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PRECISE DETERMINATION OF THE CRYSTAL STRUCTURE OF BERTRANDITE $Be_4[Si_2O_7](OH)_2$

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In 1961 we deciphered [1] the crystal structure of beryllium (diortho) silicate (bertrandite) $Be_4[Si_2O_7](OH)_2$; a = 8.73; b = 15.31; c = 4.56 A; Z = 4. The rhombic hemimorphic structure with Fedorov group C_{2v}^{12} in the $Cmc2_1$ arrangement was solved by "direct methods" with the Harker-Kasper inequalities at the first stage and the Sayer-Zachariesen statistical equation at the second, in which, apart from rotation photographs around three axes, we had only three developments: hk0, hk1, and 0k*l*.

Of the two most general inequalities

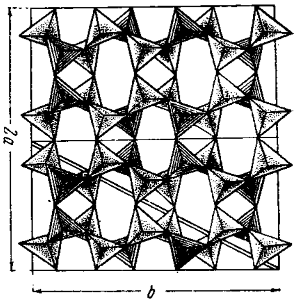
$$[|U_H| + |U_K|]^2 \leqslant [1 + S_H S_K U_{H+K}][1 + S_H S_K U_{H-K}], \tag{I}$$

$$[|U_H| - |U_K|]^2 \leqslant [1 - S_H S_K U_{H+K}][1 - S_H S_K U_{H-K}] \tag{II}$$

the first (and stronger) was mainly used. The large left-hand side of this necessarily constricts the conditions for its fulfillment. All calculations with the inequalities and the statistical equation were carried out by hand. The variance coefficients attained were: $R_{hk0} = 22.2\%$, $R_{0kl} = 21\%$.

Later we obtained a considerably larger number of experimental intensities (developments of all the layer rotations around c); besides this, in the Institute of Mathematics of the Siberian Department of the Academy of Sciences, USSR, Skoritskaya and colleagues of the Crystallochemistry Laboratory prepared [2] a program for the solution of a system of Harker-Kasper inequalities on the large computer (BÉSM). Both fundamental inequalities were solved simultaneously, which is very important, since only so can one obtain, for example, the minus signs and other valuable information which we were enable to derive from the single strong inequality.

Simultaneous solution of the inequalities leads to six variants of the sign relations:



Structure of bertrandite. Projection xy. Cleavage plane (110) is shown, the only one for which all the diorthogroups $[Si_2O_7]$ are passed by.

1. $S_H \cdot S_K = S_{H+K} = S_{H-K}$ $\quad \Pi_1 \geqslant \Sigma^2 \geqslant \Pi_2 \geqslant \Pi_3 \geqslant \Pi_4 \geqslant \Delta^2$,
2. $S_H \cdot S_K = S_{H+K}$ $\quad \Pi_1 \geqslant \Pi_2 \geqslant \Sigma^2 \geqslant \Pi_3 \geqslant \Pi_4 \geqslant \Delta^2$,
3. $S_H \cdot S_K = \pm S_{H+K} = \pm S_{H-K}$ $\quad \Pi_1 \geqslant \Pi_2 \geqslant \Pi_3 \geqslant \Sigma^2 \geqslant \Pi_4 \geqslant \Delta^2$,

excluding $S_H \cdot S_K = -S_{H+K} = -S_{H-K}$,

4. $S_H \cdot S_K = S_{H+K} = -S_{H-K}$ $\quad \Pi_1 \geqslant \Pi_2 \geqslant \Sigma^2 \geqslant \Pi_3 \geqslant \Delta^2 \geqslant \Pi_4$,
5. $S_{H+K} = -S_{H-K}$ $\quad \Pi_1 \geqslant \Pi_2 \geqslant \Pi_3 \geqslant \Sigma^2 \geqslant \Delta^2 \geqslant \Pi_4$,
6. any $\quad \Pi_1 \geqslant \Pi_2 \geqslant \Pi_3 \geqslant \Pi_4 \geqslant \Sigma^2 \geqslant \Delta^2$.

In all other cases the inequalities are incompatible.*

The electron density projections xy and yz constructed with the new signs were made still more precise by the method of least squares, using Brusentsev's program [3] on the BÉSM. Seven approximating cycles for each projection reduced the variance coefficient to $R_{hk0} = 6\%$ and $R_{0kl} = 10.4\%$ (from all nonzero F_e).

In view of the peculiarity of the xy projection of betrandite shown in the figure, namely, that in

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* $|U_H| + |U_K| = \Sigma$; $|U_H| - |U_K| = \Delta$, $(1 + |U_{H+K}|$, $(1 + |U_{H-K}|) = \Pi_1$; $(1 + |U_{H+K}|)(1 - |U_{H-K}|) = \Pi_2$; $(1 - |U_{H+K}|)(1 + |U_{H-K}|) = \Pi_3$; $(1 - |U_{H-K}|)(1 - |U_{H-K}|) = \Pi_4$.

TABLE 1. Improvement in the Structure of **Bertrandite** by the Method of Least Squares

Atoms		Before improvement	Zone *hk0*	Zone *0k1*	*hk0, 0k1, hk1, hk2, hk3*	Atoms		Before improvement	Zone *hk0*	Zone *0k1*	*hk0, 0k1, hk1, hk2, hk3*
Si	*x*	0.316	0.326	—	0.325	O(OH)$_V$	*x*	0.500	0.500	—	0.500
	y	0.116	0.115	0.115	0.114		*y*	0.253	0.256	0,263	0.255
	z	0.626	—	0.626	0.626		*z*	0.008	—	0,009	0,059
	B	1.00	0.49	0.20	0.48		*B*	1,00	0,60	1.59	0.90
O$_I$	*x*	0.316	0,290	—	0.288	O(OH)$_{VI}$	*x*	0	0	—	0
	y	0.116	0,124	0,125	0.125		*y*	0.083	0.086	0.098	0.087
	z	—0.01	—	—0,041	—0.032		*z*	0,014	—	0.006	0.068
	B	1.00	0.61	0.66	0.57		*B*	1.00	0,73	2,21	0.78
O$_{II}$	*x*	0.203	0.209	—	0.211	Be$_I$	*x*	0.203	0.167	—	0.171
	y	0,047	0.043	0.043	0.043		*y*	0.047	0,052	0.047	0.053
	z	0.490	—	0.466	0.475		*z*	0,129	—	0.095	0.097
	B	1.00	0,52	0.22	0,71		*B*	1.00	0.75	—0.43	0,96
O$_{III}$	*x*	0.303	0,293	—	0.292	Be$_{II}$	*x*	0.303	0,326	—	0.329
	y	0.216	0.208	0.208	0.209		*y*	0.216	0.219	0.212	0,221
	z	0,489	—	0.457	0.467		*z*	0.128	—	0.114	0.101
	B	1.00	0.80	0.02	0.70		*B*	1.00	0,88	0.78	0.81
O$_{IV}$	*x*	0.500	0,500	—	0.500		*R*		6%	10,4%	8.9%
	y	0,084	0.084	0.074	0.084						
	z	0.501	—	0.518	0.565						
	B	1.00	0.63	1.81	0.65						

TABLE 2

Atoms	*x*	*y*	*z*
(8) Si	0,325	0.114	0,658
(8) O$_I$	0,288	0.125	0
(8) O$_{II}$	0.211	0.043	0.507
(8) O$_{III}$	0,292	0.209	0.469
(4) O$_{IV}$	0.500	0,084	0.597
(4) O$_V$	0.500	0.255	0.091
(4) O$_{VI}$	0	0.087	0.100
(8) Be$_I$	0.171	0.053	0.129
(8) Be$_{II}$	0,329	0.221	0,133

TABLE 3

	$O_I - O_{II} = 2.67_9$
Si-tetrahedron	$O_I - O_{III} = 2.62_9$
$Si - O_I = 1.59_6$	$O_I - O_{IV} = 2.68_2$
$Si - O_{II} = 1.63_2$	$O_{II} - O_{III} = 2.64_0$
$Si - O_{III} = 1.64_7$	$O_{II} - O_{IV} = 2,63_0$
$Si - O_{IV} = 1.61_2$	$O_{III} - O_{IV} = 2.66_3$
Mean 1.61_7 A	Mean 2.65_4 A
	$O_I - O_{II} = 2.72_8$
Be$_I$-tetrahedron	$O_I - O'_{II} = 2.70_5$
$Be_I - O_I = 1.61_2$	$O_I - OH_{VI} = 2.61_6$
$Be_I - O_{II} = 1.78_0$	$O_{II} - O'_{II} = 2.66_9$
$Be_I - O'_{II} = 1.61_9$	$O_{II} - OH_{VI} = 2.70_7$
$Be_I - OH_{IV} = 1.58_3$	$O'_{II} - OH_{VI} = 2.74_8$
Mean 1.64_8 A	Mean 2,69 A
	$O_I - O_{III} = 2.62_9$
Be$_{II}$-tetrahedron	$O_I - O'_{III} = 2.64_5$
$Be_{II} - O_I = 1,63_2$	$O_I - OH_V = 2.75_7$
$Be_{II} - O_{III} = 1.72_0$	$O_{III} - O'_{III} = 2,71_7$
$Be_{II} - O'_{III} = 1.63_2$	$O_{III} - OH_V = 2.69_7$
$Be_{II} - OH_V = 1.59_4$	$O'_{III} - OH_V = 2,64_2$
Mean 1.64_4 A	Mean $2,68_1$ A

this projection both Si and Be are overlapped by O atoms, the accuracy of the corresponding coordinates raised doubts. A three-dimensional improvement was carried out (in three cycles) by the Brusentsev program, the total number of reflections used being 430. The variance coefficient for the whole three-dimensional block became 8.9%. The shifts in coordinates are shown in Table 1; the individual temperature factors appear in the same table. The rather more substantial change in the y- and z-coordinates as compared with data from the projection was probably the result of error in evaluating the intensities in the 0k*l* development. Since the z-coordinate of the O atoms arbitrarily taken as zero in the hemimorphic group undergoes correction, Table 2 contains a slightly altered list of coordinates, referred to the said z = 0.

Table 3 shows the interatomic distances in the Si-tetrahedron and in two kinds of Be-tetrahedra. One can hardly fail to notice the satisfactory way in which the mean Si to O distance of 1.617 A falls right in the middle of the range indicated by Smith in his frequently quoted papers [4] on the "standard" Si to O distances, with limits of 1.61 for the skeletal silicates and 1.63 A for orthosilicates.

In bertrandite we have the diorthogroups [Si_2O_7] "dissolved" in twice the number of $Be_2(O, OH)_7$ groups, as a result of which a beryllium-silicon-oxygen skeleton with generalized formula $(Be, Si)_2 \cdot (O, OH)_3$ of the corundum type [1] is formed.

A description of the structure of bertrandite and, in the light of this, a discussion of the physical features of the mineral are given in [1]. Here we give (see figure) a representation of the structure doubled along the a-axis in order to demonstrate the main cleavage of bertrandite (110), for which all the diorthogroups [Si_2O_7] are passed by, and which figures in the first papers on bertrandite [5]. Recently published courses on mineralogy [6] have, however, quite stubbornly indicated (001) as the chief cleavage, although from the structure shown in the figure this is clearly impossible. The extremely large difference in quality of the (001) and (00$\bar{1}$) faces, indicated in detailed descriptions and obvious from the figure, only suggest characteristic cleavage with respect with respect to (001), i.e., in this respect bertrandite appears similar to corundum.

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