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LEUCOPHOSPHITE, A NEW OCCURRENCE IN THE QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRAZIL[1]

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ABSTRACT

A sixth occurrence of leucophosphite, the third organic occurrence, is in a cave in the Serra do Tamanduá, Minas Gerais, Brazil. The mineral fills the central part of cavities, and, intimately mixed with limonite, it lines small cavities and coats wallrock of the cave. The leucophosphite was identified by *x*-ray, spectrographic, and chemical analyses. Leucophosphite from Serra do Tamanduá differs from other leucophosphites principally in its lower K_2O and higher $(NH_4)_2O$ content.

INTRODUCTION

Leucophosphite, a rare iron phosphate with the formula $(K, NH_4)(Al, Fe)_2(PO_4)_2 \cdot 2H_2O$ (Smith and Brown, 1959, p. 141–142) occurs in a cave in the Serra do Tamanduá, Minas Gerais, Brazil (Simmons, 1963, p. 71–72). Leucophosphite has been previously reported from five other localities: 1) Lake Weelhamby, Ninghanboun Hills, Western Australia (Simpson, 1932); 2) Bomi Hill, Liberia (Axelrod and others, 1952); 3) Sapucaia mine, Minas Gerais, Brazil (Lindberg, 1957); 4) Fletcher mine, North Groton, New Hampshire (Mrose, *in* Behier, 1960, p. 47); and 5) Marivolanitra, Ambatofindrakana, Malagasy Republic (Behier, 1960, p. 46–47). The Serra do Tamanduá leucophosphite is richer in ammonia and lower in potash than previously described leucophosphites.

The Serra do Tamanduá leucophosphite apparently was formed by aqueous solutions that passed over bat guano and reacted with iron oxides in the cave wallrock. The genesis is similar to that of leucophosphite at Lake Weelhamby which resulted from solutions passing over bird dung and reacting with serpentine, and that at Bomi Hill[2] which occurs in and in front of a cave and resulted from reaction of massive hematite with solutions which passed over bat guano. The Sapucaia, Fletcher, and Marivolanitra leucophosphites are pegmatite occurrences.

This study is a by-product of a joint U. S. Geological Survey—Departamento Nacional da Produção Mineral study of the iron ore deposits of the State of Minas Gerais, Brazil, under the auspices of the Agency for International Development, U. S. Department of State.

LOCATION AND ACCESSIBILITY

The cave containing leucophosphite is in the famous Brazilian iron

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] According to R. D. Jones, Republic Steel Corporation (1961, written comm.), the cave containing leucophosphite at Bomi Hill has been destroyed by mining operations.

region, the Quadrilátero Ferrífero, in the south-central part of the State of Minas Gerais. The locality is near the west end of the Serra do Tamanduá about 50 kilometers west of Belo Horizonte, the State capital. The cave, little known among local residents, lies 1,430 meters south and 3,280 meters east of the northwest corner of the Santa Bárbara quadrangle, Minas Gerais, but its position is not shown on the quadrangle map.

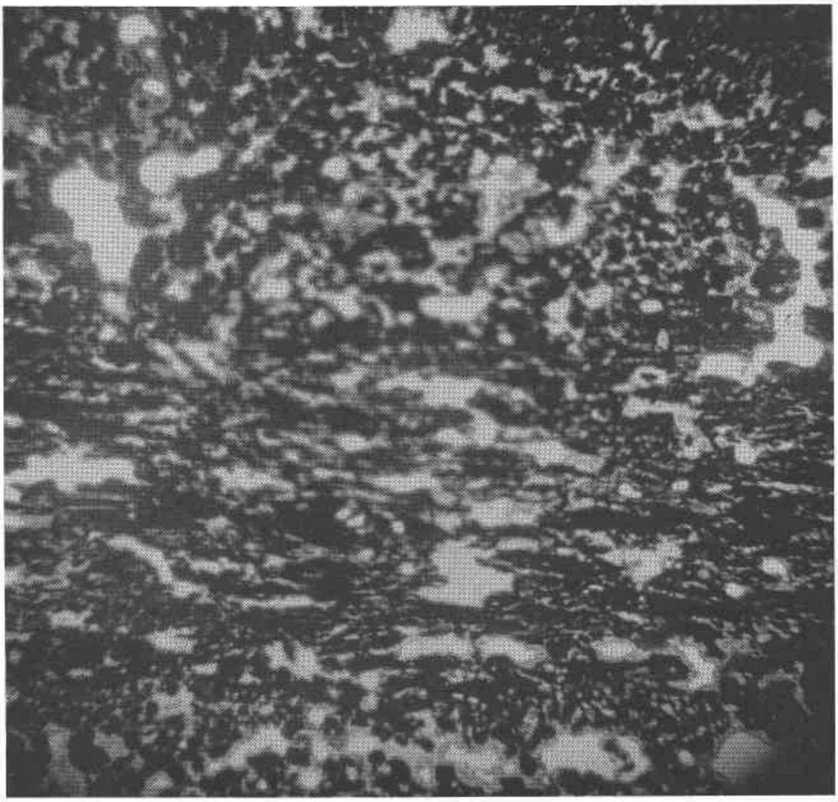

FIG. 1. Leucophosphite (light gray) lining cavities in itabirite. Diagonal of area is 5 mm.

The vicinity of the cave is reached by driving 76 kilometers east of Belo Horizonte on the asphalt highway designated BR-31, better known as "paralelo vinte" because of its proximity to the twentieth parallel south latitude. The dirt road leading south to Barão de Cocais is followed for 18 kilometers.

The cave is reached by a $1\frac{1}{2}$-kilometer hike from the road, starting 1,660 meters south and 4,360 meters east of the northwest corner of the

Santa Bárbara quadrangle. This point is about 100 meters west of a knoll marked on the quadrangle map as "T 938." A trail can be followed for the first kilometer, and the last half kilometer is over open slopes.

Occurrence and Description

Leucophosphite occurs in a thin veneer on the itabirite wall of a cave, and lines and fills microscopic and small macroscopic vugs and cavities in the itabirite (Fig. 1). The leucophosphite in the wallrock coating is intimately mixed with limonite and minor quantities of minerals tentatively identified as strengite and metastrengite, and together the minerals form a brown layer as much as 3 mm thick. Coated surfaces are smooth and have a polished appearance which contrasts with the uneven surface of uncoated itabirite. In the macroscopic cavities leucophosphite is white to pale yellow and finely crystalline.

Fig. 2. Leucophosphite in cavities. Area is 1.5 mm across. The white areas are nearly pure leucophosphite. The black areas with rough or shiny surfaces are maghemite, martite, and magnetite. The dark-gray to black areas with metacolloidal structure, particularly prominent around the cavity at upper right, are mixtures of limonite, leucophosphite, strengite, and metastrengite. The gray areas in the central part of the two larger cavities are voids.

Although pure leucophosphite is transparent in thin section, most of the mineral is translucent to nearly opaque as a result of admixed limonite and limonite coating. Most of the leucophosphite coating itabirite wallrock is translucent brown, and in this respect resembles leucophosphite in contact with vug walls. The latter, also with intimately associated limonite, forms a thin film that lines the cavities. Leucophosphite in the central part of the vugs is clear, yellowish brown, and almost free of other minerals (Fig. 2).

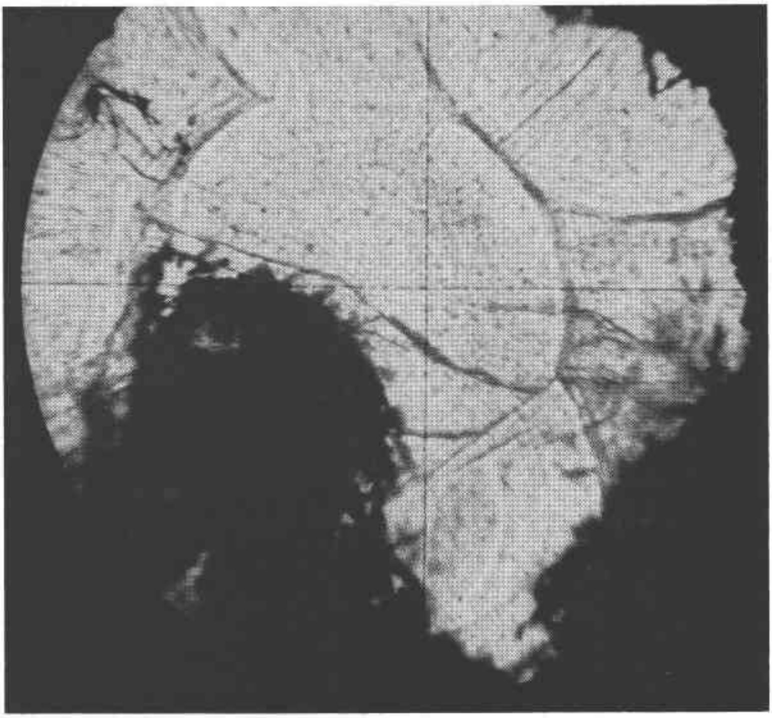

FIG. 3. Annular and acicular structures in leucophosphite. Area is 0.5 mm across.

Some clear leucophosphite has concentric annular and radiating acicular structures (Fig. 3). The concentric rings are nearly perfect circles or arcs of circles from the centers of which the acicular structures radiate. The structures have a striking appearance through crossed nicols (Fig. 4). Within each structural unit the needles from a spherulitic cross. From a few grains of this clear, annular, acicular leucophosphite the mineral was determined to have a large 2V; indices above 1.70 and under 1.74; and a mean index above 1.71.

Itabirite, the cave wallrock on and in which the leucophosphite was deposited, is a low-grade metamorphic oxide-facies iron formation, comprising alternating iron-rich and silica-rich laminae of hematite and very fine grained quartz, and may contain dolomite, magnetite, maghemite, and other minerals. The itabirite wallrock of the Serra do Tamanduá cave is exceptional in that the iron-rich laminae are composed mostly of maghemite, and contain very little hematite; and the alternating laminae, containing little quartz, consist mostly of vugs containing leucophosphite. Magnetite commonly occurs in the iron-rich layers of itabirite that have dolomite in the silica-rich layers. This suggests that the itabirite wallrock originally had a high dolomite content, and that solution of the dolomite resulted in the cavities and cave in which the leucophosphite was deposited.

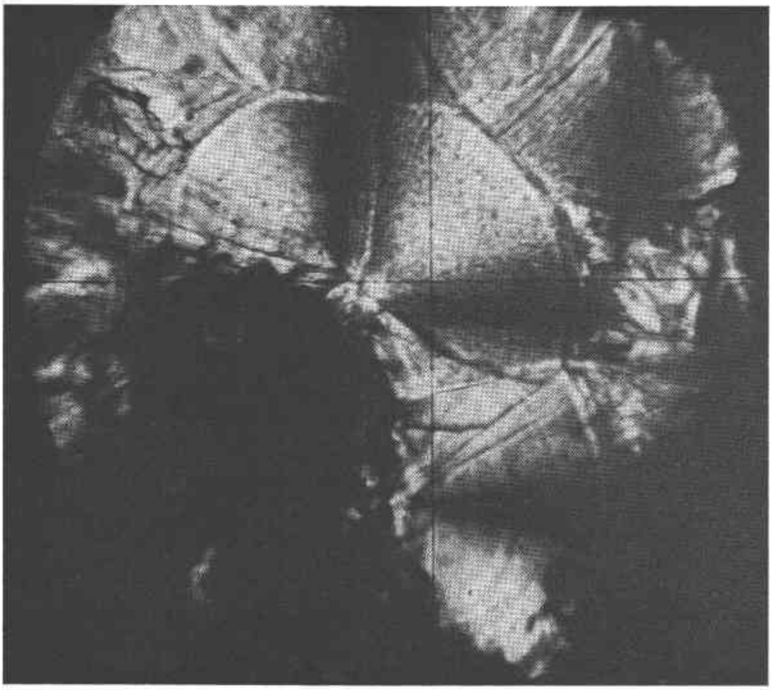

Fig. 4. Annular and acicular structures and spherulitic cross in leucophosphite. Area is 0.5 mm across.

The approximate composition of the itabirite wallrock as determined from grain counts of four thin sections is in volume per cent: maghemite, martite, magnetite, and hematite (?), 45 per cent; leucophosphite, 20 per cent; limonite, 19 per cent; voids, 12 per cent; quartz, 4 per cent. Of the leucophosphite, only 5 per cent or less (less than 1 per cent of the total rock volume) is clear leucophosphite.

SAMPLES AND CONCENTRATES

Two leucophosphite concentrates were analyzed during the present study. Both were made by crushing samples to −100 and +200 screen size, washing, drying, separating the heavy minerals with bromoform, and removing quartz from the light fraction with a Franz separator. The small concentrate made from the first sample was sufficient for only a tentative identification. A second collection of four larger samples was made, and a second series of analyses was performed with the combined concentrate made from the four samples. The two concentrates, one made from a small sample and the other from four larger samples, are referred to as Concentrate 1 and Concentrate 2, respectively, throughout this report.

Microscopic examination of the two concentrates indicated the presence of limonite. The quantity of limonite is difficult to determine because of its intimate association with the leucophosphite and the similarity in appearance of the admixed minerals regardless of the proportions. Nevertheless, it is estimated that Concentrates 1 and 2 contained 20 and 10 per cent limonite, respectively.

X–RAY DATA

The leucophosphite was first tentatively identified from an *x*-ray analysis of Concentrate 1 by M. H. Falabella, Brasil Comissão Energia Nuclear, Rio de Janeiro.

The Tamanduá leucophosphite *x*-ray pattern is slightly different from those of Lake Weelhamby, Bomi Hill, Sapucaia, and from synthetic leucophosphites in reflection intensities and d-spacings (Table 1). These differences undoubtedly result from substitution of ammonia for potash. As noted below, the Tamanduá *x*-ray pattern also contains extra reflections indicating the presence of impurities.

The original identification was verified by M. L. Lindberg, U. S. Geological Survey, Washington, D. C, from an analysis of Concentrate 2. Although intensity of the lines was not measured, a direct visual comparison was made with other leucophosphite film strips. M. L. Lindberg (1962, written comm.) reports as follows:

> "The *x*-ray powder pattern shows that leucophosphite is the chief mineral present in the sample. The extra reflections in the *x*-ray powder pattern suggest that strengite and metastrengite are present as impurities in the sample, but their concentration is not adequate to give well-defined *x*-ray patterns."

SPECTROGRAPHIC DATA

Spectrographic analyses were made of Concentrate 1 by C. V. Dutra, Instituto de Tecnologia Industrial, Belo Horizonte, Brazil, and of Concentrate 2 by H. W. Worthing, U. S. Geological Survey, Washington, D. C. These analyses appear in Table 2 with spectrographic data for the Bomi Hill leucophosphite. The amounts of the elements are concordant for all three analyses. However, it should be noted that potassium was not detected in Concentrate 1, and was reported as 0.1 per cent in Concentrate 2. Chemical analyses of the same two samples yielded 0.48 and 0.75 per cent potassium, respectively (Table 3).

TABLE 1. *X*-RAY DATA FOR LEUCOPHOSPHITE

Lake Weelhamby[1]		Bomi Hill[1]		Serra do Tamanduá[2]		Synthetic[3]		Sapucaia[4]	
d	I	d	I	d	I	d	I	d	I
7.5	5½	7.6	6	7.61	vw	7.50	.31	7.60	3
6.73	10	6.78	10	6.88	s	6.77	1.00	6.79	10
		6.11	5	6.08	vs			6.09	1
5.93	8	5.96	9			5.92	.76	5.99	7
4.71	5	4.78	5½	4.80	vw	4.73	.28	4.76	3
4.26	4	4.30	5	4.27	w	4.23	.21	4.28	2
4.17	6	4.23	5			4.20	.28	4.21	2
4.05	5	4.08	5			4.05	.14	4.08	2
3.90*	3								
3.76	5	3.80	4			3.78	.21	3.79	3
3.68H	3							3.65	1
3.51	5	3.55	2					3.54	1
3.35	6½	3.38 3.35	5	3.38	vw	3.34	.35	3.37	3B
								3.25	½
3.19	6B	3.23	4B			3.20	.14	3.23	½
						3.09	.14		
3.03	7	3.06	7	3.08	m	3.03	.59	3.06	7
etc.		etc.		#		etc.		etc.	

[1] Data from Axelrod and others, 1952, p. 899–900.

[2] Analyzed by M. H. Falabella, Brasil Comissão Energia Nuclear, Rio de Janeiro, 1961, using CuK/Ni radiation, Debye-Scherrer camera, diameter 114.6 mm.

[3] Data from Haseman and others, 1950, p. 80.

[4] Data from Lindberg, 1957, p. 219.

* Probably an unidentified impurity.

H—wholly or partly hematite; B—broad; vs—very strong; s—strong; m—medium; w—weak; vw—very weak.

Reflections below 3 Ångstrom not measured.

TABLE 2. SEMIQUANTITATIVE SPECTROGRAPHIC DATA FOR LEUCOPHOSPHITE

Bomi Hill[1]		Serra do Tamandua[2]		Serra do Tamandua[3]	
		Concentrate 1		Concentrate 2	
Elements	Per Cent	Elements	Per Cent	Elements	Per Cent
Fe, P	M	Fe, P	M	Fe, P	M
				Al	.2
Si, Al, Ti	>.1	Ti, Si, Al	>.1	K	.1
				Ti, Si	.07
				Mg, Mn, Cu	.03
Ca	>.01	Zn, Ca, Mg, Mn, Ba	>.01	Zr	.015
				Ca, Zn	.01
				Na	.007
Mg, Ba, Mn, Cu, Zr	>.001	Na	>.001	Ba, V	.003
				Cr, Mo, Ni	.001
Sr, Cr	>.0001	Cr	>.0001	Pb	.0002
				Be	.00007
				Ag	.00003
Not encountered: Ag, B, Be, Bi, Cd, Co, Ge, In, La, Mo, Na, Ni, Pb, Sn, Tl, V, W, Y, Zn		Not encountered: As, B, Be, Co, Ga, Ge, K, Li, Mo, Ni, Pb, Sr, Y, Zr		Not encountered: As, Au, B, Bi, Cd, Ce, Co, Ga, Ge, Hf, Hg, In, La, Li, Nb, Pd, Pt, Re, Sb, Sc, Sn, Sr, Ta, Te, Th, Tl, U, W, Y, Yb	

[1] Adapted from analysis by K. J. Murata *in* Axelrod and others, 1952, p. 901.

[2] Analysis by C. V. Dutra, Instituto de Tecnologia Industrial, Belo Horizonte, Brazil, 1961.

[3] Analysis by H. W. Worthing, U. S. Geological Survey, 1962. Results reported in per cent to nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc. which represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30 per cent of the time.

M major constituent.

CHEMICAL DATA

Two chemical analyses were made of the Serra do Tamanduá leucophosphite (Table 3). These analyses, a partial analysis of Concentrate 1 by Aida Espinola, Brasil Departmento Nacional da Produção Mineral, Rio de Janeiro, and a complete analysis of Concentrate 2 by Blanche Ingram, U. S. Geological Survey, Washington, D. C., indicate that the mineral has a much lower K_0O content and a higher $(NH_4)_2O$ content than all analysed leucophosphites from other localities. Unfortunately, the purity of the concentrates, the amount of limonite and possibly strengite and metastrengite, was indeterminable, and other differences may exist that are masked by the impurities.

TABLE 3. CHEMICAL ANALYSES OF LEUCOPHOSPHITE

	Lake Weelhamby Australia (1)	Bomi Hill Liberia (2)	Serra do Tamanduá Brazil (3)	Serra do Tamanduá Brazil (4)	Sapucaia Brazil (5)
			Concentrate 1	Concentrate 2	
K_2O	7.88	7.86	0.48	0.75 e	10.93
Na_2O	0.13	0.22	0.27		0.53
$(NH_4)_2O$	0.09	1.99	n.d.	2.4 d	
FeO	0.00	0.14	n.d.		0.00
CaO	trace	0.16	n.d.		
MgO	0.73	0.02	n.d.		
MnO	0.22		n.d.		
Fe_2O_3	32.82	36.85	42.3	42.3 a,b	41.02
Al_2O_3	12.73	0.88	n.d.	0.82 c	0.25
Mn_2O_3			n.d.		0.57
TiO_2		0.41	0.22		
P_2O_5	26.69	33.46	21.7	37.5 f	34.71
CO_2	0.17		n.d.		
C organic	trace	0.30	n.d.		
H_2O+	12.28	11.67	17.4	16.1 g	11.20
H_2O-	6.59	1.23	1.30		
Insoluble		(4.92)	n.d.		0.45
SiO_2		4.32	n.d.		
Total	100.33	99.51	83.67	99.9	99.96

(1) D. G. Murray, analyst (Simpson, 1932, p. 72).

(2) M. K. Carron, analyst (Axelrod and others, 1952, p. 902).

(3) Aida Espinola, Brasil Departamento Nacional da Produção Mineral, Rio de Janeiro, analyst.

(4) Blanche Ingram, U. S. Geological Survey, Washington, D. C., analyst.

(5) M. L. Lindberg, analyst. "A spectrogram (IWS-561) by Harry Bastron shows in addition .X% Mg, .X% Si, .OX% Ba, and a line detected for Cu, Sn, and Be." (M. L. Lindberg, 1957, p. 220).

n.d.—not determined.

a—A 100 mg. sample was ignited at 900° C. to constant weight. The ignited sample was fused with Na_2CO_3, leached with water and filtered. The residue was used to determine Fe_2O_3, and the filtrate was used for P_2O_5 and Al_2O_3 determinations. Separate samples were taken for $(NH_4)_2O$, K_2O and H_2O.

b—Determined volumetrically with standard $K_2Cr_2O_7$ after reduction.

c—Determined colorimetrically using alizarin red S.

d—Fifty mg. sample dissolved in H_2SO_4 and $(NH_4)_2O$ determined using the micro-Kjeldahl method.

e—One hundred mg. sample dissolved with $HF\text{-}HClO_4$ and K_2O determined flame photometrically.

f—Determined gravimetrically as $Mg_2P_2O_7$.

g—Water was determined by correction of the ignition loss for $(NH_4)_2O$. It was also determined by ignition of a sample in a modified combustion train at 900° C. in a stream of oxygen and correcting the absorbed H_2O for H_2O contributed by $(NH_4)_2O$.

The potash values of Concentrates 1 and 2, even if corrected for estimated impurities of 20 and 10 per cent limonite, respectively, are less than 1 per cent, only a small fraction of that encountered in other leucophosphites. The 2.4 per cent value determined for ammonia, which would be higher if corrected for impurities, is slightly higher than the ammonia content found in Bomi Hill leucophosphite. Only 0.09 per cent ammonia was found in the Lake Weelhamby mineral.

Comparison of chemical analyses in Table 3 shows the Serra do Tamanduá leucophosphite to most closely resemble the Bomi Hill leucophosphite. This would be expected from their similarity in origin and environment of deposition.

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