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Table 1

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Abstract

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CRYSTAL STRUCTURE OF HODGKINSONITE

$Zn_2Mn[SiO_4](OH)_2$

Hodgkinsonite with the formula indicated is assigned in mineralogical handbooks ([1,2]) a place next to norbergite $Mg_3[SiO_4](OH)_2$, on the basis of the external similarity of the formulae and the approximate similarity of the lattice parameters (Table 1). In addition, the Franklin, New Jersey, USA deposit remains the principal known occurrence for both minerals.

Table 1

Mineral		a, Å	b, Å	c, Å	β	Z	Space group	sp. gr.
Hodgkinsonite	$Zn_2Mn[SiO_4](OH)_2$	8.13	5.34	11.71	95°35′	4	$P\,2_1/a$	3.91
Norbergite	$Mg_2Mg[SiO_4](OH)_2$	8.74	4.71	10.22		4	$P\,mcn$	3.14
Clinohedrite	$Ca\,Zn[SiO_4] \cdot H_2O$						Cc	3.33

It was therefore expected that the Zn and Mn atoms, like the Mg atoms in norbergite, would occupy in hodgkinsonite half of the octahedral voids of a hexagonal closest packing of O atoms (zigzags of occupied octahedra alternating with analogous zigzags of empty octahedra; both are related by a "black-and-white" translation along one axis and by a "black-and-white" plane of (anti)symmetry normal to another axis ([3])). This assumption was not confirmed. As in a number of other compounds, Zn in hodgkinsonite has a clearly expressed fourfold tetrahedral coordination, and in structure hodgkinsonite proved closer to another Zn silicate from the same deposit, namely clinohedrite $CaZn[SiO_4] \cdot H_2O$ ([4]).

Although hodgkinsonite was first found by Hodgkinson and described by Palache and Schaller as early as 1913 ([5,6]), its parameters were given only in 1958 by Rancieperis ([7]). The objects of our structural analysis were specimens from Franklin kindly supplied by Prof. C. Frondel (Harvard). The experimental material consisted of rotation radiographs about the y and x axes; Weissenberg photographs of the 0–4th layer lines of rotation about y, and the zero layer of rotation about x ($0kl$)—all with Mo radiation. The lattice parameters determined from these photographs and the centrosymmetric space group are given

Fig. 1. Hodgkinsonite. Projection of electron density xz

Figure 1: Fig. 1. Hodgkinsonite. Projection of electron density xz

in Table 1. They are close to the data of Rancieperis and Roberts-Quodling (8). Intensities were estimated on a blackening scale with a step of $\sqrt[4]{2}$, and from them, by the usual methods, after elimination of angular factors, a set of $|F_{hkl}|$ was obtained. The analysis was begun with the xz projection, as corresponding to the shortest period ($b = 5.34$ Å) and therefore promising the least number of overlaps.

On the $h0l$ layer, 171 independent and nonzero reflections were recorded. To determine the signs of the structure amplitudes, the Harker-Kasper inequalities method (9) was used after reducing the set of amplitudes to an absolute scale according to Wilson (10) and Weinstein (11) (with coinciding

···with the results). In calculating the unit structural amplitudes, the temperature factor $B = 0.5$, determined according to Wilson, was taken into account. Eleven amplitudes with $U > 0.5$ and another 17 with $U > 0.4$ ensured the effectiveness of the inequality method. The solution of the latter was carried out on a large computer using the program of A. F. Skorikov (12). From 185 sign relations obtained, it was possible to establish the signs or symbols (“letters”) of 95 amplitudes. After fixing the origin of coordinates by arbitrarily assigning two signs (13), one symbol (letter) remained undetermined, and in this way we obtained two possible structural variants.

Fig. 1. Hodgkinsonite. Projection of electron density xz

Confidence in the results of direct sign determination is greatly aided by “minus” relations (14). In the present case, 5 relations of the type $S_{H+K} = -S_{H-K}$ and 6 of the type $S_H \cdot S_K = S_{H+K} = -S_{H-K}$ were established, which gave pure “minuses” for 8 amplitudes. In manual sign determination the corresponding relations are usually missed as the number of possible variants increases.

The signs of the remaining F_{hol} were determined from the obtained “supporting” (15) signs with the help of the Sayre-Zachariasen statistical equality (16). On the electron-density maps constructed for the two variants from the found signs, 2Zn, 1Mn, 1Si, and 6O had to be placed in the independent part of the xz projection ($h0l$). The discrepancy coefficient, calculated from the heavy atoms, proved to be 28% for one of the variants, which formed the basis for further analysis. From the x, z coordinates of the atoms Zn I, Zn II, Mn fixed from it, the signs of all F_{hol} were calculated, and in the newly constructed xz projection peaks corresponding to three O atoms were clearly distinguished (Fig. 1). The positions of the three remaining O atoms were established only after constructing the yz projection ($0kl$), since in the xz projection these O overlap–

Table 2

Hodgkinsonite. Coordinates of the basis atoms

Atom	$100\,x/a$	$100\,y/b$	$100\,z/c$	Sum of valence strengths	Atom	$100\,x/a$	$100\,y/b$	$100\,z/c$	Sum of valence strengths
Mn	4.8	25.0	39.3		O_2	36.1	14.2	46.5	2
Zn I	25.1	56.1	10.7		O_3	30.8	93.2	10.7	2
Zn II	42.2	93.4	27.3		O_4	43.3	56.8	31.6	2
Si	33.0	43.8	43.2		O_5	11.3	92.0	49.8	$1\frac{1}{6}$
O_1	20.2	45.0	33.2	$1\frac{5}{6}$	O_6	5.7	9.6	15.4	1

by the heavier Si, Zn I, Zn II. For the yz projection, determination of the signs by the inequality method gave no results, as became clear later, because of the inflated scale factor F_{0kl} to absolute values, which in turn was connected with insufficient accuracy in the parameter $a = 8.13$ Å. The y coordinates of the heavy atoms were obtained from the three-dimensional Patterson function. With known z, the values of y thus found proved sufficient for calculating F_{0kl} and constructing $\sigma(y, z)$, on which all O atoms appeared, and precise indications were obtained for the x coordinates of those three O atoms that overlapped on $\sigma(xz)$. The discrepancy factors for all nonzero reflections were: $R_{h0l} = 15.7\%$ ($\sin\vartheta/\lambda \leq 0.960$); $R_{0kl} = 17\%$ ($\sin\vartheta/\lambda \leq 0.940$). The coordinates of the 10 basis atoms (30 parameters) are given in Table 2.

In Fig. 2 is shown the xz projection of the structure of hodgkinsonite with the coordination polyhedra around the two kinds of Zn, Mn, and Si distinguished. The Si atoms are located in isolated (ortho-)tetrahedra. The Mn atoms in oxygen octahedra, by means of inversion centers in common edges, form along the short axis b zigzag chains of identically oriented octahedra. These chains are cut out of a two-layer close packing, whose planes extend parallel to (102). By a 2_1 screw axis each zigzag is coupled with an analogous zigzag of the next packing layer, etc. A "ladder" is formed, shown in Fig. 3. Being "set on edge," it plays in the structure the role of a wall bounding the cell along the coordinate planes (001). In the wide interval between the walls (Fig. 2) the remaining polyhedral material of the structure is concentrated. In the tetrahedra are found not only Si atoms, but also both kinds of Zn atoms, which excludes the presumed analogy of hodgkinsonite with norbergite. Thus, the peculiarity of zinc crystal chemistry, requiring for it tetrahedral coordination, has once again been confirmed, and hodgkinsonite has taken its place in the series of recently solved Zn minerals: hopeite (^{17}), phosphophyllite (^{18}), clinohedrite (^{4}). Both in these structures and in hodgkinsonite a characteristic feature is metazincate chains of Zn tetrahedra $|Zn_2O_6|_\infty$. The chains are polar, i.e., in them all tetrahedra face in one direction along the axis (2_1) of the chain. In the cell two chains $[Zn_2O_6]_\infty$ are connected

Fig. 2. Hodgkinsonite. Projection of the structure with the line of sight along the short axis b. Oxygen octahedra around Mn atoms and tetrahedra around

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

Si and the two kinds of Zn are distinguished. In the center of the projection are the ends of two polar metachains $[Zn_2O_6]_\infty$

Fig. 3. Wall of Mn octahedra as a cutout from close hexagonal packing

center of inversion and thus (Fig. 2) are oriented in opposite directions. Another feature of the previously deciphered Zn minerals* is repeated: the metachains are encrusted, i.e., as Fig. 4 shows, they are "paved" with orthotetrahedra $[SiO_4]$, as in clinohedrite (in goethite and phosphophyllite the paving tetrahedra are $[PO_4]$). In hodgkinsonite, however, the metazincate chains are not completely isolated. The encrusting Si tetrahedra are connected by one vertex with another metazincate chain and, in addition, have common vertices with both chains of Zn tetrahedra of another kind. The latter, together with the Si tetrahedra, are also combined into two polar metachains of "mixed type" $[ZnSiO_6]_\infty$.

Fig. 4. Metachain $[Zn_2O_6]_\infty$, encrusted with orthotetrahedra $[SiO_4]$

The mutual interweaving of the chains creates an infinite two-dimensional "cushion" of tetrahedra, which is clamped between walls of Mn octahedra. Both the cushion and the walls are the obvious cause of the optically negative sign of the crystals, although this is opposed by the metachains, all of which are parallel to the *b* axis. The different character of the walls and the cushion determines the perfect cleavage (001), which, it must be thought, specifically passes along the seam between the walls and the cushions.

The interatomic distances in the structure differ little from the commonly cited ones. In the Si tetrahedron: Si—O = 1.58 Å to 1.64 Å, with edges O—O = 2.59—2.77 Å. In Zn tetrahedra: Zn—O = 1.80—2.10 Å, with O—O = 2.89—3.40 Å. In Mn octahedra: Mn—O = 2.06—2.26 Å, O—O = 2.77—3.35 Å.

Since some O atoms overlap in both projections with heavy atoms, their positions are to be refined from three-dimensional data by the least-squares method.

The positions of the two hydrogen atoms belonging to the independent part of the cell are readily established from the balance of valence strengths. The atoms $O_5(\Sigma = 1\frac{1}{6})$ and $O_6(\Sigma = 1)$ should be regarded as hydroxyls, and these

Fig. 4

Figure 4: Fig. 4

are precisely the atoms that do not participate in the Si tetrahedra. The atom O_5 participates in a Zn1 tetrahedron. The atom O_6 is not included in any tetrahedron.

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* And also Be minerals. On the (formal) similarity of the crystal chemistry of beryllium and zinc, see (4).

Note: Figure translations are in progress. See original paper for figures.