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PHOSPHATE MINERALIZATION AT BOMI HILL AND BAMBUTA, LIBERIA, WEST AFRICA*

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ABSTRACT

An interesting suite of iron phosphate minerals formed by biogeochemical processes occurs at Bomi Hill and Bambuta in western Liberia. The phosphates at Bomi Hill form bouldery aprons on the slopes below two prominent cliffs and occur in place in caves and open fissures in cliffs of high-grade iron ore. They were formed by the interaction of bat dung, or substances derived from it, with exposed iron oxide. The minerals thus formed include strengite and its dimorph, phosphosiderite; a member of the rockbridgeite group (formerly included with dufrenite); and, most noteworthy, leucophosphite, hitherto known only from Western Australia. From chemical, optical, and α -ray data, together with a recent synthetic study, leucophosphite is established as a valid and well-defined mineral species and, so far, the only known alkali-iron phosphate mineral of sedimentary origin. Chemical studies by soils chemists have been correlated with natural occurrences, giving a better understanding of the geochemistry of phosphatic fertilizers and of phosphate minerals.

The phosphates from Bambuta differ from those at Bomi Hill; the differences, however, may reflect incomplete knowledge of the two deposits rather than any significant difference of origin. In both, the source of the phosphorus is believed to be the dung of bats.

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

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OCCURRENCE—LOCALITY AND FIELD RELATIONS

At the request of the Liberian government the iron ore deposits at Bomi Hill, 40 miles north of Monrovia, were mapped in 1943-44 by the U. S. Geological Survey. Limited exposures of a gray to cream-colored rock superficially resembling calcareous tufa were noted near the bases of two cliffs of massive magnetite-hematite ore. It was not until 1949, however, after the jungle growth had been cleared away, and analysis of some of the material showed it to be essentially ferric phosphate, that the significance of these deposits was appreciated.

The field relations of the phosphate rock were studied briefly by T. P. Thayer and G. G. Lill while on furlough with the Liberia Mining Com-



FIG. 1. Phosphate-cemented talus down slope from cliff at west end of Ore Body #1 (Monkey Hill). Note absence below lower iron ore exposures to right, and the cave at base of the 120-foot high cliff. Bomi Hill, Liberia.

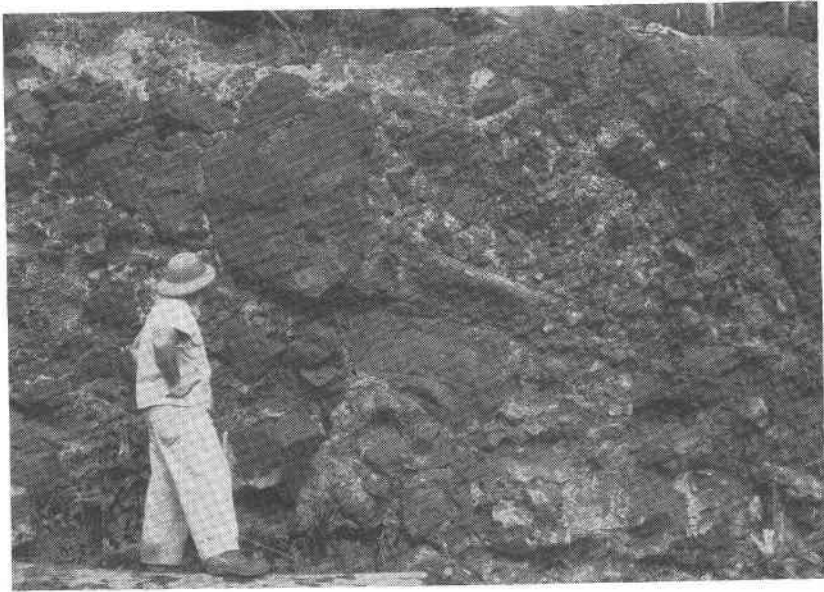


FIG. 2. Massive talus ore cemented by iron phosphate, on south slope of Bomi Hill. Blocks are massive magnetite-hematite. Bomi Hill, Liberia.

pany, Ltd., and they discovered a second occurrence near Bambuta, about 22 miles east of Bomi Hill. The mining company was interested in the high phosphorus content of the material primarily as a contaminant of several tens of thousands of tons of otherwise premium-grade float iron ore, and also because the presence of this phosphate suggested that parts of the main ore bodies might be high in phosphate.

The largest high-grade deposits are on the south slope of Bomi Hill, where they form two prominent cliffs. The phosphate forms bouldery talus aprons on the slopes below the cliffs (Fig. 1), fills joint cracks in massive ore, and replaces some layers of medium-grade ore at the base of the cliffs. The talus consists of fragments of massive iron ore in a matrix of light-colored phosphate (Fig. 2). At the margins of the phosphatic talus, the matrix grades into normal limonite. Accumulations of talus cemented with phosphate extend up into wide joints in the iron ore cliffs below the roosting places of numerous bats (Fig. 3). The talus overlies 50 feet or more of thoroughly weathered residual soil on which, in places, benches have been formed by landsliding. The phosphate is absent below low exposures of iron ore between the two cliffs.

Similar iron phosphate minerals were found on the summit of the second body of massive iron ore, about $1\frac{1}{2}$ miles west of the Boporosuehn trail and about a mile southwest of Bambuta. The phosphate

there forms pink and white cavity fillings in medium-to coarse-grained magnetite, fills narrow fractures, and cements small masses of iron ore fragments. The largest exposure of the breccia noted was about 2 feet across and lay 20 to 25 feet away from the topmost outcrop of massive ore.

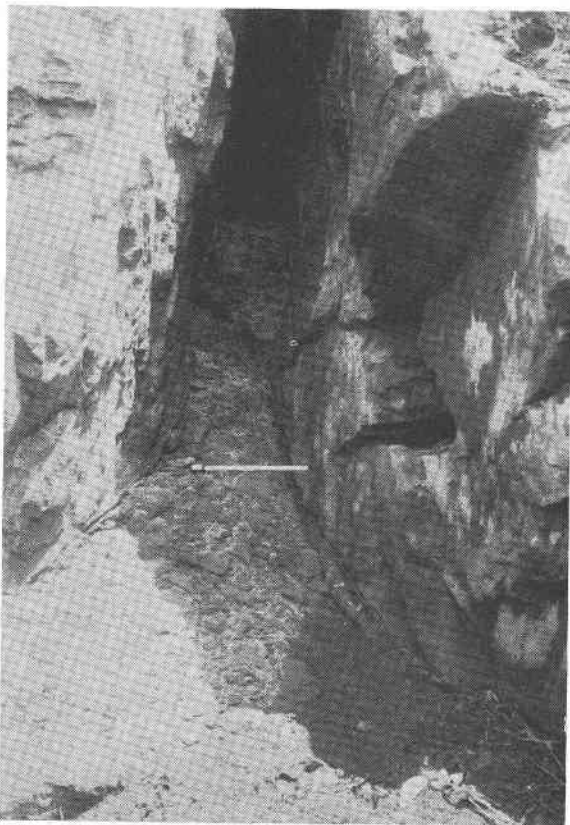


FIG. 3. Iron phosphates cementing iron ore fragments in joint in base of cliff of massive iron ore. (12 inch scale). Bomi Hill, Liberia.

The relations at Bomi Hill indicate that the phosphates form by the reaction of bat excreta with iron oxides under the extreme conditions of the rain-forest climate. Solution cavities in talus boulders of massive ore and in two caves in the highest cliff give eloquent testimony of solution of iron oxides by rain water and organic acid. Abundance of bat guano in the caves and open joints in the cliffs and markedly low phosphorus content in the massive ore itself clearly indicate that bats are the source of the phosphorus. The extent of the accumulations on the slopes below

the cliffs is explained by soil creep or minor landsliding, combined with insolubility of the phosphate. The occurrence of massive strengite on the summit of the hill southwest of Bambuta shows that the strengite, at least, must compare with magnetite and hematite in resistance to solution.

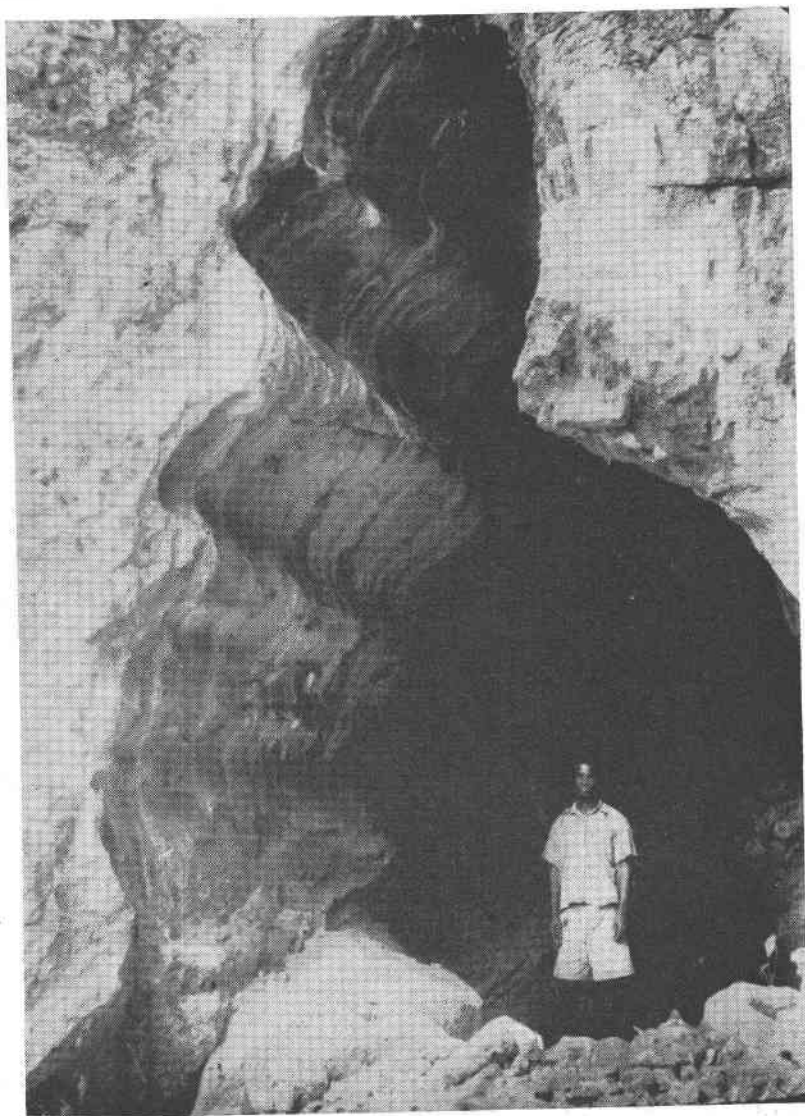


FIG. 4. Cave in massive iron ore at Bomi Hill, inhabited by bats responsible for surficial phosphatization of ore. Note solution flutings in iron ore.

Figures 1, 2, and 3 show typical field relations of the iron phosphates. Figure 4 shows one of the caves, home of the bats responsible for the remarkable phosphatization.

In describing weathering of the iron ores at Bomi Hill, E. F. Fitzhugh, Jr. (1951) stated "The ore and siliceous iron formation at Bomi Hill, Liberia, are similar in character and occurrence to the better-known deposits of Venezuela and Brazil. Iron formation forms a hanging wall and granite gneiss a footwall of the massive, high-grade ore. Ore outcrops and float show induration and recrystallization to a fine-grained, steely hematite. Similar transformations by tropical meteoric waters in Venezuela are noted. Canga capping is confined to the hanging-wall side of the Bomi Hill ore. This, together with comparable occurrences in Venezuela, suggest that the iron in porous limonitic canga is derived from iron-rich, siliceous rocks rather than from high-grade iron ore."

A general account of the Liberian iron ore deposits, by Thayer, Newhouse, and Butler (1952), is in preparation.

GENERAL CHARACTER OF SPECIMENS STUDIED

Nine specimens of phosphatized rock and ore were available for this study; no two were alike in appearance, and almost all of them were loose float and obviously heterogeneous. For this reason conclusions as to paragenesis must rest on interpretation of the mineralogy. Figures 5A, B, C, D, and 6A, B, C, illustrate the variety of the material.

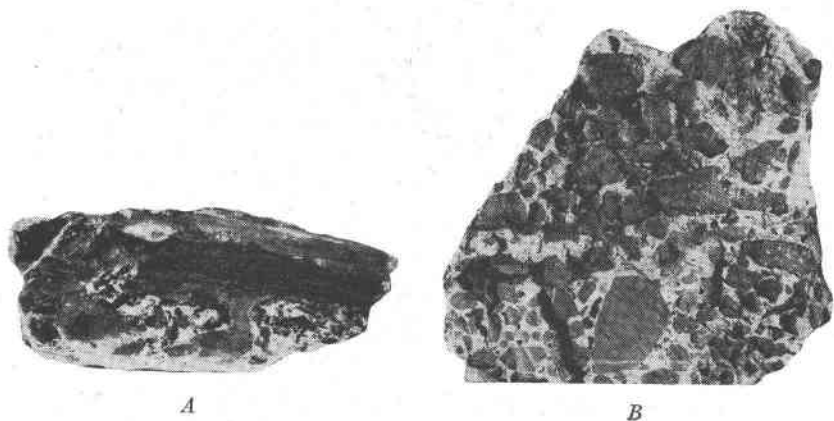


FIG. 5A. "Bomi 1 TPT" shows complex structure of phosphatized ore. The dark band across the middle is essentially limonite. The white areas are largely phosphosiderite and strengite; the black granular areas rockbridgeite; and the gray areas are leucophosphate.

FIG. 5B. "Bomi 6 TPT." Hematite-limonite fragments in phosphosiderite-strengite matrix.

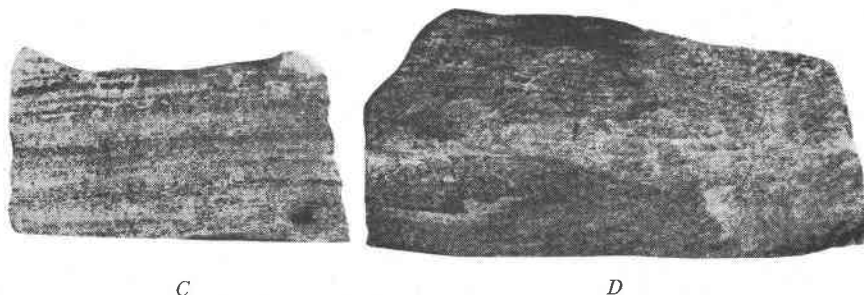


FIG. 5C. "Bomi 4 TPT." Hematite-quartz-phosphosiderite/strengite; replacement of granitic gneiss.

FIG. 5D. "Sta. 27 WHN." Strengite and hematite replacing granitic gneiss. Goethite (?) at lower right corner.

All figures are $\frac{2}{3}$ natural size.

Seven of the specimens are from the Bomi Hill locality, and two are from Bambuta. At Bomi Hill the phosphates include leucophosphate, phosphosiderite, and strengite, associated with hematite-limonite. At Bambuta, there are phosphosiderite, strengite, and (in the two specimens studied) no leucophosphate; the iron oxide is magnetite. This difference in mineralogy may indicate deeper erosion of the ore at Bambuta than at Bomi Hill.



FIG. 6A. Leucophosphate, Bomi Hill. Shows open cavities and meta-colloid structure. Six x-ray samples were studied from the face of this specimen.

Two of the Bomi Hill specimens are breccia of hematite-limonite cemented by phosphate ("Bomi 1 TPT" and "Bomi 6 TPT"), three are hematitic granitic gneiss, with iron oxide and other minerals partially replaced by phosphate ("Bomi 4 TPT," "ST 27 WHN" and "SA 34 C"), and two are massive leucophosphite ("SP 35 Ore Body IIIC"), and the

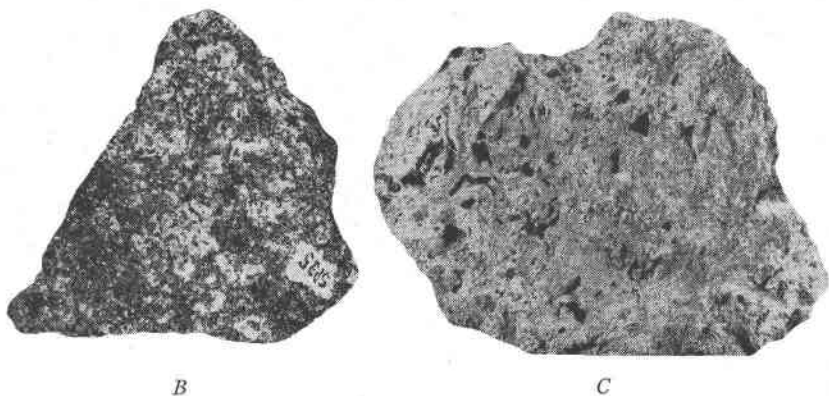


FIG. 6B. "SP 35 Ore body III C" Bambuta. Magnetite, with vugs of phosphsiderite and strengite.

FIG. 6C. Bambuta "SP 34." Massive strengite. Shows shrinkage openings and meta-colloid structure.

All figures are $\frac{2}{3}$ natural size.

two others (from Bambuta) massive microcrystalline strengite ("SP 34"), and magnetite with phosphsiderite-strengite ("SP 35").

DESCRIPTION OF SPECIMENS FROM BOMI HILL

A. Breccia of iron oxide in phosphate matrix

"Bomi 1 TPT." This is a rather small specimen a few inches across, and is shown in Fig. 5A. It was broken from rock in place at the base of the high cliff, and probably represents material formed by replacement along a fracture in magnetite-bearing gneiss. A very rough separation may be made into light brownish layers, largely phosphatic, and dark mahogany brown pebbly layers, essentially limonitic. Both layers include quartz and hematite particles. Typical areas were sectioned, and, by careful picking of the specimen under a binocular microscope, more or less apparently homogeneous phases were isolated (to correspond to individual minerals or substances perceived in thin section). The picked materials were analyzed by x -ray diffraction patterns and thereby, despite their apparent homogeneity, shown to be in general inhomogeneous aggregates of two or more compounds. Four such samples of x -rayed material, selected by color, had the following compositions:

X-ray film 5385 (brick red and black)	Hematite, strengite, trace of unidentified
X-ray film 5386 (black)	Rockbridgeite group
X-ray film 5387 (brown and black)	Leucophosphite, goethite, trace of unidentified
X-ray film 5388 (light reddish crust)	Strengite with traces of quartz and of unidentified.

Applying these data to the interpretation of the thin sections (Figs. 7 and 8) it appears that the light brown areas of the hand specimen (pale yellow in section) consist essentially of apparently isotropic leucophosphite and crystalline colorless strengite. The specific characters and relationships of these minerals will be considered further on. Here it may be noted that leucophosphite varies from optically isotropic to weakly birefringent, resembling chert in this respect, and that strengite and phosphosiderite are so similar optically that in fine-grained mixtures their differentiation is impractical microscopically. There are also present with these phosphate minerals quartz grains which show strikingly corroded outlines (see Figs. 7 and 8), and brown to black masses of limonite with outlines suggesting original magnetite.



FIG. 7. "Bomi 1 TPT." Bomi Hill, Liberia. $\times 8$ Thin section. Hematite-limonite (black), quartz (white) and leucophosphite (gray). Around the larger quartz particles right of center, instead of leucophosphite there is strengite (which has about the same relief and hence does not show up under ordinary light); at the lower left corner is a fragment of hematite almost completely replaced by phosphate.



FIG. 8. "Bomi 1 TPT." Bomi Hill, Liberia. $\times 8$ Thin section. Hematite (most of the black areas), quartz (white) and rockbridgeite (very dark or black—indicated by R) in a groundmass of strengite (gray areas).

The darker bands are mainly brown-black limonite, with much light brown iron phosphate (?) and colorless phosphate. Some, at least, of the "limonite" may be hematite.

Where the colorless crystalline strengite is abundant, there is seen a mineral of the rockbridgeite group (Fron del, 1949) which is well crystallized, sometimes in radial aggregates. It is black in the hand specimen, and characteristically pleochroic in reddish brown and bluish green in thin section. Its optics resemble those of dufrenite, with which it was formerly included. As shown by Fron del, dufrenite and rockbridgeite differ crystallographically, as well as chemically: dufrenite being best represented by $\text{Fe}''\text{Fe}_4'''(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$, whereas rockbridgeite may be $\text{Fe}''\text{Fe}_4'''(\text{PO}_4)_3(\text{OH})_5$.

"Bomi 6 TPT." This is a breccia consisting of slightly rounded hematite fragments up to 2 cm. across (some partly altered to limonite) in a flesh-colored dense phosphate matrix.

Microscopically, the flesh colored matrix is mostly isotropic (leucophosphate) where it adjoins the ore fragments it is definitely crystalline, and x -ray analysis shows the crystalline material to be phosphosiderite and strengite, with a little unidentified substance, and a trace of quartz (x -ray film 5301).

The rock is illustrated in Fig. 5B; a typical thin section is shown in Fig. 9.

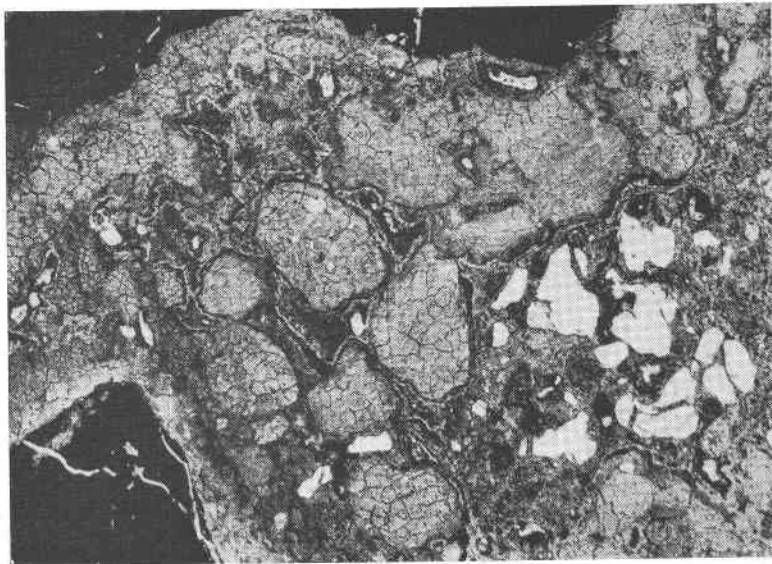


FIG. 9. "Bomi 6 TPT." Bomi Hill, Liberia. $\times 8$. The rounded masses are apparently homogeneous and isotropic, and are referred to leucophosphite; their matrix however is anisotropic and is shown to be phosphosiderite-strengite. The white areas are quartz, showing characteristic corroded outlines; the black is hematite-limonite (the thin white lines are cracks). Note shrinkage (?) cracks in the leucophosphite.

B. Hematitic granitic gneiss

"Bomi 4 TPT." This specimen (Fig. 5C) superficially resembles a sandstone, although it is a granitic gneiss containing iron ore with the original structure emphasized by the banding of dark hematite and light quartz and phosphate. The microstructure is similar to that of "Sta. 27 WHN" and "Sta. 34 c" described in detail below.

"Sta. 27 WHN." This is a banded rock consisting of alternate streaks of minute grains of black hematite and pinkish strengite. At one end of the specimen is a deep red-brown translucent substance, probably goethite. Its appearance is shown in Fig. 5D.

In thin section, granular quartz and hematite are abundant in an obscurely crystallized or isotropic matrix identified by x -rays as strengite. Figures 10 and 11 show the microscopic character of this rock.

C. Leucophosphite from Liberia and Australia

Presumably the least changed material from the original phosphatized ore is that represented by a buff to liver-brown stony mass, generally dense and taking a high polish, but containing numerous open cavities. It is shown in Fig. 6A. Inspection of the polished surface shows a hetero-

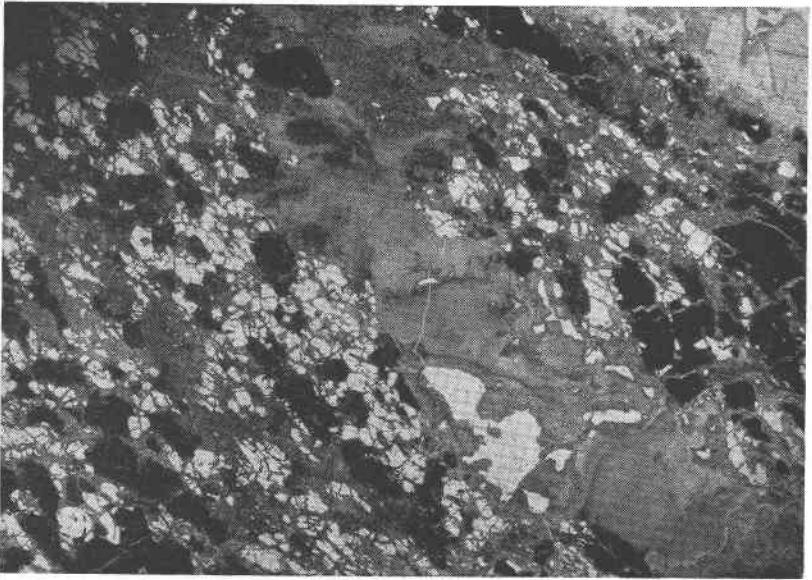


FIG. 10. "Sta. 27 WHN." Bomi Hill, Liberia. $\times 8$ Thin section. Ore-bearing granite gneiss partly replaced by strengite. The largest white area (lower center) is a void; the others are quartz grains.

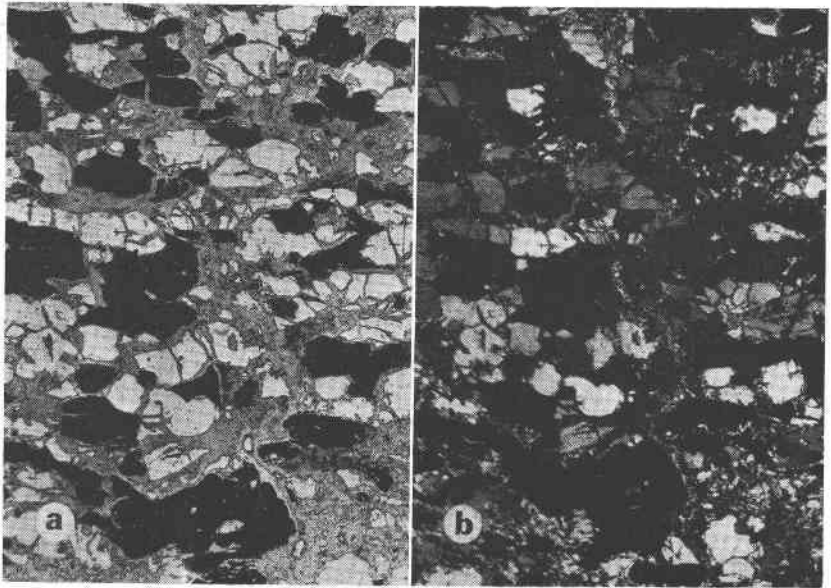


FIG. 11. (a) ordinary light. (b) crossed nicols. "Liberia Sta. 27 WHN." Bomi Hill, Liberia. $\times 12\frac{1}{2}$. Hematite-quartz in phosphosiderite-strengite matrix. Under crossed nicols the anisotropy of the matrix is clearly seen.

geneous metacolloid structure suggesting brecciation of an original gel-structure, with marked contrast in depth of the color of successive zones and of matrix and fragments. Small irregular grains of quartz and hematite are strewn through the mass. The microstructure of the Liberian leucophosphate is shown in Fig. 12.

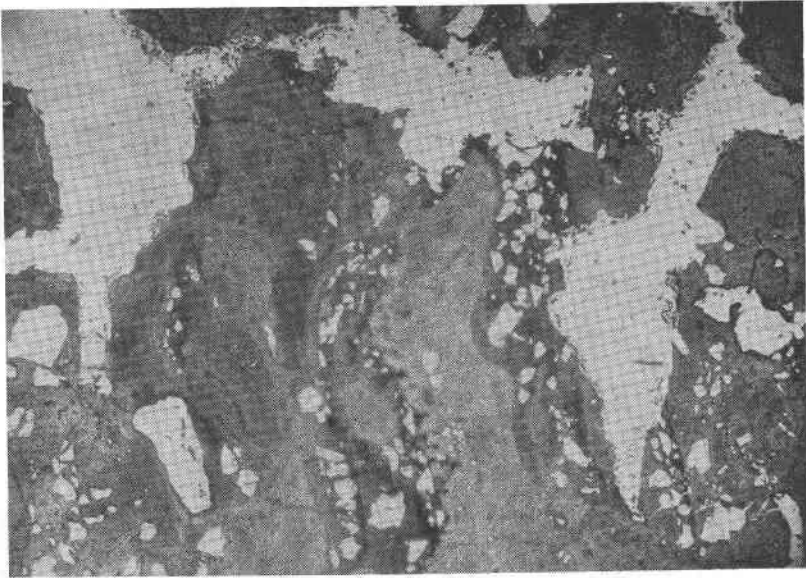


FIG. 12. Leucophosphate. Bomi Hill, Liberia. $\times 8$. Shows meta-colloid structure. The clear large white areas are voids in the specimen probably caused by shrinkage. The smaller white areas are mostly quartz grains. The varying shades of gray correspond to minor variations in texture and possibly composition.

The Australian leucophosphate is markedly different in appearance. It is far more obviously heterogeneous with bright green (talc?) areas and hematitic streaks. It is soft and friable, and has a distinct, by no means unpleasant aromatic odor. The freshly scratched surface is white, but in time turns to a light purplish brown. The microstructure is shown in Fig. 13. At a casual glance, and even with chemical analyses available, there would be nothing to suggest the essential identity of the African and Australian material, but the x -ray data demonstrate this beyond question.

DESCRIPTION OF SPECIMENS FROM BAMBUTA

A. Magnetite with Phosphosiderite, etc.

Specimen "SP 35 Ore body III C Bambuta" is massive magnetite with its grains peripherally martitized (Fig. 16) and with countless vugs filled



FIG. 13. Leucophosphate. U.S.N.M. 96772. Australia. $\times 8$ Thin section. Shows highly irregular variation in texture and, no doubt, composition. The black areas are opaque grains probably hematitic; the rest of the section, different kinds of fine grained material, much of which, however, yields a characteristic x -ray diffraction pattern.

with excellently developed rose-colored clear crystals of phosphosiderite and colorless crusts of strengite (illustrated in Fig. 6B, 14, and 15).

The association of the dimorphous phosphates, phosphosiderite and strengite, appears to be fairly common. The crystallographic relations of these minerals, their isodimorphous aluminum homologues, meta-variscite and variscite, and the mixed iron-aluminum dimorphs, barrandite and clinobarrandite have been summarized by Strunz and Sztrokay (1939).

Hutchinson (1950) points out that these minerals presumably "represent the normal products of phosphatization of igneous and other aluminosilicate rocks in tropical and subtropical regions of markedly seasonal rainfall." He cites Lacroix who compared this process to lateritization, involving loss of silica and soluble bases, which occurs

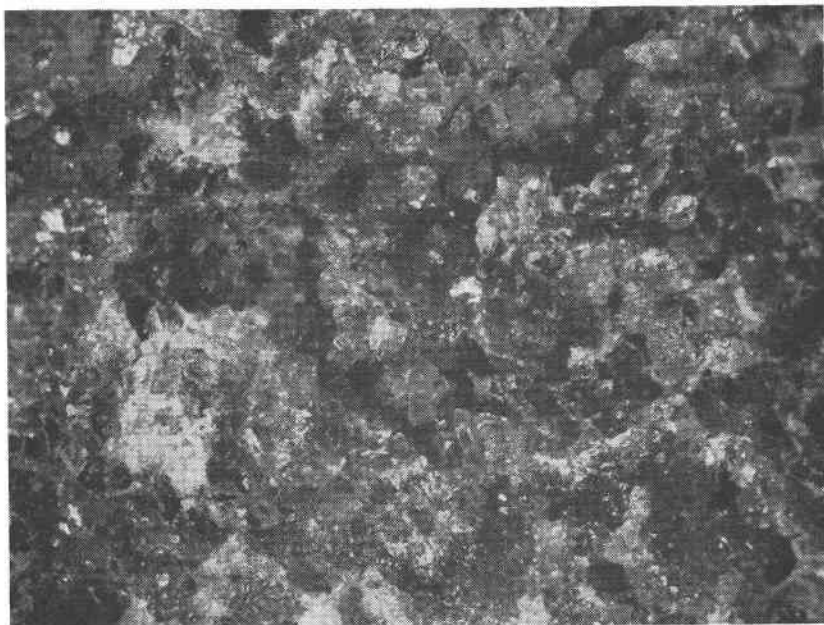


FIG. 14. "SP 35 Ore Body III C Bambuta." $\times 7$. Bambuta, Liberia. Vugs in magnetite lined with sharp-edged red crystals of phosphosiderite.

when phosphate is absent. Phosphosiderite, however, has been reported (six localities) only from Europe (Laubmann and Steinmetz, 1920).

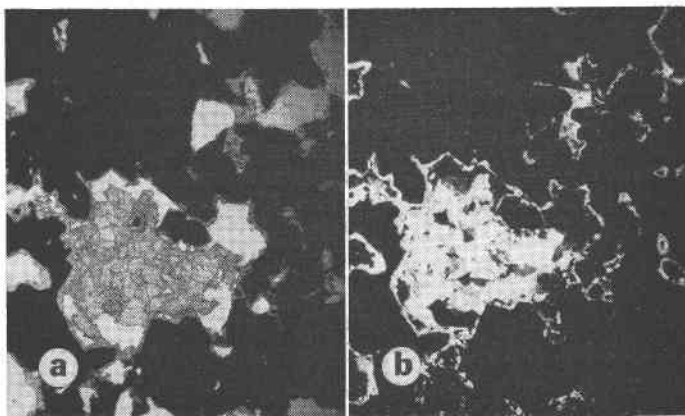


FIG. 15. (a) Ordinary Light. $\times 6$. (b) Crossed nicols. "SP 35 Ore body III C Bambuta." Bambuta, Liberia. Magnetite ore with phosphosiderite. The clear areas (left) are open cavities. Phosphosiderite (gray) lines and partly fills the vugs. Some strengite is also present, but cannot be distinguished in the figures. Crossed nicols shows twinning in phosphosiderite.

B. *Strengite (rock)*

A second massive phosphate, with merest traces of iron oxide minerals and very little quartz, is represented by "SP 34 Ore body III C Bambuta" and is illustrated in Fig. 6C. This is a light brownish, rather porous, but firmly coherent aggregate, more or less stony in texture, and, with a

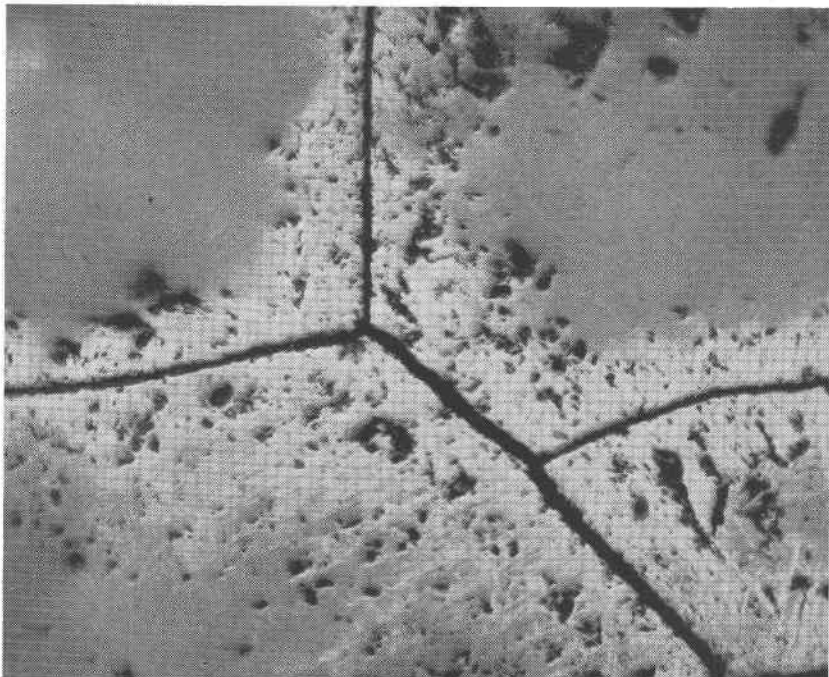


FIG. 16. "SP 35 Ore Body III C Bambuta." $\times 200$. Bambuta, Liberia. (Polished section.) Magnetite oxidized to hematite along grain boundaries. The hematite follows octahedral planes in the magnetite (martitization) as is clearly seen in the lower right corner. This ore is porous, and the pores are more or less lined with pink to red phosphosiderite, accompanied by minor strengite. (Figs. 6B, 14, and 15.)

hand lens, clearly shows colloform structure like that of the leucophosphate. Very rarely, in the numerous open cavities, extremely minute crystals are visible. Both crystals and the main mass give the x -ray pattern of strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (x -ray film 5299). It will be noted that this is simply the formula of leucophosphate after deduction of $(\text{K}, \text{NH}_4)_2\text{O}$ and part of the water. The work of Cole and Jackson (1950), cited in detail below, shows that the related mineral minyulite dissociates at a pH near 7 to produce variscite as a stable phase, and thus throws light on the relations of leucophosphate to phosphosiderite-strengite.

INVESTIGATION OF LEUCOPHOSPHITE

X-ray data for natural and synthetic leucophosphate

Numerous *x*-ray diffraction patterns, made of variously-appearing particles of this substance, were the same with insignificant variations. Table 1 gives the *x*-ray data for the Liberian mineral, for the type Australian leucophosphate (which likewise shows a varied degree of crystallinity from "statistically isotropic to barely visible crystals"), and for synthetic leucophosphate (Haseman, Lehr and Smith, 1950). It will be seen that these three patterns are substantially the same, the minor discrepancies being assignable to impurities in the natural compounds and to variation in isomorphous replacement of NH₄ and K, and of Al and Fe.

It was suspected that the better crystallized material might be fine-grained strengite or phosphosiderite, but careful examination of eight

TABLE 1. X-RAY DATA FOR LEUCOPHOSPHITES FROM LAKE WHEELHAMBY, S.W. AUSTRALIA AND BOMI HILL, LIBERIA, AND FOR SYNTHETIC LEUCOPHOSPHITE. FILTERED IRON RADIATION, $\lambda = 1.937\text{\AA}$

Australia		Africa		Synthetic "I" ¹	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I/I</i> ₁
7.5	5½	7.6	6	7.50	.31
6.73	10	6.78	10	6.77	1.00
		6.11	5		
5.93	8	5.96	9	5.92	.76
4.71	5	4.78	5½	4.73	.28
4.26	4	4.30	5	4.23	.21
4.17	6	4.23	5	4.20	.28
4.05	5	4.08	5	4.05	.14
3.90*	3				
3.76	5	3.80	4	3.78	.21
3.68H	3				
3.51	5	3.55	2		
3.35	6½	3.38	5	3.34	.35
		3.35			
3.19	6b	3.23	4b	3.20	.14
				3.09	.14

H = wholly or partly hematite.

* = probably an unidentified impurity.

b, vb = broad, very broad.

¹ Haseman, Lehr, and Smith (1950)

Intensities, by comparison with a scale based on $\log \sqrt{2}$ so that $I_{10}/I_2 = 16$, approximate the integrated rather than the peak intensities. Weaker lines have been omitted.

(Table continued on next page)

TABLE 1—(continued)

Australia		Africa		Synthetic "T"	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I/I₁</i>
3.03	7	3.06	7	3.03	.59
				3.00	.28
2.95	5	2.98	4	2.97	.28
2.88	6	2.91	6	2.90	.37
2.79	6b	2.83	6	2.81	.41
2.70H	6				
2.64	6b	2.68	4	2.66	.35
		2.66	6	2.64	.37
		2.58	4		
2.52H	7			2.53	.17
		2.54	2		
2.47*	5			2.48	.17
		2.49	3½		
		2.446	3		
2.358}	5	2.382	2	2.38	.17
2.318}		2.343	4	2.33	.21
2.210H		4b			
		2.279	2b		
2.130	5b	2.154	2½	2.14	.21
1.995	2	2.000	5b		
		1.966	3b		
1.920	1	1.928	4b		
1.907*	1b	1.896	4b		
1.842H	2b				
		1.819	4		
1.758	2b	1.786	4b		
		1.706	3b		
1.692H	6b				
1.645	4b	1.658	4b		
1.598	4b	1.588	2		
		1.570	2		
1.532}	3	1.526	2		
1.503}					
1.490H}	6	1.498	4b		
1.479 }		1.454	3b		
		1.259	3b		
		1.228	2b		
		1.130	2b		
		1.081	3vb		
		1.067	2vb		2vb
	1.020	3vb			
		1.009	3vb		

x-ray patterns of various parts of the specimens failed to show the strongest line of either of these minerals.

The smaller cell size of the Australian mineral is in accord with the presumed substitution of aluminum for some of the iron. Some of the leucophosphate powder patterns were spotty, which confirms the observation that all of it is not cryptocrystalline.

Hutchinson (1950) mentions Bannister as having proved by *x*-ray diffraction that the Australian leucophosphate is amorphous, which is not in accord with our findings. However, this seeming conflict was resolved on further investigation of the type specimen (U. S. National Museum 96772). The visible heterogeneity of this material persists in the microscopic range; that is to say, it is impossible to take a small *x*-ray sample of seemingly uniform material and say in advance whether it will be "amorphous" or give a definite crystalline pattern. Of three trials, one was amorphous, two gave good or poor, but consistent, *x*-ray patterns of leucophosphate.

It should also be noted in this connection that Haseman, Lehr and Smith expressly note that their synthetic "I" (leucophosphate), unlike most of their other preparations, "gave a weak pattern"; although this is rather surprising in view of the relatively large size of crystals illustrated in their paper (some 200 microns in length).

Spectrographic analysis of leucophosphate

Spectrographic analysis by K. J. Murata of the Liberian leucophosphate showed:

%	
>1	Fe, P
.X	Si, Al, Ti
.0X	Ca
.00X	Mg, Ba, Mn, Cu, Zr
.000X	Sr, Cr

not found: B, Be, Sn, Zn, Cd, V, Ni, Co, Ag, Bi, Mo, W, Pb, Tl, Ge, In, Y, La, Na.

The material selected for spectrographic and chemical analysis was freed as much as possible from quartz. Also it should be noted that the alkali metals were not sought spectrographically; the wave-length range photographed did not include their most sensitive lines. Otherwise the agreement between the spectroscopic data and the analysis is good. Murata also noted the possible presence of ammonia, judging from the behavior of the sample during arcing. This was the first indication of its presence in the Liberian mineral.

Chemical analysis

TABLE 2. ANALYSES OF NATURAL AND SYNTHETIC LEUCOPHOSPHITE

	A	B	C	D
Insoluble	(4.92)			
SiO ₂	4.32	.00		
Al ₂ O ₃	.88	12.73		
Fe ₂ O ₃	36.85	32.82	38.9	40.55
Cr ₂ O ₃	—	.00		
FeO	.14	.00		
CaO	.16	tr		
MgO	.02	.73		
MnO	—	.22		
NiO	—	tr		
(NH ₄) ₂ O	1.99	.09		
K ₂ O	7.86	7.88	12.2	11.96
Na ₂ O	.22	.13		
H ₂ O+	11.67	12.28		
H ₂ O-	1.23	6.59		
TiO ₂	.41	—		
P ₂ O ₅	33.46	26.69	37.4	36.07
CO ₂	—	.17		
C (organic)	.30	tr		
Cl	—	—		
SO ₃	—	—		
Ignition loss	—	—	11.6	11.42
	99.51	100.33	(100.1)	100.00
Sp. gr.	2.6	2.45	2.93	
<i>Ratios</i>				
Fe ₂ O ₃ +Al ₂ O ₃	1.90	3.71		2
(NH ₄) ₂ O+K ₂ O+Na ₂ O	1.00	1.00		1
P ₂ O ₅	1.87	2.11		2
H ₂ O+	5.14	7.66		5

A. Leucophosphite, Bomi Hill, Liberia.

M. K. Carron, analyst.

B. Leucophosphite, Ninghanboun Hills, Lake Weelhamby, Southwest Australia.

D. G. Murray, analyst.

C. Leucophosphite, synthetic.

Haseman, Lehr, and Smith (1950).

D. Theoretical K₂O · 2Fe₂O₃ · 2P₂O₅ · 5H₂O.

Discussion of analyses

Allowing for about 5% of siliceous impurity in the African material, and for replacement of K₂O by (NH₄)₂O there appears to be a satisfac-

tory agreement between the analysis of this leucophosphate and the theoretical $K_2O \cdot 2Fe_2O_3 \cdot 2P_2O_5 \cdot 5H_2O$. The Australian leucophosphate, although in general chemically comparable, contains hematite and other impurities, and a notable Al_2O_3 content probably, in part, in isomorphous replacement of Fe_2O_3 . The similarity in composition and the common x-ray diffraction pattern indicate a species rank for the African and Australian minerals; comparison with the synthetic preparation shows that this is justified.

Synthesis of leucophosphate

If possible, a new mineral of complex composition should be synthesized as assurance of the validity of the formula proposed from the analysis. A formula obtained from a synthetic substance of known composition, homogeneity, and physical properties is much more acceptable than one inferred from analysis of a complex mixture. Happily, while the natural impure leucophosphate was being studied, Haseman, Lehr and Smith (1950) prepared and described in completely satisfying detail a substance whose properties establish it beyond question as artificial leucophosphate. In brief, they added to precipitated ferric phosphate (from ferric chloride and orthophosphoric acid) potassium hydroxide, to a pH of 3. The resulting precipitate, after washing, was suspended in KOH solutions of alkalinity up to pH 8, with concentrations of potassium phosphate from .001 to 3.5M. (PO_4 basis). After sealing, the suspensions were digested from 1 to 54 days at constant temperatures between 27° C. and 145° C.

Morphology and optical data for synthetic leucophosphate

The excellent synthetic study of Haseman, Lehr, and Smith gives satisfactory morphological and crystallographic data for this mineral species. They show photomicrographs of leucophosphate crystals with formula $K_2O \cdot 2Fe_2O_3 \cdot 2P_2O_5 \cdot 5H_2O$ (and of the homologous $(NH_4)_2O \cdot 2Fe_2O_3 \cdot 2P_2O_5 \cdot 6H_2O$). They report for the synthetic: pale yellow color; indices 1.706, 1.720, and 1.741; monoclinic symmetry; $Z \wedge c = 2^\circ - 3^\circ$; habit, stout prisms terminated by clinodomes. This color agrees with the yellowish brown of the Liberian mineral whose mean refractive index lies close to 1.723. The density of the Liberian mineral was 2.6, against 2.93 for the synthetic; the Liberian mineral however is porous and contains about 5% of quartz, and ammonium replaces part of the potassium.

MINERALS RELATED TO LEUCOPHOSPHITE

Leucophosphate is one of a genetically closely related group of naturally occurring alkali iron-aluminum phosphates, including the sub-

stances that have been named paratooite, taranakite, minervite, palmerite, and minyulite.

Paratooite is somewhat sketchily described from Elder Rock, in the desert about 160 miles north of Adelaide, South Australia, by Mawson and Cooke (1907). It is formed by the action of bird droppings on ferruginous (magnetite and hematite) quartzite. "Much" ammonium is mentioned in their account, although the two analyses given do not show any. Their analyses vary widely, with alkalis in one not mentioned and in the other determined by difference; both analyses sum to 100.00. In the latter 1.22% of "alkalies, etc." are cited. The refractive indices are not given, beyond a mention of "yellowish-brown birefringent globules" with double refraction about .023, and index (sic) much above quartz; this is for the substance without alkalis; the other is "isotropic, light yellow." These data are inadequate to define the substances. The analyses compute approximately to $2(\text{Fe,Al})_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ and $(\text{Al,Fe})_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, respectively. The paratooite minerals need further study.

L. R. Catalano (1933) described a deposit off the coast of Argentina, essentially potassium aluminum phosphate, formed by penguins nesting on an island composed of quartz porphyry and granite. No optical or *x*-ray data are given. He describes and gives an analysis of "whitish nodules, whose diameter varies from a few millimeters to 5 centimeters. They crumble in the fingers giving a white, unctuous powder in which are sandy particles. . . ." Catalano derives a different formula from that ascribed to palmerite, but his data are too vague for any definite characterization of the material.

A much more satisfactory situation exists with regard to taranakite, minervite, and palmerite, the recent work of Bannister and Hutchinson (1947) having shown their identity. Although the *x*-ray patterns and optical constants of the poorly crystallized natural minerals are identical, there is considerable variation in the reported analyses, which approximate $\text{K}_2\text{O} \cdot 3(\text{Al, Fe})_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$. The synthetic study of Haseman, Lehr, and Smith shows that the composition of taranakite is $2\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5 \cdot 26\text{H}_2\text{O}$, and deviations from this in analyses of the natural substances may be referred to impure material.

Minyulite, $\text{KAl}_2(\text{PO}_4)_2(\text{OH, F}) \cdot 4\text{H}_2\text{O}$ is mentioned by Bannister and Hutchinson (1947) as being the only potassium aluminum phosphate defined precisely, chemically and crystallographically; with no potassium iron phosphate so defined. Leucophosphate and taranakite (Haseman, Lehr, and Smith, 1950) may also now be listed as well-defined species.

The taranakite minerals and minyulite, though containing essential K_2O , differ sharply from leucophosphate in morphology and optical character, as well as chemically.

GEOCHEMISTRY OF LEUCOPHOSPHITE AND RELATED PHOSPHATES

Within the last year three important papers have appeared which help elucidate the relationships of the Liberian phosphates: one by Haseman, Lehr, and Smith (1950), and two by Cole and Jackson (1950), all of which deal with the physical chemistry of the systems and minerals in question; but first, we should consider the source of the components that enter these systems—potassium, ammonium, phosphorus, and iron (aluminum).

Sources of constituent elements

The potassium has two obvious sources—one organic and one inorganic. The former is the excreta of birds and mammals (bats, etc.). The latter is potassium feldspar, a common and abundant constituent of many igneous, metamorphic, and sedimentary rocks.

Analyses of fresh guano from both birds and bats show notable quantities of K₂O. In Table 3, taken from Hutchinson (1950) three analyses, one of bird, two of bat guano, show respectively 2.51, 3.85, and 1.57% K₂O. (In the bird guano cited, there is also 3.51% Na₂O.

TABLE 3. ANALYSES OF FECES AND GUANO

	A	B	C	D	E	F
H ₂ O	9.40	43.96	29.40	22.28	83.65	82.63
Organic matter	81.75	18.94	17.74	56.03		
Total N	21.66	2.33	2.86	17.41	10.25	11.73
P ₂ O ₅	4.30	16.34	16.80	7.14	6.95	7.42
Alkalies, etc.	3.70	20.36	27.84			
Sand	.85	.40	8.22			
Insol.				1.47	.16	1.39
Na ₂ O				3.51		
K ₂ O				2.51	3.85	1.57
CaO				3.67	2.36	4.56
MgO				.50	1.40	1.03
Al ₂ O ₃					.00	.49
Fe ₂ O ₃					.38	.78
SO ₃					3.00	3.80

- A. Excrement of *Pelecanus occidentalis thagus* (pelicans), air dried apparently.
- B. Feces of *Otaria byronica* (sea lion).
- C. Guano from seal feces, Peru.
- D. Guano (bird) Peru.
- E. Fresh bat guano, Lares, Puerto Rico.
- F. Fresh bat guano, San German, Puerto Rico.

The data in Table 3 also show a nitrogen content varying from 2.33% to 21.66%. (It should be noted that the low figures are for feces of sea-mammals; were the nitrogen content of their liquid urine added, the

figure would be far higher.) The analyses of bat guano, presumably including solid and liquid excreta, run over 10% N, while the two analyses of bird guano, in which all of the excreta are solid, run twice as high.

No attempt will be made to unravel the complicated chemistry whereby this nitrogen is converted, in part or wholly, into ammonium. That this does occur cannot be questioned, nor that some of the other strong base, K_2O , is likewise liberated or made available for fixation in inorganic phosphate compounds. An abundance of phosphorus is at hand in the guano.

The commonly present additional source of K_2O in the phosphatized country rock has already been mentioned. It is not probable that such a source of K_2O is of any great significance in the formation of complex potassium phosphates. Iron and aluminum, however, are practically absent in feces and guano, and must be derived wholly from the country rock, whatever it may be, on which the guano was deposited. On destruction of the (felspathic) rock, some potash may be released along with the alumina.

One aspect of the geochemistry of the nitrogen should be mentioned. In birds the semisolid urine consists, more or less, of relatively stable and insoluble uric acid. The liquid urine of mammals, however, is characterized by urea, unstable and soluble. This changes first to ammonia, which in turn oxidizes to nitric acid. This explains the nitrate often found in caves frequented by bats. The intense alteration of original rock or ore shown in Liberia and elsewhere, effected by bat excreta, may in part be explained by a secondary action of nitric acid, as well as the first-formed alkaline ammonia and potash solutions.

Replacement of siliceous (and carbonate) rocks by phosphatizing solutions has been described by many writers. The extensive phosphate deposits of oceanic coral islands need only be mentioned; less familiar is phosphatization of igneous rocks, as described by McConnell (1943), where augite-andesite has been replaced by phosphosiderite-strengite. An analysis gave:

Phosphosiderite and strengite	87.2
Ilmenite (Ti-magnetite)	3.0
Quartz and opaline silica	4.3
Leucosene (TiO_2)	3.9
H_2O- , H_2O+ (opal), organic	1.6
	100.0

On the same island, an amygdaloidal scoria has been partially replaced, most of the feldspar laths being replaced by either clear quartz or variscite with metavariscite (both $AlPO_4 \cdot 2H_2O$). The source of the phos-

phate was guano from sea birds (masked booby, *Sula dactylotra*). Similarly, Willemse (1949) described a South African occurrence in which a dolerite has been converted to aluminum-iron phosphate (77–89 per cent, the balance essentially SiO_2). The source of the phosphate is droppings from birds and dassies (i.e. rabbits). A laterite derived from the unphosphatized dolerite contained only 0.4% P_2O_5 .

In these occurrences, it will be noted that the phosphate formed is non-potassic. However, Lacroix (1936) described lava changed to taranakite in a bat cave in basalt; and further that minervite (taranakite) has changed to redondite (barrandite) by loss of alkalis. Very likely then, the occurrences described by McConnell and Willemse were originally potassic (or ammoniac) but have altered by loss of alkali.

Physical chemistry of alkali iron-aluminum phosphates

Haseman, Lehr, and Smith (1950) have shown that taranakite, leucophosphite (and homologous aluminum and ammonium compounds), and minyulite, can form under soil conditions. Other possible compounds of the same constituents may be synthesized, but are not known to form under ordinary, natural conditions. Their observations in reference to the role of potassium and ammonium are noteworthy: "The digestion of precipitated phosphates of iron and aluminum in solutions of potassium or ammonium phosphate invariably resulted in the absorption of potassium or ammonium by the solid to form a complex phosphate of the respective uni- and ter-valent cations. Similar digestions in solutions of the phosphates of lithium, cesium, calcium or magnesium phosphates yielded variscite, strengite, or berlinite" ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, and AlPO_4 , respectively). That is, complex alkali compounds of the leucophosphite-taranakite-minyulite type form when the proper alkali is available; any simple iron-aluminum phosphates changing into the alkali compounds. At first glance, this might seem to be opposed to the findings of Cole and Jackson (1950) who investigated the solubility behavior of minyulite $\text{K}[\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4]_2\text{OH}$ and variscite $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$. They found that minyulite transforms to variscite, which is the reverse of the reaction indicated above. However, in the reaction variscite (strengite) \rightarrow taranakite (minyulite, leucophosphite) an excess of K or NH_4 ion was present, whereas in the reverse reaction minyulite \rightarrow variscite, an aqueous suspension of minyulite was treated with dilute NaCl solution containing HCl or NaOH to establish a pH of 2, 3, 4 . . . 9. Thus, removal of K or NH_4 ion, regardless of other alkali or alkali-earth ions present, would result in the formation of variscite, etc., in agreement with the findings of both groups of workers. Cole and Jackson note that suspensions of minyulite in $\text{N}/_{20}\text{NaCl}$ are nearly neutral (pH 6.5 after one day). How-

ever, in two weeks the pH changes to 4.6, corresponding to the formation of a second solid phase in the suspension, namely variscite. In suspensions more acid than pH 4.0, solution of variscite occurs, the excess hydrogen ion going into water perhaps according to a reaction such as $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4 + 2\text{H}^+ \rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O}$. On the other hand, in suspensions more alkaline than pH 4.0 hydroxyl ions are removed perhaps in the reaction $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4 + (\text{OH})^- \rightleftharpoons \text{Al}(\text{OH})_3 + \text{H}_2\text{PO}_4^-$. In other words, variscite is amphoteric, with pH 4 the neutral (isoelectric) point.

From this summary of Cole and Jackson's data, it is seen that the initial (metastable) equilibria in suspensions of minyulite at varying pH in the absence of K, reach a final stable equilibrium at a pH corresponding to the existence of variscite as the solid phase present. Extrapolating from the experimental relations of minyulite and variscite, to the analogous iron-bearing system, a similar formation of strengite $\text{Fe}(\text{OH}(\text{OH})_2\text{H}_2\text{PO}_4$ is proposed by these writers, who point out in this connection the well-known isomorphism in the variscite-barrandite-strengite crystal series, and, also, the similar isoelectric pH values of 4.0 for variscite and 3.4 for strengite (Swenson, Cole, and Seiling, 1949).

From this, it is to be concluded that the complex alkali compounds found in nature (leucophosphite, taranakite, minyulite) form in the presence of an excess of the proper alkali (K, NH_4) ion; and that such compounds are unstable in water free of K and NH_4 passing by loss of alkali into the far more commonly-found variscite-barrandite-strengite minerals.

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