Crystal structure of synthetic lipscombite: A redetermination

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Abstract

The synthetic compound $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$ is tetragonal, space group $P4_32_12$, with $a = 7.310(3)$, $c = 13.212(7)$ Å, $V = 706.0$ Å³, $Z = 4$, and $D_{calc} = 3.68(1)$ g/cm³. The structure was solved by the heavy-atom technique and refined by least-squares to an R value of 0.102 for 300 observed reflections. The structure consists of two disordered Fe^{2+} ions in special positions and one Fe^{3+} ion in the general position, all octahedrally coordinated by PO_4^{3-} ligands and an $(OH)^-$ group. The octahedra form infinite face-sharing chains alternatively in the [110] and [1Ī0] directions. The shortest distances between Fe atoms along the chains are $Fe(1)-Fe(3) = 2.75(4)$ and $Fe(2)-Fe(3) = 2.44(4)$ Å, the latter being shorter than in α-Fe. Other unusual features of the structure include a Fe^{3+}-OH distance of 2.24(4) Å and a mean value of 2.74 Å for the O-O edges of the shared octahedral faces.

Introduction

During a series of hydrothermal syntheses to obtain barbosalite and lipscombite, two dimorphous mixed-valence iron phosphates, only lipscombite was obtained. Gheith (1953) applied the name lipscombite to synthetic compounds with tetragonal symmetry and composition varying between $Fe_8^{2+}(PO_4)_4(OH)_4$ and $Fe_{5.3}^{3+}(PO_4)_4(OH)_4$. The synthetic lipscombite having the composition $Fe_7(PO_4)_4(OH)_4$ shows tetragonal, $I4_122$, symmetry with $a = 5.37$ and $c = 12.81$ Å (Katz and Lipscomb, 1951). However, according to Lindberg (1962), natural manganoan lipscombite has the parameters $a = 7.40$ and $c = 12.81$ Å, with space group $P4_12_12$. More recently, Vochten and De Grave (1981) and Vochten et al. (1983) conducted Mössbauer spectroscopic and electrokinetic studies of synthetic lipscombite and also crystallographic studies on powder samples with a Guinier-Hägg camera. They found the cell parameters $a = 5.3020(5)$ and $c = 12.8800(5)$ Å.

As the crystal-structure data for lipscombite (Katz and Lipscomb, 1951) are quite unsatisfactory—with only a proposed structure without refinement—and since in our synthesis, single crystals were obtained with suitable dimensions for crystallographic measurements, we decided to redetermine the crystal structure of this phosphate.

Experimental details

The crystals of lipscombite were obtained by hydrothermal synthesis using the reaction of an acid ferric phosphate solution (phosphate B) and synthetic vivianite (phosphate A) for a week at 238 °C in a Parr steel commercial vessel. In this method, 2.5 cm of phosphate B was put in the bottom of a quartz tube (2.0 cm in inside diameter and 13 cm in height), and phosphate A was put in a 5-cm-long Teflon cartridge with a perforated bottom that fitted into the top part of this tube (Fig. 1). Finally the quartz tube was filled with water until approximately 90% of the volume of the vessel was occupied.

Phosphate B was obtained by gradually adding 10 g of Fe_2O_3 to 40 mL of boiling H_3PO_4 (density 1.71). The volume of the acid solution was kept constant by slowly adding water to the reaction mixture. The end of the reaction was indicated by the clear violet color and syrupy aspect of the acid phosphate, whose viscosity increases with cooling. Phosphate A was prepared according to method A described in Mattievich and Danon (1977).

As a result of the hydrothermal synthesis, two kinds of crystals were observed in the bottom of the quartz tube, one prismatic and the other octahedral. The prismatic crystals were transparent and gray colored and were shown by single-crystal X-ray diffractometry to be triclinic with cell parameters $a = 7.971(1)$, $b = 9.531(1)$, $c = 6.389(2)$, Å, $\alpha = 68.84(2)°$, $\beta = 78.40(2)°$, and $\gamma = 66.93(1)°$. The octahedral crystals were lustrous, black, and opaque. One single crystal (Fig. 2) was selected for crystal-structure analysis.

In the quartz tube, a hard crust of crystals strongly adhered to the walls with the same octahedral crystals

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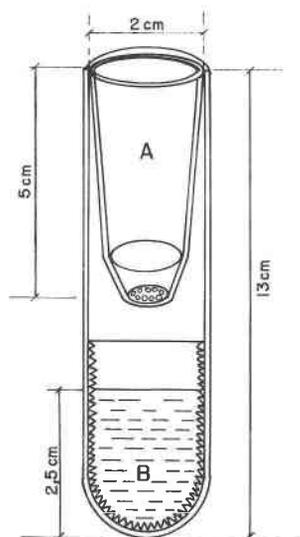
Fig. 1. Diagram of apparatus used in the hydrothermal synthesis of synthetic lipscombite.

Fig. 2. A crystal of synthetic lipscombite showing the form $a\{111\}$: (**A**) plan; (**B**) clinographic projection.

taken from the *International Tables for X-ray Crystallography* (1974).

STRUCTURE DETERMINATION AND REFINEMENT

The crystal-lattice parameters of our synthetic product differ from those of Katz and Lipscomb (1951) and approximately agree with those of Lindberg (1962). Owing to the presence of three weak reflections (002, 006, and 0.0.14), we tried unsuccessfully to solve the crystal structure of our compound in space group $P4_22_12$ (with systematic absences 00*l*, $l \neq 2n$; *h*00, $h \neq 2n$). Supposing that those reflections are due to the Renninger effect, the space group can be taken as $P4_12_12$ or $P4_32_12$ with systematic absences (00*l*, $l \neq 4n$; *h*00, $h \neq 2n$). The successful determination of the structure by Patterson and difference-Fourier methods in the latter resolved the space-group ambiguity.

The space-group symmetry and electrostatic charge balance require that the Fe(3) atom be Fe^{3+}, and the Fe(1) and Fe(2) atoms both be Fe^{2+}. Atoms Fe(1) and Fe(2) were found by difference-Fourier syntheses in two independent crystallographic sites in special positions; their refined occupancy factors are 0.391(5) (= 3.13 atoms) and 0.082(5) (= 0.66 atom), respectively. The isotropic refinement with unit weights converged to $R = 0.129$. Probably owing to the disorder of the structure, which certainly is also reflected in the internal agreement factor, the anisotropic refinement of the Fe(3) atom gave physically unacceptable results; i.e., it became nonpositive definite. We therefore decided to fix the U_{ij} with $i \neq j$ of

described above. The crystals forming the hard crust have the same color and morphology as the octahedral crystals from the bottom of the quartz tube. When powdered, they showed a very dark green color. Powder diffractometry of this material gave the data in Table 1, which when used in a least-squares refinement yielded the tetragonal cell parameters $a = 7.30$ and $c = 13.19$ Å. From this we conclude that the crust material is equivalent to the crystal chosen for structural determination, as the same unit cell was obtained for the latter crystal by single-crystal diffractometry.

A single-crystal of dimensions $0.15 \times 0.18 \times 0.18$ mm was selected for intensity measurement on a CAD-4 Enraf-Nonius diffractometer using graphite-monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation. The lattice parameters [$a = 7.310(3)$, $c = 13.212(7)$ Å] were determined by a least-squares procedure applied to the setting angles of 25 strong reflections in the range $9.2° < \theta < 13.4°$. The diffraction intensities were measured by the θ-2θ scan technique up to ($\sin \theta/\lambda$) = 0.573 Å^{-1} in the range $-8 \leq h \leq 8$, $0 \leq k \leq 8$, $0 \leq l \leq 15$, using a variable scan speed between 3.3° min^{-1} and 10.0° min^{-1} determined by a fast prescan of 10.0° min^{-1} and scan width of 1°. Two standard reflections measured every hour showed no significant deviations during the data-collection period. A total of 1270 reflections were collected. The intensities were corrected for the Lorentz-polarization factor, but no absorption correction was applied because of the modest linear absorption coefficient of 63.14 cm^{-1}, the favorable crystal shape, and similar intensities among equivalent reflections. Equivalent reflections were merged into a set of 583 independent reflections, with $R_{int} = 7.8\%$. Of these, 300 with $I \geq 3\sigma(I)$ were used in the structure analysis; $\sigma(I)$ was estimated from counting statistics. The atomic scattering factors and anomalous dispersion factors were

TABLE 1. X-ray powder-diffraction data for synthetic lipscombite

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
10	6.30	6.396	0 1 1	10	2.064	2.047	1 3 3
10	4.89	4.901	0 1 2	20	2.021	2.026	1 1 6
45	4.82	4.814	1 1 1	5	1.877	1.894	1 3 4
5	3.73	3.772	0 1 3	5	1.866	1.866	0 2 6
100	3.352	3.352	1 1 3	10	1.823	1.828	0 4 0
50	3.304	3.303	0 0 4	5	1.800	1.791	0 3 5
45	3.232	3.198	0 2 2	10	1.756	1.757	1 4 1
40	3.152	3.173	1 2 1	20	1.676	1.676	2 2 6
10	2.645	2.625	1 2 3	20	1.653	1.651	0 0 8
20	2.607	2.584	2 2 0	10	1.622	1.622	2 4 1
30	2.318	2.312	1 3 0	20	1.603	1.605	3 3 3
20	2.283	2.277	1 3 1	5	1.600	1.599	0 4 4
5	2.102	2.108	0 1 6	10	1.576	1.587	2 4 2

Note: Powder diffractogram, 1°/min, Cu$K\alpha$ radiation. Indices are based on strong single-crystal reflections and cell parameters stated in the text.
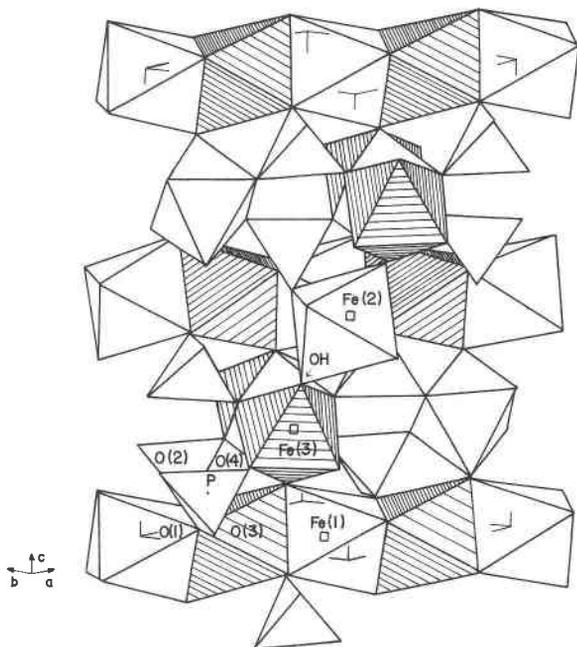
Fig. 3. Polyhedral projection of the synthetic lipscombite. The c axis is in the plane of the paper and vertical. The a axis is directed into the plane of the page at an angle of approximately 45°. The origin is that closest to Fe(1) in the diagram.

Fe(3) at zero. Convergence was reached at $R = 0.102$ for the observed reflections, also with unit weights, and $R = 0.20$ for all reflections. The number of refined parameters was 70. Further anisotropic refinements neither improved the R value nor the calculated interatomic bond distances and angles. An IBM/4341 computer was used to perform all the calculations with the SHELX-76 program system (Sheldrick, 1976). The projection shown in Figure 3 was drawn with the help of the program ORTEP (Johnson, 1965), which is incorporated in the Enraf-Nonius Structure Determination Package.

Final coordinates and anisotropic thermal parameters are given in Table 2. Selected interatomic distances and angles are given in Table 3. The calculated and observed structure factors are presented in Table 4.[1]

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[1] A copy of Table 4 may be ordered as Document AM-89-401 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.
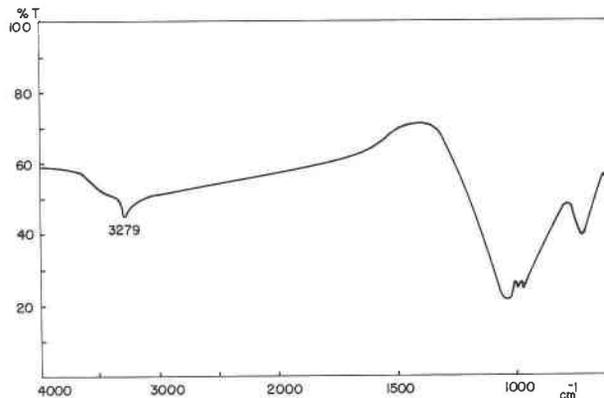
Fig. 4. Infrared absorption spectrum of synthetic lipscombite in KBr pellets. The stretching vibration ν occurs at 3279 cm^{-1}.

STRUCTURE DESCRIPTION

The Fe^{3+} [= Fe(3)] coordination octahedron is formed by two *trans* (OH)$^-$ groups and by four different oxygen atoms, O(1), O(2), O(3), and O(4), from phosphate groups. The Fe^{2+} [= Fe(1)] octahedron is formed by two *trans* (OH)$^-$ groups and by two O(1) atoms plus two O(2) atoms. The Fe^{2+} [= Fe(2)] octahedron is also formed by two *trans* (OH)$^-$ groups and by two O(3) atoms plus two O(4) atoms. The presence of the hydroxyl group was verified with an infrared-absorption spectrum (Fig. 4), obtained with a Perkin Elmer 1320 spectrometer using KBr pellets. The stretching vibration ν occurs at 3279 cm^{-1}, indicating an (OH)$^-$ group, according to Baur (1972).

The structure represented in projection in Figure 3 is formed by octahera sharing opposite faces in infinite chains along the directions [110] and [1$\bar{1}$0]. For the dimorphic variety of lipscombite that crystallizes in space group $I4_122$, Katz and Lipscomb (1951) found chains of octahedra along the [100] and [010] directions. In our structure, each chain is composed of alternating Fe^{2+} and Fe^{3+} octahedra sharing faces according to the scheme Fe(1)-Fe(3)-Fe(2)-Fe(3)-Fe(1)-···, where Fe(1) and Fe(2) have the combined occupancy factor of 0.47. The latter would be 0.50 for the ideal stoichiometric composition $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$. It is worth noting that Katz and Lipscomb did not distinguish between Fe^{2+} and Fe^{3+} ions, but they mentioned incomplete occupation of equivalent Fe sites.

TABLE 2. Atomic coordinates, site occupancy factors (k), and anisotropic thermal-vibration parameters (Å²) for synthetic lipscombite

Atom	k	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.391(5)	0.368(1)	0.368(1)	0	0.046(5)	0.046(5)	0.016(6)	0.002(6)	−0.002(6)	−0.026(7)
Fe(2)	0.082(5)	0.138(6)	0.138(6)	½	0.031(12)	0.031(12)	0.038(15)	0.027(14)	−0.027(14)	−0.017(14)
Fe(3)	1	0.1489(8)	0.3821(7)	0.2458(8)	0.0006(25)	0.008(3)	0.030(3)	0.0	0.0	0.0
P	1	0.257(2)	−0.000(2)	0.124(1)	0.021(6)	0.007(5)	0.017(4)	0.010(6)	0.005(8)	0.003(5)
O(1)	1	0.386(5)	0.0112(5)	0.053(3)	0.028(13)	0.021(13)	0.034(12)	−0.012(12)	0.010(13)	0.007(12)
O(2)	1	0.134(5)	0.129(5)	0.184(2)	0.029(12)	0.014(12)	0.037(11)	−0.002(13)	0.009(13)	−0.005(11)
O(3)	1	0.138(6)	−0.132(6)	0.062(3)	0.046(13)	0.036(13)	0.048(12)	0.001(13)	−0.006(14)	0.000(12)
O(4)	1	0.372(5)	−0.113(6)	0.193(3)	0.028(13)	0.029(13)	0.032(13)	0.002(13)	−0.015(13)	−0.004(12)
OH	1	0.012(4)	0.235(4)	0.373(3)	0.015(10)	0.015(11)	0.010(8)	0.005(13)	0.004(12)	−0.002(12)

TABLE 3. Interatomic distances (Å) and angles (°) for synthetic lipscombite

Fe(1)			Fe(2)			Fe(3)			P		
Fe(1)-O(1)	2.00		Fe(2)-O(3)^D	2.18		Fe(3)-O(1)^I	2.03		P-O(1)	1.56	
-O(2)^A	2.13		-O(4)^E	1.97		-O(2)	2.03		-O(2)	1.52	
-OH^A	2.08		-OH	2.04		-O(3)^E	1.83		-O(3)	1.54	
-O(1)^B	2.00		-O(3)^F	2.18		-O(4)^J	1.99		-O(4)	1.49	
-O(2)^C	2.13		-O(4)^G	1.97		-OH	2.24		average	1.53	
-OH^C	2.08		-OH^H	2.04		-OH^A	2.06				
Average	2.07		average	2.06		average	2.03				
	O-O	O-Fe-O		O-O	O-Fe-O		O-O	O-Fe-O		O-O	O-P-O
O(1)-OH^A	3.19	103	O(3)^D-OH	2.82*	84	O(1)^I-O(2)	2.63*	81	O(1)-O(2)	2.53	110
-O(1)^B	3.16	104	-O(3)^F	3.24	96	-O(4)^J	2.82	89	-O(3)	2.55	111
-O(2)^C	2.63*	79	-O(4)^G	2.69*	81	-OH	2.74*	80	-O(4)	2.48	109
-OH^D	2.74*	84	-OH^H	2.99	90	-OH^A	3.07	97	O(2)-O(3)	2.49	109
O(2)^A-OH^A	2.77*	82	O(4)^E-OH	3.00	97	O(2)-O(3)^E	2.95	100	-O(4)	2.48	111
-O(1)^B	2.63*	79	-O(3)^F	2.69*	81	-OH	2.77*	81	O(3)-O(4)	2.43	107
-O(2)^C	3.23	98	-O(4)^G	3.07	102	-OH^A	3.06	97	average	2.49	109
-OH^C	2.98	90	-OH^H	2.80*	89	O(3)^E-O(4)^J	2.69*	90			
OH^A-O(1)^B	2.74*	84	OH-O(3)^F	2.99	90	-OH	2.88	90			
-O(2)^C	2.98	90	-O(4)^G	2.80*	89	-OH^A	2.82*	93			
O(1)^B-OH^C	3.19	103	O(3)^F-OH^H	2.82*	84	O(4)^J-OH	3.09	94			
O(2)^C-OH^C	2.77*	82	O(4)^G-OH^H	3.00	97	-OH^A	2.80*	88			
average	2.92	90	average	2.91	90	average	2.86	90			

Note: Estimated standard deviations are 0.04 Å and 2° for interatomic distances and angles, respectively. A: ½ − y, ½ + x, −¼ + z; B: y, x, − z; C: ½ + x, ½ + y, ¼ − z; D: −x, −y, ½ + z; E: ½ − y, ½ − x, ¼ + z; F: −y, − x, ½ − z; G: ½ − x, ½ + y, ¾ − z; H: y, x, 1 − z; I: −½ + x, ½ − y, ¼ − z; J: −y, 1 − x, ½ − z.
* Octahedral shared faces.

Our synthetic lipscombite structure is similar to the iron lazulite structure given by Katz and Lipscomb. The cell contents of the $I4_122$ space-group structure can be approximately transformed to the $P4_32_12$ space-group structure with the matrix 1̄10/110/001 followed by a translation of the origin such that $x' = x$, $y' = y − 0.250$, $z' = z + 0.375$.

The Fe^{3+} octahedra are ruled in Figure 3. The chains make angles of 90° with one another and are joined via the (OH)⁻ ligand. Each (OH)⁻ ligand is a common vertex of four octahedra: one Fe(1), one Fe(2), and two Fe(3). The chains are also interconnected by the phosphate tetrahedral groups, which share vertices with the octahedra. The shortest distances between metal atoms are along the chains, with Fe(1)-Fe(3) = 2.75(4) Å and Fe(2)-Fe(3) = 2.44(4) Å. The latter is shorter than the Fe-Fe distance in α-Fe (2.482 Å). The shortness of these distances suggests a high probability of electron transfer along the chains.

The mean Fe^{3+}-O distance agrees within experimental error with the values for the iron phosphates determined by Moore and Araki (1976), Moore et al. (1974), and Vencato et al. (1986). An exception is Fe^{3+}-OH = 2.24(4) Å, a surprisingly long distance for iron phosphates. Severe cation-cation repulsion across the shared faces results in short O-O distances, which have a mean value of 2.74 Å. The corresponding deformation at the other octahedral faces can be seen as greater O-O and O-Fe-O distances. The tetrahedral P-O and O-O distances are within the reported values for numerous well-refined structures.

The shortest distances between (OH)⁻ and each of the four oxygen atoms O(1), O(2), O(3), and O(4) of the phosphate group are 2.74, 2.77, 2.82, and 2.80 Å, respectively.

All these oxygen atoms belong to the Fe coordination polyhedra. As no H atom can be localized on the edges of the coordination polyhedra around cations, it is concluded that the H atom of the (OH)⁻ group is disordered.

A calculation of the empirical bond-valence sums (Brown and Altermatt, 1985) around cations and anions (Table 5) shows satisfactory agreement for Fe(3), P, and O atoms. The contribution of oxygen atoms to the electrostatic balance of charges of Fe(1) and Fe(2) atoms has been taken in proportion to their occupancy factors. It should be noted that calculated sum of the valence contribution of Fe(1) and Fe(2) atoms is 1.16 v.u., which is in disagreement with the ideal value of 1.00 v.u. (their ideal combined occupation factor is ½). We believe that this may be due to the disorder present in the structure. The bond-valence sum of 1.08 v.u. for OH shows that it is a hydroxyl, as confirmed by the infrared spectrum (Fig. 4).

The Mössbauer spectrum of the crust material is identical to that of synthetic barbosalite (Mattievich and Danon, 1977), both in the relative intensities and in the I.S. and Q.S. parameters. The reason for this identity can be attributed to the structural resemblance between monoclinic barbosalite and tetragonal lipscombite, as shown

TABLE 5. Bond valences in synthetic lipscombite

	Fe(1)	Fe(2)	Fe(3)	P	Sum
O(1)	0.38		0.48	1.17	2.03
O(2)	0.27		0.48	1.30	2.05
O(3)		0.05	0.83	1.23	2.11
O(4)		0.09	0.54	1.41	2.04
OH	0.30	0.07	0.71		1.08
	0.95	0.21	3.04	5.11	9.31

by Moore (1970). It is notable that the occupancy factor of the Fe^{2+} ions relative to the Fe^{3+} ions in the present structure is 0.47, very close to 0.50, the value for the ordered barbosalite structure. The resemblance is further reflected in the great similarity between the X-ray diffraction pattern of lipscombite (Table 1) and that of barbosalite (Lindberg and Pecora, 1955).

REFERENCES CITED

Baur, W. (1972) Predictions of hydrogen bonds and hydrogen atom positions in crystalline solids. Acta Crystallographica, B28, 1456–1465.

Brown, I.D., and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Crystallographica, B41, 244–247.

Gheith, M.A. (1953) Lipscombite: A new synthetic iron lazulite. American Mineralogist, 38, 612–628.

International Tables for X-ray Crystallography. (1974) J.A. Ibers and W.C. Hamilton, Eds., vol. IV. Kynoch Press, Birmingham, England.

Johnson, C.K. (1965) ORTEP: A Fortran thermal-ellipsoid plot program for crystal structure illustrations. Oak Ridge National Laboratory, Tennessee.

Katz, L., and Lipscomb, W.N. (1951) The crystal structure of iron lazulite, a synthetic mineral related to lazulite. Acta Crystallographica, 4, 345–348.

Lindberg, M.L. (1962) Manganoan lipscombite from the Sapucaia pegmatite mine, Minas Gerais, Brazil. First occurrence of lipscombite in nature. American Mineralogist, 47, 353–359.

Lindberg, M.L., and Pecora, W.T. (1955) Tavorite and barbosalite, two new phosphate minerals from Minas Gerais, Brazil. American Mineralogist, 40, 952–966.

Mattievich, E., and Danon, J. (1977) Hydrothermal synthesis and Mössbauer studies of ferrous phosphates of the homologous series $Fe_3^{2+}(PO_4)_2(H_2O)_n$. Journal of Inorganic and Nuclear Chemistry, 39, 569–580.

Moore, P.B. (1970) Crystal chemistry of the basic iron phosphates. American Mineralogist, 55, 135–169.

Moore, P.B., and Araki, T. (1976) A mixed-valence solid solution series: Crystal structures of phosphoferrite, $Fe_e^{II}(H_2O)_3[PO_4]_2$, and kryzhanovskite, $Fe_3^{III}(OH)_3[PO_4]_2$. Inorganic Chemistry, 15, 316–321.

Moore, P.B., Kampf, A.R., and Irving, A.J. (1974) Whitmoreite, $Fe^{2+}Fe_2^{3+}(OH)_2(H_2O)[PO_4]_2$, a new species: Its description and atomic arrangement. American Mineralogist, 59, 900–905.

Sheldrick, G.M. (1976) SHELX-76. Programme for crystal structure determination. University of Cambridge, England.

Vencato, I., Mascarenhas, Y.P., and Mattievich, E. (1986) The crystal structure of $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$: A new synthetic compound of mineralogic interest. American Mineralogist, 71, 222–226.

Vochten, R.F., and De Grave, E. (1981) Crystallographic, Mössbauer, and electrokinetic study of synthetic lipscombite. Physics and Chemistry of Minerals, 7, 197–203.

Vochten, R.F., van Acker, P., and De Grave, E. (1983) Mössbauer, electrokinetic, and refined parameters study of synthetic manganoan lipscombite. Physics and Chemistry of Minerals, 9, 263–268.