American Mineralogist, Volume 64, pages 390–401, 1979

Magnussonite, manganese arsenite, a fluorite derivative structure

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Abstract

A single crystal of magnussonite, end-member formula unit Mn^{2+}_{18} $[As^{3+}_{6}Mn^{1+}O_{18}]_2Cl_2$, was studied in detail by three-dimensional X-ray diffractometry. The mineral is cubic, space group $Ia3d$, $Z = 8$, $a = 19.680(4)$A. $R = 0.112$ ($R_w = 0.097$) for 1373 independent reflections. X-ray diffraction data to $\sin\theta/\lambda = 0.80$ (Mo$K\alpha$ radiation) were collected on a Pailred diffractometer, and the structure was solved by Patterson, Fourier, and least-squares refinement techniques.

The structure is an anion-deficient derivative of the fluorite structure type and possesses a pronounced substructure $a' = a/4$. The cell contains 64 fluorite cells and the general fluorite-like formula can be written $X_{32}O_{36}\square_{28}$, $Z = 8$ where $\square$ are ordered vacancies over the anion frame. Its underlying principle is a large cluster of composition $[As^{3+}_{6}Mn^{1+}O_{18}]$, where the oxygens define a polyhedron of point symmetry $\bar{3}$ consisting of 36 edges, 18 vertices, 2 hexagonal faces, 12 triangular faces, and 6 quadrilateral faces. The arsenite oxygens reside on the periphery, and the central core consists of six As^{3+} octahedrally coordinated to central Mn^{1+} with an average bond distance As^{3+}–Mn^{1+} = 2.65A, 0.08A longer than Mn–As = 2.57A found in the structure of MnAs (nickel arsenide structure type). This unusual structure is interpreted as satisfying the 18-electron rule with $2 \times 6 = 12$ electrons donated by the As^{3+} plus 6 d^6 electrons from Mn^{1+}. The Cl^- ions reside outside the large hexagonal faces of the oxygen polyhedron.

The rest of the structure consists of $Mn(1)O_8$ distorted cubes, $Mn(2)O_4$ distorted squares, $Mn(3)O_6$ distorted trigonal prisms, and $Mn(4)O_6$ distorted octahedra.

Introduction

Magnussonite is an arsenite mineral originally described from the Långban mine in Värmland, Sweden (Gabrielson, 1956), and subsequently found in geochemically similar environments at Sterling Hill, Sussex County, New Jersey (Frondel, 1961), and the Brattfors mine, Nordmark in Värmland, Sweden (Moore, 1970b). It occurs as granular masses ranging in color from grass-green, emerald green, bluish-green, passing into yellowish-green and orange. It is optically isotropic ($n = 1.980 \pm 0.005$), with vitreous luster, fracture conchoidal, hardness about 4 on Mohs scale (Gabrielson, 1956). Locally it is not rare, and its paragenetic settings suggest that its field of stability, although confined to basic and reduced conditions, may extend over a considerable temperature range.

Earlier study by Moore (1970b) showed it to be cubic, space group $Ia3d$, $a = 19.7$A, $Z = 32$ for the composition $(Mn,Mg,Cu)_5(AsO_3)_3(OH,Cl)$. A pronounced fluorite-like subcell was recognized, $a' = a/4$. This property, compounded with a rather complex cell for such a simple composition, attracted us to the problem. Many fluorite derivative structures, some of considerable complexity, have been recently characterized (Moore and Araki, 1976a, 1977). The present study not only confirms the fluorite-related structure but also affords evidence on the first *bona fide* example of a metal cluster in an oxide matrix for an inorganic natural product.

Experimental section

Minerals, unlike synthetic materials, usually have crystallized in systems where the number of available components is greater than the end-member composition would suggest, and magnussonite is no exception. Therefore, two problems arise: the determination of the structure type and the assessment of mixed cation populations over the non-equivalent sites in the structure. The three known chemical analyses (Table 1) show that twelve components may play some role in the structure. Solid solution must occur at some of the non-equivalent sites, but even worse, magnussonite's space group (*Ia*3*d*) has a range of equipoint rank numbers (from 16 to 96), and therefore structure refinement is sensitive to site population refinement. This, coupled with a pronounced pseudocell for magnussonite ($a' = a/4$), suggested a nasty structural problem.

Actually, we solved the structure two years ago, but the crystal was too small and only about one-third of the independent reflections were recovered. *R* converged to 0.27 and the structure could not be refined further; we then selected a rather large crystal, covered as much reciprocal space as possible, and employed a slow scan speed on a Pailred diffractometer with graphite monochromator and Mo tube (Table 2). After data collection was completed, "unobserved" reflections where $I_o < 2\sigma(I)$ were set $I_o = \sigma(I)$, the estimated errors of the intensities being calculated according to a published procedure (Moore and Araki, 1976c). A total of 60 *independent* I_o belonged to this category.

The crystal size, which was carefully measured on a two-circle goniometer with micrometer ocular, provided the data for absorption correction. The chip was described by 12 planes, and we used 7 divisions for the Gaussian integral (Burnham, 1966). This correction was substantial since the extrema in transmission factors ranged from 0.088 to 0.191. Symmetry-equivalent F_o's were then inspected, found satisfactory, then averaged to yield 1373 F_o which constitute the basis of the structure analysis.

Table 2. Experimental details of magnussonite

a, Å	19.680(4)
Space group	Ia3d
Z	16
Formula	$(Mn,Mg)_9^{2+}[As_6^{3+}Mn^{1+}O_{18}](Cl,OH)$
ρ(calcd), g cm^{-3}	4.55
Specific gravity	4.14 to 4.49
μ, cm^{-1}	164.5
Crystal size, mm	$0.21(\lVert a_1)$, $0.19(\lVert a_2)$, $0.24(\lVert a_3)$
Reciprocal space covered	$\bar{h}k\ell$ and $hk\ell$, with $k \geq \ell$, $\ell \leq 2$
Max $(\sin\theta)/\lambda$	0.80
Scan speed, deg per min	1.0
Base scan width	3.2 (min) to 3.6 (max)
Background counts	Stationary, 20s at beginning and end of scan
Radiation	MoKα_1 (λ 0.7926Å), graphite monochromator
Largest $\lvert F_o \rvert$	$\lvert F_o \rvert = 4239$ for (880).
Independent F_o	1373

	Above $\lvert F_o \rvert = 0$ (No. F_o)	Above $\lvert F_o \rvert = 40$	Above $\lvert F_o \rvert = 120$
R	0.112(1373)	0.109(1320)	0.046(598)
R_w	0.097	0.097	0.056
Scale factor		0.329(2)	
Goodness of fit		1.05	
Coefficient of extinction		2.4(2)x10^{-8}	

Table 1. Chemical analyses on magnussonite

	a	b	c	d
Mn_2O	---	---	---	4.82
CaO	---	0.84	2.0	---
MgO	1.47	0.74	2.5	1.67
MnO	47.24	45.82	48.1	43.00
FeO	---	1.35	0.2	---
CuO	2.07	---	---	3.29
ZnO	---	2.17	---	---
SiO_2	---	1.40	---	---
As_2O_3	43.49	---	47.2	45.42
As_2O_5	---	47.42	---	---
Cl	0.84	nil	---	2.17
H_2O	1.16	0.58	---	0.14
Insol.	3.68	---	---	---
-O = Cl	0.19	---	---	0.51
	99.76	100.32	100.0	100.00

[a] R. Blix analysis in Gabrielson (1956). Insoluble = barite ($BaSO_4$). Specific gravity = 4.30. Långban, Sweden.

[b] L. H. Bauer analysis in Frondel (1961). Specific gravity = 4.14 ± 0.05. Sterling Hill, New Jersey.

[c] B. Rajandi analysis in Moore (1970). Olive-green variety from the Brattfors mine, Nordmark, Sweden. Specific gravity = 4.49.

[d] Calculated for $(Mn_{0.88}^{2+}Mg_{0.06}^{2+}Cu_{0.06}^{2+})_9[As_6^{3+}Mn^{1+}O_{18}](Cl_{0.80}OH_{0.20})$. The calculated density is 4.55 g cm^{-3}.

Structure determination and refinement

Programs used in determining and refining the structure were listed earlier (Moore and Araki, 1976c). Three-dimensional Patterson syntheses, $P(uvw)$, gave a map with pronounced substructure, $a' = a/4$. Within this subcell, strong vectors occurred at the face-centered positions and medium-sized peaks appeared at tetrahedral sites between them, suggesting a ZnS-type arrangement. The immediate choices for the arrangement of substructure cations are either (1) 96 M(1) at 1/8 1/8 0, 96 M(2) at 1/8 − 1/8 0, and 48 M(3) at 1/4 0 0; or (2) 96 M(1) at 0 1/8 0, 48 M(2) at 1/8 1/4 0, 48 M(3) at 1/8 3/8 1/8, 24 M(4) at 1/4 3/8 0 and 24 M(5) at 1/4 1/8 0, yielding in either case a defect-fluorite type arrangement. Choice (1) was ruled out in the subsequent β-synthesis (Ramachandran and Srinivasan, 1970). Choice (2) led to a map clearly showing As ≈ 0 1/8 0 and

Table 3. Site population and distribution results on magnussonite*

	Mn^{2+}	Mg^{2+}	Cu^{2+}
Mn(1)	0.95(3)	0.05(3)	-------
Mn(2)	0.66(5)	-------	0.34(6)
Mn(3)	0.94(2)	0.06(2)	-------
Mn(4)	0.90(2)	0.10(2)	-------
MX	Mn° 0.95(5), □(hole) 0.05(5)		
ClW	Cl^{1-} 0.80(6), O^{1-} 0.20(6)		
As	As° 1.00		
O(1), O(2), O(3)	O^{1-} 1.00		

*Employing the scattering curves from Cromer and Mann (1968) and anomalous dispersion of Mn, Cu and As from Cromer and Liberman (1970).

three non-equivalent oxygens, O(1), O(2) and O(3), defining a stable trigonal geometry, and acceptable distances (As–O ≈ 1.76A) expected for the $(AsO_3)^{3-}$ trigonal pyramid. In addition to the cations mentioned above, densities appeared at 0 0 0 and 1/8 1/8 1/8. The first cycle of atomic coordinate parameter refinement was then inaugurated. A subsequent γ-synthesis revealed that the positions at 1/8 1/8 1/8 (called ClW), 0 0 0 (called MX), and 1/4 1/8 0 [called Mn(2)] were split, displaced about 0.3A away from these special positions. Therefore, the next cycle admitted split-atom models.

At $R = 0.22$, it was necessary to assess the possible solid solutions over the non-equivalent sites. Mn(1), Mn(3), and Mn(4) indicated average atomic number somewhat less than Mn^{2+} and we assigned $Mn^{2+}_{1-x}Mg^{2+}_x$ to these sites. Mn(2) possessed somewhat larger atomic number than Mn^{2+} and, combined with its distorted square-planar coordination, we assumed Cu^{2+} reported in the analysis substituted here. Accordingly, we applied $Mn^{2+}_{1-x}Cu^{2+}_x$ at this site. Likewise, the site ClW was assigned $Cl^-_{1-x}OH^-_x$. MX was assigned $Mn^0_{1-x}\square_x$, where $\square$ = vacancy on the basis of crystal chemical arguments (*vide infra*). Thus, *in toto* 75 parameters were varied, namely independent atomic coordinates (19), anisotropic thermal vibration parameters (48), solid-solution pairs (5), fractional site occupancy (1, for MX), scale factor (1), and coefficient of secondary extinction (1). This leads to a data-to-variable parameter ratio of 18:1.

Full-matrix refinement converged to the results in Table 2, where

$$R = \frac{\Sigma \left|\, |F_o| - |F_c| \,\right|}{\Sigma |F_o|}, \quad R_w = \frac{\Sigma_w(|F_o| - |F_c|)^2}{\Sigma_w F_o^2}$$

Magnussonite possesses a pronounced substructure whose largest $|F_o|$ on an arbitrary scale is 4239 for the (880) reflection. Those reflections with $|F_o| < 40$ were not observable, which gives an idea of the difficulty encountered in selecting a suitable crystal for a complete data recovery. From this standpoint, the convergence is excellent. A final difference synthesis failed to reveal any residues in excess of two electrons. The site MX at 0 0 0, which on crystal-chemical grounds is the most interesting feature of the structure (*vide infra*), was carefully inspected. We were forced to conclude (1) from the refinement, (2) from deliberate omission in one difference synthesis and subsequent mapping of the electron density profile, and (3) from chemical analyses, that it is a Mn atom. Deliberate omission of MX, with subsequent least-squares refinement, led to $R = 0.143$ and $R_w = 0.184$. For $|F_o| > 120$, the results were $R = 0.082$ and $R_w = 0.162$. The final site populations and distributions appear in Table 3; it is seen that MX = Mn^0 is practically completely occupied, the indication of a minor omission at the site being more likely a result of its splitting and the high correlation between site population and thermal vibration parameters. We repeated Fourier synthesis on data from the original small crystal (which were also corrected for absorption) and obtained the same broad electron density at the origin indicative of occupancy by a Mn atom. The final site distributions were then used to calculate a chemical composition (Table 1, d). The results are quite satisfactory but indicate that Cl^- may have not been fully recovered in the chemical analyses.

A rather large number of equivalent points had to

Table 4. List of equivalent points used in this study

1	1/2-y	1/2-z	1/2-x	16	3/4-y	3/4-x	3/4-z
2	y	1/2-z	1/2+x	17	1/4+z	3/4-y	1/4-x
3	3/4-x	1/4+z	3/4+y	18	1/2+z	x	1/2-y
4	3/4+x	1/4+z	1/4-y	19	y	z	x
5	-x	1/2-y	z	20	1/4-x	1/4-z	1/4-y
6	z	-x	1/2-y	21	z	x	y
7	1/2-y	-z	1/2+x	22	-x	-y	-z
8	1/4+z	3/4+y	3/4-x	23	1/2+x	1/2-y	-z
9	3/4-y	3/4+x	1/4-z	24	z	1/2-x	1/2+y
10	1/4-z	3/4-y	3/4+x	25	-z	1/2+x	1/2-y
11	1/4+y	3/4-x	1/4-z	26	1/2+y	z	1/2-x
12	1/2-x	y	-z	27	1/2-x	1/2+y	z
13	3/4+y	3/4-x	1/4+z	28	-y	1/2+z	1/2-x
14	y	-z	1/2-x	29	1/2-z	-x	1/2+y
15	1/4+x	1/4-z	3/4+y				

Table 5. Magnussonite atomic coordinate parameters[a]

			x	y	z	x	y	z	D,A
Mn(1)	24	$\bar{4}$	1/4	3/8	0	1/4	3/8	0	0.00
Mn(2)	24[b]	222[b]	0.23263(35)	1/8	1/4-x	1/4	1/8	0	0.48
Mn(3)	48	2	3/8	0.26423(15)	y-1/4	3/8	1/4	0	0.40
Mn(4)	48	2	0.11266(13)	1/4+x	1/8	1/8	3/8	1/8	0.34
As	96	1	0.49912(4)	0.36620(4)	0.00839(4)	1/2	3/8	0	0.24
O(1)	96	1	0.56979(33)	0.32014(38)	0.03660(41)	9/16	5/16	1/16	0.55
O(2)	96	1	0.46116(30)	0.31841(34)	-0.05683(32)	7/16	5/16	-1/16	0.49
O(3)	96	1	0.44445(31)	0.33379(37)	0.07270(31)	7/16	5/16	1/16	0.48
ClW	16[c]	32[c]	0.14136(110)	1/4-x	1/8	1/8	1/8	1/8	0.46
MX	16[d]	$\bar{3}$[d]	0.00750(225)	0.01336(88)	-0.00073(267)	0	0	0	0.30
□(1)	32	3				1/16	1/16	1/16	
□(2)	96	1				-1/16	1/16	1/16	
□(3)	96	1				3/16	1/16	1/16	

[a] Listed along a row are atom designation, equipoint rank number, point symmetry, atomic coordinates for refined structure, ideal (fluorite-type) atomic coordinates, and D, the displacement of real atomic positions away from fluorite-type positions in Angström units.

[b] Half occupancy ("split atom") of position 48f. The locus of the symmetry 222 is 1/4 1/8 0.

[c] Half occupancy ("split atom") of position 32e. The locus of the symmetry 32 is 1/8 1/8 1/8.

[d] One-sixth occupancy ("split atom") of position 96h. The locus of the symmetry $\bar{3}$ is 0 0 0.

be employed in the structure description. We assigned numbers to these and then applied these numbers to the appropriate atoms as superscripts in parentheses. The relationship between number and equipoint appears in Table 4 and these can be directly applied to the atomic coordinate parameters in Table 5. Table 6[1] presents the anisotropic thermal vibration parameters; MX is non-positive definite, doubtless owing to its equal splitting into six pieces. Table 7[1] lists the crystallographic orientations of their principal vibration directions, and pertinent bond distances and angles are given in Table 8. Table 9[1] is a list of the structure factors.

Description of the structure

Magnussonite as a fluorite derivative structure

Magnussonite is an ordered anion-deficient fluorite (CaF_2, $Z = 4$, $a = 5.45$A, $Fm3m$) derivative structure. We represent its general formula by noting that the $a_1(\mathrm{m}) = 4a_1(\mathrm{f})$. The cell contains 64 fluorite cells, *i.e.* $X_{256}\phi_{512}$, where X are the available cation sites and ϕ the anion sites. Setting $Z = 8$ (the formula unit), we see that the distribution over $X_{32}\phi_{64}$ is 32 X = 3 Mn(1) + 3 Mn(2) + 6 Mn(3) + 6 Mn(4) + 12 As + 2 ClW and 64 ϕ = 12 O(1) + 12 O(2) + 12 O(3) + 4 $\square$(1) + 12 $\square$(2) + 12 $\square$(3), where $\square$ correspond to the ordered vacancies. Thus, in terms of populated sites, the general formula can be written $X_{32}O_{36}\square_{28}$. The formula unit also contains 2 MX (= Mn^{1+}), *not* associated with the fluorite frame but occurring as the core of a compact [As_6Mn] cluster.

We adopt the conventions and symbols of the earlier studies (Moore and Araki, 1976a, 1977) describing fluorite derivative structures. Since magnussonite contains four fluorite repeats along a_3, it must contain eight "checkerboards" within its cell. We partition the symmetry elements, $\{\cdots\}$, of the space group $Ia3d$ into the sheet group $\{pbab\}$; the permuted cubic coordinates (xyz, zxy, yzx), written $\{3\}$; and the pole group $\{4_1\}$. With suitable arrangement of the elements, it can be shown that $\{pbab\}\cdot\{3\}\cdot\{4_1\} = Ia3d$ where "$\cdot$" denotes a generation of the elements[2]. Note that we need describe only two checkerboards, at $z = 0$ and 1/8, since the 4_1-screw generates the remaining six. The ideal checkerboard designs appear

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[1] To obtain copies of Tables 6, 7 and 9, order Document AM-79-095 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

[2] The subgroups are *factorizations* of the space group, and the products between them constitute products of ordered pairs or a *generation* of the space group elements by the subgroup elements. The order of the space group, $|G|$, is the product of the orders of the subgroups, $|H_1|\cdot|H_2|\cdots$. Thus $96 = 8\cdot 3\cdot 4$.

Table 8. Magnussonite polyhedral interatomic distances (A) and angles (°)^a

MX	
2 MX–MX$^{(21)}$	0.341(74)
2 MX–MX$^{(1)}$	0.498(34)
1 MX–MX$^{(22)}$	0.604(53)
average	0.456
1 MX–As$^{(23)}$	2.381(18)
1 MX–As$^{(7)}$	2.522(44)
1 MX–As$^{(24)}$	2.630(53)
1 MX–As$^{(25)}$	2.681(56)
1 MX–As$^{(26)}$	2.783(45)
1 MX–As$^{(27)}$	2.904(18)
average	2.650

Mn(1)		O-Mn-O′ angle (deg.)	Ideal cube angles (deg.)
4 Mn(1)–O(3)$^{(1)}$	2.230(7)		
4 Mn(1)–O(1)$^{(1)}$	2.611(8)		
average	2.420		
4 O(1)$^{(1)}$–O(3)$^{(1)}$	2.581(9)^b	63.9(2)	
4 O(1)$^{(1)}$–O(3)$^{(4)}$	2.797(10)^c	70.1(2)	
4 O(1)$^{(1)}$–O(3)$^{(2)}$	3.124(11)^c	80.0(2)	
average	2.834	71.3	70.52
Body Diagonal:			
4 O(1)$^{(1)}$–O(3)$^{(3)}$		162.8(2)	180.00
Face Diagonal:			
2 O(1)$^{(1)}$–O(1)$^{(2)}$		96.4(3)	
4 O(3)$^{(1)}$–O(3)$^{(3)}$		102.3(1)	
4 O(1)$^{(1)}$–O(1)$^{(3)}$		116.3(2)	
2 O(3)$^{(1)}$–O(3)$^{(2)}$		125.0(3)	
average		109.8	109.46

As–As Distances and Angles		
1 As$^{(25)}$–As$^{(27)}$	3.601(2)	80.2(10)
1 As$^{(25)}$–As$^{(26)}$	3.601(2)	82.4(18)
1 As$^{(7)}$–As$^{(27)}$	3.601(2)	82.8(8)
1 As$^{(23)}$–As$^{(26)}$	3.601(2)	88.1(11)
1 As$^{(7)}$–As$^{(24)}$	3.601(2)	88.6(20)
1 As$^{(23)}$–As$^{(24)}$	3.601(2)	91.7(13)
1 As$^{(26)}$–As$^{(27)}$	3.857(2)	85.4(9)
1 As$^{(24)}$–As$^{(27)}$	3.857(2)	88.2(10)
1 As$^{(24)}$–As$^{(26)}$	3.857(2)	90.8(7)
1 As$^{(7)}$–As$^{(25)}$	3.857(2)	95.6(8)
1 As$^{(23)}$–As$^{(25)}$	3.857(2)	99.1(16)
1 As$^{(7)}$–As$^{(23)}$	3.857(2)	103.7(13)
average	3.729(2)	89.7

Mn(2)		
2 Mn(2)–O(2)$^{(3)}$	2.008(9)	
2 Mn(2)–O(2)$^{(4)}$	2.197(9)	
average	2.102	
1 Mn(2)–C1W	2.796(16)	
1 Mn(2)–Mn(2)$^{(12)}$	0.967(10)	
Square Plane:		
2 O(2)$^{(3)}$–O(2)$^{(14)}$	2.806(12)	83.6(3)
2 O(2)$^{(3)}$–O(2)$^{(4)}$	3.096(12)	94.7(3)
average	2.951	89.2
Face Diagonal:		
2 O(2)$^{(3)}$–O(2)$^{(7)}$	4.014(15)	
Pyramidal:		
1 C1W–O(2)$^{(7)}$	3.473(17)	91.1(4)
1 C1W–O(2)$^{(3)}$	3.526(17)	93.0(4)
1 C1W–O(2)$^{(14)}$	4.007(18)	106.1(4)
1 C1W–O(2)$^{(4)}$	4.375(18)	121.9(4)
average	3.845	103.0

in Figures 1a and 1b respectively. It is readily seen that at $z = 0$ (which has a pattern according to the sheet group *pbab*) and at $z = 1/8$ (pattern according to *pba*2), coordination numbers and maximal point symmetries can be obtained; it is convenient to discuss the point symmetries as (point symmetry of player on idealized checkerboards; point symmetry in magnussonite, space group *Ia*3*d*). Thus, Mn(1)O$_8$ = u^8 ($4/m\bar{3}\ 2/m$; $\bar{4}$), Mn(2)O$_4$ = $u^4d^4(3)$ ($2/m\ 2/m\ 2/m$; 222), Mn(3)O$_6$ = $u^6d^2(1)$ ($2mm$; 2), Mn(4)O$_6$ = $u^6d^2(3)$ ($\bar{3}\ 2/m$; 2), and AsO$_3$ = $u^3d^5(1)$ (m; 1). The actual point symmetries in the crystal are therefore seen as subgroups of the point symmetries of the players on the checkerboard; specifically, the crystal point symmetries are devoid of reflections (m) and $\bar{3}$. The kinds of oxygen polyhedra furthermore can be described as Mn(1)O$_8$ = distorted cube, Mn(3)O$_6$ = distorted trigonal prism, Mn(4)O$_6$ = distorted octahedron, and AsO$_3$ = distorted triangle.

Polyhedral diagrams of the magnussonite crystal structure appear in Figures 2a and 2b. At $z = 0$, Mn(1)O$_8$, Mn(2)O$_4$, Mn(3)O$_6$ and AsO$_3$ exploit

Table 8. (continued)

Mn(3)			
2 Mn(3)–O(1)$^{(4)}$	2.033(7)		
2 Mn(3)–O(3)$^{(3)}$	2.251(7)		
2 Mn(3)–O(2)	2.443(7)		
average	2.242		
A. Base Edges:			
2 O(2)–O(3)	2.588(9)[b]	66.8(2)	70.52
2 O(1)$^{(5)}$–O(3)	3.124(11)[c]	93.5(3)	70.52
2 O(1)$^{(5)}$–O(2)	3.345(12)	96.3(2)	109.46
B. Prism Edges:			
1 O(3)–O(3)$^{(3)}$	2.751(12)[c]	75.3(3)	70.52
2 O(1)$^{(4)}$–O(2)	2.864(9)[c]	79.0(2)	70.52
average of A and B	2.955	82.9	79.18 81.70[d]
2 O(2)–O(3)$^{(3)}$		123.1(3)	109.46
2 O(1)$^{(4)}$–O(3)		127.6(3)	109.46
1 O(1)$^{(4)}$–O(1)$^{(5)}$		129.8(5)	180.00
1 O(2)–O(2)$^{(3)}$		169.0(3)	180.00
average		133.4	132.97 135.53[d]

Mn(4)		
2 Mn(4)–O(3)$^{(1)}$	2.144(6)	
2 Mn(4)–O(2)$^{(12)}$	2.161(6)	
2 Mn(4)–O(1)$^{(3)}$	2.275(7)	
average	2.193	
1 O(3)$^{(1)}$–O(3)$^{(10)}$	2.751(12)[c]	79.8(4)
2 O(1)$^{(3)}$–O(3)$^{(1)}$	2.797(10)[c]	78.5(3)
1 O(2)$^{(12)}$–O(2)$^{(13)}$	2.807(12)[c]	81.0(4)
2 O(1)$^{(3)}$–O(2)$^{(12)}$	2.864(9)[c]	80.4(3)
2 O(1)$^{(3)}$–O(2)$^{(13)}$	3.272(12)	95.0(3)
2 O(2)$^{(12)}$–O(3)$^{(1)}$	3.298(12)	100.0(3)
2 O(1)$^{(3)}$–O(3)$^{(10)}$	3.535(13)	106.2(3)
average	3.091	90.1
Body Diagonals:		
1 O(1)$^{(3)}$–O(1)$^{(6)}$		174.0(4)
2 O(2)$^{(13)}$–O(3)$^{(1)}$		173.1(3)

As		
1 As–O(1)	1.750(6)	
1 As–O(2)	1.758(6)	
1 As–O(3)	1.779(6)	
average	1.762	
1 O(1)–O(3)	2.581(9)[b]	94.0(3)
1 O(2)–O(3)	2.588(9)[b]	94.0(3)
1 O(1)–O(2)	2.820(9)	107.0(3)
average	2.663	98.3

[a] Estimated standard deviations refer to the last digit. Equivalent atoms are denoted with numbers in superscripts. Refer to Table 4 for the corresponding coordinates.

[b] O–O′ edge shared between As–O and Mn–O polyhedra. [c] O–O′ edge shared between Mn–O and Mn–O polyhedra. [d] Ideal angles for equivalent trigonal prism.

shared edges and vertices; and at $z = 1/8$, Mn(4)O$_6$ occurs in addition. The composite is a highly rigid framework built upon extensive polyhedral edge-sharing and dictated according to those anions remaining in the fluorite-type frame. Figure 3 outlines, as Schlegel diagrams, the shared edges. Mn(1)O$_8$ shares all twelve of its edges (compare with braunite, Mn^{2+}Mn$_6^{3+}$SiO$_{12}$, another fluorite derivative, see Moore and Araki, 1976a), Mn(2)O$_4$ two of its four edges, Mn(3)O$_6$ seven of its nine edges, Mn(4)O$_6$ six of its twelve edges (compare with Mn(2)O$_6$ in braunite), and AsO$_3$ two of its three edges. There can be little doubt that the magnussonite polyhedral framework is highly stable, the unusual coordinations among its component polyhedra and the high degree of edge-sharing being dictated by the inherent electrostatic stability of a fluorite-type arrangement. As seen in Table 5, the displacement of the cations and anions away from ideal fluorite positions are 0.55A at most, which substantiates the statement that magnussonite is indeed based on ordered anion vacancies over a fluorite framework. Since the fluorite arrangement is highly stable, the unusual coordinations of anions about cations obtain directly from the manner in which the vacancies are ordered.

The cavity at 0 0 0 and the As$_8^{3+}$Mn^{1+} cluster

Figure 1a shows that eight anion vacancies occur in the coordination sphere about 0 0 0. This central position would be empty in a fluorite arrangement since it corresponds to an empty cube in that structure. However, refinement and chemical analyses

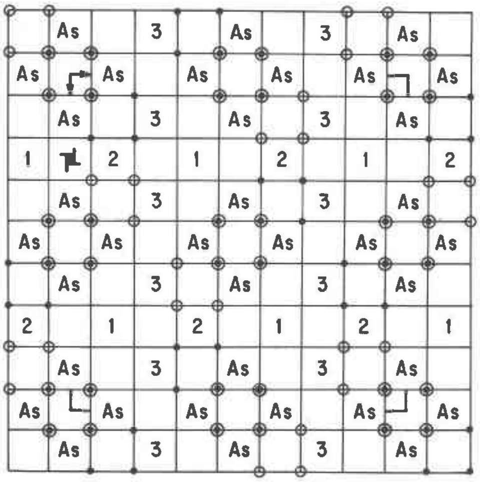

Fig. 1a. Idealized checkerboard for magnussonite, $z = 0$. The numbers 1, 2 and 3 refer to Mn(1), Mn(2) and Mn(3) respectively. Solid disks indicate anion vacancies on the cubic domain above the plane, open circles below the plane. The 4_1-screw translates this checkerboard along z. Note the large open region produced at the origin and the maximal 8-coordination of Mn(1) by oxygens.

conclusively show that an atom resides in this position and that the atom is Mn (= MX). Difference synthesis toward the conclusion of the structure refinement showed that MX is actually displaced 0.30A away (Table 5) from the center and is split into six equivalent points ranging from 0.34 to 0.60A from each other (Table 8).

We submit the argument that the presence of MX is the key to the unusual distribution of the $[AsO_3]^{3-}$ trigonal pyramids in the structure: the triangles of coordinating oxygens are situated away from the central cavity so that the lone electron pairs at the opposing empty vertices point into the central cavity. Both the Figure 1 and 2 series show that the As atoms are distributed at the vertices of a distorted octahedron with As–As edge distances of 3.601(×6) and 3.857(×6)A, resulting in an average As–As edge length of 3.73A and a calculated mean distance from the octahedral vertex to the center of $3.73/\sqrt{2} = 2.64$A, corresponding to a mean MX–As distance of 2.65A in the structure refinement. Since the average residency of MX is displaced away from the origin, six non-equivalent MX–As distances result, ranging from 2.38 to 2.90A.

We compare the MX–As distance of 2.65A to that calculated from MnAs (2.57A), which possesses the NiAs structure (hexagonal close-packing, space group $P6_3/m\ 2/m\ 2/c$, $Z = 2$) (Wyckoff, 1963, p. 124). In the MnAs structure, the Mn atoms are surrounded by six As atoms in a compressed octahedral coordination, and the As atoms are surrounded by six Mn atoms in a trigonal prismatic coordination. The As–As edge distances are 3.56(×6)A and 3.71(×6)A (average 3.64A) with As–Mn–As angles of 87.7°(×6) and 92.4°(×6) respectively. Thus, the As_6Mn cluster in magnussonite is expanded by about 3 percent. Compression of the As_6Mn octahedron in MnAs is a result of the structure geometry and bonding character: the octahedra share edges in a plane forming a sheet, and the sheets are stacked by octahedral face-sharing. Compression occurs along the axis normal to the shared faces, owing to a Mn–Mn metal–metal bond with separation of 2.85A.

The $[AsO_3]^{3-}$ trigonal pyramid is somewhat distorted, since two of its three edges are shared with other oxygen polyhedra in the structure. The four independent atoms in the trigonal pyramid exhibit no disorder, and the oxygens contribute the anion framework for the entire structure. The mean As^{3+}–O distance is 1.762A, in accord with 1.79A in hematolite $(Mn^{2+},Mg,Al)_{15}(OH)_{23}(AsO_3)(AsO_4)_2$ (Moore and Araki, 1978); 1.76A in synadelphite, $Mn_9(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2$ (Moore, 1970a); 1.80A, 1.79, 1.81A in trigonite, $Pb_3Mn(AsO_3)_2(AsO_2OH)$ (Pertlik, 1978), compounds which occur in a paragenetic setting similar to magnussonite. The O–As–O′ angle average is 98.3° compared with 94.2° in hematolite and 95.7° in synadelphite. The $[SbO_3]^{3-}$ anion is geometrically similar to $[AsO_3]^{3-}$: O–Sb^{3+}–O′ angles ranging from 79.8° to 98.1° have been found for valentinite, orthorhombic Sb_2O_3 (Svensson, 1974) and 92.1° in derbylite, $Fe^{3+}_4Ti^{4+}_3(Sb^{3+}O_3)O_{10}(OH)$

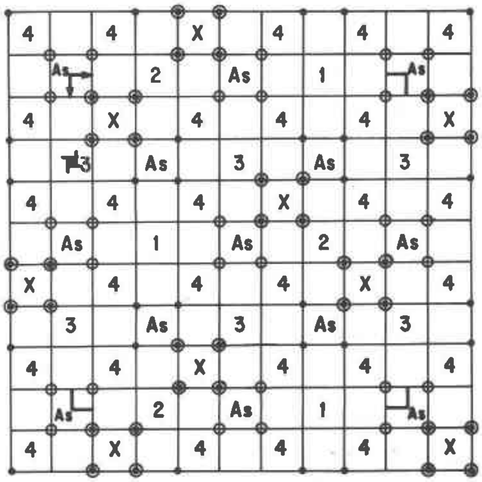

Fig. 1b. Idealized checkerboard for magnussonite, $z = 1/8$. The site "X" is the ClW position. Note that it resides in an open region in the structure. The 4_1-screw translates this checkerboard along z and, along with Fig. 1a, completes the ideal structure.

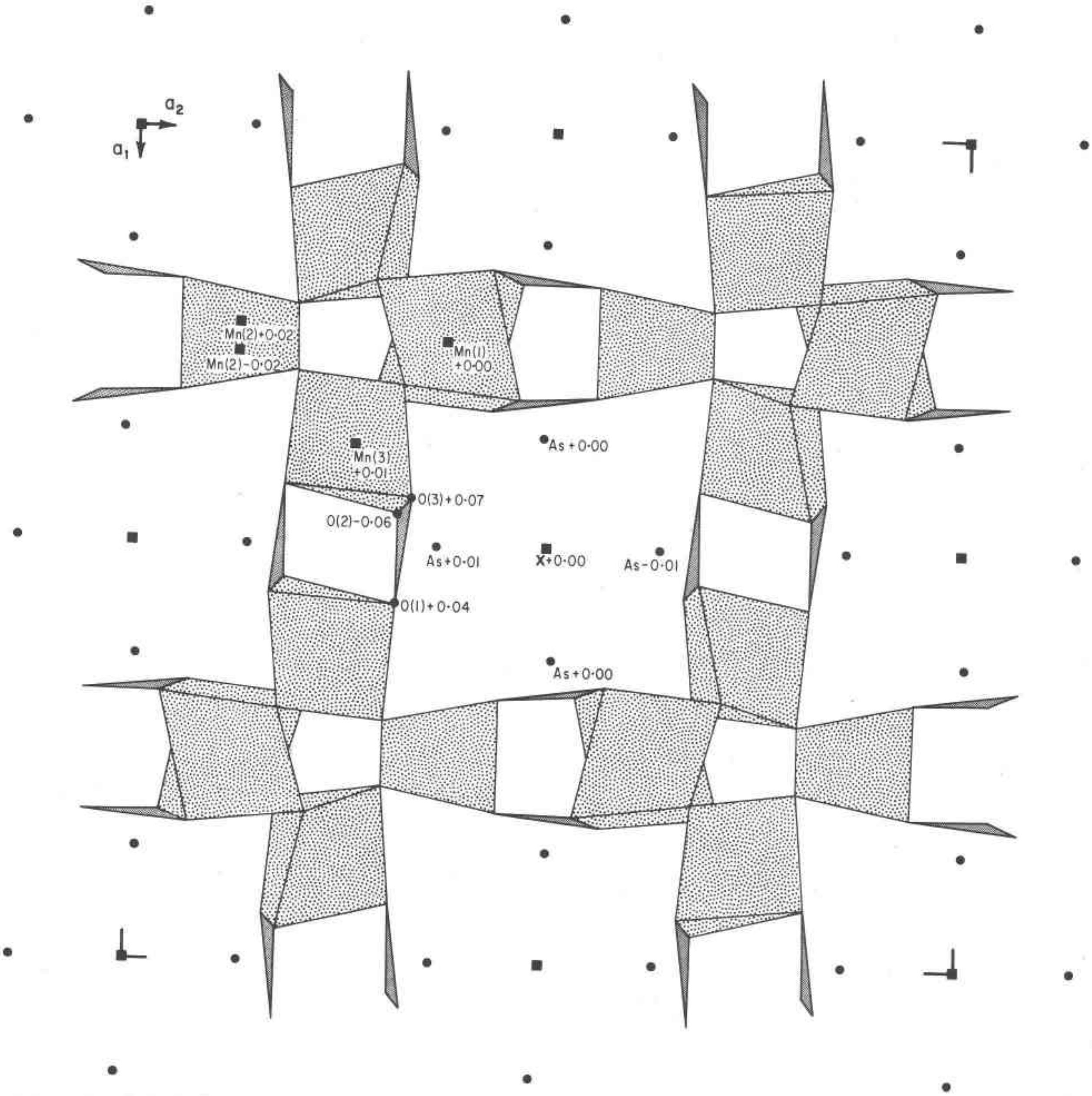

Fig. 2a. Polyhedral representation of the magnussonite crystal structure, $z = 0$. The basal oxygens associated with (AsO_3) form a shaded triangle. The site "X" corresponds to $MX(= Mn^{1+})$ centrally located and octahedrally coordinated by six As atoms, four of which occur in the section of the structure. Heights are given as fractional coordinates in z.

(Moore and Araki, 1976b). Discussion on the antimonite anion by Moore and Araki (1976b) and Andersson *et al.* (1973) and the results on hematolite and synadelphite reveal that the lone pair electrons in dense-packed structures involving $[SbO_3]^{3-}$ and $[AsO_3]^{3-}$ anions are situated in anion voids in these structures and that these voids are separated from each other by substantial distances owing to electrostatic repulsion. Magnussonite is unique chemically in that a total of six electron pairs point into the same cavity.

We believe that the underlying principle accounting for magnussonite's stability is the $[As_6MnO_{18}]$ cluster. It is clearly seen in Figure 2a that the convex hull of this cluster is a sphere of 10A diameter and that these spheres pack according to body-centered

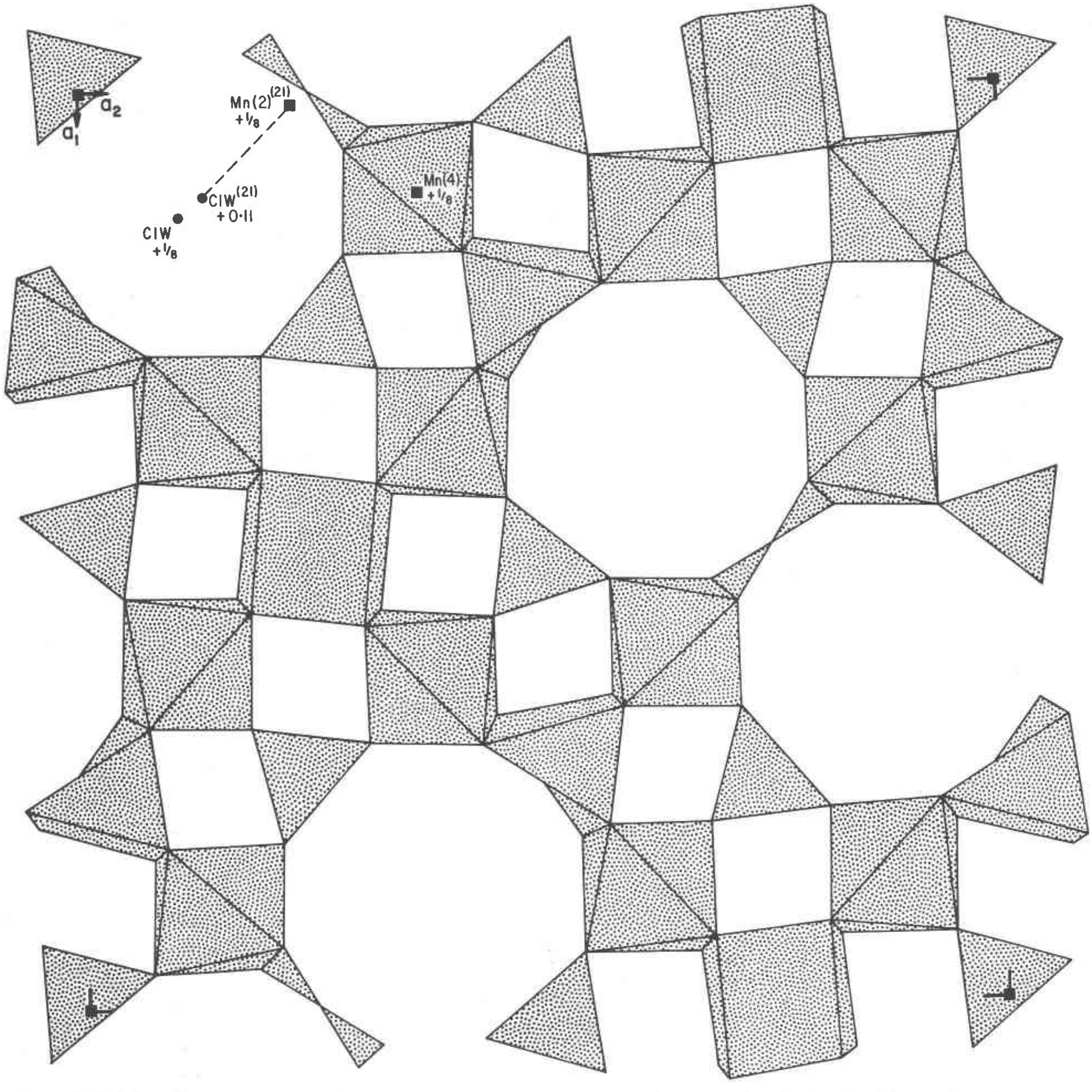

Fig. 2b. Polyhedral representation of the magnussonite crystal structure, $z = 1/8$. Note the split ClW position centered in the large cavities. The trigonal prismatic coordination of Mn(3) and the cubic coordination of Mn(1) are readily noticeable in this section.

cubic packing. It is tempting to suggest that these clusters are stable in the fluid coexisting with the growing crystal and that the unusual geometry of the rest of the structure is "forced" in part by these clusters. We suggest that a high degree of stability is conferred upon the cluster according to the 18 electron rule. Counting electrons, we have $2 \times 6 = 12$ electrons contributed by As^{3+} plus 6 electrons contributed by $3d^6$ Mn^{1+}. In the absence of spectroscopic or other independent evidence, we are forced to conclude, for the present, that the formal charge is Mn^{1+}.

To our knowledge, magnussonite is the first example in a natural crystal of a metallic core embedded in an ionic oxide matrix. Armangite's structure has been refined ($R = 0.15$), but we are presently collecting data on a larger crystal to obtain more complete recovery of the weak reflections. Its formula is $Mn_{26}^{2+}[As_6^{3+}O_{14}(OH)_4][As_6^{3+}\square O_{18}]_2(CO_3)$, $Z = 1$,

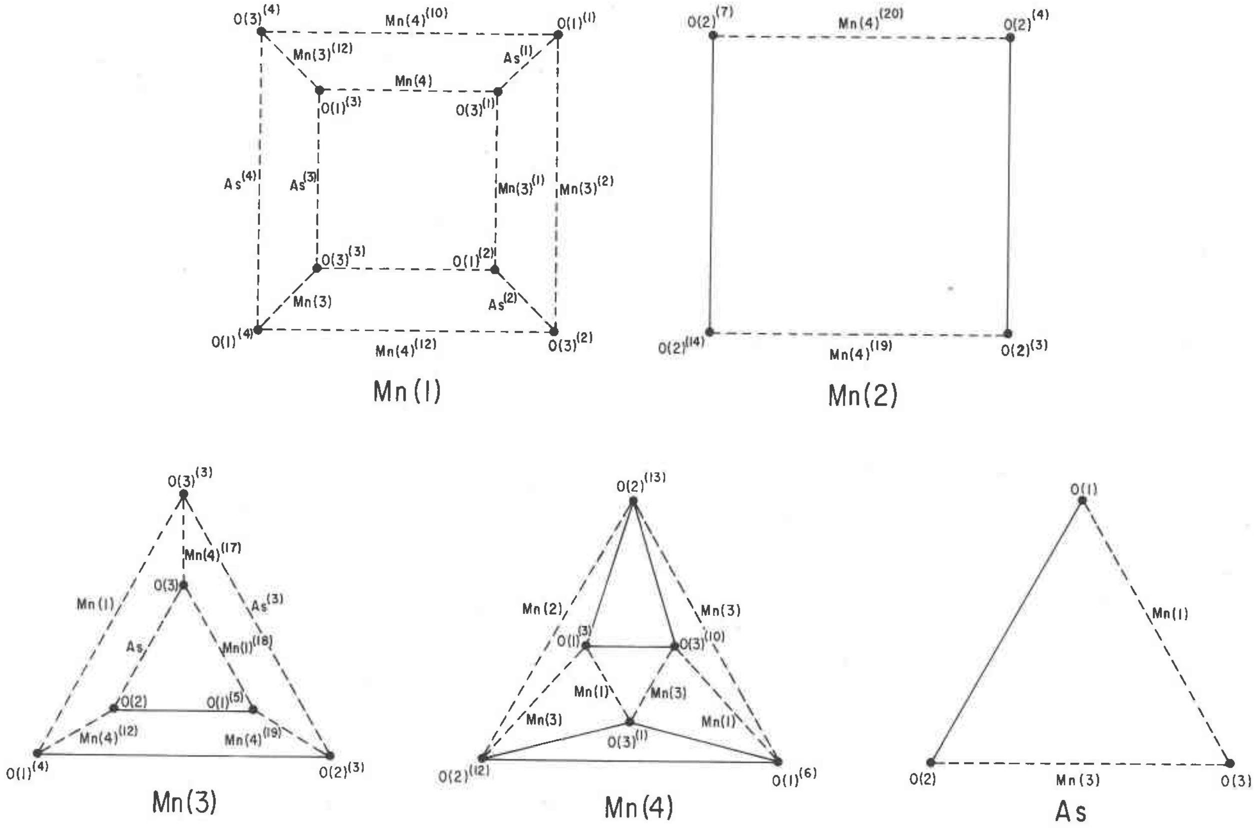

Fig. 3. Schlegel diagrams of the coordination oxygen polyhedra in magnussonite showing shared edges (dashed). The neighboring atom is identified with each shared edge. Superscripts in this and other figures refer to equivalent points in Table 4 acting upon atomic coordinate parameters listed in Table 5.

space group $P\overline{3}$. Therefore, we inquire further about its paragenesis.

Specimens of magnussonite (and armangite) present the following features. The crystals grew in open fissures which cut manganese (braunite + hausmannite) and iron (hematite + magnetite) oxide ores at Långban. The associated minerals indicate basic and reduced conditions of formation: native lead, Pb^0, trigonite, $Pb_3Mn(AsO_3)_2(AsO_2OH)$; dixenite, $Mn_{11}^{2+}Mn_4^{3+}(OH)_8(AsO_3)_6(SiO_4)_2$; pyrochroite, $Mn(OH)_2$; α-domeykite, α-Cu_3As; barite, $BaSO_4$; and basic lead carbonates (hydrocerussite and plumbonacrite). At Sterling Hill, magnussonite coexists with pyrochroite, basic arsenates and arsenites of Mn^{2+} and barite. These geochemically peculiar assemblages are indicative of highly basic and reducing conditions. Indeed, it has been proposed by Boström (1965) that Pb^0, hydrocerussite $[Pb_3(OH)_2(CO_3)_2]$, $Mn(OH)_2$, and sulfate ions are stable together at pH ≈ 10.5 and $e \approx -0.42$ volts (25°C). Such conditions geochemically require reactions under stagnant conditions, and the probable source of these was the earlier reaction of sulfides (ZnS and PbS), common as remnants in some of these veins, with oxides of Mn^{2+} and Mn^{3+} in carbonate host rocks.

The Mn(3)O$_6$ trigonal prism

A distorted trigonal prismatic oxygen coordination for Mn(3) is achieved by the removal of two anions on the edge of a cube (Figs. 1a, 1b). Figure 2b clearly shows that the triangular faces are nearly eclipsed. Seven of the nine edges are shared by other polyhedra (Fig. 3). The three independent Mn(3)–O distances range from 2.03 to 2.44A (average 2.24A) which corresponds to $Mn^{2+}O_6$. We can more fully appreciate the geometry of this polyhedron by comparing its O–Mn(3)–O′ angles with those of the sectioned cube and the "ideal" trigonal prism (all nine edges equal); see Table 8. The sectioned cube would have angles of 70.52° to the edges and 109.46° to the face diagonals. For the ideal trigonal prism, the nine edge angles would be 81.70° and the six square face diagonals would be 135.53°. It is clearly seen that the polyhedron in magnussonite resembles the ideal trigonal

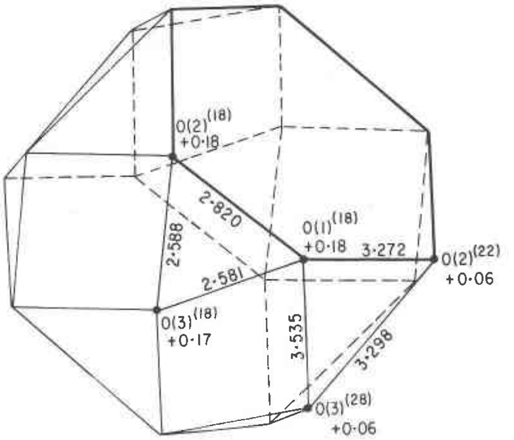

Fig. 4. The oxygen polyhedron, consisting of eighteen vertices, which is centered on MX at 1/2 1/2 0. It possesses point symmetry $\bar{3}$. The asymmetric unit of vertices and edge lengths are labelled.

prism more than the sectioned cube, and this is achieved by small movements (<0.55A) of the anions away from the ideal fluorite cube positions. The unusually acute O(2)–Mn(3)–O(3) = 66.80° angle is a consequence of edge-sharing with the [AsO_3] trigonal pyramid, resulting in the short O(2)–O(3) = 2.588A distance.

The Mn(1)O₈ cube

Mn(1), which occurs in the special position $\bar{4}$ of equipoint rank number 24 and exhibits no disorder, is a distorted cube whose eight vertices in the fluorite frame are occupied by oxygens. All twelve edges are shared by other polyhedra, a feature also found in the related structure of braunite, $Mn^{2+}Mn_6^{3+}SiO_{12}$, another fluorite derivative structure (Moore and Araki, 1976a). The Mn(1)–O = 2.420A average is identical to that found in the related structure of parwelite, $Mn_{10}^{2+}Sb_2^{5+}As_2^{5+}Si_2^{4+}O_{24}$, reported by Moore and Araki (1977). In braunite, the Mn(1)–O average is 2.327A, and we suspect that the Ca^{2+} reported is ordered over the cube position in magnussonite, as we suggested earlier for parwelite. This conclusion is reached since it is not possible to discriminate between (Mn,Ca) and (Mn,Mg) solid solution when the site distributions are allowed to vary, and we are forced to make appeal to ionic radius relationships. Inspection of the bond angles in Table 8 suggests that the distortion of the cube is largely a result of the kinds of polyhedra sharing edges with it: O(1)–O(3) = 2.581A, O(1)–Mn(1)–O(3) = 63.9° also associated with the small tightly bound [AsO_3] trigonal pyramid.

The "cavity" at 1/8 1/8 1/8 and the Mn(2) site

As seen in Figure 1b, the "fluorite" cation position at 1/8 1/8 1/8 (point symmetry 32) is surrounded by eight vacancies, resulting in a large open cavity. The cavity is occupied by 16 atoms per cell (called ClW) although they are substantially disordered, their positions displaced 0.46A away from the invariant point and along the two-fold rotor. Thus, they occupy on the average 1/3 of the site of point symmetry 2, with minimum ClW–ClW = 0.789A separation. According to our site refinement and from the chemical analysis, the atoms are chlorine and oxygen. The refinement converged to average 0.80 Cl and 0.20 O, leading to 12.8 Cl in the cell, substantially larger than 5.17 Cl based on the chemical analysis. The ClW–ClW separation is too short for a Cl–Cl bond, and we believe that chlorine and oxygen at this site are formally Cl^- and OH^-. They are coordinated to two disordered Mn(2) atoms resulting in Mn(2)–ClW = 2.80A. This distance is 0.30A longer than the predicted $^{[5]}Mn^{2+}$–Cl^- = 2.51A distance based on ionic radii.

The Mn(2) site on the two-fold rotor is another curiosity piece. It is clearly seen in Figures 1a and 1b as a slightly twisted square plane of oxygens with the Mn(2) atoms displaced 0.48A away from the special positions of point symmetry 222. Thus, it is disordered in the same way as ClW. Including ClW in its coordination sphere, the resulting polyhedron is on the average a distorted elongate square pyramid. The Mn(2)–O distances are Mn(2)–O(2)$^{(3)}$ = 2.008A(×2) and Mn(2)–O(2)$^{(4)}$ = 2.197A(×2) with an Mn(2)–O = 2.102A average.

We cannot at present offer a satisfactory explanation for the anomalously long Mn(2)–ClW distance based solely on its coordination to Mn(2). However, a provisional interpretation is offered. If the [As_6MnO_{18}] cluster is considered, the oxygen vertices define a polyhedron of point symmetry $\bar{3}$ with 36 edges, 18 vertices, 2 hexagonal faces, 12 triangular faces, and 6 quadrilateral faces (Fig. 4). The edge lengths range from 2.58A to 3.54A. The two hexagonal "windows" are the only open regions in the cluster. The windows are normal to the 3-fold axis and the ClW are situated above and below these windows (see Fig. 1b in conjunction with Fig. 4). We suspect that a substantial net bond toward the window is experienced by ClW. This geometry is advanced as a clue to possible new types of compounds involving the [As_6MnO_{18}] cluster.

Concluding remarks

We summarize the unusual structural properties found in magnussonite. First, the compound is an anion-deficient fluorite derivative structure of general formula $X_{32}O_{36}\square_{28}$ and, at first glance, would appear to be yet another example of a complex ionic solid. Second, two of the X's are not cations but disordered (Cl,OH) anions. Third, twelve of the X's are As^{3+} ions which octahedrally coordinate to central Mn^{1+} not included in the above general formula. That fraction of the structure can be written $[As_6^{3+}Mn^{1+}O_{18}]_2$. Fourth, the remaining 18 Mn^{2+} cations exhibit a range of coordinations by oxides. By writing the coordination numbers as bracketed superscripts, we can cast magnussonite's formula unit as

$$^{[8]}Mn_3^{2+}\,^{[4+1]}(Mn^{2+},Cu^{2+})_3\,^{[6]}Mn_6^{2+}\,^{[6]}Mn_6^{2+}\ [^{[3]}As_6^{3+}\,^{[6]}Mn^{1+}O_{18}]_2Cl_2, \qquad Z = 8$$

Few ionic crystals enjoy such a variety of exotic structural features!

At least locally, magnussonite and the related armangite occurred in fairly sizeable crystalline masses, suggesting that the compounds should be synthesizable. Solid masses of magnussonite up to several grams in weight are known, and armangite has been found as hexagonal crystals up to a centimeter on an edge. A variety of possible compounds can be conceived, and several questions can be asked. By isomorphic substitution is it possible to "isolate" the central cluster, *viz.* $Ca_3Mg_{15}[As_6XO_{18}]_2Cl_2$ in place of $Mn_{18}^{2+}[As_6^{3+}Mn^{1+}O_{18}]_2Cl_2$? If so, then it would be interesting to examine which metals can substitute for X. For example, can X correspond to an isoelectronic series Cr^0, Mn^{1+}, Fe^{2+}? Is it possible to form a closed xenon core, that is $X = Mo^0, Tc^{1+}, Ru^{2+}$? Finally, is it possible to isolate $[As_6XO_{18}]$ as a discrete ion in solution or as $[As_6^{3+}X(n)O_{18-y}(OH)_y]^{n+y-18}$? If the polyhedron in Figure 4 is intrinsically stable, is it possible to form the simple adduct $FeCl_2 + 6\ As(OH)_3 \rightarrow [As_6^{3+}Fe^{2+}(OH)_{18}]Cl_2$? We hope to address these questions through attempted synthesis of magnussonite and these related compositions.

Acknowledgments

This study was supported by NSF grant EAR-19483 (Geochemistry) and a Materials Research Laboratory grant (NSF) awarded to The University of Chicago. We appreciate donation of a fragment of type magnussonite by Dr. Eric Welin of the Swedish Natural History Museum.

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Manuscript received, May 22, 1978;
accepted for publication, October 3, 1978.