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THE CRYSTAL STRUCTURE OF KURNAKOVITE

$$Mg_2B_6O_{11} \cdot 15H_2O = 2Mg[B_3O_3(OH)_5] \cdot 5H_2O$$

Hydrous magnesium borate—kurnakovite—was first discovered by M. N. Godlevskii in 1938 (1) at the Inder deposit (USSR, Western Kazakhstan). In (1) the chemical formula of the mineral is given with a somewhat underestimated water content ($Mg_2B_6O_{11} \cdot 13H_2O$), the density is stated as $d = 1.85$, and the hardness as $H = 3$. In 1946 Heinrich (2), for single crystals of kurnakovite from the Kramer deposit (California), determined the parameters of the triclinic cell ($a = 8.14$, $b = 10.47$, $c = 6.33$ Å; $\alpha = 96°56'$, $\beta = 106°28'$, $\gamma = 106°03'$, $V = 485.4$ Å^3) and refined the chemical composition ($Mg_2B_6O_{11} \cdot 15H_2O$); density $d = 1.86$, hardness $H = 3$. Perfect cleavage is parallel to [010] and good cleavage to $[1\bar{1}0]$. However, Heinrich considered his specimens to be inderite and not kurnakovite. Schaller and Mrose (3) established that kurnakovite and inderite are dimorphous modifications of composition $Mg_2B_6O_{11} \cdot 15H_2O$ and that in (2) kurnakovite, not inderite, had been studied.

In 1963 kurnakovite was found in China (4). For the Chinese specimens the cell parameters reported are: $a = 8.36$, $b = 10.68$, $c = 6.44$ Å; $\alpha = 98°10'$, $\beta = 108°32'$, $\gamma = 106°04'$; $V = 506.9$ Å^3; Fedorov group $P\bar{1}$ on the basis of morphological data; $d = 1.847$, $H = 3$ (4,5). In the following report (6) an unsuccessful attempt was made to determine the crystal structure of kurnakovite from the Patterson projection $P(x, y)$, based on the previously noted similarity of the boron-oxygen radicals of kurnakovite and inderite (7–9) (the structure of inderite was published in 1962 (10,11)). For the structure in (6), the discrepancy factor R_{hk0}, calculated from the nonzero reflections measured by us, was 55.6%.

Table 1

Coordinates of the basis atoms of the kurnakovite structure

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Mg	0.653	0.232	0.802	O_9*	0.150	0.441	0.352

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
O_1**	0.923	0.321	0.920	O_{10}*	0.251	0.412	0.739
O_2**	0.593	0.410	0.775	O_{11}	0.128	0.220	0.414
O_3**	0.331	0.133	0.667	O_{12}*	0.016	−0.012	0.245
O_4**	0.672	0.036	0.810	O_{13}**	0.284	0.242	0.051
O_5*	0.651	0.194	0.471	B_I	0.767	0.227	0.354
O_6*	0.670	0.260	0.141	B_{II}	0.110	0.352	0.505
O_7	0.809	0.103	0.272	B_{III}	0.930	0.104	0.308
O_8	0.932	0.334	0.508				

* O atom in a hydroxyl group.
** O atom in a water molecule.

Colorless transparent crystals of kurnakovite from the California deposit were obtained by us from Prof. C. Frondel. From rotation photographs and Weissenberg photographs ($hk0, 0kl, h0l$) we established the unit-cell parameters $a = 8.28$, $b = 10.66$, $c = 6.40$ Å; $\alpha = 99.0°$, $\beta = 108.5°$, $\gamma = 105.4°$; $V = 498.2$ Å^3, which proved to be fairly close

from the results of ($^{4-6}$). The unit cell contains one formula unit of $Mg_2B_6O_{11} \cdot 15H_2O$. From Weissenberg photographs (Mo radiation) 253 nonzero F^2_{hk0}, $635F^2_{hk1}$, $502F^2_{hk2}$, $583F^2_{hk3}$, $130F^2_{0kl}$, $314F^2_{1kl}$, and $71F^2_{h0l}$ were recorded. The intensities were estimated from blackening standards with a step of $\sqrt[4]{2}$ and were reduced to an absolute scale by Wilson’ s method (^{12}). The presence of a center of symmetry follows from the distribution of F^2_{hk0} (^{13}), i.e., the Fedorov group $P\bar{1}$ is unambiguously established.

In the formula of kurnakovite atoms with close atomic numbers are present (hydrogen atoms excluded). Therefore, for determining the structure, direct methods for determining signs were used—the Harker-Kasper inequalities (^{14}) and the statistical relations of Sayre-Cochran-Zachariasen ($^{15-17}$). From the total number of 2235 nonzero reflections, reflections with unit amplitudes satisfying the condition $|U_{hkl}| > 0.26$ ($|E_{hkl}| > 1.5$) were selected—a total of 267 “basis” U_{hkl}. Application of the H.-K. inequalities to them gave 114 effective relations, which made it possible to express the signs of most of the basis group through 14 letters. Each of the basis signs was then analyzed once more with the aid of the statistical relations S.-C.-Z.; as a result, for 170 S_{hkl} the number of letters was reduced to five, three of which, fixing the origin of the cell, were assigned arbitrary signs (^{18}). The selected S_{hkl} became the basis for the statistical determination of the signs of 60% of the largest, in modulus, U_{hkl}; among them, only for 26% (570 U_{hkl}) was a result obtained in the form of signs or combinations of two unknown letters. Their specification led to four variants of sets of S_{hkl}.

Fig. 1. Structure of kurnakovite in coordination polyhedra. Projection along the a axis. The numbers denote the basis atoms. Dotted lines indicate hydro-

Fig. 1. Structure of kurnakovite in coordination polyhedra. Projection along the *a* axis. The numbers denote the basis atoms. Dotted lines indicate hydrogen bonds. Shaded circles are H_2O molecules not included in the coordination polyhedra.

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Fig. 2. Projection of the structure of kurnakovite along the *c* axis

Figure 2: Fig. 2. Projection of the structure of kurnakovite along the *c* axis

gen bonds. Shaded circles are H_2O molecules not included in the coordination polyhedra.

The three-dimensional Fourier synthesis constructed on the basis of the first set of signs for 560 U_{hkl} made it possible to identify the elements of the structure and, in particular, the Mg octahedron, whose position approximately corresponded to the drawing of the Chinese model (^{6}). However, the interatomic distances in this variant proved far from standard values, and the discrepancy factor R_{hk0} could not be reduced below 41% (and R_{0kl} below 46%). One more variant of signs was rejected as a result of analysis of the three-dimensional electron-density map, with only a single high maximum and an almost complete absence of any other significant peaks.

The third set of signs was recognized as the true one. The sharpened Fourier distribution (constructed from the corresponding 560 U_{hkl}) contained, in addition to spurious peaks, all the maxima corresponding to the atoms of the structure, which were readily identified by analysis of interatomic distances. The atomic coordinates, fixed from the subsequent synthesis $\rho(x, y, z)$ on the basis of all measured F_{hkl} (51 numerical parameters), are collected in Table 1. The discrepancy factor, with allowance for the averaged isotropic temperature correction over all 1973 nonzero reflections of the type $hk0$—$hk3$, is $R_{hkl} = 19.0\%$ ($\sin\vartheta/\lambda \leq 0.85$ Å^{-1}, $B = 1.9$ Å^{2}).

Fig. 2. Projection of the structure of kurnakovite along the *c* axis

The structural motif of kurnakovite is seen in Figs. 1 and 2. The boron-oxygen polyanions each consist of two $BO_2(OH)_2$ tetrahedra and one $BO_2(OH)$ triangle, joined by common O vertices into a three-membered ring $[B_3O_3(OH)_5]^{2-}$, which confirms the assumptions put forward in ($^{7-9}$). The Mg atoms are located inside fairly regular octahedra made up of two groups of OH and four H_2O. Similar structural elements were established by us in the monoclinic modification –inderite (^{10,11}).

With the same chemical formula in the boron-oxygen radicals of the two structures, a substantial difference is found: in the inderite ring the (OH) vertices of the two tetrahedra that do not lie in the plane of the ring are situated on one side of this plane, whereas in kurnakovite the B-tetrahedra "look" in opposite directions. Among the structures of hydrous borates determined in our laboratory, the inderite ring has also been found in inderborite ([19]) and, as an element of more complex radicals, in the chain hydroboracite ([20]) and probertite ([21]), as well as in the layered *p*-vitchite ([22]). The kurnakovite ring is the second constituent element of the complex probertite chain ([21]).

The principal interatomic distances in the structure of kurnakovite, given in Table 2, agree well with those found in other borates ([11,19–22]). Also, unlike inderite ([10,11]), where each Mg-octahedron is connected by a pair of adjacent vertices to one boron-oxygen ring, in kurnakovite each Mg-octahedron is linked to a pair of boron-oxygen radicals by two opposite vertices. Accordingly, in the less compact structure of inderite, island complexes $MgB_3O_3(OH)_5 \cdot 4H_2O$ are formed, whereas

In kurnakovite, Mg octahedra are joined through boron-oxygen radicals into infinite chains of the same composition. They extend along the *c* axis and are combined by parallel and hydrogen bonds both directly and through isolated water molecules, which also participate in the system

Table 2

Interatomic distances in the structure of kurnakovite (in angstroms)

B_I-tetrahedron	Distance	B_{II}-tetrahedron	Distance	B_{III}-triangle	Distance
$B_I—O_5^*$	1.40	$B_{II}—O_8$	1.44	$B_{III}—O_7$	1.36
$B_I—O_6^*$	1.49	$B_{II}—O_9^*$	1.52	$B_{III}—O_{11}$	1.38
$B_I—O_7$	1.51	$B_{II}—O_{10}^*$	1.49	$B_{III}—O_{12}^*$	1.38
$B_I—O_8$	1.45	$B_{II}—O_{12}$	1.50	Average	1.37
Average	1.46	Average	1.49	$O_7—O_{11}$	2.39
$O_5^*—O_6^*$	2.37	$O_8—O_9^*$	2.44	$O_7—O_{12}^*$	2.39
$O_5^*—O_7$	2.37	$O_8—O_{10}^*$	2.41	$O_{11}—O_{12}^*$	2.34
$O_5^*—O_8$	2.32	$O_8—O_{11}$	2.43	Average	2.37
$O_6^*—O_7$	2.38	$O_9^*—O_{10}^*$	2.45	Mg-octahedron	
$O_6^*—O_8$	2.47	$O_9^*—O_{11}$	2.42	$Mg—O_1^{**}$	2.01
$O_7—O_8$	2.43	$O_{10}^*—O_{11}$	2.40	$Mg—O_2^{**}$	2.10
Average	2.39	Average	2.43	$Mg—O_3^{**}$	2.04
$B_I—B_{II}$	2.57			$Mg—O_4^{**}$	2.14
$B_I—B_{III}$	2.52			$Mg—O_5^*$	2.10
$B_{II}—B_{III}$	2.51			$Mg—O_6^*$	2.10
				Average	2.08

of hydrogen bonds (in their redistribution), similarly to what occurs in inderite

([11]). In kurnakovite the isolated H_2O particle is linked with four boron-oxygen rings and one Mg octahedron; in inderite each H_2O is connected by hydrogen bonds with three boron-oxygen groups and one Mg octahedron. The structural formula of kurnakovite may be written as $\{Mg[B_3O_3(OH)_5] \cdot 4H_2O\} \cdot H_2O$.

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