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The Crystal Structure of Hurlbutite: A Comparison with Danburite and Anorthite

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Abstract

The crystal structure of hurlbutite, $CaBe_2P_2O_8$ ($a = 8.299$ Å; $b = 8.782$ Å; $c = 7.798$ Å; $\beta = 90.5°$; space group $P2_1/a$) has been refined to an R factor of 0.062. The refinement converged only when the signs of the z-coordinates reported by Bakakin and Belov (1959) were interchanged.

Hurlbutite is a framework of alternating BeO_4 and PO_4 tetrahedra with Ca in an irregular coordination polyhedron, which may be considered either 7- or 9-coordinated: $\langle Ca^{VII} - O\rangle = 2.469$ Å, $\langle Ca^{IX} - O\rangle = 2.620$ Å. The mean Be-O distances are 1.620 and 1.629 Å, and the mean P-O distances are 1.527 and 1.533 Å.

The trends observed between T-O bond lengths, oxygen coordination number, and Mulliken bond overlap populations for Be-O→P and P-O→Be bonds in hurlbutite are similar to those in anorthite and danburite. It is also demonstrated that the overlap populations account for part of the extrinsic effects of the Ca atoms, even though Ca was not included in the extended Hückel molecular orbital calculations.

Introduction

Hurlbutite, $CaBe_2P_2O_8$, is a rare pegmatitic mineral which was first described by Mrose (1952). She reported that the space group was *Pmmm* with $a = 8.29$, $b = 8.80$, and $c = 7.81$ Å. The following year Machatschki and Stradner (1953) compared Mrose's hurlbutite data with that of danburite and concluded that the two minerals were isostructural. However, Bakakin and Belov (1959) determined the structure of hurlbutite and showed that despite similarities the two minerals are not strictly isostructural. Both have topologically identical frameworks, but PO_4 and BeO_4 tetrahedra are in perfect alternation in hurlbutite whereas Si_2O_7 and B_2O_7 tetrahedral groups alternate in danburite. Furthermore, hurlbutite is monoclinic ($P2_1/a$, $\beta \sim 90°$) whereas danburite is orthorhombic (*Pnam*). It was apparent to us upon reviewing the structure analysis of hurlbutite that better data were needed to provide the precise bond lengths and angles required in an analysis of chemical bonding in this mineral.

Experimental Procedure

The hurlbutite studied is from Smith Mine, Newport, New Hampshire, and was donated by J. E. Arem and J. S. White, Jr. of the Smithsonian Institution. A single crystal, distinguished by its characteristic pale yellow color, was picked from a matrix of pale smoky quartz, as was the sample studied by Mrose (1952). A chemical analysis of hurlbutite from Smith Mine is given by Mrose (Table 3, 1952). Precession and Weissenberg X-ray photographs were used to verify the $P2_1/a$ space group determined by Bakakin and Belov (1959). Lattice parameters ($a = 8.299(1)$, $b = 8.782(2)$, $c = 7.798(3)$ Å, $\beta = 90.5°$) were obtained by least-squares refinement of Picker single-crystal diffractometer data. The intensity data, recorded with the diffractometer using Nb-filtered Mo radiation, were corrected for Lorentz-polarization effects using a program prepared by C. T. Prewitt. However, no absorption corrections were made because of the small size of the crystal ($0.1 \times 0.1 \times 0.2$ mm). The resulting 980 structural amplitudes were then submitted to the least-squares program of Busing, Martin, and Levy (1962), using the positional parameters reported by Bakakin and Belov (1960) as a trial structure, atomic scattering curves from Doyle and Turner (1968), and a weighting scheme similar to that devised by Hanson (1965). The refinement failed to converge, but a close correspondence found between $|F_{hkl(obs)}|$ and $|F_{hk\bar{l}(calc)}|$ suggested that the z-coordinates of hurlbutite were of

the wrong sign and that Bakakin and Belov (1959) had chosen an incorrect set of reciprocal lattice basis vectors, probably because they did not detect the small departure of β from 90°. To test this possibility, the z-coordinates of the atoms in the asymmetric unit were changed to $-z$ and the resulting parameters were submitted to least-squares refinement, yielding a final R-factor of 0.062. The refined positional and thermal parameters are given in Table 1. Using the Busing, Martin, and Levy (1964) function and error program, the interatomic distances, selected angles, and their associated e.s.d.'s were computed and are presented in Table 2. The Mulliken bond overlap populations listed in Table 2 were computed for the T-O bonds in $(T_5O_{16})^{n-}$ ions by the EHMO method summarized by Gibbs, Louisnathan, Ribbe, and Phillips (1974), using the valence orbital ionization potentials and orbital exponents given in Table 3, clamping all Be-O bonds at 1.62 Å, all P-O bonds at 1.54 Å, and using the observed O-T-O and T-O-T angles.

Discussion of the Structure

The structure of hurlbutite (Fig. 1) consists of alternating BeO_4 and PO_4 tetrahedra forming a framework of 4-, 6-, and 8-membered rings analogous to danburite, $CaB_2Si_2O_8$, which was described in detail and compared with the feldspar structures by Phillips, Gibbs, and Ribbe (1974). The primary difference between hurlbutite and danburite was discerned by Bakakin, Kravchenko, and Belov (1959): BeO_4 and PO_4 tetrahedra are ordered in hurlbutite whereas B_2O_7 and Si_2O_7 groups are ordered in danburite (see Fig. 2).

TABLE 1. Positional Parameters and Isotropic Temperature Factors (B) for Hurlbutite

Atom	x	y	z	B(Å^2)
M (Ca)	0.3869(2)*	0.0863(2)	0.2440(2)	0.66(3)
T_1m (P)	.2626(2)	.4177(2)	.4395(2)	.72(12)
$T_1$0 (Be)	.2680(10)	.4215(10)	.0707(11)	.75(12)
$T_2$0 (P)	.0588(2)	.1976(2)	-.0606(2)	.38(2)
T_2m (Be)	.0566(10)	.1949(10)	.5698(11)	.72(12)
$O_1$0	.1928(5)	.0888(5)	.0028(6)	.60(7)
O_1m	.1881(5)	.0737(5)	.4965(6)	.59(7)
$O_2$0	.1224(5)	.3634(5)	-.0550(6)	.54(7)
O_2m	.1296(6)	.3689(6)	.5630(6)	.78(7)
$O_3$0	.4215(6)	.3096(5)	.0675(6)	.72(7)
O_3m	.4034(5)	.3065(5)	.4371(6)	.61(7)
O_4	.4999(5)	.6553(5)	.2388(6)	.73(7)
O_5	.1854(5)	.4199(5)	.2591(6)	.77(7)

*The estimated standard errors are given in brackets and refer to the last decimal place.

TABLE 2. Interatomic Distances and Angles and Bond Overlap Populations (n) in Hurlbutite*

P-O distances (Å)		n(P-O)	O-O distances (Å)		and O-P-O angles (°)
T_1m-O_1m	1.513(5)	0.664	O_1m-O_2m	2.398(7)	103.9(3)
O_2m	1.532(6)	0.653	O_1m-O_3m	2.522(7)	112.3(3)
O_3m	1.523(5)	0.672	O_1m-O_5	2.554(7)	113.5(3)
O_5	1.541(5)	0.663	O_2m-O_3m	2.543(8)	112.7(3)
Mean	1.527		O_2m-O_5	2.460(7)	106.3(3)
			O_3m-O_5	2.479(7)	108.0(3)
$T_2$0-$O_1$0	1.544(5)	0.662	$O_1$0-$O_2$0	2.521(7)	109.2(2)
$O_2$0	1.549(5)	0.658	$O_1$0-$O_3$0	2.478(7)	107.8(3)
$O_3$0	1.523(6)	0.655	$O_1$0-O_4	2.529(7)	111.5(3)
O_4	1.515(5)	0.671	$O_2$0-$O_3$0	2.455(7)	106.1(3)
Mean	1.533		$O_2$0-O_4	2.530(7)	111.1(3)
			$O_3$0-O_4	2.500(7)	110.8(3)
Be-O distances (Å)		n(Be-O)	O-O distances (Å)		and O-Be-O angles (°)
$T_1$0-$O_1$0	1.611(10)	0.288	$O_1$0-$O_2$0	2.535(6)	102.8(5)
$O_2$0	1.631(9)	0.270	$O_1$0-$O_3$0	2.684(6)	112.9(6)
$O_3$0	1.609(10)	0.302	$O_1$0-O_5	2.726(7)	114.7(6)
O_5	1.627(10)	0.295	$O_2$0-$O_3$0	2.694(7)	112.5(6)
Mean	1.620		$O_2$0-O_5	2.549(7)	103.0(5)
			$O_3$0-O_5	2.657(8)	110.4(6)
T_2m-O_1m	1.631(10)	0.298	O_1m-O_2m	2.689(7)	110.3(6)
O_2m	1.645(10)	0.278	O_1m-O_3m	2.624(6)	107.0(5)
O_3m	1.632(9)	0.282	O_1m-O_4	2.695(8)	112.7(6)
O_4	1.606(10)	0.309	O_2m-O_3m	2.613(7)	105.7(6)
Mean	1.629		O_2m-O_4	2.663(8)	110.0(6)
			O_3m-O_4	2.666(7)	110.8(6)

T-O-T angles (°)		Ca-O distances (Å)	
T_1m-O_1m-T_2m	130.9	Ca-$O_1$0	2.466(7)
T_1m-O_2m-T_2m	123.2	O_1m	2.583(7)
T_1m-O_3m-T_2m	126.2	$O_2$0	2.451(5)
T_1m-O_5 -T_1m	130.5	O_2m	2.435(5)
		$O_3$0	2.414(5)
$T_2$0-$O_1$0-$T_1$0	126.7	O_3m	2.454(5)
$T_2$0-$O_2$0-$T_1$0	124.2	O_5	2.479(5)
$T_2$0-$O_3$0-$T_1$0	129.2	$O_2$0'	3.087(8)
$T_2$0-O_4 -$T_2$0	134.8	*Ca-$T_1$0*	*3.117*
		Ca-T_1m	*3.143*
		O_2m'	3.211(8)

* Estimated standard errors are in parentheses and refer to the last decimal place.

There is also a difference in Ca coordination. In danburite there are seven Ca-O distances shorter than 2.50 Å and two at ~3.02 Å; in hurlbutite there are seven Ca-O distances shorter than 2.50 Å, an eighth at 3.087 Å and a ninth at 3.211 Å (Table 2). But intermediate between the eighth and ninth oxygens are two Ca-T distances. The question thus arises as to the coordination number of Ca. A 7-fold coordination model is more consistent with structurally similar danburite, anorthite, reedmergnerite and albite, as indicated by the strong correlation between

TABLE 3. Valence Orbital Ionization Potentials (VOIP) and Orbital Exponents (ζ) for Be, P, and O

Atom	Atomic Orbital	VOIP	ζ
Be	2s	0.956	-9.89
	2p	0.905	-5.94
P	3s	1.881	-18.76
	3p	1.629	-10.11
O	2s	2.246	-32.34
	2p	2.227	-15.79

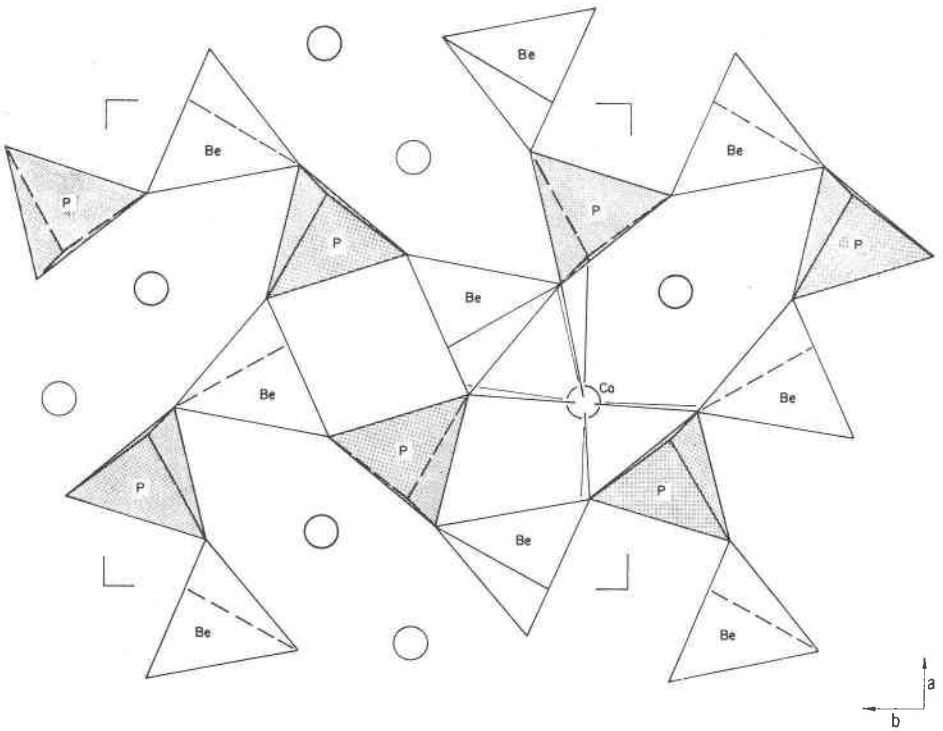

FIG. 1. A portion of the hurlbutite structure viewed down c^* showing the framework of 4- and 8-membered rings formed by alternating Be- and P-containing tetrahedra. The open circles represent Ca atoms in 9-fold coordinaiton.

mean Ca-O and Na-O bond lengths and the isotropic temperature factors for the 7-coordinated Ca and Na atoms in these structures (Fig. 3). If nothing more, this correlation indicates that the nearest-neighbor oxygens control the magnitude of the apparent "thermal" vibration parameter. On the other hand, just as the 9-fold coordination model was more satisfying in terms of explaining mean Si-O and B-O bond-length variations in danburite as a function of coordination number and bond overlap population

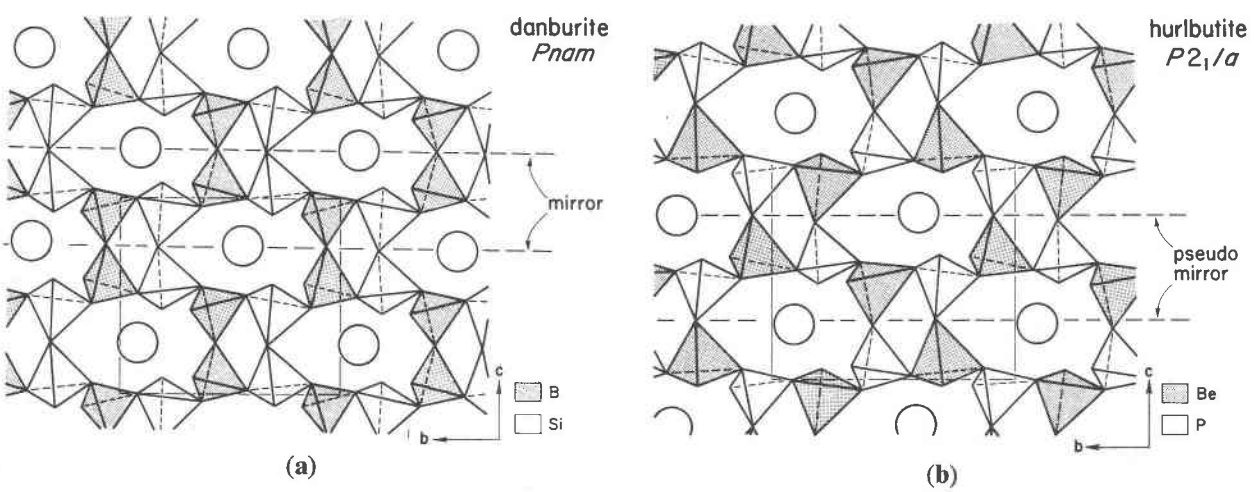

FIG. 2. Schematic drawings of (a) hurlbutite and (b) danburite viewed down a^*, showing their similar topologies and their contrasting ordering schemes (modified after Craig, Louisnathan, and Gibbs, in preparation).

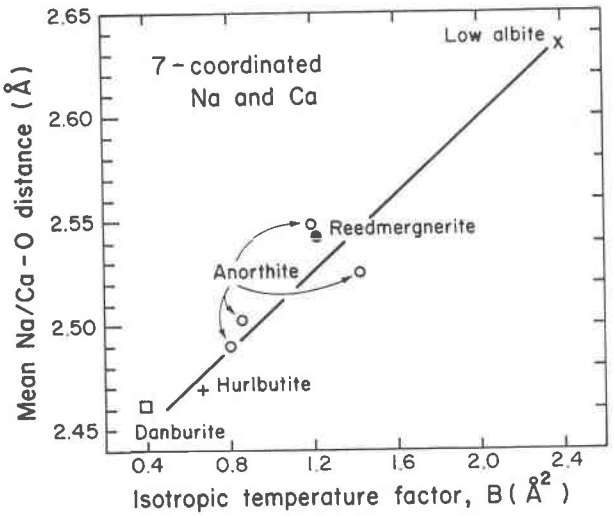

FIG. 3. A plot of mean Ca-O distances for hurlbutite, danburite, and anorthite and mean Na-O distances for reedmergnerite and low albite vs the individual isotropic temperature factors for 7-coordinated Ca and Na. *Cf* Phillips *et al* (1974, Fig. 1, p. 82).

(Phillips *et al*, 1974, Fig. 4, p. 84), an 8- or 9-fold coordination model for hurlbutite also gives better correlation with these parameters (Fig. 4). Furthermore, when the O_20 and O_2m atoms are considered to be 4-coordinated (*i.e.*, C.N.(Ca) = 9), the longest *T*-O bond in three of the four tetrahedra involves one or the other of these atoms. As expected, the shortest P-O bond in the T_20 tetrahedron and the shortest Be-O bond in the T_2m tetrahedron are to the 2-coordinated O_4 atom (Table 2).

In a comparison of the structures of danburite and the feldspars, Phillips *et al* (1974) found that Mulliken bond-overlap populations, $n(T\text{-O})$, are strongly correlated with mean observed *T*-O distances and the coordination number of the oxygens involved in the *T*-O bond. Figure 4 shows that the same trends are observed for the Be-O → P and P-O → Be bonds in hurlbutite, regardless of whether the Ca atom is assumed to be 7- or 9-coordinated. Here the bond-overlap parameter is normalized by subtracting the mean overlap populations for *T*-O bonds involving 4-coordinated oxygen atoms from those involving 4-, 3- and 2-coordinated oxygens:

$$\Delta n \equiv \langle n(T - O^{II,III,IV})\rangle - \langle n(T - O^{IV})\rangle.$$

In order to taken into account the effects of both the coordination number of oxygen and the individual Ca-O distances on tetrahedral bond lengths, Phillips *et al* (1973) introduced the parameter $\Sigma[1/(\text{Ca-O})^2]$ and found it to be strongly correlated with the individual Al-O ($r = 0.84$) and Si-O ($r = 0.90$) distances in anorthite, where r is the correlation coefficient. When mean values of $\Sigma[1/(\text{Ca-O})^2]$ for

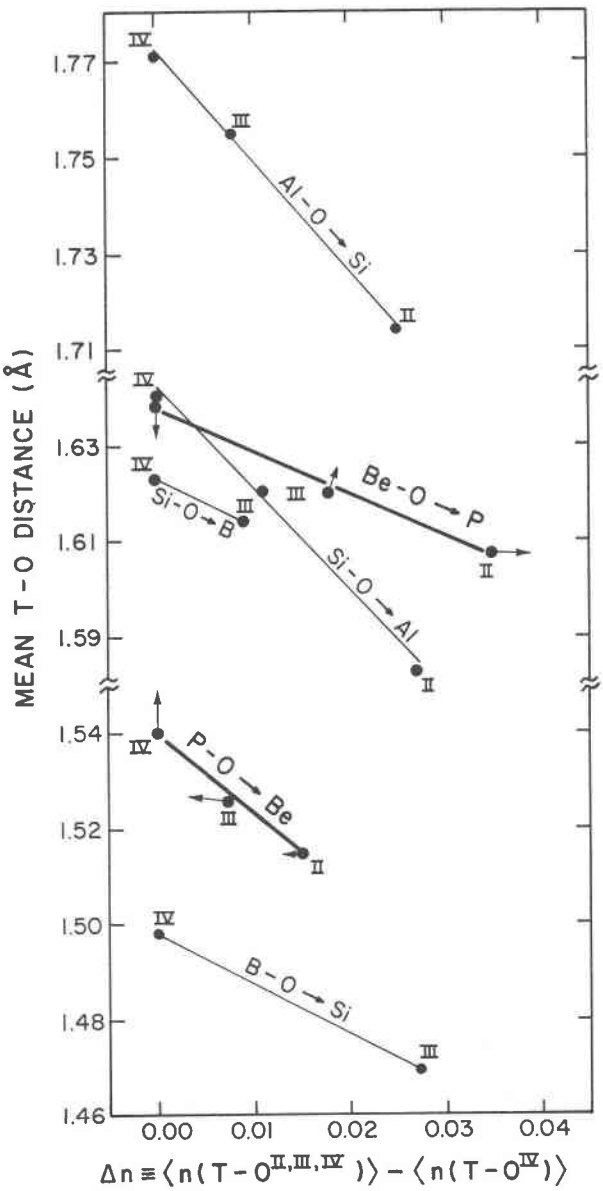

FIG. 4. The differences in the mean Mulliken bond overlap populations for *T*-O bonds involving 4-coordinated oxygen atoms and those involving 4-, 3- and 2-coordinated oxygens plotted against mean *T*-O distances for Al-O→Si and Si-O→Al bonds in anorthite, for Si-O→B and B-O→Si bonds in danburite, and for Be-O→P and P-O→Be bonds in hurlbutite. The tips of the arrows indicate data points for a 7-coordinated Ca atom in hurlbutite, whereas the solid dots represent data points for the 9-coordinated model. The Roman numerals indicate the coordination number of oxygen.

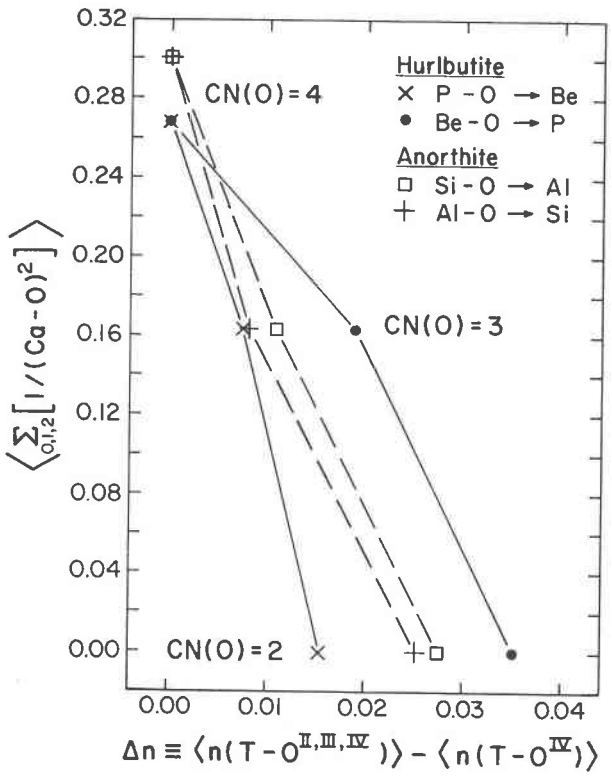

FIG. 5. A plot of Δn versus the mean values of $\Sigma[1/(Ca\text{-}O)^2]$ for 4-, 3- and 2-coordinated oxygens involved in Be-O→P and P-O→Be bonds in hurlbutite and Si-O→Al and Al-O→Si bonds in anorthite.

4-, 3- and 2-coordinated oxygens in anorthite are plotted against Δn, we find the expected relationship: larger Δn values are associated with smaller coordination number and $\Sigma[1/(Ca\text{-}O)^2]$ values. These relationships hold as well for the P-O → Be and Be-O → P bonds in hurlbutite as they do for the Si-O → Al and Al-O → Si bonds in anorthite (see Fig. 5). Inasmuch as the bond-overlap populations, n, were calculated for T_5O_{16} ions assuming fixed T-O distances, and using only the observed T-O-T and O-T-O angles, it is evident that the molecular orbital calculations retain part of the extrinsic effects of the Ca atoms, even though they were not included in the computations.

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