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HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF SEAMANITE

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ABSTRACT

Seamanite, Mn^{2+}_3 $[B(OH)_4]$ $[PO_4]$ $(OH)_2$ is orthorhombic, *a* 7.8231(9), *b* 15.1405(14), *c* 6.6999(7) Å, *V* 793.50(14) Å^3, space group *Pbnm*, *Z* = 4. The structure was refined to an *R* index of 1.8% on the basis of 1160 observed [$|F_o| > 5\sigma F$] reflections measured with Mo$K\alpha$ X-radiation using a single-crystal diffractometer, and all the H atoms were located in the refinement. The structure consists of face-sharing $[Mn_3\,\phi_{12}]$ trimers (ϕ: O, {OH}) of octahedra that link by sharing octahedron edges to form an $[Mn_3\,\phi_{10}]$ chain that extends in the *c* direction. This chain is decorated by $(B\{OH\}_4)$ and (PO_4) groups in a staggered configuration on either side of the chain. These chains condense in pairs by sharing octahedron–octahedron and octahedron–tetrahedron vertices to form columns that link together in the *a* and *b* directions by sharing vertices to form a heteropolyhedral framework. There are five crystallographically distinct H-atom sites in the structure. Two of the H atoms are displaced off their special positions on a mirror plane, presumably driven by local bond-valence requirements, but the displacement seems to be disordered, as refinement was completely satisfactory in the centrosymmetric space-group *Pbnm*. One of the anions of the phosphate group is not bonded to any other cations and is an acceptor anion for four hydrogen bonds.

Keywords: seamanite, crystal-structure refinement, electron-microprobe analysis.

SOMMAIRE

La seamanite, Mn^{2+}_3 $[B(OH)_4]$ $[PO_4]$ $(OH)_2$, est orthorhombique, *a* 7.8231(9), *b* 15.1405(14), *c* 6.6999(7) Å, *V* 793.50(14) Å^3, groupe spatial *Pbnm*, *Z* = 4. Nous avons affiné la structure jusqu'à un résidu *R* de 1.8% en utilisant 1160 réflexions observées [$|F_o| > 5\sigma F$] et mesurées sur cristal unique en diffraction X avec rayonnement Mo$K\alpha$ au moyen d'un diffractomètre; tous les atomes d'hydrogène ont été localisés dans notre affinement. La structure contient des trimères d'octaèdres à faces partagées, $[Mn_3\,\phi_{12}]$ (ϕ: O, {OH}), liés par partage d'arêtes d'octaèdres pour former une chaîne $[Mn_3\,\phi_{10}]$ allongée selon la direction *c*. Cette chaîne est décorée avec des groupes $(B\{OH\}_4)$ et (PO_4) en alternance de chaque côté de la chaîne. Ces chaînes sont agencées en paires par partage de vertex octaèdre–octaèdre et octaèdre–tétraèdre pour former des colonnes liées entre elles dans les directions *a* et *b*, et ainsi, une trame hétéropolyédrique. Les atomes d'hydrogène occupent cinq sites distincts. Deux de ceux-ci sont déplacés par rapport à leurs positions spéciales sur le plan miroir, probablement à cause des exigeances locales des valences de liaison, mais ces déplacements semblent désordonnés, parce que l'affinement est complètement satisfaisant dans le groupe spatial centrosymétrique *Pbnm*. Un des anions du groupe de phosphate n'est lié à aucun autre cation, et serait donc un récepteur de quatre liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: seamanite, affinement de la structure cristalline, analyse à la microsonde électronique.

INTRODUCTION

Seamanite, Mn^{2+}_3 $\{B(OH)_4\}$ (PO_4) $(OH)_2$, was described by Kraus *et al*. (1930) from the Chicagon mine, east of Iron River, Iron County, Michigan, U.S.A. It occurs there as slender translucent vertically striated acicular crystals, the color of which varies from pale yellow to distinct wine yellow where larger; crystals are up to 10 mm long and 2 mm wide, and occur in crevices in highly fractured ferruginous siliceous rock. Seamanite is also reported from the Bengal (Cannon) mine, Iron River, by DeMark (2000). The specimens described by him were not found in place, but were in the collection of a recently deceased miner, and are stated to be "quite dissimilar from the type-locality material" (DeMark 2000). McConnell & Pondrom (1941) determined the space group of seamanite to be *Pbnm*. Moore & Ghose (1971) solved the crystal structure of seamanite, and showed it to have an extremely unusual structural unit consisting of a chain of non-linear trimers of face-

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sharing ($Mn\phi_6$) octahedra (ϕ: O, {OH}) decorated by ($B\{OH\}_4$) tetrahedra. As part of our continuing interest in the role of hydrogen bonding in oxysalt minerals, we have refined the structure of seamanite, located the positions of the hydrogen atoms, and established the hydrogen bonds present in the structure; we present the results here.

EXPERIMENTAL

Crystals of seamanite from the Chicagon mine were used in this work. A fragment of an acicular crystal was ground to a spheroidal shape of diameter 160 μm and attached to a glass fiber.

X-ray diffraction

The unit-cell dimensions were determined using a Siemens *P*4 automated four-circle diffractometer with a graphite monochromator and a Mo*K*α X-ray tube. Twenty-five reflections between 10 and 30°2θ were centered, and a constrained orthorhombic cell was determined from the setting angles and refined using least-squares (Table 1). Single-crystal intensity data were measured from 4 to 60°2θ over the range $0\ 0\ \overline{10}$ to $12\ 22\ 10$ with a scan range of 1.2° and scan-speeds from 2.0 to 20.0°/min. A total of 2573 intensities was measured for a quarter of the Ewald sphere. Psi-scan data were measured for 15 reflections out to 60°2θ at increments of 5°, and an absorption correction, the crystal modeled as a triaxial ellipsoid, reduced *R*(azimuthal) from 1.2 to 0.9%. Intensities were corrected for Lorentz, polarization and background effects, and then reduced to structure factors; of the 1256 unique reflections, 1160 were classed as observed ($|F_o| > 5\sigma F$). Twenty-one observed reflections violated the diffraction conditions for *Pbnm* symmetry. A Ψ-scan on the most intense of these reflections showed that it is not due to Bragg diffraction, but rather to double diffraction.

Chemical analysis

The same crystal used for collection of the single-crystal X-ray intensity data was mounted in a perspex disc, ground, polished and coated with carbon for chemical analysis using a Cameca SX–50 electron microprobe. The crystal was analyzed for Mn, Mg, Fe, Ca, P and F in wavelength-dispersion mode. Ten points were analyzed with the following conditions: excitation voltage: 15 kV, specimen current: 20 nA, beam size: 10 μm, peak count-time: 20 s, background count-time: 10 s. The standards and crystals used for *K*α X-ray lines for the elements of interest were: Mn: spessartine, LiF; Mg: forsterite, TAP; Fe: marićite, LiF; Ca: diopside, PET; P: marićite, PET; F: fluorine equivalent of riebeckite, TAP. The resulting chemical composition and unit formula are given in Table 2; the amounts of B_2O_3 and H_2O were calculated on the basis of stoichiometry.

CRYSTAL-STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC^{TM} PC Plus system of programs; *R* indices are of the form given in Table 1, and are expressed as percentages. Structure refinement was initiated with the atom coordinates of Moore & Ghose (1971), and refinement converged to an *R* index of 2.6% for anisotropic-displacement parameters. An extinction correction further reduced the *R* index to 1.8%. At this stage of the refinement, a difference-Fourier map was calculated, and the coordinates of the H positions were determined. It is well known that refinement of H positions using X-ray intensity data results in anomalously short O–H bond-lengths because the center of gravity of the electron density associated with the H atom is displaced significantly toward the donor O atom by chemical bonding. The H positions were allowed to refine to optimal positions around respective O atoms with reasonable fixed displacement-parameters. A soft constraint was then imposed on the refinement (whereby the O–H distances should be ~0.98 Å) by adding extra weighted observational equations to the least-squares matrix, and the displacement parameters were allowed to refine. When the positional constraints on the H(1) and H(3) sites were removed, these sites refined off their special positions at *c* = ¼ (mirror plane), indicating positional disorder. Final refinement of all parameters converged to an *R* index of 1.8%. Final atom positions and displacement parameters are given in Table 3, selected interatomic distances and angles are listed in Table 4, and a bond-valence table is given in Table 5. Observed and calcu-

TABLE 1. MISCELLANEOUS INFORMATION FOR SEAMANITE

a (Å)	7.8231(9)	radiation	Mo*K*α/graphite
b	15.1405(14)	Total no. of *I*	2573
c	6.6999(7)	No. of *F*	1256
V (Å^3)	793.57(14)	No. of $\lvert F_o\rvert > 5\sigma F$	1160
Sp. Gr.	*Pbnm*	*R*(merge) %	1.4
Z	4	*R*(obs) %	1.8
μ (mm^{-1})	4.95	*wR*(obs) %	2.1

$R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$

$wR = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1$

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*)* FOR SEAMANITE

MnO	56.55	Mn^{2+}	3.07
MgO	0.12	Mg	0.01
FeO	0.06	Fe^{2+}	0.00
P_2O_5	17.84	Σ	3.08
B_2O_3 **	9.05		
H_2O **	14.05	P	0.97
Σ	97.67	B	1
		OH	6

* calculated based on 10 anions *pfu*
** determined by stoichiometry

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR SEAMANITE

Site	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	0.27819(5)	0.47584(3)	1/4	0.0114(1)	0.0128(2)	0.0112(2)	0.0103(2)	0	0.0005(2)	0.0114(1)
Mn(2)	0.35076(4)	0.64067(2)	0.50166(4)	0.0116(1)	0.0143(1)	0.0112(1)	0.0093(1)	0.0004(1)	0.0003(1)	0.0116(1)
P	0.69328(8)	0.55408(4)	1/4	0.0072(2)	0.0078(3)	0.0069(3)	0.0078(3)	0	–0.0006(2)	0.0072(2)
B	0.0071(4)	0.3151(2)	1/4	0.0110(7)	0.0099(13)	0.0091(12)	0.0139(13)	0	–0.0003(10)	0.0110(7)
O(1)	0.4608(2)	0.3688(1)	1/4	0.0135(5)	0.0126(9)	0.0132(9)	0.0145(9)	0	–0.0002(7)	0.0135(5)
O(2)	0.1866(2)	0.6162(1)	1/4	0.0135(5)	0.0106(9)	0.0172(9)	0.0128(9)	0	–0.0032(7)	0.0135(5)
O(3)	0.0393(2)	0.4094(1)	1/4	0.0148(4)	0.0208(7)	0.0122(6)	0.0115(6)	–0.0022(5)	0.0019(5)	0.0148(4)
O(4)	–0.1846(2)	0.3027(1)	1/4	0.0121(6)	0.0102(9)	0.0102(9)	0.0158(11)	0.0093(48)	0.0012(7)	0.0121(6)
O(5)	0.0812(2)	0.2733(1)	0.0734(2)	0.0159(6)	0.0113(9)	0.0090(9)	0.0275(12)	0.0023(99)	0.0002(7)	0.0159(6)
O(6)	0.7244(2)	0.4964(1)	0.0646(2)	0.0179(4)	0.0247(8)	0.0131(6)	0.0160(7)	0.0032(5)	0.0050(6)	0.0179(4)
O(7)	0.5040(2)	0.5846(2)	1/4	0.0136(6)	0.0154(10)	0.0110(10)	0.0143(10)	–0.0009(53)	0.0031(8)	0.0136(6)
O(8)	0.8110(2)	0.6348(1)	1/4	0.0129(6)	0.0105(8)	0.0151(10)	0.0130(10)	0.0121(42)	–0.0005(8)	0.0129(6)
H(1)	0.399(5)	0.314(2)	0.218(9)	0.0436(106)						
H(2)	0.0616(5)	0.621(3)	1/4	0.0391(111)						
H(3)	–0.041(5)	0.446(3)	0.327(6)	0.0458(122)						
H(4)	–0.216(5)	0.2400(7)	1/4	0.0713(114)						
H(5)	0.101(4)	0.317(1)	–0.031(3)	0.0561(190)						

The occupancy of H(1) and H(3) of ½.

lated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Cation polyhedra

There are two *Mn* sites, each of which is surrounded by six oxygen atoms and (OH) groups in an octahedral arrangement. The *Mn*(1) site lies on a mirror plane at $z = ¼$ and is coordinated by three O atoms and three (OH) groups; the *Mn*(2) site lies at the general position 8*i* and is coordinated by two O atoms and four (OH) groups. The <*Mn*–O> distances are 2.207 and 2.205 Å, in accord with complete occupancy of the *Mn*(1) and *Mn*(2) sites by Mn^{2+}, as indicated by both the X-ray scattering from these sites and the unit formula (Table 2) calculated from the electron-microprobe results. The $\{Mn(1)\phi_6\}$ octahedron is quite distorted from holosymmetric geometry, with a range in bond lengths from 2.12 to 2.42 Å. Inspection of the bond-valence table (Table 5) shows that this range in bond lengths is a result of the topology of the structure: ignoring the role of the hydrogen atoms for the moment, the anion coordination numbers vary from [1] for O(8) to [4] for O(7). The O(7) anion is bonded to P and Mn^{2+} at *Mn*(1) and *Mn*(2) × 2. The very long *Mn*(1)–O(7) distance of 2.415 Å is hence the result of the bond-valence requirements of the O(7) anion; O(7) has an excess of formal bond-strength ($0.33 \times 3 + 1.25 = 2.24$ *vu*); lengthening of *Mn*(1)–O(7) compensates for this excess and results in an incident bond-valence sum in accord with the valence-sum rule.

The *P* site is occupied completely by P and is surrounded by four O atoms in a tetrahedral arrangement. The <P–O> distance, 1.540 Å, is close to the grand <P–O> distance for inorganic phosphate structures (Baur 1974). The *B* site is occupied completely by B and is surrounded by four (OH) groups in a tetrahedral arrangement, with a <B–O> distance of 1.470 Å, close to the grand <B–O> distance of 1.476 Å given for borate minerals by Hawthorne *et al.* (1996).

Topology of the structure

As noted by Moore & Ghose (1971), the structure of seamanite is based on chains of $(Mn\phi_6)$ octahedra; they consist of face-sharing $[Mn_3\,\phi_{12}]$ trimers (Fig. 1a) that link by sharing octahedron edges to form an $[Mn_3\,\phi_{10}]$ chain, which extends in the *c* direction (Fig. 1b). The rather unusual $[Mn_3\,\phi_{12}]$ trimer is apparently stabilized by the $(B\{OH\}_4)$ group that spans the apical vertices of the *Mn*(2) octahedra (Moore & Ghose 1971). Additional linkage along the length of the chain is provided by (PO_4) tetrahedra that link apical vertices on neighboring *Mn*(2) octahedra such that the $(B\{OH\}_4)$ and (PO_4) groups adopt a staggered configuration on either side of this $[Mn_3\,(B\{OH\}_4)\,(PO_4)\,\phi_6]$ chain (Fig.1b). These chains condense in pairs by sharing both octahedron–octahedron and octahedron–tetrahedron vertices (Fig. 1c) to form columns of the form $[Mn_3\,(B\{OH\}_4)\,(PO_4)\,\phi_4]$. These columns link together in the *a* and *b* directions by sharing vertices between tetrahedra and octahedra (Fig. 2). The resulting structure is a heteropolyhedral framework, and the acicular habit is parallel to the chains of octahedra that extend in the *c* direction.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SEAMANITE

Mn(1)–O(1)	2.161(2)	O(1)–*Mn*(1)–O(3)	103.1(1)
Mn(1)–O(2)	2.243(2)	O(1)–*Mn*(1)–O(6)a,b	98.8(1)
Mn(1)–O(3)	2.123(2)	O(1)–*Mn*(1)–O(7)	91.6(1)
Mn(1)–O(6)a,b	2.149(1)	O(2)–*Mn*(1)–O(3)	99.7(1)
Mn(1)–O(7)	2.415(2)	O(2)–*Mn*(1)–O(6)e,f	79.1(1)
<*Mn*(1)–O>	2.207	O(2)–*Mn*(1)–O(7)	65.7(1)
		O(3)–*Mn*(1)–O(6)e,f	94.9(1)
Mn(2)–O(1)b	2.227(1)	O(7)–*Mn*(1)–O(6)e,f	82.7(1)
Mn(2)–O(2)	2.152(1)		
Mn(2)–O(4)c	2.279(1)	O(1)a–*Mn*(2)–O(4)c	81.7(1)
Mn(2)–O(5)d	2.138(1)	O(1)a–*Mn*(2)–O(5)d	94.1(1)
Mn(2)–O(6)b	2.197(1)	O(1)a–*Mn*(2)–O(6)b	88.5(1)
Mn(2)–O(7)	2.237(1)	O(1)a–*Mn*(2)–O(7)	100.6(1)
<*Mn*(2)–O>	2.205	O(2)–*Mn*(2)–O(4)c	107.2(1)
		O(2)–*Mn*(2)–O(5)d	97.2(1)
P–O(6),e	1.539(2)	O(2)–*Mn*(2)–O(6)b	80.1(1)
P–O(7)	1.551(1)	O(2)–*Mn*(2)–O(7)	70.4(1)
P–O(8)	1.530(2)	O(4)b–*Mn*(2)–O(5)d	87.8(1)
<*P*–O>	1.54	O(4)b–*Mn*(2)–O(6)b	93.6(1)
		O(5)d–*Mn*(2)–O(7)	92.6(1)
B–O(3)	1.450(3)	O(7)–*Mn*(2)–O(6)b	86.0(1)
B–O(4)	1.512(3)		
B–O(5),e	1.460(2)	O(6)–*P*–O(6)e	107.7(1)
<*B*–O>	1.47	O(6)–*P*–O(7)	108.7(1)
		O(6)–*P*–O(8)	111.0(1)
O(1)–H(1)	0.98(3)	O(6)e–*P*–O(7)	108.7(1)
O(2)–H(2)	0.980(4)	O(6)e–*P*–O(8)	111.0(1)
O(3)–H(3)	0.98(4)	O(7)–*P*–O(8)	109.7(1)
O(4)–H(4)	0.98(2)		
O(5)–H(5)	0.98(2)	O(3)–*B*–O(4)	107.1(2)
		O(3)–*B*–O(5)	111.0(1)
H(1)···O(5)	2.74(4)	O(3)–*B*–O(5)e	111.0(1)
H(2)···O(8)f	1.97(6)	O(4)–*B*–O(5)	109.9(1)
H(3)···O(6)f	2.12(4)	O(4)–*B*–O(5)e	109.9(1)
H(4)···O(8)g	1.76(2)	O(5)–*B*–O(5)e	108.0(1)
H(5)···O(8)a	1.78(2)		
		O(1)–H(1)···O(5)	136(3)
		O(2)–H(2)···O(8)f	178(4)
		O(3)–H(3)···O(6)f	160(3)
		O(4)–H(4)···O(8)g	169(4)
		O(5)–H(5)···O(8)a	158(2)

Symmetry operators: a: 1–*x*, 1–*y*, –*z*; b: 1–*x*, 1–*y*, ½+*z*; c: –*x*, 1–*y*, ½+*z*; d: ½–*x*, ½+*y*, ½–*z*; e: *x*, *y*, ½–*z*; f: –1+*x*, *y*, ½–*z*; g: ½–*x*, –1+½+*y*, ½–*z*

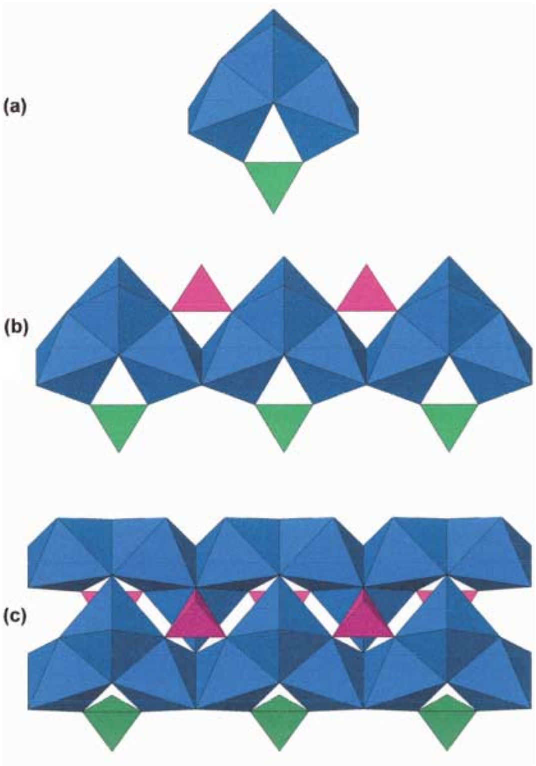

FIG. 1. Perspective view of aspects of the crystal structure of seamanite: (a) The [Mn_3 ϕ_{10} (B{OH}$_4$)] trimer; (b) the [Mn_3 (B{OH}$_4$) (PO_4) ϕ_6] chain; (c) the [Mn_3 (B{OH}$_4$) (PO_4) ϕ_4] column. The (*Mn*O_6) octahedra are shown in blue, the (B{OH}$_4$) groups, green, and the (PO_4) groups, in pink.

TABLE 5. EMPIRICAL BOND-VALENCES (*vu*)* FOR SEAMANITE

	Mn(1)	*Mn*(2)	*P*	*B*	Σ	H(1)	H(2)	H(3)	H(4)	H(5)	Σ
O(1)	0.37	$0.31^{\times2}\rightarrow$			0.99	0.95					1.94
O(2)	0.29	$0.38^{\times2}\rightarrow$			1.05		0.90				1.95
O(3)	0.41			0.81	1.11			0.90			2.01
O(4)		$0.27^{\times2}\rightarrow$		0.68	1.13				0.80		1.93
O(5)		0.39		$0.78^{\times2}\downarrow$	1.07	0.05				0.80	1.92
O(6)	$0.38^{\times2}\downarrow$	0.33	$1.23^{\times2}\downarrow$		1.94			0.10			2.04
O(7)	0.18	$0.30^{\times2}\rightarrow$	1.20		1.98						1.98
O(8)			1.26		1.26		0.10		0.20	$0.20^{\times2}\rightarrow$	1.96
Σ	2.01	1.98	4.92	3.05		1.0	1.0	1.0	1.0	1.0	

* Bond valences in (*vu*: valence units) calculated using the curves of Brown & Altermatt (1985).

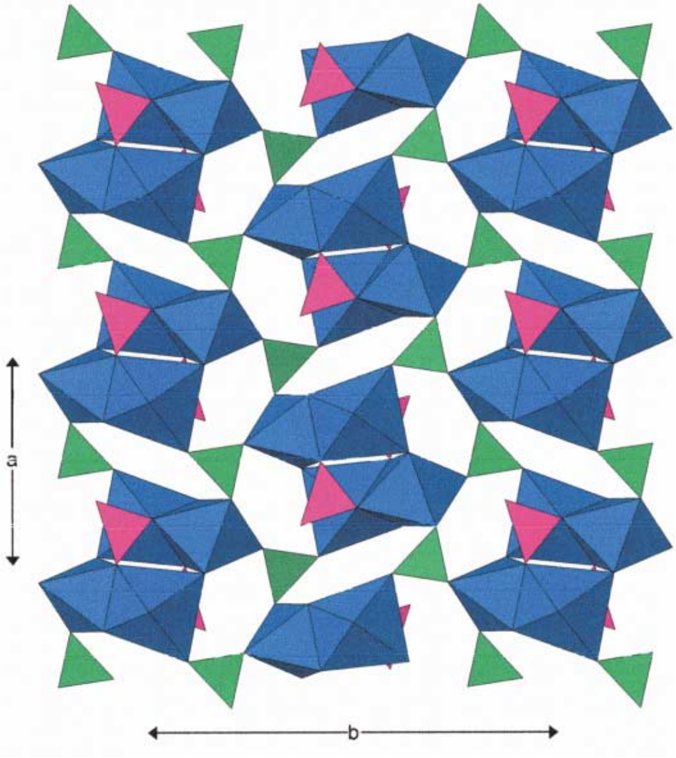

FIG. 2. The crystal structure of seamanite projected onto (001); legend as in Figure 1.

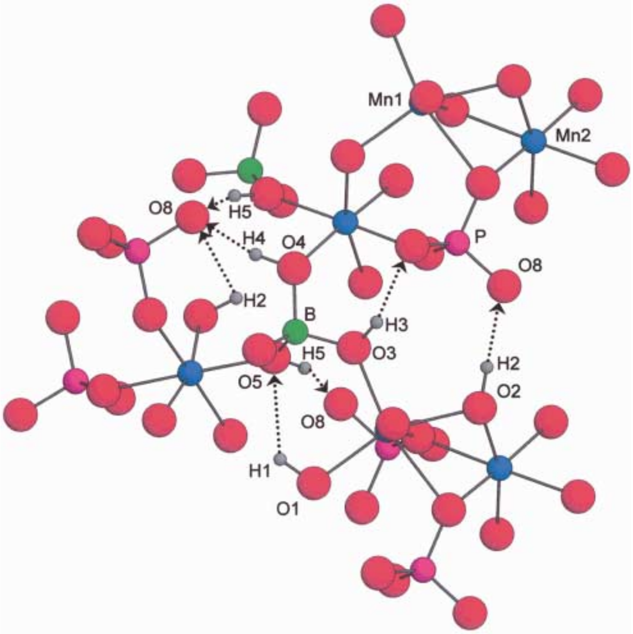

FIG. 3. Perspective view of hydrogen bonds in the crystal structure of seamanite. *B* atoms: green circles, *P* atoms: pink circles, *Mn* atoms: blue circles, O atoms: large red circles, H atoms: small grey circles, and hydrogen bonds: dotted lines.

Inspection of Table 5 shows that the incident bond-valence from the cations (excluding the H atoms) are ~1 *vu* (valence units) for the O(1) to O(5) anions; hence these anions are (OH) groups, in accord with the refined H-atom positions determined in the structure refinement. The O(1) atom is the donor oxygen for the H(1) atom (Fig. 3). When the H(1) atom was confined to the mirror plane at $z = ¼$, it was not sufficiently close to the O(5) atom to form a hydrogen bond. Moreover, the H(1) atom is on a mirror plane where there are two symmetrically equivalent O(5) atoms at equal distances from H(1). When the H(1) position was not restricted to the mirror plane, it refined off $z = ¼$, and the distance between it and one of the O(5) atoms became shorter (Table 4). The resulting H(1)–O(5) distance is 2.74 Å, with an O(1)–O(5) distance of 3.51 Å. This value exceeds the maximum donor–acceptor distance for hydrogen bonding suggested by Baur (1972), 3.1 Å. However, Brown (1976) made a persuasive argument that donor–acceptor distances of up to 3.1 Å are indicative of (weak) hydrogen bonding. Using this criterion, there is a weak hydrogen bond between H(1) and O(5), and the bond valences were assigned accordingly (Table 5). Similarly, the H(3) atom refined off the special position at $z = ¼$, producing a short hydrogen-bond to the O(6) anion (Table 5). As both H(1) and H(3) disorder off the mirror plane, each produces a hydrogen bond to one of the symmetrically equivalent pairs of O(5) and O(6) anions. Rather than having a static disorder in which there is a hydrogen bond to one O(5) anion and no hydrogen bond to the mirror-symmetric O(5) equivalent, it seems more reasonable to postulate dynamic disorder of the H(1) atom across the mirror plane such that each O(5) atom of a pair receives a hydrogen bond approximately half the time; a similar situation is suggested for H(3) and O(6).

The O(8) anion of the (PO_4) group is not bonded to Mn or B, and the bond valence incident at the O(8) atom, an anion of the phosphate group, is quite low, 1.26 *vu*. It must obtain the balance of its incident bond-valence requirements from hydrogen bonds, and the positions of the H-atom sites are in accord with this conclusion (Fig. 3). The H(2), H(4) and H(5) atoms all have reasonable acceptor distances, ~1.84 (± 0.13 Å), to O(8), and the O(donor)–H....O(acceptor) angles are all ~168° (±10°). The H(2)...O(8) distance is somewhat longer than the H(4)...O(8) and H(5)...O(8) distances (Table 4), and this is in accord with the assignment of bond valences in Table 5. The H(4)...O(8) and H(5)...O(8) bond-valences of 0.20 *vu* (for distances of ~1.77 Å) are more than the H(4)...O(8) bond-valence of 0.10 *vu* (for a distance of 1.97 Å). This assignment is in accord with the incident bond-valence requirements of the O(2), O(4) and O(5) anions.

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