American Mineralogist, Volume 64, pages 187–195, 1979

Hilgardite, $Ca_2[B_5O_9]Cl \cdot H_2O$: a piezoelectric zeolite-type pentaborate

SUBRATA GHOSE AND CHE'NG WAN

Department of Geological Sciences, University of Washington
Seattle, Washington 98195

Abstract

Hilgardite, $Ca_2B_5O_9Cl \cdot H_2O$, from Choctow Salt Dome, Iberville Parish, Louisiana, is monoclinic, space group *Aa*, with unit-cell dimensions a = 11.438(2), b = 11.318(2), c = 6.318(1)A, β = 90.06(1)°, and Z = 4. The crystal structure has been determined from three-dimensional Patterson and Fourier syntheses and refined by full-matrix least-square methods to an R-factor of 0.017 based on 1487 reflections, measured on an automatic single-crystal X-ray diffractometer. The absolute configuration and the hydrogen positions have been determined.

The structure of hilgardite is an open three-dimensional borate framework, whose building block is the anhydrous pentaborate polyanion $[B_5O_{12}]^{9-}$, consisting of three (BO_4) tetrahedra and two (BO_3) triangles. The average tetrahedral and triangular B–O distances are 1.474 and 1.363A respectively. The polyanions form three-tetrahedral-repeat single chains (6.3A c axis) by sharing tetrahedral corners with those belonging to adjacent polyanions. Within each chain, corners of two borate tetrahedra point along $+\mathbf{a}$ and $+\mathbf{b}$ directions, whereas corners of two borate triangles point along $-\mathbf{a}$ and $-\mathbf{b}$ directions; these corners are shared with four adjacent chains, such that tetrahedral corners of one chain are shared with triangular corners of the other. The resulting framework has ~6 and ~5A diameter open channels parallel to the a and c axes respectively. The water molecules and the chlorine atoms within the channels form quasi-linear hydrogen-bonded chains parallel to the c axis. Hilgardite may be the precursor of a new family of borate zeolites.

The calcium atoms occur within channels parallel to the a and b axes. The $[Ca(1)O_5Cl(H_2O)]$ and $[Ca(2)O_6Cl_2]$ coordination polyhedra are slightly distorted pentagonal and hexagonal bipyramids, with average Ca–O distances 2.465 and 2.535A, and average Ca–Cl distances 2.817 and 2.905A respectively. By sharing opposite Cl corners the Ca(2) polyhedra form linear chains parallel to the a axis, crosslinked into a sheet by the Ca(1) polyhedra sharing polyhedral corners and edges.

Hilgardite is mildly piezoelectric, the strongest electric axis being parallel to the a axis. The piezoelectricity along b is zero or nearly zero, because the borate triangles point alternately along $+\mathbf{b}$ and $-\mathbf{b}$, whereas along the a axis, all borate triangles point along $-\mathbf{a}$. All borate tetrahedra point along $-\mathbf{c}$, the c axis presumably being the intermediate piezoelectric axis.

Introduction

The hydrated calcium chloroborate minerals hilgardite and parahilgardite were found in the insoluble residue from a brine well in the Choctow Salt Dome, Iberville Parish, Louisiana, in association with anhydrite, danburite, boracite, dolomite, magnesite, calcite, quartz, sulphur, and other minerals (Hurlbut and Taylor, 1937, 1938; Hurlbut, 1938). Hilgardite occurs as colorless hemimorphic triangular plates. It is monoclinic, crystal class *m*. The lack of a center of symmetry is clearly indicated by the morphology, further confirmed by positive tests for piezoelectricity (Hurlbut, 1938). The unit-cell dimensions were determined by Hurlbut and Taylor (1937), who suggested the space group to be *Pc* or *Pm*, and the chemical composition as $Ca_8(B_6O_{11})_3Cl_4 \cdot 4H_2O$, which implies a close relationship to colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$. Braitsch (1959) confirmed the unit-cell dimensions and found the correct space group to be *Cc*. In addition, he described a new triclinic strontiohilgardite phase, whose unit-cell volume is one-fourth that of hilgardite; on this basis, he suggested the chemical composition of hilgardite and

0003–004X/79/0102–0187$02.00

Table 1. Hilgardite: crystal data

Hilgardite, $Ca_2[B_5O_9]Cl \cdot H_2O$. Colorless transparent triangular plates
Choctow Salt Dome, Iberville Parish, Louisiana

Monoclinic, *m*

a(Å) = 11.438(2)	Space group: *Aa*
b(Å) = 11.318(2)	Unit cell content: $4[Ca_2B_5O_9Cl \cdot H_2O]$
c(Å) = 6.318(1)	D_m 2.71 g cm^{-3}
β(°) = 90.06(1)	D_c 2.693 g cm^{-3}
V(Å^3) = 817.82(26)	$\mu_{MoK\alpha}$: 16.90 cm^{-1}

parahilgardite to be $Ca_2[B_5O_8(OH)_2Cl]$. Ghose and Wan (1977) in a brief report showed that hilgardite and parahilgardite are zeolite-type framework pentaborates and the correct chemical composition for both phases is $Ca_2[B_5O_9]Cl \cdot H_2O$.

Experimental

A clear single-crystal fragment of hilgardite was ground to a sphere with a diameter of 0.30 mm (Bond, 1951), and mounted on the computer-controlled four-circle single-crystal X-ray diffractometer (Syntex $P\bar{1}$). The unit-cell dimensions were determined by the least-squares refinement of 15 reflections, with 2θ values lying between 25 and 50°, measured with Mo$K\alpha$ radiation (Table 1).

For hilgardite we have chosen the unit-cell orientation of Hurlbut and Taylor (1937), in which c is the shortest axis (space group *Aa*). Intensities of all reflections with 2θ values $\leq 65°$ were measured by the 2θ–θ scan method with Mo$K\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal, and a scintillation counter. A variable scan method was used, the minimum scan rate being 2°/min (50 kV, 10mA). A total of 1487 reflections were measured, of which 10 reflections were below $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measurement of the intensity, I, as determined by the counting statistics. The intensity data were corrected for Lorentz, polarization, and absorption factors.

Determination and refinement of the structure

An interpretation of the three-dimensional Patterson map indicated the positions of two Ca and one Cl atoms. A structure-factor calculation using these atomic positions yielded an R-factor of 0.37 for all reflections. Fourier and difference Fourier syntheses subsequently calculated indicated the positions of all the boron and oxygen atoms. Least-squares refinement of these atomic positions and anisotropic temperature factors lowered the R-factor to 0.033. A difference Fourier synthesis calculated at this stage yielded the positions of the two hydrogen atoms attached to the water molecule. Atomic scattering factors for Ca, Cl, B, O, and H were taken from Cromer and Mann (1968), corrected for anomalous dispersion (Cromer and Liberman, 1970). The observed structure factors were weighted by $1/\sigma^2(Fo)$, where $\sigma(Fo)$ is the standard deviation of the measurement of Fo. Three cycles of full-matrix least-squares refinement using anisotropic temperature factors for all atoms except hydrogens, for which isotropic temperature factors were used, yielded a final R-factor of 0.017.

The final atomic positional and thermal parameters are listed in Table 2 and a comparison of the observed and calculated structure factors in Table 3[1].

Interatomic bond distances and angles and their standard deviations, which include the standard deviations of the unit-cell dimensions, are listed in Table 4. Least-squares planes through B–O rings, calculated by the method of Schomaker *et al.* (1959), are listed in Table 5.

The average standard deviations in Ca–O, Ca–Cl, and B–O distances are 0.002, 0.001 and 0.002A respectively, and in O–Ca–O and O–B–O angles 0.04 and 0.1° respectively.

Programs incorporated in the X-RAY SYSTEM-72 (Stewart *et al.*, 1972) including CRY LSQ and BONDLA have been used for the computations.

Absolute configuration

Since hilgardite is monoclinic-noncentrosymmetric, with a glide plane normal to the b axis, two configurations of the crystal structure with reference to a right-handed coordinate system are possible; the first configuration is represented by the atomic coordinates x, y, z and the second by $\bar{x}, y, \bar{z}$. A least-squares refinement, carried out using the latter set of coordinates, resulted in a R-factor (0.020), significantly higher than that (0.017) obtained by using the x, y, z set of coordinates. This indicates that the x, y, z set, as listed in Table 2, represents the absolute configuration.

Description of the structure

The crystal structure of hilgardite consists of the pentaborate polyanion, $[B_5O_{12}]^{9-}$ $(5{:}3T + 2\Delta)$[2],

---

[1] For a copy of Table 3, order Document AM-78-075 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

[2] Nomenclature after Christ and Clark (1977): 5: pentaborate, T: borate tetrahedron, Δ: borate triangle.

Table 2. Hilgardite: atomic positional and thermal parameters (with standard deviations in parentheses)

Atom	*x*	*y*	*z*	u_{11}^*	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ca(1)	0.00000	0.25023(3)	0.00000	1.07(1)	1.16(1)	0.73(1)	0.05(1)	0.02(1)	-0.07(1)
Ca(2)	0.27346(5)	0.47081(3)	0.84144(9)	1.01(1)	0.92(1)	0.61(1)	0.11(1)	0.02(1)	0.12(1)
Cl	0.02385(6)	0.49169(4)	0.90054(11)	1.22(2)	1.23(2)	2.02(2)	0.00(1)	-0.17(2)	-0.13(2)
B(1)	0.2604(2)	0.1951(2)	0.6460(3)	0.66(7)	0.59(7)	0.52(7)	-0.01(5)	0.02(6)	0.08(5)
B(2)	0.2710(2)	0.0280(2)	0.8833(3)	0.91(8)	0.60(7)	0.67(8)	-0.04(6)	-0.03(7)	0.00(6)
B(3)	0.2252(2)	0.3065(2)	0.3208(3)	0.56(7)	0.56(7)	0.51(6)	0.08(6)	-0.02(5)	0.06(6)
B(4)	0.3361(2)	0.2296(2)	0.0083(3)	0.61(8)	0.60(7)	0.47(7)	-0.01(6)	-0.01(6)	0.04(6)
B(5)	0.0602(2)	0.2573(2)	0.5415(3)	0.51(8)	0.84(7)	0.71(7)	0.07(6)	-0.02(6)	-0.05(6)
O(1)	0.2668(1)	0.0652(1)	0.6779(2)	1.60(6)	0.55(5)	0.61(5)	-0.07(4)	-0.16(5)	0.09(4)
O(2)	0.3458(1)	0.2565(1)	0.7813(2)	0.69(6)	0.76(5)	0.47(5)	-0.15(4)	-0.12(4)	0.02(4)
O(3)	0.1411(1)	0.2367(1)	0.6981(2)	0.52(6)	1.39(6)	0.69(5)	0.22(4)	-0.04(4)	0.07(4)
O(4)	0.2894(1)	0.2121(1)	0.4268(2)	0.86(5)	0.70(5)	0.42(5)	0.24(4)	0.02(4)	0.09(4)
O(5)	0.2953(1)	0.1055(1)	0.0429(2)	1.67(6)	0.57(5)	0.62(5)	-0.25(5)	-0.07(4)	-0.01(4)
O(6)	0.4494(1)	0.2436(1)	0.1134(2)	0.48(6)	1.64(6)	0.69(6)	-0.21(4)	-0.03(4)	-0.01(4)
O(7)	0.2528(1)	0.3138(1)	0.0991(2)	0.89(6)	0.84(5)	0.47(5)	0.28(4)	0.12(4)	0.05(4)
O(8)	0.2479(1)	0.4161(1)	0.4462(2)	1.68(6)	0.54(5)	0.71(5)	-0.27(4)	-0.03(4)	-0.01(4)
O(9)	0.0949(1)	0.2834(1)	0.3389(2)	0.58(5)	1.32(6)	0.67(5)	-0.05(4)	-0.04(4)	0.26(4)
O(w)-(H_2O)	0.0101(2)	0.0492(2)	0.9092(3)	2.83(9)	1.32(7)	2.38(8)	0.25(7)	0.44(7)	0.36(6)
H(1)	0.034(4)	0.026(3)	0.789(6)	4.2(1.0)					
H(2)	0.041(6)	0.495(6)	0.521(8)	10.3(1.6)					

**Temperature-factor expression* ($\times 10^2$), $\exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}\ell^2c^{*2}+2u_{12}hka^*b^*\cos\gamma+2u_{13}h\ell a^*c^*\cos\beta^*+2u_{23}k\ell b^*c^*\cos\alpha^*)]$

linked into chains by sharing tetrahedral corners, which in turn are cross-linked into an open three-dimensional framework. Ca(1), Ca(2), and Cl atoms and the water molecules occur within open channels of the pentaborate framework.

The configuration of the pentaborate polyanion

The $(B_5O_{12})^{9-}$ polyanion in hilgardite is formed by two six-membered boron–oxygen rings, joined through a common tetrahedral boron atom (Fig. 1). Each ring consists of two (BO_4) tetrahedra and a (BO_3) triangle, with the $[B(1)O_4]$ tetrahedron being common to the two ring systems. The polyanion has the point symmetry *1* and the two (BO_3) triangles are in *cis*-configuration with respect to the central borate tetrahedron (Fig. 1).

The two boron–oxygen rings are nearly perpendicular to each other, the angle between the two mean ring planes being 85.8°. The average B–B separations within ring 1[B(1)–O(1)–B(2)–O(5)–B(4)–O(2)] and ring 2[B(1)–O(3)–B(5)–O(9)–B(3)–O(4)] are 2.474 and 2.448A, and the average inter-ring B–O–B angles are 118.2 and 116.5° respectively. Compared to the isolated pentaborate $[B_5O_6(OH)_6]^{3-}$polyanion in ulexite, where the average B–B separations within two six-membered B–O rings are 2.498 and 2.505A (Ghose *et al.*, 1978), the two rings in hilgardite are more distorted, ring 2 being more so than ring 1. The maximum deviation of a boron atom from the mean plane in ring 1 is 0.60A and in ring 2 0.68A. The average tetrahedral and triangular B–O bond lengths (1.474 and 1.363A respectively) are in agreement with corresponding values in other borates. However, within each borate tetrahedron two B–O distances (av. 1.490A) involving oxygen atoms, further bonded to a triangular boron, are significantly longer than the other two (av. 1.457A); the latter involve oxygen atoms which are further bonded to a tetrahedral boron. However, the B(4)–O(6) bond is an exception. Each of the three oxygen atoms belonging to a borate triangle is further bonded to a tetrahedral boron and a Ca atom; hence all the triangular B–O distances are expected to be very similar. However, within each borate triangle, two B–O distances are similar (av. 1.369A) and are significantly longer than the third one (av. 1.350A).

The pentaborate $[B_5O_{11}]^{7-}$ chain

The pentaborate polyanions form chains parallel to the *c* axis, by sharing two borate tetrahedral cor-

Table 4. Hilgardite: interatomic distances (A) and angles (°) (with standard deviations in parentheses)

The Ca(1) Pentagonal bipyramid

Ca(1)-O(2)	2.506(1)
Ca(1)-O(3)	2.504(2)
Ca(1)-O(4)	2.489(2)
Ca(1)-O(6)	2.510(2)
Ca(1)-O(9)	2.429(2)
Ca(1)-O(w)	2.350(2)
Ca(1)-Cl	2.817(1)
Mean of 6 Ca-O distances	2.465

The Ca(2) - Hexagonal Bipyramid

Ca(2)-O(1)	2.380(2)
Ca(2)-O(2)	2.590(1)
Ca(2)-O(4)	2.789(2)
Ca(2)-O(5)	2.438(2)
Ca(2)-O(7)	2.421(2)
Ca(2)-O(8)	2.589(2)
Ca(2)-Cl	2.890(1)
Ca(2)-Cl'	2.919(1)
Mean of 6 Ca-O distances	2.535
Mean of 2 Ca-Cl distances	2.905

The B(1) - Tetrahedron

B(1)-O(1)	1.486(3)	O(1)-O(2)	2.435(2)	O(1)-B(1)-O(2)	110.9(1)
B(1)-O(2)	1.471(2)	O(1)-O(3)	2.420(2)	O(1)-B(1)-O(3)	109.3(1)
B(1)-O(3)	1.481(2)	O(1)-O(4)	2.313(2)	O(1)-B(1)-O(4)	104.6(1)
B(1)-O(4)	1.438(2)	O(2)-O(3)	2.409(2)	O(2)-B(1)-O(3)	109.4(1)
Mean	1.469	O(2)-O(4)	2.384(2)	O(2)-B(1)-O(4)	110.1(1)
		O(3)-O(4)	2.429(2)	O(3)-B(1)-O(4)	112.7(1)
		Mean	2.398	Mean	109.5

The B(2) - Triangle

B(2)-O(1)	1.365(2)	O(1)-O(5)	2.373(2)	O(1)-B(2)-O(5)	120.7(2)
B(2)-O(5)	1.365(2)	O(1)-O(8)	2.402(2)	O(1)-B(2)-O(8)	124.1(2)
B(2)-O(8)	1.353(2)	O(5)-O(8)	2.294(2)	O(5)-B(2)-O(8)	115.1(2)
Mean	1.361	Mean	2.356	Mean	120.0

The B(3) - Tetrahedron

B(3)-O(4)	1.459(2)	O(4)-O(7)	2.405(2)	O(4)-B(3)-O(7)	112.3(1)
B(3)-O(7)	1.438(2)	O(4)-O(8)	2.361(2)	O(4)-B(3)-O(8)	106.1(1)
B(3)-O(8)	1.495(2)	O(4)-O(9)	2.431(2)	O(4)-B(3)-O(9)	109.5(1)
B(3)-O(9)	1.518(2)	O(7)-O(8)	2.480(2)	O(7)-B(3)-O(8)	115.5(1)
Mean	1.478	O(7)-O(9)	2.383(2)	O(7)-B(3)-O(9)	107.4(1)
		O(8)-O(9)	2.403(2)	O(8)-B(3)-O(9)	105.8(1)
		Mean	2.411	Mean	109.4

The B(4) - Tetrahedron

B(4)-O(2)	1.471(2)	O(2)-O(5)	2.447(2)	O(2)-B(4)-O(5)	111.2(1)
B(4)-O(5)	1.496(2)	O(2)-O(6)	2.413(2)	O(2)-B(4)-O(6)	110.6(1)
B(4)-O(6)	1.464(2)	O(2)-O(7)	2.364(2)	O(2)-B(4)-O(7)	107.3(1)
B(4)-O(7)	1.465(2)	O(5)-O(6)	2.397(2)	O(5)-B(4)-O(6)	108.1(1)
Mean	1.474	O(5)-O(7)	2.434(2)	O(5)-B(4)-O(7)	110.5(1)
		O(6)-O(7)	2.387(2)	O(6)-B(4)-O(7)	109.1(1)
		Mean	2.407	Mean	109.5

The B(5) - Triangle

B(5)-O(3)	1.374(3)	O(3)-O(6)	2.268(2)	O(3)-B(5)-O(6)	112.9(2)
B(5)-O(6)	1.347(3)	O(3)-O(9)	2.389(2)	O(3)-B(5)-O(9)	120.9(2)
B(5)-O(9)	1.372(3)	O(6)-O(9)	2.424(2)	O(6)-B(5)-O(9)	126.1(2)
Mean	1.364	Mean	2.360	Mean	120.0

B - B Separations

B(1)-B(2)	2.417(3)	B(2)-B(4)	2.527(3)
B(1)-B(3)	2.444(2)	B(3)-B(4)	2.503(3)
B(1)-B(4)	2.477(3)	B(3)-B(5)	2.413(3)
B(1)-B(5)	2.485(3)	B(4)-B(5)	2.577(3)
B(2)-B(3)	2.591(3)		

The Hydrogen Bonds

O(w)-H(1)	0.85(4)	H(1)-O(w)-H(2)	109(4)
O(w)-H(2)	1.00(5)	O(w)-H(1)...Cl	156(3)
H(1)...Cl	2.49(4)	O(w)-H(2)...Cl'	133(4)
H(2)...Cl'	2.41(5)	Ca(1)-O(w)-H(1)	122(3)
O(w)-Ca(1)	2.350(2)	Ca(1)-O(w)-H(2)	116(3)
O(w)-Cl	3.283(2)		
O(w)-Cl'	3.175(2)		

ners with two other borate tetrahedra in adjacent polyanions (Fig. 2). The backbone of this chain is a three-tetrahedral-repeat borate chain (*Dreierkette*), accounting for the ∼6.3A *c* axis. This feature is common to all hilgardite group minerals (Braitsch, 1959). The B–B separations within this chain are 2.444 [B(1)–B(3)], 2.477 [B(1)–B(4)], and 2.503A [B(3)–B(4)] and the B–B–B angles are 138.8° [B(3)–B(1)–B(4)], 113.6° [B(1)–B(3)–B(4)], and 127.4° [B(3)–B(4)–B(1)].

The open pentaborate $[B_5O_9]^{3-}$ framework

Within each borate chain, corners of two borate tetrahedra point along +**a** and +**b** directions, whereas corners of two borate triangles point along −**a** and −**b** directions; these corners are shared with four adjacent chains, such that the tetrahedral corners of one chain are shared with triangular corners of the other. An open borate framework is created this way, which has channels parallel to the *a, b,* and *c* axes (Fig. 3). The chlorine atoms and the water molecules occur within straight channels parallel to *c*, whereas Ca(1) and Ca(2) occur within zigzag and straight channels parallel to the *b* and *a* axes respectively.

The calcium polyhedral sheet

The linkage of two adjacent borate chains along the *a* axis (likewise along the *b* axis) creates an open borate sheet, with nine-membered B–O rings, consisting of seven (BO_4) tetrahedra and two (BO_3) triangles (Fig. 4). Ca(1) and Ca(2) occur within these B–O rings, such that five or six nearly coplanar oxygen atoms are within 3A of the Ca atom. The chlorine atom and the water molecule act as apical ligands. The $[Ca(1)O_5Cl(H_2O)]$ and the $[Ca(2)O_6Cl_2]$ polyhedra are slightly distorted pentagonal and hexagonal bipyramids respectively (Fig. 5). The average Ca–O distances are 2.465 and 2.535A, and the average Ca–Cl distances 2.817 and 2.905A within the Ca(1) and Ca(2) polyhedra respectively. The Ca(1) polyhedron shares one edge each with a B(2) tetrahedron and a B(5) triangle, whereas the Ca(2) polyhedron shares one edge each with the B(1) and B(4) tetrahedra and the B(2) triangle.

By sharing opposite apical Cl corners, the Ca(2) polyhedra form linear polyhedral chains parallel to the *a* axis. These chains are cross-linked into a polyhedral sheet through the Ca(1) polyhedra, by sharing a polyhedral corner, O(2) and an edge [O(4)–Cl] with the Ca(2) polyhedra (Fig. 6).

Table 5. Ring angles, planes, and deviations from ring planes for the pentaborate polyanion in hilgardite

Ring	*Ring atoms*	*B-O-B angles*	
1	B(1) - O(1) - B(2) - O(5) - B(4) - O(2)	B(1) - O(1) - B(2) B(1) - O(2) - B(4) B(2) - O(5) - B(4)	115.8(1) 114.7(1) 124.0(1)
2	B(1) - O(4) - B(3) - O(9) - B(5) - O(3)	B(1) - O(3) - B(5) B(1) - O(4) - B(3) B(3) - O(9) - B(5)	120.9(2) 115.1(1) 113.1(1)

Parameters of planes* defined by ring oxygens

	A	B	C	D
1	10.6099	-4.1791	-0.3659	2.3107
2	3.4823	10.6486	0.9359	3.6656

Angle between ring planes 85.79°

Deviations from ring planes defined by three oxygens

Ring 1		Ring 2	
Atom	Deviation (Å)	Atom	Deviation (Å)
B(1)	-0.599	B(1)	-0.076
B(2)	+0.125	B(3)	-0.209
B(4)	-0.074	B(5)	+0.682
O(6)	+1.032	O(6')	-0.538
O(7)	-1.032	O(7')	0.649
O(8)	+0.324	O(8')	+2.046

**The equations of the planes in direct space are of the form Ax + By + Cz = D, where x, y, z are the atomic coordinates in Å units and D is the distance of the plane from the origin in Å unit.*

The hydrogen bonding

The water molecule is bonded to only one of the two calcium atoms [Ca(1)-O(w) 2.350A]. The O(w)-H(1) and O(w)-H(2) distances are 0.85 and 1.0A, and the H-O-H angle is 109°. Both hydrogen atoms are hydrogen-bonded to two adjacent chlorine atoms. The H(1)-Cl and H(2)-Cl distances are 2.49 and 2.41A, and the O(w)-H(1) · · · Cl and O(w)-H(2) · · ·

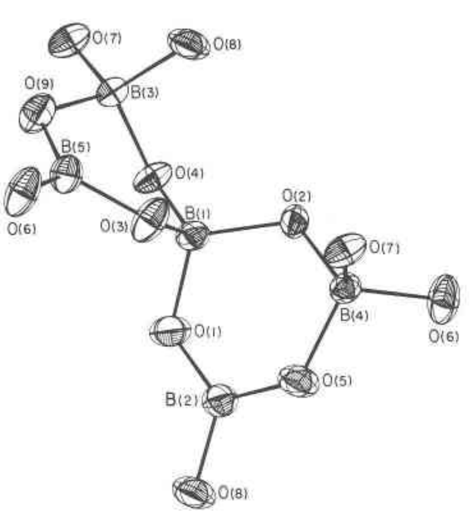

Fig. 1. A view of the $[B_5O_{12}]^{9-}$ polyanion in hilgardite, showing the ellipsoids of thermal vibration.

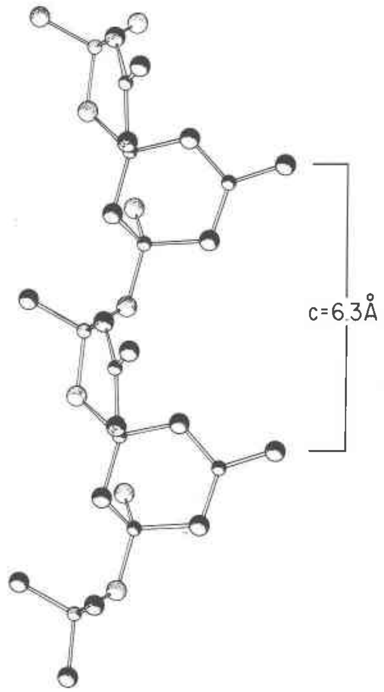

Fig. 2. The three-tetrahedral-repeat pentaborate $[B_5O_{11}]^{7-}$chain in hilgardite parallel to the *c* axis.

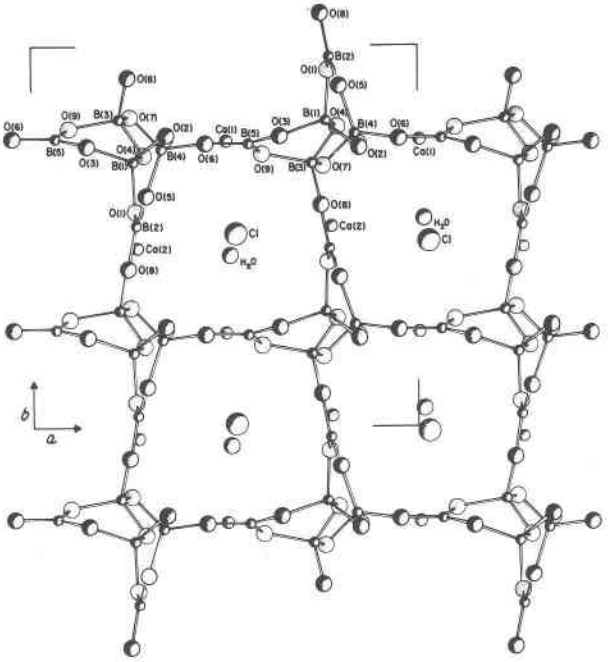

Fig. 3. The zeolite-type $[B_5O_9]^{3-}$ framework in hilgardite viewed down the *c* axis. Note the chlorine atoms and the water molecules occurring within the channels parallel to *c*.

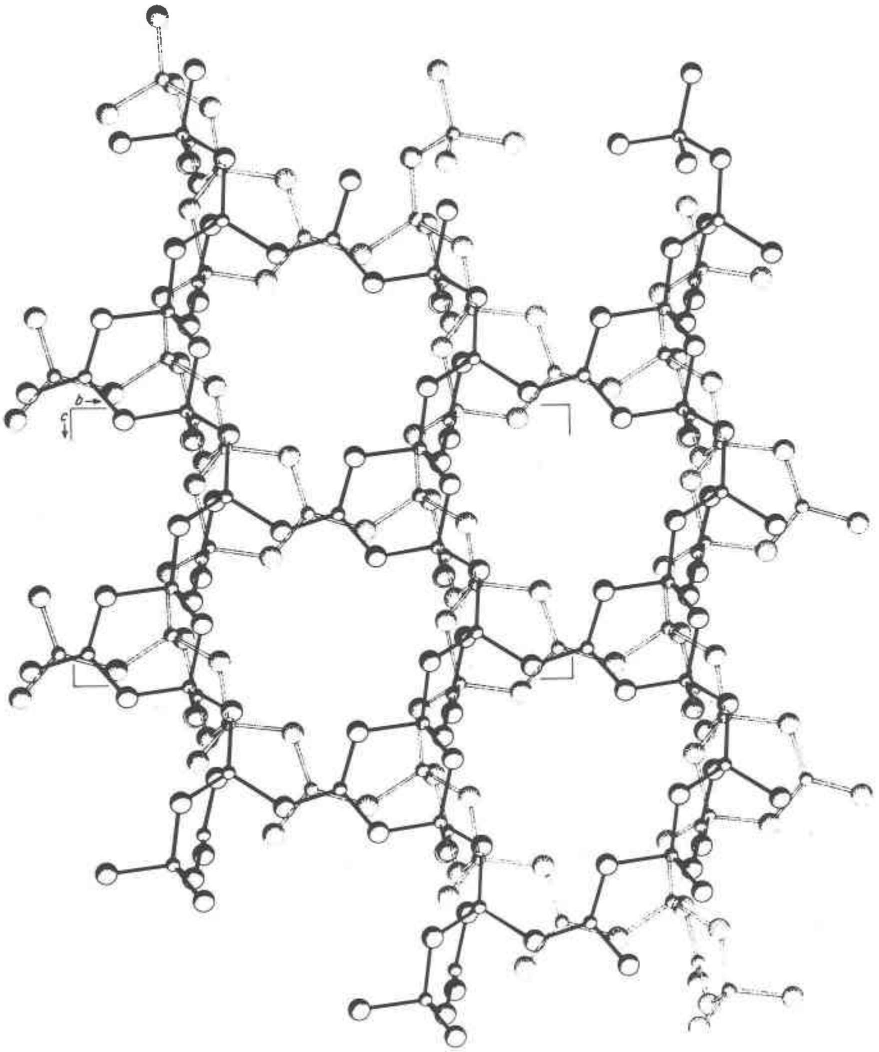

Fig. 4. A view of the pentaborate framework in hilgardite down the *a* axis. The borate sheet between *a* ~0.0 and ~0.5 is shown in full lines; the sheet between *a* ~0.5 and ~1.0 shown in dotted lines. Note the open channels parallel to the *a* axis, which are occupied by Ca(2) atoms (not shown).

Cl angles are 156 and 133° respectively. Thus, the chlorine atoms and the water molecules form quasi-linear hydrogen bonded chains parallel to the *c* axis (Fig. 7). The average Cl–O distance in hilgardite is 3.229A, as compared to 3.296 in hydrochlorborite (Brown and Clark, 1978).

The Ca(1)–O(w)–H(1) and Ca(1)–O(w)–H(2) angles are 122 and 116° respectively. These two angles, along with the H–O–H angle of 109°, indicate a nearly trigonal planar (sp^2) configuration for the water molecule. Such trigonal planar configurations have been found for the water molecules bonded to Mg in the structure of the magnesium tetraborate complex hungchaoite, $[Mg(H_2O)_5B_4O_5(OH)_4]\cdot 2H_2O$ (Wan and Ghose, 1977).

Anisotropic thermal vibration

As would be expected in a framework borate structure, the boron atoms are mildly anisotropic, the triangular boron atoms slightly more so than tetrahedral boron atoms. The thermal vibration ellipsoid for the triangular borons is a prolate spheroid, the maximum vibration direction being perpendicular to the (BO_3) plane. The oxygen atoms bonded to two tetrahedral boron atoms are nearly isotropic, whereas the oxygen atoms bonded to a triangular and a

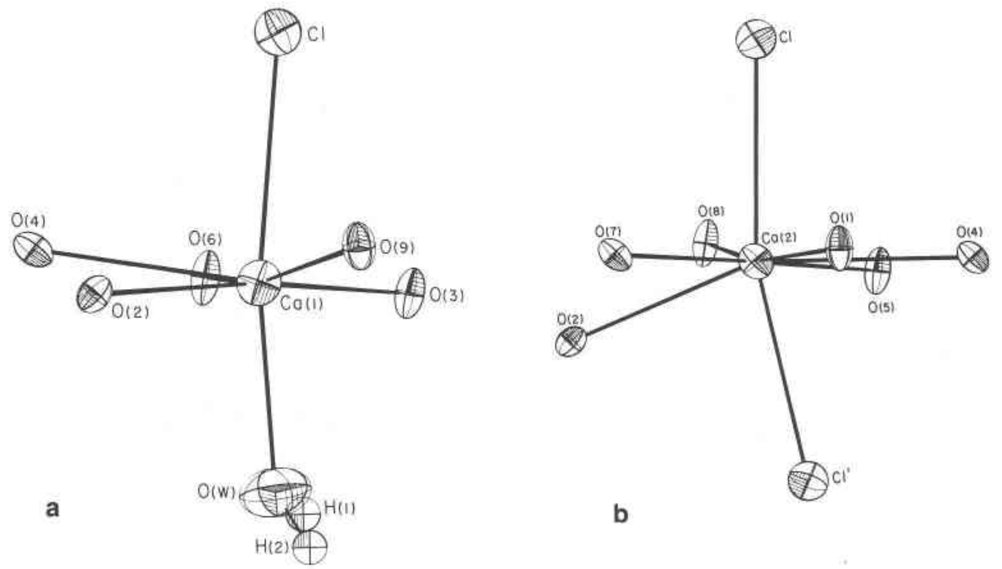

Fig. 5. The [Ca(1)O_5Cl(H_2O)] pentagonal bipyramid (a), and [Ca(2)O_6Cl_2] hexagonal bipyramid (b) in hilgardite, showing ellipsoids of thermal vibration.

tetrahedral boron atom are markedly anisotropic; the thermal vibration ellipsoid is also a prolate spheroid with the maximum vibration direction normal to the B–O–B plane (Fig. 1). The channel atoms, Ca(1), Ca(2), Cl, and the water molecule, are strongly anisotropic, the water molecule showing twice as much thermal vibration as the other channel atoms. The thermal vibration ellipsoids for Ca(1) and Ca(2) and H_2O are oblate spheroids; the minimum vibration direction of the water molecule is along the Ca–OH_2 bond. The chlorine atom lies within a triangle of three calcium atoms, and the thermal vibration ellip-

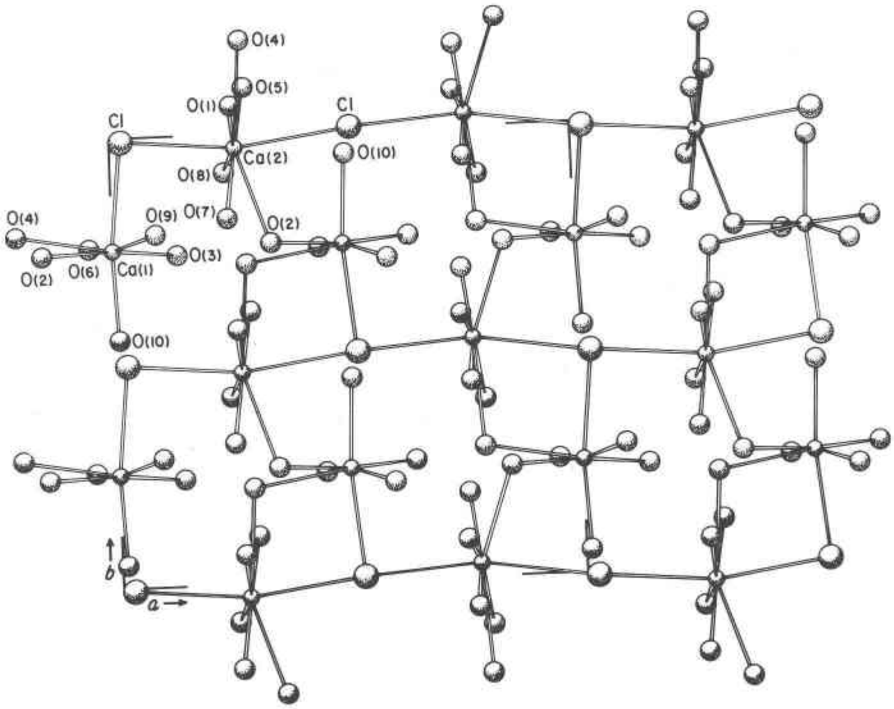

Fig. 6. The calcium polyhedral sheet in hilgardite.

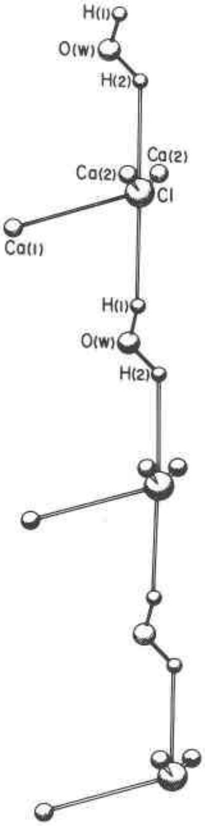

Fig. 7. The hydrogen bonded quasi-linear Cl···H–O–H···Cl chain in hilgardite, parallel to the *c* axis. Note the five-fold trigonal bipyramidal coordination of the chlorine atom.

soid is a prolate spheroid; the maximum vibration direction is normal to the plane of the three calcium atoms (Fig. 5).

Comparison of the crystal structures of hilgardite and the triclinic hilgardite-type phase

The structure of triclinic hilgardite $Ca_2[B_5O_9]Cl \cdot H_2O$ [$a = 6.463$, $b = 6.564$, $c = 6.302$A, $\alpha = 61°31'$, $\beta = 118°46'$, $\gamma = 105°47'$; $V = 205.8$A^3, space group *P1*], determined by Rumanova *et al.* (1977), closely resembles the hilgardite structure. The framework is built up of pentaborate chains which share tetrahedral and triangular corners. However, in triclinic hilgardite, which lacks any crystallographic symmetry, the borate triangles all point along −**a** and −**b** (or +**a** and +**b** directions, since the absolute configuration is unknown). Hence, the piezoelectric constants are expected to be the same along both **a** and **b** axes.

In triclinic hilgardite the coordination of the pentagonal and hexagonal bipyramids is slightly different from that of hilgardite, in that within each polyhedron the apical ligands are chlorine and a water molecule. The Ca(1) and Ca(2) polyhedra form a dimer by sharing a polyhedral edge; these dimers share Cl corners and form linear chains parallel to [110], which are crosslinked by O–H···Cl type hydrogen bonds.

Polymerization of the pentaborate polyanion and the genesis of hilgardite

The fully hydrated pentaborate polyanion $[B_5O_6(OH)_6]^{3-}$ can polymerize by splitting out water molecules to form chains, sheets, and eventually a three-dimensional framework (Christ, 1960). The isolated polyanion exists in ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ (Clark and Appleman, 1964; Ghose *et al.*, 1978). The anhydrous analog of this polyanion, $[B_5O_{12}]^{9-}$, has been found in garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose *et al.*, 1976). Pentaborate polyanion chains, formed by sharing an oxygen atom common to a borate triangle of one polyanion and a tetrahedron of the next, have been found in the structure of probertite, $NaCaB_5O_7(OH)_4 \cdot 3H_2O$ (Rumanova *et al.*, 1966). These polyanions, further linked into sheets, are found in the structures of heidornite, $Na_2Ca_3Cl[B_5O_8(OH)_2]\ [SO_4]_2$ (Burzlaff, 1967) and synthetic $Na_3B_5O_8(OH)_2 \cdot H_2O$ (Menchetti and Sabelli, 1977). The borate framework in hilgardite represents the culmination of this polymerization process. The progressive polymerization of the pentaborate polyanion can be represented by the following reactions:

$[B_5O_6(OH)_6]^{3-}$	$\rightarrow$	$[B_5O_7(OH)_4]^{3-}$	$+ H_2O$
ulexite		probertite	
$[B_5O_7(OH)_4]^{3-}$	$\rightarrow$	$[B_5O_8(OH)_2]^{3-}$	$+ H_2O$
probertite		heidornite	
$[B_5O_8(OH)_2]^{3-}$	$\rightarrow$	$[B_5O_9]^{3-}$	$+ H_2O$
heidornite		hilgardite	

Hence, the lowering of the activity of water and most likely rising temperatures will favor the formation of hilgardite rather than ulexite. Within the Choctow Salt Dome the presence of anhydrite indicates low water activity. Formation of borosilicates, such as danburite, probably indicates temperatures above 100°C.

Piezoelectricity in hilgardite and its structural basis

Two hilgardite crystals were tested for second harmonic generation, using a Nd glass laser. Both gave signals comparable to quartz, confirming their acentricity (J. Kramer and R. E. Newnham, private communication, 1977). The signals were small compared to ferroelectric perovskites, indicating that they are not strong piezoelectrics. G. W. Pierce (quoted in Hurlbut, 1938) positively determined the presence of piezoelectricity in hilgardite, with a strong electric axis parallel to or nearly parallel to the *a* axis.

The origin of the piezoelectricity in hilgardite lies in the way the borate tetrahedra and the borate triangles are oriented within the structure. Due to the glide plane normal to the *b* axis, the borate triangles parallel to *b* point alternately along $+\mathbf{b}$ and $-\mathbf{b}$. Hence, piezoelectricity along *b* would be zero or nearly zero. However, along the *a* axis, the borate triangles all point along $-\mathbf{a}$ direction (Fig. 3), which explains the strong electric axis along *a*. An intermediate electric axis presumably exists parallel to *c*, since all the borate tetrahedra within the borate chains point along the $-\mathbf{c}$ direction.

Hilgardite as a potential borate zeolite

The open borate framework structure of hilgardite with straight ~6A diameter channels parallel to *a* axis and ~5A diameter channels parallel to the *c* axis is the precursor of a potential new family of zeolites. In hilgardite itself, these channels are filled by Ca and Cl atoms and water molecules. Ion-exchange experiments on hilgardite are currently in progress.

Acknowledgments

We are indebted to Dr. Joan R. Clark, U. S. Geological Survey, for the donation of the hilgardite crystals and for discussions on the crystal chemistry of borates, to Professors J. Kramer, University of Delaware, and R. E. Newnham, Pennsylvania State University, for checking the hilgardite crystals for piezoelectricity, and to Floyd Bardsley, University of Washington, for the diagrams. Drs. C. L. Christ and Joan R. Clark of the U. S. Geological Survey and Dr. S. Guggenheim, University of Illinois at Chicago, critically reviewed the paper. This research has been supported by the Graduate School Research Fund of the University of Washington and in part by NSF grant EAR 76-13373.

References

Bond, W. L. (1951) Making small spheres. *Rev. Sci. Inst., 22*, 344–345.

Braitsch, O. (1959) 1 Tc-Strontiohilgardit $(Ca,Sr)_2[B_5O_8(OH)_2Cl]$ und seine Stellung in der Hilgardit-gruppe $X_2^{II}[B_5O_8(OH)_2Cl]$. *Beitr. Mineral. Petrogr., 6*, 233–247.

Brown, G. E., and J. R. Clark (1978) Crystal structure of hydrochlorborite, $Ca_2[B_3O_3(OH)_4 \cdot OB(OH)_3]Cl \cdot 7H_2O$., a seasonal evaporite mineral. *Am. Mineral.*, 63, 814–823.

Burzlaff, H. (1967) Die Struktur des Heidornits $Ca_3Na_2Cl(SO_4)_2B_5O_8(OH)_2$. *Neues Jahrb. Mineral. Monatsh.*, 157–169.

Christ, C. L. (1960) Crystal chemistry and systematic classification of hydrated borate minerals. *Am. Mineral., 45*, 334–340.

——— and J. R. Clark (1977) A crystal-chemical classification of borate structures with emphasis on hydrated borates. *Phys. Chem. Minerals, 2*, 59–87.

Clark, J. R. and D. E. Appleman (1964) Pentaborate polyanion in the crystal structure of ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$. *Science, 145*, 1295–1296.

Cromer, D. T. and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys., 53*, 1891–1898.

——— and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr., A24*, 321–324.

Ghose, S. and C. Wan (1977) Hilgardite and parahilgardite piezoelectric zeolite type phases. *Nature, 270*, 594–595.

———, ——— and J. R. Clark (1978) Ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$: structure refinement, polyanion configuration, hydrogen bonding and fiber optics. *Am. Mineral., 63*, 160–171.

———, ——— and H. H. Ulbrich (1976) Structural chemistry of borosilicates. I. Garrelsite, $NaBa_3Si_2O_7O_{16}(OH)_4$: a silicoborate with the pentaborate $[B_5O_{12}]^{9-}$ polyanion. *Acta Crystallogr., B32*, 824–832.

Hurlbut, Jr., C. S. (1938) Parahilgardite, a new triclinic pedial mineral. *Am. Mineral., 23*, 765–771.

——— and R. E. Taylor (1937) Hilgardite, a new mineral species from Choctow Salt Dome, Louisiana. *Am. Mineral., 22*, 1052–1057.

——— and ——— (1938) Notes on minerals associated with hilgardite. *Am. Mineral., 23*, 898–902.

Menchetti, S. and C. Sabelli (1977) The crystal structure of synthetic sodium pentaborate monohydrate. *Acta Crystallogr., B33*, 3730–3733.

Rumanova, I. M., Kh. M. Kurbanov and N. V. Belov (1966) Crystal structure of probertite, $CaNa[B_5O_7(OH)_4] \cdot 3H_2O$. *Sov. Phys. Crystallogr., 10*, 513–522.

———, Z. I. Yorish and N. V. Belov (1977) The crystal structure of triclinic hilgardite $Ca_2[B_5O_9]Cl \cdot H_2O = Ca_2[B_3^tB_2^{\Delta}O_9]Cl \cdot H_2O$. (in Russian) *Dokl. Akad. Nauk SSSR, 236*, 91–94.

Schomaker, V., J. Waser, R. E. Marsh and G. Bergman (1959) To fit a plane or a line to a set of points by least squares. *Acta Crystallogr., 12*, 600–604.

Stewart, J. M., G. J. Kruger, H. L. Ammon, C. Dickinson and S. R. Hall (1972) The X-RAY SYSTEM-version of June, 1972. *Tech. Rep. TR-192*. Computer Science Center, University of Maryland, College Park, Maryland.

Wan, C. and S. Ghose (1977) Hungchaoite, $Mg(H_2O)_5B_4O_5(OH)_4 \cdot 2H_2O$: a hydrogen bonded molecular complex. *Am. Mineral., 62*, 1135–1143.

Manuscript received, March 20, 1978;
accepted for publication, May 19, 1978.