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Holdenite, a novel cubic close-packed structure

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Abstract

Holdenite, $(Mn_{0.91}Mg_{0.09})_6Zn_3(OH)_8(AsO_4)_2(SiO_4)$, $Z = 8$, orthorhombic, space group *Abma*, $a = 11.99(1)$, $b = 31.46(4)$, $c = 8.697(6)$A, is a novel structure type based on cubic close-packing of oxygens. $R = 0.064$ for 3478 independent reflections.

The complex structural formula can be written on the basis of cation coordination numbers in superscripts: $^{[6]}Mn_6(OH)_2{}^{[4]}[Zn(OH)_4]^{[4]}[Zn_2(OH)_2(AsO_4)_2(SiO_4)]$. An open tetrahedral sheet of composition $^2_\infty[Zn_2SiO_6(OH)_2]$, oriented parallel to {010}, further links to AsO_4 tetrahedra to form thick slabs of composition $^2_\infty[Zn_2As_2SiO_{12}(OH)_2]$. Insular $Zn(OH)_4$ tetrahedra also occur in the structure. These link to complex aggregates of $Mn(O,OH)_6$ condensed octahedra to form a framework structure. One plane of close-packing is (051); the structure derives from the ordering of different cations over $M_3T_3\phi_{10}$ (where M = octahedral populations, T = tetrahedral populations, ϕ = anions). The $M_3T_3\phi_{10}$ scheme preserves the same space group and cell shape as holdenite, so the compound is not an ordered derivative structure of some simpler arrangement.

Bond distance averages are Mn(1)–O = $Mn_{0.53}Mg_{0.47}$–O = 2.15A, Mn(2)–O = $Mn_{0.92}Mg_{0.08}$–O = 2.21A, Mn(3)–O = 2.21A, Mn(4)–O = 2.22A, Zn(1)–O = 1.98A, Zn(2)–O = 1.95A, As–O = 1.69A and Si–O = 1.64A. Five distinct hydrogen bonds were located, ranging from OH···O = 2.89 to 3.22A.

Introduction

Holdenite, a supposed complex basic arsenate of manganese and zinc, occurs as an extremely rare fissure mineral from the famous zinc mines at Franklin, Sussex County, New Jersey. Evidently, only one specimen is known, and a portion of that was sacrificed for the original study of Palache and Shannon (1927). The mineral occurs implanted upon franklinite ore along a slickenside; associated minerals are barite, galena, pyrochroite, and willemite, indicating rather basic conditions for its formation.

Our interest in holdenite's atomic structure was drawn not from its rarity, but from an X-ray study by Prewitt-Hopkins (1949), the cell parameters of which suggested oxygen cubic close-packing. She proposed the formula $(Mn,Ca)_{25}(Zn,Mg,Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}$, $Z = 2$. In the initial portion of this study, we elected the simpler formula $Mn_4Zn_2(AsO_4)O_2(OH)_5$ proposed by Palache and Shannon. The present work on holdenite, therefore, constitutes a portion of a general study on complex ordering schemes of cations over a dense-packed anion frame, as well as being a step toward unravelling the gargantuan structure of the related mineral macgovernite, $Mg_4Mn_9Zn_2(SiO_4)_2(AsO_4)_2O(OH)_{14}$, $R\bar{3}c$, $a_h = 8.22$A, $c_h = 205.5$A (Wuensch, 1960).

Experimental section

Earlier investigations on holdenite include the original study by Palache and Shannon (1927), who presented the descriptive and chemical details of the new species including careful morphological examination, and X-ray single-crystal and powder investigation by Prewitt-Hopkins (1949). Unfortunately, those studies yielded results which are not entirely correct, and reinterpretation of the species was required, based on the success of the crystal structure analysis.

A single crystal from the holotype (Harvard University number 89996) was kindly provided by Professor C. Frondel, who permitted its removal from the only known specimen. Calibrated precession photographs using Mo$K\alpha$ radiation gave cell parameters

a = 11.99(1), b = 31.46(4), c = 8.697(6)A, space group *Abma*. The cell parameters agree fairly well with the earlier study of Prewitt-Hopkins who reported a = 11.99, b = 31.21, c = 8.60A,[1] but we cannot agree on her space-group orientation *Bmam*. Extinction criteria, observed on precession films and from the three-dimensional diffractometric data, are: hkl, $k + l \neq 2n$, $0kl$, $k \neq 2n$, $hk0$, $h \neq 2n$. The success of the crystal structure analysis and the holosymmetric development reported by Palache and Shannon support the space group *Abma*.

The crystal, a fragment of irregular pyramidal shape, was carefully measured and aligned with its c axis parallel to the rotation axis of a *Pailred* semi-automated diffractometer. Salient details: Mo$K\alpha$ (λ = 0.7093A) radiation with graphite monochromator; scan speed 1°/min; 20-second stationary background counts on each side of the peak; full scan widths 2.8° widening out to 6.0° for strong intensities and higher levels; scan range to $\sin\theta/\lambda$ = 0.8 for each level. Data were collected up through the l = 12 level.

We assumed the formula and specific gravity of 4.11 proposed by Prewitt-Hopkins (1949); we obtained μ = 133.8 cm^{-1} (Mo$K\alpha$) for the linear absorption coefficient based on the formula $Mn_4Zn_2(AsO_4)O_2(OH)_5$; Z = 14. This value is practically identical (μ = 133.9 cm^{-1}) to that calculated from the correct formula discussed further on. The crystal shape was approximately described by nine planes, and using the Gaussian integral method with a division of seven grid points (Burnham, 1966), an absorption correction was applied. The symmetry equivalent pairs, $I_o(hkl)$ and $I_o(\bar{h}kl)$, were then averaged, and after applying Lorentz and polarization corrections 3478 independent F_o were obtained. "Unobserved reflections" are those with $I(hkl) < \sigma(I)$, and their intensities were readjusted to $I(hkl) = \sigma(I)$. Weights assigned to the individual F_o's included factors related to counting statistics, crystal misorientation (±0.025°), inclination angle missetting error (±0.1°), and $\Delta\mu$ = 1.5 cm^{-1}. Supplemental tests for centrosymmetry included the $N(z)$ test calculated on the sets hkl, $h0l$, $hk0$, $0kl$ (Srikrishnan and Parthasarathy, 1970), all of which indicated a centrosymmetric crystal structure.

Solution and refinement of the structure

A three-dimensional Patterson map $P(u,v,w)$ revealed a halite-like substructure $a = c/2$, $a/2\sqrt{2}$, $b/5\sqrt{2}$ with additional vectors at the tetrahedral interstices. It was immediately realized that the solution of the structure would prove a very difficult problem. Based on a halite cubic close-packing, all atoms must have coordinates related by $x \pm q/8$, $y \pm r/20$, $z \pm s/8$, where q, r, s are integers. A halite grid was then constructed, and it was noted that the origin of the cell could be placed on either an octahedral edge or an octahedral center. The problem then reduced to the combinatorial ways of distributing octahedral populations over the asymmetric unit; tetrahedral populations would be automatically defined on electrostatic grounds. For complete cubic close-packing, there must be 160 anions in the cell which, with assumed $Mn_4Zn_2[AsO_4]O_2(OH)_5$, requires about 14 such formula units. We then assumed that Mn^{2+} occurred in octahedral coordination, and Zn and As in tetrahedral coordination, and derived patterns for 56 octahedral populations in the cell.

One arrangement gave R = 0.45 for 56 octahedra (Mn^{2+}), 16 As^{5+} tetrahedra, and 24 Zn^{2+} tetrahedra. A β synthesis (Ramachandran and Srinivasan, 1970) suggested eight of these octahedra were empty. In addition, a small electron density contribution appeared at 1/4 1/4 z. Subsequent syntheses revealed all oxygens in the cell, and a bond-distance calculation suggested that the small contribution corresponds to Si^{4+}. The ideal formula now stood at $Mn_6Zn_3As_2SiO_{12}(OH)_8$. Convergency by least-squares refinement was rapid.

Scattering curves for Mn^{2+}, Mg^{2+}, Zn^{2+}, As^{5+}, Si^{4+}, and O^{1-} were obtained from Cromer and Mann (1968), and anomalous dispersion corrections, $\Delta f''$, for Mn, Zn, and As from Cromer and Liberman (1970). Since the earlier-reported chemical analysis showed the presence of MgO, two curves were applied to the independent Mn positions, $x Mn^{2+}$ and $(1 - x)Mg^{2+}$, initially setting x = 1.0. Subsequent refinement converged to R = 0.064, and R_w = 0.081 for all 3478 reflections, where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \text{ and } R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma_w|F_o|^2}\right]^{1/2}$$

with $w = \sigma^{-2}$ of F_o. Refinement minimized $w(F_o - F_c)^2$. The secondary extinction coefficient used was c_o = 1.3(1) × 10^{-7} and the overall scale factor, s = 1.011(3). The "goodness-of-fit," $\Sigma_w(F_o - F_c)^2/\Sigma(n - m)$, where n = number of independent data and m = number of parameters is 1.26. The data-to-variable parameter ratio is about 50:1.

Table 1 lists the refined atomic coordinates and isotropic thermal vibration parameters for holdenite,

[1] After conversion from kX to Angström units (1A = 1.00202 kX).

Table 1. Holdenite. Atomic coordinate parameters and isotropic thermal vibration parameters†

Atom			x	y	z	B(Å²)	Ideal		
Mn(1)*	2	8	0	0.10108(4)	0	0.91(3)	0	2/20	0
Mn(2)**	2	8	0	0.20493(3)	0	0.79(2)	0	4/20	0
Mn(3)	1	16	0.37353(6)	0.05137(2)	0.21843(8)	1.00(1)	3/8	1/20	2/8
Mn(4)	1	16	0.36297(6)	0.15428(2)	0.22701(8)	0.84(1)	3/8	3/20	2/8
Si	2	8	1/4	1/4	0.1150(2)	0.59(2)	2/8	5/20	1/8
O(1)	1	16	0.1347(2)	0.2522(1)	0.0142(3)	0.80(4)	1/8	5/20	0
O(2)	1	16	0.2473(3)	0.2063(1)	0.2158(3)	0.89(4)	2/8	4/20	2/8
As	1	16	0.12961(3)	0.10069(1)	0.36268(5)	0.64(1)	1/8	2/20	3/8
O(3)	1	16	0.1346(3)	0.1453(1)	0.4742(4)	0.89(4)	1/8	3/20	4/8
O(4)	1	16	0.1382(3)	0.0578(1)	0.4761(4)	1.04(4)	1/8	1/20	4/8
O(5)	1	16	0.0089(3)	0.1010(1)	0.2597(4)	0.99(4)	0	2/20	2/8
O(6)	1	16	0.2396(3)	0.1020(1)	0.2405(4)	0.95(4)	2/8	2/20	2/8
Zn(1)	m	8	0.11099(6)	0	0.10650(8)	0.86(1)	1/8	0	1/8
OH(1)	m	8	0.2517(4)	0	0.2276(5)	0.89(6)	2/8	0	2/8
OH(2)	m	8	-0.0034(4)	0	0.2700(5)	0.95(6)	0	0	2/8
OH(3)	1	16	0.1173(3)	0.0511(1)	-0.0247(4)	0.92(4)	1/8	1/20	0
Zn(2)	1	16	0.13073(4)	0.20123(2)	0.36797(5)	0.79(1)	1/8	4/20	3/8
OH(5)	1	16	-0.0092(3)	0.2022(1)	0.2552(4)	0.89(4)	0	4/20	2/8
OH(4)	1	16	0.1113(3)	0.1502(1)	-0.0308(4)	0.91(4)	1/8	3/20	0

†Estimated standard errors in parentheses refer to the last digit. *Ideal* refers to perfect packing. Point symmetries and rank numbers follow the atom designations.

*Refined to 0.53(1) Mn^{2+} + 0.47(1) Mg^{2+}.

**Refined to 0.92(1) Mn^{2+} + 0.08(1) Mg^{2+}.

and Table 2 presents the structure factors.[2] There are four Mn, two Zn, one As, one Si, and eleven O atoms in the asymmetric unit. The isotropic thermal vibration parameters range between $0.59A^{-2}$ (Si) to $1.04A^{-2}$ (O), and are reasonable for a dense-packed oxide structure. In addition, Mn(1) and Mn(2) are partly replaced by Mg^{2+}, the site occupancies having refined to $0.53(1)Mn^{2+} + 0.47(1)Mg^{2+}$ and $0.92(1)Mn^{2+} + 0.08(1)Mg^{2+}$ respectively. There is no indication of substitution over any other site, and the interatomic distances and electrostatic bond strength sums essentially substantiate the formula $Mn_{5.45}Mg_{0.55}Zn_3(OH)_8(AsO_4)_2(SiO_4)$, which, referred to an ideal end-member, is $Mn_6Zn_3(OH)_8(AsO_4)_2(SiO_4)$, $Z = 8$.

This final composition is at variance with the chemical results given by Palache and Shannon (1927), which are repeated in Table 3. We note, however, that SiO_2 was attributed to presence of willemite and was deducted as that mineral. CO_2 was shown to be present as calcite. Owing to the great rarity of the species, only a few hundred milligrams could be sacrificed for the analysis. We agree well on MnO and H_2O, but their As_2O_5 and SiO_2 appear to be too low, and ZnO too high. Our cell contents give a calculated density of 4.11 g cm^{-3}, in perfect agreement with the observed specific gravity of 4.11 ± 0.01 (Prewitt-Hopkins, 1949). Owing to sensitivity of thermal vibration parameters with assigned scattering curves, the structure analysis is in effect a chemical analysis, subsequently confirmed by the bond distance and electrostatic bond-strength sum calculations. An electron microprobe analysis, utilizing a solid-state detector, revealed an average of 5.48 percent SiO_2, thus confirming the results of the structure study (Table 3). Ca and Fe were sought but not detected (<0.05%).

From the structure data, we calculated a powder pattern; its stronger reflections above 1.50A are com-

[2] To obtain a copy of Table 2, order document No. AM-77-041 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.

Table 3. Holdenite. Chemical analysis and theoretical composition based on structure refinement

	1	2	3	4
CaO	3.80	2.47	<0.05	---
MnO	37.75	38.71	37.25	38.10
ZnO	28.08	28.79	25.52	24.06
MgO	1.45	1.49	n.d.	2.18
FeO	1.80	1.85	<0.05	---
SiO_2	2.01	2.06	5.48	5.92
As_2O_5	17.40	17.84	19.25	22.65
H_2O	6.62	6.79	n.d.	7.09
CO_2	[1.09]	---	---	---
	100.00	100.00	[87.60]	100.00

[1]Palache and Shannon (1927). CO_2 was assumed by difference. Specific gravity = 4.11 (Prewitt-Hopkins, 1949).

[2]Recalculated to 100% after deducting 2.48% $CaCO_3$.

[3]Electron probe analysis (this study). Also found 0.43% Al_2O_3. n.d. = present but not determined. The analysis employed a solid state detector for Mn, Zn, Si and As. Standards include wyllieite (Mn), synthetic ZnO (Zn), anorthite (Si) and $CoAs_2$ (As). Operating conditions: 0.1 μA, 15kV. Corrections were applied to Mn, Zn and Si using the local program SSOLID developed by Dr. I. M. Steele. No correction was applied for As. Mg was not determined owing to overlap with AsLα.

[4]For $Mn_{5.45}Mg_{0.55}Zn_3(OH)_8(AsO_4)_2(SiO_4)$, ρ = 4.11 g cm^{-3}.

pared in Table 4 with the data given by Prewitt-Hopkins (1949) and our redetermination of powder data from a pattern taken by a Gandolfi camera. We suspect that many reflections were overlooked in the earlier study; indeed, examination of the reproduced powder film in that study reveals an inferior pattern. The new data are in good agreement with the calculated pattern, although the effect of absorption is pronounced. We did not correct for this effect, because powder patterns are often used as determinative tools and so should be reported without that correction. The calculated pattern affords the best reference material for future samples corrected for the absorption effect. Agreement with the Prewitt-Hopkins data is poor at best.

Description of the structure

Holdenite represents one of the more elaborate examples of ordered octahedral and tetrahedral populations distributed over a cubic close-packed anion frame. The formula, stating coordination numbers as bracketed superscripts, is $^{[6]}Mn_6^{2+}{}^{[4]}[Zn_3As_2Si]O_{12}(OH)_8$. The c axis is the sum of four M–O bonds, the a axis the sum of four octahedral

Table 4. Holdenite. Observed and calculated powder patterns

Observed*		Observed†		Calculated			Observed*		Observed†		Calculated		
I/Io	d(obs)	I/Io	d(obs)	I/Io	d(calc)	hkℓ	I/Io	d(obs)	I/Io	d(obs)	I/Io	d(calc)	hkℓ
				7	7.864	040	5	2.704	1	2.72	17	2.721	133
				2	5.993	200	8	2.583	2	2.60	45	2.601	213
5	5.740	6	5.83	18	5.844	131	2	2.546			9	2.566	362
				1	5.243	060					19	2.493	1.10.2
3	4.617	2	4.69	11	4.691	151	7	2.464	8	2.47	41	2.474	2.11.1
				3	4.465	231	3	2.368	4	2.38	11	2.387	173
3	4.311			10	4.348	002	3	2.246	2	2.34	9	2.257	531
		1	4.15	4	4.191	022	2	2.196	1	2.25	5	2.207	1.12.2
3	4.038			8	4.088	102			1	2.20	5	2.173	2.13.1
2	3.920	1	3.93	7	3.956	122	3	2.161			7	2.170	4.10.0
				3	3.805	042	1	2.137			6	2.149	3.10.2
2	3.765	1	3.76	6	3.788	171	3	2.092	2	2.09	7	2.099	502
8	3.582	9	3.61	28	3.627	142	2	2.083			4	2.090	482
				27	3.607	311	2	2.051	1	2.04	8	2.055	571
				7	3.520	202	2	2.005	1	2.01	4	2.013	3.13.1
6	3.406	2	3.43	38	3.431	331	2	1.942			3	1.949	562
2	3.304	1	3.31	12	3.323	271	1	1.898			1	1.903	084
				12	3.288	280	2	1.828			4	1.836	1.13.3
				7	3.224	162	5	1.781	2	1.79	11	1.788	0.10.4
3	3.124	1	3.14	11	3.146	0.10.0	2	1.763	1	1.77	4	1.769	1.10.4
4	2.981	10	2.99	42	2.997	400	2	1.755			5	1.760	404
				5	2.944	420	3	1.741	1	1.75	8	1.746	5.10.2
3	2.922			10	2.942	302	4	1.695			14	1.701	691
				15	2.892	322	3	1.660			8	1.668	215
10	2.838			100	2.852	291	4	1.640	2	1.63	9	1.643	613
				7	2.834	182	3	1.625			6	1.632	3.10.4
				20	2.824	371	4	1.605	1	1.60	4	1.609	6.11.1
5	2.789			26	2.806	113	4	1.569	1	1.56	20	1.573	0.20.0
				3	2.800	440	2	1.556			2	1.561	742
				6	2.785	2.10.0	8	1.531	3	1.53	60	1.536	4.10.4
				5	2.756	342							

*This study. Single crystal Gandolfi camera (114.6 mm diameter), FeK_α radiation. The film was corrected for shrinkage but the sample was not corrected for absorption. About sixty more lines were observed, with intensities less than 5, below 1.53Å.

†Prewitt-Hopkins (1949).

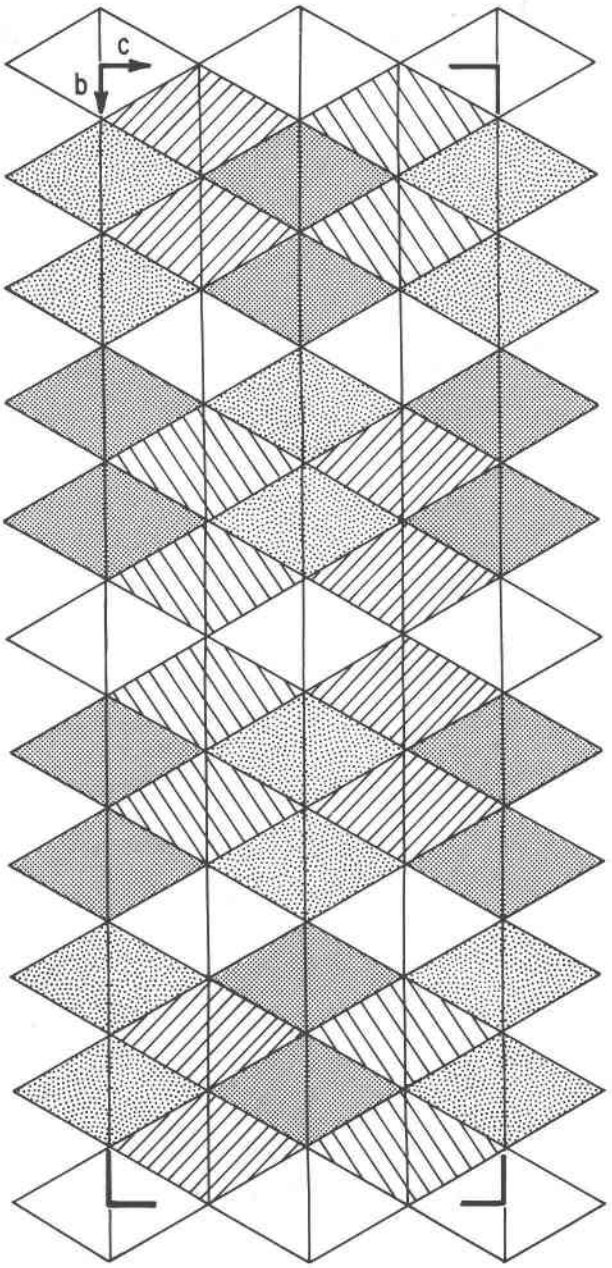

Fig. 1. Idealization of octahedral population between $0 \leq x \leq \frac{1}{2}$. Populations at $x = 0$ are light stippled, $x = 1/8$ hatched NW–SE, $x = 3/8$ hatched NE–SW, and $x = 1/2$ dark stippled. Unpopulated octahedral positions within the region are unshaded.

O–O′ edges, and the b axis the sum of ten O–O′ edges. Referring to the simplest orthogonal unit for oxygen cubic close-packing, the metrical properties are ($m \times$ 4.2A, $n \times$ 3.0A, and $p \times$ 3.0A) where m is some multiple of twice the M–O distance, and n and p are each a multiple of the octahedral edge. All cubic close-packings can be referred to this unit, and it is noted that projections along octahedral edges correspond to the [110] direction and projections along M–O to the [100] direction of the halite anion frame. In addition, there exist $2mnp$ anions to the unit for full occupancy in dense-packing. Thus, holdenite has $m = 2$, $n = 10$, and $p = 4$ with 160 anions in the cell.

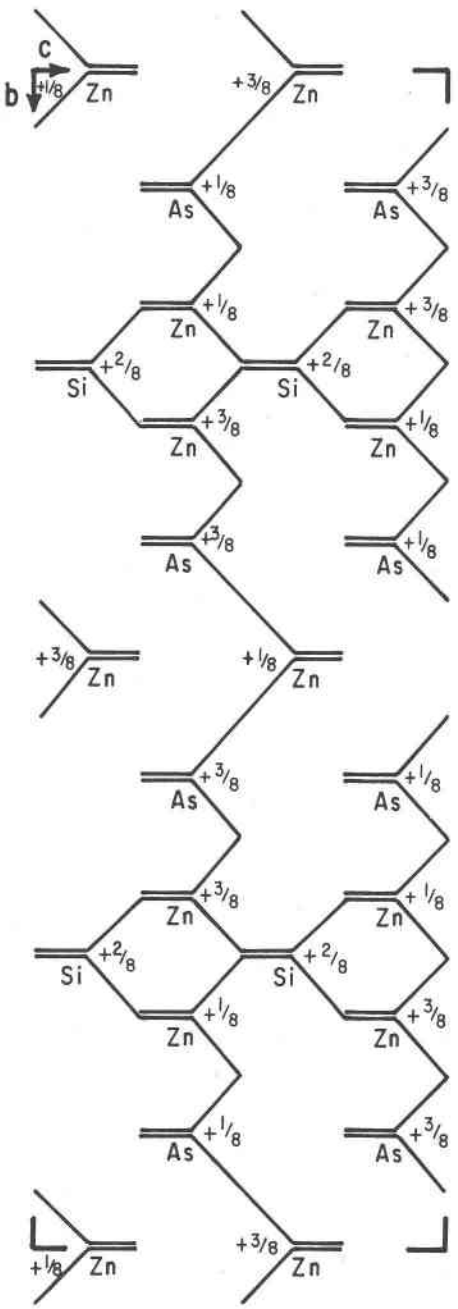

Fig. 2. Idealization of tetrahedral populations as T–O spokes between $0 \leq x \leq \frac{1}{2}$. Heights are given as fractional coordinates in x.

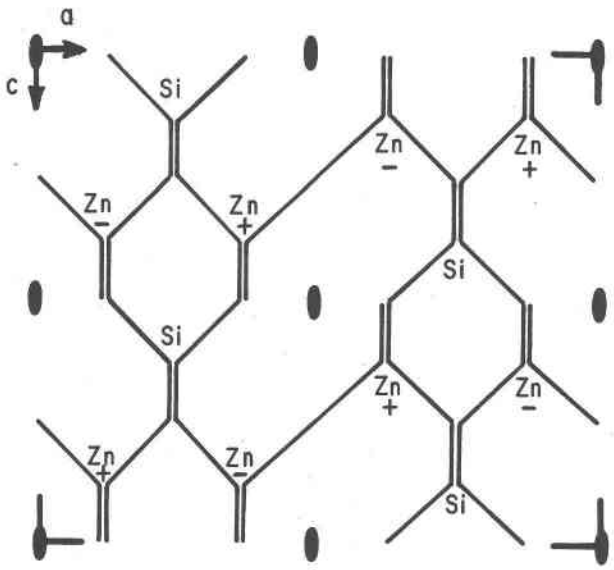

Fig. 3. Idealization of tetrahedral broken sheet drawn as T–O spokes on either side of $y = 1/4$. The "+" and "−" refer to Zn atoms above and below Si. The two-fold rotors are shown.

The general formula can be written $M_6T_6\phi_{20}$ or $M_3T_3\phi_{10}$, where M are octahedral occupancies, T are tetrahedral occupancies, and ϕ are the anions. Thus, three-tenths of the available octahedral voids and three-twentieths of the available tetrahedral voids are occupied by cations. To more fully appreciate the complexity of the holdenite structure, it is noted that if no distinction is made among the *kinds* of cations populating the sites, and if a perfect undistorted model is constructed based on $M_3T_3\phi_{10}$, the space group and cell parameters remain unchanged, *i.e.*, holdenite is a novel structure type, and not a derivative of a simpler arrangement achieved by ordering of different kinds of cations.

The structure is best examined in sections. In Figure 1, an ideal model of the octahedral populations between $0 \leq x \leq ½$ is featured. One of the planes of dense-packed anions is (051). Octahedral voids are populated at $x = 1/8$ and $3/8$ (also $5/8$ and $7/8$) to form edge-sharing arrays four octahedra in length along the [010] direction; and at $x = 0$ and $1/2$ to form edge-sharing doublets along [010]. No octahedral voids are populated at $x = 1/4$ (and $3/4$). According to the structure analysis, the octahedral positions are populated by Mn^{2+} and Mg^{2+}, with Mg^{2+} preferentially occupying the doublets.

The tetrahedral populations are even more complicated. In Figure 2, an ideal model of the tetrahedral populations between $0 \leq x \leq ½$ is featured. $Zn(1)(OH)_4$ is insular and does not link to other tetrahedra. The As and Zn(2) link to form a corner-sharing dimer which is bridged by the SiO_4 tetrahedra to form an incompleted sheet parallel to {010}. A slice of this sheet is seen on either side of $y = 1/4$ in Figure 3. One terminus of the Zn(2)–O tetrahedron does not bridge the other tetrahedra and is an hydroxyl group. The open sheet has composition $^{2}_{\infty}[Zn_2O_2(OH)_2SiO_4] = {}^{2}_{\infty}[Zn_2SiO_6(OH)_2]$, the oxide anions not associated

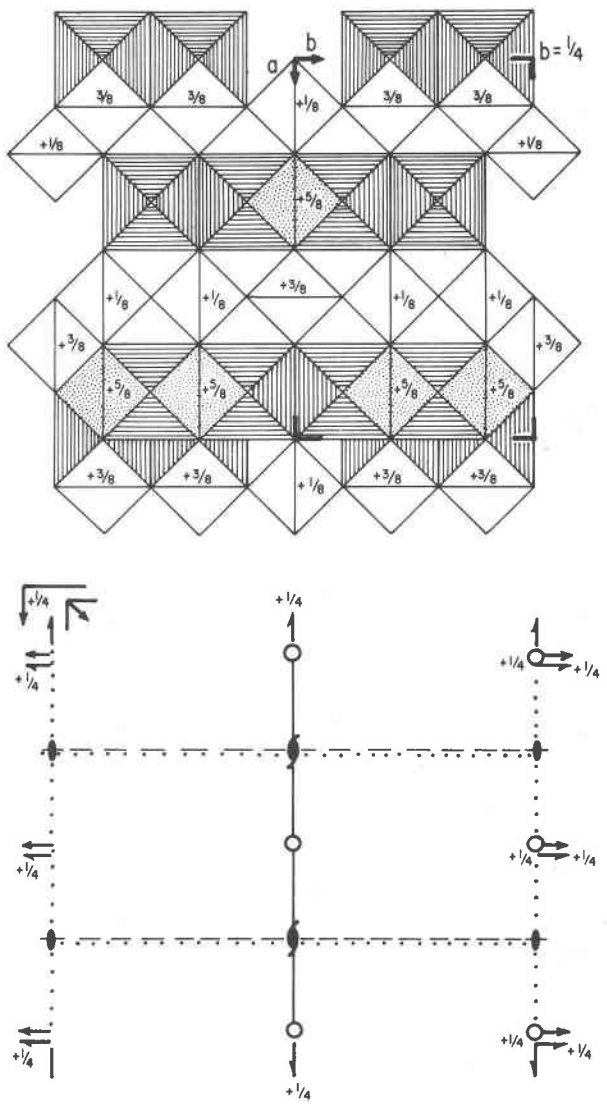

Fig. 4. Idealization of octahedral and tetrahedral populations down the c axis between $-¼ \leq y \leq +¼$. Atoms at $z = 3/4$ and $7/8$ are omitted. Octahedra at $z = 0$ and $1/4$ are ruled. Tetrahedra at $z = 1/8$ and $3/8$ are unshaded and at $5/8$ are stippled. The symmetry diagram which applies to the sketch is shown at the bottom.

Table 5. Holdenite. Bond distances and angles*

Mn(1)		
2 Mn(1)-OH(4)	2.059(4)	
2 Mn(1)-OH(3)	2.121(4)	
2 Mn(1)- O(5)	2.261(4)	
average	2.147Å	
1 OH(4)-OH(4)$^{(4)}$	2.722(6)*	82.7(2)
1 OH(3)-OH(3)$^{(4)}$	2.845(6)	84.3(2)
2 O(5)-OH(4)$^{(4)}$	2.904(6)*	84.3(1)
2 O(5)-OH(3)$^{(4)}$	2.988(6)*	85.9(1)
2 OH(3)-OH(4)	3.119(6)	96.5(2)
2 O(5)-OH(3)	3.205(6)	94.0(1)
2 O(5)-OH(4)	3.207(6)	95.7(1)
average	3.034	90.0
Mn(2)		
2 Mn(2)-OH(4)	2.194(4)	
2 Mn(2)- O(1)	2.199(4)	
2 Mn(2)-OH(5)	2.224(4)	
average	2.206	
1 OH(4)-OH(4)$^{(4)}$	2.722(6)*	76.6(2)
2 OH(5)-OH(4)$^{(4)}$	2.825(6)*	79.5(1)
2 OH(5)- O(1)	3.136(6)	90.4(1)
2 OH(5)- O(1)$^{(4)}$	3.198(6)	92.6(1)
1 O(1)- O(1)$^{(4)}$	3.239(6)	94.9(2)
2 O(1)-OH(4)	3.245(6)	95.2(2)
2 OH(5)-OH(4)	3.308(6)	97.0(1)
average	3.115	90.1
Si		
2 Si - O(2)	1.632(3)	
2 Si - O(1)	1.638(3)	
average	1.635	
2 O(1)-O(2)$^{(1)}$	2.604(5)	105.6(2)
2 O(1)-O(2)	2.643(5)	107.9(2)
1 O(2)-O(2)$^{(1)}$	2.753(7)	115.3(2)
1 O(1)-O(1)$^{(1)}$	2.767(7)	115.0(2)
average	2.669	109.6
Hydrogen Bonds		
OH(1)···O(4)	3.135(6)	
OH(2)···O(4)	3.066(6)	
OH(3)···O(4)$^{(6)}$	2.938(6)	
OH(4)···O(2)	3.220(6)	
OH(5)···O(1)$^{(7)}$	2.888(6)	

Mn(3)		
Mn(3) - O(4)$^{(6)}$	2.122(4)	
Mn(3) -OH(1)	2.180(4)	
Mn(3) -OH(2)$^{(2)}$	2.190(4)	
Mn(3) -OH(3)$^{(6)}$	2.237(4)	
Mn(3) - O(5)$^{(2)}$	2.260(4)	
Mn(3) - O(6)	2.269(4)	
average	2.210	
OH(1) -OH(2)$^{(2)}$	2.936(6)*	84.4(2)
OH(3)$^{(6)}$- O(5)$^{(2)}$	2.988(6)*	83.3(1)
OH(3)$^{(6)}$-OH(2)$^{(2)}$	2.999(6)	85.3(1)
O(4)$^{(6)}$- O(6)	3.060(6)	88.3(1)
OH(3)$^{(6)}$- O(6)	3.111(6)	87.3(1)
OH(3)$^{(6)}$-OH(1)	3.113(6)	89.6(1)
O(4)$^{(6)}$-OH(1)	3.136(6)	93.6(1)
O(5)$^{(2)}$-OH(2)$^{(2)}$	3.182(6)	91.3(2)
O(4)$^{(6)}$- O(5)$^{(2)}$	3.199(6)	93.7(1)
OH(1) - O(6)	3.214(6)	92.5(2)
O(6) - O(5)$^{(2)}$	3.228(6)*	90.9(2)
O(4)$^{(6)}$-OH(2)$^{(2)}$	3.286(6)	99.3(2)
average	3.121	90.0
Mn(4)		
Mn(4) -OH(4)$^{(6)}$	2.133(4)	
Mn(4) - O(2)	2.146(4)	
Mn(4) -OH(5)$^{(2)}$	2.155(4)	
Mn(4) - O(6)	2.214(4)	
Mn(4) - O(3)$^{(6)}$	2.217(4)	
Mn(4) - O(5)$^{(2)}$	2.425(4)	
average	2.215	
OH(4)$^{(6)}$-OH(5)$^{(2)}$	2.825(6)*	82.4(1)
OH(4)$^{(6)}$- O(5)$^{(2)}$	2.904(6)*	78.9(1)
O(2) -OH(5)$^{(2)}$	2.932(6)	86.0(2)
OH(4)$^{(6)}$- O(6)	3.074(6)	90.0(1)
O(3)$^{(6)}$- O(6)	3.081(6)	88.1(1)
O(3)$^{(6)}$- O(2)	3.176(6)	93.5(1)
OH(5)$^{(2)}$- O(5)$^{(2)}$	3.191(6)	88.1(1)
O(3)$^{(6)}$- O(5)$^{(2)}$	3.203(6)	87.1(1)
O(5)$^{(2)}$- O(6)	3.228(6)*	88.1(1)
O(6) - O(2)	3.286(6)	97.8(2)
OH(4)$^{(6)}$- O(2)	3.291(6)	100.6(1)
O(3)$^{(6)}$-OH(5)$^{(2)}$	3.317(6)	98.6(1)
average	3.126	89.9

Zn(1)		
2 Zn(1) -OH(3)	1.972(4)	
1 Zn(1) -OH(2)	1.976(5)	
1 Zn(1) -OH(1)	1.988(5)	
average	1.977	
1 OH(1) -OH(2)	3.080(8)	102.0(2)
2 OH(1) -OH(3)	3.161(5)	105.9(1)
1 OH(3)$^{(3)}$-OH(3)	3.215(5)	109.1(2)
2 OH(2) -OH(3)	3.354(5)	116.3(1)
average	3.221	109.3
Zn(2)		
Zn(2) - O(2)	1.931(3)	
Zn(2) - O(1)$^{(5)}$	1.940(4)	
Zn(2) -OH(5)	1.943(4)	
Zn(2) - O(3)	1.988(4)	
average	1.951	
O(2) -OH(5)	3.096(6)	106.1(2)
O(3) -OH(5)	3.131(6)	105.6(1)
O(1)$^{(5)}$-OH(5)	3.179(6)	109.9(1)
O(1)$^{(5)}$- O(2)	3.203(6)	111.7(1)
O(1)$^{(5)}$- O(3)	3.243(6)	111.3(2)
O(2) - O(3)	3.249(6)	112.0(1)
average	3.184	109.4
As		
As - O(4)	1.673(4)	
As - O(6)	1.694(4)	
As - O(5)	1.702(4)	
As - O(3)	1.707(4)	
average	1.694	
O(3) - O(6)	2.751(5)	108.0(2)
O(3) - O(4)	2.751(6)	109.0(2)
O(4) - O(6)	2.758(5)	110.0(2)
O(5) - O(6)	2.771(6)	109.4(2)
O(3) - O(5)	2.774(5)	108.9(2)
O(4) - O(5)	2.791(5)	111.6(2)
average	2.766	109.5

*Estimated standard errors in parentheses refer to the last digit. The equivalent positions (referred to Table 1) are (1) = ½-x, ½-y, z; (2) = ½+x, y, ½-z; (3) = x, -y, z; (4) = -x, y, -z; (5) = x, ½-y, ½+z; (6) = ½-x, y, ½+z; (7) = -x, ½-y, ½-z.

Table 6. Holdenite. Relations in bond strength-bond length*

	Coordinating Cations											Bond Length Deviations							
Anions	Si	As	Zn(1)	Zn(2)	Mn(1)	Mn(2)	Mn(3)	Mn(4)	H_d	H_a	Δp_x	Si	As	Zn(1)	Zn(2)	Mn(1)	Mn(2)	Mn(3)	Mn(4)
O(1)	1	-	-	1	-	1	-	-	-	-	+0.00	+0.00	-----	-----	-0.01	-----	-0.01	-----	-----
O(2)	1	-	-	1	-	-	1	-	-	1	+0.00	+0.00	-----	-----	-0.02	-----	-----	-----	-0.07
O(3)	-	1	-	1	-	-	-	1	-	-	+0.08	-----	+0.01	-----	+0.04	-----	-----	-----	+0.00
O(4)	-	1	-	-	-	-	1	-	-	2	-0.08	-----	-0.02	-----	-----	-----	-----	-0.09	-----
O(5)	-	1	-	-	1	-	1	1	-	-	+0.25	-----	+0.01	-----	-----	+0.11	-----	+0.05	+0.21
O(6)	-	1	-	-	-	-	1	1	-	-	-0.08	-----	+0.00	-----	-----	-----	-----	+0.06	+0.00
OH(1)	-	-	1	-	-	-	2	-	1	-	+0.00	-----	-----	+0.01	-----	-----	-----	-0.03	-----
OH(2)	-	-	1	-	-	-	2	-	1	-	+0.00	-----	-----	+0.00	-----	-----	-----	-0.02	-----
OH(3)	-	-	1	-	1	-	1	-	1	-	+0.00	-----	-----	-0.01	-----	-0.03	-----	+0.03	-----
OH(4)	-	-	-	-	1	1	-	1	1	-	-0.17	-----	-----	-----	-----	-0.09	-0.01	-----	-0.08
OH(5)	-	-	-	1	-	1	-	1	1	-	+0.00	-----	-----	-----	-0.01	-----	+0.02	-----	-0.06

*Δp_x is the deviation of the bond strength sum from neutrality (p_x=2.00). A bond length deviation is the polyhedral average subtracted from the individual bond distance.

with Si being linked to form Zn–O–As bridges. The inclusion of the AsO_4 tetrahedra above and below the slice at $y = 1/4$ leads to $^{2}_{\infty}[Zn_2(OH)_2(AsO_4)_2(SiO_4)]$ or $^{2}_{\infty}[Zn_2As_2SiO_{12}(OH)_2]$. Thus, the structural formula can be written $^{[6]}Mn^{2+}_{6}(OH)_2{}^{[4]}[Zn(OH)_4]^{[4]}[Zn_2(OH)_2(AsO_4)_2(SiO_4)]$, with the hydroxyl not associated with tetrahedra being identified with OH(4). Thus, holdenite is a complex basic manganous zincosilicoarsenate.

Since holdenite possesses three axes such that nonequivalent atoms overlap in any projection, a two-dimensional representation of its structure is most difficult. A projection down [001] is desirable, and a section is shown in Figure 4. It features the region between $-1/4 \leq y \leq +1/4$. The Mn(3)–and Mn(4)–O octahedra at $z = 1/4$ are shaded as well as the Mn(1)– and Mn(2)–O octahedra at $z = 0$. The edge-sharing array four octahedra in length along [010] and the edge-sharing array two octahedra in length can be immediately recognized. A symmetry diagram is placed alongside the sketch of the structure, and polyhedra at $z = 3/4$ and $7/8$ have been omitted for clarity.

Owing to the rather even distribution of bonds in three dimensions, holdenite possesses no well-developed cleavage direction. Despite the complexity of the structure, the only chromophore present is $^{[6]}Mn^{2+}$, so holdenite possesses a pale pink to reddish-pink color. One wonders how many as yet unknown structures of similar complexity exist, hidden by the mimetic appearance of their crystals and grains with already-defined species.

Bond distances and angles

Individual bond distances, angles, and their averages are listed in Table 5. The polyhedral averages are Mn(1)–O = 2.15A, Mn(2)–O 2.21A, Mn(3)–O 2.21A, Mn(4)–O 2.22A, Zn(1)–O 1.98A, Zn(2)–O 1.95A, As–O 1.69A and Si–O 1.64A. The relatively short Mn(1)–O distance clearly reflects the replacement of about half Mn^{2+} by Mg^{2+}.

The individual distances deviate in accordance with deviations in local electrostatic neutrality of cations about anions. The tetrahedra do not share edges either with themselves or with octahedra. The shortest O–O′ edge distances associated with the octahedra tend be those whose edges are shared between two octahedra. Edges associated with O(5) violate this condition in two notable instances: $O(5)^{(2)}$–O(6) associated with Mn(4) and Mn(3). The explanation lies in the unusually long $Mn(4)–O(5)^{(2)} = 2.43A$ distance, a result of the cation oversaturation about O(5).

Hydrogen bonds and electrostatic valence balances

The complex crystal structure of holdenite presents difficulties in locating hydrogen bonds, and the following technique was adopted to ascertain them. Since OH···O bonds should not occur along edges of occupied octahedra, each hydrogen atom donor, OH(1) to OH(5), was sketched along with its twelve nearest neighbor anions in the cuboctahedral array. Bonds in the cuboctahedron which corresponded to populated octahedral edges were eliminated until the bonds remained which could be potential OH···O bonds. Five bonds could be readily identified: OH(1)···O(4) = 3.14A, OH(2)···O(4) = 3.07A, $OH(3)\cdots O(4)^{(6)}$ = 2.94A, OH(4)···O(2) = 3.22A and $OH(5)\cdots O(1)^{(7)}$ = 2.89A. This arrangement requires that O(4) receives on the average two hydrogen bonds [one from OH(1) and OH(2) each in special positions and one from OH(3)]; O(2) receives one hydrogen bond from OH(4); and O(1) receives one bond from OH(5).

Adopting $s = 5/6$ for a hydrogen-bond donor and $s = 1/6$ for a hydrogen bond acceptor (Baur, 1970), a tabulation of deviations from electrostatic neutrality, Δ_{P_x}, and individual bond distance from the polyhedral average, Δd, can be constructed (Table 6). It is seen that only O(5) and OH(4) deviate significantly from neutrality, with $\Delta_{P_x} = +0.25$ for O(5) and $\Delta_{P_x} = -0.17$ for OH(4). In accordance with these deviations, the deviations in Δd are all positive for O(5) and negative for OH(4). Although we propose that O(2) receives one hydrogen bond and is consequently locally neutral, the distance deviations for Zn(2) and Mn(4) are significantly negative, suggesting that OH(4)···O(2) is a weak bond, which is also supported by the rather long distance for this bond.

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