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Í N D I C E

Phosphate Minerals from the Sapucaia Pegmatite Mine, Minas Gerais Por M. L. LINDBERG e W. T. PECORA .....	5
Notas à margem de "O Paládio e a Platina no Brasil" de E. Hussak Por DJALMA GUIMARÃES .....	15
Meteorito encontrado à margem do Córrego Areado, Município de Patos, Minas Gerais Por DJALMA GUIMARÃES .....	33
Age of Gold Mineralizations at the Morro Velho and Raposos Mines, Minas Gerais Por JACOB E. GAIR .....	39
Geologia da Serra do Macaia, Minas Gerais Por PAULO MARQUES DE ALMEIDA ROLFF .....	47
Symposium of the Stratigraphy of the Minas Series in the Quadrilátero Ferrífero, Minas Gerais, Brazil. Por GEOLOGISTS OF THE JOINT DNPM-USGS TEAM....	57
Geochemistry of trace element concentrations in the Poços de Caldas Plateau, Brazil Por GENE E. TOLBERT .....	71
Preliminary spectrochemical and age determination results on some granitic rocks, of the Quadrilátero Ferrífero, Minas Gerais Brazil Por NORMAN HERZ e C. V. DUTRA .....	81

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# PHOSPHATE MINERALS FROM THE SAPUCAIA PEGMATITE MINE, MINAS GERAIS (\*)

Por

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## ABSTRACT

Twenty-two phosphate minerals, identified in collections from the granite pegmatite locality in Minas Gerais known as the Sapucaia pegmatite mine, are described in summary fashion in this paper. Most are rare minerals, and a few are known only from this locality. The list includes apatite, avelinoite (= cyrilovite), barbosalite, bermanite, childrenite, faheyite, frondelite, gordonite, heterosite, hureaulite, leucophosphate, lipscombite, metastrengite, montebbrasite, moraesite, roscherite, saléite, strengite, tavorite, triphylite, variscite, and vivianite.

## INTRODUCTION

In 1942-45, W. T. Pecora of the U. S. Geological Survey and A. L. de M. Barbosa, then of the Departamento Nacional da Produção Mineral, studied and mapped the Sapucaia mine as part of their joint investigations of pegmatites in eastern Minas Gerais. Mineral specimens collected by them, and supplemented by additional material in later years, were studied in preliminary fashion by Pecora in Washington, D. C. Since 1948 mineralogical investigation of this suite has been undertaken by Pecora's colleague Mrs. Lindberg and has resulted in a number of separate papers (see bibliography).

The mine has been a principal producer of muscovite and beryl. These commercial minerals were recovered from different zones within an oval-shaped pegmatite, as described by Pecora and others (1950, p. 254). Within the central zone, essentially composed of quartz, perthite, muscovite, and beryl, is an irregular body of triphylite, several hundred tons in mass, that was altered partly by hydrothermal solutions during consolidation of the pegmatite and partly by surficial waters during weathering. Both agencies have resulted in a complex assortment of rare phosphate minerals, six of which were first identified from this deposit as new species. Four of the six (avelinoite, barbosalite, moraesite, and tavorite) were named in honor

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

of Brazilian geologists and two (faheyite and frondelite) in honor of North Americans.

For purposes of identification and reference, the phosphate minerals are described in alphabetical order below.

## MINERAL DESCRIPTIONS

### Apatite

Pale aquamarine-colored crystals of apatite occur in association with saléeite in vugs in albite. Apatite is uniaxial negative (—), with variable indices of refraction:  $\omega = 1.649$  to  $1.654$ ,  $\epsilon = 1.645$  to  $1.650$ . A spectrographic examination shows between 1 and 5 per cent manganese. Small white crystals of apatite occur with roscherite, and also in quartz-variscite-montebbrasite veins in muscovite.

### Barbosalite

Barbosalite,  $(\text{Fe}^{2+}, \text{Mn}^{2+})\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2$ , occurs as jet-black crystals, usually twinned, and as square crystal aggregates (4 crystals growing at right angles, in one plane, with bases attached at center) together with crystals of hureaulite in vugs in triphylite rock. Barbosalite also occurs in a dark blue-green, nearly black, massive layer, admixed with tavorite, in a zone between porous triphylite rock and massive purple heterosite (Lindberg and Pecora, 1955). The specific gravity is 3.60. The principal X-ray powder diffraction  $d$ -spacings for barbosalite are 3.361, 3.313, 4.84, 3.239, 3.160, 2.327, 2.614, 2.292, and 2.027. This new species was named in honor of Dr. A. L. de M. Barbosa and is isostructural with scorzalite, the ferrous aluminum phosphate from the Corrego Frio pegmatite mine, Minas Gerais, described by Pecora and Fahey (1949).

### Avelinoite (= cyrilovite)

Avelinoite,  $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , an iron phosphate mineral isostructural with wardite, occurs as yellow crystals in vugs in frondelite. Avelinoite is tetragonal; the space group is  $P4_12_12_1$ ; the cell dimensions are  $a = 7.32$ ,  $c = 19.4$  Å. Avelinoite grows in squat crystals, with crystal forms (001), (113), and (012). The principal reflections on the X-ray powder pattern occur at  $d$ -spacing (\*) 4.85, 3.186, 2.658, 3.101, 3.60, 2.020, 1.833, 4.05, and 3.230. The measured specific gravity is  $3.081 \pm 0.005$ . Avelinoite is uniaxial negative (—);  $\omega = 1.803$ ,  $\epsilon = 1.769$ . This new species was named in honor of Dr. Avelino I. Oliveira (Lindberg and Pecora, 1954b), and is probably identical with cyrilovite (Lindberg, 1957a).

(\*) Throughout this paper  $d$ -spacings are listed in order of decreasing intensity.

## Bermanite

Bermanite,  $(\text{Mn}, \text{Mg})_5(\text{Mn}, \text{Fe})_8(\text{PO}_4)_8(\text{OH})_{10} \cdot 15\text{H}_2\text{O}$ , \* occurs as reddish-brown crystals and crystal aggregates that line vugs in frondelite. Spectrographic analyses show that manganese is the major constituent and iron and phosphorus are minor constituents. The principal X-ray powder reflections occur at  $d$ -spacings 9.67, 5.10, 4.82, 2.916, 3.28, and 3.67 Å.

## Childrenite

Childrenite,  $(\text{Fe}, \text{Mn})\text{Al}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$ , occurs as pale honey-colored crystals associated with roscherite in pockets in muscovite. Childrenite is biaxial negative (—);  $\alpha = 1.648$ ,  $\beta = 1.679$ ,  $\gamma = 1.688$ ; the indices of refraction suggest that the childrenite is near the iron end-member of the childrenite-eosphorite series. The X-ray powder diffraction pattern gives strong reflections at 2.839, 5.22, 1.536, 4.41, 4.13, 2.444, 2.405, 6.79, 3.569, and 3.410 Å.

## Faheyite

Faheyite,  $(\text{Mn}, \text{Mg}, \text{Na})\text{Be}_2\text{Fe}_2(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ , occurs as bluish-white tufted fibers in pockets in muscovite. The fibers form an efflorescence on roscherite, frondelite, manganoan variscite, and quartz. The X-ray powder diffraction pattern of faheyite may be completely indexed on the basis of a primitive hexagonal cell with dimensions  $a = 9.43$ ,  $c = 16.00$  Å; strong reflections occur at  $d$ -spacings 5.72, 7.28, 3.244, 3.085, 3.029, and 3.962. The measured specific gravity is 2.660. Faheyite is uniaxial positive (+);  $\omega = 1.631$  and  $\epsilon = 1.652$ . This new species was named in honor of Joseph J. Fahey of the U. S. Geological Survey (Lindberg and Pecora, 1953).

## Frondelite

The principal occurrence of frondelite,  $\text{Mn}^{2+}\text{Fe}^{3+}_4(\text{PO}_4)_3(\text{OH})_5$ , is in large brown fibrous botryoidal masses, which form the host rock for many other phosphate minerals. Minute doubly-terminated crystals with high luster have also been noted, together with crystals of avelinoite (= cyrilovite), metastrengite, and leucophosphite, in a vuggy zone in the larger fibrous botryoidal masses. Frondelite is orthorhombic, the space group is  $B2_212$ ;  $a = 13.89$ ,  $b = 17.01$ ,  $c = 5.21$  Å. The crystal forms include (100), (010), (110), and (101). The X-ray powder  $d$ -spacings data include strong reflections at 3.195, 3.381, 1.598, 3.61, 3.045, 2.779, 2.444, 1.979, and 1.849. The specific gravity is 3.476.

(\*) Formula in doubt.

The name frondelite is given to material containing, in per cent, MnO 7.74, Mn<sub>2</sub>O<sub>3</sub> 1.75, Fe<sub>2</sub>O<sub>3</sub> 48.85 (Lindberg, 1949). In addition to type frondelite, which is brown in color and contains a high ratio of manganous manganese, a green member of the frondelite-rockbridgeite series, containing an increased proportion of ferrous iron, also occurs at the Sapucaia pegmatite mine in fibrous masses and as thin plates between the cleavages in muscovite. The latter contains, in per cent, FeO 6.70, MnO 5.54, and Fe<sub>2</sub>O<sub>3</sub> 41.93. The new species frondelite was named in honor of Professor Clifford Frondel of Harvard University.

#### Gordonite

Gordonite occurs in buff-colored crystals in association with variscite and metastrengite, as a crust on albite. Gordonite is biaxial negative (—);  $\alpha = 1.548$ ,  $\beta = 1.588$ ,  $\gamma = 1.600$ ;  $r > v$ . Spectrographic examination shows Al, P, Fe, Mg, and minor quantities of Mn. The high indices, high birefringence, and negative character of the gordonite suggest that the iron present is in the form of ferric iron substituting for aluminum in the formula  $MgAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$ ; the birefringence is greater than that consistent with the substitution of ferrous iron for magnesium. The principal reflections on the X-ray powder diffraction pattern occur at  $d$ -spacings 9.8, 6.45, 4.88, 3.22, 2.860, 2.592, and 2.010 Å.

Gordonite, with indices of refraction near those of quartz occurs in colorless vitreous crystals, tabular in habit, sometimes diamond-shaped, together with leucophosphite, saléite, and apatite, in vugs in albite. The spectrographic examination of this gordonite shows major quantities of P, Ca, Mg, Al, Fe, and minor quantities of Mn.

#### Heterosite

A member of the heterosite-purpurite series,  $(Fe^{III}, Mn^{III})(PO_4)_2$ , occurs in massive crystalline blocks which are purple in color. A partial analysis shows that the mineral is in the iron-rich portion of the series: Fe<sub>2</sub>O<sub>3</sub> = 33.98 per cent, Mn<sub>2</sub>O<sub>3</sub> = 9.79 per cent, and MnO<sub>2</sub> = 6.00 per cent.

Heterosite is found in association with triphylite, from which it formed by oxidation of the iron and manganese. Excess lithium probably results in the formation of tavorite. In the heterosite are numerous dense black seams of admixed oxidized manganese minerals intimately intergrown. Individual manganese oxides which have been identified include lithiophorite,  $\gamma$ -MnO<sub>2</sub>, and cryptomelane.

#### Hureaulite

Hureaulite,  $(Mn, Fe)_5H_2(PO_4)_4 \cdot 4H_2O$ , occurs as clear, flesh-colored crystals in vugs in triphylite rocks, and also in association with green,



relatively unoxidized frondelite. Hureaulite is biaxial positive (+);  $\alpha = 1.648$ ,  $\beta = 1.656$ ,  $\gamma = 1.662$ ;  $v > r$ , strong. The specific gravity is 3.211. An analysis gives FeO 18.02, MnO 27.57, MgO 1.73, ZnO 0.14, P<sub>2</sub>O<sub>5</sub> 39.37, H<sub>2</sub>O 12.46, total 99.29. The principal reflections on the powder pattern occur at  $d$ -spacings 3.152, 8.12, 2.990, 8.76, 2.185, and 2.623 Å.

#### Leucophosphite

Aluminum-bearing leucophosphite occurs in pink spherulitic and flat fan-shaped aggregates of radiating diamond-shaped crystals intimately intergrown with saléite in vugs in albite rock. Leucophosphite is biaxial positive (+);  $\alpha = 1.673$ ,  $\beta = 1.688$ , and  $\gamma = 1.710$ ,  $v > r$ , strong. The spectrographic analysis shows that iron and phosphorus are major constituents and aluminum is a minor constituent.

The ferric iron end-member,  $\text{KFe}^{2+}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ , occurs as buff-colored crystals with avelinoite (= cyrilovite), in vugs in frondelite, and in pink spherulitic masses intergrown with frondelite. The indices of refraction of the buff-colored crystals are  $\alpha = 1.707$ ,  $\beta = 1.721$ ,  $\gamma = 1.739$ ; biaxial positive (+). The specific gravity is 2.948. The principal X-ray powder  $d$ -spacings occur at 6.79, 5.99, 3.06, 2.916, 2.829, 7.60, and 4.76. (See Lindberg, 1957).

#### Lipscombite

Manganous lipscombite,  $(\text{Mn}^{2+}, \text{Fe}^{2+})\text{Fe}^{2+}_2(\text{PO}_4)_2(\text{OH})_2$ , occurs in olive-green to black fine-grained aggregates together with avelinoite (= cyrilovite), leucophosphite, and metastrengite in vugs in frondelite. It is tetragonal, with  $a = 7.40$ ,  $c = 12.81$  Å; the transformation matrix is  $110/110/001$  \* from the orientation of Katz and Lipscomb (1951) to the orientation of Lindberg. Reflections corresponding to the body-centered cell of Katz and Lipscomb are strong, but the presence of additional weak reflections of the type  $(0kl)$ , with  $k$  odd, and  $l$  even or odd (orientation of Lindberg) indicate a primitive lattice. The analysis includes, in per cent, MnO 7.91, FeO 3.75, Fe<sub>2</sub>O<sub>3</sub> 50.45, P<sub>2</sub>O<sub>5</sub> 33.37, and H<sub>2</sub>O 4.45. The measured specific gravity is  $3.66 \pm 0.01$ . Strong reflection on the powder diffraction pattern occur at 3.314, 3.206, 1.656, 1.601, 4.84, 2.304, and 2.054 Å (Lindberg, in preparation).

#### Metastrengite

Metastrengite,  $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , occurs as buff-colored, stubby crystals and lavender, bladed crystals in vugs in frondelite, and as lavender encrustations on frondelite, heterosite, hureaulite, and albite. The composition of metastrengite, as indicated by the indices of refraction, varies in different

(\*) Darker numbers signify negative.

samples from the pegmatite, but is always near the iron end-member. Indices of refraction of the buff-colored crystals are  $\alpha = 1.684$ ,  $\beta = 1.718$ ,  $\gamma = 1.730$ ; for the lavender crystals,  $\alpha = 1.688$ ,  $\beta = 1.720$ , and  $\gamma = 1.735$ ;  $r > v$ , strong; biaxial negative (—); large 2V. The principal reflections on the X-ray powder diffraction pattern occur at  $d$ -spacings 2.792, 4.372, 4.71, 3.613, and 2.014 Å. Metastrengite, strengite, and variscite crystals have been found in close association.

#### Montebrasite

Massive quartz-montebrasite veins occur in triphylite, heterosite, frondelite, muscovite, and albite rock. Crystals of montebrasite occur with well-developed crystal faces or with sawtooth edges, indicative, of partial solution in muscovite and in albite. The indices of refraction are  $\alpha = 1.614$ ,  $\beta = 1.624$ ,  $\gamma = 1.644$ ;  $r > v$ , strong; biaxial positive (+); medium 2V. These indices correspond to the Li and OH end-member,  $\text{LiAl}(\text{PO}_4)(\text{OH})$ , and are higher than those previously recorded for members of the amblygonite-montebrasite series. The analysis gives  $\text{Li}_2\text{O}$  10.11,  $\text{Na}_2\text{O}$  0.14,  $\text{Al}_2\text{O}_3$  35.50,  $\text{Fe}_2\text{O}_3$  0.28,  $\text{P}_2\text{O}_5$  48.14,  $\text{H}_2\text{O}$  5.70, total 99.87; specific gravity 3.01. The principal reflections on the powder photograph occur at  $d$ -spacings 2.971, 4.68, 3.221, 3.169, 2.405, 1.610, 3.351, 3.285, and 2.137 Å.

#### Moraesite

Moraesite,  $\text{Be}_2\text{PO}_4(\text{OH}) \cdot 4\text{H}_2\text{O}$ , occurs as spherulitic masses composed of radiating, white to clear, needlelike crystals and crusts with a coarse fibrous texture. Moraesite is monoclinic,  $C2/c$ , or  $C-c$ ,  $a = 8.55$ ,  $b = 36.90$ , and  $c = 7.13$  Å. The crystal forms include (100), (130), and (131). It is biaxial negative (—) with 2V = 65°;  $\alpha = 1.462$ ,  $\beta = 1.482$ , and  $\gamma = 1.490$ . The principal reflections on the X-ray powder diffraction pattern occur at  $d$ -spacings 7.00, 3.278, 4.24, 3.023, 2.819, 6.15, 2.325, and 2.050 Å. This new species was named in honor of Dr. Luciano Jacques de Moraes (Lindberg, Pecora, and Barbosa, 1953).

#### Roscherite

Roscherite occurs as brown, single prismatic crystals, crystal aggregates, and granular masses, in vugs in muscovite, and as crusts on beryl. It is also closely associated with quartz, with frondelite, and with tufts of faheyite. It is monoclinic prismatic, space group  $C2/c$  or  $C-c$ ; the cell dimensions are  $a = 15.95$ ,  $b = 11.95$ , and  $c = 6.62$  Å;  $\beta = 94^\circ 50'$ . Crystal forms observed include: (100), (010), (111), (111), (102), (201), (101), (201), and (301). The cell contents, as derived from the chemical analyses, are:  $\text{Ca}_{3.0}\text{Mn}_{3.2}\text{Fe}_{5.8}\text{Be}_{11.4}(\text{PO}_4)_{12.0}(\text{OH})_{12.8}\text{H}_2\text{O}$ . The specific gravity is 2.934. The principal reflections on the X-ray powder diffraction pattern occur at

*d*-spacings 5.96, 9.58, 3.18, 2.796, 4.84, 2.652, and 1.656 Å. Roscherite is biaxial positive (+);  $\alpha = 1.636$ ,  $\beta = 1.641$ ,  $\gamma = 1.651$ ;  $r > v$ , strong. The indices of refraction for roscherite are variable. A paper redefining roscherite as a beryllium phosphate mineral is in press (Lindberg).

#### Saléeite

Saléeite occurs as lemon-yellow tabular crystals, usually square in outline, with micaceous cleavage, in vugs and in seams in albite. Saléeite is uniaxial negative (-);  $\omega = 1.570$ ,  $\varepsilon = 1.554$ . Spectrographic analysis shows: U and P, over 10 per cent; Mg, 5 to 10 per cent; Si, 0.5 to 1 per cent; and Ca, Fe, 0.1-0.5 per cent (Si, Ca, and Fe probably are impurities). The X-ray powder diffraction data for saléeite include reflections at *d*-spacings 10.0, 3.493, 4.69, 4.44, and 2.194 Å.

#### Strengite

Strengite forms a vitreous coating on "green" frondelite and also strings of white beady crystals in vugs in "green" frondelite. Strengite, in contrast to its dimorph metastrengite, apparently is limited in its occurrence to partially oxidized mineral environments in which the iron phosphates are of mixed valence, and where hureaulite and sulfides are present.

The crystal forms (001), (201), and (111) have been observed on strengite. Strengite is biaxial positive (+);  $\alpha = 1.728$ ,  $\beta = 1.729$ ,  $\gamma = 1.758$ ;  $r > v$ , strong. The principal reflections on the X-ray powder diffraction pattern occur at *d*-spacings 4.37, 5.51, 3.118, 2.998, 2.953, 2.537, and 3.990.

#### Tavorite

Tavorite,  $\text{LiFe}^{III}(\text{PO}_4)(\text{OH})$ , the ferric iron equivalent of montebasite, occurs in yellow-green, fine-grained aggregates forming veinlets in heterosite and barbosolite, and as flakes disseminated in the cleavage planes of triphylite. The aggregates have a mean index of refraction near 1.807 and a specific gravity of 3.29. The X-ray powder pattern gives strong reflections at *d*-spacings 3.045, 3.285, 4.99, 2.474, 4.68, 1.662, 3.323, 2.360, and 2.206 Å. This new species was named in honor of Dr. Elysiario Tavora (Lindberg and Peccra, 1955).

#### Triphylite

Large crystalline masses of gray-green triphylite occur as the primary phosphate mineral from which many of the secondary minerals have derived their iron, manganese, and phosphorus. Triphylite is biaxial positive (+); small 2V;  $\alpha = 1.638$ ,  $\beta = 1.689$ ,  $\gamma = 1.695$ ;  $r > v$ , strong. The chemical

analysis of the triphylite shows, in per cent, FeO 29.58, MnO 14.55, MgO 1.12, Li<sub>2</sub>O 9.33, Na<sub>2</sub>O 0.08, P<sub>2</sub>O<sub>5</sub> 45.16, H<sub>2</sub>O 0.20, total 100.02. The specific gravity is 3.525.

#### Variscite

Manganooan variscite occurs as single crystals, aggregates of crystals, or as spherulitic masses in pockets in muscovite; as a crust in albite; as a replacement product of beryl; or as spherulitic masses in frondelite. Variscite grows in squat crystals with curved faces showing growth lines of successive accretions with varying composition, with (001) concave, (010) convex, and (111) concave. The crystals are a brilliant raspberry-red in color, the depth of color varying with the manganese content. The MnO content of the variscite ranges from 0.04 to 2.46 per cent; the Fe<sub>2</sub>O<sub>3</sub> content from 12.90 to 18.28 per cent. Indices of refraction vary with the iron and manganese content and with the growth habits, the indices being less where successive accretions are separated by films of air or moisture. The principal reflections on the X-ray powder diffraction pattern occur at *d*-spacings 3.045, 4.27, 5.39, 2.920, 2.881, 3.915, and 3.648 Å.

#### Vivianite

Vivianite, Fe<sup>2+</sup><sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O, occurs as thin plates in cleavage planes in triphylite and as dendritic seams which invade massive triphylite. The blue color of vivianite gives a bluish cast to the gray-green triphylite. Vivianite is biaxial positive (+); 2V large;  $\alpha = 1.583$ ,  $\beta = 1.605$ ,  $\gamma = 1.634$ . The chemical analysis of vivianite is FeO 34.71, MnO 2.67, MgO 2.00, ZnO 0.06, Fe<sub>2</sub>O<sub>3</sub> 2.85, P<sub>2</sub>O<sub>5</sub> 28.65, H<sub>2</sub>O 28.50, insoluble 0.20, total 99.64.

#### Unidentified minerals

A few phosphate minerals as yet have remained unidentified. Some of them may be alteration products or variations of the minerals described above.

### MINERAL ASSOCIATIONS

A detailed study of mineral associations in hundreds of specimens has revealed a number of separate environments of geochemical relations. For simplicity of reference these are enumerated below with examples:

#### A. Associations with triphylite:

1. Fracture filling in triphylite with vein deposition: montebasite, quartz, sphalerite, pyrite, zircon, tourmaline, and siderite.

2. Solution of triphylite, essentially along cleavage directions, with replacement by.
  - a) hydrous unoxidized phosphates: vivianite (enrichment in Fe) and hureaulite (enrichment in Mn).
  - b) anhydrous oxidized phosphates: heterosite with manganese oxides.
  - c) hydrous oxidized phosphates: metastrengite, tavorite, barbosalite, and frondelite.

**B** Associations with frondelite:

1. Residual phosphates enclosed by frondelite: triphylite, heterosite, and montebrasite.
2. Massive replacement of frondelite: leucophosphate, avelinoite, and cryptomelane.
3. Minerals on walls vugs in frondelite: leucophosphate, avelinoite, lipscombite, metastrengite, variscite, bermanite, opal, and goethite.

**C.** Associations with silicate minerals:

1. Secondary crusts on altered albite: saléeite, gordonite, leucophosphate, apatite, variscite, metastrengite, tourmaline, and goethite.
2. Alterations of beryl: variscite, moraesite, faheyite, and roscherite.
3. Replacement and vug-filling in muscovite: apatite, montebrasite, childrenite, variscite, faheyite, frondelite, roscherite, and bermanite.

### SUMMARY

An impressive array of new and rare phosphates minerals is now known from the Sapucaia pegmatite mine and additional minerals are in process of identification. Among those described here briefly, but described in more detail in other publications listed in the bibliography are some that have no apparent structural relation to known phosphate minerals. Others are isostructural with known species but differ principally in that ferric iron has substituted completely for aluminum in the formula. Intermediate compositions between the ferric iron and aluminum end-members are not represented in the rocks studied. Abundant evidence supports the conclusion that most of the phosphate minerals were formed by oxidation and/or hydration of earlier minerals resulting in redistribution of the available elements. Both hydrothermal alteration and weathering played a role in developing assortment of phosphate minerals known.

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