

A NOVEL FACE-SHARING OCTAHEDRAL TRIMER  
IN THE CRYSTAL STRUCTURE OF SEAMANITE

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ABSTRACT

The atomic arrangement of seamanite,  $Mn_3^{2+}(OH)_2[B(OH)_4][PO_4]$ ,  $a$  7.811 (5),  $b$  15.114 (10),  $c$  6.691 (5) Å,  $Z=4$ , space group  $Pbnm$ , was deciphered by vector set techniques. Utilizing 1217 independent reflections, full-matrix refinement converged to  $R_{hkl}=0.062$ .

The structure is based on a novel face-sharing Mn-O octahedral trimer which links by edge-sharing with symmetry equivalent trimers to form infinite chains running parallel to the  $c$ -axis. Each chain is weakly linked to an equivalent chain through common hydroxyl groups to form a band. The ligands include  $(OH)^-$  anions, and tetrahedral  $[B(OH)_4]$  and  $[PO_4]$  groups. The tetrahedral groups bridge octahedral bands to form a fairly rigid three-dimensional edifice. One oxygen atom associated with P does not bond to the octahedral cations but accepts four possible hydrogen bonds which, with the  $P^{5+}$  cation, define a distorted trigonal bipyramid.

The peculiar trimer is apparently stabilized by the short O-O' edge associated with the borate tetrahedron. Of the three trimeric face-sharing octahedral isomers, two are now known to exist in natural crystals.

INTRODUCTION

Seamanite, a rare hydrated borate-phosphate of manganese, was first described by Kraus, Seaman, and Slawson (1930). It occurred in fractures cutting siliceous rock at the Chicagon Mine, Iron River, Michigan, as pale pink to yellow acicular crystals associated with sussexite, manganese oxyhydroxides, and calcite. Few specimens were preserved, most of which appear in the A. E. Seaman Mineralogical Museum at Michigan Technological University. McConnell and Pondrom (1941), by X-ray study and etch tests, established  $a$  7.83 (2),  $b$  15.14 (2),  $c$  6.71 (2), space group  $Pbnm$ . On the basis of powder photographs, they further concluded that seamanite, believed to be  $Mn_3(BO_3)(PO_4) \cdot 3H_2O$ , was probably not isostructural with reddingite,  $Mn_3(PO_4)_2 \cdot 3H_2O$ .

As part of a general program concerning octahedral clustering in manganese anisodesmic oxysalts, we report a detailed study of the seamanite atomic arrangement. We wish to remind readers that the rarity of a species has little bearing on the significance of formal crystal structure analysis directed toward furthering our knowledge of crystal chemistry. As a point of fact, some of the most unexpected clusters have

been revealed only through the study of more exotic species. Seamanite proved no exception; not only have we found a novel octahedral face-sharing cluster hitherto believed impossible on geometrical grounds, but we are also committed to interpret the seamanite crystal-chemical formula as a basic compound with composition  $Mn_3^{2+}(OH)_2[B(OH)_4][PO_4]$ .

## EXPERIMENTAL

A nearly perfectly symmetrical rectangular prism (U.S. National Museum No. 96282) of 0.005 mm<sup>3</sup> volume was selected for study. 3000 reflections with  $c$  as the rotation axis were collected on a PAILRED automated diffractometer using a graphite monochromator and Mo radiation to  $2\theta=65^\circ$ . The cell parameters in Table 1 were obtained from conventional least-squares refinement of the indexed powder data in Table 2. These powder data were obtained from a spherical powder mount utilizing a 114.6 mm diameter Buerger camera and Mn-filtered Fe radiation, and the corresponding Miller indices were unambiguously selected by comparison with the strong intensities of the single crystal study. Individual single crystal integrated intensities were obtained using a  $1.8^\circ$  half-angle scan, with background counting time on each side of the peak of 20 seconds.

Reflection pairs of the kind  $I(hkl)$ ,  $I(\bar{h}kl)$  were averaged since  $\omega$ -scans about the basal reflections revealed that absorption anisotropy correction amounted to only 6 percent of the mean peak value. A total of 1217 symmetry independent non-zero reflections were processed and were the only ones used in the ensuing study. Among the remaining 515 zero-reflections were the space group absences as well as weak data which were within the error of the background differences and these data were excluded from further consideration.

TABLE 1. SEAMANITE: CRYSTAL CELL DATA

$a$ (Å)	7.811 (5)
$b$ (Å)	15.114 (10)
$c$ (Å)	6.691 (5)
$V$ (Å <sup>3</sup> )	790.0 (7)
space group	$Pbnm$
formula	$Mn_3(OH)_2[B(OH)_4][PO_4]$
$Z$	4
specific gravity <sup>1</sup>	3.128
$\rho$ calc	3.132 gm/cm <sup>3</sup>

<sup>1</sup>Kraus, Seaman and Slawson (1930).

TABLE 2. SEAMANITE: POWDER DATA<sup>a</sup>

$I/I_0$	$\underline{d}(\text{obs})$	$\underline{d}(\text{calc})$	$\underline{hkl}$
6	7.551	7.557	020
10	6.917	6.939	110
5	5.420	5.431	120
5	4.807	4.817	111
6	4.204	4.217	121
5	3.899	3.906	200
7	3.777	3.781	210
6	3.467	3.469	220
5	3.394	3.401	140
3	3.313	3.345	002
3	3.286	3.290	041
5	3.057	3.059	022
8	2.843	2.848	122
2	2.713	2.715	240
3	2.617	2.625	132
2	2.581	2.566	310
2	2.555	2.519	060
7	2.502	2.506	212
6	2.393	2.397	160
1	2.351	2.357	061
2	2.309	2.310	321
3	2.263	2.269	232
2	2.184	2.186	331
4	2.111	2.117	260
		2.108	242
1	2.073	2.081	170
2	2.061	2.063	123
1	2.025	2.036	312
2	2.015	2.018	261
		2.012	062
1	1.974	1.987	171
1	1.945	1.945	252
5	1.901	1.903	332
1	1.818	1.818	271
2	1.769	1.771	181

TABLE 2. (continued)<sup>a</sup>

$I/I_0$	$\underline{d}(\text{obs})$	$\underline{d}(\text{calc})$	$\underline{hkl}$
1	1.736	1.735	440
1	1.687	1.687	402
4	1.672	1.676	412
		1.673	004
2	1.643	1.645	082
2	1.636	1.640	450
3	1.610	1.610	182
3	1.594	1.592	362
2	1.542	1.543	290
3	1.528	1.529	380
		1.529	520
2	1.502	1.501	144
3	1.488	1.488	372
1	1.419	1.418	183
2	1.402	1.401	314
		1.401	292
3	1.372	1.372	164
		1.371	254
1	1.330	1.329	472
1	1.325	1.326	542
		1.322	193
1	1.304	1.302	600
2	1.262	1.260	630
1	1.254	1.252	084

<sup>a</sup> FeK<sub>α</sub>; 114.6 mm camera diameter. Film corrected for shrinkage. When more than one reflection contributes to  $\underline{d}(\text{obs})$ , all are listed in decreasing value of spacing.

## SOLUTION OF THE STRUCTURE

Patterson projections,  $P(uv)$  and  $P(vw)$ , combined with polyhedral packing models assisted in the structure determination. The only hindrance in the experiment was the prejudice on the part of the investigators that the clusters revealed by vector set analysis were crystallochemically impossible and were rejected in the initial trial parameter refinements, thus rendering the problem more costly in time than justified.

The correct model, consisting of two symmetry independent Mn atoms and one P atom, yielded a heavy atom least-squares refinement of

$$R_{hkl} = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}|} = 0.28.$$

Difference synthesis of the phases thus produced unambiguously revealed all oxygen atoms in the asymmetric unit of the crystal structure. Inclusion of the anions in the refinement followed by further difference synthesis revealed the position of the boron atom.

## REFINEMENT

The study by McConnell and Pondrom (1941) indicated a centrosymmetric crystal and we did not find it necessary to consider lower symmetry throughout this study. All atomic free parameters in the asymmetric unit were refined according to full-matrix least-squares procedures using a local version of the familiar program of Busing, Martin, and Levy (1962). Scattering curves for  $Mn^{1+}$ ,  $P^{3+}$ ,  $B^{2+}$ , and  $O^{1-}$  were obtained from MacGillavry and Rieck (1962). The reliability index,  $R_{hkl}$ , converged to 0.062 for all 1217 non-zero reflections which were each ascribed unit weight. The atomic coordinates and isotropic thermal vibration parameters are listed in Table 3 and the  $|F_{obs}| - F_{calc}$  data appear in Table 4.<sup>1</sup> A ratio of independent data to variable parameters of 30:1, low estimated standard errors for the atomic parameters and thermal vibration parameters typical for their ionic species add confidence to the interatomic distances discussed further on.

## DESCRIPTION OF THE STRUCTURE

Seamanite is certainly a candidate for one of the most exotic of mineral structures. The Mn-O octahedral arrangement is one of the most peculiar and unexpected on record, and we shall discuss it in detail.

Figure 1 features a polyhedral diagram of the octahedral backbone and its surrounding tetrahedral  $[B(OH)_4]$  and  $[PO_4]$  ligands, projected down the  $x$ -axis. We isolate the octahedral backbone and show it in Figure 2. It consists of an octahedral face-sharing trimer which joins to identical trimers by reflection across shared edges. The resulting chain runs parallel to the prismatic  $c$ -axis of the crystal. The face-sharing trimer is the most peculiar feature of the structure since its arrangement on geometrical grounds utilizing regular octahedra with oxygen atoms

<sup>1</sup> To obtain a copy of Table 4, order NAPS Document #01519 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting \$2.00 for microfiche or \$5.00 for photocopies payable to CCMIC-NAPS.

TABLE 3. SEAMANITE: ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS.  
(Estimated standard errors in parentheses refer to the last digit.)

	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}(\text{\AA}^2)$
Mn(1)	0.2783(2)	0.4758(1)	0.2500	0.53(2)
Mn(2)	.3507(1)	.6406(1)	.5016(1)	.58(1)
P	.6931(2)	.5542(1)	.2500	.30(2)
B	.0072(12)	.3146(6)	.2500	.63(11)
O(1) = OH <sup>-</sup>	.4615(8)	.3688(4)	.2500	.91(8)
O(2) = OH <sup>-</sup>	.1862(8)	.6165(4)	.2500	.80(8)
O(3) = OH <sup>-</sup> (B)	.0399(9)	.4099(4)	.2500	1.01(9)
O(4) = OH <sup>-</sup> (B)	.1846(8)	.3027(4)	.2500	.69(8)
O(5) = OH <sup>-</sup> (B)	.0810(6)	.2739(3)	.0742(8)	1.12(7)
O(6) = O <sup>2-</sup> (P)	.7246(6)	.4961(3)	.0648(7)	.91(6)
O(7) = O <sup>2-</sup> (P)	.5042(8)	.5845(4)	.2500	.90(9)
O(8) = O <sup>2-</sup> (P)	.8112(8)	.6340(4)	.2500	.96(9)

at the vertices would be impossible. The Mn(1)-O octahedron, situated on a mirror plane, shares two adjacent faces with the Mn(2)-O octahedra.

Closer inspection of octahedral clusters in general reveals that only three kinds of topologically and geometrically distinct face-sharing trimers can exist and all three possess the stoichiometry  $M_3O_{12}$ , where M is the octahedral center and O a vertex. Figure 3 features the three trimers projected down the octahedral edge and arranged to most effectively show their point symmetries. One arrangement has point symmetry  $2/m$  and the other two possess  $mm2$  symmetry. The centrosymmetric arrangement persists in the "5.1 Å" fibrous basic ferrous-ferric phosphates, as discussed in detail by Moore (1970). In the seamanite arrangement, the trimer is the least favored geometrically since the gap between the two free vertices across the mirror plane is only 1.5 Å, referring to a regular octahedral edge of 3.0 Å. The third arrangement, which so far has not been found in crystals, is favorable on geometrical grounds.

This peculiar trimer is apparently stabilized by the B(OH)<sub>4</sub> ligand group, since the O(5)-O(5)' tetrahedral edge which bridges the free vertices is 2.35 Å. The dilation of *ca.* +0.8 Å away from the undistorted octahedral model is indicative of forced liganacy. In seamanite, the

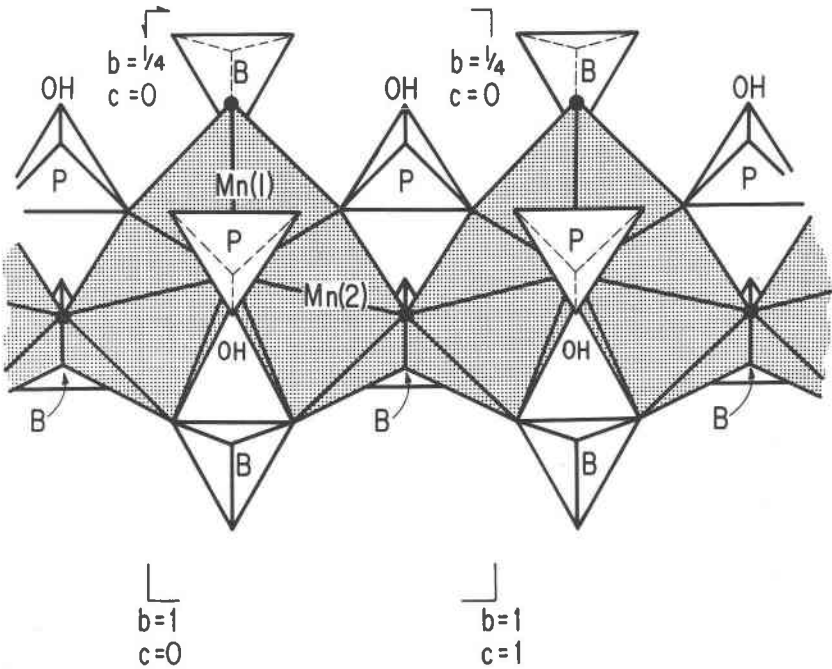


FIG. 1. Polyhedral diagram of the seamanite atomic arrangement. The octahedral backbone is stippled and the surrounding P-O and B-O tetrahedra are featured. The O(1) hydroxyl anion connects to two octahedral backbones related by the inversion operation. The O(1) position is shown on a black disk. The O(2) hydroxyl anion is situated under the stippled backbone and is bonded to  $2\text{Mn}(2) + \text{Mn}(1)$ . Its position is near the symbol "OH."

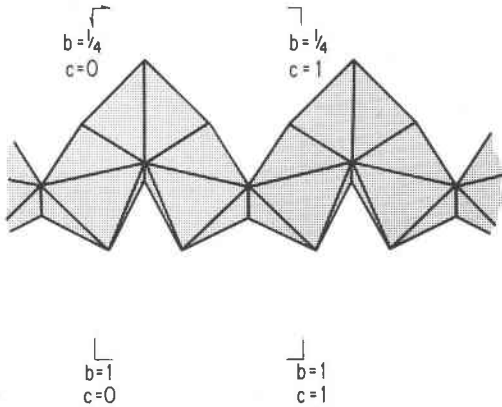


FIG. 2. The octahedral backbone in seamanite. Note the edge-sharing of the octahedral face-sharing trimers which results in the chain running parallel to the  $c$ -axis.

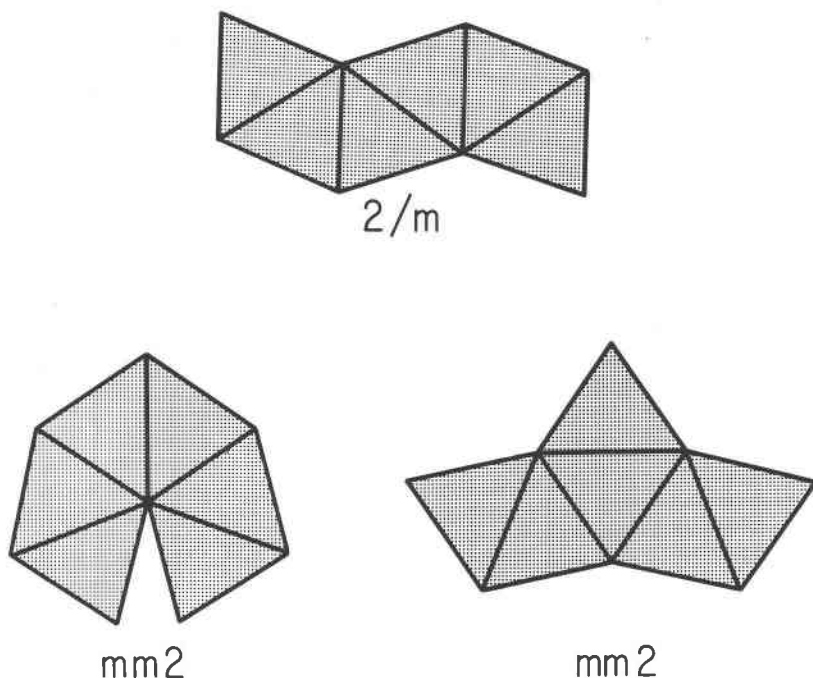


FIG. 3. The three possible topologically distinct octahedral face-sharing trimers. They are projected parallel to octahedral edges and oriented to fully show their point symmetry.

trimers share their terminal edges with each other by reflection. Here, the bridging  $O(6)-O(6)' = 2.48 \text{ \AA}$  atoms belong to the  $[PO_4]$  tetrahedral edge. The size difference between the two different tetrahedra must be accepted as a stabilizing feature for the octahedral chains and, for this reason, the B and P atoms are ordered in the non-equivalent oxygen tetrahedra. The crystal structure analysis suggests that the deviation from the 1:1 B:P ratio found in the seamanite chemical analysis of Kraus, Seaman, and Slawson (1930) is largely an analytical error.

Figure 1 reveals that the octahedral backbone is not strictly insular with respect to other octahedra but is weakly condensed with the symmetry equivalent chain related by the inversion operation. As shown in Figure 1, the two chains link by the  $O(1)$  hydroxyl ions to form a band. Individual bands are further joined by the tetrahedral ligand groups which also link to similar bands generated by the glide operations to form a three-dimensional array of corner-linked polyhedra.

#### CRYSTAL CHEMISTRY

Table 5 presents electrostatic valence balances of the cationic charge contributions to the anions. It is readily apparent that  $O(1)$ ,  $O(2)$ ,  $O(3)$ ,



O(4), and O(5) are hydroxyl groups, and O(6) and O(7) are oxide anions. Despite the fact that it is considerably oversaturated with respect to cations, O(4), with  $\Sigma = 1.42$ , has to be accepted as an hydroxyl anion. Thus, the ligand groups are  $(\text{OH})^-$ ,  $[\text{B}(\text{OH})_4]$ , and  $[\text{PO}_4]$  and the seamanite crystal formula is  $\text{Mn}_3^{2+}(\text{OH})_2[\text{B}(\text{OH})_4][\text{PO}_4]$ . No water molecules are present either as ligands or as water of hydration and the stoichiometrically similar formula  $\text{Mn}_3[\text{BO}_3][\text{PO}_4] \cdot 3\text{H}_2\text{O}$  is crystallochemically meaningless. Seamanite is an interesting example of a coordination complex where a neutral acid— $[\text{PO}_4]$ —and a basic fraction— $(\text{OH})^-$ —are present in the same crystal which includes the amphoteric  $[\text{B}(\text{OH})_4]$  group. This would suggest that the compound forms under rather restricted pH conditions which, in combination with the mutual presence of boron, phosphorus, and manganese, may be a contributing factor in the restricted occurrence of the species.

## INTERATOMIC DISTANCES

The relatively low errors in atomic positions and the unusual octahedral clustering in seamanite warrant a detailed discussion of the interatomic distances. Table 6 lists Me-O and O-O' distances in order of increasing values for each polyhedron. Most interesting are the distances associated with O(7) since this anion is considerably over-saturated electrostatically with respect to cations and since the anion occurs at the vertex common to the two Mn(1)-O shared faces. The Mn(1)-O(7) = 2.41 Å is unusually long—in excess of +0.20 Å for typical  $\text{Mn}^{2+}$ -O octahedral averages. In addition to its cation oversaturation, the Mn(2)→Mn(1)←Mn(2) cation-cation repulsions across the shared face

TABLE 5. SEAMANITE: ELECTROSTATIC VALENCE BALANCES OF CATIONS ABOUT ANIONS

			$\Sigma$	$\Delta \Sigma$
O(1) = OH <sup>-</sup>	Mn(1)+Mn(2)+Mn(2)	2/6+2/6+2/6	1.00	+0.00
O(2) = OH <sup>-</sup>	Mn(1)+Mn(2)+Mn(2)	2/6+2/6+2/6	1.00	+0.00
O(3) = OH <sup>-</sup>	Mn(1)+B	2/6+3/4	1.09	+0.09
O(4) = OH <sup>-</sup>	Mn(2)+Mn(2)+B	2/6+2/6+3/4	1.42	+0.42
O(5) = OH <sup>-</sup>	Mn(2)+B	2/6+3/4	1.09	+0.09
O(6) = O <sup>2-</sup>	Mn(1)+Mn(2)+P	2/6+2/6+5/4	1.92	-0.08
O(7) = O <sup>2-</sup>	Mn(1)+Mn(2)+Mn(2)+P	2/6+2/6+2/6+5/4	2.25	+0.25
O(8) = O <sup>2-</sup>	P	5/4	1.25	-0.75 <sup>a</sup>

<sup>a</sup>Excludes the presence of four possible hydrogen bonds.

TABLE 6. SLAMANTITE: POLYHEDRAL INTERATOMIC DISTANCES<sup>d</sup>.  
 (Estimated standard errors: Mn-O, P-O +0.006 Å, B-O +0.013 Å, O-O +0.008 Å)

P		Mn(1)		Mn(2)	
1	P - O(8)	1 Mn(1) - O(3)	2.111	1 Mn(2) - O(5) <sup>'''</sup>	2.144
2	- O(6)	2 - O(6) <sup>†</sup>	2.150	- O(2)	2.150
1	- O(7)	1 - O(1)	2.159	- O(6) <sup>†</sup>	2.188
	average	1 - O(2)	2.244	- O(1) <sup>†</sup>	2.222
		1 - O(7)	<u>2.411</u>	- O(7)	2.235
1	O(6) - O(6) <sup>''</sup>	average	2.204	- O(4) <sup>†</sup>	<u>2.277</u>
2	O(6) - O(7)			average	2.203
1	O(8) - O(7)	a <sub>1</sub> O(2) - O(7)	2.530		
2	O(6) - O(8)	b <sub>2</sub> O(2) - O(6) <sup>†</sup>	2.796	b <sub>1</sub> O(7) <sup>''''</sup> - O(2)	2.530
	average	b <sub>2</sub> O(7) - O(6) <sup>†</sup>	3.020	b <sub>1</sub> O(6) <sup>†</sup> - O(2)	2.796
		2 O(3) - O(6) <sup>†</sup>	3.137	c <sub>1</sub> O(1) <sup>†</sup> - O(4) <sup>†</sup>	2.939
		2 O(1) - O(6) <sup>†</sup>	3.274	b <sub>1</sub> O(7) - O(6) <sup>†</sup>	3.020
	B	1 O(1) - O(7)	3.276	1 O(4) <sup>†</sup> - O(5) <sup>''''</sup>	3.066
2	B - O(5)	1 O(2) - O(3)	3.324	1 O(1) <sup>†</sup> - O(6) <sup>†</sup>	3.076
1	- O(3)	1 O(1) - O(3)	<u>3.352</u>	1 O(5) <sup>''''</sup> - O(7)	3.165
1	- O(4)	average	3.078	1 O(1) <sup>†</sup> - O(5) <sup>''''</sup>	3.199
	average			1 O(2) - O(5) <sup>''''</sup>	3.217
		Mn(1) - Mn(2)	3.058	1 O(4) <sup>†</sup> - O(6) <sup>†</sup>	3.252
1	O(5) - O(5) <sup>''</sup>				
1	O(4) - O(3)	Mn(2) - Mn(2) <sup>''''</sup>	3.326	1 O(1) <sup>†</sup> - O(7)	3.432
2	O(3) - O(5)				
2	O(4) - O(5)	Mn(2) - Mn(2) <sup>''</sup>	3.369	1 O(2) - O(4) <sup>†</sup>	<u>3.564</u>
	average			average	3.105

<sup>a</sup>Mn(1) - Mn(2) shared face and Mn(2) - Mn(2)<sup>''</sup> shared edge.

<sup>b</sup>Mn(1) - Mn(2) shared face only.

<sup>c</sup>Mn(2) - Mn(2)<sup>''''</sup> shared edge only.

<sup>d</sup>Superscripts represent symmetry equivalent positions of Table 3:

<sup>†</sup> = -x, -y, 1/2 +z;

<sup>''</sup> = x, y, 1/2 -z;

<sup>'''</sup> = 1/2 -x, 1/2 +y, 1/2 -z;

<sup>''''</sup> = x, y, 3/2 -z.

are so profound that the Mn(1)-O(7) distance is affected along with the foreshortening of the octahedral edges associated with the shared faces. The O(2)-O(7)=2.53 Å edge is common to the two Mn(1)-O shared faces and a shared edge between the Mn(2)-O octahedra. This edge is foreshortened by *ca.* -0.55 Å with respect to O-O' averages associated with Mn-O octahedra, indicative of particularly violent cation-cation repulsion effects. As shown in Table 6, all O-O' distances associated with shared edges are among the shortest for their polyhedra. Thus, the unusual face-sharing trimer cannot be explained solely on the presence of Mn-Mn metallic bonds since the edge distance relationships follow the electrostatic model. Although a weak metallic bond may be present, distortion of the octahedral clusters conform to a model with predominant ionic character.

As interpreted, the O(4)=(OH)<sup>-</sup> anion is considerably oversaturated with respect to cations since it coordinates to two Mn-O octahedra and

one B atom. Consequently, the Mn(2)-O(4) and B-O(4) distances are the longest for their polyhedra. This correlation between charge balance and interatomic distances adds support to the interpretation that O(4) is an hydroxyl group.

But this means that O(8) may be severely undersaturated with respect to cations since it coordinates only to the P atom. The P-O(8) distance is the shortest for the tetrahedron but in addition O(8) potentially receives four hydrogen bonds. These bonds include 2 O(8)  $\cdots$  O(5) 2.71, O(8)  $\cdots$  O(4) 2.73, and O(8)  $\cdots$  O(2) 2.94 Å. They may be described as two lateral bonds from hydroxyl groups associated with boron atoms related by the mirror plane, one bond in the  $+z$  direction to an hydroxyl group and one in the  $-z$  direction to a boron hydroxyl group. This network of bonds through the unit cell is shown in Figure 4. Such an arrangement adds further confidence to the interpretation that O(8) is an oxide anion whereas O(4) is an hydroxyl anion. Indeed, Baur and Rama Rao (1968) have found a similar example in metavauxite,  $\text{Fe}(\text{H}_2\text{O})_6 \cdot \text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_2$ , where one phosphorus oxygen does not coordinate to octahedral cations but receives three hydrogen bonds instead. In the crystal structure of  $\text{Na}_2(\text{H}_2\text{O})_7(\text{PO}_3\text{OH})$ , Baur and Khan (1970) have found that each of the three tetrahedral oxygen atoms receives four hydrogen bonds which, including the  $\text{P}^{5+}$  cation, define a tetragonal pyramid. The range of these bonds are 2.72–3.06 Å. The

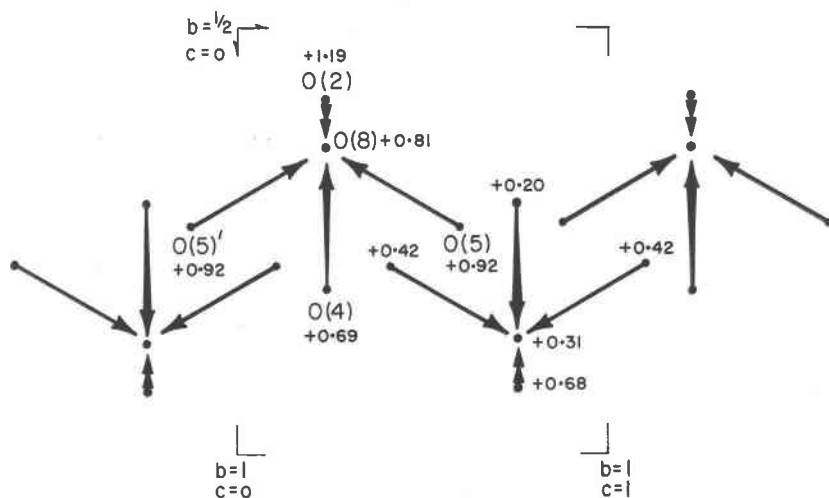


FIG. 4. The possible O-H  $\cdots$  O(8) bonds in seamanite. The tails of the arrows are located at the hydroxyl donor and the heads point toward the O(8) acceptor. Heights are given in fractional coordinates.

polyhedron in seamanite is a highly distorted trigonal bipyramid including the  $P^{5+}$  cation in the coordination sphere. We have performed a three-dimensional difference synthesis as an attempt to locate hydrogen atom positions, but the peak heights proved to have little physical meaning, doubtless arising from the presence of the heavy atoms in the structure and the feeble contribution of hydrogen atoms to the structure factors.

## ACKNOWLEDGEMENTS

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## REFERENCES

- BAUR, W. H., AND B. RAMA RAO (1967) The crystal structure of metavauxite. *Naturwissenschaften* **21**, 561-562.
- , AND A. A. KHAN (1970) On the crystal chemistry of salt hydrates. VI. The crystal structures of disodium hydrogen orthoarsenate heptahydrate and disodium hydrogen orthophosphate heptahydrate. *Acta Crystallogr.* **B26**, 1584-1596.
- BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Oak Ridge Nat. Lab. (U.S. Clearinghouse Fed. Sci. Tech. Info.) Rep. ORNL-TM-305*.
- KRAUS, E. H., W. A. SEAMAN, AND C. B. SLAWSON (1930) Seamanite, a new manganese phospho-borate from Iron County, Michigan. *Amer. Mineral.* **15**, 220-225.
- MACGILLAVRY, C. H., AND G. D. RIECK, EDS. (1962) *International Tables for X-ray Crystallography, Vol. 3*, The Kynoch Press, Birmingham, England.
- MCCONNELL, D., AND W. L. PONDROM, JR. (1941) X-ray crystallography of seamanite. *Amer. Mineral.* **26**, 446-447.
- MOORE, P. B. (1970) Crystal chemistry of the basic iron phosphates. *Amer. Mineral.* **55**, 135-169.

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