CRYSTALLOGRAPHY

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Abstract

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THE CRYSTAL STRUCTURE OF HURLBUTITE

In papers ([1],[2]) some of our results are presented on the X-ray structural study of hurlbutite, $CaBe_2P_2O_8$, considered chiefly with respect to their similarity to and difference from analogous data for danburite, $CaB_2Si_2O_8$. The absence of exact values of the coordinate x did not then make it possible to give a complete structural interpretation of hurlbutite. Below we fill this gap and at the same time have the opportunity to demonstrate one more case of a far-reaching analogy in the structure of certain phosphates and silicates.

Hurlbutite, $CaBe_2P_2O_8$; parameters of its monoclinic (pseudorhombic) cell: $a = 8.29$ Å, $b = 8.80$ Å, $c = 7.81$ Å, $\beta \approx 90°$; space group $P2_1/a$; $Z = 4CaBe_2P_2O_8$. The principal experimental material included 184 F_{hk0}, 171 F_{h0l}, and 157 F_{0kl} (KFUR camera, Mo radiation).

In paper ([2]), in comparing the structures of danburite and hurlbutite, for the latter the analysis of the yz projection was brought to a discrepancy factor of $R_{0kl} = 17.5\%$ for all nonzero reflections. Later it was possible to reduce it to 14.1% for all nonzero reflections and to 18.3% with the inclusion of 88 zero F_{expt} (to $\sin\vartheta/\lambda = 1.05$ Å^{-1}).

In its final form this yz projection is reproduced in Fig. 1; it should be compared with Fig. 2b given below, in order to demonstrate the possibility of a very clear separation of the "heavy" atoms P and the light Be in positions that in danburite are occupied either by a pair of Si atoms (from the diortho group Si_2O_7) or by a pair of B atoms (from the group B_2O_7).

The coordinates x of all atoms, which we previously established only from crystallochemical considerations, have now been refined from the projection of the electron density onto the xz plane and partly from the projection onto the xy plane, on which 10 atoms out of 13 overlap pairwise. The values of the discrepancy factors are: $R_{h0l} = 18.1\%$ and $R_{hk0} = 17.0\%$ (to $\sin\vartheta/\lambda = 1.05$, $F \neq 0$).

Fig. 1. Hurlbutite. Projection yz of electron density in isolines

Fig. 2

Figure 2: Fig. 2

The final coordinates of the basis atoms are given in Table 1. All atoms are in general positions, and, consequently, the structure of hurlbutite is characterized by 39 independent parameters.

Table 1

Coordinates of the basis atoms in the structure of hurlbutite

	x	y	z		x	y	z
Ca	0.386	0.085	0.753	O_3	0.121	0.367	0.438
Be_1	0.059	0.196	0.435	O_4	0.126	0.364	0.055
Be_2	0.265	0.421	0.933	O_5	0.412	0.308	0.565
P_1	0.264	0.418	0.560	O_6	0.415	0.309	0.931
P_2	0.059	0.197	0.060	O_7	0.006	0.150	0.247
O_1	0.188	0.083	0.508	O_8	0.184	0.421	0.745
O_2	0.189	0.085	0.993				

As was indicated earlier ([2]), the structure of hurlbutite is close to the structure of danburite $CaB_2Si_2O_8$; both are framework structures with an alternation in the framework of four-membered and elongated eight-membered centrosymmetric rings of tetrahedra of two kinds—a motif very characteristic (with a difference in the orientation of the rings) of feldspar structures. In hurlbutite the general scheme of arrangement of the atoms is the same as in danburite, but in the latter each tetrahedron is linked (by common O vertices) with one of its own kind (and the corresponding O atom lies in the plane of symmetry)

Fig. 2. Similar yz projections of the structures: a—danburite and b—hurlbutite. Hatching marks SiO_4 tetrahedra in a and PO_4 tetrahedra in b. Only in the first structure are there mirror planes passing through the central O in the groups $[Si_2O_7]$ and $[B_2O_7]$

and with three of the other kind, whereas in hurlbutite each PO_4 tetrahedron is linked with four BeO_4 tetrahedra, and vice versa (Fig. 2a and 2b). The Ca atoms are situated in seven-vertex polyhedra characteristic for it (a trigonal prism plus a half-octahedron), elongated into columns along the c axis at the centers of the pseudo-square base xy of the cell.

The principal numerical characteristics of the structure are given in Table 2. The interatomic distances P—O do not go beyond 1.55-1.60 Å, and Be—O = 1.57-1.61 Å, with O—O edges in the PO_4 and BeO_4 tetrahedra, respectively, 2.50-2.66 Å and 2.51-2.72 Å. Seven Ca—O distances are equal to 2.42-2.52 Å (the two nearest next values are > 3.1 Å).

We see that the dimensions of the PO_4 and BeO_4 tetrahedra are approximately the same, and both kinds prove to be intermediate between SiO_4 and BO_4 in danburite.

As in the case of danburite, the closeness of all Ca–O distances in the seven-vertex polyhedron around Ca is noteworthy. In other structures (minerals), 6, 7, 8 distances from the loose cation Ca to the nearest O are usually characterized by a large scatter.

As indicated above, the structures of danburite $CaB_2Si_2O_8$ and hurlbutite $CaBe_2P_2O_8$ remain sufficiently close to the structure of feldspars,

Table 2

Interatomic distances (in Å), angular values, and valence balance in the structure of hurlbutite

P_I-tetrahedron	Distance
P_I—O_I	1.60
P_I—O_{III}	1.58
P_I—O_V	1.56
P_I—O_{VIII}	1.59
O_I—O_{III}	2.51
O_I—O_V	2.62
O_I—O_{VIII}	2.66
O_{III}—O_V	2.66
O_{III}—O_{VIII}	2.50
O_V—O_{VIII}	2.54

P_{II}-tetrahedron	Distance
P_{II}—O_{II}	1.55
P_{II}—O_{IV}	1.57
P_{II}—O_{VI}	1.56
P_{II}—O_{VII}	1.58
O_{II}—O_{IV}	2.56
O_{II}—O_{VI}	2.50
O_{II}—O_{VII}	2.56
O_{IV}—O_{VI}	2.51
O_{IV}—O_{VII}	2.60
O_{VI}—O_{VII}	2.61

Be_I-tetrahedron	Distance
Be_I—O_I	1.57

Be_I-tetrahedron	Distance
Be_I—O_{III}	1.59
Be_I—O_V	1.58_5
Be_I—O_{VII}	1.58_5
O_I—O_{III}	2.62
O_I—O_V	2.52
O_I—O_{VII}	2.60
O_{III}—O_V	2.52
O_{III}—O_{VII}	2.60
O_V—O_{VII}	2.63

Be_{II}-tetrahedron	Distance
Be_{II}—O_{II}	1.60
Be_{II}—O_{IV}	1.58
Be_{II}—O_{VI}	1.59
Be_{II}—O_{VIII}	1.61
O_{II}—O_{IV}	2.51
O_{II}—O_{VI}	2.64
O_{II}—O_{VIII}	2.72
O_{IV}—O_{VI}	2.63
O_{IV}—O_{VIII}	2.52
O_{VI}—O_{VIII}	2.60

Ca-polyhedron	Distance
Ca—O_I	2.52
Ca—O_{II}	2.49
Ca—O_{III}	2.46
Ca—O_{IV}	2.42
Ca—O_V	2.43
Ca—O_{VI}	2.46
Ca—O_{VIII}	2.47
Ca—O'_{III}	3.16
Ca—O'_{IV}	3.12

P—O—Be bond angles	Angle
$\angle P_I$—O_I—Be_I	129°
$\angle P_{II}$—O_{II}—Be_{II}	127°
$\angle P_I$—O_{III}—Be_I	121°
$\angle P_{II}$—O_{IV}—Be_{II}	125°

Figure 3: comparison of two pseudotetragonal projections

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P—O—Be bond angles	Angle
$\angle P_I$—O_V—Be_I	127°
$\angle P_{II}$—O_{VI}—Be_{II}	128°
$\angle P_{II}$—O_{VII}—Be_I	135°
$\angle P_I$—O_{VII}—Be_{II}	131°
Average	128°

Valence balance	
O_I	$= 2 + 1/28$
O_{II}	$= 2 + 1/28$
O_{III}	$= 2 + 1/28$
O_{IV}	$= 2 + 1/28$
O_V	$= 2 + 1/28$
O_{VI}	$= 2 + 1/28$
O_{VII}	$= 2 - 1/4$
O_{VIII}	$= 2 + 1/28$
Check	$7/28 = 1/4$

in particular anorthite $CaAl_2Si_2O_8$. To see the alternation, characteristic of all three structures, of eight-membered rings of tetrahedra with four-membered ones, it is necessary for hurlbutite to take the pseudotetragonal projection (001) in a base-centered aspect, and then it is comparable with the pseudotetragonal projection of anorthite (Figs. 3a and 3b).

Fig. 3. Comparison of two pseudotetragonal projections: **a**—hurlbutite and **b**—anorthite, with alternating rings of tetrahedra: eight-membered and four-membered. Tetrahedra facing upward from the plane of the drawing are drawn with solid lines, and tetrahedra facing downward—with dashed lines.

The structure of hurlbutite $CaBe_2P_2O_8$ served as the key to solving the structure of paracelsian (δ-$BaAl_2Si_2O_8$). Despite the greater closeness of the cell of the latter to the cell of rhombic danburite $CaB_2Si_2O_8$, paracelsian nevertheless proved to be monoclinic and a complete analogue of monoclinic hurlbutite with strict separation of Si and Al into different positions, analogous to the P and Be positions in hurlbutite.

	a, Å	b, Å	c, Å	β	$a:b:c$	Space group
Danburite	8.01	8.75	7.71	$=90^\circ$	$0.915:1:0.891$	$D_{2h}^{16}=Pnam$
Hurlbutite	8.29	8.80	7.81	$\simeq 90^\circ$	$0.942:1:0.887$	$C_{2h}^{5}=P2_1/a$
Paracelsian	9.08	9.58	8.58	$\simeq 90^\circ$	$0.947:1:0.895$	$C_{2h}^{5}=P2_1/a$

The details of the determination of the paracelsian structure are the subject of our paper ([3]).

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