

LEUCOPHOSPHITE FROM THE SAPUCAIA PEGMATITE MINE, MINAS GERAIS, BRAZIL*

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ABSTRACT

At the Sapucaia pegmatite mine, Minas Gerais, Brazil, leucophosphite $[\text{KFe}_2^{III}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}]$ occurs sparingly as minute buff-colored crystals in vugs in frondelite. The optical constants are $\alpha=1.707$, $\beta=1.721$, and $\gamma=1.739$; biaxial positive; dispersion $v>r$ very strong. Leucophosphite is monoclinic, pseudo-orthorhombic, space group $P2_1/n$ (primitive cell); the cell dimensions are $a_0=9.73$, $b_0=9.60$, and $c_0=9.69$ Å; $\beta=102^\circ 16'$; the principal d -spacings occur at 6.79, 5.99, and 3.061 Å. The chemical analysis, in per cent, is K_2O 10.93, Na_2O 0.53, Fe_2O_3 41.02, Al_2O_3 0.25, Mn_2O_3 0.57, P_2O_5 34.71, H_2O 11.20, insoluble matter 0.45; total 99.66.

INTRODUCTION

This paper presents a detailed mineralogical description of leucophosphite, $\text{KFe}_2^{III}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, from the Sapucaia pegmatite mine, Minas Gerais, Brazil. Leucophosphite has previously been reported only from two deposits, both of sedimentary origin: (1) from Weelhamby Lake, Nighanboun Hills, Western Australia (Simpson, 1931–32), where it occurs as fine-grained chalklike masses which derive their phosphate content from bird guano; and (2) from Bomi Hill, Western Liberia (Axelrod et al., 1952) where it occurs in heterogeneous metacolloidal masses which derive their phosphate content from bat dung. The leucophosphite from the Sapucaia pegmatite mine represents not only the first known occurrence of leucophosphite in a pegmatite but also the first natural occurrence in well-defined crystals. Synthetic crystals (Haseman, Lehr, and Smith, 1950) have been prepared at temperatures ranging between 75° and 145° C., at a pH of 2.5 to 6.0, and at phosphate concentrations from 1.0 to 3.5*M*.

The Sapucaia pegmatite mine is in the municipality of Galilea in the Rio Doce valley region of eastern Minas Gerais. This mine was mapped and a suite of minerals collected by W. T. Pecora and A. L. de M. Barbosa during the years 1942–45. Minerals already described from this pegmatite include frondelite (Lindberg, 1949), faheyite (Lindberg and Murata, 1953), moraesite (Lindberg, Pecora, and Barbosa, 1953), tavorite and barbosalite (Lindberg and Pecora, 1954*a*), and avelinoite (Lindberg and Pecora, 1954*b*). The mica deposits and general features of the pegmatite have been described by Pecora and others (1950).

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OCCURRENCE

Leucophosphite occurs sparingly in close association with avelinoite† and metastrengite in crystal aggregates that line vugs in frondelite. The material replacing the frondelite walls of the vugs is crudely layered. Metastrengite is most abundant on the outside of the specimens where it occurs interstitially to compact masses of radiating fibers of frondelite. The frondelite is partly altered and the masses of fibers may form a loose meshwork interstitial to which grow crusts of crystals of avelinoite, together with minor amounts of leucophosphite. The leucophosphite crystals frequently contain a few radiating fibers of residual frondelite.

Metastrengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, avelinoite, $\text{NaFe}_3^{III}(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and leucophosphite, $\text{KFe}_2^{III}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ are secondary minerals after frondelite, $\text{MnFe}_4^{III}(\text{PO}_4)_3(\text{OH})_5$. Frondelite contains a small amount of sodium (Na_2O 0.98 per cent) and potassium (K_2O 0.12 per cent), probably substituting for manganese. Although all the chemical constituents are present in frondelite for the formation of the secondary minerals metastrengite, avelinoite, and leucophosphite, it seems likely that sodium and potassium solutions reacted with frondelite to form avelinoite and leucophosphite. The space occupied by vugs in the frondelite is insufficient to yield, through leaching of frondelite, enough sodium and potassium to form masses of avelinoite and leucophosphite.

CRYSTALLOGRAPHY

Leucophosphite occurs in minute doubly terminated diamond-shaped plates (Fig. 1). The habit and morphological measurements suggest a holohedral orthorhombic mineral. Single-crystal Weissenberg photographs by their intensity distribution and lattice level symmetry show that leucophosphite is actually monoclinic. The extinctions observed on the Weissenberg patterns are consistent with the space group $P2_1/n(C_{2h}^5)$ and the habit of the crystals confirm a center of symmetry.

The crystallographic elements for both the primitive monoclinic and for the pseudo-orthorhombic *B*-centered settings are given in Table 1. Goniometric measurements were made on eight crystals oriented parallel to the *c*-axis, and on three crystals oriented parallel to the *a*-axis, pseudo-orthorhombic *B*-centered setting. Calculated differences in ϕ and ρ angles between \pm forms (elements calculated from *x*-ray data) are smaller than the error of measurement on the two-circle goniometer. For this reason the choice of (111) and $(\bar{1}\bar{1}1)$ (morphological data, Table 1) has been made on a statistical basis—that is, data for the pair of faces symmetrical to the *ac* symmetry plane with the largest values of ϕ and ρ are

† See preceding article.

TABLE 1. MORPHOLOGICAL DATA¹

(measured)

Forms	ϕ Range	ϕ Aver- age	ρ Range	ρ Aver- age	A^2 Range	A Aver- age
100	—	90°00'	89°20'–92°30'	90°25'	—	0°00'
210	51°50'–52°37'	52°02'	89°36'–91°02'	90°21'	—	—
111	32°37'–34°08'	33°08'	57°30'–59°08'	57°54'	62°00'–63°43'	62°52'
$\bar{1}11$	–31°30'–32°46'	32°05'	55°22'–58°00'	57°07'	63°00'–64°32'	63°33'

CRYSTALLOGRAPHIC ELEMENTS AND ANGLE TABLE

(calculated from *x*-ray data)

Pseudo-orthorhombic orientation

Monoclinic; prismatic $2/m$ Space group: $B2_1/n$ (C_{2h}^5) $a:b:c=1.577:1:1.267$; $\beta=90^\circ12'$; $p_0:q_0:r_0=0.8035:1.267:1$ $r_2:p_2:q_2=0.7893:0.6342:1$; $\mu=89^\circ48'$; $p_0' 0.8035$, $q_0' 1.267$, $x_0' 0.0035$

Forms	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
100	90°00'	90°00'	0°00'	90°00'	89°48'	0°00'
210	51°45'	90°00'	0°00'	51°45'	89°51'	38°15'
111	32°30'	56°21'	51°05'	45°24'	56°15'	63°26'
$\bar{1}11$	–32°16'	56°16'	128°38'	45°18'	56°23'	116°21'

Primitive orientation

Monoclinic; prismatic— $2/m$ Space group: $P2_1/n$ (C_{2h}^5) $a:b:c=1.013:1:1.009$; $\beta=102^\circ16'$; $p_0:q_0:r_0=0.996:0.986:1$ $r_2:p_2:q_2=1.014:1.010:1$; $\mu=77^\circ44'$; $p_0' 1.109$, $q_0' 1.009$, $x_0' 0.2174$

Forms	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
110 ³	45°18'	90°00'	0°00'	45°18'	81°19'	44°42'
011	12°10'	45°53'	77°44'	45°25'	44°35'	81°19'
$\bar{1}01$	90°00'	38°43'	128°43'	90°00'	50°59'	128°43'
$\bar{1}11$	–38°28'	52°11'	128°43'	51°48'	60°21'	119°26'

¹ Pseudo-orthorhombic orientation was used in measuring these crystals.² Three crystals were measured in a position with (100) polar.³ Equivalent forms:*B*-centered orientation100
210
111
 $\bar{1}11$

Primitive orientation

 $\bar{1}01$
 $\bar{1}11$
011
110

tabulated as (111); data for the other pair of faces are tabulated $(\bar{1}\bar{1}1)$. Measured values of ϕ and ρ are considered only as indicative of which forms are present; the crystallographic elements and angle table have been calculated from the *x*-ray data which are considered more accurate.

The unit-cell dimensions as derived from rotation and Weissenberg photographs subsequently adjusted to measurements on a shrinkage-corrected powder photograph are $a_0=9.73$, $b_0=9.60$, $c_0=9.69$ Å., all

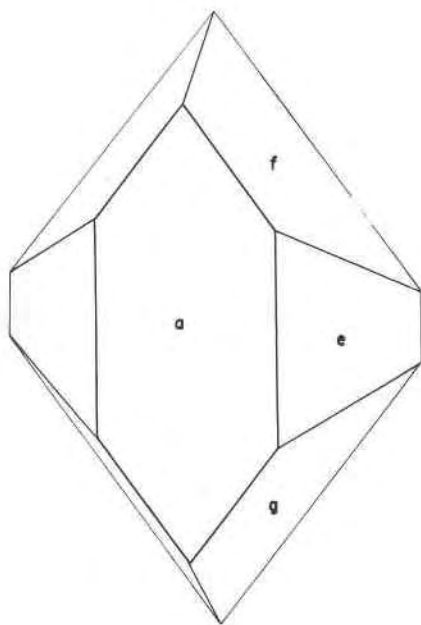


FIG. 1. Leucophosphite

	<i>a</i>	<i>e</i>	<i>f</i>	<i>g</i>
<i>B</i> -centered Forms	100	210	111	111
Primitive Forms	$\bar{1}01$	$\bar{1}11$	011	110

± 0.04 Å, $\beta=102^\circ 16' \pm 15'$, primitive monoclinic cell, and $a_0=15.14$, $b_0=9.60$, and $c_0=12.16$ Å, $\beta=90^\circ 12' \pm 15'$, pseudo-orthorhombic *B*-centered cell. The measured *d*-spacings on the Weissenberg photograph for $h0l$ and $h0\bar{l}$ establish unequivocally the position of the obtuse angle β in the *B*-centered orientation, even though β values of $90^\circ 12' \pm 15'$ may imply no choice in the position of the obtuse angle. The transformation matrix, pseudo-orthorhombic cell to the primitive cell, is $\frac{1}{2}0\frac{1}{2}/010/\frac{1}{2}0\frac{1}{2}$ and for primitive to pseudo-orthorhombic is $\bar{1}01/010/101$. *D*-spacings have been calculated for all indices possible in the space group $P2_1/n$ for values of *h*, *k*, and *l*=0, 1, 2, and 3. Those consistent with the

measured d -spacings are given in Table 2. The close agreement of axial lengths yields a multiple choice of indices in the comparison of calculated and measured d -spacings as values of h , k , and l are transposed. It is known from single-crystal Weissenberg data that the intensity of reflections with d -spacings of the same order of magnitude varies considerably. In the powder pattern weak reflections may enhance the intensity of strong reflections, or, if resolved, may not appear. The minimum difference in 2θ between reflections not resolved and those resolved has not been evaluated. Indices for reflections are therefore considered as tentative.

PHYSICAL PROPERTIES

Leucophosphite is buff-colored. It has an excellent cleavage parallel to (100) (pseudo-orthorhombic orientation). The specific gravity, as measured on the sample used for analysis by means of an Adams-Johnston pycnometer of fused silica, is 2.948. The specific gravity calculated from x -ray data for the end member without substitution by sodium or aluminum is 2.957. The small size of the crystals made determination of the hardness impracticable.

Leucophosphite from the Sapucaia pegmatite is biaxial (+), with indices of refraction $\alpha=1.707$, $\beta=1.721$, and $\gamma=1.739$ (all ± 0.002). The calculated $2V$ is 84° . The dispersion is $v>r$, very strong. The optical orientation (pseudo-orthorhombic axes) is $X=b$, $Z\wedge c=26^\circ$. The sense of $Z\wedge c$ (+ or -) has not been determined because the acute and obtuse angles ($\beta=90^\circ 12'$) were not differentiated during the microscopic examination. The optical data for the synthetic crystals (Haseman et al., 1950, p. 82) are $\alpha=1.706$, $\beta=1.720$, $\gamma=1.741$; biaxial (+); $2V=81^\circ$; $\beta=102^\circ$; $r>v$. The dispersion formula for the naturally occurring and for the synthetic crystals is reversed.

The extinction angles of Lindberg ($Z\wedge c=26^\circ$) and Haseman ($Z\wedge c=30^\circ$) seem consistent, but the choice of the c -direction by the two authors may not be identical, since the $Z\wedge c$ given by Lindberg refers to the B -centered orientation and the monoclinic β angle of Haseman is equivalent to the β angle of the primitive cell of Lindberg.

CHEMICAL PROPERTIES

Leucophosphite is a hydrous potassium iron phosphate with formula $KFe_2'''(PO_4)_2(OH)\cdot 2H_2O$. The analysis (Table 3) is in agreement with the theoretical composition of the synthetic compound (Haseman et al., 1950). It differs greatly from the analyses of the leucophosphite from the two occurrences of sedimentary origin, both samples of which contain known mineral impurities, in addition to which the samples themselves

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR LEUCOPHOSPHITE FROM THE SAPUCAIA PEGMATITE MINE AND FOR SYNTHETIC LEUCOPHOSPHITE

Sapucaia ¹		Synthetic ²		Possible indices, primitive monoclinic lattice							
<i>I</i>	<i>d</i> _{meas.}	<i>I</i>	<i>d</i> _{meas.}	<i>hkl</i>	<i>d</i> _{calc.}	<i>hkl</i>	<i>d</i> _{calc.}	<i>hkl</i>	<i>d</i> _{calc.}	<i>hkl</i>	<i>d</i> _{calc.}
3	7.60 Å	.31	7.50	10 $\bar{1}$	7.57 Å						
10	6.79	1.00	6.77	110	6.76						
1	6.09	—	—	101	6.09						
7	5.99	.76	5.92	11 $\bar{1}$	5.94						
3	4.76	.28	4.73	020	4.80	200	4.76	002	4.74		
2	4.28	.21	4.23	120	4.28	021	4.28	210	4.26	012	4.25
2	4.21	.28	4.20	21 $\bar{1}$	4.20	112	4.19				
2	4.08	.14	4.05	12 $\bar{1}$	4.05						
3	3.79	.21	3.78	20 $\bar{2}$	3.79	121	3.77				
1	3.65	—	—	211	3.63	112	3.63				
1	3.54	—	—	21 $\bar{2}$	3.52						
3 B	3.37	.35	3.34	220	3.38	022	3.37	2 $\bar{2}$ $\bar{1}$	3.35	12 $\bar{2}$	3.34
$\frac{1}{2}$	3.25	.14	3.20	301	3.22						
$\frac{1}{2}$	3.23	.14	3.09	10 $\bar{3}$	3.20						
7	3.66	.59	3.03	31 $\bar{1}$	3.05	11 $\bar{3}$	3.04	202	3.04		
				211	3.04	122	3.03	130	3.03	031	3.03
1	3.017	.28	3.00	310	3.010	013	2.998				
1	2.990	.28	2.97	22 $\bar{2}$	2.973						
1	2.956	—	—	13 $\bar{1}$	2.948						
4	2.916	.37	2.90	212	2.903						
4	2.829	.41	2.81	131	2.833	301	2.828	103	2.820		
1	2.685	.35	2.66	32 $\bar{1}$	2.675	12 $\bar{3}$	2.667				
3	2.655	.37	2.64	230	2.655	032	2.652	320	2.645	023	2.637
1	2.586	—	—	222	2.570						
1	2.542	.17	2.53	30 $\bar{3}$	2.523						
1	2.484	.17	2.48								
1	2.451	—	—								
1	2.412	—	—								
1	2.384	.17	2.38								
2	2.345	.21	2.33								
1	2.323	—	—								
1	2.220	—	—								
1	2.179	—	—								
1	2.154	.21	2.14								
1	2.091	—	—								
1	2.041	—	—								
B	1.998	—	—								
1	1.972	—	—								
1	1.960	—	—								
B	1.926	—	—								
1	1.899	—	—								
2	1.823	—	—								
1	1.786	—	—								
1	1.754	—	—								
1	1.709	—	—								
1	1.701	—	—								
B	1.687	—	—								
1	1.660	—	—								
1	1.653	—	—								
1	1.617	—	—								
1	1.602	—	—								
1	1.584	—	—								
1	1.570	—	—								
1	1.525	—	—								
1	1.512	—	—								
1	1.501	—	—								
1	1.490	—	—								
1	1.460	—	—								
1	1.452	—	—								
1	1.432	—	—								
1	1.403	—	—								
B	1.377	—	—								
1	1.360	—	—								
1	1.348	—	—								
1	1.337	—	—								
1	1.327	—	—								
1	1.313	—	—								

¹ Iron radiation FeK α =1.9373, Debye-Scherrer camera, diameter 114.59 mm. Film shrinkage negligible; values of $2\theta \pm 0.1^\circ$ for lines intensity $> \frac{1}{2}$; $\pm 0.2^\circ$ for broad lines (B) and lines of intensity $= \frac{1}{2}$. Indices are considered as tentative and intensity contribution and resolution of the several suggested indices have not been evaluated.

² Data from Haseman and others (1950).

are heterogeneous, showing a varied degree of crystallinity to x -rays, from amorphous to well crystallized. The amorphous material cannot be strictly identified with the crystalline leucophosphite as described in this paper and can be expected to show some variation in composition.

Leucophosphite is soluble in hot dilute HCl (1:1) and H₂SO₄ (1:1). When heated in the closed tube it gives off water.

TABLE 3. CHEMICAL ANALYSIS OF LEUCOPHOSPHITE

	(1)	(2)	(3)	(4)	(5)	(6)	Ratios	Metal equivalent	Oxygen equivalent	Metal atoms in unit cell*
K ₂ O	7.86	7.88	12.2	11.96	10.93	11.02	0.1170	0.2340	0.1170	3.71
Na ₂ O	0.22	0.13			0.53	0.53	0.0056	0.0112	0.0056	0.18
(NH ₄) ₂ O	1.99	0.09								
FeO	0.14	0.00			none					
CaO	0.16	trace								
MgO	0.02	0.73								
MnO		0.22								
Fe ₂ O ₃	36.85	32.82	38.9	40.55	41.02	41.35	0.2589	0.5178	0.7767	8.20
Al ₂ O ₃	0.88	12.73			0.25	0.25	0.0024	0.0048	0.0072	0.07
Mn ₂ O ₃					0.57	0.57	0.0036	0.0072	0.0108	0.11
TiO ₂	0.41									
P ₂ O ₅	33.46	26.69	37.4	36.07	34.71	34.99	0.2465	0.4930	1.2325	7.81
CO ₂		0.17								
Organic	0.30	trace								
H ₂ O ⁺	11.67	12.28			11.20	11.29	0.6267	1.2534	0.6267	9.86
H ₂ O ⁻	1.23	6.59								
Ignition loss			11.6	11.42						
Insoluble	(4.92)				0.45					
SiO ₂	4.32									
Total	99.51	100.33	100.1	100.00	99.66	100.00			2.7765	

(1) Leucophosphite, Bomi Hill, Liberia, M. K. Carron, analyst (Axelrod et al., 1952).

(2) Leucophosphite, Ninghanboun Hills, Lake Weelhamby, Southwest Australia. D. G. Murray, analyst (Simpson, 1931-32).

(3) Leucophosphite, synthetic. Haseman, Lehr, and Smith (1950).

(4) Theoretical composition of synthetic compound of formula KFe³⁺(PO₃)₂(OH)·2H₂O.

(5) Leucophosphite, Sapucaia pegmatite, Brazil; M. L. Lindberg, analyst. A spectrogram (IWS-561) by Harry Bastron shows in addition .X% Mg, .X% Si, .0X% Ba, and a line detected for Cu, Sn and Be.

(6) Analysis 5, recalculated to 100% without insoluble matter.

* Assuming 44 oxygen atoms per cell (4 formulas).

PARAGENESIS

Leucophosphite formed late in the mineral sequence at the Sapucaia granite pegmatite. Minerals formed earlier include quartz, albite, perthite, muscovite, and triphylite. Hydrothermal fluids generated within the pegmatite produced a large variety of secondary minerals. Leucophosphite together with avelinoite occur in well-formed crystals in vugs in frondelite. The close association of the two separate mineral species, one sodium-rich and the other potassium-rich, suggests that,

although a limited amount of substitution in each mineral occurs, the two mineral species do not form a complete mineral series from sodium to potassium end-members, but instead the small amount of leucophosphite present represents potassium in excess over that which will enter into the avelinoite molecule.

Leucophosphite has been synthesized in the laboratory (Haseman, Lehr, and Smith, 1950) at temperatures ranging from 75° to 145° C., at a pH of 2.5 to 6.0, and at phosphate concentrations of 1.0 to 3.5*M*. These data on synthesis are consistent with the low-temperature hydrothermal genesis indicated by the late position of leucophosphite in the observed mineral sequence.

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