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Törnebohmite, $RE_2Al(OH)[SiO_4]_2$: crystal structure and genealogy of RE(III)Si(IV) $\rightleftarrows$ Ca(II)P(V) isomorphisms

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Abstract

Törnebohmite, $RE_2Al(OH)[SiO_4]_2$, monoclinic, $a = 7.383(3)$, $b = 5.673(3)$, $c = 16.937(6)$Å, $\beta = 112.04(2)°$, $Z = 4$, space group $P2_1/c$, is structurally allied to the brackebuschite and pyrobelonite groups of minerals. It is isostructural with fornacite. $R = 0.033$ for 2586 independent reflections.

The basis of the structure consists of linear $^1_\infty[Al(OH)(O_T)_3]$ octahedral chains which run parallel to [010]. Insular $[SiO_4]$ which corner-link to the octahedral chains are arranged in *trans* configuration to these chains. These admit the large RE (rare earth) cations which form a serrated wall of linked $RE\phi_{10}$ polyhedra which is oriented parallel to the {001} plane. Average distances are $^{[10]}$RE(1)–O = 2.64, $^{[10]}$RE(2)–O = 2.68, $^{[6]}$Al–O, OH = 1.90, $^{[4]}$Si(1)–O = 1.62 and $^{[4]}$Si(2)–O = 1.63Å.

Törnebohmite is yet another example where isomorphisms of the type $RE^3Si^{4+} \rightleftarrows Ca^{2+}P^{5+}$ can be found.

Introduction

Törnebohmite is a hydrous rare earth silicate, consisting principally of the rare earth elements (= RE) lanthanum, cerium and neodymium. It was first discovered as a minor constituent of the cerite ores from the Bastnäs Mine, Riddarhyttan, Parish of Skinnskatteberg, Province of Västmanland, central Sweden. Geijer (1921) first announced the new species, and Geijer and Carlborg (1923) offered a comprehensive document from a geological and historical standpoint of this remarkable region, which is rich in mining history and has been a site of extensive mineralogical-chemical investigations. Jorpes (1966), for example, documents the journeys of Jöns Jacob Berzelius, in search of minerals which provided him with several new rare earth elements. Of the rare earth silicate species, cerite appeared to be the most predominant, along with allanite. Geijer discerned törnebohmite in thin sections, where it occurs as green, pleochroic grains embedded in the cerite ore and recognized its distinction from cerite. He named it after Alfred Elis Törnebohm (1838–1911), former Director of the Geological Survey of Sweden.

The chemical composition of törnebohmite was obtained by Mauzelius and reported by Geijer. It is listed in Table 1 along with a calculated composition derived from our structure analytical study. Agreement between the chemical analysis of Mauzelius and the theoretical end member formula $Ce_2Al(OH)[SiO_4]_2$ is good, bearing in mind that reported FeO could be Fe_2O_3 and that minor CaO probably substitutes for RE. Water was not reported; the low F content is not sufficient to warrant predominant F^-–OH^- substitution. The hydroxyl anion is so tightly bound that it may be included with "ignition". The ignition content (1.70%) and theoretical water content (1.77%) make this proposition appealing.

Despite subsequent attempts to rationalize törnebohmite's crystal chemistry, the literature is fraught

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Table 1. Törnebohmite: chemical analysis

	1	2
SiO_2	22.05	23.64
Al_2O_3	8.55	10.03
Ce_2O_3	27.52	64.56
$(La,Nd)_2O_3$	34.85	-
MgO	0.49	-
CaO	0.23	-
MnO	0.05	-
FeO	1.91	-
F_2	0.29	-
H_2O	-	1.77
Chalcopyrite	0.96	-
Insoluble	0.95	-
Ignition	1.70	-
Total	99.55	100.00

[1] Mauzelius in Geijer (1921).

[2] Theoretical weight percent for $Ce_2Al(OH)[SiO_4]_2$.

with uncertainty. Strunz (1970) hints that it may be monoclinic; Povarennykh (1972) lists the correct formula but presents a hexagonal or trigonal cell. Our structure study demonstrates a remarkable kinship with the large brackebuschite–fornacite mineral group and provides further evidence for cationic isomorphism RE(III)Si(IV) ⇄ Ca(II)P(V), thus connecting the rare earth silicates with the calcium phosphates. A later paper will stress the structural kinship between cerite and whitlockite. Finally, accepting törnebohmite's theoretical formula above and its refined cell parameters, we calculate 5.12 gm cm^{-3}, which is slightly higher than the observed specific gravity of 4.94 reported by Geijer.

Experimental procedure

Our sample of törnebohmite from Riddarhyttan, Sweden was kindly donated by the Smithsonian Institution, USNM No. 96428. We thank Mr. John S. White, Jr. for the research specimen.

The single crystal used in the final structure determination was an ellipsoid with no prominent crystal faces and measured 0.13 × 0.18 × 0.18 mm^3. Although the shape of the grain was microscopically measured, attempts at absorption correction showed no significant improvement of the raw data set and no such correction was applied in the final study. Precession and Weissenberg photographs led to the systematic absences compatible with space group $P2_1/c$ which is uniquely determined. The crystal cell parameters were refined on a PICKER automated diffractometer, using graphite monochromator and Mo$K\alpha$ radiation (λ = 0.70926Å) prior to complete data collection.

Refined cell parameters are listed here, both for the standard crystallographic orientation (International Tables, vol. 1, 1969) and for the reduced cell. We retained the standard orientation in this study.

	Standard orientation		Reduced cell orientation
a(Å)	7.383(3)	a'	15.732(6)
b(Å)	5.673(3)	b'	5.673(3)
c(Å)	16.937(6)	c'	7.383(3)
β(deg.)	112.04(2)	β'	93.73(2)
Space group	$P2_1/c$		$P2_1/n$

The transformation matrix from standard orientation to reduced cell orientation is $101/010/\bar{1}00$.

With scan speed 2° min^{-1}, base scan width of 2°, reflections to $2\theta = 70°$ ($\sin\theta/\lambda = 0.81$) were collected. Background counting times were 40 sec on each side of the peak. A total of 6029 reflections was collected, ranging from $h = -11$ to 11, $k = 0$ to 9, $l = -26$ to 26. After Lorentz-polarization correction and averaging symmetry-equivalent reflections, 2586 independent $|F_O|$ were obtained.

Solution and refinement of the structure

The structure was solved through three-dimensional P(uvw) Patterson synthesis. The structure

Table 2. Törnebohmite: atomic coordinate parameters†

Atom	x	y	z
RE(1)	0.81254(4)	0.73320(5)	0.45628(2)
RE(2)	0.21935(5)	0.78459(6)	0.36951(2)
Si(1)	0.5286(2)	0.2507(3)	0.4187(1)
Si(2)	0.9312(2)	0.2389(3)	0.3381(1)
Aℓ	0.4929(3)	0.5008(3)	0.2503(1)
O(1)	0.3822(8)	0.2133(10)	0.4665(3)
O(2)	0.7488(6)	0.2851(8)	0.4845(3)
O(3)	0.5083(6)	0.0120(7)	0.3614(3)
O(4)	0.4791(6)	-0.5097(7)	0.3600(3)
O(5)	0.0406(6)	0.1733(8)	0.2739(3)
O(6)	0.6939(6)	0.2561(7)	0.2765(2)
O(7)	0.9988(6)	0.4764(7)	0.3943(3)
O(8)	0.9811(6)	0.0234(7)	0.4057(3)
OH	0.3239(6)	0.2450(7)	0.2144(2)

†Estimated standard errors refer to the last digit.

Table 3. Törnebohmite: anisotropic thermal vibration parameters†

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{EQ}, Å^2
Ce(1)	105(1)	59(1)	73(1)	- 0(1)	58(1)	1(1)	0.58(1)
Ce(2)	128(1)	90(1)	115(1)	1(1)	88(1)	- 2(1)	0.78(1)
Si(1)	97(6)	40(5)	58(5)	10(4)	38(5)	9(4)	0.49(4)
Si(2)	87(5)	48(5)	55(5)	11(4)	32(5)	- 2(4)	0.50(4)
Aℓ	77(6)	18(5)	37(5)	3(5)	29(5)	- 2(4)	0.34(4)
O(1)	345(27)	199(22)	277(25)	96(20)	281(23)	97(19)	1.68(15)
O(2)	150(17)	122(17)	112(17)	-34(14)	8(14)	8(14)	1.01(13)
O(3)	131(16)	65(14)	72(16)	3(12)	46(14)	- 8(12)	0.58(15)
O(4)	146(17)	60(14)	68(16)	8(13)	49(14)	8(12)	0.67(13)
O(5)	133(17)	141(18)	102(16)	1(14)	71(14)	-33(14)	0.90(13)
O(6)	104(15)	66(14)	78(14)	- 9(12)	42(12)	13(12)	0.63(12)
O(7)	137(17)	46(14)	95(17)	- 7(12)	42(14)	-13(12)	0.65(14)
O(8)	109(16)	77(15)	84(17)	- 8(12)	17(14)	16(12)	0.96(17)
OH	88(15)	61(14)	78(14)	12(12)	37(12)	1(12)	0.60(11)

†Coefficients in the expression exp-$[U_{11}h^2 + U_{22}k^2 + U_{33}\ell^2 + 2U_{12}hk + 2U_{13}h\ell + 2U_{23}k\ell]$. Estimated standard errors refer to the last digit. The coefficients are each ×10^4.

initially presented a difficult problem owing to strong structural homometricity. Despite encouraging convergences to R ~ 0.20, at least ten different electron density maps were examined until the correct one was found. At this stage we had doubts about the chemical composition and the possibility of twin domains. Nevertheless, Harker sections using the heavy lanthanide atom positions led to a chemically sensible model. The problem was eventually resolved when it was realized that most atoms possessed $y \sim 0 \pm 1/4$.

Rapid convergence followed, from R = 0.18 to 0.059 after five cycles of refinement with isotropic parameters. Anisotropic refinement led to R = 0.033 for all 2586 independent reflections where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} .$$

The final cycle included 42 variable atomic coordinate parameters among the 14 non-equivalent atoms in general positions, 1 scale factor and 84 anisotropic thermal vibration parameters giving a variable parameter to data ratio of 21:1. Programs used in this study include those listed earlier (Moore and Araki, 1976) and the SHELX-76 program system at the Amdahl 470 computer facility at The University of Chicago. Scattering curves for Ce^{3+}, Al^{3+}, Si^{4+} and O^{1-} were obtained from International Tables, vol. 4 (1974) and anomalous dispersion correction, f″, for all metals from Cromer and Liberman (1970).

Atomic coordinate parameters are given in Table 2, anisotropic thermal vibration parameters in Table 3, structure factor tables in Table 4,[1] bond distances and angles in Table 5 and bond length–bond strength relations in Table 6.

Description of the structure

Törnebohmite possesses a structure which is related to a rather large family of compounds. Although we have counted over fifty species, only a few will be discussed here. Table 7 outlines some of these compounds, which have been subdivided into three categories. The first (category I) involves compounds which are probably isostructural, possessing approximately similar axial dimensions, same cell contents (although with differing ionic species) and same space group $P2_1/m$. The second (category II) include törnebohmite and fornacite both of which possess the same space group $P2_1/c$, similar cell dimensions, same structure type but differ from the first category in having a doubled *c*-axis. Category III includes orthorhombic compounds where structures are related, but pyrobelonite with probable space group *Pnma* appears to contain descloizite, which has a nearest *Zellengleich* subgroup $P2_12_12_1$.

All structures are based on an octahedral "back-

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[1] To obtain a copy of Table 4, order Document AM-82-207 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 5. Törnebohmite: bond distances and angles[†]

RE(1)		
Re(1)-O(1)$^{(1)}$	2.298(4)	
-O(8)	2.407(4)	
-O(7)	2.490(4)	
-O(8)$^{(1)}$	2.649(4)	
-O(2)	2.661(4)	
-O(7)$^{(1)}$	2.667(4)	
-OH$^{(3)}$	2.683(4)	
-O(3)	2.724(4)	
-O(4)	2.758(4)	
-O(2)$^{(1)}$	3.011(4)	
Average	2.635	
RE(1)-O(1)	4.237(5)	
O(2)-O(4)	2.572(6)†	
O(2)-O(7)$^{(1)}$	2.578(6)$^{\bigstar}$	
O(3)-OH$^{(3)}$	2.583(6)‡	
O(7)$^{(1)}$-O(8)$^{(1)}$	2.584(6)†	
O(7)-O(8)	2.584(6)$^{\bigstar}$	
O(4)-OH$^{(3)}$	2.677(6)‡	
O(3)-O(4)	2.721(6)$^{\bigstar}$	
O(2)$^{(1)}$-O(8)	2.777(6)	
O(7)-OH$^{(3)}$	2.845(6)	
O(8)-OH$^{(3)}$	2.875(6)	
O(2)$^{(1)}$-O(8)$^{(1)}$	2.940(6)	
O(1)-O(1)$^{(1)}$	2.948(6)	
O(1)$^{(1)}$-O(8)$^{(1)}$	2.950(6)	
O(1)$^{(1)}$-O(3)	3.002(6)	
O(2)-O(7)	3.006(6)	x2
O(1)$^{(1)}$-O(7)$^{(1)}$	3.023(6)	
O(8)-O(8)$^{(1)}$	3.112(6)	
O(1)$^{(1)}$-O(2)	3.197(6)	
O(1)$^{(1)}$-O(4)	3.202(7)$^{\bigstar}$	
O(3)-O(8)	3.284(7)	
O(7)-O(7)$^{(1)}$	3.584(7)	
O(4)-O(7)	3.803(7)	
Average	2.950	

RE(2)	
Re(2)-O(2)	2.427(4)
-O(8)$^{(1)}$	2.473(4)
-O(7)$^{(1)}$	2.530(4)
-O(3)$^{(1)}$	2.540(4)
-O(5)$^{(2)}$	2.546(4)
-O(4)$^{(1)}$	2.593(4)
-O(5)$^{(1)}$	2.761(4)
-O(6)$^{(2)}$	2.782(4)
-O(1)$^{(1)}$	2.929(4)
-O(1)	3.199(4)
Average	2.678
O(1)$^{(1)}$-O(3)$^{(1)}$	2.566(6)†
O(5)$^{(1)}$-O(8)$^{(1)}$	2.576(6)†
O(2)-O(7)$^{(1)}$	2.578(6)$^{\bigstar}$
O(7)$^{(1)}$-O(8)$^{(1)}$	2.584(6)$^{\bigstar}$
O(5)$^{(2)}$-O(6)$^{(2)}$	2.619(6)†
O(1)-O(2)	2.639(6)†
O(4)$^{(1)}$-O(6)$^{(2)}$	2.652(6)‡
O(3)$^{(1)}$-O(6)$^{(2)}$	2.678(6)‡
O(3)$^{(1)}$-O(4)$^{(1)}$	2.721(6)$^{\bigstar}$
O(2)-O(8)$^{(1)}$	2.777(6)
O(1)-O(1)$^{(1)}$	2.948(6)$^{\bigstar}$
O(5)$^{(1)}$-O(5)$^{(2)}$	2.949(6)
O(1)$^{(1)}$-O(8)$^{(1)}$	2.950(6)$^{\bigstar}$
O(5)$^{(2)}$-O(7)$^{(1)}$	2.971(6)
O(1)-O(3)$^{(1)}$	3.002(7)$^{\bigstar}$
O(1)$^{(1)}$-O(2)	3.197(7)
O(1)-O(4)$^{(1)}$	3.202(7)$^{\bigstar}$
O(1)$^{(1)}$-O(5)$^{(1)}$	3.298(7)
O(3)$^{(1)}$-O(5)$^{(1)}$	3.333(7)
O(5)$^{(1)}$-O(6)$^{(2)}$	3.381(7)
O(4)$^{(1)}$-O(5)$^{(2)}$	3.507(7)
O(5)$^{(2)}$-O(8)$^{(1)}$	3.586(7)
O(4)$^{(1)}$-O(7)$^{(1)}$	3.803(7)
O(2)-O(4)$^{(1)}$	3.836(7)
Average	3.015

Al		
Al-OH	1.861(4)	
-OH$^{(3)}$	1.871(4)	
-O(3)$^{(3)}$	1.890(4)	
-O(4)	1.900(4)	
-O(6)$^{(3)}$	1.935(4)	
-O(6)	1.954(4)	
Average	1.902 Å	
O(6)-OH	2.533(6)*	83.1(2)
O(6)$^{(3)}$-OH$^{(3)}$	2.533(6)*	83.5(2)
O(3)$^{(3)}$-OH$^{(3)}$	2.583(6)‡	87.0(2)
O(4)-O(6)$^{(3)}$	2.652(6)‡	87.6(2)
O(4)-OH(3)	2.677(6)	90.5(2)
O(3)$^{(3)}$-O(6)	2.678(6)‡	88.2(2)
O(4)-OH	2.685(6)	91.1(2)
O(3)$^{(3)}$-OH$^{(3)}$	2.694(6)	91.5(2)
O(3)$^{(3)}$-O(6)$^{(3)}$	2.710(6)	90.3(2)
O(6)-OH$^{(3)}$	2.713(6)	90.3(2)
O(6)$^{(3)}$-OH	2.784(6)	94.3(2)
O(4)-O(6)	2.822(6)	94.0(2)
Average	2.672	89.3°

Si(1)		
Si(1)-O(1)	1.590(5)	
-O(2)	1.601(4)	
-O(3)	1.640(4)	
-O(4)	1.643(4)	
Average	1.619	
O(1)-O(3)	2.566(6)	105.2(3)†
O(2)-O(4)	2.572(6)	104.9(2)†
O(1)-O(2)	2.639(6)	111.7(3)†
O(2)-O(3)	2.668(6)	110.8(3)
O(1)-O(4)	2.685(6)	112.3(3)
O(3)-O(4)	2.722(6)	112.0(2)
Average	2.642	109.5

Si(2)		
Si(2)-O(7)	1.616(4)	
-O(8)	1.620(4)	
-O(5)	1.622(4)	
-O(6)	1.672(4)	
Average	1.632	
O(5)-O(8)	2.576(6)†	105.2(2)
O(7)-O(8)	2.584(6)†	106.0(2)
O(5)-O(6)	2.619(6)†	105.3(2)
O(6)-O(7)	2.690(6)	109.8(3)
O(6)-O(8)	2.747(6)	113.1(2)
O(5)-O(7)	2.771(6)	117.7(2)
Average	2.665	109.5

[†] Estimated standard errors in parentheses refer to the last digit. The equivalent positions (referred to Table 2) are designated as superscripts and are (1) = -x, -y, -z; (2) = x, ½-y, ½+z; (3) -x, ½+y, ½-z.

For types of shared edges, † = RE-Si, ★ = RE-RE, ‡ = RE-Al and * = Al-Al.

bone'' which consists of a linear edge-sharing *trans*-chain which is coupled at corners by $[TO_4]$ tetrahedral groups. The orientation in Figure 1 shows the underlying structural principle where one tetrahedron links within a chain at two corners and the other links at only one corner, the latter at one of the edge-shared octahedral vertices. The remaining shared edge vertex of the octahedral chain is occupied by either $(OH)^-$ or $(H_2O)^\circ$ ligands, and results in an open region in the structure which, like the tetrahedron, alternates in *trans* fashion. This open region is the key to distinguishing categories I and II from category III. Indeed, the first two categories are monoclinic while the third is orthorhombic.

How are the first two categories distinguished? Topologically, the structural principles are the same but slight distortions away from {m} symmetry normal to the *b*-axis result in a doubling of the *c*-axial direction and relatively weak *hkl* (l = 2n + 1) reflections.

The distinction between categories I and II, and category III can be appreciated in Figures 2a and 2b, of törnebohmite and descloizite structures projected down [100] respectively. In törnebohmite,

Table 6. Törnebohmite: electrostatic valence balance of cations and anions†

Anions	RE(1)	RE(2)	Si(1)	Si(2)	Al	Δp_0
O(1)	1	2	1	------	------	-0.10
	-0.337	+0.251	-0.029	------	------	
	------	+0.521	------	------	------	
O(2)	2	1	1	------	------	-0.10
	+0.026	-0.251	-0.018	------	------	
	+0.376	------	------	------	------	
O(3)	1	1	1	------	1	+0.10
	+0.089	-0.138	-0.012	------	-0.012	
	------	------	------	------	------	
O(4)	1	1	1	------	1	+0.10
	+0.123	-0.085	+0.024	------	-0.002	
	------	------	------	------	------	
O(5)	------	2	------	1	------	-0.40
	------	-0.132	------	-0.010	------	
	------	+0.083	------	------	------	
O(6)	------	1	------	1	2	+0.30
	------	+0.104	------	+0.040	+0.033	
	------	------	------	------	+0.052	
O(7)	2	1	------	1	------	-0.10
	-0.145	-0.148	------	-0.016	------	
	+0.032	------	------	------	------	
O(8)	2	1	------	1	------	-0.10
	-0.228	-0.205	------	-0.012	------	
	+0.014	------	------	------	------	
OH	1	------	------	------	2	+0.30
	+0.048	------	------	------	-0.041	
	------	------	------	------	-0.031	

†A bond strength deviation refers to the polyhedral average subtracted from the individual bond distance. The Δp_0 = deviations of electrostatic bond strength sum from neutrality (p_0 = 2.00 e.s.u.; for OH, p_0 = 1.00 e.s.u.). Bond length deviations which conform to Δp_0 are underlined.

the interchain open regions alternate, such that the large cations (such as REE^{3+}, Pb^{2+}, *etc.*) occur in between and form a continuous slab parallel to {001}. This serrated slab does not fit the underlying structural motif in Figure 1 along the [001] direction. In descloizite, however, the tetrahedra are corner-shared to form a completed linkage of the structural motifs along [001]. A consequence of this is a distinctly different chemical stoichiometry, *viz.*

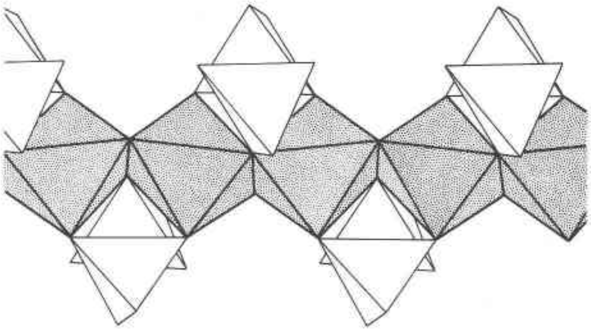

Fig. 1. Underlying octahedral-tetrahedral backbone of the törnebohmite crystal structure. Note that one tetrahedron spans two octahedral vertices within the linear octahedral edge-sharing chain and the other tetrahedron shares one vertex with two fused octahedra. Symmetry independent tetrahedra alternate in *trans* fashion with respect to an octahedron. The $(OH)^-$ ligand resides at the free octahedral vertex.

Categories I & II	törnebohmite	A(1)A(2)BXYZ	$RE_2Al(SiO_4)_2(OH)$
Category III	descloizite	$A(1)A(2)B_2XYZ_2$	$Pb_2Zn_2(VO_4)_2(OH)_2$

Yet other octahedral chain motifs may occur among the rare earth silicates. Allanite, $RECa(Fe,Mg)Al_2O(OH)[SiO_4][Si_2O_7]$, an epidote structure (Dollase, 1971); and perrierite–chevkinite, $RE_4Mg_2Ti_3O_8[Si_2O_7]_2$ (Calvo and Faggiani, 1974) both contain the linear edge-sharing octahedral column and interchain bridging tetrahedra as in Figure 1, but differ in the additional linkages, suggesting that combinatorial study on the octahedral column may be very fruitful.

Table 7. Törnebohmite and related structures†

	A_1	A_2	B	X	Y	Z	S.G.	a(Å)	b(Å)	c(Å)	β	Reference
Brackebuschite	Pb(II)	Pb(II)	Mn(II)	VO_4	VO_4	H_2O	$P2_1/m$	7.68	6.18	8.88	111°50′	Donaldson and Barnes (1955b)
Arsenbrackebuschite	Pb(II)	Pb(II)	Fe(II)	AsO_4	AsO_4	H_2O	$P2_1/m$	7.764	6.045	9.022	112°30′	Abraham et al. (1978)
Tsumebite	Pb(II)	Pb(II)	Cu(II)	PO_4	SO_4	OH	$P2_1/m$	8.70	5.80	7.85	111°30′	Bideaux et al. (1966)
Goedkenite	Sr(II)	Sr(II)	Al(III)	PO_4	PO_4	OH	$P2_1/m$	8.45	5.74	7.26	113°42′	Moore et al. (1975)
Törnebohmite	Ce(III)	Ce(III)	Al(III)	SiO_4	SiO_4	OH	$P2_1/c$	7.383	5.673	16.937	112°03′	This study
Fornacite	Pb(II)	Pb(II)	Cu(II)	AsO_4	$Cr(VI)O_4$	OH	$P2_1/c$	7.91	5.91	17.46	109°30′	Cocco et al. (1967)
Pyrobelonite	Pb(II)	Pb(II)	2Mn(II)	VO_4	VO_4	2(OH)	Pnma	7.66	6.19	9.52	--	Donaldson and Barnes (1955a)
Descloizite	Pb(II)	Pb(II)	2Zn(II)	VO_4	VO_4	2(OH)	$P2_12_12_1$	7.607	6.074	9.446	--	Qurashi and Barnes (1954)

†For general stoichiometry A_1 A_2 B X Y Z.

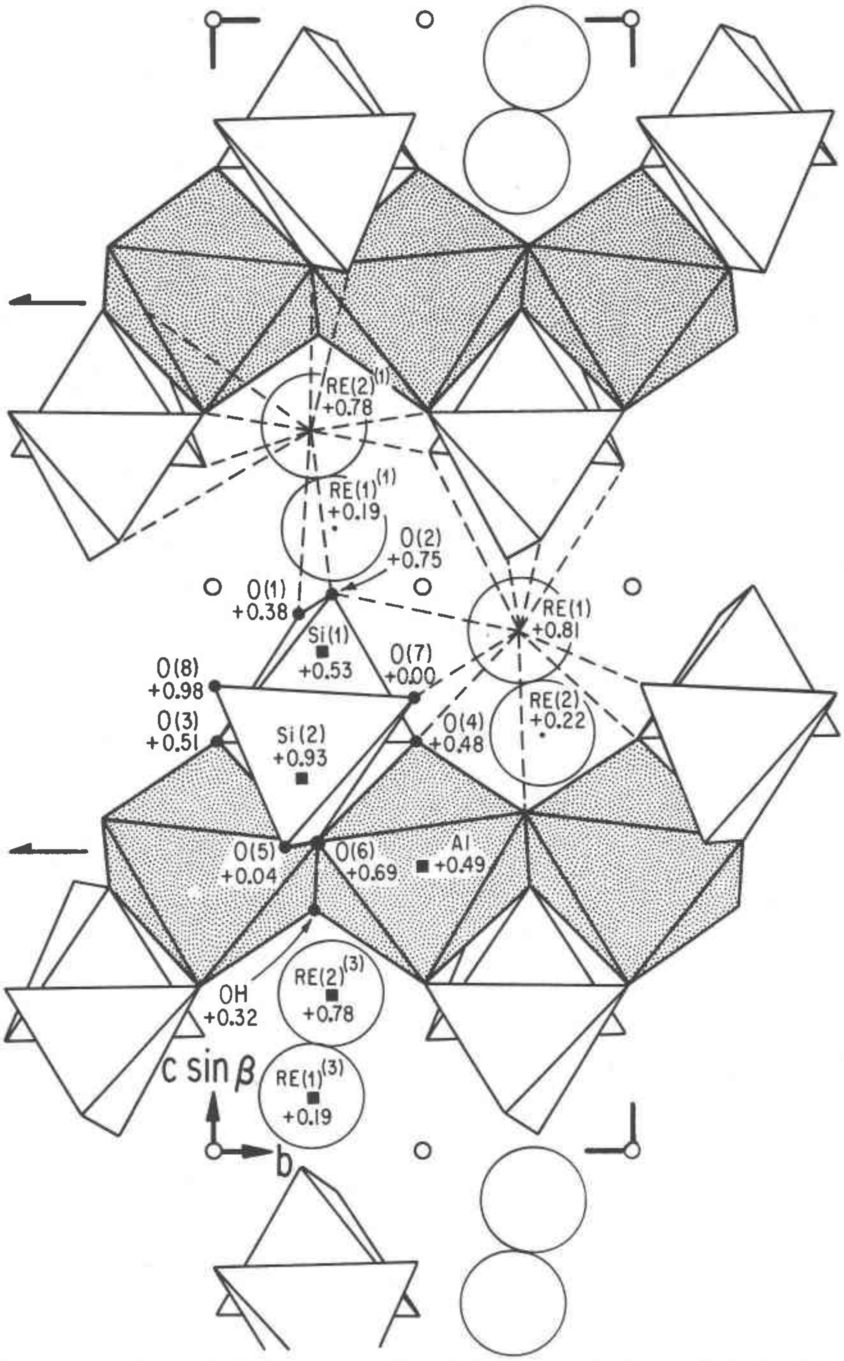

Fig. 2a. Polyhedral diagram of the törnebohmite structure down [100]. The octahedral-tetrahedral backbone can be easily seen. Inversion centers and 2_1-screw axes are drawn in. Heights are given as fractional coordinates in x. RE–O bonds are dashed in.

Bond distances and angles

Table 5 lists the polyhedral distances and angles for törnebohmite. We chose coordination numbers of ten for RE(1) and RE(2) and the RE–O distances range between 2.30 and 3.20Å; beyond these coordination spheres are cation–cation distances which are an effective cutoff value for these polyhedra of high order. The large polyhedra were triangulated and all edge distances were calculated. From Euler's Characteristic Theorem, there exist $N_0 = 10$, $N_1 = 24$ and $N_2 = 16$ geometrical elements. Ac-

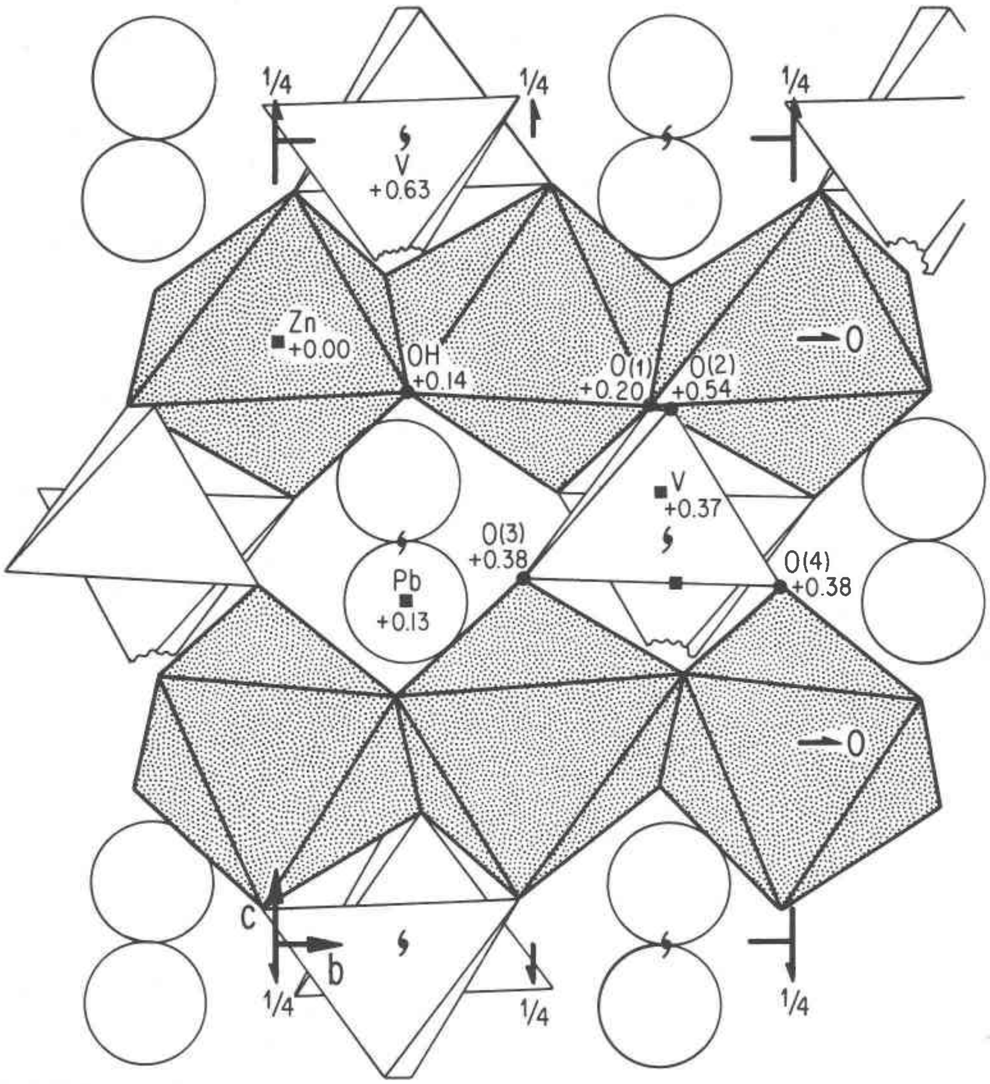

Fig. 2b. Polyhedral diagram of the descloizite crystal structure after Qurashi and Barnes (1954). Note the fusion of adjacent backbones by the (VO_4) tetrahedra. These are the free inter-octahedral vertices in törnebohmite.

counting for cation charge and its ionic radius, expected order of repulsions, or contractions of shared edges, would be (RE^{3+}–Si^{4+}), (Al^{3+}–Al^{3+}), (RE^{3+}–Al^{3+}) and (RE^{3+}–RE^{3+}) denoted by symbols †, ★, ‡ and ☆ respectively in Table 5.

Table 6 lists the deviations of individual polyhedral distances from the individual polyhedral averages. These bond length–bond strength deviations express trends. A relation between such deviations for *all* individual bonds in that crystal structure can be ascertained by taking the total number of entries which conform in both bond length and bond strength deviations and divide that number by the total entries in the tabulation (*e.g.*, Table 6). If there existed a perfect correlation level, then this ratio would be 1.00; complete contradictions would give a ratio 0.00; the ratio 0.50 would essentially state that the correlation could be either true or false. Therefore, values greater than 0.50 at least express a trend in accord with the total bond length–bond strength entries. The value for törnebohmite is 20/34 = 0.59, compared with the more complex structures fillowite, 49/84 = 0.58 (Araki and Moore, 1981) and dickinsonite, 60/93 = 0.65 (Moore *et al.*, 1981). Of course, the electrostatic model works best for ions with inert gas configurations; in Table 6, the glaring contradictions occur for OH, since the hydrogen atom was not located in the structure and the O–H bond distance is not known. Nor are the OH · · · O bonds known. In our calculation, we merely assumed $p_0 = 1.00$ e.s.u. for $(OH)^-$.

Some chemical isomorphisms

There are two interesting cases of isomorphisms where rare earth silicates can be linked structurally to the alkaline earth phosphates; and where alkali phosphates can be linked to alkaline earth silicates, *e.g.*,

$$\begin{array}{lcl} \text{(I)} & \multirow{2}{*}{and} & RE^{3+}Si^{4+} \rightleftarrows Ca^{2+}P^{5+} \\ \text{(II)} & & Na^{1+}P^{5+} \rightleftarrows Ca^{2+}Si^{4+} \end{array}$$

Examples abound for these compounds. One interesting case of (II) was noted by Moore (1975) for the pair:

$Na_2CaMg(PO_4)_2$	brianite
$Ca_2CaMg(SiO_4)_2$	merwinite

Many other examples exist, such as $NaMn(PO_4)$ (natrophilite) and $CaMn(SiO_4)$ (glaucochroite).

Even more intriguing, are the rare earth silicates and alkaline earth phosphate analogues. Some examples for (I) include:

$RE^{3+}Si^{4+}$	
$RE_2Al(OH)(SiO_4)_2$	törnebohmite
$RE_3Ca_2(OH)(SiO_4)_3$	britholite
$RE_{14}Ca_4Mg_2(SiO_4)_{12}(SiO_3OH)_2$	cerite
$Ca^{2+}P^{5+}$	
$(Sr,Ca)_2Al(OH)(PO_4)_2$	goedkenite
$Ca_5(OH)(PO_4)_3$	hydroxyl–apatite
$Ca_{14}Ca_4Mg_2(PO_4)_{12}(PO_3OH)_2$	whitlockite

We have just refined the cerite structure, confirming its isomorphism with whitlockite.

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