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THE STRUCTURE OF PRICEITE, A BASIC HYDRATED CALCIUM BORATE, BY *AB INITIO* POWDER-DIFFRACTION METHODS

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Abstract

The crystal structure of priceite, $Ca_2B_5O_7(OH)_5{\bullet}H_2O$, has been determined by direct methods from synchrotron powder X-ray-diffraction data and refined to $R_{wp} = 0.042$ and $R_p = 0.030$ using the Rietveld method. The monoclinic structure was refined in space group $P2_1/c$, a 11.623(1), b 6.976(1), c 12.350(1) Å, β 110.70(1)°, V 936.72(1) Å^3, $Z = 4$. The structure consists of infinite chains of pairs of borate rings that extend along [100] *via* corner-sharing; three corner-linked $B\phi_4$ (ϕ: OH^-, O^{2-}, or H_2O) tetrahedra form one ring linked through a common boron atom to the next ring, composed of two $B\phi_4$ tetrahedra and one $B\phi_3$ triangle. Chains of edge-sharing $Ca\phi_8$ polyhedra zigzag along [010]. The borate chains are cross-linked by $Ca\phi_8$ polyhedra *via* edge- and corner-sharing. There are three borates in addition to priceite, that contain a <3B>–<3B> chain motif, but priceite is the only one containing a 3□ ring. These chains extend perpendicular to the calcium chains of polyhedra, in contrast to colemanite, which displays a <3B> motif where the strings are parallel.

Keywords: priceite, crystal structure, Rietveld refinement, powder diffraction, synchrotron data, borate.

Sommaire

Nous avons affiné la structure cristalline de la priceïte, $Ca_2B_5O_7(OH)_5{\bullet}H_2O$, par méthodes directes à partir de données de diffraction X sur poudre prélevées avec rayonnement synchrotron, jusqu'à un résidu R_{wp} égal à 0.042 et R_p égal à 0.030 en utilisant la méthode de Rietveld. La structure monoclinique répond au groupe spatial $P2_1/c$, a 11.623(1), b 6.976(1), c 12.350(1) Å, β 110.70(1)°, V 936.72(1) Å^3, $Z = 4$. La structure contient des chaînes de paires d'anneaux de borate le long de [100] par partage de coins; trois tétraèdres $B\phi_4$ (ϕ: OH^-, O^{2-}, ou H_2O) à coins partagés forment un anneau lié, grâce à un atome de bore en commun, à l'anneau prochain, fait de deux tétraèdres $B\phi_4$ et d'un triangle $B\phi_3$. Des chaînes de polyèdres $Ca\phi_8$ à arêtes partagées, disposés en zigzag, sont alignées selon [010]. Les chaînes de borate sont interliées par les chaînes de polyèdres $Ca\phi_8$ par partage de coins et d'arêtes. Il y a trois borates en plus de la priceïte qui contiennent un motif <3B>–<3B> en chaînes, mais seule la priceïte contient un anneau 3□. Ces chaînes sont orientées perpendiculairement au chaînes de polyèdres à calcium, ce qui contraste avec la cas de la colemanite, qui possède un motif <3B> dans lequel les chaînes sont parallèles.

(Traduit par la Rédaction)

Mots-clés: priceïte, structure cristalline, affinement de Rietveld, diffraction sur poudre, rayonnement synchrotron, borate.

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INTRODUCTION

The crystal structure of many borate minerals has been determined in detail; these structures have revealed that this group of minerals has a very rich topology (Hawthorne *et al.* 1996). The diversity of borate topology is in part due to the common occurrence of both tetrahedral BO_4 and triangular BO_3 groups within the same structures. Although the structure of the majority of borate minerals has been determined, there are a number of fine-grained, microcrystalline species, including priceite, whose structures are unknown.

The recent development of profile-fitting methods for X-ray powder-diffraction analysis, together with the development of new software to accurately extract intensity data from these patterns, has made possible the *ab initio* determination of the structure of microcrystalline compounds. Louër (1998) reviewed the methods, problems and structure-solution strategies for *ab initio* determination of the structure of microcrystalline compounds. As part of an ongoing program, we are investigating the crystal structures of phosphate (Wallwork *et al.* 2002) and borate minerals that occur only in microcrystalline masses, and we report here the crystal structure of priceite. A preliminary account of this work was presented at Crystal 22 (Wallwork *et al.* 2001).

BACKGROUND INFORMATION

Priceite was first described by Benjamin Silliman Jr. in the 1870s from a locality 8 kilometers north of Chetco, Oregon, U.S.A., where it occurs as small fine-grained compact nodules with aragonite in a hot-spring deposit (Palache *et al.* 1951). The mineral has since been found at other localities, including Furnace Creek Wash, Death Valley, California, U.S.A.; Wentworth and Hillsborough, New Brunswick, Canada; Inder, Kazakstan, and Turkey (Gaines *et al.* 1997, Helvaci & Alonso 2000). Dana (1892) considered the mineral to be a massive and impure form of colemanite. Van't Hoff (1906) proposed the formula $Ca_4B_{10}O_{19}{\bullet}7H_2O$ on the basis of a synthesis and a chemical analysis of material from Turkey ("pandermite"). "Pandermite" was originally described in 1877, but was shown to be identical to priceite in 1887; see Clark (1993) for references to early literature on "pandermite". The powder pattern of priceite was reported by Kramer & Allen (1956), but they were unable to index the pattern and to determine the unit cell. Although priceite occurs at many localities in some abundance, and can readily be synthesized (Fukushige *et al.* 1981), no material suitable for investigation by conventional single-crystal X-ray-diffraction methods has been found.

TABLE 1. SUMMARY OF CRYSTALLOGRAPHIC DATA AND REFINEMENT CONDITIONS FOR PRICEITE

$Ca_2B_5O_7(OH)_5{\bullet}H_2O$		χ^2(total)	5.84
a (Å)	11.623(1)	μR	1.24
b (Å)	6.976(1)	no. of profile parameters	26
c (Å)	12.350(1)	no. of structural parameters	48
β (°)	110.70(1)	no. of constraints	27
V (Å³)	936.72(1)	no. of reflections	1931
Z	4	no. of data points	11288
d_{calc} (g/cm³)	2.427	Profile function	pseudo-Voigt
Space group	$P2_1/c$	Background function	Chebyshev type-I
R_{wp}(total)	0.042	$R_{wp} = \Sigma I_o - I_c/\Sigma I_o$	
R_p(total)	0.030	$R_p = ((\Sigma w(I_o - I_c)^2)/\Sigma w I_o^2)^{1/2}$	
R_{wpb}(total)	0.069	$R_{wpb} = \Sigma((I_o - I_c \bullet I_o - I_b)/I_o)/\Sigma I_o - I_b$	
R_{pb}(total)	0.042	$R_{pb} = ((\Sigma w((I_o - I_c)(I_o - I_b)/I_o)^2)/\Sigma w(I_o - I_b)^2)^{1/2}$	

EXPERIMENTAL

Samples of priceite were obtained from the collection of the South Australian Museum, Adelaide. The material used for structure determination was taken from specimen G3769, a compact mass, originally labeled "pandermite" from Sultancayir (Sultan Tschair), south of Panderma, Turkey. A pure sample for powder-diffraction study was broken from the bulk sample, finely crushed and loaded into a glass capillary 0.3 mm in diameter. The diffraction pattern was recorded using synchrotron radiation in a high-resolution powder diffractometer at the Photon Factory (KEK), Tsukuba, Japan. Partial diffraction-rings were collected on three concurrent image plates positioned 573 mm from the axially spinning sample; the wavelength of the X-rays was 1.3908(1) Å, calibrated using an alumina standard (NBS 674). The data were extracted from the image plates and processed using the program Python PDA (Hester *et al.* 1999). The angular range of the data is 5.00 – 42.46°, 43.16 – 82.50°, 83.70 – 120.00°, in steps of 0.0100° in 2θ. Even though the image plates are butted together, a small gap (~0.3°) occurs.

The structure analysis was done using the RIETICA (Hunter 1998), SIRPOW.92 (Altomare *et al.* 1994), GSAS (Larson & Von Dreele 1994) and EXPGUI (Toby 2001) packages. The powder pattern was indexed using the program ITO (Visser 1969), which gave a metrically monoclinic cell. The cell parameters (Table 1) were refined by fitting the whole data-set. The indexed powder pattern indicated that the unit cell is primitive. Data were extracted from the powder pattern in the form of $F_{obs}{}^2$ values using a Le Bail profile fit within RIETICA. The cell parameters, zero errors, scale factor and peak-profile parameters for each of the three histograms were refined. A pseudo-Voigt function was used to model the profile shape, with coefficients refined simultaneously while constrained to be equal for all histograms. This extraction afforded data for 1019 reflections in the form: *hkl*, FWHM, $F_{obs}{}^2$.

STRUCTURE SOLUTION AND REFINEMENT

A search of the reflection data for systematic extinctions did not provide conclusive evidence of the existence of a glide plane, but the presence of a 2_1 axis was

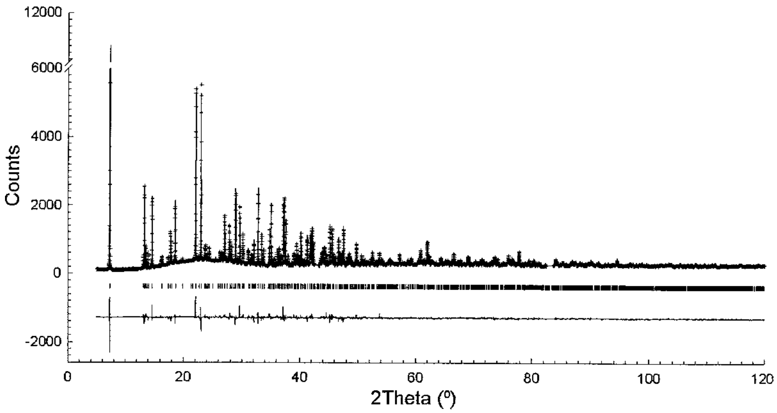

FIG. 1. Powder-diffraction trace for priceite (combined plot of the three histograms). The observed pattern is denoted by +, and the calculated pattern is superimposed. Below that profile are the positions of the Bragg diffraction maxima, and the difference pattern.

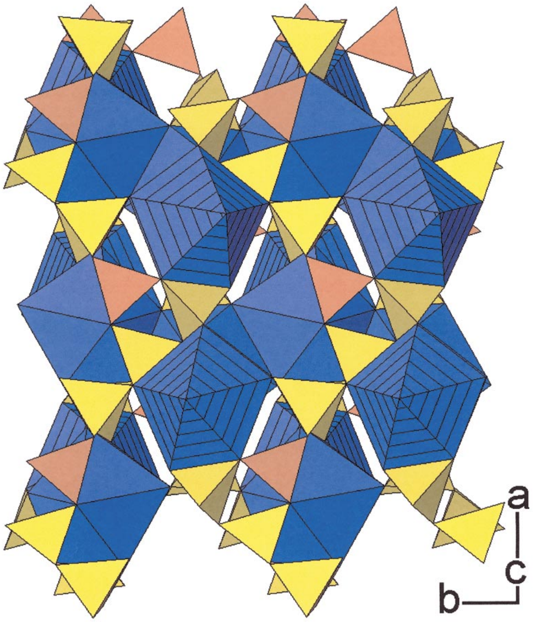

FIG. 2. The structure of priceite. Bϕ_3 and Bϕ_4 polyhedra are shown in orange and yellow, respectively. Caϕ_8 polyhedra are blue, with the polyhedra that lie above and below (001) highlighted with hatching.

TABLE 2. PRICEITE: ATOM PARAMETERS AND ISOTROPIC-DISPLACEMENT PARAMETERS

	x	*y*	*z*	U_{iso}
*Ca*1	0.4928(1)	0.2403(2)	–0.0809(1)	0.017(3)
*Ca*2	0.8085(1)	0.2554(2)	0.3790(1)	0.017(3)
O1	0.1817(3)	0.2579(5)	0.2235(2)	0.013(3)
O2 (OH)	0.7956(3)	0.5805(5)	0.4357(3)	0.013(3)
O3	0.7671(3)	0.9288(5)	0.4186(3)	0.013(3)
O4	0.6167(2)	–0.2127(5)	–0.2116(3)	0.013(3)
O5 (OH)	0.5208(4)	0.1072(5)	0.1129(3)	0.013(3)
O6 (OH)	0.4088(3)	0.8312(5)	0.2247(3)	0.013(3)
O7	0.5527(2)	0.9347(4)	0.4069(3)	0.013(3)
O8	0.7145(3)	0.8283(4)	0.5805(2)	0.013(3)
O9	0.6999(3)	0.3331(4)	0.0234(3)	0.013(3)
O10 (OH)	0.7709(3)	0.1081(4)	0.1825(3)	0.013(3)
O11 (OH)	0.9088(2)	0.2410(6)	0.0914(3)	0.013(3)
O12	0.8317(3)	0.4375(4)	0.2145(3)	0.013(3)
O13 (H_2O)	0.0112(4)	0.1530(5)	0.4003(4)	0.013(3)
*B*1	0.7497	–0.2543	–0.6451	0.015(9)
*B*2	0.5139	–0.2715	–0.1731	0.015(9)
*B*3	0.6835	–0.0350	–0.5180	0.015(9)
*B*4	0.8029	0.2799	0.1280	0.015(9)
*B*5	0.7882	–0.1241	–0.3089	0.015(9)

considered possible. With the aid of SIRPOW.92, a chemically plausible model was obtained for most of the non-hydrogen atoms in the space group $P2_1$. Additional sites for boron atoms were located by systematically searching the arrangement of oxygen atoms. A first refinement by the Rietveld (Rietveld 1969) method gave a parameter set that when tested by PLATON (Spek 1997) indicated the presence of a *c*-glide plane (P.C. Burns, pers. commun., 2002). The refinement was completed in $P2_1/c$. The EXPGUI–GSAS suite of programs was employed in this task. Three datasets were used, one from each of the image plates. The profile backgrounds were fitted by Chebyschev type-1 polynomials. This function allows the glass capillary to be properly modeled. The peak-shape parameters were constrained as described for the peak extraction. The data were corrected for absorption by applying a cylin-

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR PRICEITE

*B*1 – O1	1.46	*Ca*1 – O4	2.448(4)
O2	1.49	O5	2.478(4)
O3	1.48	O5	2.452(3)
O4	1.49	O6	2.480(4)
		O7	2.746(4)
*B*2 – O4	1.49	O7	2.392(3)
O5	1.50	O8	2.488(4)
O6	1.47	O9	2.384(3)
O7	1.47		
*B*3 – O3	1.47	*Ca*2 – O2	2.394(4)
O7	1.49	O3	2.414(4)
O8	1.49	O6	2.452(3)
O9	1.49	O9	2.597(4)
		O10	2.527(4)
*B*4 – O9	1.46	O11	2.466(3)
O10	1.48	O12	2.490(4)
O11	1.48	O13	2.386(4)
O12	1.49		
*B*5 – O1	1.36		
O8	1.37		
O12	1.39		

TABLE 4. BOND-VALENCE (*vu*) CALCULATIONS FOR PRICEITE

	*Ca*1	*Ca*2	*B*1	*B*2	*B*3	*B*4	*B*5	Σ
O1			0.79				1.00	1.78
O2 (OH)		0.32	0.72					1.04
O3		0.30	0.74		0.76			1.81
O4	0.27		0.73	0.73				1.74
O5 (OH)	0.27, 0.25			0.70				1.22
O6 (OH)	0.25	0.27		0.75				1.28
O7	0.32, 0.12			0.76	0.72			1.93
O8	0.24				0.74		1.00	2.00
O9	0.32	0.18			0.73	0.78		2.01
O10 (OH)		0.22				0.74		0.96
O11 (OH)		0.26				0.75		1.01
O12		0.24				0.73	0.98	1.95
O13 (H_2O)		0.32						0.32
Σ	2.05	2.11	2.99	2.96	2.95	2.99	2.98	

drical correction μR of 1.24. The phase scale and the zero shifts were refined, as were all atom coordinates. The final cycles of refinement were calculated using GSAS. A single isotropic-displacement parameter was refined for each of the three types of atom. Soft geometrical O–O restraints were applied to assign the $B\phi_4$ groups to tetrahedra and $B\phi_3$ groups to triangles (ϕ: unspecified ligand). The B atoms were placed geometrically at the center of these polyhedra, and their positions were not refined. Hydrogen-atom positions were not located.

The Rietveld refinement converged to $R_{wp} = 0.042$ and $R_p = 0.030$. A summary of the data collection, structure solution and refinement is given in Table 1. The refined powder-diffraction patterns are shown in Figure 1, and the structure solution is shown in Figure 2. The atom coordinates and isotropic-displacement parameters are listed in Table 2; selected interatomic distances are presented in Table 3.

STRUCTURE DESCRIPTION

Of the five crystallographically unique atoms of boron in the structure, one is [3]-coordinated and four are [4]-coordinated. Of the 13 unique O atoms, one is bonded solely to Ca; seven bridge two B atoms, and five are bonded to one B. The first is probably a molecule of H_2O, the second group, O^{2-} ions, and the third group, OH^- ions, giving the structural formula, $Ca_2B_5O_7(OH)_5 \bullet H_2O$. This assignment is confirmed by bond-valence analysis (Table 4).

Hawthorne *et al.* (1996) described the fundamental building blocks (FBBs) of borate structures in terms of $B\phi_3$ triangles (Δ) and $B\phi_4$ tetrahedra (□). The topology of the frameworks is denoted by *A:B,* where *A* is the number of borate groups in the cluster ($B\phi_3$ triangles and $B\phi_4$ tetrahedra), and *B* is a character string that contains the relevant information on connectivity. A ring of polyhedra is denoted by < >, enclosing the polyhedra members in the ring. A ring is formed through corner-sharing between adjacent polyhedra. The number of polyhedra common to both rings is indicated by –, = and ≡ for one, two and three polyhedra, respectively.

The $B\phi_3$ and $B\phi_4$ groups in priceite are arranged into rings of the type Δ4□:<3□>–<Δ2□> (Fig. 3a). Thus, the cluster consists of a ring of three corner-sharing borate tetrahedra, connected through a common boron atom to a ring of one borate triangle and two borate tetrahedra. The pairs of rings form infinite chains parallel to [001] by corner-sharing through the BO_3 group (Fig. 3b). The backbone of the priceite structure is infinite zigzag strings of edge-sharing $Ca\phi_8$ polyhedra extending parallel to [010] (Fig. 4a), linked through edge-sharing to other $Ca\phi_8$ polyhedra, that lie alternately above and below (001), making the strings stepped in two dimensions (Fig. 4b).

The Ca–O distances range from 2.386 to 2.746 Å, with a mean of 2.48 Å, similar to those reported for other calcium borates. This is in good agreement with those in colemanite, 2.51 Å (Burns & Hawthorne 1993a), probertite, 2.53 Å (Menchetti *et al.* 1982) and meyerhofferite, 2.45 Å (Burns & Hawthorne 1993b). Angles in the $Ca\phi_8$ polyhedra range from 54.70° to 158.47° (mean 99.98°). The B–O distances in the BO_4 tetrahedra range from 1.46 to 1.50 Å, and in the BO_3 triangle, they range from 1.36 to 1.39 Å. The angles in the tetrahedra range from 107.57° to 111.08°, and in the triangles, from 119.15° to 120.47°.

RELATION TO OTHER MINERALS

Whereas the structures of meyerhofferite, sussexite and borax consist of finite clusters, the rings in priceite link to form infinite chains. There are three other bo-

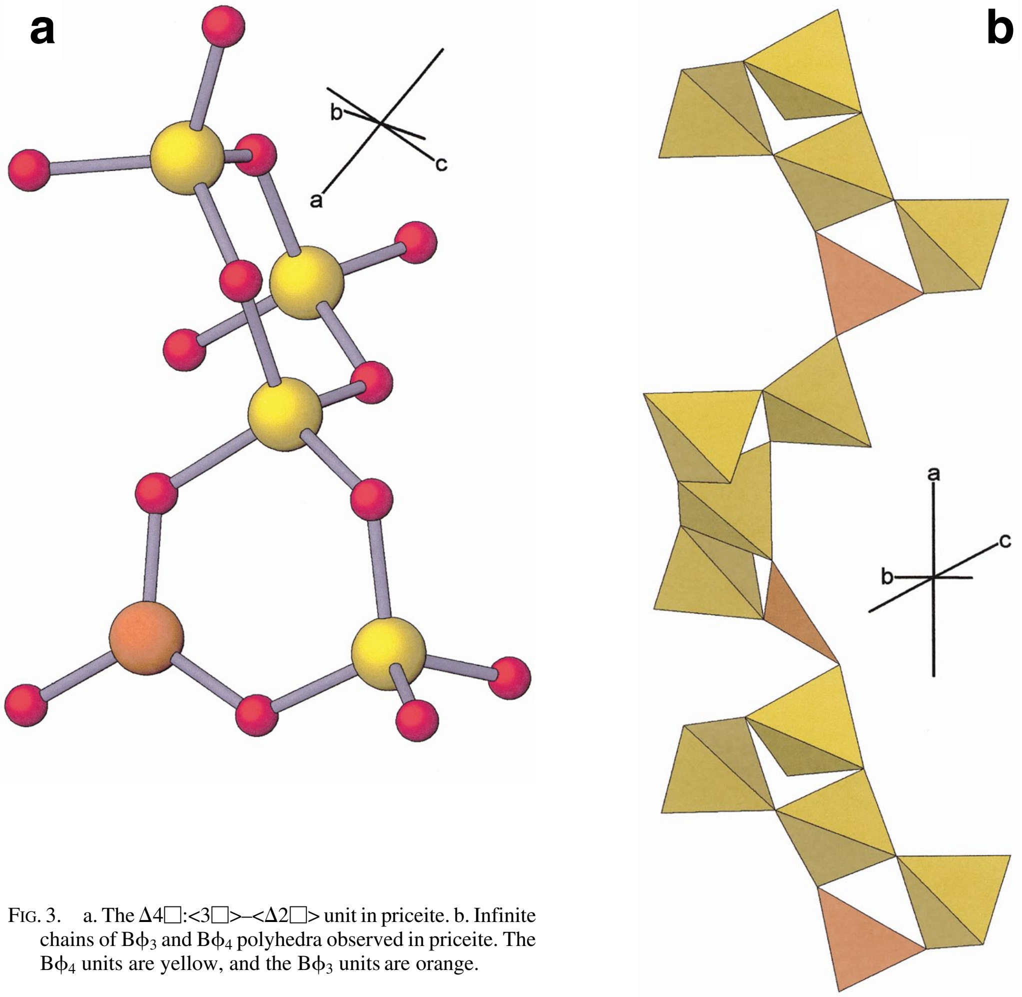

FIG. 3. a. The Δ4□:<3□>–<Δ2□> unit in priceite. b. Infinite chains of $B\phi_3$ and $B\phi_4$ polyhedra observed in priceite. The $B\phi_4$ units are yellow, and the $B\phi_3$ units are orange.

rates, probertite, laderellite and ezcurrite, that contain a <3B>–<3B> chain motif (where B denotes $B\phi_3$ or $B\phi_4$) (Hawthorne *et al*. 1996), but priceite is the only one containing a 3□ ring. The borate chains in priceite extend perpendicular to the calcium chains of polyhedra, in contrast to colemanite, where the strings are parallel (Fig. 5). Colemanite is a calcium borate chain structure displaying a <3B> motif.

Kramer & Allen (1956) reported priceite as an alteration product of colemanite. Fleet & Muthupari (2000) noted that subtraction of the sassolite formula from the colemanite formula gives rise to the formula of priceite, suggesting that this may be a path of alteration for the formation of priceite. They predicted through B *K*-edge XANES that priceite contains 80% tetrahedrally coordinated boron and that the structure contains chains or layers. The structure determination presented here shows their inferences to be correct.

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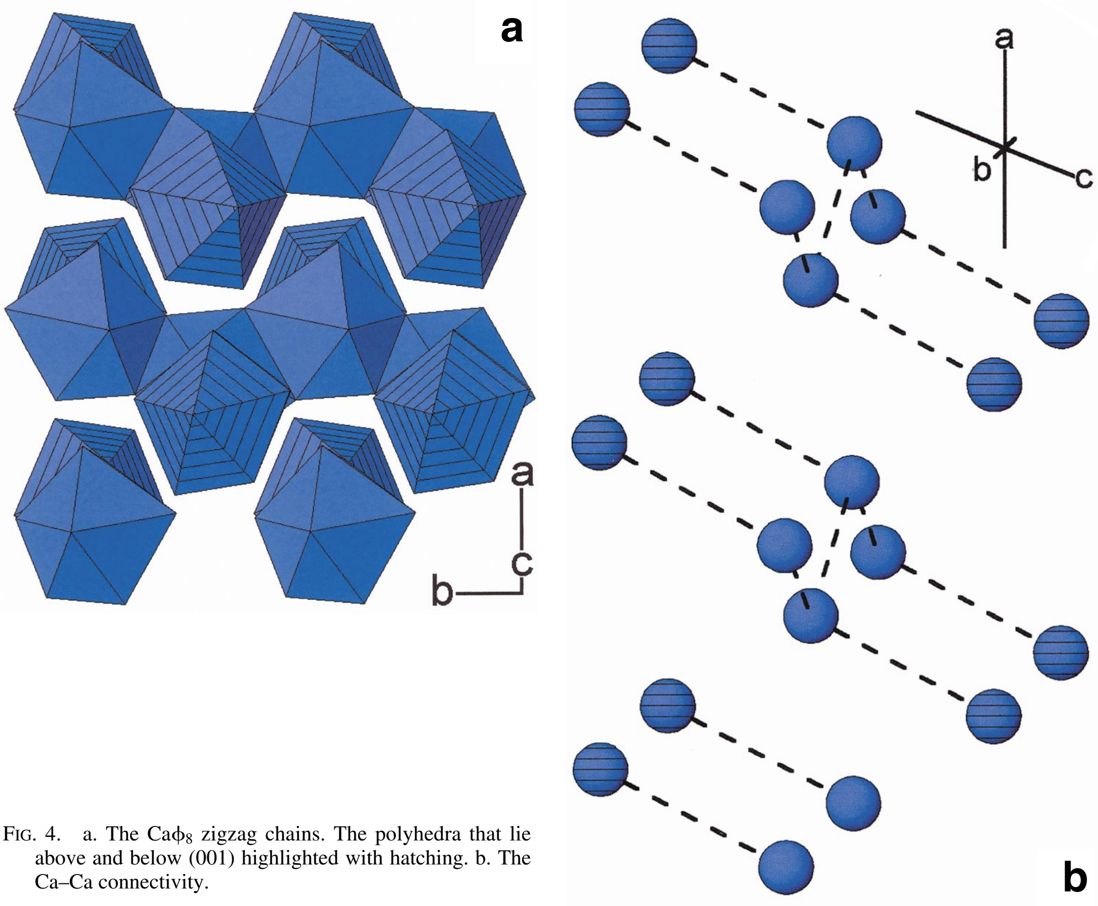

FIG. 4. a. The Caϕ_8 zigzag chains. The polyhedra that lie above and below (001) highlighted with hatching. b. The Ca–Ca connectivity.

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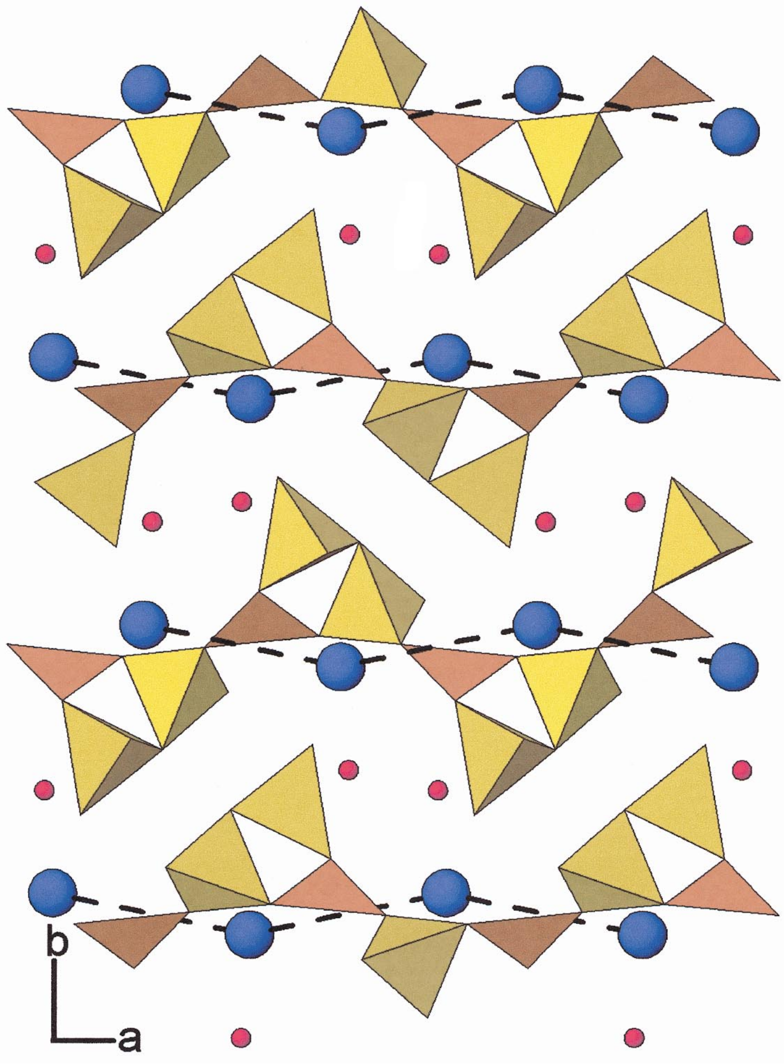

FIG. 5. The structure of colemanite, where the borate chains are parallel to the chains of calcium polyhedra. The Bϕ_4 are yellow, and the Bϕ_3 units are orange; the Ca-polyhedra are shown as blue circles for simplicity, and the direction of bonding is given by a dashed line.

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