

Akrochordite, $(\text{Mn},\text{Mg})_5(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$: A sheet structure with amphibole walls

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ABSTRACT

Akrochordite, $(\text{Mn},\text{Mg})_5(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$, monoclinic holosymmetric, $a = 5.682(2)$, $b = 17.627(5)$, $c = 6.832(1)$ Å, $\beta = 99.49(2)^\circ$, $Z = 2$, space group $P2_1/c$, $D_{\text{obs}} = 3.19, 3.26$, $D_{\text{calc}} = 3.26$ g·cm⁻³ for $(\text{Mn}_{0.80}\text{Mg}_{0.20})$, has 12 non-H atoms in the asymmetric unit. $R = 0.036$ for 1295 independent F_o . Average distances are $^{55}\text{Mn}(1)\text{—O}$ 2.174, $^{55}\text{Mn}(2)\text{—O}$ 2.232, $^{55}\text{Mn}(3)\text{—O}$ 2.188, and $^{75}\text{As}\text{—O}$ 1.686 Å. Bond-distance averages suggest that Mg^{2+} substitutes for Mn^{2+} , with a preference for the Mn(1) site followed by the Mn(3) site.

The perfect {010} cleavage results from a sheetlike structure with formula-unit composition $\frac{2}{\infty}[\text{M}_3(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2]$ parallel to this plane. Of the six unique hydrogen bonds $\text{O—H}\cdots\text{O}$, four penetrate the c -axial glide planes at $y = \frac{1}{4}, \frac{3}{4}$ and bond symmetry-equivalent sheets together. Two of these bonds involve $\text{OW}(2) \rightarrow \text{O}(3)$ 2.79 and $\text{OH}(6) \rightarrow \text{OW}(2)$ 3.02 Å, the arrows pointing to hydrogen-bond acceptors and the distances corresponding to oxygen-oxygen separations.

Upon projection along [012], it is seen that the sheets are made of fundamental building blocks based on $\frac{1}{\infty}[\text{M}_3\phi'_2\phi_{12}]$ octahedral walls of amphibole type. In amphiboles, the $\phi' = (\text{OH}^-, \text{F}^-)$, but in akrochordite it is apical O(1) of the $[\text{AsO}_4]$ tetrahedron. These walls are connected in stepwise fashion by O(2) and O(3) of $[\text{AsO}_4]$ to form the sheetlike modular units.

The remaining O(4) of $[\text{AsO}_4]$ receives three hydrogen bonds, two of which penetrate the c -axial glide planes. These have oxygen-oxygen separations $\text{OW}(1)^{(2)} \rightarrow \text{O}(4)$ 2.59 and $\text{OW}(2) \rightarrow \text{O}(4)$ 2.62 Å. The remaining bond, within the modular unit, is $\text{OW}(1) \rightarrow \text{O}(4)$ 2.62 Å. Several examples of oxide terminal to a tetrahedral anionic group are known and include seamanite, metavauxite, and minyulite, all of which possess similar relatively short $\text{O—H}\cdots\text{O}$ oxygen-oxygen distances, ranging from 2.58 to 2.80 Å.

INTRODUCTION

Determining the relationship between crystal structure and phase paragenesis is a prime motivation for any systematic analysis of mineral-chemical crystallography, and members of the $\text{Mn}_n^{2+}(\text{OH})_{2n-3z}^-(\text{H}_2\text{O})_q(\text{AsO}_4)_z^{3-}$ series are no exception (Moore and Molin-Case, 1971). The species, although rather exotic, occur in relatively close association with each other, and parageneses were early studied by Sjögren (1885). However, experimentally controlled conditions of temperature, pressure, pH, Eh, etc. are largely unexplored. It is unfortunately too early to reliably apply mineral structures *directly* to mineral paragenesis, and the feasibility of such a relationship is uncertain. One major problem is the lack of any strategy to obtain reliable thermochemical parameters directly from a crystal structure; another is the difficulty in obtaining good temperatures for the growth of successive crystallizing phases.

Akrochordite's name comes from the Greek *akrochordon*, meaning "a wart." And like a wart, its structure solution remained enigmatic. Single crystals, extremely rare, are usually splayed or tapered. Although approximate cell dimensions and space group could be obtained, the crystals were hardly suitable for structure analysis. Interest was attached to akrochordite because it usually crystallizes latest in the sequence of other arsenates.

EXPERIMENTAL DETAILS

Several radial aggregates of sharp akrochordite crystals were repeatedly broken until a crystal that yielded reasonable single-crystal precession photographs was obtained. The fragments came from the type specimen of eveite, NRMS 390274, in the Swedish Natural History Museum, which was also used in the original study of Moore (1967). The present unit-cell parameters in Table 1 are in fair agreement with the earlier study. The details of the experimental part of this investigation are summarized in Table 1.

TABLE 2. Akrochordite: Atomic coordinate and anisotropic thermal-vibration parameters ($\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq} (Å ²)
M(1)	0	0	0	163(8)	195(8)	150(8)	64(6)	-30(6)	-3(6)	1.34(6)
M(2)	0.4758(2)	0.0618(1)	0.7967(2)	120(5)	144(5)	171(5)	43(4)	-36(4)	6(4)	1.15(4)
M(3)	-0.0566(2)	0.1315(1)	0.6470(2)	159(5)	163(5)	99(5)	15(4)	-16(4)	8(4)	1.11(4)
As	0.3683(1)	0.1185(1)	0.3188(1)	118(3)	102(3)	49(3)	4(2)	-37(2)	2(3)	0.89(2)
O(1)	0.3512(9)	0.0470(3)	0.1483(7)	168(24)	106(23)	116(23)	-32(19)	-63(18)	-1(20)	1.03(18)
O(2)	0.5791(9)	0.0965(3)	0.5149(7)	142(23)	211(26)	86(22)	54(20)	-70(18)	5(21)	1.16(19)
O(3)	0.1033(10)	0.1335(3)	0.3884(7)	233(27)	254(29)	91(23)	19(21)	34(20)	37(23)	1.52(19)
O(4)	0.4380(9)	0.1973(3)	0.2037(7)	218(26)	101(23)	112(23)	-3(19)	13(19)	-22(20)	1.13(19)
OH(5)	0.1252(9)	0.0235(3)	0.7272(7)	182(24)	115(22)	62(21)	-10(18)	-12(18)	9(20)	0.95(18)
OH(6)	0.8144(8)	0.1036(3)	0.9175(7)	153(23)	131(24)	56(20)	2(18)	-22(17)	1(19)	0.89(18)
OW(1)	0.2964(9)	0.1734(3)	0.8232(7)	185(25)	128(24)	84(22)	-9(18)	-37(18)	-28(20)	1.05(19)
OW(2)	0.8588(9)	0.2483(3)	0.1566(8)	176(25)	163(25)	174(25)	6(21)	-34(20)	-7(21)	1.35(20)

Note: The U_i are coefficients in the expression $\exp[-(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. The equivalent isotropic thermal parameter is $B_{eq} = (8/3)\pi^2(U_{11} + U_{22} + U_{33})$.

boundary along [010]. We propose three unique hydrogen bonds to the O(4) acceptor, which are shown in Figure 1: OW(1)···O(4) 2.59, OW(2)···O(4) 2.62, and OW(1)⁽²⁾···O(4) 2.62 Å. In addition, since O(4) also bonds to As, it is undersaturated with electrostatic bond-strength sum $p_0 = \frac{5}{4} + \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{21}{12} = 1.75$. To evaluate the electrostatic bond-strength sum p_0 , we have used bond strengths $s = \frac{5}{6}$ valence units for the hydrogen-bond donor (the hydrogen written H_d) and $s = \frac{1}{6}$ v.u. for the hydrogen-bond acceptor (the hydrogen written H_a) (see Baur, 1970, especially p. 152). As a rather undersaturated anion, all bonds to it are comparatively short.

Baur noted that O-H···O distances between oxygens range from 2.5 to 3.3 Å based on 392 independent data. Note that these distances are between donor and acceptor oxygens. It is clear from three short OW···O(4) distances and one short As-O(4) distance that O(4) is O²⁻ and that the arsenate group is [AsO₄]³⁻ and not [AsO₃OH]²⁻. This is reminiscent of the four possible OH···O(8) bonds determined for seamanite, Mn³⁺(OH)₂[B(OH)₄][PO₄], by Moore and Ghose (1971). Three distances are 2OH(5)···O(8) 2.71 and OH(4)···O(8) 2.73 Å, and a longer OH(2)···O(8) 2.94 Å also occurs. The P-O(8) 1.517 Å individual distance is shorter than the phosphate tetrahedral average, 1.534 Å, in the structure. Unlike akrochordite, seamanite ($R = 0.062$) does not possess sheetlike units of crystal structure which are bridged by only hydrogen bonds but rather is a three-dimensional array of ···M-φ-T··· bonds. More like akrochordite is metavauxite ($R = 0.097$), which is [Fe(H₂O)₆]²⁺[Al₂(OH)₂(H₂O)₂(PO₄)₂]²⁻ (Baur and Rama Rao, 1967), in that it has insular octahedra alternating with octahedral-tetrahedral sheets separated by the {100} plane. The plane is penetrated by three different hydrogen bonds that are accepted by O(4) of the terminal [PO₄] tetrahedron of the sheets: OW(7)···O(4) 2.58, OW(7')···O(4) 2.64, and OW(8)···O(4) 2.67 Å. The remaining P-O(4) distance is about the same as the polyhedral average. Another example is O(4) in minyulite, K[Al₂F(H₂O)₄(PO₄)₂] ($R = 0.022$) which receives four hydrogen bonds (Kampf, 1977). The pertinent distances are

OW(2)···O(4) 2.70, OW(1)···O(4) 2.74, OW(2')···O(4) 2.80, and OW(1')···O(4) 2.80 Å. Here, the remaining P-O(4) 1.531 distance in minyulite matches within error the polyhedral average, (P-O) 1.532 Å. These four compounds all seem to involve one terminal P-O where that oxide achieves approximate electrostatic neutrality by coordination with three or more hydrogen-acceptor bonds.

Quite different are P-O distances in compounds that appear to have P-O-H··· termini. Termination means no continued bonding to cations other than H from the donor oxygens. In these compounds, the P-O-H··· terminal distances are considerably longer (1.57–1.59 Å) than P-O···nH ($n = 1-4$) terminal distances (1.51–1.55 Å). The shortest distance is for the extremely undersaturated P-O 1.48 Å in anhydrous compounds. This is immediately understandable in terms of local electrostatic neutrality: for P-O-H···, $p_0 = \frac{5}{4} + \frac{5}{6} = \frac{25}{12}$ and for P-O, $p_0 = \frac{15}{12}$ —oversaturated and very undersaturated oxides, respectively. Usually, OH⁻ is an acceptor of at most one hydrogen bond to the oxygen. The terminal O²⁻, on the other hand, receives three to four hydrogen bonds in hydrated crystals. For this reason, discrimination between the two is usually not difficult. We prefer to designate compounds with at least one P-OH as *acid* phosphates, and those with P-O and no OH⁻ attachments as *normal* phosphates. The same holds for arsenate; As is in the same Group 5A as P. The *oxo*-terminus in the normal compounds appears to accept several short hydrogen bonds.

In hureaulite, Mn²⁺(H₂O)₄[PO₃OH]₂[PO₄]₂ ($R = 0.058$), the hydroxyl oxygen is bonded to P(1) + H_d (Moore and Araki, 1973). It does not appear to accept hydrogen bonds. The P(1)-OH 1.57 Å distance is longer than its [PO₃OH] polyhedral average of 1.54 Å. The synthetic NH₄F₆³⁺(H₂O)₃[PO₃(OH)₃O₃]₃[PO₂(OH)₂]₃·3H₂O ($R = 0.042$), structurally investigated by Moore and Araki (1979), was crystallized from distinctly acid solutions with initial pH = 0.5–2.5, final pH = 2 for liquid coexisting with crystals. The acidities were noted in Haseman et al. (1951). The structure has three unique P-OH bonds: P(1)-OH(3) 1.58, P(2)-OH(6) 1.57 and P(2)-OH(8) 1.58 Å, all

longer than the P(1,2)-O 1.54 Å polyhedral average. The OH(3), OH(6), and OH(8) oxygens not only donate but also receive one hydrogen bond each and consequently their oxide fraction is considerably oversaturated. MacGillavry and Rieck (1962) listed the following ranges of bond lengths (in angstroms) for different types of phosphates: P-O = 1.512–1.549 (five determinations) for normal PO₄, P-O = 1.54 (two determinations) and P-OH = 1.58 (two determinations) for the two types of acid phosphates, whereas for “polyphosphates,” terminal P-O-P = 1.43–1.52 (seven determinations) and bridging P-O-P = 1.56–1.68 (nine determinations). The normal PO₄ and the acid phosphates already have been discussed. For polyphosphates, the marked difference between terminal and bridging P-O distances can be understood through general undersaturation and oversaturation, respectively, of electrostatic bond-strength sums, p_o , from 2.00.

It was initially believed that normal P-O receiving several hydrogen bonds was paragenetically distinct from acid P-OH in that the former formed only in basic fluids and the latter formed in distinctly acid fluids. If such a relation held, then a neat interpretation could be made between structure and paragenesis. Unfortunately, such a simple explanation is not the key to discriminating between these two bonding types. Haseman et al. (1951) stated that the final pH = 2.8 in minyulite formation, a distinctly acid environment where a terminal P-O receives four hydrogen bonds. Therefore, we prefer the term *normal* phosphate, as distinct from *basic* or *acid* phosphates. Nor is it at all clear whether hureaulite forms under distinctly acid, neutral or basic conditions. In fact, Haseman et al. presented several examples where such phases are evidently stable over a rather wide pH range.

Figure 1 and Table 3 outline the six unique O-H...O bonds in the akrochordite structure. The asymmetric unit and the hydrogen-bond arrows with the heads pointing toward the oxygen acceptor appear in the left quadrant. Two bonds OH(5) → O(3) 3.00 and OW(1) → O(4) 2.59 Å are confined within one sheet, a unit formula shown here bounded by the *c*-axial glide planes between $y = 1/4$ and $y = 3/4$. The remaining four unique hydrogen bonds penetrate the *c*-axial glide plane and hold adjacent sheets together. Included are OW(2) → O(3) 2.79, OH(6) → OW(2) 3.02, OW(1)⁽²⁾ → O(4) 2.59, and OW(2) → O(4) 2.62 Å. All bonds with O(4) as a receptor have already been discussed, and these are the shortest hydrogen bonds in the structure. The good to perfect {010} cleavage has a simple explanation: only O-H...O bonds are broken. As suggested by this figure, it would be desirable to project a slab of the formula unit normal to the plane of its layer. Projection of akrochordite's structure down x^* reveals the structural principle in Figure 2. Individual fundamental building blocks (fbb) are joined to each other in a staggered fashion. In this diagram, only Mn(1), Mn(2), Mn(3), and As are presented. Lines connect cations that share an oxygen. Hydrogen bonds are ignored. Inversion centers and *c*-axial glides are shown. Here, a cell transformation is required (100/012/012). The new cell, a , b'

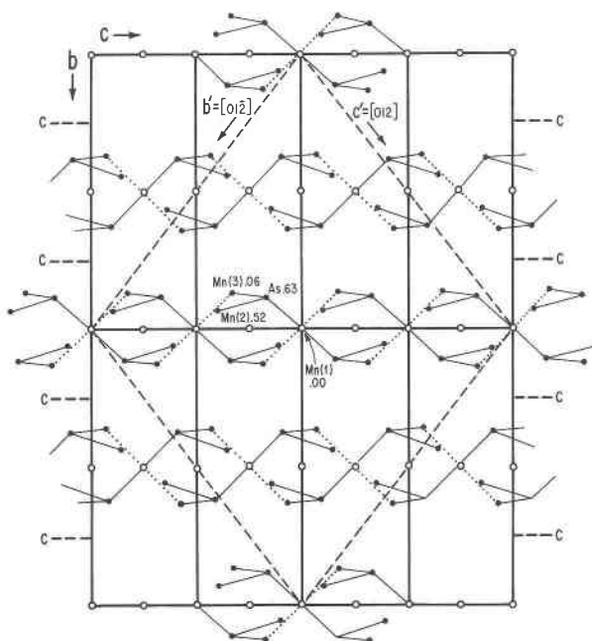


Fig. 2. The Mn and As cations along x^* . The *c*-glides and inversion centers are shown. Thin lines indicate cation connections via ligands, which are omitted. The central octahedral wall is dotted, and the transformed $b' \times c'$ cell is dashed. Note suggestion of good {010} cleavage.

= [012], $c' = [012]$ has $a = 5.682$, $b' = 22.303$, $c' = 22.303$ Å, $\alpha' = 75^\circ 34'$, $\beta' = 95^\circ 48'$, $\gamma' = 84^\circ 12'$ and contains four conventional cells of akrochordite. This cell not only presents the {010} cleavage plane, but it shows the sheet module parallel to {010}. In addition, the fbb can be easily extracted.

Dotted lines within the packets of structure indicate the Mn(1), Mn(2), and Mn(3) octahedral edge-sharing wall that runs parallel to the *a* axis. This wall is like the octahedral wall found in amphiboles. All oxygens except O(4), which is coordinated by As and 3H, are components of the wall. Note that the sequence of five Mn(1), Mn(2), and Mn(3) cations projected down x^* progresses Mn(3) ($x \approx 0$), Mn(2) ($x \approx 1/2$), Mn(1) ($x \approx 0$), Mn(2)' ($x \approx 1/2$), Mn(3)' ($x \approx 0$), and that b' and c' are alternately roughly perpendicular and parallel to these walls. Projection along $b' = [012]$ should afford a slab roughly normal to that axis, from which the packing principle can be ascertained. Along b' , the $M_5\phi_{14}$ wall is nearly normal to that axis at $y' = 1/8, 3/8, 5/8, 7/8$ and nearly parallel to that axis at $y' = 1/8, 2/8, 4/8, 6/8$. Figure 3 shows that wall at $y' \approx 7/8$ with Mn(1) fixed at $(\bar{x}y\bar{z}) = (0 \ 7/8 \ 5/8)$. The arrangement of the wall is based on a slice of cubic close-packing [ABCA]. Each wall has stoichiometry $M_5(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$; thus all atoms in the asymmetric unit are represented, and this unit is chosen as the fbb of the structure. The $[\text{AsO}_4]$ tetrahedra decorate the central $1/2[M_5\phi_{14}]$ octahedral edge-sharing wall by sharing the apical O(1) vertex above and below the projection, and the O(2) and

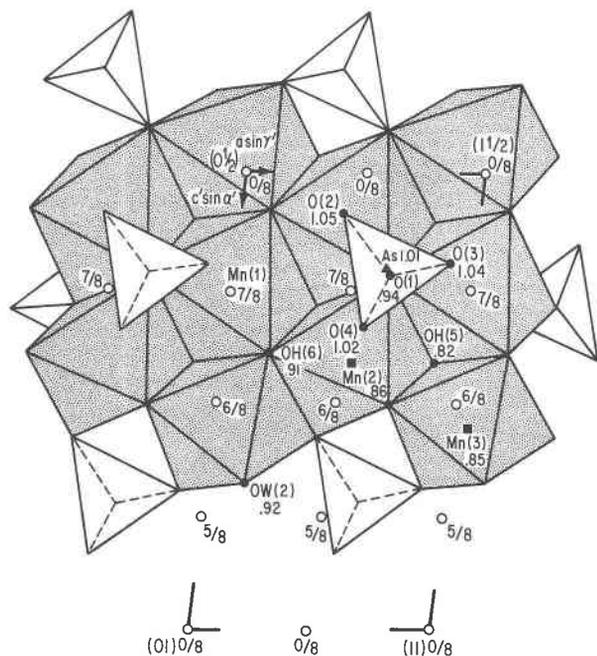


Fig. 3. A wall of polyhedra projected along $[01\bar{2}]$ in akrochordite. Note amphibole-like $\frac{1}{2}[M_3O_4]$. Inversion centers are drawn in and derive from Fig. 2.

rahedron (see Fig. 3). Also at the boundary are terminal OW(1) bonded to two octahedra and OW(2) bonded to one octahedron only. The OH(5) and OH(6) complete the coordinating anions and occur between the center and the boundary of the wall. Successive fbb's are linked via O(1), O(2), O(3), and O(4) of the $[AsO_4]$ group. The O(1) is a part of the wall, and O(2) and O(3) link to the boundary vertices of adjacent walls, while O(4) receives three hydrogen bonds.

The two orientations of these walls are automatically defined by the inversion centers and the c -axial glide implicit in $P2_1/c$ (Fig. 2). The packing efficiency or volume per oxygen atom is $V_E = 21.1 \text{ \AA}^3$, similar to other basic manganous arsenates with strips of dense-packing and close to manganosite ($4MnO$), $V_E = 21.9 \text{ \AA}^3$, which has the rock-salt structure.

The octahedral wall along $[100]$ and nearly perpendicular to $[01\bar{2}]$ shares with most of the other basic manganous arsenates strips or fragments of the pyrochroite, $Mn^{2+}(OH)_2$, sheet. A wall is intermediate between a chain, which is parallel to some axis, and a sheet, which is parallel to some plane. In other words, a wall is a chain with finite thickness. Or it can be considered a strip or a section of a sheet. For an octahedral wall, thickness can be specified by the number of octahedra, followed sequentially until the motif is repeated. In Figure 3, it is seen that the wall in the $\{01\bar{2}\}$ plane runs parallel to the $[100]$ direction and the thickness is parallel to $[001]$. In thickness, two octahedra alternate with three octahedra sequentially, or $(\cdot 23 \cdot)$. Included are octahedral strips or walls in retzian $(\cdot 11 \cdot \text{strip})$, arsenoklasite $(\cdot 12 \cdot \text{wall})$, al-

lactite $(\cdot 22 \cdot \text{wall})$, akrochordite $(\cdot 23 \cdot \text{wall})$, chlorophoenicite $(\cdot 33 \cdot \text{wall})$, and several others with fragments that further link to form edge- and corner-sharing frameworks. What controls the extent of polymerization of the fragments, strips, walls, etc., why most are based on close-packing, and what is the connection between structure and paragenesis in these interesting compounds are as yet unanswered questions.

Table 4 presents electrostatic bond-strength sums, p_o , for the eight unique O anions in akrochordite and the coordinating cations including H_d ($s = \frac{5}{6}$), H_a ($s = \frac{1}{6}$), M(1), M(2), M(3), and As. Deviations (in \AA) from polyhedral averages are listed. Of the 19 independent distance entries, 15 conform with oversaturation ($p_o > 2.00$) or undersaturation ($p_o < 2.00$) of the oxide anions by the coordinating cations. This leads to matching for bond length-bond strength deviations in about 80% of the entries, a typical value for oxysalts. The contradictions remaining are small.

Bond distances

Table 3 lists the individual bond distances for our akrochordite. The expected $^{61}Mn^{2+}-^{41}O^{2-}$ 2.20 \AA average from Shannon and Prewitt (1969) suggests that Mg^{2+} preferentially substitutes at the Mn(1) site ($\langle Mn(1)-O \rangle$ 2.17), followed by the Mn(3) site ($\langle Mn(3)-O \rangle$ 2.19 \AA). Since we applied scattering factors for neutral Mn at the M(1), M(2), and M(3) sites, the thermal-vibration parameters in Table 2 should indicate site preferences. Comparison with thermal-vibration parameters for other refined manganous arsenates indicates that B_{eq} are all somewhat high by about 25%, Mn(1) possessing the largest value. Based on the analysis of Almström in Flink (1922) for type akrochordite, the allocation for 10.0 M in the unit cell indicates a magnesian compound with $7.6Mn^{2+} + 2.4Mg^{2+}$ in the cell. Ordering of Mg is clearly not completely allocated to one site. It is likely that Mg substitutes at M(1) followed by M(3). Note that we have included M(2)-O(1) 2.627 \AA into the octahedral coordination sphere. This long distance is common among many of the basic manganous arsenates. The coordination number is difficult to assess. Perhaps the coordination number should be written $^{[5+1]}M(2)$.

For the ten unique shared edges, nine of them are the shortest for their polyhedra. The one exception, O(1)-O(1) $^{(0)}$, is associated with the long M(2)-O(1) distance.

SUMMARY

Akrochordite, $\frac{2}{3}(Mn,Mg)_3(OH)_4(H_2O)_4(AsO_4)_2$, belongs to the general family of basic manganous arsenate minerals, $Mn_n^{2+}(OH)_{2n-3s}(H_2O)_s(AsO_4)_{\frac{3-s}{2}}$. It is among the latest arsenates to crystallize in a paragenetic sequence.

The underlying unit or fundamental building block is a $\frac{1}{2}[M_3O_4]$ wall of octahedra, resembling the octahedral wall in amphibole. This wall is decorated by the $[AsO_4]$ tetrahedron, which shares the central O(1) vertex (the OH, F position of amphibole), and the O(2) and O(3) of symmetry-equivalent tetrahedra at the boundary of the wall.

The $[\text{AsO}_4]$ tetrahedron thus creates a steplike sequence of equivalent walls to form a sheetlike arrangement of polyhedra parallel to $\{010\}$, the plane of perfect cleavage.

Six independent $\text{O}-\text{H}\cdots\text{O}$ bonds occur in the structure. Two of these bonds are confined within a sheet, and four penetrate the c -axial glide planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The anion $\text{O}(4)$ is four-coordinated: in addition to receiving the As^{5+} ($s = \frac{3}{4}$ v.u.) bond, it receives three short (2.59–2.62 Å) hydrogen ($s = \frac{1}{6}$ v.u. each) bonds. It shares this property in common with several other mineral structures such as seamanite, metavauxite, and minyulite.

The common underlying structural feature among basic manganous arsenates appears to be walls of octahedra that in turn are fragments of the pyrochroite, $\text{Mn}(\text{OH})_2$ structure. What environments dictate thicknesses and close-packings of walls, and the connection between their structures and paragenesis, remain as yet unanswered questions.

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