

MANGANOAN LIPSCOMBITE FROM THE SAPUCAIA
 PEGMATITE MINE, MINAS GERAIS, BRAZIL
 FIRST OCCURRENCE OF LIPSCOMBITE IN NATURE¹

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ABSTRACT

Manganoan lipscombite (Fe^{2+} , Mn^{2+}) $\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$, a new mineral related to synthetic lipscombite, occurs with other phosphate minerals in the Sapucaia pegmatite mine, Minas Gerais, Brazil. The chemical composition of the mineral expressed in percentage is MnO 7.91, FeO 3.75, Fe_2O_3 50.45, P_2O_5 33.37, H_2O 4.45, total 99.93; the measured specific gravity is 3.66 ± 0.01 . The space group is $P4_12_12-D_2$. The unit cell dimensions are $a=7.40$, $c=12.81$ Å. Strong reflections in the powder-diffraction pattern occur at 4.84, 3.314, 3.206, 2.304, 2.054, 1.656, and 1.601 Å. Tetragonal manganoan lipscombite is structurally closely related to monoclinic barbosalite; both occur at the Sapucaia pegmatite mine.

INTRODUCTION

Manganoan lipscombite (Fe^{2+} , Mn^{2+}) $\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2$, a tetragonal mineral structurally closely related to the monoclinic mineral barbosalite, (Fe^{2+} , Mn^{2+}) $\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2$, (Lindberg and Pecora, 1955), is one of the phosphate minerals of the Sapucaia pegmatite mine, Municipio of Counselheiro Pena, Minas Gerais, Brazil (Lindberg and Pecora, 1958). It occurs in vugs in the alkali-altered zone in frondelite, $\text{Mn}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_5$ (Lindberg, 1949) intimately intergrown with avelinoite (= cyrilovite), $\text{NaFe}^{3+}(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (Lindberg and Pecora, 1954; Lindberg, 1957a), leucophosphate, $\text{KFe}^{3+}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ (Lindberg, 1957b), and metastrengite, $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$.

The name lipscombite was given to the compound synthesized by Gheith (1953), in honor of W. N. Lipscomb, who together with Katz determined its crystal structure (Katz and Lipscomb, 1951).

The occurrence of manganoan lipscombite at the Sapucaia pegmatite mine is the first recorded occurrence of lipscombite in nature.

PHYSICAL PROPERTIES

Manganoan lipscombite occurs as olive-green to black crystal aggregates of splendid luster, intimately intergrown with avelinoite and metastrengite in vugs in frondelite. The strong greenish-blue black absorption renders even very fine particles opaque. The small size of the crystals makes determination of the hardness impracticable.

The specific gravity as determined by means of an Adams-Johnston pycnometer of fused silica on the sample used for analysis is 3.66 ± 0.01 .

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CHEMICAL COMPOSITION

The theoretical composition of manganooan lipscombite is $(\text{Fe}^{2+}, \text{Mn}^{2+})\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$. The chemically analyzed sample of manganooan lipscombite from the Sapucaia pegmatite mine shows an excess of iron and manganese ions and a deficiency of phosphate and hydroxyl. Total manganese and iron, per unit cell, are 12.3 ions, analyzed; 12.0 ions, calculated; the PO_4^{3-} ions are 7.3 analyzed, 8.0 calculated; the OH ions 7.6 analyzed, 8.0 calculated. The analyzed sample contains, by grain count, 99 per cent opaque material and 1 per cent birefringent material, chiefly metastrengite. The sample does not contain sufficient quantities of iron oxide or manganese oxide minerals to be detectable by x-ray techniques.

Manganooan lipscombite from the Sapucaia pegmatite mine contains a significant substitution of manganous manganese for ferrous iron. In the sample analyzed, the ratio of Mn^{2+} to Fe^{2+} is greater than 2:1 but a new name is not here proposed for the manganooan equivalent of lipscombite. The total manganese atoms are less than half the number of metal atoms statistically filling equivalent octahedral spaces in the unit cell. The high ratio of trivalent to divalent metal atoms found in the analysis may be in part related to oxidation during the prolonged heating necessary to dissolve manganooan lipscombite in $\text{H}_2\text{SO}_4 + \text{HF}$ in the ferrous iron determination.

The chemical analyses and number of ions per unit cell of manganooan lipscombite are given in Table 1. The ions per unit cell are obtained by multiplying the metal equivalent by 1546, the gram-molecular weight of the new unit cell, and by 0.01 to convert from a per cent to a fractional scale. The gram-molecular weight of manganooan lipscombite is based upon double the cell volume of synthetic lipscombite, and a specific gravity of 3.66 ± 0.01 .

X-RAY CRYSTALLOGRAPHY

In 1951 Katz and Lipscomb described the crystal structure of iron lazulite, $\text{Fe}_{3.5}(\text{PO}_4)_2(\text{OH})_2$, a tetragonal synthetic compound. In 1953 Gheith gave the name lipscombite to related tetragonal synthesized compounds with composition varying from $\text{Fe}_8^{2+}(\text{PO}_4)_4(\text{OH})_4$ to $\text{Fe}_{5.3}^{3+}(\text{PO}_4)_4(\text{OH})_4$. Comparison of the x-ray powder data for manganooan lipscombite with the powder data given by Gheith for synthetic lipscombite suggested a similarity of the two, but a reflection with $d_{hkl} = 6.40 \text{ \AA}$ in manganooan lipscombite could not be indexed with the space group $D_4^{10}-I4_12$ and with the unit cell dimensions $a = 5.37$, $c = 12.81 \text{ \AA}$, data of Katz and Lipscomb (1951).

TABLE 1. CHEMICAL ANALYSES OF LIPSCOMBITE

	Theoretical Fe ²⁺ Fe ³⁺ (PO ₄) ₂ (OH) ₂	Analyses Synthetic experi- ment 99 (Gheith) ¹	Manganoan lipscombite ²				Ions per unit cell
			Analy- sis	Recal- culated to 100%	Ratios	Metal equiva- lent	
MnO			7.91	7.91	0.1115	0.1115	Mn ²⁺ 1.72
FeO	18.35	12.33	3.75	3.75	0.0522	0.0522	Fe ²⁺ 0.80
Fe ₂ O ₃	40.79	46.68	50.45	50.49	0.3161	0.6322	Fe ³⁺ 9.77
P ₂ O ₅	36.26	35.62	33.37	33.40	0.2353	0.4706	PO ₄ ³⁻ 7.28
H ₂ O	4.60	5.53	4.45	4.45	0.2470	0.4940	OH ²⁻ 7.64
Total	100.00	100.16	99.93	100.00			

¹ Synthetic lipscombite; FeO by Lee Peck, U. S. Geological Survey; remaining part of analysis by Gheith aided by Khalafallah (Gheith, 1953).

² Manganoan lipscombite, Sapucaia pegmatite mine, M. L. Lindberg, analyst. Spectrographic analysis, in per cent, by Katherine V. Hazel, U. S. Geological Survey, shows in addition:

0.1–0.5% Si	0.005–0.001% Mg
0.05–0.1% Zn	0.001–0.005% Cu, Pb
0.01–0.05% Al, Na	0.0001–0.0005% Be

Formula of manganoan lipscombite: (Fe²⁺, Mn²⁺)Fe₂³⁺(PO₄)₂(OH)₂; Z=4.

Single crystal studies of the manganoan variety of lipscombite indicate a primitive, pseudo-face-centered tetragonal lattice, with $a=7.40$, $c=12.81$ Å. The space group is $P4_12_12-D_4^4$ (no. 92). The transformation matrix from the body-centered lattice of Katz and Lipscomb to the primitive, pseudo-face-centered lattice of manganoan lipscombite is $\bar{1}\bar{1}0/110/001$ (Lindberg, 1958). All hOl and hhl reflections are indicative of a face-centered cell, except for the presence of very weak reflections of the type, hOl , h odd, l even or odd. If these very weak reflections are neglected, the observed extinctions lead to the smaller body-centered cell selected by Katz and Lipscomb.

Powder diffraction data for manganoan lipscombite and for synthetic lipscombite (Gheith, 1953) are given in Table 2. The large number of reflections having the same calculated d-spacing results from a $c:a$ ratio = tangent 60° . The powder pattern may be indexed with hexagonal indices, but the symmetry of the reflections is tetragonal.

Comparison of the x-ray powder pattern of manganoan lipscombite with that of barbosolite (Fig. 1) reveals a striking resemblance between the patterns of the two minerals, both in the relative succession of strong and weak reflections, and in the approximate positions of the reflections,

TABLE 2. X-RAY POWDER DIFFRACTION DATA

Manganooan lipscombite ¹ Sapucaia pegmatite mine				Synthetic lipscombite ²		
$a=7.40 \text{ \AA}; c=12.81 \text{ \AA}$				Precession Data	<i>I</i>	<i>d</i> (obs.) \AA
<i>I</i>	<i>d</i> (obs.) \AA	<i>hkl</i>	<i>d</i> (calc.) \AA			
		100	7.40	absent		
1	6.40	101	6.406	present		
		110	5.233	absent		
3	4.84	102	4.845	present	1	4.864
		111	4.845	present		
$\frac{1}{2}$	4.37	metastrengite				
		112	4.052	absent		
		103	3.700	present	2.5	3.669
		201	3.555	absent	1	3.544
10	3.314	210	3.309		10	3.329
		113	3.309	present		
6	3.206	211	3.205		7	3.200
		202	3.204	present		
		104	2.940	absent		
		212	2.940			
		203	2.796	absent	f	2.880
		114	2.731	absent		
2	2.617	220	2.616	present	2	2.616
		213	2.616			
		221	2.563	absent	f	2.544
		300	2.467	absent		
1	2.422	105	2.422	absent	1	2.422
		322	2.422			
		301	2.422	present		
		204	2.422	present		
		310	2.340			
3	2.302	311	2.302			
		214	2.302			
		115	2.302	present		
		302	2.302	present		
		223	2.231	absent	f	2.267
		320	2.231			
		312	2.198			
		321	2.198			

¹ Averaged *d*-spacings from spectrometer pattern, scale 1 in. = $\frac{1}{4}^\circ$ of 2θ , $\text{CuK}\alpha_1$, $\lambda=1.5405 \text{ \AA}$ and from powder-diffraction pattern, iron radiation, manganese filter, $\text{FeK}\alpha$, $\lambda=1.9373 \text{ \AA}$. Cut-off 11 \AA .

² Data of Gheith (1953, p. 617) lipscombite of experiment 99B; unfiltered iron radiation. The *d*-spacings have been calculated by Gheith from the measured 2θ using the same wavelength for reflections from $\text{CuK}\beta$ as from $\text{CuK}\alpha$.

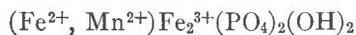
TABLE 2. (continued)

Manganoan lipscombite ¹ Sapucaia pegmatite mine				Synthetic lipscombite ²		
$a=7.40 \text{ \AA}; c=12.81 \text{ \AA}$				Precession Data	<i>I</i>	<i>d</i> (obs.) \AA
<i>I</i>	<i>d</i> (obs.) \AA	<i>hkl</i>	<i>d</i> (calc.) \AA			
		303	2.136	present		
3	2.054	313	2.052		5.5	2.056
		106	2.052	absent		
2	2.028	224	2.026	present	1.5	2.036
		215	2.026			
		323	1.977			
		304	1.954	absent		
		314	1.890			
		400	1.850	present	1	1.862
2	1.849	206	1.849	present	2	1.845
		324	1.831			
		225	1.831	absent		
		401	1.801	absent	1	1.773
1	1.730				1	1.747
4	1.656				5	1.664
1	1.613					
4	1.601				6	1.604
2	1.442				1.5	1.449
3	1.309				1	1.441
2	1.218				1	1.374
1	1.153					
1	1.140					

there being a greater number of reflections present in the barbosolite pattern. The *hOl* single crystal pattern of manganoan lipscombite has the appearance of the combination of the single crystal *OkI* and the twinned crystal *hOl* patterns of barbosolite, superimposed. The crystal structure described by Katz and Lipscomb for tetragonal iron lazulite (=lipscombite) differs from that of barbosolite chiefly in the ordered manner in which iron atoms occupy octahedral positions in barbosolite. A trial structure for the monoclinic lazulite-scorzalite-barbosolite series has been established, and has been reported elsewhere (Lindberg and Christ, 1959).

PARAGENESIS

Both the tetragonal and monoclinic forms of



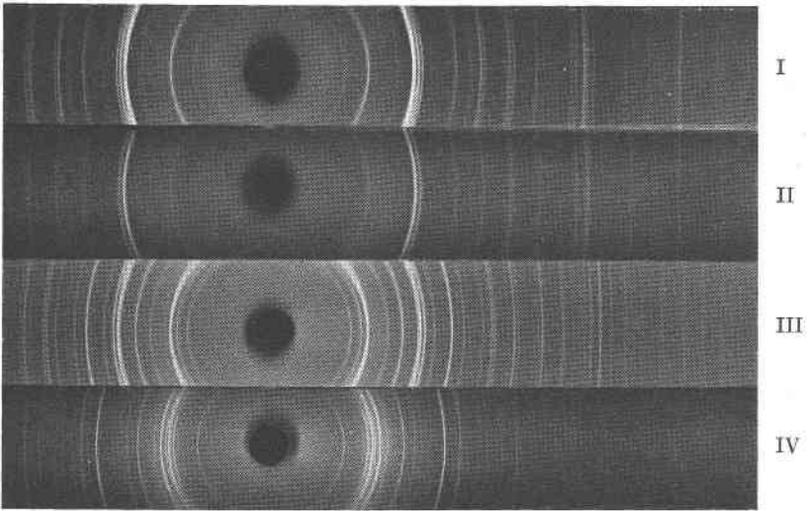


FIG. 1. X-ray powder photographs of minerals from the Sapucaia pegmatite mine, iron radiation, manganese filtered: (I) barbosalite, (II) manganooan lipscombite, (III) avelinoite (=cyrilovite), and (IV) metastrengite.

occur at the Sapucaia pegmatite mine. The tetragonal form is apparently limited in its occurrence to an alkali-altered oxidized zone in frondelite, into which avelinoite has been introduced. Barbosalite is apparently limited in its occurrence to triphylite and heterosite rock, being particularly abundant along solution channels where it occurs admixed with nonoxidized minerals such as triphylite, hureaulite, and vivianite, and with oxidized minerals such as heterosite and tavorite. The mineralogy of the occurrences of the two minerals suggests that the pH of the solutions may be one factor in determining whether manganooan lipscombite or barbosalite may form; lipscombite occurs admixed with avelinoite and leucophosphite; the latter replace frondelite and require a source of Na and K ions for their formation and hence are probably formed in an alkaline environment; barbosalite occurs associated with hureaulite, an acid phosphate with a deficiency of metal cations suggesting an acid environment for the formation of barbosalite. The presence of avelinoite as a "seed" crystal may also influence the growth of manganooan lipscombite since both avelinoite and manganooan lipscombite are intimately intergrown, avelinoite occurring free of lipscombite, but lipscombite not occurring independently of avelinoite. Both minerals are tetragonal with space group $P4_12_12$; both have a similar cell edge a , the cell edge c having a ratio 1.5:1 ($a=7.32$, $c=19.40$ Å for avelinoite and $a=7.40$, $c=12.81$ Å for manganooan lipscombite).

The tetragonal and monoclinic forms of $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ have been synthesized by Gheith (1953). He concludes that no prediction can be made as to whether the synthesized product will be the tetragonal lipscombite or the monoclinic barbosolite. The monoclinic dimorph, when formed, changes to lipscombite between 110° and 290° C. The transformation is sluggish and is accompanied by oxidation of iron.

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