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CRYSTAL STRUCTURE OF THE CALCIUM SILICOBORATE, HOWLITE

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ABSTRACT

Howlite, $Ca_2SiB_5O_9(OH)_5$, is monoclinic, $P2_1/c$, $a=12.78\pm0.03$, $b=9.33\pm0.02$m $c=8.60\pm0.02$ Å, $\beta=104.83\pm0.10°$, $Z=4$. Using the 1500 *hkl* intensities estimated visually from Weissenberg photographs, the structure was determined by locating the Ca atoms from a Patterson synthesis and placing the oxygen, boron and silicon atoms following study of a three-dimensional electron-density map based on the Ca signs. Least-squares refinement of the 861 data with $|F|>0$ reduced the conventional *R*-factor to 0.10. Study of infrared spectra had prompted the suggestion by Moenke (1960) that boron occurred in both tetrahedral and triangular coordination in the structure. The suggestion is now verified because the structure contains colemanite-like chains with two tetrahedra and a triangle. These chains are located on the edges of anion slabs which contain spirals of silicate plus borate tetrahedra in the central region between chains. The slabs are tightly held together by single and double chains of Ca coordination polyhedra. Three of the five hydroxyl ions are involved in hydrogen bonding. The absence of any observed cleavage is in accord with the structural character.

INTRODUCTION

The calcium silicoborate mineral, howlite, first known as silicoborocalcite, was discovered by How (1868) near Windsor, Hants County, Nova Scotia, Canada. Other occurrences were described during the following years (*cf.* Palache *et al.*, 1951) but no X-ray diffraction data were given until Murdoch (1957) reported the results of studies on crystals from the old Sterling Borax mine, Tick Canyon, California. Infrared absorption spectra were examined by Moenke (1960) and by Kühn and Moenke (1963). Moenke suggested that the spectra indicated the presence in the structure of both tetrahedrally and triangularly coordinated boron. Because boron had not to our knowledge previously been found in both coordination states in the presence of silicon, we decided to determine the crystal structure. The complete results, which confirm Moenke's suggestion, are reported in this paper; a preliminary note giving atomic coordinates has already appeared (Finney, Kumbasar, and Clark, 1969).

EXPERIMENTAL DATA

Crystallographic data. The crystal used for the structural study was kindly provided by Prof. J. Murdoch, UCLA, from the sample described by him (1957). Its habit resembled

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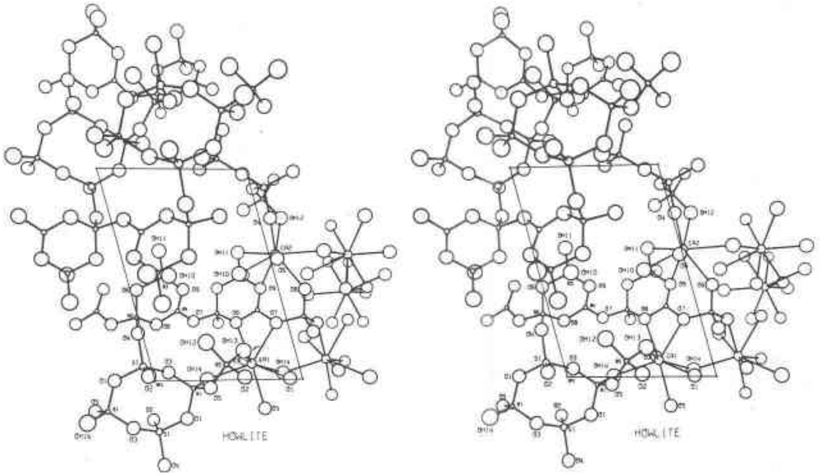

FIG. 1. Stereoscopic pair showing selected portions of the howlite structure, including Si—O, B—O, and Ca—O bonds, viewed in perspective along *b*. ORI marks the origin; the end of one unit cell is outlined, *c* horizontal. Portions of a complete polyanion slab can be seen starting upwards from about halfway along *a*; the approach to a second slab is also seen here. An eight-membered ring is shown around ORI, the center of symmetry, which is not centered because of the perspective. Drawing produced using ORTEP (Johnson, 1965).

that illustrated in his Fig. 1, and we observed no violations of the $P2_1/c$ symmetry assigned by him. No piezoelectric tests were made, but the crystal habit is in accord with the assignment of a center of symmetry. Lattice parameters and other related data are compared in Table 1 for the two studies; agreement is excellent. No cleavage directions have been reported for howlite, and the structure confirms their absence, as is shown later.

Intensity data. About 1500 *hkl* intensities were estimated visually from equi-inclination Weissenberg films taken about *a*, *b*, and *c*-axes with Zr-filtered Mo radiation. The crystal used for all exposures was 0.3×0.2×0.07 mm. Of the 1500 reflections, 861 had intensities above the threshold value and were used for the structural determination and refinement; the remaining 634 reflections were assigned the value zero and were not used in least-squares refinement. Lorentz and polarization factors were applied, and the intensities were scaled by comparison with equivalent reflections from the various films. No absorption corrections were made; the linear absorption coefficient for Mo radiation is only 13.2 cm^{-1}.

Solution and refinement of the structure. The structural problem consists of locating two Ca, 14 oxygen (including hydroxyls), one silicon, and five boron atoms in the general positions 4*e* of $P2_1/c$. Vectors between Ca atoms were identified on a three-dimensional Patterson synthesis, and positions assigned for both Ca atoms. The signs thus obtained were used to calculate a three-dimensional electron-density map, from which the locations of the remaining atoms were found. Refinement was carried out by full-matrix, least-squares methods, using *X-Ray 67, program system for x-ray crystallography*, by J. M. Stewart, University of Maryland, adapted for the IBM 360/65 computer by D. E. Appleman,

TABLE 1. CRYSTALLOGRAPHIC DATA FOR HOWLITE, $Ca_2SiB_5O_9(OH)_5$, MONOCLINIC, $P\ 2_1/c$, $Z=4$

	Murdoch (1957)	This study
a	12.93 Å	12.78(3) Å
b	9.34	9.33(2)
c	8.60	8.60(2)
β	104°50′	104.83°(0.10)
Cell volume	—	991.3(1.2) Å^3
Density, calc.	2.402 g/cm^3	2.432 g/cm^3
Specific gravity, obs.	2.53–2.59[a]	2.56[b] 2.45[c]

[a] Given by Palache *et al.* (1951), who say "Penfield and Sperry (1887) by pycnometer; the variation in ρ is due to the mode of aggregation. Porcelaneous material from Lang has $\rho=2.59$ (Mrose, Priv. comm., 1946)."

[b] Specific gravity measured by Berman balance on Lang material. The figure represents the average value for four separate determinations on samples weighing approximately 20 milligrams taken from two large specimens numbered T.M. 5638 and T.M. 701:2:1 (CSM collections).

[c] Specific gravity measured by Berman balance on Lang material. Figure is result of two determinations as stated above from a single specimen numbered Huleatt T.M. 701.2 (CSM collections).

X-ray powder photographs of crushed 20 milligram samples numbered T.M. 5638 and Huleatt T.M. 701.2 are identical.

U. S. Geological Survey. The scattering factors used were for neutral atoms, taken from MacGillavry and Rieck, 1962. Unit weights were assigned to the reflections. The initial $R=\sum|F_o|-|F|/\sum|F_o|$ was 0.54 for the two Ca atoms only. After three cycles of least-squares refinement with individual isotropic temperature factors, *R* dropped to 0.13, and the final *R*, after three cycles refining individual anistropic temperature factors, is 0.10. The errors in the temperature factors are sufficiently large to preclude any meaningful examination of thermal ellipsoids, so only the equivalent isotropic temperature factors are included with the final atomic positional parameters in Table 2. A final difference Fourier is relatively featureless, a maximum of $3e/\text{Å}^3$ occurring in the vicinity of the Ca atoms and representing about 7 percent of the peak height observed for these cations on the electron-density synthesis. The observed and calculated structure factors are compared in Table 3.[1]

DISCUSSION OF STRUCTURE

General. The structure is illustrated in the stereoscopic pair of Figure 1, which clearly shows the overall three-dimensional character, compatible with the observed absence of cleavage. The structure can be considered

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[1] Table 3 may be ordered as NAPS Document No. 00943 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue New York, N. Y. 10022, remitting in advance $2.00 for microfiche or $5.00 for photocopies, payable to CCMIC-NAPS. The standard deviation in $|F|$ is 8.2 (unit-weight refinement).

TABLE 2. ATOMIC PARAMETERS FOR HOWLITE[a]

Atom	x	y	z	B(Å^2) equivalent isotropic
Ca(1)	0.1171(5)	0.1838(8)	0.1493(8)	0.8(1)
Ca(2)	.4118(5)	.8216(8)	.5228(8)	0.7(1)
Si	.1411(8)	.5549(11)	.0115(11)	0.7(2)
B(1)	.039(3)	.471(5)	.257(4)	1.2(6)
B(2)	.323(3)	.384(5)	.033(4)	1.0(6)
B(3)	.492(3)	.423(5)	.256(5)	1.4(7)
B(4)	.343(3)	.261(5)	.284(4)	1.1(6)
B(5)	.157(3)	.650(5)	.476(5)	1.3(7)
O(1)	.081(2)	.512(3)	−.174(3)	0.9(4)
O(2)	.127(2)	.723(3)	.047(3)	1.4(5)
O(3)	.102(2)	.450(2)	.137(3)	0.8(4)
O(4)	.269(2)	.525(3)	.030(3)	0.9(4)
O(5)	.061(2)	.597(3)	.355(3)	0.5(4)
O(6)	.438(2)	.407(3)	.078(3)	1.1(4)
O(7)	.292(2)	.171(2)	.364(3)	0.8(4)
O(8)	.287(2)	.282(3)	.130(3)	1.0(4)
O(9)	.438(2)	.333(2)	.352(2)	0.8(4)
OH(10)	.497(2)	.570(3)	.294(3)	1.1(4)
OH(11)	.601(2)	.356(3)	.272(3)	0.9(4)
OH(12)	.246(2)	.685(3)	.398(3)	1.0(4)
OH(13)	.197(2)	.542(3)	.599(3)	0.8(4)
OH(14)	.055(2)	.338(2)	.351(2)	0.5(4)

[a] Values in parentheses are standard deviations.

with respect to three important features. First, the colemanite-like chains, which are linked *via* an oxygen atom to the second feature, the silicoborate spirals. Large anion slabs oriented approximately in (100) are thus formed. The polyhedral chains associated with each of the two distinct Ca atoms are a third structural feature, linking adjacent anion slabs. These features are considered in detail and compared with those in related structures in the following sections. The hydrogen bonding in howlite is also considered separately.

The colemanite-like chains. The basic unit of these chains can be described by reference to the $[B_3O_3(OH)]^{2-}$ polyanion first discovered in the structure of meyerhofferite (Christ and Clark, 1960). The polyanion is composed of two tetrahedra and a triangle linked at corners to form a six-membered boroxol ring. Such polyanions may polymerize, according to Christ's fourth rule (Christ, 1960), to form the chains found in colemanite (Christ, Clark and Evans, 1958), the schematic reaction being

$$n[B_3O_3(OH)_5]^{2-} = [B_3O_4(OH)_3]_n^{2n-} + nH_2O.$$

The chains are produced by having an oxygen common to a tetrahedron of one ring and a triangle of an adjacent ring; their orientation in howlite is illustrated in Figure 2a. Within the rather large limits of error associated with the distances and angles for howlite, the colemanite-like chains are in all respects comparable to those in colemanite, and the minor deviations from polyhedral regularity appear to be similar in both structures (Table 4).

The silicoborate spirals. The unique portion of this structural feature consists of the silicate tetrahedron, one borate tetrahedron with two hydroxyls, and one borate tetrahedron with one hydroxyl, all sharing corners to create infinite spirals along the *b* direction (Fig. 2b). Each spiral is also linked *via* corners to its own centrosymmetric equivalent, thus forming an eight-membered ring with alternating B, O, and Si atoms (Figs. 1, 3). Similar centrosymmetric eight-membered rings are found in the structures of datolite ($CaBSiO_4(OH)$, Ito and Mori, 1953), danburite ($CaB_2Si_2O_2$, Dunbar and Machatschki, 1930), and reedmergnerite ($NaBSi_3O_8$, Appleman and Clark, 1965). Despite the relatively large errors associated with the howlite distances and angles, the rings appear similar in all four structures (Table 5), although the Si—O distances are unusually long in datolite and hence the angles within the ring are somewhat different. Nevertheless, the values exhibit similar tendencies and this kind of ring is apparently a frequent structural feature in borosilicates containing tetrahedral boron. The distances and angles for the complete silicoborate spiral in howlite are given in Table 6, and are those to be expected for the elements involved, within the associated errors.

Linkage of the colemanite-like chains and silicoborate spirals. These two structural features link through O(4) oxygen atoms, which are common to the silicate tetrahedra and borate tetrahedra of two colemanite-like chains. The linkage is illustrated in Figures 1 and 3. A schematic polymerization of the two structural groups can be written as:

$$[B_3O_4(OH)_3]_n^{2n-} + [SiB_2O_4(OH)_4]_n^{2n-}$$
$$= [B_3O_4(OH)_2SiB_2O_5(OH)_3]_n^{4n-} + nH_2O.$$

The structural formula for howlite would contain the polyanion on the right side of this equation, but because this version is cumbersome, we believe the usual form, $Ca_2SiB.O_3(OH)'$, should be retained.

The calcium polyhedra. The two crystallographically distinct calcium

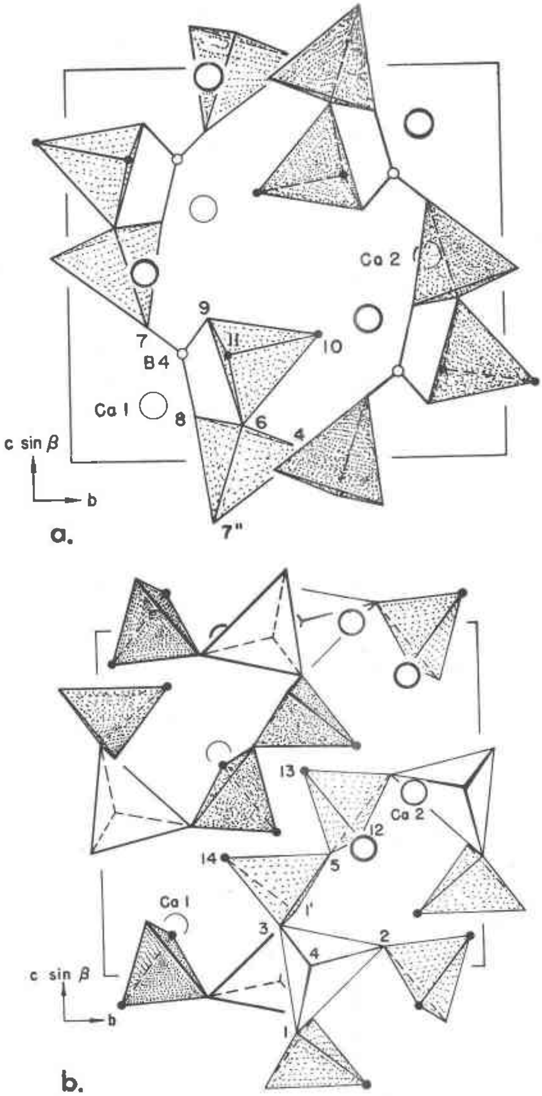

Fig. 2. Portions of the howlite structure viewed along *a;* black dots represent hydroxyl ions. (a) The colemanite-like chains with two tetrahedra and a BO_3 triangle; open circle marks B. (b) The silicoborate spirals; borate tetrahedra shaded, silicate tetrahedra unshaded.

cations in howlite are each coordinated by eight oxygen (including hydroxyl) atoms at an average distance of 2.47 Å (Table 7). The coordination and distances are common for Ca in numerous other structures.

TABLE 4. COMPARISON OF DISTANCES AND ANGLES IN THE BORATE CHAINS OF COLEMANITE AND HOWLITE

Colemanite Clark *et al.* (1964)		Howlite This study	
Atoms	Distances (Å)	Atoms	Distances (Å)
B(1)—O(1)	1.386(8)	B(4)—O(9)	1.38(4)
B(1)—O(2)	1.368(8)	B(4)—O(8)	1.35(4)
B(1)—O(4)	1.362(8)	B(4)—O(7)	1.35(5)
Average	1.376	Average	1.36
B(2)—O(1)	1.493(8)	B(3)—O(9)	1.47(5)
B(2)—O(3)	1.467(8)	B(3)—O(6)	1.52(5)
B(2)—OH(5)	1.476(9)	B(3)—OH(10)	1.41(5)
B(2)—OH(6)	1.484(8)	B(3)—OH(11)	1.50(5)
B(3)—O(2)	1.517(8)	B(2)—O(8)	1.42(5)
B(3)—O(3)	1.453(8)	B(2)—O(6)	1.44(5)
B(3)—O(7)	1.478(8)	B(2)—O(7)″	1.50(4)
B(3)—OH(8)	1.454(8)	B(2)—O(4)	1.48(5)
Average of 8	1.473	Average of 8	1.47
B(1)—B(2)	2.503(10)	B(4)—B(3)	2.49(6)
B(1)—B(3)	2.461(9)	B(4)—B(2)	2.40(6)
B(2)—B(3)	2.498(9)	B(3)—B(2)	2.52(5)
	Angles (°)		Angles (°)
O(1)—B(1)—O(2)	120.8(6)	O(9)—B(4)—O(8)	122(3)
O(1)—B(1)—O(4)	113.9(5)	O(9)—B(4)—O(7)	125(3)
O(2)—B(1)—O(4)	125.3(6)	O(8)—B(4)—O(7)	113(3)
Σ	360.0	Σ	360
O(1)—B(2)—O(3)	110.7(5)	O(9)—B(3)—O(6)	110(3)
O(1)—B(2)—OH(5)	111.0(5)	O(9)—B(3)—OH(10)	115(4)
O(1)—B(2)—OH(6)	103.8(5)	O(9)—B(3)—OH(11)	106(3)
O(3)—B(2)—OH(5)	106.7(5)	O(6)—B(3)—OH(10)	108(3)
O(3)—B(2)—OH(6)	112.9(5)	O(6)—B(3)—OH(11)	103(3)
OH(5)—B(2)—OH(6)	111.7(5)	OH(10)—B(3)—OH(11)	114(3)
O(2)—B(3)—O(3)	109.0(5)	O(8)—B(2)—O(6)	114(3)
O(2)—B(3)—O(7)	107.2(5)	O(8)—B(2)—O(7)″	107(3)
O(2)—B(3)—OH(8)	106.2(5)	O(8)—B(2)—O(4)	113(3)
O(3)—B(3)—O(7)	109.5(5)	O(6)—B(2)—O(7)″	108(3)
O(3)—B(3)—OH(8)	113.2(5)	O(6)—B(2)—O(4)	108(3)
O(7)—B(3)—OH(8)	111.4(5)	O(7)″—B(2)—O(4)	106(2)
Average of 12	109.2	Average of 12	109.3
B(1)—O(1)—B(2)	120.7(5)	B(4)—O(9)—B(3)	122(3)
B(2)—O(3)—B(3)	117.6(5)	B(3)—O(6)—B(2)	117(3)
B(3)—O(2)—B(1)	117.0(5)	B(2)—O(8)—B(4)	120(3)

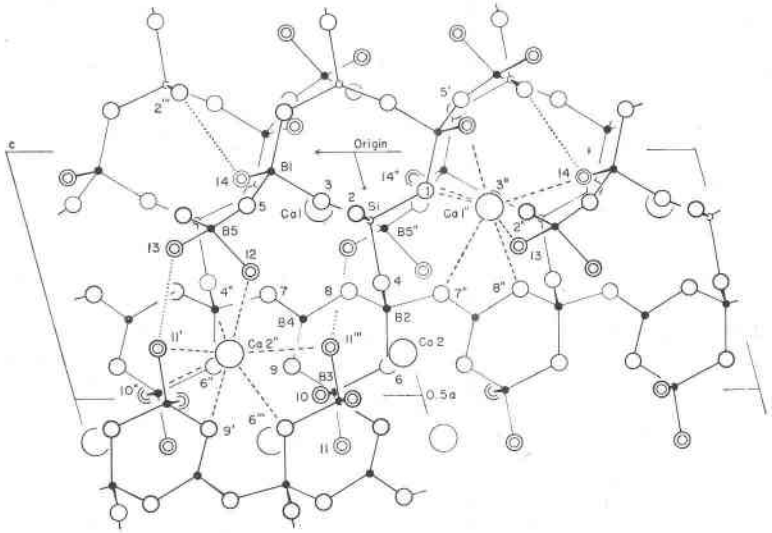

Fig. 3. A portion of the howlite structure viewed along *b*. Intermediate size open circles, oxygen atoms; double circles, hydroxyl ions. Dashed lines indicate Ca—O bonds; dotted lines, hydrogen bonds. The eight-membered centrosymmetric rings (see text) can be traced around the origin.

The Ca(1) cation is coordinated by six atoms of the silicoborate-spiral group and by only two from the colemanite-like chains. This polyhedron shares hydroxyl corners with adjacent glide equivalents to form single zig-zag chains along *c*, illustrated in Figure 4. The Ca(2) cation is coordinated by seven atoms of the colemanite-like chains, including O(4) which links to the silicoborate spirals, and by only one, OH(12), which is wholly associated with the spirals. The Ca(2) polyhedron also shares hydroxyl corners with adjacent glide equivalents to form zig-zag chains along *c*. However, in addition it shares an O(6)—O(6) edge of 2.90 Å with the equivalent centrosymmetric polyhedral chain, so that double Ca(2) polyhedral chains along *c* are thus created (Fig. 4). These double chains are located at the junction of two colemanite-like chains in adjacent polyanion slabs (Figs. 1, 3), and so bind the structure tightly in three dimensions. The single Ca(1) and double Ca(2) chains are separate in the structure, further emphasizing a distinction between one region that is essentially silicoborate spirals plus Ca(1) single polyhedral chains, and another that is chiefly colemanite-like chains plus Ca(2) double polyhedral chains. The closest Ca-Ca approach in the structure is 4.09 Å, between the Ca(2) cations across the shared edge. The Ca-Ca separations in the single chains are about 4.5 Å.

TABLE 5. COMPARISON OF EIGHT-MEMBERED CENTROSYMMETRIC RINGS IN HOWLITE, DANBURITE, DATOLITE, AND REEDMERGNERITE

Howlite This study		Danburite Johansson (1959)		Datolite Pant and Cruickshank (1967)		Reedmergnerite Appleman and Clark (1965)	
Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Si—O(1)	1.63(2)	Si—O(1)	1.62(1)	Si—O(4)	1.653(11)	Si2(*m*)—OC(O)	1.606(4)
O(1)—B(1)	1.52(4)	O(1)—B	1.47(2)	O(4)—B	1.449(22)	OC(O)—B(O)	1.443(9)
B(1)—O(3)	1.48(5)	B—O(3)	1.47(2)	B—O(2)	1.450(22)	B(O)—OD(O)	1.467(6)
O(3)—Si′	1.62(3)	O(3)—Si′	1.61(1)	O(2)—Si′	1.671(11)	OD(O)—Si′2(*m*)	1.614(3)
Si—B(1)	2.86(4)	Si—B	2.83(1)	Si—B	2.84(2)	Si2(*m*)—B(O)	2.850(4)
Si′—B(1)	2.82(4)	Si′—B	2.76(1)	Si′—B	2.72(2)	Si′2(*m*)—B(O)	2.706(7)
	Angle (°)		Angle (°)		Angle (°)		Angle (°)
O(1)—Si—O(3)	111(1)	O(1)—Si—O(3)	111(1)	O(2)—Si—O(4)	107.17(67)	OC(O)—Si2(*m*)—OD(O)	114.2(2)
Si—O(3)—B(1)	135(2)	Si—O(3)—B	128(1)	Si—O(4)—B	132.19(1.21)	Si2(*m*)—OD(O)—B(O)	135.4(3)
O(3)—B(1)—O(1)	110(3)	O(3)—B—O(1)	112(1)	O(4)—B—O(2)	112.86(1.57)	OD(O)—B(O)—OC(O)	111.1(4)
B(1)—O(1)—Si	127(2)	B—O(1)—Si	133(1)	B—O(2)—Si′	120.92(1.17)	B(O)—OC(O)—Si′2(*m*)	124.9(3)

TABLE 6. DISTANCES AND ANGLES FOR THE SILICOBORATE SPIRAL IN HOWLITE

Atoms	Distance (Å)	Atoms	Angle (°)
Si—O(1)	1.63(2)	O(1)—Si—O(2)	112
Si—O(2)	1.61(3)	O(1)—Si—O(3)	110
Si—O(3)	1.62(3)	O(1)—Si—O(4)	105
Si—O(4)	1.63(2)	O(2)—Si—O(3)	113
average	1.62	O(2)—Si—O(4)	108
		O(3)—Si—O(4)	108
		average	109.3
B(1)—O(1)′	1.52(4)	O(1)′—B(1)—O(3)	110
B(1)—O(3)	1.48(5)	O(1)′—B(1)—O(5)	102
B(1)—O(5)	1.43(5)	O(1)′—B(1)—OH(14)	109
B(1)—OH(14)	1.47(5)	O(3)—B(1)—O(5)	117
		O(3)—B(1)—OH(14)	104
		O(5)—B(1)—OH(14)	113
B(5)—O(2)	1.43(5)	O(2)—B(5)—O(5)	108
B(5)—O(5)	1.48(4)	O(2)—B(5)—OH(12)	109
B(5)—OH(12)	1.50(5)	O(2)—B(5)—OH(13)	110
B(5)—OH(13)	1.46(5)	O(5)—B(5)—OH(12)	110
average of 8	1.47	O(5)—B(5)—OH(13)	111
Si—B(1)	2.86(4)	OH(12)—B(5)—OH(13)	108
Si—B(5)	2.78(5)	average of 12	109.2
B(1)—B(5)	2.67(6)		

Hydrogen bonds and charge balance in the structure. Based on the ideal ionic model according to the principle established by Pauling (1929), each Ca—O bond has a strength of 0.25 valence units (v.u.), each tetrahedral B—O bond, 0.75 v.u., and each triangular B—O and tetrahedral Si—O bond, 1.00 v.u. Summing over each oxygen and hydroxyl ion on this basis, exact agreement of 2.00 or 1.00 v.u., respectively, is found for all except four: O(2) and O(5), deficient with only 1.75 v.u., and OH(11) and OH(14), overcompensated with 1.25 v.u.

Any hydrogen bonds can be assumed to be in the range of 2.6 to 3.0 Å, but most of the hydroxyl-oxygen distances in this range are edges of the Ca coordination polyhedra. They are therefore unlikely locations for the protons, which are expected to be directed away from the cations (Templeton, 1960). However, three possibilities can be considered in connection with the observed charge balance.

A distance of 2.90 Å between OH(14) and O(2) is undoubtedly a true hydrogen bond. Its existence helps decrease the excess charge otherwise associated with OH(14) and increase that of the nominally deficient O(2), as well as providing an additional link within the silicoborate

TABLE 7. CALCIUM-OXYGEN DISTANCES IN HOWLITE

Ca atom				Oxygen atom				Distance (Å)
Number	*x*	*y*	*z*	Number	*x*	*y*	*z*	
(1)	0.1171	0.1838	0.1493	(1)	0.081	−0.012	0.326	2.49(3)
				(3)	0.102	0.450	0.137	2.49(2)
				(5)	−0.061	0.097	0.145	2.41(3)
				(7)	0.292	0.171	0.364	2.51(2)
				(8)	0.287	0.282	0.130	2.40(3)
				OH(13)	0.197	−0.042	0.099	2.43(3)
				OH(14)	0.055	0.338	0.351	2.53(2)
				OH(14)	0.055	0.162	−0.149	2.49(2)
	average of 8							2.47
(2)	0.4118	0.8216	0.5228	(4)	0.269	0.975	0.530	2.33(2)
				(6)	0.562	0.907	0.422	2.43(3)
				(6)	0.438	1.093	0.578	2.58(3)
				(9)	0.562	0.667	0.648	2.42(2)
				OH(10)	0.497	0.930	0.794	2.52(2)
				OH(11)	0.399	0.643	0.728	2.46(3)
				OH(11)	0.399	0.857	0.228	2.52(2)
				OH(11)	0.246	0.685	0.398	2.47(2)
	average of 8							2.47

spirals (Fig. 3). A distance of 2.70 Å between OH(11) and OH(13) must also be considered a true hydrogen bond, with OH(11) as the probable donor because its excess charge can thereby be distributed between the two hydroxyl ions. In addition this bond is an important structural link between the two essentially distinct regions of the structure (Fig. 3). A

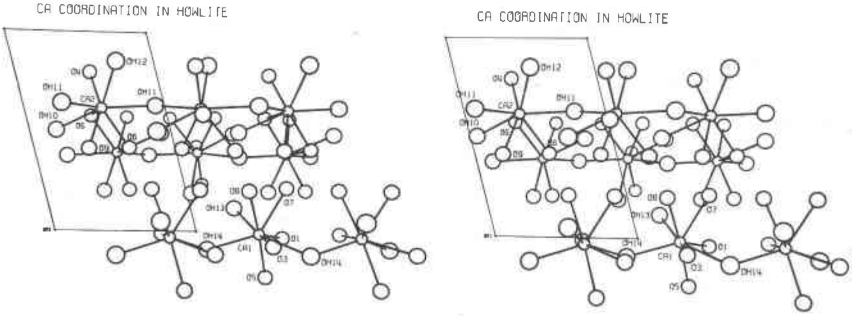

FIG. 4. Stereoscopic pair perspective view along *b*, showing the Ca(1) single polyhedral chains and the Ca(2) double polyhedral chains in the howlite structure (see also Table 7). ORI marks the origin; the end of one unit cell is outlined, *c* horizontal. Drawing produced using ORTEP (Johnson, 1965).

third distance of 3.03 Å between OH(12) and O(2) is probably not a hydrogen bond, because both OH(12) and O(2) are apparently satisfactorily balanced. Thus, of the five hydroxylions, only three appear to participate in hydrogen bonding, OH(14), and OH(11) with OH(13).

The charge balance throughout the structure is adequately explained by consideration of the hydrogen bonds in conjunction with the ideal ionic model, with the single exception of the deficient O(5). A short bond to Ca might logically be expected for this oxygen, but its Ca—O distance of 2.41 Å, although shorter than the average value (Table 7), is not the shortest Ca—O distance of the structure. Presumably it is short enough to satisfy the oxygen, however.

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