties and occur as microcrystalline intergrowths thus preventing separation in quantity by sizing, specific gravity, or magnetic methods. Optical determinations on hand-picked material showed that the aggregate index of refraction of millisite ($n = 1.63$) is higher than that reported for the type millisite from Fairfield, Utah, whereas the aggregate index of refraction of pseudowavellite ($n = 1.59$-1.61) is in the lower range of known pseudowavellite.

X-ray studies showed that millisite and pseudowavellite have similar X-ray patterns in some respects. Significant differences exist at certain positions especially at 4.72 A and 2.80 A where millisite has strong lines. Other minerals known to be present in the rock are quartz, goethite, wavellite, and accessory heavy minerals.

INTRODUCTION

This report summarizes mineralogic studies of a sample of leached-zone rock from the Homeland mine of the Virginia-Carolina Chemical Corp. The work was done as part of a program undertaken by the Geological Survey on behalf of the Atomic Energy Commission.

The sample was collected from the east-west cut of the mine approximately 100 yards east of Florida State highway 17. The mine is located at the northeast corner SW1/4 sec. 33, T. 30 S., R. 25 E., Polk County, Fla.

The leached zone in this area is well developed and approximately 10 to 13 ft thick. The lower portion of this zone is coarsely vesicular. The sample described here was taken about 5 ft above the base of the leached zone.

The work done on this sample is part of the program of systematic petrographic study of the leached zone which was described in a previous report (Altschuler, 1952) containing some early results. The sample was selected as representative of pseudowavellite material (crandallite, Palache et al., 1951) from the leached zone. During the course of the work it was found that the sample also contains millisite as a major constituent.

The main objectives of this work were to study the mineralogy and uranium distribution of the rock and the possible methods of fractionating the rock and thereby concentrating its uranium.

The sample studied consists of phosphate-cemented quartz sand. The phosphate matrix is nonclastic; all coarse fragments of the material are rock fragments rather than original pebbles or granules. Hence disaggregation was not a problem and the rock was merely rough-crushed and split after drying for 24 hours at 100 C. The material was then stage-ground to 200 mesh at which size a fourfold concentration of the phosphate was established because the quartz, which constituted from 75 to 80 percent of the rock, was only 20 percent of the 200 mesh material.

MINERALOGIC STUDIES

Megascopic characteristics

The sample of leached-zone rock is a coarsely porous, ivory-colored, phosphate-cemented, medium-grained, quartz sandstone. Its porosity is approximately 50 percent of the volume, and the individual cavities range from microscopic pores to holes 1 mm in diameter. A thin glazed greenish coating of secondary phosphate lines most of the cavities, occurs as septa separating cavities, and is dispersed generally throughout the rock. In addition, a secondary coating of goethite causes patchy orange-colored staining. Goethite is also found as small nodules in some of the cavities. As a result of the secondary phosphatic and ferruginous cements, the rock is indurated although friable. The bulk specific gravity of the rock ranges from 1.5 to 1.7. No apatite pebbles were observed.

Microscopic characteristics

Under the microscope the rock is seen to be composed of isolated quartz grains, ranging in size from medium sand to silt, in a matrix of brown phosphatic cement (fig. 1). The quartz is clear, subangular to subrounded, and lacks evidence of strain or inclusions.

The phosphatic matrix is optically isotropic or only faintly birefrigent, the birefrigence being distributed in patches of pin-point extinction somewhat like 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 $(\varepsilon - \omega = < 0.003)$ is associated with the secondary cement, in other words with the greenish coatings visible in the hand specimen. In addition, the birefringent material has higher

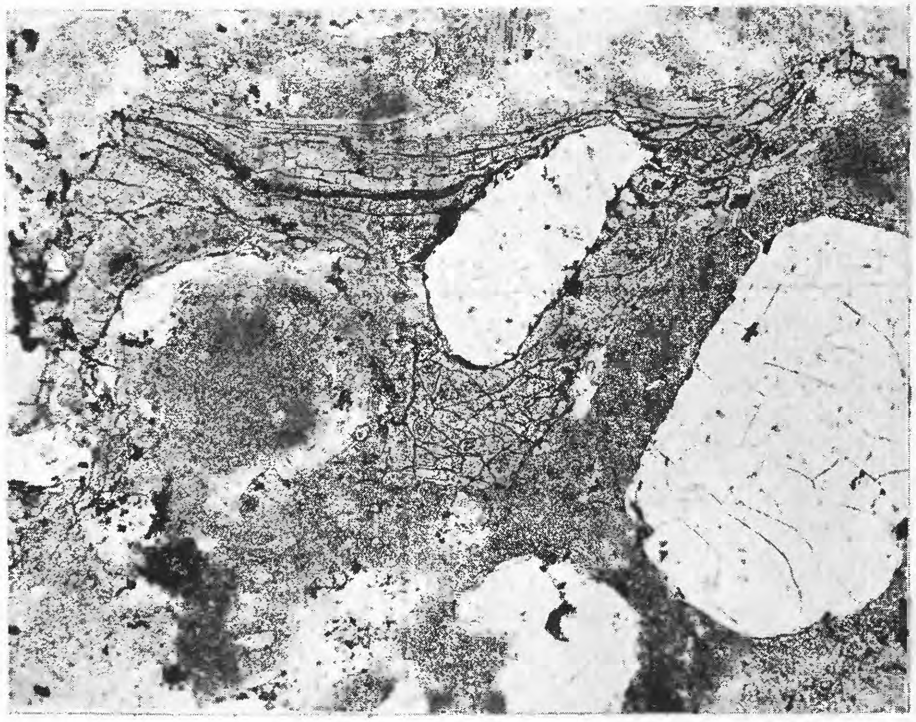

Figure 1.--Photomicrograph of phosphatic quartz sand containing millisite and pseudowavellite (x 100). Uncrossed nicols.

indices, generally from 1.625 to 1.630. The interstitial matrix is a fine-grained mixture of isotropic low-index material (1.615) and of birefringent high-index material (1.630). 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. This material proved to be millisite 1/ when X-rayed (figs. 2 and 3). The lower index material was never successfully isolated but it is presumed to be pseudowavellite which is known to be present from the X-ray data.

A birefringent deep-yellow to dark-brown material is present as secondary crusts or nodules. The mass index of the secondary crusts varies from 1.70 to 1.80; that of the nodules is as high as 1.93. Goethite was found in all this material by X-ray studies. The lower index material is impure, being presumably mixed with secondary phosphate minerals.

Chemical and spectrographic analysis

Chemical and spectrographic analyses were made on the -200 mesh concentrate of the leached-zone rock. The results are listed in tables 1 and 2.

The chemical analysis in table 1 is not complete; the difference between the total shown and 100 is accounted for by the constituents that are shown in the spectrographic analysis but were not determined chemically. The figure for acid insoluble is practically identical with SiO_2 as quartz is essentially the only mineral present that would be undissolved in 1:1 nitric acid. The figure for loss on ignition is essentially equal to water of constitution as the sample was dried at 105 C before processing

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1/ The formula for millisite is $(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O$. The formula for pseudowavellite (crandallite) is $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$. Wardite $[Na_4CaAl_{12}(PO_4)_8(OH)_{18} \cdot 6H_2O]$ forms a series with millisite, and is found with it at Fairfield, Utah (Palache et al., 1951).

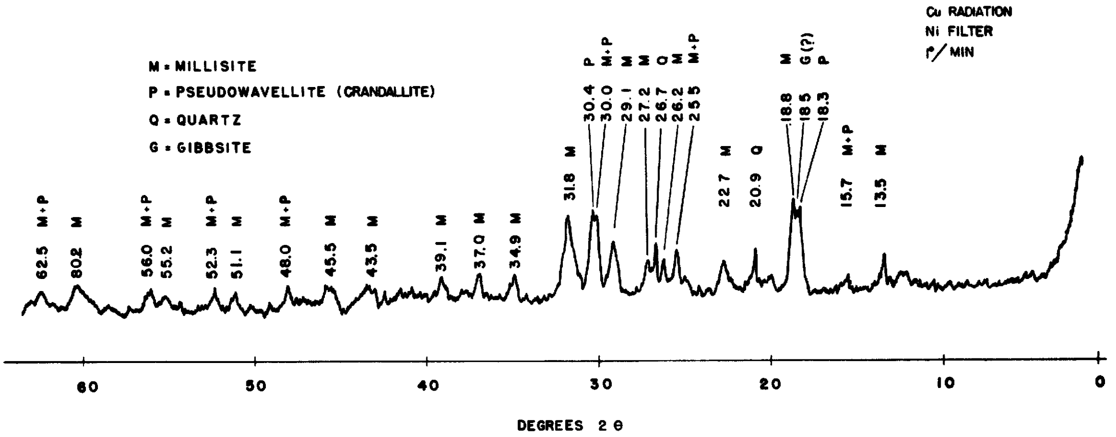

Figure 2. X-RAY SPECTROGRAM OF ROCK MINUS MOST OF THE QUARTZ.

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Figure 3. PORTIONS OF X-RAY SPECTROGRAM OF ROCK (Figure 2) RUN AT SLOWER SPEED.

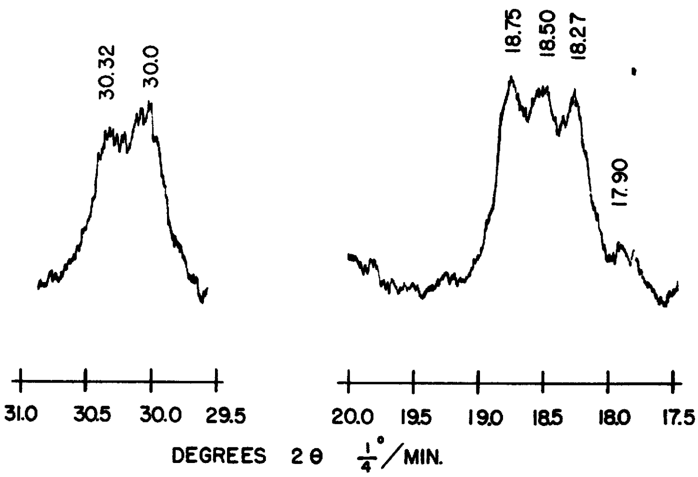

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Table 1.--Chemical analysis of -200 mesh concentrate of leached-zone rock. (Analyst: S. J. Lundine, M. Delevaux, and A. Sherwood).

Constituents	Percentage
Al_2O_3	26.1
Fe_2O_3	4.9
P_2O_5	21.9
CaO	6.4
U	0.033
Loss on ignition	14.9
Acid insoluble in HNO_3 (1 + 1)	22.9
Na_2O	1.35
K_2O	0.27
Total	98.6

Table 2.--Semiquantitative spectrographic analysis, in percent, of -200 mesh concentrate of leached-zone rock. (Analyst: H. W. Worthing).

Over 10	1.0-10.0	0.1-1.0	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

and does not contain detectable carbonates or organic matter.

X-ray studies

As the material studied is a microcrystalline intergrowth (with the exception of the quartz, some goethite, and stray accessory minerals), it was necessary to use X-ray studies to identify the principal phosphate constituents. The thorough descriptions of the phosphate minerals occurring at Fairfield (Larsen, 1942) and the availability at the U. S. National Museum of pure standards based on these descriptions greatly aided these studies.

A comparison of the spectrograms of the quartz-free fraction and of the green, secondary, birefringent materials with spectrograms of pure standards shows the green material to be a member of the wardite-millisite series. The other major constituent, exclusive of quartz, is pseudowavellite.

Wardite and millisite have similar X-ray patterns but they differ in detail, both in d spacings and in the presence or absence of some lines. The material from the Homeland mine corresponds most closely to millisite. Table 3 contains a list of spacings and intensity measurements of wardite, millisite, and pseudowavellite from Fairfield, Utah, and of millisite and pseudowavellite as measured on spectrograms of the Homeland rock. X-ray powder patterns of the Homeland millisite and of the standard material from Fairfield (fig. 4) show them to be nearly identical.

Iron phosphates were at first investigated because phosphosiderite had been reported in a similar ore (Hill et al., 1950) and because an appreciable quantity of iron was recorded from the chemical analysis. A survey of X-ray patterns of the isodimorphous series, variscite-strengite and metavariscite-phosphosiderite, (McConnell, 1939) as well as those of other iron-

Table 3.--Interplanar spacings of millisite, wardite, and pseudowavellite from X-ray powder patterns (A) (CuKα radiation).

Wardite		Millisite		Millisite		Pseudowavellite		Pseudowavellite	
Fairfield, Utah		Fairfield, Utah		Homeland pit, Florida		Fairfield, Utah		Homeland pit, Florida	
d	I	d	I	d	I	d	I	d	I
6.65	3	6.58	3	6.56	3	5.72	4	5.68	1
5.68	3	5.68	3	5.66	1	4.86	4	4.85	10*
5.04	3	4.98	1	4.95	1/2	3.51	4	3.49	3
4.74	10	4.74	10	4.72	10	2.98	5	2.98	7
3.95	4	3.93	4	3.93	2	2.95	10	2.95	10
3.48	4	3.48	3	3.49	1	2.70	1	-	-
3.10	9	3.40	1	3.40	1	2.37	1/2	-	-
3.00	9	3.29	1	3.28	1	2.21	3	-	-
2.83	7	3.09	9	3.07	6	2.16	4	-	-
2.62	1/2	2.99	9	2.97	8	1.993	1	1.993	1
2.60	7	2.80	9	2.81	8	1.895	4	1.895	3
2.55	1/2	2.59	2	2.57	2	1.755	4	-	-
2.39	1	2.42	1/2	2.43	1	1.514	1/2	-	-
2.33	1	2.30	1	2.30	1	1.492	1/2	-	-
2.262	1	2.25	1	2.25	1	1.469	1/2	-	-
2.166	1	2.166	1/2	2.08	1	1.431	1	-	-
2.115	2	2.108	1	1.993	1				
2.076	1/2	2.058	1	1.899	1				
2.036	1/2	1.997	1/2	1.781	1				
2.006	1/2	1.965	1/2	1.768	1				
1.969	1	1.933	1/2	1.669	2				
1.93	1	1.888	1/2	1.645	2				
1.87	1/2	1.838	1	1.542	1				
1.84	1/2	1.790	1/2	1.486	1				
1.82	1/2	1.768	1						
1.77	3	1.746	1						
1.655	1	1.725	1/2						
1.636	1/2	1.667	1						
1.59	1/2	1.637	1						
1.558	1/2	1.532	2						
1.535	2	1.514	2						
1.516	2	1.461	1/2						
1.46	1	1.423	1						
1.410	1								

*Intensities in this sample are in doubt as result of the intimate intergrowth of this mineral with millisite.

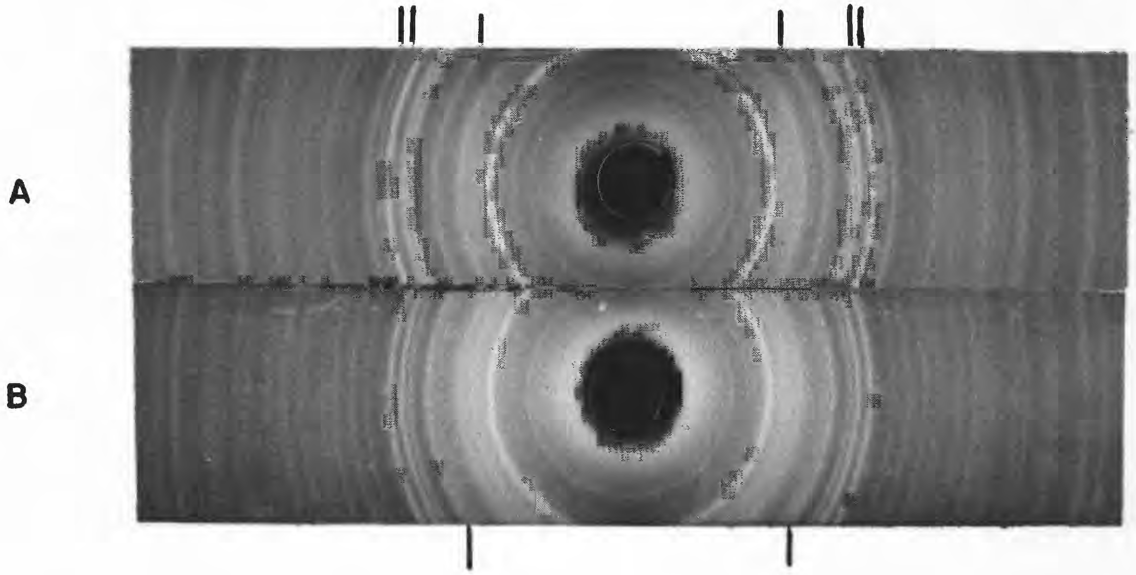

Figure 4.--X-ray powder patterns of millisite. The notches above pattern A indicate apatite lines, those below pattern B indicate quartz lines.

A = millisite from Fairfield, Utah

B = millisite from Homeland mine, Florida bearing phosphate minerals proved fruitless in identifying our material. Although parts of the pattern of phosphosiderite correspond to patterns of the Homeland rock, two moderately strong lines of phosphosiderite ($\underline{d}$ = 4.37 A and $\underline{d}$ = 3.62 A) are consistently absent.

In many spectrograms of Homeland rock three peaks, occurring consistently between 18.2 and 18.8 degrees 2θ (fig. 3), were equal to or higher in intensity than any other peaks in the pattern. A line at 18.8 corresponds to the strongest line of millisite and one at 18.3 corresponds to a moderately strong line of pseudowavellite. The other line (18.5) can be accounted for by gibbsite but not by pseudowavellite or millisite. Gibbsite is a mineral with very few lines in its pattern and only one very strong line. Therefore, the fact that the only peak unaccounted for corresponds to the only strong line of gibbsite makes plausible the assumption that gibbsite is present. In addition a computation of the metal balances of the rock shows an excess of alumina after all oxide deductions for minerals proved to be present.

The fact that the pseudowavellite peak in this rock at 18.3 degrees 2θ has an unusual intensity is explained by its proximity to the two strong peaks at 18.5 and 18.75 (figs. 2 and 3).

The identification of pseudowavellite in this rock need discussion. Almost every peak in a pseudowavellite pattern corresponds to the position of a millisite peak. Two strong lines, however, are distinct--one at 30.3 and the other at 18.3 degrees 2θ. Study of these regions at slow speed and enhanced resolution (fig. 3) proves both peaks to be present. Further proof of the presence of pseudowavellite is obtained by comparing the intensities of the lines of the X-ray pattern of the whole rock from Homeland with those of lines of virtually pure millisite from Homeland.

Thus the peak at 25.5 in figure 2 has a relative intensity of 4. The same peak in the film pattern of Homeland millisite (table 1), d = 3.49 A, has an intensity of 1. The greater intensity in the spectrogram of the whole rock is explained by the coincidence of pseudowavellite and millisite at that position.

Mineral composition

Because of the impossibility of determining the complete mineral composition optically or by mechanical separation methods, the mineral composition of the rock shown in table 4 has been calculated from the chemical composition (table 2). 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. All the remaining CaO was then used to compute pseudowavellite, the only other lime-bearing mineral found. After corresponding deductions of Al_2O_3 and P_2O_5 for pseudowavellite, small amounts of Al_2O_3 and P_2O_5 remained unassigned. All of this remaining P_2O_5 was assigned to wavellite with corresponding deductions of Al_2O_3. The basis of the last step was the microscopic identification of trace amounts of wavellite. There still remained about 3 percent of Al_2O_3. As kaolinite and probably gibbsite were shown to be present by X-ray patterns, the remaining Al_2O_3 was assigned collectively to these minerals. It was not deemed worth while to analyze for soluble silica as a guide to the quantity of kaolinite because both kaolinite and gibbsite are minor constituents. The 23 percent insoluble residue was examined and found to be almost entirely quartz.

It is known (Palache et al., 1951) that the ratio of Na to K in pure millisite is 10:4 whereas that in wardite is approximately 10:1. The ratio

Table 4.--Mineral composition of the rock from Homeland pit, Florida

Constituents	Percentage
Quartz	23
Millisite	32
Pseudowavellite	30
Goethite	6
Wavellite	2
Gibbsite + kaolinite	5
Miscellaneous 1/	Tr
Total	98

1/ Miscellaneous includes zircon, rutile, sillimanite, ilmenite, and tourmaline.

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of Na to K in the Homeland material is 10:2 which would make it more nearly like the millisite from Fairfield than wardite. This variation in chemical composition may explain the minor differences in the X-ray patterns of the millisites. However, it is possible that the ratio of Na to K may be slightly in error because these Homeland determinations were done on the whole rock. The Na and K may exist in trace amounts in other minerals. A calculated composition of the Homeland millisite is listed in table 5, based on the Na:K ratio of 10:2.

Table 5.--Composition of millisite from Homeland, calculated on basis of Na:K ratios

Constituents		Percent
Na_2O		4.16
K_2O		0.85
CaO		6.00
Al_2O_3		36.40
P_2O_5		34.00
H_2O		18.00
	Total	99.41

SUMMARY AND CONCLUSIONS

The deposit at the Homeland mine is the second reported occurrence and the largest known concentration of millisite in the United States. These facts plus the recent report of millisite found in quantity in Senegal (Visse, 1952) probably indicate that the mineral is more widespread than has been supposed.

Millisite is found as an alteration product of pre-existing phosphate minerals in sedimentary deposits and is usually associated with pseudowavellite and other secondary phosphate minerals.

The chemical composition of millisite seems to vary with the ratio of Na to K. This ratio is 10:2 in Florida, 5:2 in Utah, with K absent in the Senegal deposit, This chemical variation may explain some anomalous results obtained from the Florida millisite. For example, the aggregate index of refraction of the Florida millisite ($n = 1.63 \pm 0.005$) is higher than any of the indices of the Utah millisite, $\alpha = 1.584$, $\beta = 1.598$, and

$\gamma = 1.602$ (Larsen and Shannon, 1930). The X-ray patterns of the minerals from both areas match in the low-angle range but show variations in the high-angle range. The Florida millisite is pale green, whereas the Utah millisite is white to light gray.

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