

## Holdenite, a novel cubic close-packed structure

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### Abstract

Holdenite,  $(\text{Mn}_{0.91}\text{Mg}_{0.09})_8\text{Zn}_3(\text{OH})_6(\text{AsO}_4)_2(\text{SiO}_4)$ ,  $Z = 8$ , orthorhombic, space group *Abma*,  $a = 11.99(1)$ ,  $b = 31.46(4)$ ,  $c = 8.697(6)\text{Å}$ , 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:  $^{[6]}\text{Mn}_6(\text{OH})_2^{[4]}\text{Zn}(\text{OH})_4^{[4]}\text{Zn}_2(\text{OH})_2(\text{AsO}_4)_2(\text{SiO}_4)$ . An open tetrahedral sheet of composition  $^2[\text{Zn}_2\text{SiO}_6(\text{OH})_2]$ , oriented parallel to  $\{010\}$ , further links to  $\text{AsO}_4$  tetrahedra to form thick slabs of composition  $^2[\text{Zn}_2\text{As}_2\text{SiO}_{12}(\text{OH})_2]$ . Insular  $\text{Zn}(\text{OH})_4$  tetrahedra also occur in the structure. These link to complex aggregates of  $\text{Mn}(\text{O},\text{OH})_6$  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,  $\phi$  = 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  $\text{Mn}(1)\text{-O} = \text{Mn}_{0.53}\text{Mg}_{0.47}\text{-O} = 2.15\text{Å}$ ,  $\text{Mn}(2)\text{-O} = \text{Mn}_{0.92}\text{Mg}_{0.08}\text{-O} = 2.21\text{Å}$ ,  $\text{Mn}(3)\text{-O} = 2.21\text{Å}$ ,  $\text{Mn}(4)\text{-O} = 2.22\text{Å}$ ,  $\text{Zn}(1)\text{-O} = 1.98\text{Å}$ ,  $\text{Zn}(2)\text{-O} = 1.95\text{Å}$ ,  $\text{As-O} = 1.69\text{Å}$  and  $\text{Si-O} = 1.64\text{Å}$ . Five distinct hydrogen bonds were located, ranging from  $\text{OH}\cdots\text{O} = 2.89$  to  $3.22\text{Å}$ .

### 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  $(\text{Mn},\text{Ca})_{25}(\text{Zn},\text{Mg},\text{Fe})_{15}(\text{AsO}_4)_7(\text{OH})_{33}\text{O}_{13}$ ,  $Z = 2$ . In the initial portion of this study, we elected the simpler formula  $\text{Mn}_4\text{Zn}_2(\text{AsO}_4)_2\text{O}_2(\text{OH})_5$  proposed by Palache and Shannon. The present work on holdenite, therefore, constitutes a portion of a general study on complex ordering schemes of cat-

ions over a dense-packed anion frame, as well as being a step toward unravelling the gargantuan structure of the related mineral macgovernite,  $\text{Mg}_4\text{Mn}_9\text{Zn}_2(\text{SiO}_4)_2(\text{AsO}_4)_2\text{O}(\text{OH})_{14}$ ,  $R3c$ ,  $a_h = 8.22\text{Å}$ ,  $c_h = 205.5\text{Å}$  (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  $\text{MoK}\alpha$  radiation gave cell parameters

$a = 11.99(1)$ ,  $b = 31.46(4)$ ,  $c = 8.697(6)$ Å, space group *Abma*. The cell parameters agree fairly well with the earlier study of Prewitt-Hopkins who reported  $a = 11.99$ ,  $b = 31.21$ ,  $c = 8.60$ Å,<sup>1</sup> 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: MoK $\alpha$  ( $\lambda = 0.7093$ Å) 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  $\mu = 133.8$  cm<sup>-1</sup> (MoK $\alpha$ ) for the linear absorption coefficient based on the formula  $Mn_4Zn_2(AsO_4)O_2(OH)_6$ ;  $Z = 14$ . This value is practically identical ( $\mu = 133.9$  cm<sup>-1</sup>) 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 ( $\pm 0.025^\circ$ ), inclination angle missetting error ( $\pm 0.1^\circ$ ), and  $\Delta\mu = 1.5$  cm<sup>-1</sup>. 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  $Mn_4Zn_2[AsO_4]O_2(OH)_6$ , requires about 14 such formula units. We then assumed that Mn<sup>2+</sup> 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<sup>2+</sup>), 16 As<sup>5+</sup> tetrahedra, and 24 Zn<sup>2+</sup> tetrahedra. A  $\beta$  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<sup>4+</sup>. The ideal formula now stood at  $Mn_6Zn_3As_2SiO_{12}(OH)_8$ . Convergency by least-squares refinement was rapid.

Scattering curves for Mn<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, As<sup>5+</sup>, Si<sup>4+</sup>, and O<sup>1-</sup> 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,  $xMn^{2+}$  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

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

with  $w = \sigma^{-2}$  of  $F_o$ . Refinement minimized  $w(F_o - F_c)^2$ . The secondary extinction coefficient used was  $c_o = 1.3(1) \times 10^{-7}$  and the overall scale factor,  $s = 1.011(3)$ . The "goodness-of-fit,"  $\sum w(F_o - F_c)^2 / \sum (n - m)$ , 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,

<sup>1</sup> After conversion from kX to Angström units (1Å = 1.00202 kX).

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

Atom		x	y	z	B(Å <sup>2</sup> )	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<sup>2+</sup> + 0.47(1) Mg<sup>2+</sup>.

\*\* Refined to 0.92(1) Mn<sup>2+</sup> + 0.08(1) Mg<sup>2+</sup>.

and Table 2 presents the structure factors.<sup>2</sup> 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 0.59 Å<sup>-2</sup> (Si) to 1.04 Å<sup>-2</sup> (O), and are reasonable for a dense-packed oxide structure. In addition, Mn(1) and Mn(2) are partly replaced by Mg<sup>2+</sup>, the site occupancies having refined to 0.53(1)Mn<sup>2+</sup> + 0.47(1)Mg<sup>2+</sup> and 0.92(1)Mn<sup>2+</sup> + 0.08(1)Mg<sup>2+</sup> 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<sub>5.45</sub>Mg<sub>0.55</sub>Zn<sub>3</sub>(OH)<sub>8</sub>(AsO<sub>4</sub>)<sub>2</sub>(SiO<sub>4</sub>), which, referred to an ideal end-member, is Mn<sub>6</sub>Zn<sub>3</sub>(OH)<sub>8</sub>(AsO<sub>4</sub>)<sub>2</sub>(SiO<sub>4</sub>), 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<sub>2</sub> was attributed to presence of willemite and was deducted as that mineral. CO<sub>2</sub> 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<sub>2</sub>O, but their As<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> appear to be too low, and ZnO too high. Our cell contents give a calculated density of 4.11 g cm<sup>-3</sup>, 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<sub>2</sub>, 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 1.50 Å are com-

<sup>2</sup> 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.



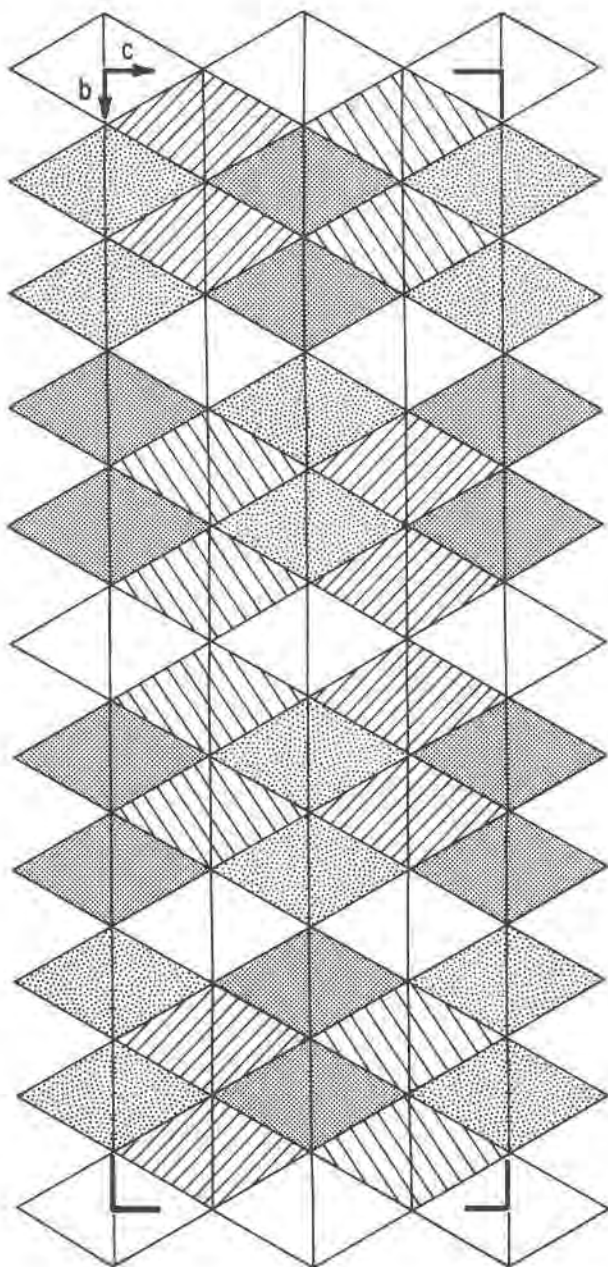


Fig. 1. Idealization of octahedral population between  $0 \leq x \leq 1/2$ . Populations at  $x = 0$  are light stippled,  $x = 1/8$  hatched NW-SE,  $x = 3/8$  hatched NE-SW, and  $x = 1/2$  dark stippled. Unpopulated octahedral positions within the region are unshaded.

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 ( $m \times 4.2\text{\AA}$ ,  $n \times 3.0\text{\AA}$ , and  $p \times 3.0\text{\AA}$ ) 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.

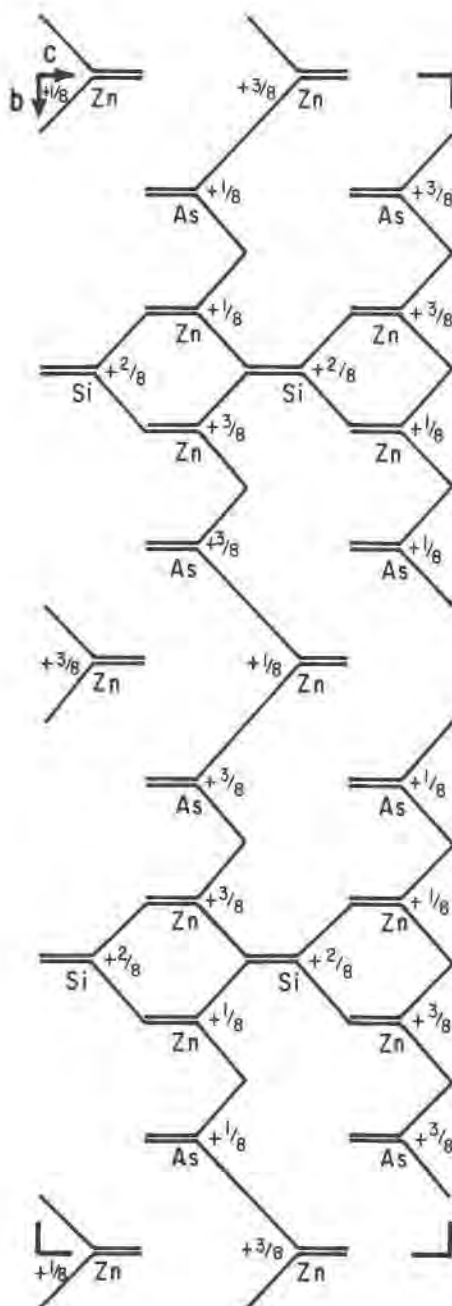


Fig. 2. Idealization of tetrahedral populations as T-O spokes between  $0 \leq x \leq 1/2$ . Heights are given as fractional coordinates in  $x$ .

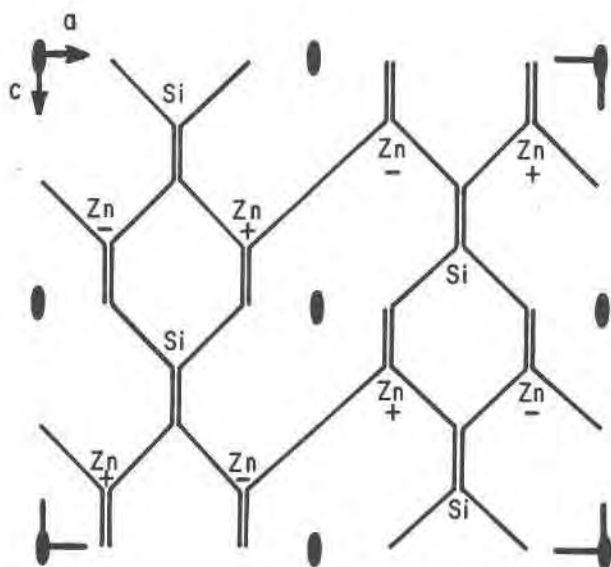


Fig. 3. Idealization of tetrahedral broken sheet drawn as  $T-O$  spokes on either side of  $y = 1/4$ . The "+" and "-" refer to Zn atoms above and below Si. The two-fold rotors are shown.

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  $\phi$  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  $0 \leq x \leq 1/2$  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  $0 \leq x \leq 1/2$  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 incomplete 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  ${}_{\infty}^2[Zn_2O_2(OH)_2SiO_4] = {}_{\infty}^2[Zn_2SiO_6(OH)_2]$ , the oxide anions not associated

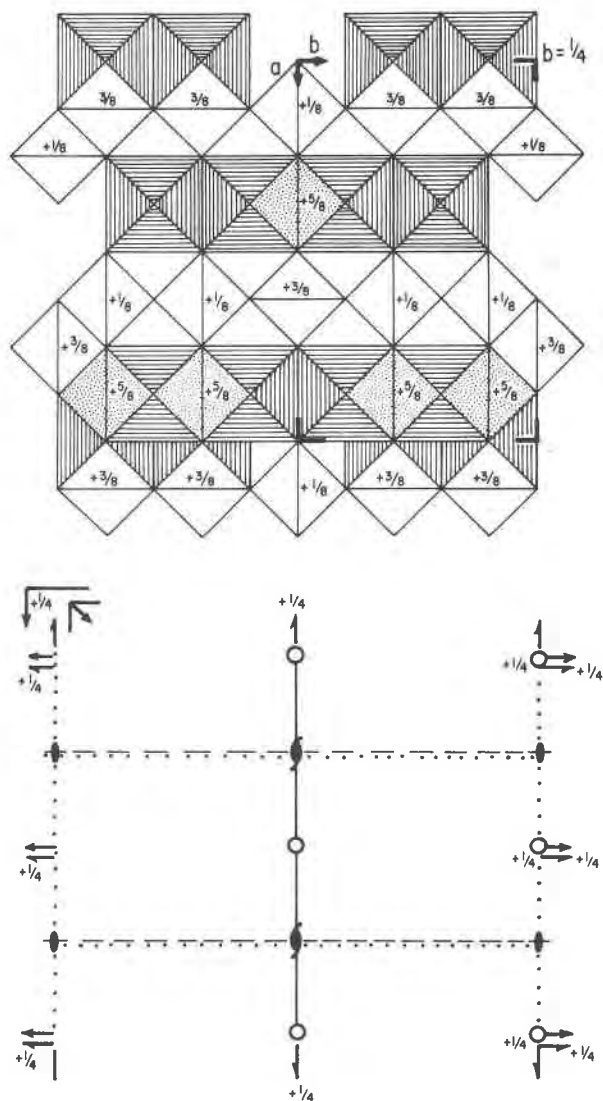


Fig. 4. Idealization of octahedral and tetrahedral populations down the  $c$  axis between  $-1/4 \leq y \leq 1/4$ . Atoms at  $z = 3/4$  and  $7/8$  are omitted. Octahedra at  $z = 0$  and  $1/4$  are ruled. Tetrahedra at  $z = 1/8$  and  $3/8$  are unshaded and at  $5/8$  are stippled. The symmetry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



with Si being linked to form Zn–O–As bridges. The inclusion of the  $\text{AsO}_4$  tetrahedra above and below the slice at  $y = 1/4$  leads to  ${}^2_2[\text{Zn}_2(\text{OH})_2(\text{AsO}_4)_2(\text{SiO}_4)]$  or  ${}^2_2[\text{Zn}_2\text{As}_2\text{SiO}_{12}(\text{OH})_2]$ . Thus, the structural formula can be written  ${}^{6l}\text{Mn}_8^{2+}(\text{OH})_2{}^{4l}[\text{Zn}(\text{OH})_4]{}^{4l}[\text{Zn}_2(\text{OH})_2(\text{AsO}_4)_2(\text{SiO}_4)]$ , 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 non-equivalent 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  ${}^{6l}\text{Mn}^{2+}$ , 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 = 2.15Å, Mn(2)–O 2.21Å, Mn(3)–O 2.21Å, Mn(4)–O 2.22Å, Zn(1)–O 1.98Å, Zn(2)–O 1.95Å, As–O 1.69Å and Si–O 1.64Å. The relatively short Mn(1)–O distance clearly reflects the replacement of about half  $\text{Mn}^{2+}$  by  $\text{Mg}^{2+}$ .

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 to be those whose edges are shared between two octahedra. Edges associated with O(5) violate this condition in two notable instances: O(5)<sup>(2)</sup>–O(6) associated with Mn(4) and Mn(3). The explanation lies in the unusually long Mn(4)–O(5)<sup>(2)</sup> = 2.43Å 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) = 3.14Å, OH(2)...O(4) = 3.07Å, OH(3)...O(4)<sup>(6)</sup> = 2.94Å, OH(4)...O(2) = 3.22Å and OH(5)...O(1)<sup>(7)</sup> = 2.89Å. 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,  $\Delta_{p_x}$ , and individual bond distance from the polyhedral average,  $\Delta d$ , 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  $\Delta d$  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.

### Acknowledgments

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