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HYDROGEN BONDING IN COLEMANITE: AN X-RAY AND STRUCTURE-ENERGY STUDY

PETER C. BURNS AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of colemanite, $CaB_3O_4(OH)_3{\cdot}H_2O$, monoclinic, *a* 8.712(2), *b* 11.247(3), *c* 6.091(1) Å, β 110.12(2)°, *V* 560.4(2) $Å^3$, $Z = 4$, space group $P2_1/a$, has been refined by full-matrix least-squares to an *R* index of 2.8% and a *wR* index of 3.5% for 1408 unique observed $[|F_O| \geq 5\sigma(F_O)]$ reflections measured with Mo*K*α X radiation. The H-positions were located on difference-Fourier maps and refined using the "soft" constraints that H–O distances are approximately 0.97 Å. Colemanite is a complex inoborate. Each chain element consists of two $B\phi_4$ (ϕ: unspecified anion) tetrahedra and a $B\phi_3$ triangle linked through corners to form rings of composition $[B_3O_5(OH)_3]^{4-}$; these rings link *via* corner-sharing to form chains of composition $[B_3O_4(OH)_3]^{2-}$ that extend along [100]. The eight-coordinate Ca polyhedra share corners to form chains parallel to [100]. These link with the B polyhedral chains *via* corner sharing to form complex heteropolyhedral sheets parallel to (010). The linkage between these sheets is weak, consisting of a small number of B–ϕ–Ca linkages together with a network of hydrogen bonds, and accounts for the perfect {010} cleavage in colemanite. Minimum-energy calculations of the hydrogen positions done with a directionally isotropic H–O potential function predict the positions of three of the five hydrogen atoms, but fail to give the correct positions for two hydrogen atoms. This is attributed to the lack of a directional component in the potential function.

Keywords: colemanite, borate, structure refinement, hydrogen bonding, inoborate, crystal structure, energy minimization.

SOMMAIRE

Nous avons affiné la structure cristalline de la colemanite, $CaB_3O_4(OH)_3{\cdot}H_2O$, phase monoclinique, *a* 8.712(2), *b* 11.247(3), *c* 6.091(1) Å, β 110.12(2)°, *V* 560.4(2) $Å^3$, $Z = 4$, groupe spatial $P2_1/a$, par moindres carrés avec matrice entière, jusqu'à un indice *R* de 2.8% ($wR = 3.5\%$) en utilisant 1408 réflexions uniques observées $[|F_O| \geq 5\sigma(F_O)]$, mesurées avec rayonnement Mo*K*α. La position des atomes d'hydrogène a été localisée sur des projections de Fourier par différence, et affinée suivant la contrainte non rigoureuse que les distances H–O devraient avoir une longueur d'environ 0.97 Å. La colemanite est en fait un inoborate complexe. Chaque chaîne est faite de deux tétraèdres $B\phi_4$ (ϕ: anion non spécifié) et un triangle $B\phi_3$ liés par leurs coins pour former un anneau $[B_3O_5(OH)_3]^{4-}$; ces anneaux sont articulés par partage de coins pour former des chaînes de composition $[B_3O_4(OH)_3]^{2-}$ le long de [100]. Les polyèdres autour du Ca, à coordinence huit, partagent leurs coins pour former des chaînes parallèles à [100]. Celles-ci sont liées avec les chaînes de polyèdres B par partage de coins pour former des feuillets hétéropolyédriques complexes parallèles à (010). Les liens entre ces feuillets sont faibles, impliquant un petit nombre de liaisons B–ϕ–Ca et un réseau de liaisons hydrogène–oxygène, ce qui rend compte du clivage {010} parfait. Un calcul de la position des atomes d'hydrogène compatible avec une énergie minimum, effectué au moyen d'une fonction du potentiel H–O directionnellement isotrope, réussit à prédire la position de trois des cinq atomes, mais non des deux autres. Nous attribuons cette situation au manque d'une composante directionnelle dans l'expression du potentiel utilisée.

(Traduit par la Rédaction)

Mots-clés: colemanite, borate, affinement de la structure, liaisons de l'hydrogène, structure cristalline, minimisation d'énergie.

INTRODUCTION

Colemanite, $CaB_3O_4(OH)_3{\cdot}H_2O$, is a complex inoborate mineral that is a common constituent of borate deposits. Its crystal structure was determined by Christ *et al.* (1958) and refined by Clark *et al.* (1964).

Considerable effort has recently been focused on finding a suitable potential energy function for H-bonding in mineral structures (*e.g.*, Abbott 1991, Abbott *et al.* 1989). The work has resulted in the development of a directionally isotropic potential that gives reasonable H-positions in such minerals as trioctahedral micas, tremolite and chlorite (Abbott *et al.* 1989). We have completed a study of H-positions in colemanite by energy-minimization methods and compare the results to the positions determined from X-ray data.

EXPERIMENTAL

Colemanite from San Bernardino County, California,

TABLE 1. MISCELLANEOUS INFORMATION FOR COLEMANITE

Space Group	$P2_1/a$	Crystal size (mm)	0.24x0.08 x0.20
a (Å)	8.712(2)	Total Ref.	1819
b (Å)	11.247(3)	$\lvert F_O \rvert \geq 5\sigma(F_O)$	1408
c (Å)	6.091(1)	R(int.)	1.8%
β (°)	110.12(2)	Final R	2.8%
V (Å^3)	560.4(2)	Final wR	3.5%
		R (all data)	3.6%
F(000)	416	wR (all data)	4.0%
μ	1.09 mm^{-1}		

Unit-cell contents 4[$CaB_3O_4(OH)_3 \cdot H_2O$]

$R = \Sigma\,(\lvert F_O \rvert - \lvert F_C \rvert)/\,\Sigma\,\lvert F_O \rvert$

$wR = [\,\Sigma\, w(\lvert F_O \rvert - \lvert F_C \rvert)^2/\,\Sigma\, F_O^2]^{1/2}$, $w=1$

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR COLEMANITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	94(2)	118(2)	73(2)	3(1)	2(1)	7(1)
B(1)	65(6)	87(6)	69(6)	3(5)	19(5)	-1(5)
B(2)	59(6)	69(6)	65(6)	-4(4)	14(5)	2(4)
B(3)	69(6)	80(6)	58(5)	-1(4)	23(5)	-5(4)
O(1)	63(4)	114(4)	88(4)	-31(3)	17(3)	18(3)
O(2)	49(4)	112(4)	74(4)	26(3)	11(3)	-9(3)
OH(3)	83(4)	115(4)	72(4)	-20(3)	-20(3)	18(3)
O(4)	88(4)	142(5)	69(4)	36(3)	-3(3)	-44(4)
O(5)	74(4)	63(4)	72(4)	-1(3)	0(3)	-4(3)
OH(6)	172(5)	100(4)	103(4)	12(4)	26(4)	57(4)
OH(7)	120(5)	128(5)	90(4)	-12(4)	54(4)	-18(4)
OW(8)	190(5)	166(5)	173(5)	28(4)	56(4)	-3(4)

was obtained from the R.B. Ferguson Mineralogy Museum at the University of Manitoba. A small cleavage fragment was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Twenty-five reflections were centered using graphite monochromated Mo$K\alpha$ X radiation. The cell dimensions (Table 1) were derived from the setting angles of twenty-five automatically aligned reflections by least-squares techniques. A total of 1819 reflections was measured over the range ($3° < 2\theta < 60°$), with index ranges $0 \leq h \leq 12$, $0 \leq k \leq 15$, $-9 \leq l \leq 9$. Two standard reflections were measured every fifty reflections; no significant changes in their net intensities occurred during data collection. An empirical absorption correction based on 11 reflections measured at 10° intervals in Ψ was applied, reducing R(azimuthal) from 2.1% to 1.8%. The data were corrected for Lorentz, polarization and background effects; of the 1819 reflections measured, there were 1408 unique observed reflections [$\lvert F_O \rvert \geq 5\sigma(F_O)$].

STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with corrections for anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this work.

Refinement of the structure was carried out in the space group $P2_1/a$, with the structure parameters given

TABLE 2. ATOMIC PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR COLEMANITE

	x	y	z	$U_{equiv.}$
Ca	0.63480(3)	0.21106(3)	0.73664(5)	102(1)
B(1)	0.3343(2)	0.2126(1)	0.3136(3)	75(4)
B(2)	0.0397(2)	0.1709(1)	0.1622(2)	66(4)
B(3)	0.2207(2)	0.0523(1)	0.4962(2)	69(4)
O(1)	-0.0182(1)	0.24675(9)	0.3156(2)	91(3)
O(2)	0.1886(1)	0.2314(1)	0.1390(2)	81(3)
OH(3)	-0.0798(1)	0.1639(1)	-0.0724(2)	102(3)
O(4)	0.3422(1)	0.1480(1)	0.5098(2)	107(3)
O(5)	0.0872(1)	0.05558(9)	0.2710(2)	76(3)
OH(6)	0.2945(1)	-0.0660(1)	0.5144(2)	130(3)
OH(7)	0.1668(1)	0.0770(1)	0.6972(2)	108(3)
OW(8)	0.6137(2)	0.0187(1)	0.9008(2)	178(4)
H(1)	-0.075(3)	0.085(1)	-0.130(5)	200
H(2)	0.334(3)	-0.101(2)	0.669(3)	200
H(3)	0.080(2)	0.025(2)	0.699(5)	200
H(4)	0.701(2)	-0.025(2)	1.010(4)	200
H(5)	0.516(2)	-0.013(2)	0.919(5)	200

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å), ANGLES (°) AND POLYHEDRAL EDGE-LENGTHS (Å) FOR COLEMANITE

B(1)-O(1)a	1.360(2)	Ca-O(1)a	2.496(1)
B(1)-O(2)	1.363(2)	Ca-O(2)b	2.419(1)
B(1)-O(4)	1.380(2)	Ca-OH(3)c	2.414(1)
<B(1)-O>	1.368	Ca-OH(3)b	2.885(1)
		Ca-O(4)	2.547(1)
B(2)-O(1)	1.476(2)	Ca-OH(6)d	2.455(1)
B(2)-O(2)	1.514(2)	Ca-OH(7)a	2.421(1)
B(2)-OH(3)	1.452(2)	Ca-OW(8)	2.416(1)
B(2)-O(5)	1.451(2)	<Ca-O>	2.507
<B(2)-O>	1.473		
B(3)-O(4)	1.492(2)		
B(3)-O(5)	1.462(2)		
B(3)-OH(6)	1.465(2)		
B(3)-OH(7)	1.480(2)		
<B(3)-O>	1.475		
B(1) triangle			
O(1)a-O(2)	2.419(1)	O(1)a-B(1)-O(2)	125.3(1)
O(1)a-O(4)	2.295(2)	O(1)a-B(1)-O(4)	113.8(1)
O(2)-O(4)	2.386(1)	O(2)-B(1)-O(4)	120.9(1)
<O-O>	2.367	<O-B(1)-O>	120.0
B(2) tetrahedron			
O(1)-O(2)	2.402(2)	O(1)-B(2)-O(2)	106.9(1)
O(1)-OH(3)	2.423(2)	O(1)-B(2)-OH(3)	111.6(1)
O(1)-O(5)	2.390(2)	O(1)-B(2)-O(5)	109.5(1)
O(2)-OH(3)	2.373(1)	O(2)-B(2)-OH(3)	106.3(1)
O(2)-O(5)	2.414(2)	O(2)-B(2)-O(5)	109.0(1)
OH(3)-O(5)	2.425(1)	OH(3)-B(2)-O(5)	113.3(1)
<O-O>	2.404	<O-B(2)-O>	109.4
B(3) tetrahedron			
O(4)-O(5)	2.431(1)	O(4)-B(3)-O(5)	110.7(1)
O(4)-OH(6)	2.444(2)	O(4)-B(3)-OH(6)	111.5(1)
O(4)-OH(7)	2.339(2)	O(4)-B(3)-OH(7)	103.9(1)
O(5)-OH(6)	2.343(1)	O(5)-B(3)-OH(6)	106.3(1)
O(5)-OH(7)	2.457(2)	O(5)-B(3)-OH(7)	113.3(1)
OH(6)-OH(7)	2.432(2)	OH(6)-B(3)-OH(7)	111.3(1)
<O-O>	2.408	<O-B(3)-O>	109.5
Ca polyhedron			
O(1)a-OH(6)d	2.814(2)	O(1)a-Ca-OH(6)d	69.3(0)
O(1)a-OH(7)a	3.011(2)	O(1)a-Ca-OH(7)a	75.5(0)
O(2)b-OW(8)	3.126(1)	O(2)b-Ca-OW(8)	80.6(0)
O(2)b-OH(3)b	2.373(1)	O(2)b-Ca-OH(3)b	52.3(0)
O(2)b-OH(3)c	2.984(2)	O(2)b-Ca-OH(3)c	76.2(0)
OH(3)c-OW(8)	3.085(2)	OH(3)c-Ca-OW(8)	79.4(0)
OH(3)c-OH(6)d	2.915(2)	OH(3)c-Ca-OH(6)d	73.5(0)
OH(3)b-OH(7)a	3.101(2)	OH(3)b-Ca-OH(7)a	70.9(0)
O(4)-O(1)a	2.295(2)	O(4)-Ca-O(1)a	54.1(0)
OH(6)d-OW(8)	2.951(2)	OH(6)d-Ca-OW(8)	74.6(0)
OW(8)-O(4)	3.083(2)	OW(8)-Ca-O(4)	76.8(0)
<O-O>	2.885	<O-CA-O>	71.25
H-bonding			
OH(3)-H(1)	0.96(2)	H(1)...O(5)h	1.78(2)
OH(6)-H(2)	0.96(2)	H(2)...O(2)i	2.27(2)
OH(7)-H(3)	0.96(2)	H(3)...O(5)j	1.78(2)
OW(8)-H(4)	0.96(2)	H(4)...OH(7)g	1.86(2)
OW(8)-H(5)	0.96(2)	H(5)...OW(8)g	1.83(3)
H(4)-H(5)	1.52(3)	H(4)-OW(8)-H(5)	105(2)
OH(3)-O(5)h	2.425(1)	OH(3)-H(1)-O(5)h	172(2)
OH(6)-O(2)i	3.075(2)	OH(6)-H(2)-O(2)i	141(2)
OH(7)-O(5)i	2.457(2)	OH(7)-H(3)-O(5)j	171(3)
OW(8)-OH(7)g	2.755(2)	OW(8)-H(4)-OH(7)g	156(2)
OW(8)-OW(8)g	2.686(3)	OW(8)-H(5)-OW(8)g	146(2)

a = x+1/2, -y+1/2, z; b = x+1/2, -y+1/2, z+1;
c = x+1, y, z+1; d = 1-x, -y, 1-z;
e = 1-x, 1-y, 1-z; f = -x+1/2, y+1/2, 1-z;
g = 1-x, -y, -z+2; h = -x, -y, -z;
i = -x+1/2, y-1/2, 1-z; j = -x, -y, 1-z.

TABLE 5. BOND-VALENCE* ANALYSIS FOR COLEMANITE

	Ca	B(1)	B(2)	B(3)	H(1)	H(2)	H(3)	H(4)	H(5)	Σ
O(1)	0.231	1.016	0.743							1.990
O(2)	0.279	1.008	0.670			0.09				2.047
OH(3)	0.293 0.090		0.793		0.80					1.966
O(4)	0.204	0.963		0.711						1.935
O(5)			0.765	0.771	0.18		0.19			1.936
OH(6)	0.256			0.765		0.80				1.821
OH(7)	0.278			0.735			0.80	0.16		1.973
OW(8)	0.281							0.81	0.80 0.16	2.051
Σ	1.959	2.987	3.001	2.982	0.98	0.89	0.99	0.97	0.96	

* Bond-valence parameters from Brown (1981)

by Christ *et al.* (1958) as the starting model. Refinement of the positional parameters and isotropic displacement parameters converged to an R index of 5.3%. Conversion to an anisotropic displacement model, together with refinement of all parameters, converged to an R index of 3.2%. A three-dimensional difference-Fourier map was calculated at this stage of the refinement, and the positions of the five hydrogen atoms were determined. Subsequent cycles of refinement showed that the hydrogen positions were not well behaved, as indicated by anomalously short O–H bond distances, a common feature of hydrogen positions refined using X-ray data. The "soft" constraint that each O–H bond distance should be ~0.97 Å was imposed by adding the constraints as additional weighted observations in the least-squares matrix. Note that only the O–H distances were constrained, and that each H position was free to refine around the associated oxygen. Refinement of all parameters, with the inclusion of a refinable weighting scheme of structure factors and a correction for isotropic extinction, converged to a final R index of 2.8% and a wR index of 3.5%. Final positional parameters and equivalent isotropic-displacement factors are given in Table 2, anisotropic displacement factors in Table 3, selected bond-distances, bond angles and polyhedral edge-lengths in Table 4, and a bond-valence analysis in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Description of the structure

Colemanite contains three unique boron positions. B(1) is triangularly coordinated by three oxygen anions at a mean distance of 1.368 Å, a typical value for $^{[3]}$B–O triangles. B(2) and B(3) are tetrahedrally coordinated by three oxygen atoms and one hydroxyl group, and two oxygen atoms and two hydroxyl groups, respectively; the mean $^{[4]}$B–O distances, 1.473 and 1.475 Å, respectively, fall in the typical range for [4]-coordinate boron polyhedra. These three boron–(O,OH) polyhedra link by sharing corners to form a ring of composition $[B_3O_5(OH)_3]^{4-}$ (Fig. 1A) that can be considered a fundamental building block of the structure. These rings link by sharing vertices between the $(B\phi_3)$ and $(B\phi_4)$ polyhedra (ϕ: unspecified anion) to form borate chains of composition $[B_3O_4(OH)_3]^{2-}$ that extend parallel to [100] (Fig. 2).

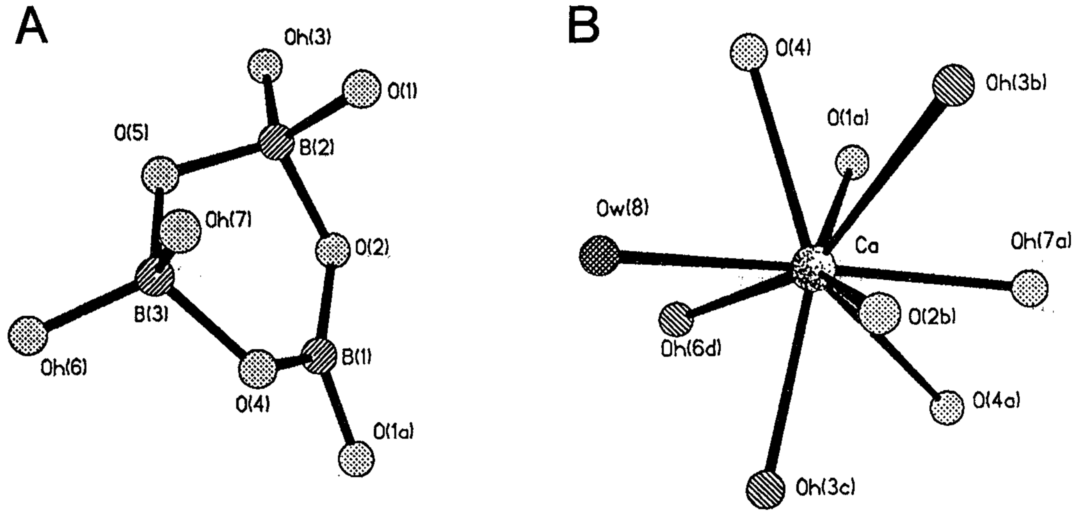

FIG. 1. The $[B_3O_5(OH)_3]^{4-}$ rings (A) and $Ca\phi_8$ (B) polyhedra in colemanite.

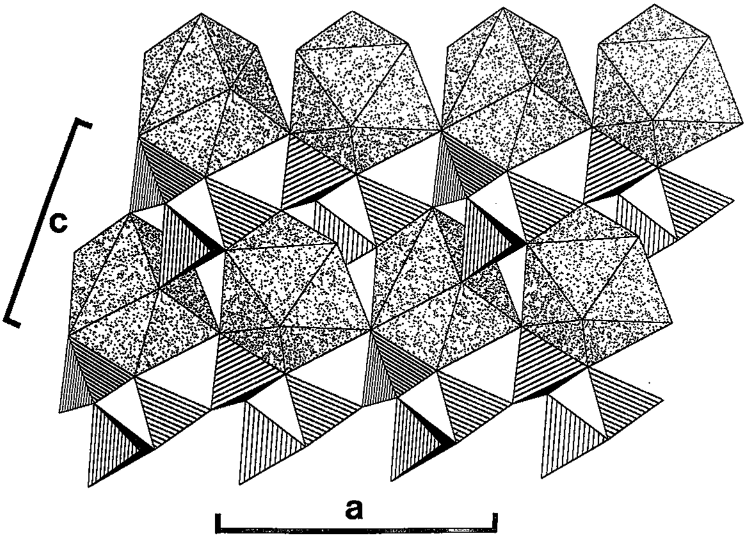

FIG. 2. The heteropolyhedral sheet in colemanite. Calcium polyhedra are shaded with a random dot pattern, and boron tetrahedra and triangles are shaded with parallel lines.

There is one unique Ca position that is coordinated by three oxygen atoms, four hydroxyl groups and an H_2O group, the anions being in an irregular dodecahedral arrangement (Fig. 1B). The $Ca\phi_8$ polyhedra link by sharing corners to form chains extending along [100]. The $[B_3O_4(OH)_3]^{2-}$ and $[Ca_2O_5(OH)_8(H_2O)_2]^{-16}$ chains link by sharing edges and corners to form a heteropolyhedral sheet of composition $[Ca_2B_3O(OH)(H_2O)]$ parallel to (010) (Fig. 2). Bonding within these sheets is quite strong, whereas the bonding between the sheets is much weaker. These sheets stack in a staggered arrangement along [010] (Fig. 3). Cross-sheet linkage occurs *via* corner-sharing between a $B\phi_4$ tetrahedron and a $Ca\phi_8$ polyhedron (Fig. 4, two linkages per unit-cell repeat along [100]) and through an extensive network of hydrogen-bonding. This weak linkage between the sheets accounts for the perfect {010} cleavage of colemanite.

Hydrogen bonding in colemanite

The constrained refinement of hydrogen positions resulted in a hydrogen-bonding scheme that is reasonable in terms of bond distances, bond angles (Table 4) and bond-valence requirements of both the anions and the hydrogen atoms (Table 5). Hydrogen is an important feature of the colemanite structure, as linkage between the heteropolyhedral sheets occurs largely *via* hydrogen bonding, and most hydrogen bonding is directed between the sheets. The arrangement of hydrogen bonds is illustrated in Figure 5, with the O–H bonds shown as solid lines and the H...O bonds shown as broken lines; their contributions to the bond-valence requirements of the anions are shown in Table 5.

The hydrogen bonds involved in the OH(3)–H(1)...O(5) and OH(7)–H(3)...O(5) configurations directly link adjacent sheets, and play a major role in the satisfaction of the bond-valence requirements around the O(5) anion (Table 5); without the bond-valence contributions by hydrogen, the bond-valence sum around O(5) would be 1.566 v.u., and it is only as an acceptor anion of the two hydrogen bonds that its bond-valence requirements can be satisfied. The OH(6) anion is the only anion directly bonded to adjacent sheets (Fig. 5). The OH(6)–H(2)...O(2) configuration involves a hydrogen bond to the sheet that is more weakly linked to OH(2) [through the Ca–OH(2) bond], and the H(2)...O(2) hydrogen bond thus provides additional intersheet linkage, albeit weaker than is the case for the other OH groups (Table 5).

The hydrogen-bonding scheme involving the H_2O group [OW(8)] in colemanite is a little more complicated than is the case for the OH groups. The H(4) hydrogen is involved in a simple OW(8)–H(4)...OH(7) configuration that hydrogen bonds across adjacent sheets (Fig. 5). However, the H(5) hydrogen is involved in an OW(8)–H(5)...OW(8) configuration, whereby adjacent H_2O groups hydrogen-bond to each other, forming a four-bond ring of the form "donor – acceptor – donor – acceptor" (Fig. 5). As the two H_2O groups involved in the ring bond to Ca atoms in different sheets, this arrangement also results in intersheet linkage *via* hydrogen bonding.

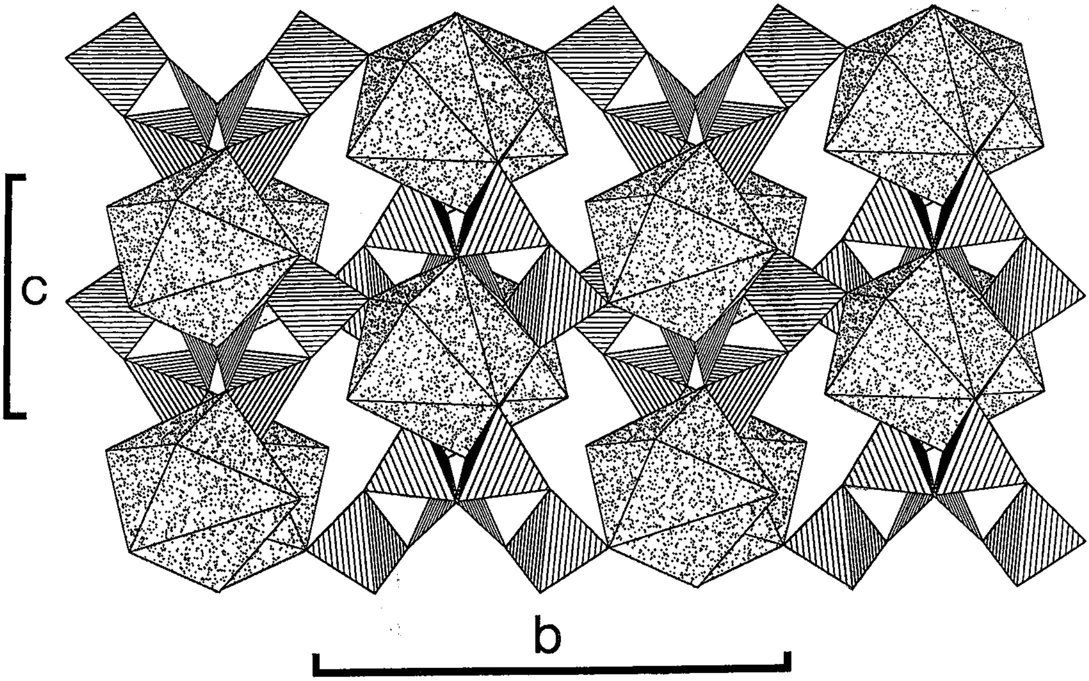

FIG. 3. The structure of colemanite projected onto (100). Shading as in Figure 2.

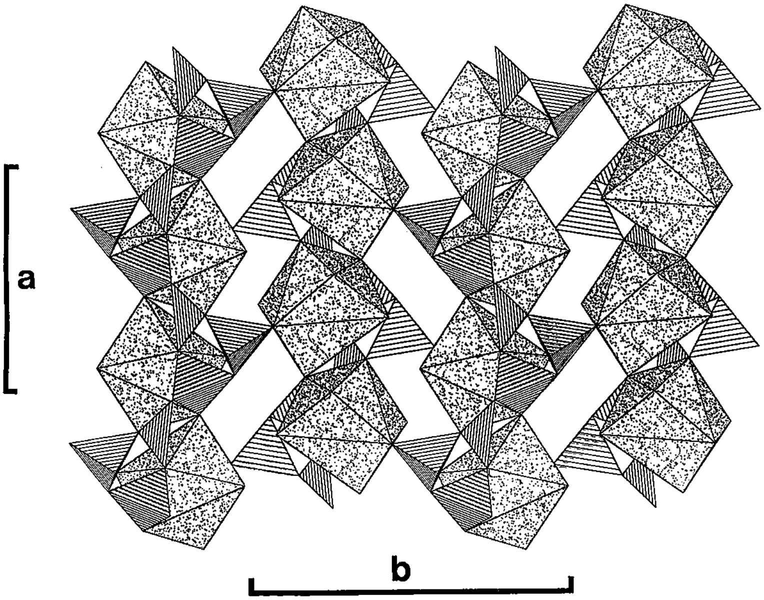

FIG. 4. The structure of colemanite projected onto (001). Shading as in Figure 2.

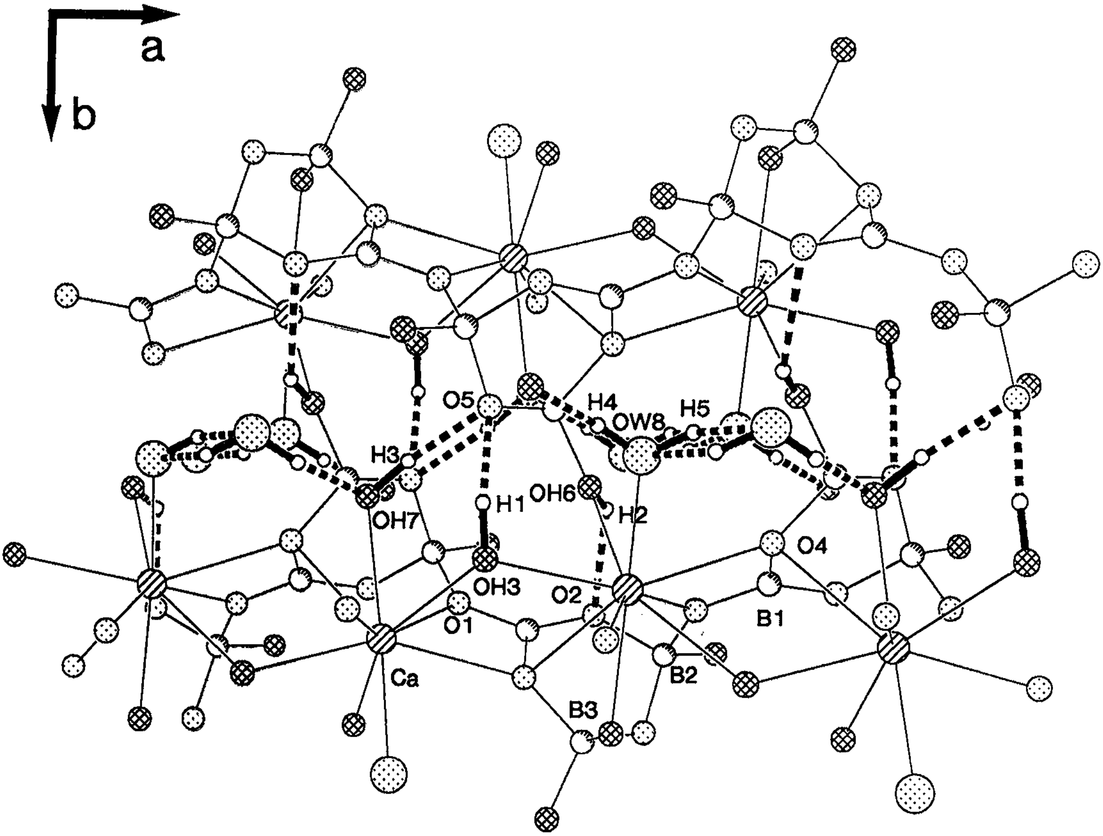

FIG. 5. The structure of colemanite projected onto (001). H–O are given as heavy solid lines, and H...O bonds are given as broken lines. Calcium atoms are shaded with parallel lines, simple oxygen atoms with regular dot pattern, OH oxygen atoms with crossed lines, H_2O oxygen atoms (larger circles) with a regular dot pattern, and hydrogen atoms are open circles.

It should be emphasized that these hydrogen bonds are not minor features of the structure. These bonds control many of the physical and chemical properties (*e.g.*, thermal stability, solubility) of the mineral, and a mechanistic interpretation of dissolution and crystallization must take hydrogen bonds into account.

The structure reported here verifies much of the previous work of Clark *et al.* (1964). However, due to the poor quality of their data (R = 14%), Clark *et al.* were unable to obtain direct information on hydrogen positions; the assignment of possible hydrogen-bond donor and acceptor pairs was based on anion–anion separations. This study provides directly determined hydrogen positions that verify most of the hydrogen bonding assignments given by Clark *et al.* (1964), except in the case of the OH(6)–H(2)...O(2) donor–acceptor pair, which Clark *et al.* (1964) gave as OH(6)–H(2)...O(1). Clark *et al.* (1964) assumed that OW(8) accepts a proton half the time from OW(8)g, and donates a proton half the time to OW(8)g, with the net result being that half the time there is one proton of the OW(8) group that does not make a hydrogen bond. The hydrogen bonding scheme reported here indicates that adjacent OW(8) groups hydrogen-bond to each other forming a four-bond "donor – acceptor – donor – acceptor" ring that does not include any part-time bonds or protons that do not form hydogen bonds.

TABLE 6. MINIMUM-ENERGY H-POSITIONS COMPARED TO X-RAY REFINEMENT H-POSITIONS

		X-ray	Minimum Energy		X-ray*	Minimum Energy
H(1)	x	-0.075(3)	-0.117	H(1)-OH(3)	0.96(2)	0.98
	y	0.085(1)	0.095	H(1)...O(5)h	1.78(1)	1.84
	z	-0.130(5)	-0.176	OH(3)-H(1)-O(5)h	172(2)	152
H(2)	x	0.334(3)	0.365	H(2)-OH(6)	0.96(2)	0.94
	y	-0.101(2)	-0.118	H(2)...O(2)i	2.27(2)	2.37
	z	0.669(3)	0.625	H(2)...O(1)	-------	1.98
				OH(6)-H(2)-O(2)i	141(2)	131
				OH(6)-H(2)-O(1)	------	147
H(3)	x	0.080(2)	0.075	H(3)-OH(7)	0.96(2)	0.99
	y	0.025(2)	0.041	H(3)...O(5)i	1.78(2)	1.78
	z	0.699(5)	0.734	OH(7)-H(3)-O(5)i	171(3)	161
H(4)	x	0.701(2)	0.699	H(4)-OW(8)	0.96(2)	0.96
	y	-0.025(2)	-0.015	H(4)...OH(7)g	1.86(2)	1.81
	z	1.010(4)	1.031	OW(8)-H(4)-OH(7)g	156(2)	169
H(5)	x	0.516(2)	0.506	H(5)-OW(8)	0.96(2)	0.91
	y	-0.013(2)	0.029	H(5)...OW(8)g	1.83(3)	2.37
	z	0.919(5)	0.815	H(5)...O(4)	------	2.34
				H(5)...OH(6)	-------	2.36
				OW(8)-H(5)-OW(8)g	146(2)	100
				OW(8)-H(5)-O(4)	------	139
				OW(8)-H(5)-OH(6)	------	140

* Distances are in Å and angles in °.

Energy minimization of H-positions

Energy minimization of the H-positions was carried out with the program WMIN (Busing 1981). The B^{3+}, O^{2-} and Ca^{2+} ions were held fixed during energy minimization, whereas the minimum-energy positions for all H^+ ions were obtained simultaneously by six cycles of steepest-descent minimization followed by six cycles of minimization by Newton's method. The H–O and H...O interactions were modeled using the direction-

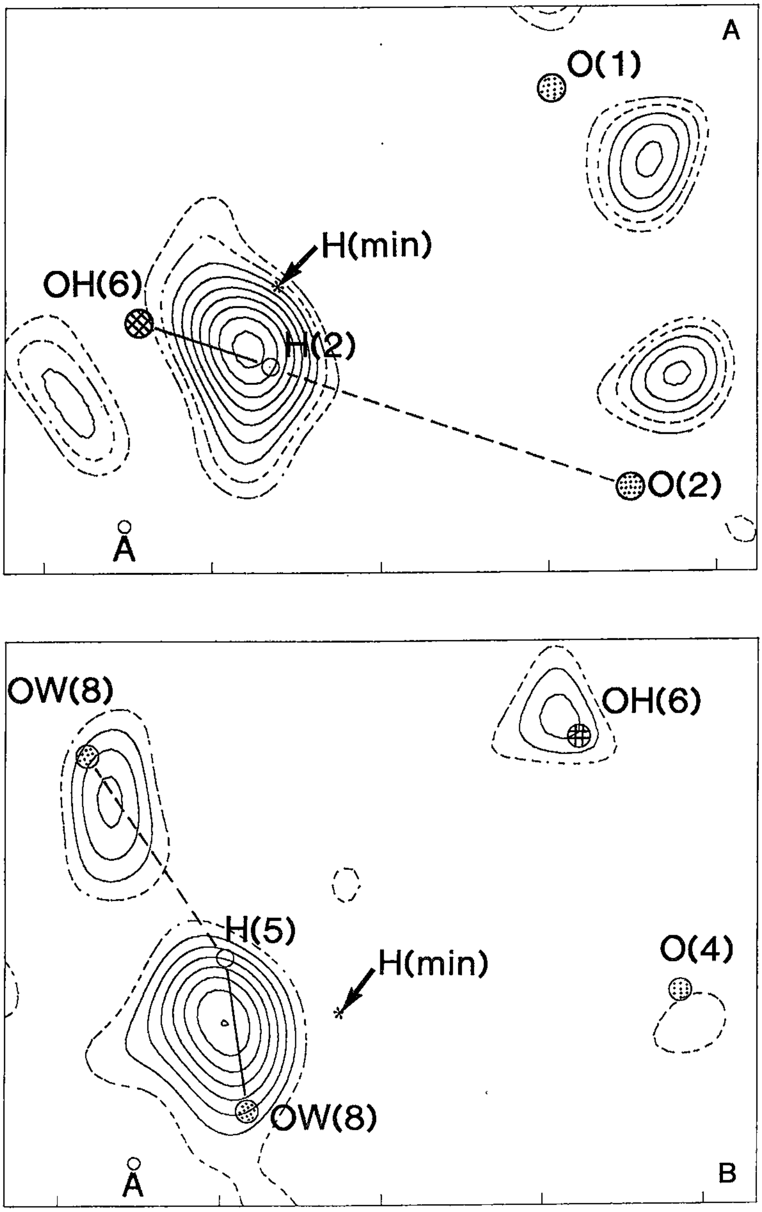

FIG. 6. Difference-Fourier maps of selected H positions in colemanite: (A) around H(2), H(2) position, Hw = structure-energy position; (B) around H(5), H(5) position, Hw = structure-energy position. The plane of projection in each case is a least-squares weighted average of the atom locations. Scale = 1 Å.

ally isotropic potential proposed by Abbott *et al.* (1989), where the energy W_{ij} for the ion pair i–j is given as

$$W_{ij} = W_{C,ij} + W_{R,ij} \qquad (1)$$

where $W_{C,ij}$ is the Coulombic electrostatic energy, and $W_{R,ij}$ is the short-range repulsive energy. The Coulombic electrostatic energy is given by:

$$W_{C,ij} = q_i q_j \,/\, r_{ij} \qquad (2)$$

where q_i and q_j are the formal charges of ions i and j, and r_{ij} is the internuclear separation. The Born-type short-range repulsion energy (Born & Huang 1954) is given by:

$$W_{R,ij} = \lambda_{ij}\exp(-r_{ij}/\rho_{ij}) \qquad (3)$$

where λ_{ij} and ρ_{ij} are pair-specific parameters. Throughout their work, Abbott *et al.* (1989) used ρ_{ij} = 0.25 Å for H–O and H...O interactions. They found that the value of λ_{ij} is structurally dependent; 30000 kJ/mol was found to work well for trioctahedral micas and tremolite, whereas 24250 kJ/mol was found to work best for chlorite.

Energy minimizations of H-positions in colemanite were done with ρ = 0.25 Å and λ_{ij} ranging from 24250 to 30000 kJ/mol, the best agreement with the X-ray-refined positions being obtained for λ_{ij} = 26500 kJ/mol. The minimum-energy positions for the H(1), H(3) and H(4) ions agree well with the positions obtained from the constrained X-ray refinement (Table 6). However, the minimum-energy positions for the H(2) and H(5) positions are markedly different from the X-ray positions (Table 6).

Concerning the disagreement between the X-ray positions and the minimum-energy positions for the H(2) and H(5) ions, there are two possibilities: (1) the calculated minimum-energy positions are not where the H ions are located, or (2) the H ions are located at the calculated minimum-energy positions, and the X-ray-derived positions are incorrect.

To resolve which of these is the case, difference-Fourier maps were calculated around the H(2) and H(5) positions with the hydrogen positions vacant. The resulting maps are given in Figure 6, and indicate that the electron density is located along the O–H bonds, as indicated by the X-ray structure refinement. The minimum-energy positions also are shown in Figure 6 and lie outside the electron density attributable to the H^+ ions. It seems reasonable to conclude that the minimum-energy positions for the H(2) and H(5) ions are not the true positions of the hydrogen atoms.

The potential given by Abbott *et al.* (1989) is specifically for OH^- interactions, and has not been previously tested for H_2O interactions. However, the H(2) position belongs to a hydroxyl group, and also is not well predicted. Hence, there must be some factor affecting the application of this specific O–H potential. In Figure 6, it can be seen that for both H(2) and H(5), there is more than one anion position sufficiently close to the H position to form a hydrogen bond. In each case, the minimum-energy hydrogen has taken up a much more central position with respect to the surrounding anions, as in fact would be predicted from simple Coulombic arguments. It is well known that the hydrogen bond has a very strong directional character, and it may not always be appropriate in the energy-minimization procedure to consider all possible O...H interactions. This point should become clearer on application of this type of potential to a large number of OH^- and H_2O-bearing minerals.

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