Crystal structures of bobierrite and synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$

Shozo Takagi, Mathai Mathew, Walter E. Brown

Paffenbarger Research Center, American Dental Association Health Foundation, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A.

Abstract

The crystal structures of two forms of $Mg_3(PO_4)_2 \cdot 8H_2O$, bobierrite (I) and the synthetic polymorph (II), have been determined by single-crystal X-ray diffraction. Crystal data for polymorph I are space group $C2/c$, $a = 4.667(1)$, $b = 27.926(8)$, $c = 10.067(3)$ Å, $\beta = 105.01(2)°$, $Z = 4$, $R = 0.041$ for 963 reflections. Crystal data for polymorph II are space group $C2/m$, $a = 10.034(1)$, $b = 13.407(2)$, $c = 4.657(1)$ Å, $\beta = 105.09(1)°$, $Z = 2$, $R = 0.025$ for 510 reflections. The structure of polymorph I is closely related to that of the vivianite group, whereas polymorph II is isostructural with vivianite. Both structures consist of octahedral edge-sharing dimers $Mg_2O_6(H_2O)_4$ and independent $MgO_2(H_2O)_4$ octahedra linked together by PO_4 tetrahedra to form complex sheets parallel to (010). The arrangement of these sheets along **b** is different in the two structures.

Introduction

Bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$, has been considered to be a member of the vivianite group of minerals with the general formula $M_3(XO_4)_2 \cdot 8H_2O$, where M = Fe, Mg, Ni, Co, or Zn and X = As or P. However, bobierrite has been reported to have a space group different from that of vivianite (Barth, 1937; Lehr et al., 1967; Kanazawa et al., 1979). Preparations of synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$ have been found to crystallize in two different space groups, one corresponding to that of the mineral bobierrite and the other to that of the vivianite group (Kanazawa et al., 1979). As part of a study of the structures of hydrated phosphates, we have determined the crystal structures of the two forms of $Mg_3(PO_4)_2 \cdot 8H_2O$.

Experimental procedure

Crystals of bobierrite from Wodgina, Australia, were kindly supplied by John S. White, U.S. National Museum, Division of Mineralogy (USNM 128218). Synthetic samples were prepared by the method reported by Kanazawa et al. (1979) in the presence of various metal ions. The crystal used in the structure analysis was prepared in the presence of Cu^{2+} ions, and subsequent analysis of the sample confirmed the presence of Cu.

Bobierrite has been assigned space group $P2_1/c$ (with an interchange of a and c from the present setting) (Barth, 1937; Lehr et al., 1967). Kanazawa et al. (1979) reported the space group to be $P2_1/m$ or $P2_1$ based on the presence of one weak $h0l$ reflection with both h and l odd. However, our studies with precession photographs indicated a C-centered cell, but with the same cell dimensions reported for the primitive cells (except for interchange of a and c). Systematic absences showed the space group to be $C2/c$ or Cc. However, intensity data were collected assuming a primitive cell. There were a few reflections (26 hkl reflections with $h + k = 2n + 1$ and 11 $h0l$ reflections with h, l or both odd) that appeared to be observed, but violated the systematic absences for $C2/c$ or Cc. However, all these reflections were only marginally observable, most of them in the range $3–5\sigma(I)$, max-

imum $10\sigma(I)$. These 37 reflections constitute less than 4% of the total additional reflections possible for the primitive cell. Of the 11 such reflections of the $h0l$ type, 9 are with $h = 2n + 1$ (which violate $P2_1/c$ with interchange of a and c as reported by Barth, 1937), 8 with $l = 2n + 1$ and 5 with $h + l = 2n + 1$. Thus it was not possible to assign specific categories of systematic absences for $h0l$ type reflections. If all these reflections were truly present, the space group would be $P2_1/m$ or $P2_1$, as reported by Kanazawa et al. (1979). A closer examination of the intensity data revealed that every one of these 37 reflections was associated with a strong reflection having a k index within ± 1 and very similar angular settings. For example, when $11\bar{2}$ was very intense, both $10\bar{2}$ and $12\bar{2}$ were "observable." This may be related to the close spacing of reflections along **b***, particularly with Mo radiation. Thus, we conclude that the true space group of bobierrite is $C2/c$ or Cc. The choice of $C2/c$ was confirmed by the structure analysis.

Data from precession photographs of the synthetic material (polymorph II) are consistent with space group $C2/m$, $C2$, or Cm and the cell dimensions reported by Kanazawa et al. (1979). The space group $C2/m$ initially chosen was confirmed by the structure analysis.

All measurements were made on a Syntex $P2_1$ diffractometer with graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). The cell parameters were obtained by least-squares fit of 2θ values for 15 reflections measured by automatic centering. The intensity data were measured using the $\theta–2\theta$ scan technique, with a variable scan rate of 0.5 to 29.3° min^{-1} depending on the intensity of the reflection. Three standard reflections monitored periodically indicated that there was no significant variation in intensity during the data collection. Additional crystal data and details of the data collection are given in Table 1. The data were corrected for Lorentz, polarization, and absorption effects using the program XRAY76 (Stewart et al., 1976).

Structure solution and refinement

The positions of Mg and P atoms in the structure of bobierrite were deduced from a three-dimensional Patterson synthesis and the remaining atoms (except for H)

Table 1. Crystal data, experimental conditions, and refinement parameters for bobierrite (polymorph I) and synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$ (polymorph II)

	I	II
Crystal size (mm)	$0.02 \times 0.17 \times 0.33$	$0.03 \times 0.13 \times 0.31$
a (Å)	4.667(1)	10.034(1)
b (Å)	27.926(8)	13.407(2)
c (Å)	10.067(3)	4.657(1)
β (°)	105.01(2)	105.09(1)
Z	4	2
Space group	$C2/c$	$C2/m$
Calculated ρ (mg m^{-3})	2.133	2.234
	Data collection	
2θ max (°)	50	50
μ (mm^{-1})	5.62	5.89
Absorption correction to F_o, max	1.09	1.08
min	1.01	1.02
Unique set	1131	558
Reflections with $I \geq 3\sigma(I)$*	963	510
	Refinement**	
R	0.041	0.025
R_w	0.053	0.030
w^{-1}	$\sigma^2(F_o) + (0.02\ F_o)^2$	$\sigma^2(F_o) + (0.01\ F_o)^2$
Goodness of fit S	1.15	1.51
Average shift/error	0.01	0.030
Max shift/error	0.11	0.15

* Only these reflections were used in the refinements.
** Values from the final cycle.

were located in subsequent Fourier syntheses. In the case of the synthetic material (polymorph II), the initial parameters were from those of vivianite (Mori and Ito, 1950). Positions of the H atoms for both compounds were obtained from difference Fourier syntheses.

The refinement of bobierrite proceeded normally. However, in the case of the synthetic sample, refinements resulted in a negative isotropic thermal parameter for Mg(1), which indicated the presence of heavier atoms at this site. The crystal used for the data collection was prepared in a medium containing Cu^{2+} ions. The presence of Cu was confirmed by energy-dispersive X-ray analysis. The occupancy factors of Cu and Mg for both cation sites were refined with the constraint that the total occupancy at each site was unity. The results were 0.915(5) Mg and 0.085 Cu for Mg(1); 1.004(4) Mg and −0.004 Cu for Mg(2). The

Table 2. Final atomic parameters of non-H atoms in bobierrite (polymorph I) and synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$ (polymorph II)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
				Bobierrite (polymorph I)						
Mg(1)	0	0.87840(5)	¼	98(8)	124(8)	44(7)	0	−26(6)	0	0.8
Mg(2)	0	0.06681(5)	¼	104(8)	113(8)	54(8)	0	−19(6)	0	0.8
Mg(3)	0	0.17283(5)	¼	118(8)	98(8)	70(8)	0	−17(6)	0	0.8
P	0.3861(2)	0.11913(3)	0.06483(8)	74(5)	111(5)	26(4)	2(3)	−25(3)	−1(3)	0.6
O(1)	0.3715(5)	0.11974(8)	−0.0916(2)	99(11)	162(11)	54(11)	−1(10)	−8(9)	12(8)	0.9
O(2)	0.7142(5)	0.11951(7)	0.1452(2)	77(11)	148(11)	62(10)	−13(9)	−37(9)	−11(8)	0.8
O(3)	0.2291(5)	0.16505(8)	0.0958(2)	118(12)	125(12)	74(11)	6(9)	−9(9)	−6(8)	0.9
O(4)	0.2312(5)	0.07345(8)	0.0958(2)	101(12)	111(12)	87(12)	−7(9)	−4(9)	−3(8)	0.8
O(w1)	0.3191(6)	0.32540(8)	0.3571(3)	151(14)	179(13)	90(14)	−4(11)	−6(11)	−9(9)	1.2
O(w2)	0.3088(7)	0.43350(9)	0.3473(3)	123(13)	184(13)	71(13)	−12(10)	−22(11)	0(9)	1.1
O(w3)	0.2857(7)	0.22389(10)	0.3534(3)	181(16)	136(15)	302(16)	−16(11)	−10(12)	−71(11)	1.7
O(w4)	0.2800(6)	0.01297(10)	0.3507(3)	149(15)	154(14)	199(14)	−23(10)	−4(11)	28(11)	1.4
				Synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$ (polymorph II)						
Mg(1)	0	0	0	72(6)	101(7)	66(6)	0	12(4)	0	0.6
Mg(2)	0	0.39054(7)	0	101(5)	92(5)	84(5)	0	30(3)	0	0.7
P	0.31452(7)	0	0.3843(1)	78(4)	104(4)	71(4)	0	26(3)	0	0.7
O(1)	0.1575(2)	0	0.3709(4)	90(10)	173(11)	95(10)	0	31(8)	0	0.9
O(2)	0.3947(2)	0	0.7144(4)	113(10)	129(10)	86(10)	0	26(8)	0	0.9
O(3)	0.3455(1)	0.0956(1)	0.2303(3)	124(7)	125(8)	111(6)	5(5)	41(5)	8(6)	0.9
O(w1)	0.4013(1)	0.3866(1)	0.1916(3)	140(8)	196(8)	135(7)	7(6)	37(6)	−24(6)	1.2
O(w2)	0.1010(2)	0.2787(1)	0.2802(3)	250(9)	167(9)	147(9)	20(7)	42(7)	11(6)	1.5

Note: The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and are multiplied by 10^4. Estimated standard deviations given in parentheses here and in all subsequent tables are in the least significant digits. Values without e.s.d.'s are fixed by symmetry.

Table 3. Final atomic parameters of H atoms in bobierrite and synthetic $Mg_3(PO_4)_2\cdot 8H_2O$

Atom	x	y	z	B (Å²)
Bobierrite (polymorph I)				
H(11)	0.158(12)	0.337(2)	0.361(5)	3(1)
H(12)	0.428(15)	0.325(2)	0.440(7)	7(2)
H(21)	0.159(11)	0.423(1)	0.363(4)	2(1)
H(22)	0.434(12)	0.438(2)	0.418(5)	3(1)
H(31)	0.482(14)	0.221(2)	0.375(6)	6(2)
H(32)	0.292(9)	0.252(2)	0.351(4)	2(1)
H(41)	0.462(15)	0.020(2)	0.361(6)	6(2)
H(42)	0.274(11)	−0.013(2)	0.303(5)	4(1)
Synthetic $Mg_3(PO_4)_2\cdot 8H_2O$ (polymorph II)				
H(11)	0.381(3)	0.414(2)	0.330(7)	2.9(7)
H(12)	0.325(4)	0.376(2)	0.060(8)	2.9(6)
H(21)	0.126(3)	0.299(2)	0.444(8)	3.3(8)
H(22)	0.048(3)	0.226(3)	0.286(7)	3.6(7)

Table 6. Selected bond distances (Å) and angles (°) for bobierrite and synthetic $Mg_3(PO_4)_2\cdot 8H_2O$

Bobierrite (polymorph I)			
P–O(1)	1.559(2)	Mg(1)–O(1)	2.030(2) × 2
–O(2)	1.535(2)	–O(w1)	2.130(3) × 2
–O(3)	1.548(2)	–O(w2)	2.139(3) × 2
–O(4)	1.537(2)		
		Mg(2)–O(2)	2.081(2) × 2
O(1)–P–O(2)	108.0(1)	–O(4)	2.116(2) × 2
–O(3)	107.2(1)	–O(w4)	2.076(2) × 2
–O(4)	108.3(1)		
O(2)–P–O(3)	110.3(1)	Mg(3)–O(2)	2.093(2) × 2
–O(4)	110.8(1)	–O(3)	2.112(2) × 2
O(3)–P–O(4)	112.0(1)	–O(w3)	2.043(3) × 2
Synthetic $Mg_3(PO_4)_2\cdot 8H_2O$ (polymorph II)			
P–O(1)	1.561(2)	Mg(1)–O(1)	2.015(2) × 2
–O(2)	1.539(2)	–O(w1)	2.133(2) × 4
–O(3)	1.539(1) × 2		
		Mg(2)–O(2)	2.075(1) × 2
O(1)–P–O(2)	107.4(1)	–O(3)	2.110(1) × 2
–O(3)	107.8(1) × 2	–O(w2)	2.071(2) × 2
O(2)–P–O(3)	110.4(1) × 2		
O(3)–P–O(3′)	112.8(1)		

occupancy of the Mg(2) site was fixed at 1.00 Mg in all subsequent calculations. The final value of the occupancy factors of the Mg(1) site was 0.910(5) Mg and 0.090 Cu.

All refinements were carried out utilizing the full-matrix least-squares programs XRAY76 (Stewart et al., 1976) for bobierrite and RFINE4 (Finger and Prince, 1975) for the synthetic sample (polymorph II). The scattering factors for neutral atoms were taken from the *International Tables for X-ray Crystallography* (1974). Details of the refinement parameters are listed in Table 1. Final atomic parameters are listed in Tables 2 and 3 and the observed and calculated structure amplitudes in Tables 4 and 5.[1]

DESCRIPTION OF THE STRUCTURE

The structure of bobierrite is closely related to that of vivianite, whereas the synthetic sample (polymorph II) is isostructural with vivianite. Selected bond lengths and angles are listed in Table 6.

The structures of both compounds consist of compact assemblies of MgO_6 octahedra and PO_4 tetrahedra forming complex sheets parallel to (010). These sheets are linked together by H bonds only (Figs. 1–3). The structures of the sheets in bobierrite and the synthetic sample are nearly identical. However, the arrangements of these sheets along the **b** axis are different. In the synthetic sample, adjacent slabs 6.70 Å thick equivalent to $b/2$ are displaced by ½a. In bobierrite, there are four crystallographically equivalent sheets per unit cell; alternate sheets are related by n-glides and c-glides perpendicular to the **b** axis (Fig. 2). Pairs of sheets, related by the c-glides, have nearly the same separation (6.69 Å) as in the synthetic sample. Note that the c-glide in bobierrite is equivalent to the ½a translation in the synthetic sample because of interchange of a and c in the two compounds. In the pairs of sheets related by n-glides, the H bonds linking the two sheets are nearly parallel to the **b** axis (Fig. 2). The distance between these

pairs of sheets increases to 7.27 Å (as compared to 6.69 Å) to avoid short $O_w\cdots O_w$ contacts. This increase in separation of the sheets corresponds to half the difference in the dimension b in the two compounds ($b/2 = 13.963$ Å in polymorph I, b = 13.407 Å in polymorph II). All separations between sheets were calculated on the basis of the midpoints of the dimeric Mg octahedra.

Mg octahedra

All Mg atoms in both structures are octahedrally coordinated. There are two types of MgO_6 octahedra in each structure, one forming independent MgO_6 octahedra and the other edge-sharing Mg_2O_{10} dimeric units.

Mg(1) in both structures is coordinated to two O atoms from PO_4 groups and to four water molecules to form $MgO_2(H_2O)_4$ monomer units. The corresponding Mg–O bonds and O–Mg–O angles are not significantly different in the two structures (Table 6).

The dimeric unit in bobierrite contains two crystallographically independent Mg atoms, Mg(2) and Mg(3), but
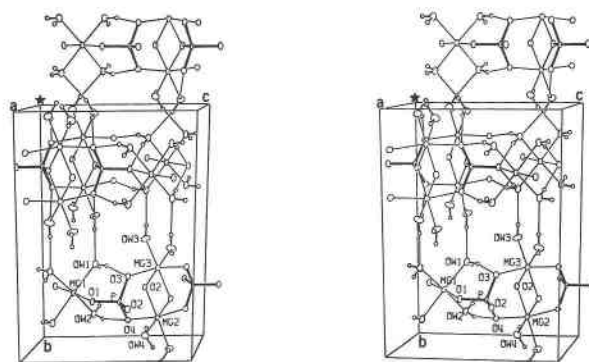

Fig. 1. Stereoscopic view of the structure of bobierrite. Only one-half of the unit cell along **b** is shown. The origin is marked by a star (*).
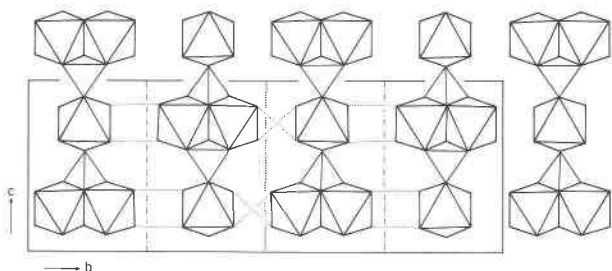
Fig. 2. Polyhedral diagram of the structure of bobierrite (polymorph I), projected down a^*. The PO₄ tetrahedra are bonded to octahedral levels above and below. The n-glides are represented by dash-dot lines and the c-glides by dotted lines. H bonds between the layers are also marked.

Fig. 3. Polyhedral diagram of the structure of synthetic Mg₃(PO₄)₂·8H₂O (polymorph II), projected down c^*. The PO₄ tetrahedra are bonded to octahedral levels above and below. H bonds between the layers are marked by dotted lines.

the dimeric unit in the synthetic sample possesses $2/m$ (C_{2h}) symmetry as in the vivianite group, and the two Mg atoms are crystallographically equivalent. The Mg atoms in both phases are bonded to two water molecules in a *cis* configuration and to four O atoms from PO₄ groups, two of which link the two Mg octahedra to form dimeric units. The Mg···Mg separation within the dimers is 2.961 and 2.936 Å in polymorphs I and II, respectively. Bond lengths and angle variations within and between the octahedra in the two polymorphs are relatively small (Table 6) in spite of the difference in the symmetries of the dimeric units. In addition, they compare very well with those in kottigite, Zn₃(AsO₄)₂·8H₂O (Hill, 1979), one of the comparatively well-refined structures among the vivianite group of minerals. The distortions usually expected in edge-shared coordination polyhedra are not evident in either structure. The O–Mg–O angles involving the shared edge are close to 90.0° whereas the corresponding O–Zn–O angle in kottigite is 85.4°.

PO₄ group

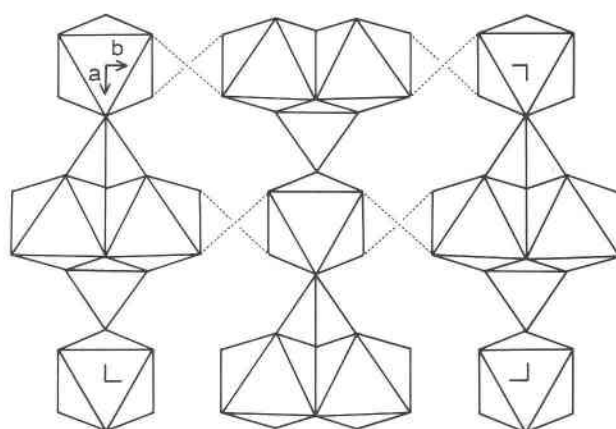The PO₄ group in bobierrite is at a site with no symmetry restrictions, whereas in polymorph II it lies on a

crystallographic mirror plane. The environments of the PO₄ groups are nearly identical in the two forms; one O is bonded to two Mg atoms to form the dimeric unit, whereas each of the remaining O atoms is bonded to only one Mg, but is involved in two H bonds.

The ranges of P–O distances in the two structures are 1.536–1.561 Å and 1.535–1.559 Å, respectively. In each case, the longest P–O bond length involves the O atom that has the shortest Mg–O bond as well as two of the shortest H bonds. The largest O–P–O angle is associated with the tetrahedral edge bonded to the two Mg atoms in the dimeric unit, as expected.

Water molecules and H bonding

The distance and angle parameters involving the water molecules and the H bonding are listed in Table 7. All O–H distances are in the range 0.79–0.89 Å, with a mean value 0.84(4) Å.

All available H atoms are involved in H bonding. The H-bonding schemes are nearly identical in the two structures and are in agreement with that observed in kottigite (Hill, 1979) rather than that proposed for the vivianite structure by Mori and Ito (1950). Only one of the four H bonds in the synthetic sample is between pairs of water molecules. In bobierrite, there are twice as many water molecules in the asymmetric unit, and two of the eight H bonds are between water molecules. These H bonds between the water molecules provide the sole linkage between the sheets in both structures. All other H bonds are within the same sheet.

DISCUSSION

The structures of the two polymorphs of Mg₃(PO₄)₂·8H₂O are very similar. There are no structural features that would indicate one structure being favored over the other in the presence of Cu²⁺ ions. The putative site for Cu²⁺ ion is present in both structures. Although the present studies have shown the presence of Cu²⁺ ions in the

Table 7. Probable H bonds in bobierrite and synthetic Mg₃(PO₄)₂·8H₂O

D-H ··· A*	D-H (Å)	H ··· A (Å)	D ··· A (Å)	D-H ··· A (°)
Natural bobierrite (polymorph I)				
O(w1)–H(11) ··· O(1)	0.83(6)	1.95(5)	2.745(4)	160(5)
–H(12) ··· O(3)	0.86(6)	1.83(7)	2.670(4)	164(6)
O(w2)–H(21) ··· O(1)	0.81(5)	1.94(5)	2.721(4)	163(4)
–H(22) ··· O(4)	0.81(5)	1.99(5)	2.762(4)	162(5)
O(w3)–H(31) ··· O(3)	0.89(6)	2.03(6)	2.737(4)	135(5)
–H(32) ··· O(w1)	0.79(6)	2.05(6)	2.839(4)	177(5)
O(w4)–H(41) ··· O(4)	0.85(7)	2.03(6)	2.776(4)	145(6)
–H(42) ··· O(w2)	0.87(5)	2.09(5)	2.940(4)	167(5)
Synthetic Mg₃(PO₄)₂·8H₂O (polymorph II)				
O(w1)–H(11) ··· O(1)	0.81(3)	1.92(3)	2.727(2)	170(3)
–H(12) ··· O(3)	0.86(4)	1.92(4)	2.742(1)	159(3)
O(w2)–H(21) ··· O(3)	0.79(4)	2.04(3)	2.773(2)	155(3)
–H(22) ··· O(w2)	0.89(4)	2.07(4)	2.944(2)	166(3)

* Donor H acceptor.

synthetic sample, Kanazawa et al. (1979) have prepared crystals of $Mg_3(PO_4)_2 \cdot 8H_2O$, corresponding to polymorph II in the absence of inorganic ions like Cu^{2+}. Thus the presence of Cu^{2+} does not appear to be an essential constituent of polymorph II.

It is of interest in this respect that the molar volume of bobierrite (polymorph I) is 4.8% larger than that for the synthetic sample (polymorph II), indicating that polymorph II may be the thermodynamically more stable phase. However, this is contraindicated by the fact that polymorph I is the natural form. Well-developed crystals of synthetic bobierrite (polymorph I) can be prepared by allowing crystals of $Mg_3(PO_4)_2 \cdot 22H_2O$ to stand in water for about two months (Lehr et al., 1967). Polymorph II was not identified in such preparations. On the contrary, direct synthesis from mixed solutions invariably resulted in the coexistence of both polymorphs (Kanazawa et al., 1979).

ACKNOWLEDGMENTS

REFERENCES

Barth, T.F.W. (1937) Crystallographic studies in the vivianite group. American Mineralogist, 22, 325–341.
Finger, L.W., and Prince, Edward. (1975) RFINE4. Technical Note 854. National Bureau of Standards, Washington, D.C.
Hill, R.J. (1979) The crystal structure of kottigite. American Mineralogist, 64, 376–382.
International tables for X-ray crystallography, volume IV (1974) J.A. Ibers and W.C. Hamilton, Eds. Kynoch, Birmingham, England.
Kanazawa, Takafumi, Umegaki, Takao, and Shimizu, Masao. (1979) The synthesis of $Mg_3(PO_4)_2 \cdot 8H_2O$ and its new polymorphism. Chemical Society of Japan Bulletin, 52, 3713–3717.
Lehr, J.R., Brown, E.H., Frazier, A.W., Smith, J.P., and Thrasher, R.D. (1967) Crystallographic properties of fertilizer compounds. Chemical Engineering Bulletin 6, Tennessee Valley Authority.
Mori, Hiroshi, and Ito, Teiichi. (1950) The structure of vivianite and simplesite. Acta Crystallographica, 3, 1–6.
Stewart, J.M., Machin, P.A., Dickinson, D.W., Ammon, H.L., Heck, H., and Flack, H. (1976) XRAY76. Technical Report TR446. Computer Science Center, University of Maryland, College Park, Maryland, U.S.A.