

## The crystal structure of kolicite, $\text{Mn}_7(\text{OH})_4[\text{As}_2\text{Zn}_4\text{Si}_2\text{O}_{16}(\text{OH})_4]^1$

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### Abstract

Kolicite,  $\text{Mn}_7(\text{OH})_4[\text{As}_2\text{Zn}_4\text{Si}_2\text{O}_{16}(\text{OH})_4]$ , is orthorhombic, space group *Cmca*,  $a = 18.59(3)$ ,  $b = 8.789(5)$ ,  $c = 12.04(1)\text{\AA}$ , with  $Z = 4$ . The structure is based on cubic-closest-packing of anions with As, Zn, and Si tetrahedra linked to form a continuous vertex-sharing slab oriented normal to  $c$ , with composition  $\text{As}_2\text{Zn}_4\text{Si}_2\text{O}_{16}(\text{OH})_4$ . These link units of seven edge-sharing Mn octahedra to form a three-dimensional structure. A basic unit of structure is common to the structure of holdenite,  $\text{Mn}_6\text{Zn}_3(\text{OH})_8(\text{AsO}_4)_2(\text{SiO}_4)$ .

### Introduction

Kolicite is a rare mineral present in a few specimens from the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey (Dunn *et al.*, 1979). Dr. Akira Kato pointed out (personal communication) that it appeared to be closely related to some other unusual Franklin and Sterling Hill minerals. These complex manganese-containing phases have structures with tetrahedrally-coordinated Zn, As, and/or Si and are generally based on anion closest-packing. Two such phases with cubic closest-packed structures are holdenite,  $\text{Mn}_6\text{Zn}_3(\text{OH})_8(\text{AsO}_4)_2(\text{SiO}_4)$ , and gerstmannite,  $(\text{Mn},\text{Mg})\text{Mg}(\text{OH})_2[\text{ZnSiO}_4]$ , as determined by Moore and Araki (1977a,b). They pointed out that these orthorhombic "structures involve one axis which is some integral multiple of twice the octahedral M-O distance, a second axis which is some integral multiple of an octahedral edge, and a third which is also a multiple of an octahedral edge. The simplest unit for oxygen cubic close-packing has metrical properties ( $m \times 4.2\text{\AA}$ ,  $n \times 3.0\text{\AA}$ ,  $p \times 3.0\text{\AA}$ )" (Moore and Araki, 1977a). The lattice parameters of kolicite are consistent with these relations. Its crystal structure thus appeared to represent yet another in a complex series of related Franklin and Sterling Hill phases, and the solution of the structure was carried out in order to further clarify the apparently complex relations among these minerals.

### Experimental

As reported in Dunn *et al.* (1979), single-crystal analysis showed that kolicite is orthorhombic with extinctions consistent with either space group *C2cb* or *Cmca*. Space group *Cmca* was eventually confirmed through statistical analysis of intensities and structure analysis. The lattice parameters, as obtained using least-squares refinement of powder diffraction data, are  $a = 18.59(3)$ ,  $b = 8.789(5)$  and  $c = 12.04(1)\text{\AA}$ . This unit cell has  $Z = 4$ .

The intensities of 1052 symmetry-independent reflections were measured with a Supper-Pace diffractometer, which uses Weissenberg equi-inclination geometry.  $\text{MoK}\alpha$  radiation, monochromated by a flat crystal of graphite, was used and intensities of reflections having  $\sin \theta \leq 0.46$  were measured, although the restrictions on upper levels were more severe due to mechanical limitations of the diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The latter was significant as the crystal was approximately 0.13 mm in diameter, and  $\mu_1 = 131.0 \text{ cm}^{-1}$ . The set of 1052 structure factors included 159 which were less intense than minimum observable values.

### Structure solution and refinement

An attempt was first made to solve the structure by direct methods using the program MULTAN (Main *et al.*, 1971), but this led to an unreasonably large number of possible solutions, which was attributable to the pseudo-symmetry due to cubic closest-packing of

<sup>1</sup> Contribution No. 356 from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan.

Table 2. Atomic coordinates for kolicite

Atom	Equipoint rank	x	y	z
O(1)	8	0	.2668(7)	.9944(6)
O(2)	16	.0738(3)	.5244(5)	.1370(4)
O(3)	16	.2547(3)	.9865(6)	.1355(4)
O(4)	8	0	.2610(9)	.2628(6)
O(5)	16	.1763(3)	.2840(6)	.2524(4)
OH(1)	16	.1697(3)	.2664(6)	.0078(4)
OH(2)	16	.0847(3)	.0332(5)	.1126(4)
M(1)	4	0	0	0
M(2)	8	.17519(9)	0	0
M(3)	16	.08776(6)	.2739(1)	.13633(9)
As	8	0	.6373(1)	.12816(7)
Zn	16	.16817(5)	.63219(9)	.13180(6)
Si	8	1/4	.3847(2)	1/4

the anions. However, the  $N(z)$  test provided by this program did show that kolicite is apparently centric and therefore has space group  $Cmca$ .

A successful solution to the structure was obtained by applying reasonable crystal-chemical principles to possible cation distributions in the anion closest-packed array, in the following manner. A three-dimensional Patterson function,  $P(uvw)$ , was first calculated. This had peaks at positions consistent with a structure based on cubic closest-packing, verifying the conclusions reached earlier on the basis of chemistry and lattice parameters. It was then noted that because there are 28 Mn per unit cell, and because equipoints of space group  $Cmca$  have ranks 4, 8, and 16, 4 Mn must be on one of the two equipoints of symmetry  $2/m$  and rank 4 at 000 or 1/200. Assuming that Mn is octahedrally coordinated, this fixed the ideal coordinates of the anions. Furthermore, the coordinates of the 96 octahedrally-coordinated sites and 192 tetrahedrally-coordinated sites per unit cell were specified. These were divided into their proper equipoints. All Mn was assumed to be octahedrally coordinated, while Zn, As, and Si were assumed to be tetrahedrally coordinated. Assuming 4 Mn on equipoint 4a or 4b, additional cations were assigned to sites only if cation-cation distances were not unreasonably short, or if face-sharing of polyhedra was avoided. In addition, octahedral occupancies were derived as consistent with octahedral edge-sharing in the  $a$ -axis direction as indicated by peaks in  $P(uvw)$ . Only four cation distributions proved to be possible with these restrictions and these were shown to be identical with appropriate changes of origin. Hydroxyl ions were readily identified by utilizing considerations of local charge balance.

The atomic parameters were refined by least-squares utilizing the program RFINE2 (Finger and Prince, 1975). Neutral atom scattering factors of

Doyle and Turner (1968) were used, and the weighting scheme was that of Cruickshank (1965, p. 114). Refinement proceeded normally through determination of anisotropic temperature factors. Near the final stages an attempt was made to refine occupancy factors for the octahedrally-coordinated cations M(1), M(2), and M(3) in order to locate the small proportion of Mg (0.24 Mg per 6.77 Mn) assumed to be substituting for Mn. The refined occupancy factors for all three sites differed by less than  $1\sigma$  from their starting values and therefore no unambiguous conclusion could be reached regarding the Mg distribution. The values did change slightly in a direction consistent with Mg only in M(1), however. The final residual  $R$  value was 7.1% for all reflections and 5.9% for unrejected reflections. Reflections for which the individual  $R$  value was greater than 0.5 were rejected. The final values of structure factors are listed in Table 1.<sup>2</sup> Atomic coordinates and anisotropic temperature factors are listed in Tables 2 and 3, respectively.

### Structure description

The crystal structure of kolicite is, as assumed in the structure solution, based on cubic closest-packing of anions. There are 96 anions (64 O and 32 OH) per cell. Some 28 of the 96 octahedrally-coordinated sites and 32 of the 192 tetrahedrally-coordinated sites are occupied. This complex array of polyhedra is difficult to illustrate clearly in its entirety, but some sense of the relations can be obtained from Figures 1 and 2, which illustrate the arrays of octahedra and tetrahedra, respectively. As is further detailed below,

<sup>2</sup> To obtain a copy of Table 1, order Document AM-80-130 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, DC 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Anisotropic temperature factors for kolicite

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O(1)	.0008(2)	.0025(8)	.0027(4)	0	0	.0004(5)
O(2)	.0008(2)	.0011(6)	.0033(4)	.0001(2)	.0002(2)	.0006(3)
O(3)	.0012(2)	.0023(5)	.0025(3)	-.0001(3)	.0003(2)	.0012(3)
O(4)	.0012(2)	.0040(8)	.0023(4)	0	0	.0018(5)
O(5)	.0014(2)	.0040(6)	.0018(3)	-.0001(2)	-.0005(2)	.0014(3)
OH(1)	.0016(2)	.0023(6)	.0019(3)	.0003(3)	.0004(2)	.0003(3)
OH(2)	.0013(2)	.0002(6)	.0029(4)	.0000(2)	.0001(2)	.0004(3)
M1	.0009(1)	.0039(2)	.0025(2)	0	0	-.0015(2)
M2	.0008(1)	.0020(2)	.0022(1)	0	0	-.0002(1)
M3	.0009(1)	.0019(2)	.0021(1)	-.0000(1)	.0001(1)	-.0003(1)
As	.0009(1)	.0021(1)	.0019(1)	0	0	-.0002(1)
Zn	.0008(1)	.0018(1)	.0020(1)	-.0001(1)	.0000(1)	-.0000(1)
Si	.0008(1)	.0001(3)	.0015(1)	0	.0000(1)	0

these diagrams are similar to those shown by Moore and Araki (1977b) for the closely-related holdenite structure. Their diagrams are not duplicated here, but part of the discussion requires reference to them.

Figure 1 illustrates the array of octahedra included within the range  $z = 0-1/2$ , and is drawn as an ideally closest-packed structure, neglecting the small deviations from the geometry present in the actual structure. The relationship to cubic closest-packing geometry can be seen from the fact that one of the four two-dimensionally closest-packed sets of planes is (130), corresponding to a plane containing parallel octahedron faces.

The basic octahedral unit can be seen by reference to the seven labeled octahedra at the center of Figure 1. Three octahedra ( $z = 0$ ) share edges (oriented parallel to  $c$ ) with M(1) as the center octahedron between 2 M(2) octahedra. Two edge-sharing M(3) oc-

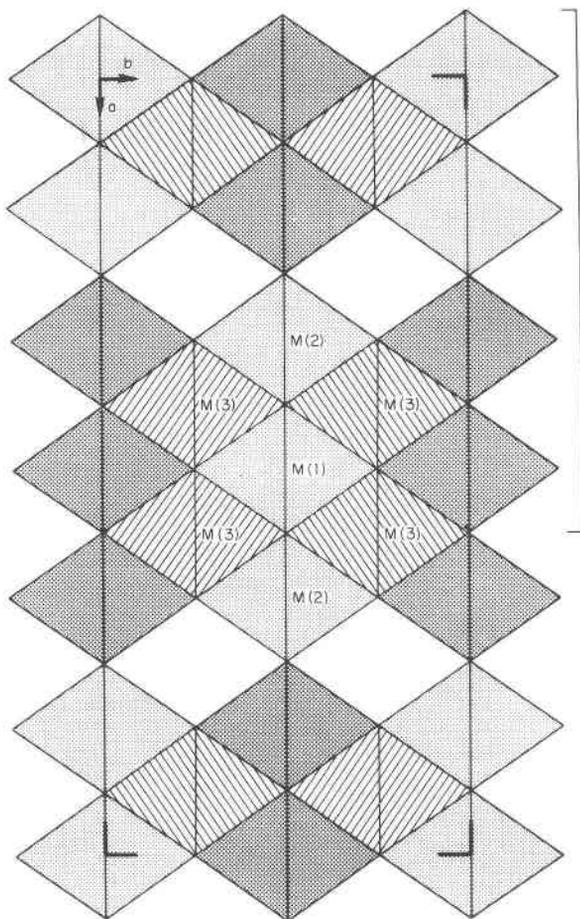


Fig. 1. Distribution of idealized octahedra,  $z = 0-1/2$ . Octahedra at  $z = 0$ , light stippled;  $z = 1/8$ , ruled NW-SE;  $z = 3/8$ , ruled NE-SW;  $z = 1/2$ , dark stippled. The vertical bar on the right denotes the unit common to the holdenite structure.

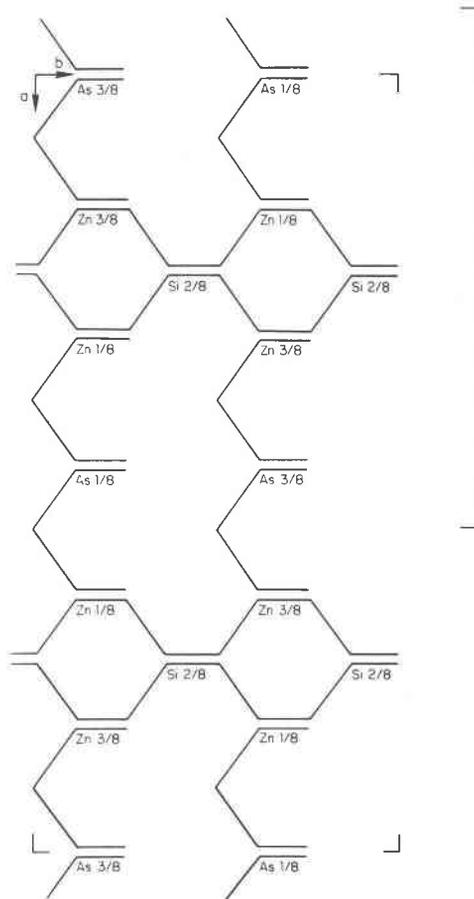


Fig. 2. Distribution of idealized tetrahedra,  $z = 0-1/2$ . The vertical bar on the right denotes the unit common to the holdenite structure.

tahedra at  $z = 1/8$  (on the right) and two at  $z = 7/8$  [left of M(1) and M(2)] share edges with the M(2) and M(1) polyhedra to create an integral seven-octahedron unit of composition  $M_7\Phi_{24}$ . These octahedral units are not bonded through anions in common with other symmetrically-equivalent units. Octahedral cations occupy sites at all levels in the structure which have  $z$  coordinates as multiples of  $1/8$ , except for levels  $2/8$  and  $6/8$ . This relationship is the same as in holdenite, except that the levels are normal to the  $a$  axis in that structure. A principal difference between the octahedral units of holdenite and kolicite is that in holdenite there are four octahedra sharing edges to form a short chain, rather than three as in kolicite.

Figure 2 is a diagram of the tetrahedra within the interval  $z = 0-1/2$ , and is also drawn as an ideally closest-packed array. In this spoke diagram, the tetrahedrally-coordinated cation is at the line intersection nearest its element symbol. Tetrahedrally-

Table 4. Interatomic distances for kolicite

<u>As tetrahedron</u>				<u>M(1) octahedron</u>			
As	0(1)	1.699(7)A		M(1)	4 OH(2)	2.098(6)A	
	2 0(2)	1.697(6)			2 0(1)	2.346(7)	
	0(4)	1.704(7)			ave.	2.180	
	ave.	1.699		OH(2)	2 OH(2)	2.774(11)	82.7(3) <sup>c</sup>
0(1)	0(4)	2.798(11)	110.6(4) <sup>o</sup>		2 OH(2)	3.148(12)	97.2(3)
0(2)	0(2)	2.745(12)	108.0(4)		4 0(1)	2.953(8)	83.1(2)
	2 0(1)	2.784(8)	110.2(2)		4 0(1)	3.330(8)	96.9(2)
	2 0(4)	2.768(8)	108.9(2)		ave.	3.081	90.0
	ave.	2.775	109.5				
<u>Si tetrahedron</u>				<u>M(2) octahedron</u>			
Si	2 0(3)	1.646(5)		M(2)	2 OH(1)	2.249(5)	
	2 0(5)	1.631(6)			2 OH(2)	2.181(6)	
	ave.	1.638			2 0(3)	2.205(6)	
0(3)	0(3)	2.762(10)	114.1(4)	OH(2)	OH(2)	2.774(11)	79.0(3)
0(5)	0(5)	2.739(12)	114.3(4)		2 0(3)	2.199(10)	93.7(2)
	2 0(3)	2.606(7)	105.4(3)		2 OH(1)	2.812(7)	78.8(2)
	2 0(3)	2.666(8)	108.9(3)		2 OH(1)	3.322(8)	9712(2)
	ave.	2.674	109.5	0(3)	0(3)	3.272(10)	95.8(3)
					2 OH(1)	3.232(7)	93.0(2)
					2 OH(1)	3.161(8)	90.4(2)
					ave.	3.125 <sup>a</sup>	90.1
<u>Zn tetrahedron</u>				<u>M(3) octahedron</u>			
Zn	OH(1)	1.950(5)		M(3)	OH(1)	2.178(5)	
	0(2)	1.994(6)			OH(2)	2.135(5)	
	0(3)	1.923(6)			0(1)	2.364(6)	
	0(5)	1.935(5)			0(2)	2.218(5)	
	ave.	1.951			0(4)	2.235(5)	
0(3)	0(5)	3.209(5)	112.6(2)		0(5)	2.162(6)	
	OH(1)	3.177(7)	110.3(2)		ave.	2.215	
	0(2)	3.205(10)	109.8(2)	OH(1)	0(2)	3.345(7)	99.1(2)
0(5)	OH(1)	3.097(7)	105.7(2)		0(1)	3.161(8)	88.1(2)
	0(2)	3.257(7)	111.9(2)	OH(2)	OH(1)	2.812(7)	81.4(2)
OH(1)	0(2)	3.157(7)	106.3(2)		0(1)	2.953(8)	81.9(2)
	ave.	3.184	109.4		0(4)	3.124(9)	91.2(2)
					0(5)	3.256(8)	98.5(2)
				0(2)	0(1)	3.156(8)	87.0(2)
					0(4)	3.089(8)	87.8(2)
					0(1)	3.233(11)	89.3(2)
				0(4)	OH(1)	2.959(7)	86.0(2)
					0(2)	3.167(7)	92.6(2)
					0(4)	3.287(8)	96.7(2)
					ave.	3.129	90.0

coordinated cations occupy levels 2/8 and 6/8 (Si) and 1/8, 3/8, 5/8, and 7/8 (As, Zn). The vertex-sharing scheme is as follows: two Zn and one As tetrahedron, all at the same level (e.g.  $z = 1/8$  or  $3/8$ ), share vertices to form short chain units parallel to  $a$ . These are crosslinked in turn through vertex-sharing with Si tetrahedra at level  $z = 2/8$  (the only cation at this level), each Si tetrahedron being central to four such short three-tetrahedron chain units. The complete vertex-sharing tetrahedron units extend infinitely as two-dimensional slabs, with thickness extending from  $z = 1/8$  to  $3/8$  or  $5/8$  to  $7/8$ . The composition of such a slab is  $\text{AsZn}_2\text{SiO}_8(\text{OH})_2$ . Such a cation-to-

anion ratio of 4 to 10 might ordinarily be interpreted to correspond to an infinitely extended tetrahedral sheet where each tetrahedron shares three vertices, as in micas. However, in this case the Si tetrahedron shares four vertices, the Zn three, and the As two, the average of which is three.

As noted in several places above, the structure of kolicite is closely related to that of holdenite. Indeed, it was this relationship in two species from the same geologic environment, each of which is extremely complex in itself, which led to our interest in this structure. Such relations are frequently the result of combining, in a regular way, rather simple but differ-

ent structure units to create a seemingly complex array of variants, as in mixed-layer polytypism or composite structures. Wuensch (1974) has reviewed such a theme in composite structures having subunits of the rocksalt structure. The holdenite and kolicite structures appear to be similarly related. On the right-hand sides of Figures 1 and 2 are vertical bars which extend over a range of slightly less than  $x = 0$  to more than  $x = \frac{1}{2}$ . This unit of structure, including both the octahedral and tetrahedral units, is identical in both holdenite and kolicite. Because the holdenite structure is already diagrammed in the paper by Moore and Araki (1977b) it is not reproduced here. Note, however, that some reorientation of their Figures 1 and 2 is necessary to visualize this relation. In particular, each figure must be rotated  $180^\circ$  (corresponding to an inversion in the directions of  $b$  and  $c$ ). Approximately the upper 40% of their figures are then identical with the corresponding units of kolicite. The symbolism for designating all polyhedra in the kolicite structure diagrams has been made identical to that for holdenite in order to facilitate visualization of the relations. Mr. Pete Dunn of the Smithsonian Institution has recently reported (personal communication) finding a specimen from Sterling Hill in which holdenite and kolicite coexist. Such materials should be thoroughly investigated for the possibility of finding oriented intergrowths, perhaps of a regular nature, or other variants of the same structural theme, in light of the relations exhibited by the holdenite and kolicite structures.

Interatomic distances as listed in Table 4 exhibit no significant differences from predictable values. Average As–O (1.699Å), Si–O (1.638Å), and Zn–O (1.951Å) distances are very similar to the corresponding values for holdenite, for example (1.694Å, 1.635Å, and 1.951Å, respectively; the value for Zn–O does not include values for an isolated tetrahedron). Deviations of individual distances from average values generally reflect local imbalances in charge and thus will not be further described here. The average

M–O distances are very similar to one another [M(1)–O, 2.180Å; M(2)–O, 2.212Å; M(3)–O, 2.215Å], and to the generally-expected value of about 2.21Å for Mn–O. It is of interest to speculate as to their significance relative to the small degree of substitution of Mg for Mn, and thus to possible cation ordering in examples of kolicite which may be found with significantly larger proportions of Mg. The slightly smaller average distance for M(1)–O is consistent with partial occupancy by Mg. Ordinarily, such a small difference might be dismissed as being not significant. However, for the M(1) site refinement of site occupancies also indicated partial occupancy by Mg, although this result was non-definitive. It therefore seems likely, although by no means proven, that substitution for Mn by smaller cations such as Mg will occur on the M(1) site.

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