# Howlite, $Ca_2SiB_5O_9(OH)_5$: Structure refinement and hydrogen bonding

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## Abstract

The crystal structure of howlite, $Ca_2SiB_5O_9(OH)_5$, was refined in space group $P2_1/c$ using 3085 unique, observed reflections collected with an automated four-circle X-ray diffractometer. Unit-cell parameters are $a = 12.820(3)$, $b = 9.351(1)$, $c = 8.608(2)$ Å, $\beta = 104.84(2)°$, and $V = 997.5(2)$ Å$^3$. The final conventional residual is $R = 0.023$. Positions of all five H atoms were located by difference-Fourier synthesis. The principal structural units are $[Si_2B_4O_{10}(OH)_6 \cdot B_3O_4(OH)_2]$ polyanions infinitely connected along $\mathbf{c}$. The polyanions comprise $Si_2B_4O_{12}(OH)_6$ fragments attached to one another to form corrugated walls parallel to (100) and $B_3O_6(OH)_2$ fragments chained together in the same direction. Single $Ca(1)O_8$ polyhedral chains strengthen the corrugated walls and double $Ca(2)O_8$ chains help to connect adjacent polyanionic chains along $\mathbf{a}$. All hydroxyls participate in hydrogen bonds of various strengths; four form single, moderately bent hydrogen bonds, and the fifth takes part in a bifurcated hydrogen bond. Most of the hydrogen bonding strengthens the borosilicate fragments of the polyanions, whereas two of the bonds serve, like $Ca(2)$, to hold adjacent polyanionic chains together along $\mathbf{a}$. Detailed analysis of the hydrogen-bonding system shows that knowledge of $O\cdots O$ separations is inadequate for identifying weak hydrogen bonds, and dependence on them may even lead to a spurious assignment of weak bonds. Current bond-length–bond-strength curves for O–H bonds probably slightly overestimate the strengths of weak hydrogen bonds and should be revised to yield a bond strength of 0.05 valence units at a $H\cdots O$ distance of 2.40 Å.

## Introduction

The crystal structure of howlite was solved by Finney et al. (1970) and was described as consisting of slabs of silicoborate spirals and colemanite-like chains cross-linked by chains of Ca-containing polyhedra. Intensities were estimated from Weissenberg photographs, however, so the accuracy of the refinement ($R = 0.10$) was lower than that attainable with modern instruments, and the standard deviations reported for interatomic distances and angles were correspondingly large (0.02 to 0.06 Å and 1° to 3°, respectively). The present work was undertaken to provide a more precise set of structural parameters for howlite for use in a study of the stereochemistry of borosilicates. It is reported here partly to make available atomic coordinates of greater precision than heretofore determined, but also because location of the H atoms sheds additional light on the hydrogen-bonding scheme.

The crystal used in this study was a natural specimen from Iona, Nova Scotia. It was provided by the U.S. National Museum, Smithsonian Institution, Washington, D.C., and is catalogued as specimen number USNM C6987.

## Structure refinement

The crystal fragment selected is a rectangular parallelepiped measuring $0.29 \times 0.17 \times 0.25$ mm. A Nicolet R3 four-circle single-crystal diffractometer with graphite-monochromatized $MoK\alpha$ radiation was used for data collection, and unit-cell parameters [$a = 12.820(3)$ Å, $b =$ 9.351(1) Å, $c = 8.608(2)$ Å, $\beta = 104.84(2)°$, and $V = 997.5(2)$ Å$^3$] were obtained by least-squares refinement of 25 reflections, $42° < 2\theta < 62°$, automatically centered at $+2\theta$ and $-2\theta$. The density, measured with a Berman balance, is 2.62 g/cm$^3$, and that calculated from the unit-cell volume, assuming the ideal formula, is 2.61 g/cm$^3$; on the strength of this agreement, ideal chemistry was postulated (and effectively confirmed by the success of the model) for purposes of the structure refinement. A total of 4072 intensities to $\sin \theta/\lambda = 0.76$, from a unique quadrant of the Ewald sphere, were measured in the $\theta$-$2\theta$ mode with the scan rate automatically varied from 3.9° to 29.3° per min, depending on intensity. Of these, 3602 reflections were unique, and 3085 were considered observed [$I > 3\sigma(I)$]. Three standards were collected once in every 100 reflections. Background and Lorentz-polarization corrections were applied, as was an empirical absorption correction ($\mu = 12.4$ cm$^{-1}$) based on psi-scans for nine reflections covering the range $6° < 2\theta < 63°$. Initial data reduction suggested a data set of very high quality, inasmuch as $R_{int}$, from merging equivalent reflections, was only 0.009.

Space group $P2_1/c$ was assumed after Finney et al. (1970) and confirmed by the refinement. No supercell or other space-group anomalies were revealed by partial rotation photographs taken about each crystallographic axis. Starting parameters for least-squares refinement were also taken from Finney et al. (1970), and the program package SHELXTL (Sheldrick, 1983) was used for all data processing. Atomic scattering factors were taken from Cromer

TABLE 2. Fractional coordinates and anisotropic-temperature-factor coefficients ($\times 10^4$) for howlite

| Atom | x | y | z | $U_{11}$* | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|---|---|---|-----------|----------|----------|----------|----------|----------|
| Ca(1) | 0.11738(2)** | 0.18339(3) | 0.14917(3) | 80(1) | 80(1) | 91(1) | −8(1) | 26(1) | −6(1) |
| Ca(2) | 0.41192(2) | 0.82088(3) | 0.52253(3) | 71(1) | 88(1) | 101(1) | 10(1) | 23(1) | 16(1) |
| Si | 0.14127(3) | 0.55510(4) | 0.01101(4) | 54(1) | 55(1) | 54(1) | 3(1) | 18(1) | −1(1) |
| B(1) | 0.0371(1) | 0.4728(2) | 0.2559(2) | 61(5) | 78(5) | 66(5) | 4(4) | 15(4) | −3(4) |
| B(2) | 0.3226(1) | 0.3834(2) | 0.0268(2) | 61(5) | 70(6) | 64(5) | 1(4) | 12(4) | 0(4) |
| B(3) | 0.4927(1) | 0.4209(2) | 0.2508(2) | 73(5) | 73(6) | 89(5) | 2(4) | 19(4) | 10(4) |
| B(4) | 0.3425(1) | 0.2623(2) | 0.2862(2) | 74(5) | 74(6) | 80(5) | −1(4) | 22(4) | 4(4) |
| B(5) | 0.1573(1) | 0.6489(2) | 0.4697(2) | 72(5) | 69(5) | 77(5) | −5(4) | 14(4) | −6(4) |
| O(1) | 0.0803(1) | 0.5138(1) | −0.1738(1) | 59(4) | 117(4) | 67(4) | 3(3) | 6(3) | −15(3) |
| O(2) | 0.1251(1) | 0.7217(1) | 0.0502(1) | 146(4) | 58(4) | 108(4) | 21(3) | 62(3) | 15(3) |
| O(3) | 0.0992(1) | 0.4525(1) | 0.1349(1) | 98(4) | 78(4) | 93(4) | 8(3) | 58(3) | 9(3) |
| O(4) | 0.2687(1) | 0.5237(1) | 0.0306(1) | 57(4) | 65(4) | 101(4) | 6(3) | 17(3) | −4(3) |
| O(5) | 0.0614(1) | 0.5997(1) | 0.3529(1) | 75(4) | 78(4) | 95(4) | 1(3) | 8(3) | −25(3) |
| O(6) | 0.4387(1) | 0.4088(1) | 0.0801(1) | 54(4) | 110(4) | 64(4) | −2(3) | 11(3) | 7(3) |
| O(7) | 0.2914(1) | 0.1692(1) | 0.3631(1) | 86(4) | 106(4) | 64(4) | −20(3) | 11(3) | 19(3) |
| O(8) | 0.2870(1) | 0.2812(1) | 0.1290(1) | 80(4) | 96(4) | 86(4) | −22(3) | 12(3) | 25(3) |
| O(9) | 0.4372(1) | 0.3332(1) | 0.3539(1) | 76(4) | 93(4) | 76(4) | −21(3) | 17(3) | 4(3) |
| O(10) | 0.4964(1) | 0.5711(1) | 0.2940(1) | 175(5) | 87(4) | 134(4) | −19(4) | 16(4) | −8(3) |
| O(11) | 0.6014(1) | 0.3568(1) | 0.2724(1) | 58(4) | 115(4) | 130(4) | −6(3) | 8(3) | 14(3) |
| O(12) | 0.2477(1) | 0.6851(1) | 0.3994(1) | 104(4) | 156(5) | 106(4) | −37(4) | 46(3) | −16(4) |
| O(13) | 0.1975(1) | 0.5421(1) | 0.5987(1) | 122(4) | 104(4) | 118(4) | −5(3) | 7(3) | 39(3) |
| O(14) | 0.0549(1) | 0.3363(1) | 0.3524(1) | 87(4) | 83(4) | 88(4) | −7(3) | 22(3) | 21(3) |
| H(10)† | 0.534 | 0.593 | 0.385 | 371(68) | | | | | |
| H(11)† | 0.345 | 0.598 | 0.681 | 308(61) | | | | | |
| H(12)† | 0.225 | 0.685 | 0.298 | 522(82) | | | | | |
| H(13)† | 0.185 | 0.574 | −0.308 | 367(66) | | | | | |
| H(14)† | 0.007 | 0.704 | −0.342 | 258(57) | | | | | |

*Note:* Numbers in parentheses are esd's and refer to last digit given.
\* $U_{ij}$ are coefficients in the expression $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.
† Positions of H atoms were not refined, but were fixed at positions located by difference-Fourier synthesis. Isotropic-temperature-factor coefficients for H atoms were refined.

and Mann (1968), and anomalous-dispersion factors from Cromer and Liberman (1970). During the early stages of the refinement, H atoms were excluded from the model, and isotropic temperature factors were used, resulting in rapid convergence to $R = 0.039$. Further refinement with anisotropic temperature factors reduced the residual to 0.027. At this stage, a difference-Fourier synthesis was calculated, and it clearly revealed the locations of all five H atoms at expected distances (for X-ray data) from their respective oxygens. The heights of the H peaks ranged from 0.92 to 0.74 e⁻ per Å³, whereas the next highest peak was 0.46 e⁻ per Å³.

The peaks on the difference map were closer to the oxygen positions than the 0.96 Å generally accepted as reasonable for the O–H distance (Brown, 1981), and with refinement of the H coordinates, they moved even closer. [This is also typical of the behavior of H positions in X-ray diffraction work; see, for example, Lager et al. (1987).] For the final refinement, the H positions were fixed at the positions of the peaks on the difference synthesis, but their isotropic temperature factors were allowed to vary. This approach resulted in quite reasonable temperature factors, suggesting that the positions were determined as well as they could be with the present data set.

Examination of the observed and calculated structure factors at this stage revealed a slight but apparently systematic problem with extinction, and so an isotropic extinction correction was made. The final residuals were $R = 0.023$ and $R_w = 0.025$, with weights proportional to $1/\sigma^2(F_o)$. The final difference map was essentially featureless, with maximum and minimum of 0.51 and −0.29 e⁻ per Å³, respectively. Table 1 contains the observed and calculated structure amplitudes.[1] Final atomic coordinates and temperature-factor coefficients are given in Table 2, and selected interatomic distances and angles are shown in Table 3.

## DISCUSSION

### Crystal structure

The topology determined by Finney et al. (1970) is confirmed, although the details of polyhedral geometry reported in their paper and this one differ considerably because of the greater precision of the present work. Only a structural summary, from a different viewpoint than they took and supplemented by Figures 1 through 3, is therefore given here. The major structural units are polyanions of composition $[Si_2B_4O_{10}(OH)_6 \cdot B_3O_4(OH)_2]^\infty$ (Fig. 1), linked to form infinite chains extending in the c crystallographic direction. Each polyanion can be divided into two parts with different structural roles, a borosilicate fragment [composition $Si_2B_4O_{12}(OH)_6$ ignoring polymerization, which reduces the number of oxygens in the formula because some are shared with identical adjacent fragments] and a borate fragment [$B_3O_6(OH)_2$, again ig-

TABLE 3. Interatomic distances (Å) and bond angles (°) in howlite

| | | | |
|---|---|---|---|
| Si–O(1) | 1.629 | O(1)–(2) | 2.694 | 112.1 |
| –O(2) | 1.618 | –O(3) | 2.668 | 110.1 |
| –O(3) | 1.625 | –O(4) | 2.601 | 106.1 |
| –O(4) | 1.625 | O(2)–O(3) | 2.664 | 110.4 |
| | | –O(4) | 2.646 | 109.3 |
| | | O(3)–O(4) | 2.640 | 108.6 |
| B(1)–O(1) | 1.495 | O(1)–O(3) | 2.429 | 109.7 |
| –O(3) | 1.477 | –O(5) | 2.318 | 104.4 |
| –O(5) | 1.437 | –O(14) | 2.442 | 108.8 |
| –O(14) | 1.509 | O(3)–O(5) | 2.473 | 116.1 |
| | | –O(14) | 2.357 | 104.3 |
| | | O(5)–O(14) | 2.464 | 113.5 |
| B(2)–O(4) | 1.488 | O(4)–O(6) | 2.369 | 107.0 |
| –O(6) | 1.459 | –O(7) | 2.374 | 107.9 |
| –O(7) | 1.448 | –O(8) | 2.412 | 110.3 |
| –O(8) | 1.451 | O(6)–O(7) | 2.403 | 111.5 |
| | | –O(8) | 2.407 | 111.7 |
| | | O(7)–O(8) | 2.350 | 108.3 |
| B(3)–O(6) | 1.458 | O(6)–O(9) | 2.464 | 112.0 |
| –O(9) | 1.513 | –O(10) | 2.354 | 108.1 |
| –O(10) | 1.450 | –O(11) | 2.357 | 106.5 |
| –O(11) | 1.484 | O(9)–O(10) | 2.447 | 111.3 |
| | | –O(11) | 2.393 | 105.9 |
| | | O(10)–O(11) | 2.447 | 113.0 |
| B(4)–O(7) | 1.360 | O(7)–O(8) | 2.259 | 111.8 |
| –O(8) | 1.368 | –O(9) | 2.434 | 125.8 |
| –O(9) | 1.375 | O(8)–O(9) | 2.403 | 122.4 |
| B(5)–O(2) | 1.505 | O(2)–O(5) | 2.373 | 106.9 |
| –O(5) | 1.449 | –O(12) | 2.441 | 109.9 |
| –O(12) | 1.478 | –O(13) | 2.391 | 106.3 |
| –O(13) | 1.483 | O(5)–O(12) | 2.452 | 113.8 |
| | | –O(13) | 2.433 | 112.1 |
| | | O(12)–O(13) | 2.389 | 107.6 |
| Ca(1)–O(8) | 2.407 | Ca(2)–O(4) | 2.356 | |
| –O(5) | 2.418 | –O(9) | 2.428 | |
| –O(13) | 2.433 | –O(6) | 2.448 | |
| –O(14) | 2.481 | –O(12) | 2.455 | |
| –O(7) | 2.508 | –O(11) | 2.462 | |
| –O(1) | 2.515 | –O(10) | 2.522 | |
| –O(3) | 2.528 | –O(11) | 2.523 | |
| –O(14) | 2.542 | –O(6) | 2.582 | |

*Note:* esd's as follows: Ca–O and Si–O distances, 0.001 Å; B–O and O–O distances, 0.002 Å; all angles, 0.1°.

noring polymerization]. The borosilicate fragment is composed of a four-membered centrosymmetric ring of alternating Si and B(1) tetrahedra, oriented essentially parallel to (010), with nonring B(5) tetrahedra linked to the Si tetrahedra through O(2) (see Figs. 1 and 2). Adjacent polyanions of this type are connected along [011]
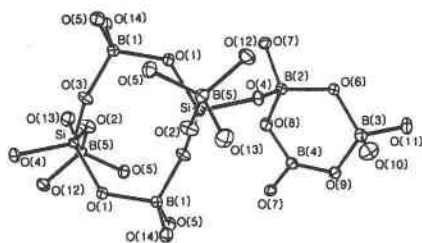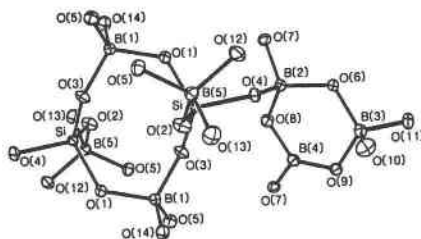
and [01$\bar{1}$] through oxygen O(5), shared by B(1) and B(5), to form (100) corrugated walls (Fig. 3). Attached to these walls through O(4), and forming chains parallel to **c** by sharing O(7) with one another, are the borate fragments, consisting of the B(2) and B(3) tetrahedra and the B(4) triangle. Finney et al. (1970) recognized the borate fragments as forming chains topologically identical to those in colemanite (Christ et al., 1958); the similarity ends with topology, as there is essentially no correlation between either bond lengths or bond angles for the borate fragments of howlite and the borate chains of colemanite.

Charge balance is provided by the two kinds of 8-co-ordinated Ca atoms, each kind forming a chain extending along **c** as shown in Figure 3, in which the chains project out of the page. Ca(1) strengthens the linkage of adjacent [Si$_2$B$_4$O$_{10}$(OH)$_6$·B$_3$O$_4$(OH)$_2$]$^\infty$ polyanions in the **b** direction. Ca(2) is bonded to oxygen atoms in what are otherwise entirely separate chains of borate fragments; except for the H(11)···O(13) and the weak H(10)···O(9) hydrogen bonds (see below), Ca(2) is the only structural entity that links separate polyanions together in the **a** crystallographic direction.

**Hydrogen bonding**

The bond-strength sums in the left-hand column of Table 4 show clearly that O(10) through O(14) are the hydroxyl anions and that O(2) is substantially underbonded, whereas O(1), O(5), and O(9) may be slightly underbonded. (In fact, these last three oxygens are no more underbonded than O(4) and O(8) are *over*bonded, but below it is shown that the H···O distances for them suggest weak hydrogen bonding.) Finney et al. (1970) also noted that O(5) was underbonded as judged by simple Pauling bond strengths, but they did not have sufficiently precise bond lengths to recognize the solution to that problem. They concluded that O(11), overbonded when hydrogen H(11) is taken into account, is the donor for a hydrogen bond with O(13), and that O(14) is the donor for a hydrogen bond with O(2). However, addition of both a full valence unit for the H(13)–O(13) bond and the residual hydrogen bond strength from H(11) required by this bonding scheme to the bond-strength sum received by O(13) from other cations results in an unacceptably large bond-strength sum for that anion. A redistribution of hydrogen bond strengths
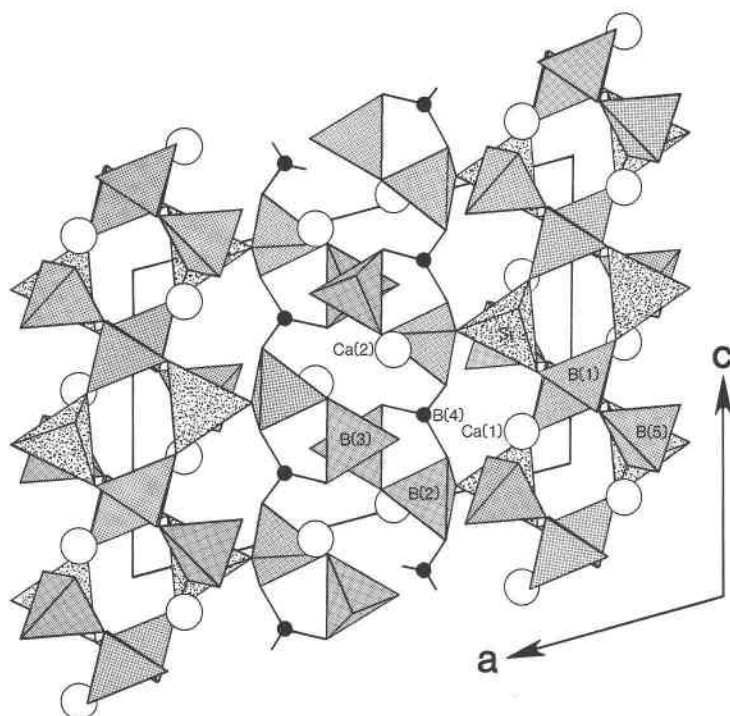


Fig. 1. A stereoscopic projection of the borosilicate polyanion of howlite, viewed down **b** (with **c** vertical in the plane of the page, as in Fig. 2). Thermal ellipsoids represent 70% probability. Although the composition of the polyanion derived from simply counting atoms shown in the figure is [Si$_2$B$_7$O$_{17}$(OH)$_8$], sharing of oxygen atoms between adjacent polyanions reduces the number of independent ones to 14. Written in a more structurally informative way, the composition is thus [Si$_2$B$_4$O$_{10}$(OH)$_6$·B$_3$O$_4$(OH)$_2$].

Fig. 2. The structure of howlite viewed down **b**. H atoms are omitted for clarity, as are Ca–O bonds and labels on oxygens. Stippled tetrahedra are occupied by Si, the shaded ones by B.
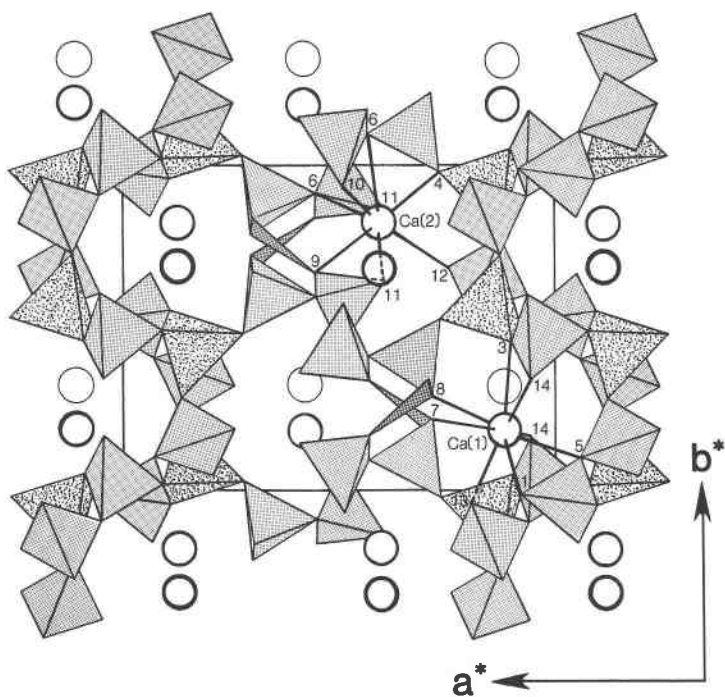


Fig. 3. View of the structure down **c**, showing the corrugated walls along (100) unit-cell boundaries, with chains of attached $B_3O_6(OH)_2$ polyanions running through the middle of the cell in the **c** direction. H atoms are omitted for clarity. Stippling and shading as in Fig. 2, except that darker-shaded triangles (rather than "balls-and-sticks") represent $B(4)O_3$. Thicknesses of circles suggests heights along **c** of Ca(1) atoms relative to one another, and of Ca(2) atoms relative to one another [but not of Ca(1) atoms relative to Ca(2) atoms]. Numerals are oxygen designations [4 = O(4), etc.].

TABLE 4. Bond-strength distribution and bond-strength sums (Σs) for anions and H atoms (expressed in valence units)

|       | Σs*  | H(10) | H(11) | H(12)   | H(13)   | H(14)    | Σs** |
|-------|------|-------|-------|---------|---------|----------|------|
| O(1)  | 1.93 | —     | —     | —       | 0.12    | (0.07)†  | 2.05 |
| O(2)  | 1.72 | —     | —     | 0.10    | (0.08)† | 0.13     | 1.95 |
| O(3)  | 1.97 | —     | —     | —       | —       | —        | 1.97 |
| O(4)  | 2.06 | —     | —     | —       | —       | —        | 2.06 |
| O(5)  | 1.90 | —     | —     | (0.06)† | —       | 0.06     | 1.96 |
| O(6)  | 2.01 | —     | —     | —       | —       | —        | 2.01 |
| O(7)  | 2.04 | —     | —     | —       | —       | —        | 2.04 |
| O(8)  | 2.08 | —     | —     | —       | —       | —        | 2.08 |
| O(9)  | 1.92 | 0.08  | —     | —       | —       | —        | 2.00 |
| O(10) | 1.01 | 0.93  | —     | —       | —       | —        | 1.94 |
| O(11) | 1.20 | —     | 0.81  | —       | —       | —        | 2.01 |
| O(12) | 1.00 | —     | —     | 0.93    | —       | —        | 1.93 |
| O(13) | 1.00 | —     | 0.19  | —       | 0.81    | —        | 2.00 |
| O(14) | 1.13 | —     | —     | —       | —       | 0.82     | 1.95 |
| Σs for H |   | 1.01  | 1.00  | 1.03    | 0.93    | 1.01     |      |

* Bond-strength sums for oxygens ignoring H in hydroxyl groups.
** Bond-strength sums for oxygens including H in hydroxyl groups.
† Unlikely hydrogen bonds involving oxygens common to a borate tetrahedral edge. These are not included in the bond-strength sums.

TABLE 5. M–O–H angles (°) for howlite

| B(3)–O(10)–H(10) | 116.7 | B(5)–O(13)–H(13) | 109.8 |
| Ca(2)–O(10)–H(10) | 141.5 | Ca(1)–O(13)–H(13) | 86.9 |
| Mean | 129.1 | Mean | 98.4 |
| B(3)–O(11)–H(11) | 119.9 | B(1)–O(14)–H(14) | 108.1 |
| Ca(2)–O(11)–H(11) | 102.0 | Ca(1)–O(14)–H(14) | 97.1 |
| Ca(2)–O(11)–H(11) | 112.8 | Ca(1)–O(14)–H(14) | 96.8 |
| Mean | 111.6 | Mean | 100.7 |
| B(5)–O(12)–H(12) | 108.6 | | |
| Ca(2)–O(12)–H(12) | 118.7 | | |
| Mean | 113.7 | | |

within this scheme can be devised that leaves O(11) and O(13) overbonded by only ~5%, but it results in poor agreement between predicted H···O distances, obtained by using Figure 1 of Brown (1981), and distances calculated geometrically (on the basis of the assumptions about the correct H positions, discussed below). It appears that the hydrogen-bonding scheme is somewhat more complicated than that proposed by Finney et al. (1970).

An analysis of hydrogen bonding from X-ray diffraction data is not without ambiguities. In considering the hydrogen bonding in howlite, two assumptions were made. In a study of hydrogrossular, Lager et al. (1987) found that the hydrogens, as located by neutron diffraction, were positioned nearly along the O–H vectors found by X-ray
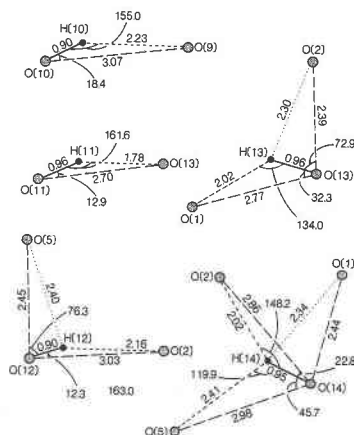
diffraction for the same crystal, but were further from their respective oxygen atoms than suggested by the X-ray data. In a comparison of H locations from neutron and X-ray diffraction work, Baur (1972) observed that H(X)–O–H(N) angles (where X and N refer to H positions from X-ray and neutron data, respectively) differed by an average of only 12°. The first assumption made here, then, was that the actual O–H distances were longer than those required by the positional parameters in Table 2, but that the hydrogens were located in the same directions from their respective oxygen atoms as were the peaks on the difference map (i.e., the positions in Table 2). The second assumption derives from the purported accuracy of the bond-length–bond-strength curves of Brown (1981)—namely, 0.05 valence units. [See also Brown and Shannon (1973), who claimed generally 5% accuracy for the sum of bond strengths about an atom.] A consequence of accepting this estimate of accuracy is that any H···O distance less than ~2.5 Å [the distance corresponding to 0.05 valence units, or 5% of the required hydrogen bond strength, in Fig. 1 of Brown (1981)] must be considered a possible hydrogen-bonded contact. This upper limit for hydrogen-bonded distances is obviously somewhat arbitrary, but it is reasonably consistent with the recommendation of Hamilton and Ibers (1968) that 2.4 Å be considered the maximum.

Table 4 shows the hydrogen-bonding scheme proposed here, and Figure 4 provides geometrical details. The O···O separations and H–O···O angles are from the results of the structure refinement, whereas H–O and H···O distances (and thus O–H···O angles) were determined by trial-and-error to yield bond strengths consistent with the second assumption above. (The distances shown in Fig. 4 are not absolutely unique, of course, but they could not vary by significant amounts and still meet the imposed constraints.) All of the usual criteria for hydrogen bonding (see Hamilton and Ibers, 1968; Baur, 1972) are met by this scheme except for one M–O–H angle (see Table 5), where M is the cation to which the donor hydroxyl is bonded. These angles are expected to exceed 90°, and the single exception measures 87°; it is, however, a Ca–O–H angle with a long Ca-H distance anyway, so the violation is not a serious one. Baur (1972), in fact, relaxed this criterion in the case of large cations, on the basis of a neutron-diffraction structure refinement that showed a clear violation of it.
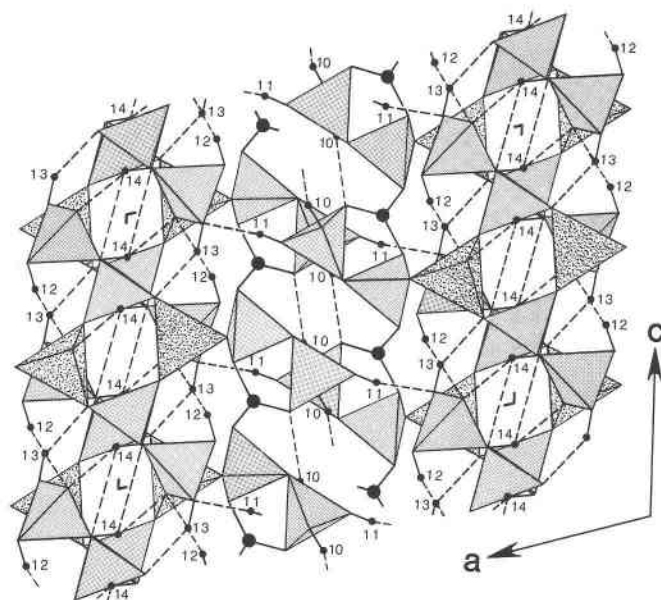


Fig. 4. Arrangement of oxygen atoms about H atoms, shown schematically. O···O distances and O···O–H angles are from the structure refinement; H–O and H···O distances, and O–H···O angles, are calculated as explained in the text. Dashed H···O contacts are hydrogen bonds proposed in Table 4; dotted H···O contacts are less likely to be hydrogen bonds because they involve oxygens common to a polyhedral edge.

Fig. 5. The crystal structure viewed down **b**, showing hydrogen bonds as dashed lines. Hydrogens are shown as small filled circles labeled with the numerical designation from Table 2 [10 = H(10), etc.], and joined with solid lines to the appropriate oxygen atoms. Ca atoms are omitted for clarity, as are other atom designations, which can be determined by comparison with Figs. 1 through 3.

Examination of Figure 4 reveals that even oxygen atoms considered unlikely to be hydrogen-bond acceptors, because they are common to a polyhedral edge with the potential donor oxygens (Donnay and Allmann, 1970), may nonetheless influence the geometry of the hydrogen bond. O–H···O angles involving hydrogen bonds that are clearly single in howlite are 153.6° and 159.7°, while the O(14)–H(14)···O(2) angle is only 146.0° because of the weak bond formed to O(5) as well. Given the quite small angle of 134.0° involving H(13), it appears that the H(13)···O(2) contact might well be considered a weak hydrogen bond, even though O(13) and O(1) form an edge of the B(5) tetrahedron; this possibility is supported by the relatively low bond-strength sum to H(13) when the contribution from O(2) is not considered. On the other hand, the angle of 163.5° involving H(12) suggests that there is essentially no hydrogen-bonding interaction of significance between H(12) and O(5), and, indeed, the bond-strength sum at H(12) does not require it. The foregoing arguments depend, of course, on the assumption that the true H locations and those determined here are not very different. Supporting the present interpretation of the X-ray data is the fact that O–H distances increase as O···O distances decrease, as observed for structures refined from neutron-diffraction data (Hamilton and Ibers, 1968).

## Conclusion

Figure 5 shows the structure of howlite projected onto (010), with the hydrogen bonds proposed in Table 4 shown as dashed lines. (Unlikely or less likely hydrogen bonds, as discussed above, are omitted.) Note that, other than

Ca(2), which has four bonds to one polyanionic chain and four to another (Fig. 3), only the H(11)···O(13) and H(10)···O(9) hydrogen bonds (the latter of which is quite weak) connect the structure in the **a** direction. Most of the hydrogen bonding serves to strengthen the borosilicate fragment of the polyanion. O(2), bonded directly to only one Si and one B(5) atom, receives contributions from at least two hydrogen bonds to achieve charge balance.

Baur (1972) pointed out that, given the nature of electrostatic interactions, there is really no such thing as "no hydrogen bond" in a structure containing both H and oxygen, although H···O attractions must necessarily become too weak to be considered significant beyond some distance. Thus for very weak hydrogen bonds with O–H···O angles as small as, say, 150°, O···O separations could be in excess of 3.3 Å; for bonds closer to linear, the separation could approach 3.5 Å. These distances are somewhat greater than the 3.0–3.2 Å that is often considered the critical nonbonded oxygen separation below which hydrogen bonding can be invoked (e.g., Finney et al., 1970). It can thus be concluded that, while short O···O approaches are expected to reveal the strongest hydrogen bonds in a structure, interactions that are weak but nonetheless play a significant role in overall charge balance can be missed by relying on this criterion, and only experimental resolution of the H atoms can unequivocally reveal the hydrogen-bonding scheme in a crystal. (In fact, some of the O···O approaches *not* indicative of hydrogen bonding in howlite are closer than some of the O···O distances that do involve hydrogen bonds; for example, an O(10)···O(9) distance of 2.981 Å and an O(10)···O(11) separation of 2.940 Å are both closer than

the hydrogen-bonded $O(10)\cdots O(9)$ approach of 3.065 Å, but they do not represent hydrogen bonds because the orientation of the O–H vectors makes the associated $H\cdots O$ distances too long.)

Finally, although the bond-length–bond-strength curves given by Brown (1976, 1981) appear to yield appropriate values for strong hydrogen bonds, they seem to overestimate the strengths of weak ones. Baur (1972) cited an example of a structure containing a H atom surrounded by three oxygens each 2.46 Å from it, but in which the O–H stretching frequency is not different from that of the free hydroxyl radical or of water vapor. This example suggests that 2.40 Å is a better upper limit for the hydrogen-bonded $H\cdots O$ distance than is 2.50 Å and that the bond-length–bond-strength curve for the O–H bond should be reconstructed so that it decreases to 0.05 valence units (at most) at the shorter distance. Such a curve would yield slightly lower bond strengths for the weak bonds in Table 4 (and might negate the probably fortuitous result that the mean bond-strength sums about the oxygens and H are 2.00 and 1.00, respectively) but would result in a quantitatively better scheme for both the oxygens and the hydrogens, while not requiring any qualitative changes in the proposed model for hydrogen bonding in howlite.

## ACKNOWLEDGMENTS

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