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A Refinement of the Crystal Structure of Herderite, $CaBePO_4OH$

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Abstract

The crystal structure of herderite [$a = 9.789(2)$, $b = 7.661(1)$, $c = 4.804(1)$ Å, $\beta = 90.02(1)°$, $P2_1/a$] has been refined by least-squares methods to an unweighted R of 0.036. The PO_4 tetrahedra in the $(BePO_4OH)_\infty$ sheet are more regular than the BeO_3OH tetrahedra, reflecting the more directional nature of the P–O bond and the absence of any shared $O \cdots O$ edges in the PO_4 tetrahedra. Plots of $\langle O\text{–}T\text{–}O \rangle_3$, the average of the three tetrahedral angles common to a T–O bond, *vs* the length of the bonds in the two tetrahedra are consistent with extended Hückel molecular orbital theory. Variations in the P–O bond lengths can be rationalized in terms of Mulliken bond-overlap populations, the Baur (1970) extended electrostatic valence rule, and the Brown-Shannon (1973) relationship between bond length and bond strength.

Introduction

Herderite, $CaBePO_4OH$, is a rare phosphate occurring primarily in pegmatites. Its cell dimensions and space group symmetry were first determined by Strunz (1936) who recognized its structural similarity with datolite, $CaBSiO_4(OH)$. A determination of the herderite structure by Pavlov and Belov (1959) later confirmed that the two minerals are isostructural. Pant and Cruickshank (1967) have since examined the herderite structure and have found that much of its P-O bond length variation can be related to balancing of valences. However, herderite was not studied in detail because of the imprecise nature of Pavlov and Belov's refinement. In our investigation, the crystal structure of herderite has been refined, and the resulting bond length and angle data are examined in terms of the predictions of extended Hückel molecular orbital (EHMO) theory, Baur's extended electrostatic valence rule, and Brown and Shannon's (1973) bond length-bond strength relationships.

Experimental Procedure

The herderite crystal used in the analysis was hand-picked from a homogeneous sample collected at Golconda Mines, Minas Gerais, Brazil. We thank Dr. Joel Arem, then of the Smithsonian Institute, Washington, D.C., for providing the sample (121024). The crystal selected for the study was optically homogeneous, clear, and nearly equidimensional with a diameter of slightly less than 0.1 mm. An examination of zero through second level precession and Weissenberg photographs, recorded using Nb-filtered Mo radiation, confirmed the space group symmetry as $P2_1/a$, in agreement with Pavlov and Belov (1959). The cell dimensions ($a = 9.789(2)$, $b = 7.661(1)$, $c = 4.804(1)$ Å, $\beta = 90.02(1)°$) were obtained from least-squares refinement of single crystal diffractometer data. Nb-filtered Mo radiation was used to collect 1150 raw intensities. Intensity data were corrected for Lorentz-polarization effects and converted to $|F_{obs}|$ using a program written by C. T. Prewitt. Absorption effects were not considered significant because of the composition and the small size of the crystal. Corrected structural amplitudes were submitted to a least-squares refinement using the ORFLS program of Busing, Martin, and Levy (1962) and the atomic coordinates of Pavlov and Belov (1959) as starting parameters in the refinement. Only structural amplitudes with magnitudes four times larger than their estimated standard deviations were used in the refinement. Atomic scattering factors were taken from Doyle and Turner (1968) assuming neutral atoms, and the weighting scheme employed was similar to that proposed by Hanson (1965). Isotropic and anisotropic refinements, with 999 reflections, yielded final unweighted residuals of 0.044 and 0.036, respectively. At this point in the refinement a difference

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TABLE 1. Positional Parameters, Anisotropic Temperature Factors (×10^4), and Equivalent Isotropic Temperature Factors for Herderite

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
O(1)	0.0396(2)*	0.3988(3)	0.2466(5)	13(1)	26(3)	70(8)	0(2)	-3(3)	13(4)	0.59(4)
O(2)	0.4585(2)	0.2835(3)	0.6521(5)	7(2)	25(3)	67(8)	3(2)	11(3)	10(4)	0.51(4)
O(3)	0.1935(2)	0.3445(3)	0.6669(5)	8(1)	33(3)	54(8)	-8(1)	-2(3)	-5(4)	0.53(4)
O(4)	0.1428(2)	0.1059(3)	0.3305(5)	17(2)	16(3)	77(9)	4(2)	18(4)	-0(5)	0.61(4)
OH	0.3332(2)	0.4123(3)	0.2039(5)	12(2)	31(3)	41(7)	3(2)	-3(3)	2(4)	0.60(4)
Ca	0.3309(1)	0.1116(1)	0.9974(1)	10(1)	19(1)	54(2)	-0(1)	4(1)	-7(1)	0.45(1)
P	0.0815(1)	0.2710(1)	0.4708(1)	5(1)	9(1)	35(2)	-0(1)	2(1)	3(1)	0.26(2)
Be	0.3398(4)	0.4141(5)	0.5370(9)	16(3)	13(5)	51(3)	-0(3)	-3(6)	6(7)	0.44(7)

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

fourier map was computed to determine the possible location of the hydrogen atom. The only significant peak (approximately 0.76e^-/Å^3) on the difference map was found at (0.386, 0.481, 0.137) at a distance of approximately 0.8 Å from O(5). This was assumed to represent the hydrogen atom. The position was chemically reasonable and consistent with the hydrogen position in datolite (Foit, Phillips, and Gibbs, 1973). Subsequent least-squares refinements with the H included failed to reduce *R* significantly, and consequently the atom was not included in the final refinement.

The atomic coordinates and temperature factors are tabulated in Table 1. The bond distances, angles, and their associated e.s.d.'s were computed using the function and error program of Busing, Martin, and Levy (1964) and are given in Table 2. The observed structural amplitudes and the calculated structure factors are compared in Table 3.

Discussion

Herderite consists of sheets of corner-sharing PO_4 and BeO_3OH tetrahedra (Fig. 1a) linked along

TABLE 2a. Bond Lengths and Angles in the PO_4 and BeO_3OH Tetrahedra in Herderite*

PO_4 Tetrahedron

P-O Bond Lengths		O-P-O Angles		O-O Distances	
P-O(1)	1.513(3)	O(1)-P-O(2')	111.4(1)	O(1)-O(2')	2.524(4)
P-O(2')	1.543(3)	O(1)-P-O(3)	112.9(1)	O(1)-O(3)	2.554(4)
P-O(3)	1.552(3)	O(1)-P-O(4)	108.9(1)	O(1)-O(4)	2.494(3)
P-O(4)	1.554(3)	O(2')-P-O(3)	107.9(1)	O(2')-O(3)	2.502(3)
<P-O>	1.541	O(2')-P-O(4)	109.0(1)	O(2')-O(4)	2.521(4)
		O(3)-P-O(4)	106.6(1)	O(3)-O(4)	2.490(4)
		<O-P-O>	109.5	<O-O>	2.514

BeO_3OH Tetrahedron

Be-(O,OH) Bond Lengths		O-Be-(O,OH) Angles		O-(O,OH) Distances	
Be-O(2)	1.630(5)	O(2)-Be-OH	111.3(3)	O(2)-O(3)**	2.637(3)
Be-O(3)	1.651(5)	O(2)-Be-O(3)	107.0(3)	O(2)-O(4')	2.663(3)
Be-O(4')	1.610(5)	O(2)-Be-O(4')	110.5(3)	O(2)-OH	2.668(4)
Be-OH	1.602(5)	O(3)-Be-OH	109.8(3)	O(3)-O(4')**	2.565(3)
<Be-(O,OH)>	1.623	O(4')-Be-OH	114.0(3)	O(3)-OH	2.662(4)
		O(3)-Be-O(4')	103.7(3)	O(4')-OH	2.694(4)
		<O-Be-(O,OH)>	109.4	<O-(O,OH)>	2.648

P-O-Be Angles

P-O(2')-Be	122.1(2)	P-O(4)-Be	127.7(2)
P-O(3)-Be	120.1(2)		

* *Estimated standard deviations are in parentheses and refer to the last decimal place.*
** *Shared edge.*

TABLE 2b. Bond Lengths and Angles in the $CaO_6(OH)_2$ Polyhedron in Herderite*

O-Ca-(O,OH) Angles

O(1')-Ca-O(2)	76.31(11)	O(3)-Ca-OH'	81.57(10)
O(1')-Ca-O(3)	115.02(8)	O(3)-Ca-O(1")	137.54(9)
O(1')-Ca-O(4")	135.59(9)	O(3)-Ca-O(3')	145.23(4)
O(1')-Ca-OH'	73.96(9)	O(3)-Ca-OH"	68.63(9)
O(1')-Ca-O(1")	76.46(10)	O(4")-Ca-OH'	75.51(9)
O(1')-Ca-O(3')	79.40(9)	O(4")-Ca-O(1")	108.58(10)
O(1')-Ca-OH"	145.17(9)	O(4")-Ca-O(3')	60.85(9)
O(2)-Ca-O(3)	60.65(7)	O(4")-Ca-OH"	76.34(8)
O(2)-Ca-O(4")	146.67(8)	OH'-Ca-O(1")	138.91(9)
O(2)-Ca-OH'	113.93(9)	OH'-Ca-O(3')	72.08(10)
O(2)-Ca-O(1")	85.47(9)	OH'-Ca-OH"	138.08(5)
O(2)-Ca-O(3')	151.76(8)	O(1")-Ca-O(3')	74.97(10)
O(2)-Ca-OH"	76.73(8)	O(1")-Ca-OH'	79.82(9)
O(3)-Ca-O(4")	91.22(8)	O(3')-Ca-OH"	118.38(8)

<O-Ca-(O,OH)> 100.17

Ca-(O,OH) Bond Lengths

Ca-O(1')	2.375(3)	Ca-O(3')	2.616(3)
Ca-O(1")	2.369(3)	Ca-O(4")	2.439(4)
Ca-O(2)	2.459(3)	Ca-OH'	2.418(3)
Ca-O(3)	2.741(3)	Ca-OH"	2.509(3)

<Ca-(O,OH)> 2.491

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

Table 3. Observ.d and Calculated Structure Factors for Herderite

h	k	l	F(obs)	F(calc)
8	-7	1	21.58	17.78
1	-7	3	21.59	18.12
11	-1	1	21.65	21.93
14	-2	0	21.78	22.81
7	-8	0	21.90	17.47
9	-2	4	21.94	18.87
2	-10	2	22.07	18.89
3	-4	5	22.13	26.69
2	-4	1	22.15	17.73
8	-7	-1	22.32	15.55
1	-2	2	22.43	21.21
5	-6	-3	22.46	27.45
1	-5	0	22.64	19.95
11	-7	0	22.69	17.23
2	-2	-5	22.73	22.96
5	-1	4	22.85	20.21
6	-8	0	23.01	20.37
8	-8	1	23.06	22.61
5	-6	-5	23.18	19.02
7	-1	6	23.19	17.99
5	-3	1	23.20	26.90
6	-6	0	23.24	21.91
12	-1	-2	23.26	17.36
5	-5	4	23.28	15.56
0	-11	1	23.35	16.21
10	-4	4	23.41	20.09
12	-1	-3	23.41	26.81
4	10	1	23.44	21.12
2	0	4	23.44	23.44
2	-8	-1	23.47	20.86
8	-2	-6	23.51	23.07
8	-8	-3	23.57	26.41
10	-3	-5	23.59	22.44
7	-5	0	23.61	20.73
2	-9	-2	23.61	20.37
2	-8	-2	23.62	25.43
6	0	2	23.63	22.84
11	-3	-1	23,65	21.59
9	-2	-4	23.65	20.30
0	-8	5	23.72	23.30
4	-8	5	23.75	21.47
3	-8	1	23.75	21.56
11	-6	3	23.75	20.19
10	-1	2	23.77	21.40
3	-4	-6	23.88	22.82
13	-4	1	24.10	29.87
12	-7	0	24.11	23.84
0	-6	3	24.17	24.48
0	-5	5	24.17	28.10
9	-4	5	24.19	24.19
1	-8	1	24.21	26.75
10	-4	-1	24.23	21.78
6	-2	5	24.28	23.97
11	-5	1	24.30	23.58
7	-5	-3	24.36	23.51
5	-4	6	24.37	24.56
7	-7	1	24.40	25.52
1	-3	5	24.43	26.82
7	-3	2	24.46	28.12
10	-8	-1	24.51	22.52
5	-10	2	24.57	23.26
0	-5	3	24.62	18.04
5	-7	-1	24.64	24.97
6	-8	4	24.69	26.63
1	-10	2	24.71	25.36
1	-10	0	24.71	29.00
3	-4	4	24.84	23.17
9	-4	2	24.88	25.23
8	-3	-4	24.88	22.03
1	-1	-6	24.88	24.13
7	-1	4	24.90	25.55
2	-6	0	25.10	23.74
12	-7	0	25.11	23.84
6	-1	-3	25.13	21.76
0	-4	-2	25.15	24.21
6	-2	-6	25.18	24.53
9	-6	0	25.24	23.22
0	-5	-4	25,24	21.52
9	-3	0	25.36	31.29
6	-9	1	25.38	26.16
4	10	0	25.43	23.02
0	-5	-6	25.48	21.75
1	-7	-2	25.50	31.51
2	-5	5	25.54	29.47
0	-2	6	25.57	26.12
8	-4	0	25.57	21.90
10	5	-2	25.59	26.90
12	-1	-1	25.66	27.05
8	-6	-5	25.73	28.78
1	-8	-2	25.74	24.68
15	-1	0	25.75	26.19
5	-4	5	25.87	25.16
3	-1	-5	25.87	23.51
3	-3	6	25.92	24.24
7	-7	-2	25.92	25.71
3	-5	0	25.93	23.19
13	-4	2	25.95	27.00
6	-8	-2	25.98	26.41
6	-3	0	26.02	27.83
7	-9	0	26.03	22.41
7	-6	5	26.11	25.38
13	-3	-2	26.15	25.41
0	-4	2	26.17	24.21
9	-6	-1	26.29	24.27
0	-2	-6	26.27	26.12
1	-6	5	26.33	25.13
3	-5	0	26.38	23.19
8	0	2	26.39	24.42
3	-7	2	26.41	28.01
7	-9	0	26.53	22.41
9	-4	-3	26.60	22.88
2	-3	-5	26.61	27.78
6	-5	6	26.63	26.04
5	-9	4	26.64	25.44
14	-2	1	26.65	20.36
0	-7	-2	26.65	28.02
2	-1	2	26.70	24.64
6	-3	5	26.77	23.54
0	-8	1	26.92	23.40
11	-7	2	26.96	23.91
10	-5	4	26.99	29.35
7	-10	1	27.07	28.72
0	-2	7	27.12	23,65
8	-9	-1	27.13	23.52
2	-7	0	27.28	25.05
9	-9	1	27.40	27.71
8	-4	4	27.47	27.86
4	-2	-6	27.48	29.62
1	-7	5	27.60	26.53
5	-5	-2	27.60	24.09
2	-7	0	27.67	25.05
0	-6	6	27.67	29.01
5	-4	-2	27.72	25.48
0	-6	-6	27.84	29.01
3	-8	4	27.86	29.06
5	-7	5	27.92	23.78
1	-2	-4	27.98	25.38
12	-1	3	28.05	26.61
7	-9	-3	28.05	25.34
6	-5	5	28.08	27.75
4	-6	6	28.09	25.95
6	-1	2	28.18	27.19
8	-4	3	28.20	28.28
9	-3	-2	28.24	30.90
11	-6	-3	28.26	27.92
4	-7	-3	28.29	27.25
2	-5	0	28.36	30.22
7	-9	2	28.38	22.51
2	-5	0	28.40	30.22
13	-2	0	28.40	28.05
10	-1	5	28.42	28.49
9	-1	-5	28.48	28.73
7	-4	-5	28.51	36.30
7	-3	3	28.54	28.78
11	-7	1	28.58	30.47
10	-2	-2	28.61	24.50
9	-1	0	28.71	31.29
14	-2	-2	28.78	22.88
5	-2	-5	28.78	27.51
1	-2	-6	28.80	24.74
3	-8	-2	28.86	29.92
11	-2	1	28.89	26.78
2	-8	-3	28.90	30.97
5	-5	6	28.98	33.89
4	-4	-2	28.98	28.66
0	-2	-3	29.02	28.96
0	-9	3	29.04	28.83
3	-5	3	29.10	28.14
8	-3	4	29.18	25.68
0	-9	-3	29.31	28.83
14	-2	0	29.32	22.81
3	-9	0	29.44	30.30
1	-3	-1	29.47	28.08
7	-8	-4	29.55	30.73
4	-7	5	29.56	28.17
1	-10	0	29.57	29.00
2	-5	-5	29.63	30.33
1	-7	5	29.65	28.75
8	-4	-2	29.76	27.16
2	-4	-5	29.76	28.11
10	-2	-1	29.76	27.68
6	-1	6	29.77	29.84
9	-7	2	29.79	30.40
5	-5	5	29.79	25.35
5	-1	-5	29.85	27.64
13	-2	0	29.89	28.05
4	0	5	29.90	30.54
2	-1	4	29.95	27.53
6	-4	1	29.95	28.40
6	-3	0	30.05	27.83
1	-10	1	30.10	30.05
8	-2	-4	30.11	31.31
4	-1	5	30.11	31.73
5	-4	2	30.20	33.44
10	-2	5	30.21	26.22
8	-4	0	30.24	21.90
12	-2	4	30.25	26.48
8	-8	-2	30.26	29.55
0	-5	1	30.47	29.83
11	-2	-4	30.50	27.22
1	-4	6	30.53	31.78
2	-6	-1	30.57	24.30
4	-2	-5	30.63	33.71
0	-5	-1	30.64	29.83
1	-10	1	30.67	27.69
2	-11	2	30.69	29.65
3	-5	-6	30.79	30.98
2	-6	6	30.80	29.07
5	-4	-3	30.82	34.78
0	0	5	30.88	28.92
9	-8	1	30.95	27.55
7	-3	0	30.99	32.18
3	-5	1	31.23	33.30
2	-5	-1	31.25	28.09
3	-3	-5	31.28	30.37
8	-5	-2	31.28	29.10
12	-2	-4	31.28	30.44
5	-7	-3	31.31	29.91
1	-3	-1	31.33	31.41
1	-3	7	31.44	28.89
3	-8	-4	31.47	31.14
0	0	-5	31.47	28.92
5	-1	-4	31.57	33.02
4	-9	2	31.58	31.36
11	-2	-2	31.62	32.67
1	-4	-1	31.63	29.86
7	-3	0	31.65	32.18
13	-4	-2	31.68	33.08
2	-5	1	31.72	30.59
8	-1	-5	31.79	31.05
9	-2	-1	31.82	33.79
1	-6	-5	31.84	31.01
9	-7	3	31.86	32.62
2	-2	-1	31.90	32.56
5	-11	0	31.95	31.69
5	-7	-2	32.00	32.18
12	-1	4	32.04	29.69
2	-3	3	32.12	28.98
5	-7	2	32.13	31.94
8	-6	2	32.18	30.45
9	-7	0	32.19	32.74
14	-2	2	32.20	31.43
4	-3	2	32.28	31.40
1	-5	6	32.29	32.50
8	-6	-3	32.38	31.71
7	-1	1	32.41	30.23
12	-2	2	32.44	33.05
6	-2	6	32.51	28.14
3	-6	0	32.65	32.01
4	-5	-5	32.67	29.00
5	-3	6	32.68	32.71
1	-5	-4	32.68	33.17
12	-3	1	32.79	36.34
2	-3	6	32.91	30.27
4	-2	-4	32.91	36.66
13	-1	0	32.92	26.19
9	-8	3	32.99	32.23
9	-4	0	32.99	36.32
5	-6	0	33.04	32.01
8	-2	2	33.08	31.71
9	-2	-5	33.11	33.84
8	-2	4	33.21	34.20
3	-11	0	33.27	30.42
5	-8	3	33.32	33.71
4	0	2	33.33	34.49
11	-1	-2	33.34	34.44
4	-10	2	33.35	31.89
3	-3	-4	33.42	35.61
13	-3	-2	33.52	34.61
4	0	6	33.53	32.27
5	-11	0	33.61	31.69
3	-2	5	33.63	32.73
7	-11	0	33.69	30.05
4	-8	3	33.74	32.40
8	-6	3	33.75	32.25
1	-5	-6	33.75	33.42
10	-4	1	33.79	33.55
8	-5	-5	33.79	33.61
7	-8	2	33.83	36.98
9	-6	3	33.92	33.66
9	-6	2	34.11	33.60
2	-9	-1	34.11	35.49
7	-8	3	34.14	34.87
3	-8	2	34.14	35.16
5	-10	-2	34.22	33.13
3	-6	-2	34.38	38.03
13	-2	3	34.39	32.00
3	-5	5	34.55	32.50
4	-4	-1	34.56	33.44
6	-3	6	34.60	29.11
3	-6	5	34.64	33.36
9	-1	5	34.69	32.58
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8	-8	0	34.71	35.63
3	-6	-6	34.72	32.40
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10	-1	-3	35.70	32.50
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5	-1	-3	70.23	69.87
6	-8	3	70.24	72.92
10	-4	-4	70.29	72.30
6	-4	-4	70.49	70.94
7	-1	-2	70.61	70.85
8	-2	-1	70.69	69.50
8	-1	-2	70.80	71.21
13	-2	-3	70.91	74.36
9	-1	1	70.95	68.73
12	-4	-1	71.17	71.04
2	-4	-2	71.19	69.11
3	-5	4	71.22	72.25
8	0	5	71.43	69.74
9	-5	-3	71.67	72.89
9	-5	1	71.71	72.55
8	-1	-6	71.89	72.92
8	-2	5	72.04	70.78
10	0	1	72.56	71.13
9	-9	-1	73.20	75.50
5	-1	3	73.22	73.13
13	-2	1	73.79	72.85
5	-7	0	74.01	74.01
8	-4	5	74.13	81.04
6	-7	-4	74.20	70.85
6	-4	-6	74.23	75.36
0	-1	4	74.55	76.34
2	-4	6	74.56	78.99
11	-2	-1	74.60	74.14
0	-4	5	74.65	80.52
0	-1	-4	75.43	76.34
5	-1	-1	75.49	73.72
3	-7	0	75.74	74.01
3	-3	3	75.89	76.71
3	-5	2	75.94	75.83
2	-5	-2	76.22	75.79
2	-1	-1	76.32	77.00
10	-7	3	76.51	78.97
10	-3	4	77.23	77.68
1	-9	2	77.60	76.84
1	-8	0	77.92	76.88
6	-1	3	77.96	75.57
5	-10	0	78.44	81.55
9	-1	-3	78.52	78.26
3	-3	0	78.54	79.84
1	-4	-2	78.85	78.17
1	-4	3	78.94	84.28
1	-3	4	79.15	80.80
8	-5	-1	79.75	82.93
0	-6	-4	79.81	81.37
4	-5	-1	80.15	78.03
1	-3	0	80.40	85.82
1	-9	-4	80.44	80.47
1	-6	3	80.66	83.57
0	-4	-5	80.99	80.52
5	-5	0	81.08	79.84
2	-6	1	81.19	83.86
10	-5	2	81.41	83.25
0	-6	4	81.61	81.37
9	-5	3	81.73	81.39
8	-7	2	81.75	82.48
14	-3	0	81.81	89.79
5	-10	0	81.83	81.55
2	-3	-4	82.12	83.90
5	-8	0	82.17	81.85
5	-6	1	82.23	83.20
8	-3	-5	82.24	84.30
4	-7	4	82.36	85.95
4	-7	2	82.41	83.06
1	-2	-5	82.49	83.93
10	-7	-1	82.74	83.66
1	-8	-1	83.27	82.24
10	-1	1	83.51	84.34
1	-9	4	83.59	84.61
7	-1	-1	83.61	82.05
5	-6	-1	84.41	84.09
5	-9	0	84.80	81.85
5	-5	-4	84.94	85.74
10	-3	-4	85.36	85.85
4	-7	-6	85.40	85.31
10	-1	3	85.77	85.32
5	-8	-1	86.05	86.88
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8	-7	-2	86.21	86.20
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10	-3	2	87.42	93.51
0	-3	1	87.87	89.50
0	-8	0	88.00	89.64
3	-1	-1	88.01	87.56
0	-8	0	88.25	89.64
8	-4	1	88.44	94.99
1	-1	4	88.77	87.81
1	-1	0	88.88	85.82
14	-3	0	89.08	89.79
3	-6	1	89.36	89.48
12	-4	1	89.46	100.86
3	-5	-1	89.66	88.65
3	-8	-1	89.88	88.35
2	-4	2	91.12	91.44
2	-1	1	91.35	92.70
3	-1	3	91.59	89.28
7	-4	-3	92.09	92.66
3	-3	-1	92.38	84.70
12	0	0	92.59	92.32
12	0	2	92.71	91.98
12	0	0	93.68	92.32
4	-5	1	93.84	93.82
1	-3	-2	93.84	93.97
4	-1	3	94.00	91.15
1	-6	0	95.75	95.62
6	-6	-1	96.08	94.43
0	-3	-3	96.26	89.50
12	0	4	96.39	96.43
4	-3	0	96.49	101.11
4	-1	-2	96.54	91.17
11	-2	3	96.58	96.77
2	0	5	96.83	97.23
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8	-2	-2	97.48	97.76
1	-6	0	98.46	95.62
8	-1	-4	98.58	99.83
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0	0	3	99.73	101.57
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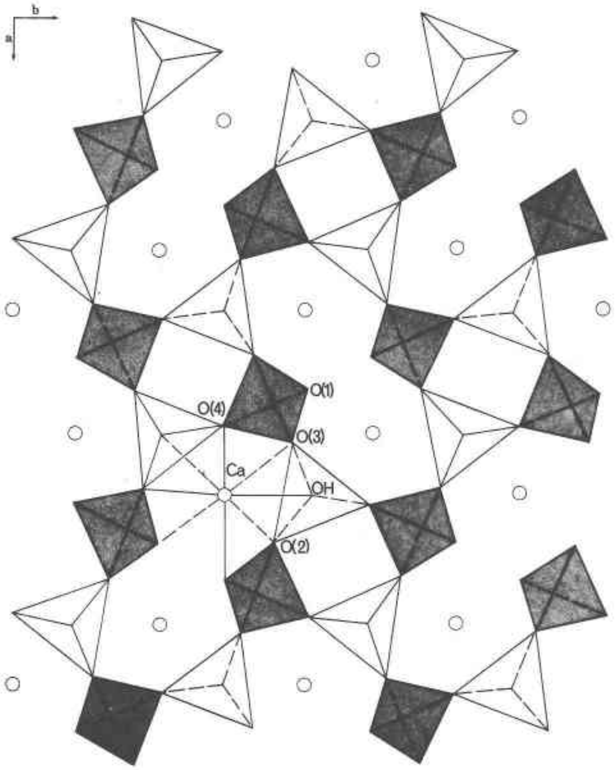
3	-8	-1	101.82	103.99
3	-5	-1	104.41	101.69
1	-3	1	105.84	107.72
6	-3	1	106.15	114.01
8	-3	-1	106.62	107.23
6	-4	4	107.47	113.42
4	-3	0	107.54	101.11
5	-5	2	107.80	108.43
2	-2	0	108.51	102.02
0	0	-6	108.65	109.67
0	0	6	109.36	109.67
4	-3	3	109.48	107.27
2	-2	0	110.37	102.02
1	-2	-1	110.44	109.11
1	-6	-2	112.03	126.40
6	-2	0	113.38	112.65
3	-1	-1	113.87	115.54
3	-5	-2	114.19	113.41
6	-2	0	114.26	112.65
4	-1	0	114.40	117.80
3	-2	-1	114.58	117.37
9	-1	2	114.67	114.38
10	-1	-1	115.08	116.88
5	-1	-2	115.67	108.02
4	-1	0	116.17	127.80
7	-2	2	119.43	120.49
1	-1	-2	119.53	118.43
8	-1	0	119.90	121.57
8	0	4	120.27	117.86
9	-1	0	121.30	121.57
4	-1	-2	122.66	126.70
5	-5	1	123.31	124.58
4	-7	0	123.41	126.73
4	-1	3	123.54	122.32
2	-1	-3	123.60	125.18
0	-4	1	124.44	130.30
2	-4	0	125.71	133.84
4	-4	-1	126.14	129.81
4	-2	1	126.33	138.29
2	-3	0	126.41	135.14
4	0	0	126.47	126.79
0	0	4	126.92	133.41
[illegible]	0	0	127.16	123.92
3	-2	-2	127.26	129.42
10	0	-4	127.71	133.41
1	-2	-4	127.99	129.54
4	-2	0	128.20	126.73
2	0	-2	128.32	129.44
2	-2	1	128.78	117.34
2	0	1	128.89	129.64
1	-2	-2	129.94	122.02
4	0	0	130.34	126.79
0	-5	1	130.53	134.80
7	-2	-2	131.24	130.50
10	-4	0	133.50	145.87
0	-4	-1	135.07	136.30
4	-1	1	137.94	128.56
2	-1	0	138.09	135.14
2	-4	0	138.54	133.84
2	0	-1	138.94	141.40
3	-3	2	139.13	137.96
2	-4	-2	139.26	145.71
8	0	0	139.77	141.94
8	0	1	140.30	141.26
2	0	-2	140.76	144.65
8	0	0	141.13	141.94
5	-2	0	141.42	140.20
5	-2	0	141.90	140.20
2	-3	-1	143.10	147.99
3	-1	2	143.73	139.30
0	0	1	144.52	148.31
10	-1	0	146.84	145.87
4	-1	-1	147.55	147.47
4	-2	-1	148.48	152.06
6	-4	-2	148.90	152.28
0	-6	0	149.55	156.90
4	-4	0	151.03	147.38
4	0	1	155.06	155.94
0	-4	-1	155.57	160.97
0	-6	0	155.62	156.90
0	-4	1	155.88	160.97
0	-2	-1	162.72	158.25
1	-2	-1	163.36	164.22
4	0	-1	163.63	170.95
4	-2	1	172.45	172.20
4	-1	2	178.36	178.31
0	-4	0	192.24	192.06

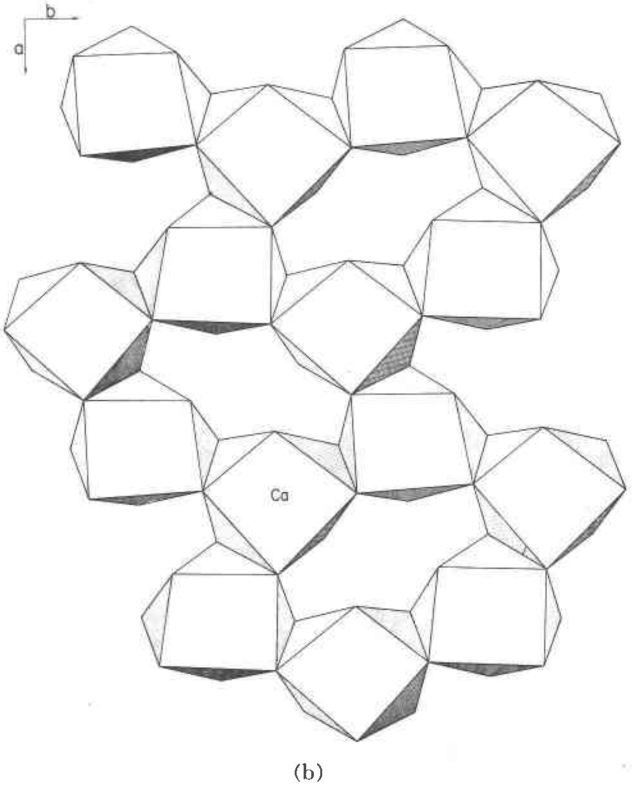


(a)

c^* by sheets of edge-sharing Ca-containing polyhedra (Fig. 1b). Each tetrahedral sheet contains alternating PO_4 and BeO_3OH polyhedra which form a network of four- and eight-membered centrosymmetric rings extending parallel to (001). The $CaO_6(OH)_2$ polyhedra (Fig. 2) are best described as slightly distorted tetragonal antiprisms which share edges to form a sheet of six-membered rings.

The phosphate tetrahedra are nearly regular with a tetrahedral angle variance of 5.3[2] (Robinson, Gibbs, and Ribbe, 1971). There are two possible explanations for this regularity: (1) the absence of shared O···O edges in the tetrahedron, and (2) the strongly directional nature of the [sp^3] bonds. In regard to the latter explanation, one would expect the directional nature of the bonds to permit better overlap with the orbitals of the coordinating oxygen atoms when the O-P-O angles are close to 109.47°. Pant and Cruickshank (1967) suggest that the small differences in the P-O bond lengths may be related to the similar 'ionicities' of the Ca-O and Be-O bonds.

Recently Baur (1970) examined the bonding in phosphates in terms of his extended electrostatic valence rule (EEVR) and found good correlations between observed P-O bond lengths and the sum of the electrostatic bond strengths to oxygen, $\zeta(O)$. An inspection of the calculated bond strengths in Table 4 indicates that the observed P–O bond length variation in herderite conforms well with Baur's model. The charges on O(3) and O(1) are balanced in the structure by a shortening of the P–O(1) bond (1.513 Å) and a lengthening of the P–O(3) bond (1.552 Å). This same line of reasoning, however, cannot be used to rationalize the length of the P–O(4) bond, which is slightly longer (1.554 Å) than expected from charge considerations (see Table 4).



(b)

FIG. 1. The herderite structure viewed down c^* showing (**a**) the sheet of four- and eight-membered rings of alternating PO_4 (shaded) and BeO_3OH (unshaded) tetrahedra and (**b**) the sheet of edge-sharing $CaO_6(OH)_2$ polyhedra. The open circles in (**a**) define the Ca-atoms of the $CaO_6(OH)_2$ polyhedral sheet (**b**). The herderite structure is generated when the latter sheet is stacked above the tetrahedral sheet so that the centers of the $CaO_6(OH)_2$ polyhedra superimpose the open circles of (**a**).

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[2] $\sigma^2 = \sum_{i=1}^{6} (\theta_i - 109.47°)^2/5$.

More recently, Lager and Gibbs (1973) have shown that the P–O bond length variations in a number of ortho- and pyrophosphates are consistent with a bonding model based on extended Hückel molecular orbital (EHMO) theory. An advantage of the model is that it relates bond length variations to O-P-O angle variations. For example, EHMO calculations carried out on hypothetically distorted PO_4^{3-} ions with P–O distances fixed at 1.50 Å predict that the shorter P–O bond lengths should be associated with the wider tetrahedral angles. The correlation in Figure 3 between $\langle O–P–O \rangle_3$, the mean of the three tetrahedral angles common to a P–O bond, and the observed bond length for the phosphate tetrahedra in herderite is consistent with the prediction (see Louisnathan and Gibbs, 1972a, b). An equation deduced by Lager and Gibbs (1973), which is based on a relationship between the bond length and the bond overlap population, n(P–O), has been used to estimate the P–O bond lengths in herderite. These estimated bond lengths are included in Table 4 for comparison with observed values and those predicted by Baur's (1970) EEVR (see Lager and Gibbs, 1973 for a more detailed discussion).

TABLE 4. Observed P-O Bond Lengths for Herderite Compared with Electrostatic Bond Strengths and with Estimated Bond Lengths Using Equations 1 and 2 (See Footnote)

	P	Be	Ca	$\Sigma\zeta$(O)	P-O(obs)	P-O(est.)[1]	P-O(est.)[2]
O(1)	1.25		2(.25)	1.75	1.513	1.510	1.522
O(2)	1.25	0.50	.25	2.00	1.543	1.537	1.537
O(3)	1.25	0.50	2(.25)	2.25	1.552	1.564	1.542
O(4)	1.25	0.50	.25	2.00	1.554	1.537	1.552
(OH)		0.50	2(.25)	1.00			

[1] P-O(est.) = 1.537 + 0.109 $\Delta\zeta$(O) Baur (1970).

[2] P-O(est.) = 1.537 + 2.479 Δn(P-O) Lager and Gibbs (1973).

The BeO_3OH tetrahedra (tetrahedral angle variance = 12.93) are more distorted than the PO_4 tetrahedra, with angles varying from 103.7° to 114.0°. The narrowest angles are opposite the two O···O edges shared with the Ca-tetragonal antiprism. Except for the Be–O(3) bond, variations in the bond lengths canont be rationalized in terms of ζ(O) because the charges on O(2), O(4), and OH are balanced in the classical sense. In Figure 3 the Be–O distances are plotted against $\langle O–Be–O \rangle_3$. As in the phosphate tetrahedron, the longer bond lengths are associated with the narrower tetrahedral angles. The correlation in Figure 3, coupled with the results of recent EHMO calculations on the BeO_4

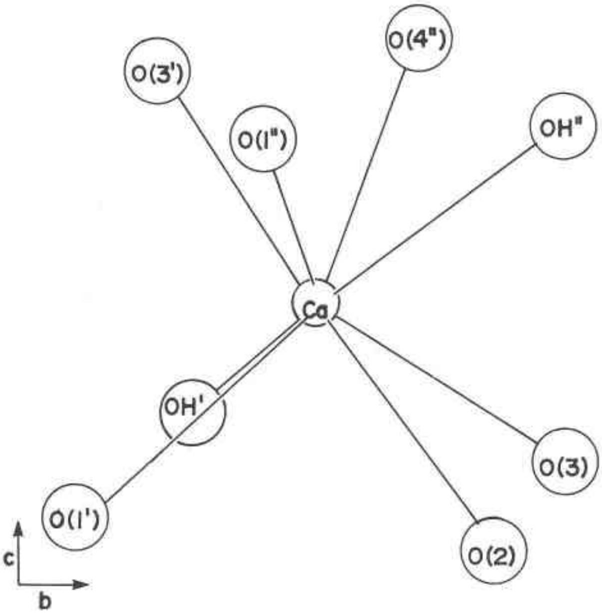

FIG. 2. The $CaO_6(OH)_2$ polyhedron designated in Figure 1(a) viewed down a^* showing the nature of the coordination. The labelling of the atoms is consistent with Table 2b.

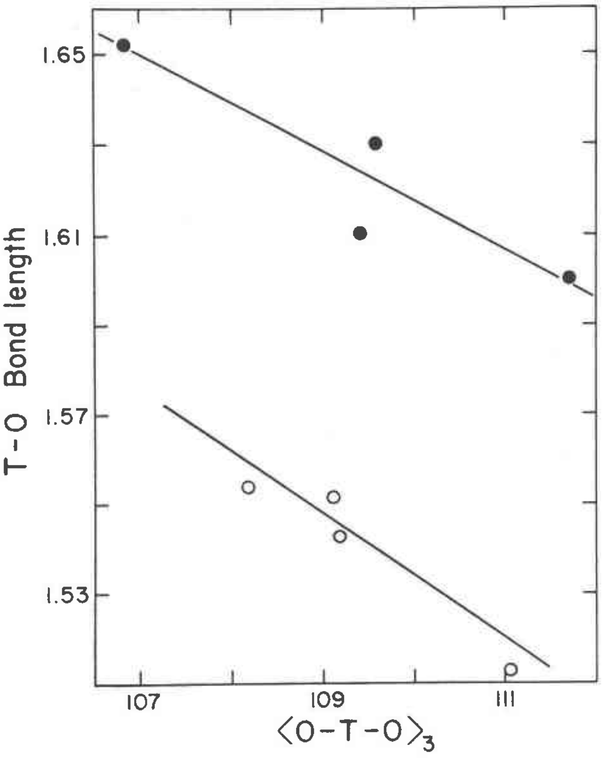

FIG. 3. Plot of $\langle O\text{-}T\text{-}O \rangle_3$, the average of the three tetrahedral angles common to a bond *vs* the observed lengths of P-O (open circles) and the Be-O (solid circles) bonds in herderite.

tetrahedra (Griffen, Schlenker, Gibbs, and Phillips, 1973) suggests that the bonding in the BeO_3OH tetrahedron can also be rationalized, in part, in terms of EHMO theory.

The Ca-tetragonal antiprism in herderite shares five edges, three with adjoining Ca-containing polyhedra and two with BeO_3OH tetrahedra. Because of electrostatic and antibonding considerations, no edges are shared with phosphate tetrahedra. As expected, the shared edges are short, compared with the average O···O distance (3.686 Å), ranging from 2.565 Å (those shared with tetrahedra) to 2.966 Å (those shared with Ca-containing polyhedra). A valence balance is apparently achieved by a shortening of the two Ca–O(1) bonds and a lengthening of the two Ca–O(3) bonds.

In conclusion, Pant and Cruickshank (1967) have demonstrated that the Pauling-Zachariasen method of balancing valences provides a qualitative description of the bond length variations in the structurally similar mineral datolite (values in parentheses in Table 5). However, they were unable to discuss the herderite structure in terms of the method because the bond length errors were too large. As the present study has provided a precise refinement, we have undertaken a balancing of valences using the Brown and Shannon (1973) empirical bond strength (ζ)-bond length (R) relationship

$$\zeta = S_0\left(\frac{R_0}{R}\right)^N \tag{1}$$

where S_o is the bond strength associated with a bond length R and where R_o and N are constants. Examination of Table 6 shows that the Brown-Shannon relations are consistent with the bond length variations in herderite. We have also used the Brown-Shannon relations to balance the valences in datolite. The agreement with the balance suggested by Pant and Cruickshank is good (see Table 5).

TABLE 5. Comparison of Valence Balance in Datolite

	Si	B	H	Ca	$\zeta(O)$*
O(1)	1.17**(1.30)***			0.41 (0.35)	1.98 (2.00)
				0.40 (0.35)	
O(2)	0.94 (0.90)	0.76 (0.80)		0.26 (0.25)	1.96 (1.95)
O(3)	0.93 (0.90)	0.74 (0.74)		0.18 (0.20)	2.01 (2.04)
				0.16 (0.20)	
O(4)	0.91 (0.90)	0.78 (0.80)		0.28 (0.25)	1.97 (1.95)
O(5)		0.72 (0.66)	1.00	0.16 (0.20)	2.10 (2.06)
				0.22 (0.20)	
$\zeta(M)$	3.95 (4.00)	3.00 (3.00)	1.00	2.09 (2.00)	10.02 (10.00)

* $\zeta(O)$ = *sum of the bond strengths from the metal atoms* (M) *to each anion.*

** *Values obtained using equation* 1, *the bond lengths given by Foit et al (1973) and the constants given in* Table IV-1 *of Brown and Shannon (1973).*

*** *Values (in parentheses) suggested by Pant and Cruickshank (1967).*

TABLE 6. Valence Balance in Herderite

	P	Be	H	Ca	$\zeta(O)$*
O(1)	1.31	–	–	0.32	1.95
	–	–	–	0.32	
O(2)	1.23	0.51	–	0.26	2.00
O(3)	1.20	0.48	–	0.13	1.99
	–	–	–	0.18	
O(4)	1.20	0.54	–	0.27	2.01
O(5)	–	0.55	1.0	0.23	2.06
	–	–	–	0.28	
$\zeta(M)$**	4.94	2.08	1.0	1.99	10.01

* $\zeta(O)$ *is the sum of bond strengths from the metal atoms* (M) *to each anion. The bond strengths were obtained using equation 1, the bond lengths given in* Table 2 *and the following constants,* S_O *and* R_O, *obtained by Brown and Shannon:* P 1.25, 1.534; Be 0.5, 1.639 and Ca 0.25, 2.468.

** $\zeta(M)$ *is the sum of bond strengths to each metal atom.*

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References

BAUR, WERNER H. (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Am. Crystallogr. Assoc.* **6,** 129–155.

BROWN, I. D., AND R. D. SHANNON (1973) Empirical bond strength-bond length curves for oxides. *Acta Crystallogr.* **A29,** 266–282.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) A Fortran crystallographic least-squares program. *U.S. Atomic Energy Comm. Rep.* ORNL-TM-**305.**

———, ———, AND ——— (1964) A Fortran crystallographic function and error program. *U.S. Atomic Energy Comm. Rep.* ORNL-TM-**306.**

DOYLE, P. A., AND P. S. TURNER (1968) Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Crystallogr.* **A24,** 390–397.

FOIT, F. F., M. W. PHILLIPS, AND G. V. GIBBS (1973) A refinement of the structure of datolite, $CaBSiO_3(OH)$. *Am. Mineral.* **58,** 909–914.

GIBBS, G. V., M. M. HAMIL, S. J. LOUISNATHAN, L. S. BARTELL, AND H. YOW (1972) Correlations between Si-O bond length, Si-O-Si angle, and bond overlap populations calculated using extended Hückel molecular orbital theory. *Am. Mineral.* **57,** 1578–1613.

GRIFFEN, D. C., J. L. SCHLENKER, G. V. GIBBS, AND M. C.

PHILLIPS (1973) EHMO bond overlap populations for Be and B oxyanions (abstr.). *Program, 54th Annu. Meet. Am. Geophys. Union,* Washington, D.C., p. 44.

HANSON, A. W. (1965) The crystal structure of the azulene, S-trinitro-benzene complex. *Acta Crystallogr.* **19,** 19–26.

LAGER, G. A., AND G. V. GIBBS (1973) The effect of O-P-O and P-O-P angular variations on bond overlap population for some selected ortho- and pyrophosphates. *Am. Mineral.* **58,** 756–764.

LINDBLOOM, J. T. (1972) *A Refinement of the Crystal Structure of Hurlbutite, $CaBe_2P_2O_8$.* M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

LOUISNATHAN, S. JOHN, AND G. V. GIBBS (1972a) Bond length variation in TO_4^{n-} tetrahedral oxyanions of the third row elements: T = Al, Si, P, S, and Cl. *Mater. Res. Bull.* **7,** 1281–1292.

———, AND ——— (1972b) The effect of tetrahedral angles on Si-O bond overlap populations in isolated tetrahedra. *Am. Mineral.* **57,** 1614–1642.

PANT, A. K., AND D. W. J. CRUICKSHANK (1967) A re-examination of the structure of datolite, $CaBSiO_4(OH)$. *Z. Kristallogr.* **125,** 286–297.

PAULING, L. (1960) *The Nature of the Chemical Bond, 3rd Ed.* Cornell University Press, Ithaca, N.Y.

PAVLOV, P. V., AND N. V. BELOV (1959) The structures of herderite, datolite, and gadolinite determined by direct methods. *Kristallografiya,* **4,** 324–340 (in Russian); *Sov. Phys. Crystallogr.* **4,** 300–314.

ROBINSON, K., G. V. GIBBS, AND P. H. RIBBE (1971) Quadratic elongation: A quantitative measure of distortion in coordination polyhedra. *Science,* **172,** 567–570.

STRUNZ, H. (1936) Datolith und Herderit. *Z. Kristallogr.* **93,** 146–150.

ZACHARIASEN, W. H. (1963) The crystal structure of monoclinic metaboric acid. *Acta Crystallogr.* **16,** 385–389.

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