

Paratobermorite, $\text{Ca}_4(\text{Al}_{0.5}\text{Si}_{0.5})_2\text{Si}_4\text{O}_{16}(\text{OH})\cdot 2\text{H}_2\text{O}\cdot (\text{Ca}\cdot 3\text{H}_2\text{O})$, a new tobermorite-supergrout mineral with a novel topological type of the microporous crystal structure

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ABSTRACT

A new mineral paratobermorite with the ideal crystal-chemical formula $\text{Ca}_4(\text{Al}_{0.5}\text{Si}_{0.5})_2\text{Si}_4\text{O}_{16}(\text{OH})\cdot 2\text{H}_2\text{O}\cdot (\text{Ca}\cdot 3\text{H}_2\text{O})$ is a member of the tobermorite group within the tobermorite supergroup. It was found at the Bazhenovskoe chrysotile asbestos deposit, Central Urals, Russia, in cavities of grossular rodingite in association with prehnite, pectolite, thomsonite-Ca, and calcite. Paratobermorite occurs as well-shaped prismatic to acicular crystals up to $1 \times 1.5 \times 8 \text{ mm}^3$ typically assembled in spray- or bush-like radial clusters or open-work aggregates up to 1.5 cm across, which form interrupted crusts up to $3 \times 5 \text{ cm}^2$. Paratobermorite is transparent, colorless, pale yellowish, pale beige, or pinkish, with a vitreous luster. The mineral is brittle, with the (001) perfect cleavage. The Mohs hardness is ca. 3½. $D_{\text{meas}} = 2.51 (2)$ and $D_{\text{calc}} = 2.533 \text{ g/cm}^3$. Paratobermorite is optically biaxial (+), $\alpha = 1.565 (2)$, $\beta = 1.566 (2)$, $\gamma = 1.578 (2)$, $2 V_{\text{meas}} = 25 (10)^\circ$ and $2 V_{\text{calc}} = 32^\circ (589 \text{ nm})$. Optical orientation is: $X = c$, $Y = b$, $Z = a$. The chemical composition of paratobermorite (electron microprobe, H_2O by selective sorption from gaseous products of heating) is Na_2O 0.40, K_2O 0.28, CaO 36.60, MnO 0.04, BaO 0.07, Al_2O_3 6.46, SiO_2 42.32, H_2O 14.10, total 100.27 wt%. The empirical formula calculated on the basis of 22 O atoms per formula unit and $(\text{O},\text{OH})_{17}\cdot 5\text{H}_2\text{O}$ is $\text{Na}_{0.09}\text{K}_{0.04}\text{Ca}_{4.72}\text{Al}_{0.92}\text{Si}_{5.09}\text{O}_{15.69}(\text{OH})_{1.31}\cdot 5\text{H}_2\text{O}$. Like other members of the tobermorite supergroup, paratobermorite displays OD character, with two MDO (maximum degree of order) structures: one (MDO1), with non-standard space group $F2/d11$ and the second (MDO2), just corresponding to the structure-type of the new mineral, with non-standard space group $C112_1/m$; its unit-cell parameters obtained from single-crystal X-ray diffraction data are: $a = 11.2220(4)$, $b = 7.3777(2)$, $c = 22.9425(8) \text{ \AA}$, $\gamma = 89.990(3)^\circ$, $V = 1899.46(10) \text{ \AA}^3$, and $Z = 4$; polytype $2M$. The structure of paratobermorite is solved on a single crystal, $R = 8.36\%$. Like structures of other “tobermorites 11 Å,” it is based on the complex layer built of a sheet of sevenfold Ca-centered polyhedra with wollastonite-type chains of T tetrahedra attached to the Ca-sheet from both sides. The tetrahedral (T) sites $T1$ and $T2$ are fully occupied by Si, while alternating $T3$ and $T4$ sites are filled by Al and Si in the ratio 1:1. The chains of tetrahedra belonging to neighboring complex layers share common oxygen vertices of the bridging $T3,4$ tetrahedra to form xonotlite-type ribbons $[\text{Si}_6\text{O}_{17}]^{6-}$. The heteropolyhedral Ca- T -O scaffolding appears as a microporous quasi-framework with wide channels, which contain additional Ca atoms and H_2O molecules. The complex Ca- T -O layers in paratobermorite (so-called “complex modules of type A”) significantly differ in topology (mutual arrangement of T tetrahedra and Ca polyhedra) from the complex Ca- T -O layers in tobermorite (“complex modules of type B”). IR spectrum confirms the presence of nonequivalent H_2O molecules and nonequivalent T -O- T angles involving T atoms of two neighboring wollastonite-type chains. Due to the original topological type of the structure and the presence of significant amount of Al, which substitutes Si, paratobermorite can be considered as a novel microporous material, a perspective cation-exchanger.

Keywords: Paratobermorite, tobermorite group, new mineral, calcium silicate hydrate, OD character, crystal structure, IR spectroscopy, Portland cement, ion exchanger, rodingite, Bazhenovskoe deposit

INTRODUCTION

Tobermorite-supergrout members (or “tobermorites”) belong to a large family of calcium silicate hydrate (C-S-H) compounds, which includes many natural and synthetic representatives. For

many years, “tobermorites” have been the focus of research by crystal chemists and material scientists due to their close relationships with the C-S-H compounds formed during the Portland cement hydration (Richardson 2008). In addition, “tobermorites” demonstrate cation exchange properties and can be used in waste disposal (Bonaccorsi and Merlino 2005).

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Natural “tobermorites” are united in the tobermorite supergroup. Until recently, this supergroup included five mineral species: tobermorite, kenotobermorite (forming the tobermorite group), clinotobermorite, plombiérite, and riversideite (Biagioni et al. 2015; see below for details).

In this paper we describe a new representative of the tobermorite group which differs from other members of the tobermorite supergroup not only in chemical features, symmetry, and unit cell metrics but also in the topology of the crystal structure, which is the most significant individual feature of the new mineral. It is named “paratobermorite” from the Greek *παρά* for “near” and the relationship to tobermorite. Both the new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2020-100). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under catalog number 97513.

TOBERMORITE-SUPERGROUP MINERALS: HISTORICAL BACKGROUND AND GENERAL CRYSTAL-CHEMICAL FEATURES

Historically, among “tobermorites” three types of minerals, so-called tobermorites 14, 11, and 9 Å were distinguished in correspondence with the strongest basal *d*-spacing in a powder X-ray diffractogram. In terms of mineral names, they correspond to plombiérite, tobermorite, and riversideite, respectively (Taylor 1953, 1964; McConnell 1954). The name tobermorite was introduced by Heddle (1880) for a new mineral described from four localities in Scotland, including three near Tobermory. Claringbull and Hey (1952), who re-examined the Heddle’s material, found that tobermorite is an individual natural C-S-H phase, which exhibits a main basal reflection in powder X-ray diffraction (XRD) pattern with *d* = 11.3 Å. Based on this, McConnell (1954) applied the mineral name tobermorite to the C-S-H compounds with a 11 Å main basal spacing.

The structure model for tobermorite (tobermorite *s.s.*, or “tobermorite 11 Å”) was first suggested by Megaw and Kelsey (1956) and later elaborated by Mamedov and Belov (1958) and Hamid (1981). The real structure of “tobermorite 11 Å,” its

structural variations, and polytypism was studied by Merlino et al. (1999, 2001) and Merlino and Bonaccorsi (2008). Hydrogen-bearing groups in one of the varieties of “tobermorite 11 Å” were examined in detail by Churakov (2009). Clinotobermorite, a natural C-S-H phase with a 11 Å main basal *d*-spacing, dimorphous with tobermorite, was described as a new mineral species from Fuka, Okayama Prefecture, Japan (Henmi and Kusachi 1992). Its sub-cell structure was determined by Hoffmann and Armbruster (1997), whereas the real structure was defined by Merlino et al. (2000).

In 2015, the IMA-approved nomenclature of the tobermorite supergroup was published. In the frame of this nomenclature (Biagioni et al. 2015), five valid mineral species were distinguished and clearly defined. “Tobermorites 14 Å” are represented by plombiérite with the idealized, end-member formula $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$, “tobermorites 9 Å” by riversideite with the end-member formula $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ and “tobermorites 11 Å” include three species. Tobermorite and clinotobermorite are defined as dimorphs with the idealized, end-member formula $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$. Besides this pair, “tobermorites 11 Å” include kenotobermorite with the end-member formula $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Table 1).

The fundamental building unit in the structures of all tobermorite-super group minerals is the complex module (or complex layer) consisting of a sheet of sevenfold-coordinated Ca-centered polyhedra decorated from both sides by Si-centered tetrahedra (*T*) belonging to wollastonite-type chains $[\text{Si}_3\text{O}_6]^\infty$ (Merlino and Bonaccorsi 2008). This complex module is C-centered and has the periods *a* ≈ 11.2 Å, *b* ≈ 7.3 Å, and thickness *c*₀ ≈ 11.2 Å (Merlino et al. 1999, 2000, 2001; Biagioni et al. 2015). In Figure 1, the complex module is illustrated by the examples taken from “tobermorites 11 Å.” As distinct from plombiérite, in “tobermorites 11 Å” the stacking of the complex modules gives rise to the condensation of wollastonite-type chains of tetrahedra to form the $[\text{Si}_6\text{O}_{17}]^\infty$ double chains (Merlino and Bonaccorsi 2008), also known as xonotlite-type ribbons. In cavities (channels) within the resulting heteropolyhedral Ca-*T*-O quasi-framework, additional cations (typically, Ca, up to one atom per formula unit, below apfu) and H₂O molecules occur (Fig. 2). In particular, the presence or absence of Ca in these cavities is a cause of the difference

TABLE 1. Crystal data of tobermorite-super group minerals belonging to “tobermorites 11 Å”: tobermorite, clinotobermorite, kenotobermorite and paratobermorite (all polytypes known in nature are included)

Mineral	Paratobermorite	Tobermorite	Kenotobermorite		Clinotobermorite	
Simplified formula	$\text{Ca}_2\text{AlSi}_5\text{O}_{16}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	$\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$	$\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$		$\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$	
Ideal (structural) formula ^a	$[\text{Ca}_4(\text{Al}_{0.5}\text{Si}_{0.5})_2\text{Si}_4\text{O}_{16}(\text{OH})_2 \cdot 2\text{H}_2\text{O}] \cdot (\text{Ca} \cdot 3\text{H}_2\text{O})$	$[\text{Ca}_4\text{Si}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}] \cdot (\text{Ca} \cdot 3\text{H}_2\text{O})$	$[\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 2\text{H}_2\text{O}] \cdot (3\text{H}_2\text{O})$		$[\text{Ca}_4\text{Si}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}] \cdot (\text{Ca} \cdot 3\text{H}_2\text{O})$	
Polytype	2M	2M	2M	4O	2M	1A
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$\text{C}112_1/m$	$B11m$	$B11m$	$F2dd$	Cc	$C1$
<i>a</i> , Å	11.2220(4)	6.732	6.735	11.265	11.276	11.274
<i>b</i> , Å	7.3777(2)	7.369	7.385	7.385	7.343	7.344
<i>c</i> , Å	22.9425(8)	22.680	22.487	44.970	22.642	11.468
α , °	90	90	90	90	90	99.18
β , °	90	90	90	90	97.28	97.19
γ , °	89.990(3)	123.18	123.25	90	90	90.02
<i>V</i> , Å ³	1899.46(10)	942	935	3742	1860	930
<i>Z</i>	4	2	2	8	4	2
Source	This work	Merlino et al. (2001); Biagioni et al. (2015)	Merlino et al. (1999, 2001); Biagioni et al. (2015)		Merlino et al. 1999, 2000; Biagioni et al. 2015	

Notes: Unit cells of all listed minerals are given in the same setting corresponding to the orientation of layers of Ca-polyhedra in the *ab* plane. Plombiérite (“tobermorite 14 Å”) and insufficiently studied riversideite (“tobermorite 9 Å”) are not included.

^a Written in accordance with the IMA-accepted nomenclature of tobermorite-super group minerals (Biagioni et al. 2015).

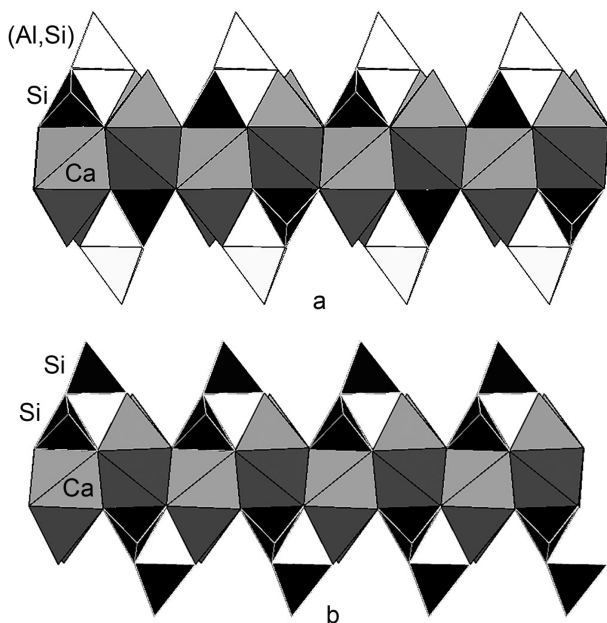


FIGURE 1. Two topological types of the complex Ca-T-O module, a fundamental building unit in the crystal structures of tobermorite-super group minerals: (a) complex module of type A in paratobormorite and (b) complex module of type B in tobermorite [drawn after Merlino et al. (2001)].

in the number of Ca apfu between tobermorite $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$ and kenotobormorite $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Biagioni et al. 2015). The presence of these wide channels confers the properties of “tobermorites” as ion-exchangers.

Bonaccorsi and Merlino (2005) stressed that there are two geometrically distinct ways to place the chains of tetrahedra on the two sides of the calcium sheet in the complex module. In the first one, the bridging tetrahedra are placed at right on one side and at left on the other side (or vice versa), with respect to the disilicate groups of the corresponding chain. Such a layer was marked as a “complex module of type A.” In a second way, the bridging tetrahedra on both sides are all placed at left (or all placed at right) with respect to the corresponding disilicate groups. The layer of this type was called “complex module of type B” (Bonaccorsi and Merlino 2005; Biagioni et al. 2015). Thus, the complex modules of types A and B are topologically different (Fig. 1). The complex module of type B is known in tobermorite and kenotobormorite, whereas the complex module of type A is known in clinotobormorite. Now it is found in paratobormorite.

POLYTYPIC ASPECTS IN TOBERMORITE GROUP OF MINERALS

The various members of the “tobermorite supergroup” present an order-disorder (OD) character (Dornberger-Schiff 1956, 1964, 1966; Ferraris et al. 2008) related to the metrical relationships between the calcium polyhedral module, with a repeat of 3.56 Å, and the wollastonite-type chains, with a periodicity of 7.3 Å. The chains may be connected to the calcium layers in two distinct but equivalent positions, shifted by 3.65 Å in the **b**

direction. Consequently, the various phases of the tobermorite supergroup can be described in terms of OD layers, which may stack in two different ways along c^* , giving rise to a whole family of disordered or ordered sequences (polytypes).

In all the polytypes of a family (but also in the disordered sequences), pairs of adjacent layers are geometrically equivalent (principle of OD structures). In each family, two main polytypes exist, corresponding to the sequences in which not only pairs but also triples, quadruples, ... n -tuples of layers are geometrically

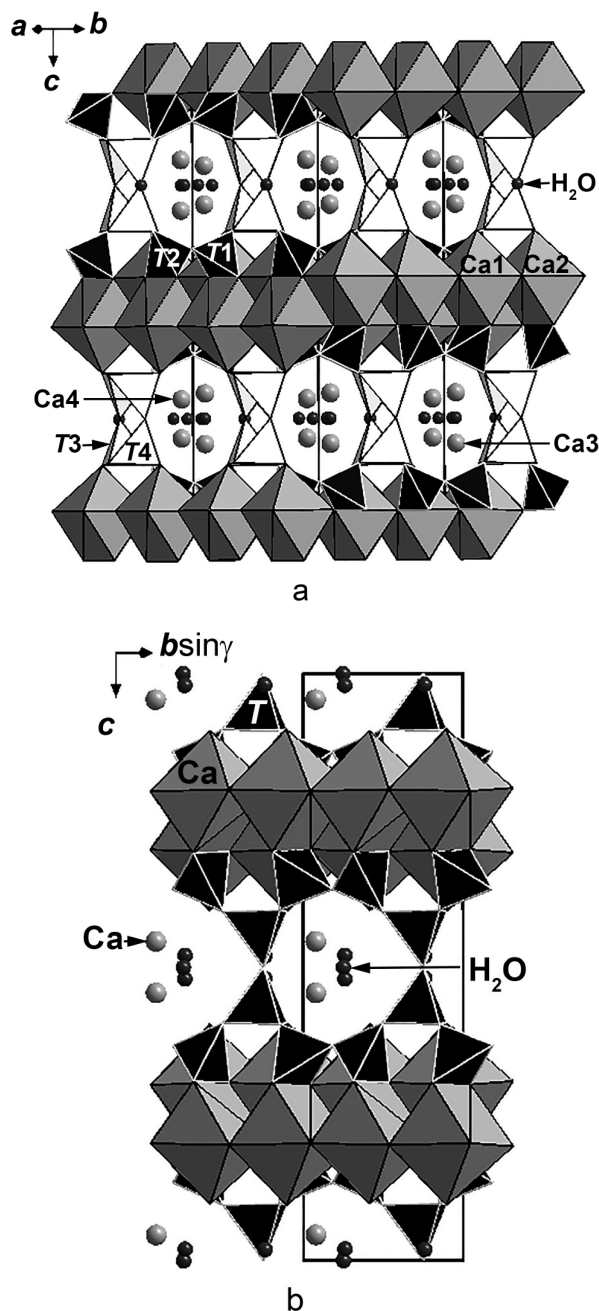


FIGURE 2. The crystal structures of paratobormorite (a) and tobermorite [drawn after Merlino et al. (2001)] (b). The unit cells are outlined.

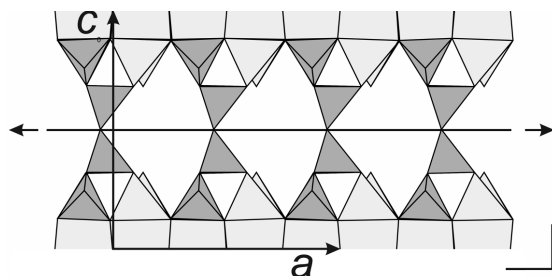


FIGURE 3. OD Layer in tobermorite 11 Å [taken from Merlino et al. (2001)]. The λ operations are indicated.

equivalent, corresponding to the maximum degree of order (MDO) structures.

In the case of tobermorite (tobermorite 11 Å), kenotobermorite and paratobormorite, the OD layer (Fig. 3) presents layer symmetry $C2m(m)$ (one of the possible 80-layer groups) with translation vectors $\mathbf{a}$ and $\mathbf{b}$, third vector $\mathbf{c}_0$ ($a \sim 11.3$, $b \sim 7.35$, $c_0 \sim 11.2$ Å). The parentheses in the last position of the symbol for the layer group indicate the direction of missing periodicity.

For a layer with symmetry $C2m(m)$, there are two possible sets of σ -operations (operations that relate to adjacent layers) compatible with the set of λ -operations (Dornberger-Schiff and Fichtner 1972; Ferraris et al. 2008):

$$\begin{array}{cc} C 2 m (m) & C 2 m (m) \\ \{ 2_s n_{2,s} (n_{s,r}) \} & \{ n_{r,2} 2_r (2_2) \} \end{array} \quad (1)$$

The first of them, with value $\frac{1}{2}$ for both s and r parameters, results in the OD groupoid family symbol:

$$\begin{array}{c} C 2 m (m) \\ \{ 2_{1/2} n_{2,1/2} (n_{1/2,1/2}) \} \end{array}$$

which just consents the derivation of the real structure of tobermorite and kenotobermorite and the definition of their two main polytypes (MDO structures) (Merlino et al. 1999, 2001; Biagioni et al. 2015).

It seems proper to recall that the symbols used for the σ operations are in keeping with those used in the normal space group operations: $2_{1/2}$ represents a rotation of 180° followed by a translation along $\mathbf{a}$ of $a/4$; $n_{2,1/2}$ represents a glide normal to $\mathbf{b}$ with translational components $\mathbf{c}_0$ and $\mathbf{a}/4$; $n_{1/2,1/2}$ represents a glide normal to $\mathbf{c}_0$, with translational components $\mathbf{a}/4$ and $\mathbf{b}/4$.

Layers of $C2mm$ symmetry follow each other in the $\mathbf{c}$ direction, related by the operator $n_{1/2,1/2}$ ($= n_{-1/2,-1/2}$ due to the C centering of the single layer) normal to $\mathbf{c}$, or by the operator $n_{1/2,-1/2}$ ($= n_{-1/2,1/2}$).

The polytype MDO1 corresponds to the sequence in which the operators $n_{1/2,1/2}$ and $n_{1/2,-1/2}$ regularly alternate, resulting in a structure with $F2dd$ symmetry and cell parameters $a \sim 11.3$, $b \sim 7.35$, $c \sim 45.2$ Å (Merlino et al. 2001). MDO2 corresponds to the sequence in which the operator $n_{1/2,1/2}$ is constantly applied, resulting in a structure with C centered cell, with parameters $a \sim 11.3$, $b \sim 7.35$, $c \sim 22.6$ Å, $\gamma \sim 90^\circ$, presenting additional lattice points at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{2}$ (Fig. 3 in Merlino et al. 2001).

A convenient cell may be derived through the transformations $\mathbf{a}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$, thus obtaining a B centered monoclinic cell, space group $B11m$ and cell parameters $a \sim 6.73$, $b \sim 7.35$, $c \sim 22.6$ Å, $\gamma \sim 122.9^\circ$.

In a paper by Merlino and Bonaccorsi (2008), attention has been given to the second set of σ -operations compatible with the layer group symmetry $C2m(m)$. By assuming the value $\frac{1}{2}$ for the r parameter a new OD groupoid family was obtained, which has the symbol:

$$\begin{array}{c} C 2 m (m) \\ \{ n_{1/2,2} 2_{1/2} (2_2) \} \end{array}$$

and by which a new family of OD structures may be obtained.

Merlino and Bonaccorsi (2008) indicated that also in the present case two main polytypes exist: MDO1 is obtained through the constant application of the $[n_{1/2,2} - -]$ operation and presents non-standard space group $F2/d11$, with $a = 11.3$, $b = 7.35$, $c = 45.2$ Å, $\alpha = 90^\circ$; MDO2 is obtained through the regular alternation of the operations $[n_{1/2,2} - -]$ and $[n_{-1/2,2} - -]$ and presents non-standard space group $C112_1/m$, with $a = 11.3$, $b = 7.35$, $c = 22.6$ Å, $\gamma = 90^\circ$. The unit-cell dimensions, space group, and structural arrangement of the last polytype closely correspond to those of paratobormorite.

Tobormorite and kenotobermorite share the same OD family, but show distinct chemical compositions, $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$ for tobermorite and $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ for kenotobermorite. With regard to polytypism, both main polytypes of kenotobermorite have been observed in nature: kenotobermorite-2M ($B11m$, $a = 6.735$, $b = 7.385$, $c = 22.487$ Å, $\gamma = 123.25^\circ$) and kenotobermorite-4O ($F2dd$, $a = 11.265$, $b = 7.385$, $c = 44.97$ Å); whereas only the monoclinic polytype tobermorite-2M ($B11m$, $a = 6.732$, $b = 7.369$, $c = 22.680$ Å, $\gamma = 123.18^\circ$) has been found. Paratobormorite, $\text{Ca}_5\text{AlSi}_5\text{O}_{16}(\text{OH}) \cdot 5\text{H}_2\text{O}$ has a peculiar OD character, pertaining to a different OD family. Similar to the case of tobermorite, so far only the polytype paratobormorite-2M has been found in nature.

ANALYTICAL METHODS AND DATA PROCESSING DETAILS

The chemical composition of paratobormorite was determined by electron microprobe in the Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University (MSU), using a Jeol JSM-6480LV scanning electron microscope (SEM) equipped with an INCA-Wave 500 wavelength-dispersive spectrometer, with an acceleration voltage of 20 kV, a beam current of 10 nA; the electron beam was rastered to the $5 \times 5 \mu\text{m}^2$ area. The standards used are listed in Table 2. The morphology of paratobormorite crystals and aggregates was characterized using the same SEM.

H_2O content was determined by the Alimarin method [the Penfield method modified for small samples and involving selective sorption of H_2O on $\text{Mg}(\text{ClO}_4)_2$ from gaseous products obtained by heating the mineral at 1080°C in oxygen at 1 atm]. Two measurements were performed, and the results were averaged. The attempt to measure CO_2 content was made using the method of selective sorption of CO_2 on askarite (an asbestiform material saturated with NaOH) from gaseous products obtained by heating the mineral at 1080°C in oxygen at 1 atm. This experiment showed the absence of CO_2 in paratobormorite, which is in agreement with both IR spectroscopy and structure data (see below).

To obtain infrared (IR) absorption spectrum, powdered sample of paratobormorite was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1} . A total of 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a

TABLE 2. Chemical composition (wt%) of paratobormorite

Constituent	Mean ^a	Range	St.dev. (σ)	Probe standard
Na ₂ O	0.40	0.29–0.47	0.08	NaCl
K ₂ O	0.28	0.23–0.33	0.04	microcline
CaO	36.60	36.26–36.82	0.26	plagioclase
MnO	0.04	0.00–0.11	0.04	MnTiO ₃
BaO	0.07	0.00–0.14	0.06	BaF ₂
Al ₂ O ₃	6.46	6.30–6.72	0.19	plagioclase
SiO ₂	42.32	42.03–42.71	0.32	diopside
H ₂ O	14.10	13.83–14.37		
Total	100.27			

^a Averaged for four spot analyses. Contents of other elements with atomic numbers higher than that of carbon are below detection limits.

reference. A sample of tobermorite (tobermorite-2M) from the Pervomaiskiy quarry, Mt. Bol'shoy Kermen, Bakhchisaray district, Crimea Peninsula was prepared and studied using the same procedures for comparison.

Powder XRD study of paratobormorite was carried out using a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a curved image plate detector (Debye-Scherrer geometry, $r = 127.4$ mm) and CoK α radiation source (rotating anode; 40 kV, 15 mA, and 12 min exposure time; powdered sample of spherical form prepared with X-ray amorphous glue was studied), with Rigaku VariMax microfocus mirror optics. Imaging plate-to-profile data conversion was performed using *osc2xrd* software (Britvin et al. 2017).

Single-crystal XRD studies of paratobormorite were carried out on a crystal of $0.21 \times 0.30 \times 0.63$ mm³ in size using an Xcalibur S single-crystal diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using CrysAlisPro version 1.171.39.46 (Rigaku Oxford Diffraction 2018). The data were corrected for Lorentz factor and polarization effect.

The crystal structure of paratobormorite was solved by direct methods and refined using the SHELX software package (Sheldrick 2015) to $R = 0.0831$ for 2076 unique reflections with $I > 2\sigma(I)$ in the frame of monoclinic space group $P2_1/m$ [unit-cell parameters: $a = 6.7149(2)$, $b = 22.9441(8)$, $c = 6.7162(3)$ Å, $\beta = 113.358(4)^\circ$]. In this setting, the a and c parameters of the unit cell have nearly the same values, and the transition to a pseudo-orthorhombic unit cell can be performed by applying the matrix $10\bar{1}/101/0\bar{1}0$. The unit cell obtained is comparable with those suggested for tobermorite ("tobermorite 11 Å") and other closely related tobermorite-supergroup minerals reported (Merlino et al. 1999, 2000, 2001; Merlino and Bonaccorsi 2008; Biagioni et al. 2015) (Table 1). We have re-analyzed single-crystal XRD data and refined the structure of paratobormorite in the non-standard space group $C112_1/m$ to $R = 0.0836$ for 2055 unique reflections with $I > 2\sigma(I)$. For ease of comparison with other "tobermorite 11 Å" phases, $C112_1/m$ is chosen as the "natural" space group for paratobormorite (Table 1). In both structure models of paratobormorite, microtwinning has been observed. The transition matrices $001/0\bar{1}0/100$ (space group $P2_1/m$) and $\bar{1}00/010/001$ (space group $C112_1/m$) are found, and the refined twin ratio is 0.53:0.47. Complete sets of crystallographic data for both models, with the space groups $P2_1/m$ and $C112_1/m$, can be retrieved from the Online Materials¹ CIF file.

All attempts to obtain a reasonable structure model for paratobormorite in the frame of orthorhombic symmetry were unsuccessful. The PLATON program (Spek 2003) did not detect higher metrics or crystallographic symmetry for the monoclinic model.

RESULTS AND DISCUSSION

Occurrence

Paratobormorite was found at the Bazhenovskoe deposit of chrysotile asbestos located at the eastern border of the city of Asbest, Sverdlovsk Oblast, Central (Middle) Urals, Russia.

The Bazhenovskoe deposit related to the Bazhenovsky gabbro-harzburgite intrusion is one of the world's largest deposits of high-quality chrysotile asbestos. It was discovered in 1885 and has been operating since 1889. From the mineralogical viewpoint, Bazhenovskoe is mainly known due to rodingites formed as a result of low-grade metamorphism after numerous gabbro dikes hosted by serpentinites. Geological and mineralogical data on Bazhenovskoe rodingites were summarized by Erokhin (2017).

One of the unique mineralogical features of the Bazhenovskoe deposit is the abundance and diversity of C-S-H minerals in late, hydrothermal parageneses related to rodingites. Some of them are known here in the form of large and perfect crystals, which is unusual for these minerals. The studies of samples from Bazhenovskoe gave a significant contribution to the mineralogy and crystal chemistry of calcium silicate hydrates, namely tobermorite, plombiérite (Zadov et al. 1995, 2001; Merlino et al. 2001), rosenhahnite (Zadov et al. 2000), and oyelite (Pekov et al. 2019). The discovery of paratobormorite again highlights the important role of the Bazhenovskoe deposit for the mineralogy of calcium silicate hydrates.

The new mineral specimens were collected in 2019 from a rodingite vein uncovered in the eastern part of the Southern open pit operating on the Bazhenovskoe deposit. This steeply dipping (with a dipping angle of 70–80°) vein about 0.5 m thick is seated in serpentinites and has a near-meridional orientation. In the area where paratobormorite was found, the main rodingite-forming mineral is white, colorless, or grayish massive, fine-grained grossular, and the subordinate mineral is prehnite. Paratobormorite occurs in cavities together with pectolite (represented by both $1A$ and $M2abc$ polytypes), thomsonite-Ca, and calcite. Paratobormorite is a hydrothermal mineral crystallized in a Ca-rich assemblage related to rodingite, a rock formed as a result of metasomatic alteration (rodingitization) of a gabbroid dike cross-cutting serpentinite (Erokhin 2017 and references therein).

General appearance, crystal morphology, physical properties, and optical data

Paratobormorite forms prismatic to acicular crystals, elongated along [010], up to $1 \times 1.5 \times 8$ mm. They are well-shaped, perfectly terminated (Figs. 4, 5a, and 5b) or crude (Fig. 5c), sometimes divergent, and typically assembled in open-work aggregates (Figs. 5c and 6a) up to 1×1.5 cm, spray- or bush-like radial clusters (Fig. 6b) up to 1.3 cm across. Crystal crusts, usually interrupted, of paratobormorite up to 3×5 cm in area and up to 1 cm thick cover grossular and prehnite aggregates, whereas pectolite, thomsonite-Ca and calcite overgrow paratobormorite.

Noteworthy, unlike other "tobermorites," which typically occur (in particular, at Bazhenovskoe) as thin acicular to hair-like individuals (tobermorite, clinotobormorite) or scales (plombiérite), paratobormorite forms relatively thick prismatic crystals (Figs. 4–6). The prismatic zone of paratobormorite crystals is formed by the {100} and {001} faces, and the terminations are formed by the {011} faces (Fig. 4: the pseudo-orthorhombic setting with $\gamma = 90^\circ$ is used). Contact twins on {100} were observed under the microscope in polarized transmitted light; microtwinning with the same plane (100) as a twinning operator (the matrix is $\bar{1}00/010/001$) was found during the crystal structure determination.

Paratobormorite is transparent, colorless, pale yellowish, pale beige, or pinkish, with white streak and vitreous luster. The mineral does not fluoresce in ultraviolet light. Paratobormorite is brittle, the (001) perfect cleavage is observed, and the fracture is stepped. The Mohs hardness is ca. 3½. Density measured by flotation in heavy liquids (bromoform + heptane) is 2.51(2) g/cm³. Density calculated using the empirical formula and unit-cell volume determined from the single-crystal XRD data is 2.533 g/cm³.

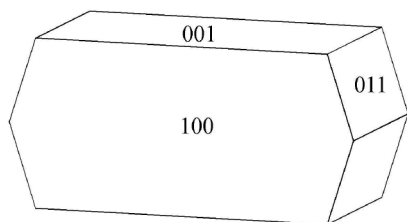


FIGURE 4. Paratobermorite crystal.

Under the microscope, in plane-polarized transmitted light paratobermorite is colorless and non-pleochroic. It is optically biaxial (+), $\alpha = 1.565(2)$, $\beta = 1.566(2)$, $\gamma = 1.578(2)$, $2 V_{\text{meas}} = 25(10)^\circ$ and $2 V_{\text{calc}} = 32^\circ$ (589 nm). Dispersion of optical axes was not observed. Extinction is parallel and elongation is negative. Orientation is as follows: $X = c$, $Y = b$, $Z = a$.

Chemical composition

The chemical composition of paratobermorite in wt% is given in Table 2. The charge-balanced empirical formula calculated on the basis of 22 O atoms per formula unit (apfu) and $(\text{O}, \text{OH})_{17} \cdot 5\text{H}_2\text{O}$ pfu (in accordance with structural data, see below) is $\text{Na}_{0.09}\text{K}_{0.04}\text{Ca}_{4.72}\text{Al}_{0.92}\text{Si}_{5.09}\text{O}_{15.69}(\text{OH})_{1.31} \cdot 5\text{H}_2\text{O}$. The simplified formula is $\text{Ca}_5\text{AlSi}_5\text{O}_{16}(\text{OH}) \cdot 5\text{H}_2\text{O}$. The ideal crystal-chemical formula of paratobermorite written in accordance with the scheme proposed in the frame of the IMA-accepted nomenclature of tobermorite-supergroup minerals (Biagioni et al. 2015) is $\text{Ca}_4(\text{Al}_{0.5}\text{Si}_{0.5})_2\text{Si}_4\text{O}_{16}(\text{OH}) \cdot 2\text{H}_2\text{O} \cdot (\text{Ca} \cdot 3\text{H}_2\text{O})$ (see structure data below).

The compatibility index $1 - (\text{K}_p/\text{K}_c) = -0.008$ if D_{meas} is used and $= 0.001$ if D_{calc} is used. Both values are rated as “superior,” according to Mandarin (1981).

Infrared spectroscopy

In the IR spectra of paratobermorite and tobermorite (Fig. 7), absorption bands are observed in the ranges of $3200\text{--}3600\text{ cm}^{-1}$ (O-H stretching vibrations), $1620\text{--}1650\text{ cm}^{-1}$ (H-O-H bending vibrations of H_2O molecules), $920\text{--}1220\text{ cm}^{-1}$ (Si-O stretching vibrations), $870\text{--}910\text{ cm}^{-1}$ (stretching vibrations involving Al-O bonds), $650\text{--}770\text{ cm}^{-1}$ ($\text{Ca} \cdots \text{O-H}$ and/or O-T-O bending vibrations) and below 600 cm^{-1} (lattice modes involving Si-O stretching, Si-O-Si bending, and H_2O librational vibrations). For the assignment of the IR bands see Zadov et al. (2001, 2006), Organova et al. (2002), and Chukanov and Chervonnyi (2016).

The main differences between the IR spectra of tobermorite and paratobermorite are observed in the ranges of $650\text{--}770$, $870\text{--}910$, $1100\text{--}1220$, and $3200\text{--}3600\text{ cm}^{-1}$, which may be due to significant differences between these minerals in the Al:Si ratio, stacking of wollastonite-type chains, and hydrogen bonding. In particular, the strong IR band at 878 cm^{-1} is a specific feature of paratobermorite, and is not observed in IR spectra of Al-poor tobermorite-group minerals. As shown earlier (Chukanov 2014), in silicates with polymerized SiO_4 tetrahedra, the position of the most high-frequency Si-O-stretching band $\nu_{\text{Si-O}}(\text{max})$, observed in the range of $1000\text{--}1220\text{ cm}^{-1}$, depends on the value of the greatest Si-O-Si angle, ϕ_{SiOSi} . At $\phi_{\text{SiOSi}} = 180^\circ$ the value $\nu_{\text{Si-O}}(\text{max})$ is close to 1200 cm^{-1} . For example, in the IR spectrum of xonotlite [with $\phi_{\text{SiOSi}} = 180^\circ$ at the stacking of wollastonite-type chains: see

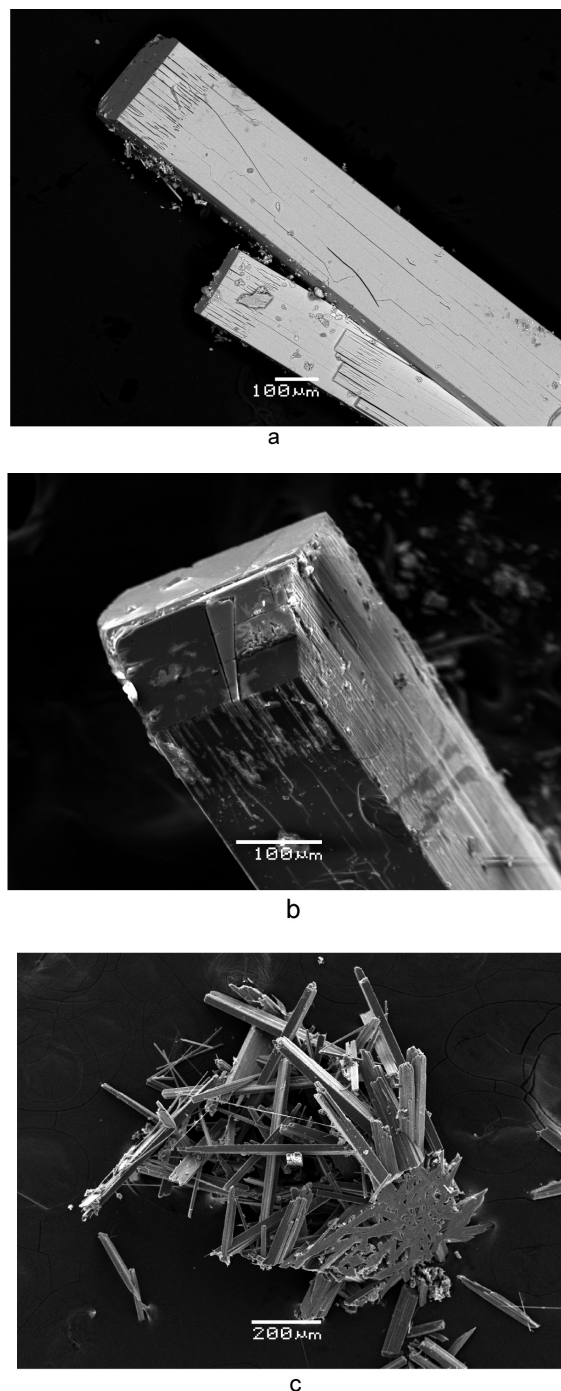


FIGURE 5. Crystals (a and b) and open-work crystal cluster of paratobermorite. SEM images: a = BSE mode; b and c = SE mode.

Kudoh and Takéuchi (1979)] $\nu_{\text{Si-O}}(\text{max})$ is 1203 cm^{-1} . The structure of tobermorite is also based on xonotlite-like ribbons with the ϕ_{SiOSi} angle close to 180° (Merlino et al. 2001). For Al-free tobermorite the $\nu_{\text{Si-O}}(\text{max})$ value is in the range of $1200\text{--}1215\text{ cm}^{-1}$. In the IR spectra of minerals belonging to the palygorskite and sepiolite groups and structurally related minerals [“palysepiolites,” with $\phi_{\text{SiOSi}} \approx 180^\circ$ at the stacking of bands of tetrahedra (Cámara

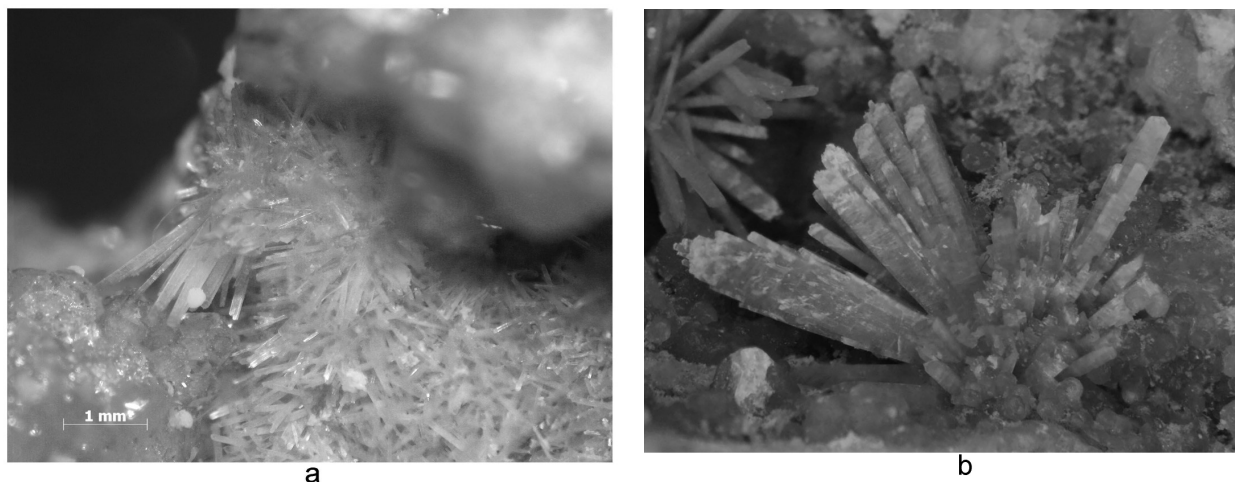


FIGURE 6. Paratobermorite aggregates. (a) Open-work aggregates on almost colorless grossular crystal crust with small milky-white spherulites of pectolite-1A (photo: I.V. Pekov and A.V. Kasatkin). (b) Radial cluster of prismatic crystals (length of the largest, divergent crystal is 8 mm) on prehnite spherulitic crust, which covers a wall of cavity in grossular rodingite (photo: N.N. Koshlyakova). FOV width: **a** = 7.5 mm, **b** = 1.5 cm.

et al. 2002; Ferraris and Gula 2005; Chukanov et al. 2012)] $\nu_{\text{Si-O}}(\text{max})$ varies from 1160 to 1212 cm^{-1} . Another example is suolunite $\text{Ca}_2[\text{Si}_2\text{O}_5(\text{OH})_2] \cdot \text{H}_2\text{O}$ (Ma et al. 1999) with $\phi_{\text{SiOSi}} = 180^\circ$ and $\nu_{\text{Si-O}}(\text{max}) = 1191 \text{ cm}^{-1}$. In contrast to these examples, for cuspidine $\text{Ca}_8(\text{Si}_2\text{O}_7)_2\text{F}_4$ (Saburi et al. 1977) $\phi_{\text{SiOSi}} = 155.4^\circ$, $\nu_{\text{Si-O}}(\text{max}) = 1057 \text{ cm}^{-1}$; for kilchoanite $\text{Ca}_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)$ (Taylor 1971) $\phi_{\text{SiOSi}} = 117^\circ$, $\nu_{\text{Si-O}}(\text{max}) = 1047 \text{ cm}^{-1}$.

The presence of the bands at 1120 and 1167 cm^{-1} in the IR spectrum of paratobermorite (unlike tobermorite: Fig. 7b) indicates the presence of two kinds of the Si-O-Si bridges with large (but significantly smaller than 180°) Si-O-Si angles and is in good agreement with the values of the $T4\text{-}O\text{-}T4$ and $T3\text{-}O\text{-}T3$ angles [$161(2)^\circ$ and $174.0(12)^\circ$, respectively]. In contrast, the IR spectra of tobermorite contain a single band in the range of 1160–1220 cm^{-1} [typically, $1200 \pm 20 \text{ cm}^{-1}$ (Chukanov 2014)],

which corresponds to a Si-O-Si angle close to 180° .

As compared with tobermorite, paratobermorite is characterized by lower wavenumbers of the bands corresponding to O-H stretching vibrations and, consequently, by stronger hydrogen bonds. Based on the correlation reported by Libowitzky (1999), the $\text{D}\cdots\text{A}$ distances for hydrogen bonds in paratobermorite corresponding to the bands at 3220, 2446, and 3538 cm^{-1} are equal to 2.71, 2.83, and 2.97 Å, respectively. Bands of carbonate and orthoborate anions are not observed in the IR spectrum of paratobermorite.

X-ray diffraction data and crystal structure

Powder XRD data of paratobermorite are given in Table 3. Parameters of the monoclinic unit cell calculated from powder data are: $a = 11.245(3)$, $b = 7.391(2)$, $c = 23.01(1)$ Å, $\gamma = 90.00(5)^\circ$, and $V = 1912(2)$ Å³.

The unit-cell parameters obtained for paratobermorite from single-crystal XRD data are: $a = 11.2220(4)$, $b = 7.3777(2)$, $c = 22.9425(8)$ Å, $\gamma = 89.990(3)^\circ$, and $V = 1899.46(10)$ Å³.

The crystal structure description of paratobermorite is reported here for the model in the space group $C112_1/m$. Selected interatomic distances are given in Table 4 and bond valence calculations in Table 5.

The crystal structure of paratobermorite (Fig. 2), like structures of other “tobermorites 11 Å” (Merlino et al. 2001), is based on the complex module built of sheet of Ca-centered polyhedra, parallel to (001), with chains of *T* tetrahedra running along the *b* axis and attached to Ca-sheet. Paratobermorite possesses the “complex module of type A” (Fig. 1a). There are three main *T* sites; according to interatomic distances, *T*1 and *T*2 are fully occupied by Si atoms, while the *T*3 site, as well as the additional *T*4 site (these sites could be only alternatively occupied due to a short *T*3–*T*4 distance), are filled by Al and Si in the ratio 1:1; the site occupancy factors of *T*3 and *T*4 are 0.70 and 0.30, respectively. The chains of tetrahedra belonging to neighboring complex modules share common oxygen vertices of the bridging *T*3,4 tetrahedra to form double chains (xonotlite-type ribbons);

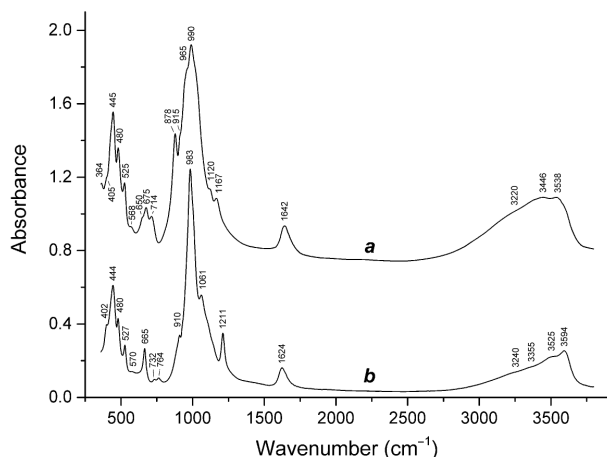


FIGURE 7. Powder infrared absorption spectra of (a) paratobermorite and (b) Al-free tobermorite-2M with the empirical formula $\text{Ca}_{4.68}\text{Si}_6\text{O}_{16.36}(\text{OH})_{0.64} \cdot n\text{H}_2\text{O}$ ($n \sim 5$) from the Pervomaiskiy quarry, Mt. Bol'shoy Kermen, Bakhchisaray district, Crimea Peninsula.

TABLE 3. Powder X-ray diffraction data (*d* in angstroms) of paratobermorite

<i>l</i> _{obs}	<i>D</i> _{obs}	<i>I</i> _{calc} ^a	<i>D</i> _{calc} ^b	<i>hkl</i>
100	11.52	100	11.471	002
5	6.17	1	6.165	110
5	5.97	1, 1	5.954, 5.954	111, $\bar{1}11$
3	5.76	3	5.736	004
24	5.46	17, 1, 2	5.450, 5.431, 5.431	201, 112, $\bar{1}12$
2	4.808	3	4.800	113
3	3.836	2	3.824	006
4	3.650	2, 3	3.681, 3.642	115, 021
17	3.562	13	3.552	205
11	3.329	1, 5, 1	3.337, 3.323, 3.302	310, 023, 311
4	3.259	6	3.249	116
3	3.211	1	3.204	312
51	3.088	18, 16, 2	3.083, 3.083, 3.058	220, $\bar{2}20$, $\bar{3}13$
50	2.982	20, 14	2.977, 2.977	222, 222
10	2.878	3, 1, 1, 6	2.894, 2.884, 2.875, 2.868	117, 314, 025, 008
20	2.838	18	2.830	207
11	2.813	9	2.806	400
6	2.729	3, 1, 1	2.725, 2.715, 2.715	402, 224, $\bar{2}24$
9	2.526	6	2.520	404
7	2.456	6	2.450	027
9	2.328	9	2.321	209
7	2.302	7	2.294	0, 0, 10
10	2.148	3, 4	2.144, 2.144	423, 423
7	2.104	2, 1, 3	2.100, 2.100, 2.097	228, $\bar{2}28$, 029
14	2.013	7, 6	2.008, 2.008	425, 425
22	1.848	5, 9, 11, 2, 2	1.846, 1.846, 1.844, 1.840, 1.840	427, 427, 040, 2, 2, 10, $\bar{2}, 2, 10$
3	1.823	2	1.821	042
2	1.736	2	1.732	605
8	1.685	2, 4, 4	1.683, 1.680, 1.680	2, 0, 13, 429, $\bar{4}29$
8	1.672	4, 4	1.668, 1.668	620, 620
3	1.641	1, 1	1.639, 1.637	0, 0, 14, 245
7	1.629	6	1.624	607
1	1.603	1	1.600	339
2	1.555	2	1.551	048
3	1.549	2, 2	1.545, 1.545	247, $\bar{2}47$
1	1.530	1, 1	1.531, 1.528	3, 3, 10, 442
1	1.480	1	1.476	2, 0, 15
3	1.447	1, 2	1.444, 1.444	249, $\bar{2}49$
2	1.406	3	1.403	800
2	1.395	2	1.392	802

^a For the calculated pattern, only reflections with intensities ≥ 1 are given.^b For the unit-cell parameters calculated from single-crystal data; the strongest reflections are marked in bold.

in general, the heteropolyhedral Ca-*T*-O scaffolding appears as a microporous quasi-framework. Two main Ca sites (Ca1 and Ca2) occupy sevenfold polyhedra, which build the (001) layers of the complex module. Wide channels in the quasi-framework contain two sites partially occupied by Ca (additional Ca sites labeled as Ca3 and Ca4 in Tables 4 and 5 and Fig. 2) and five partially occupied H₂O sites. Water molecules (labeled as Ow1–Ow5 in Tables 4 and 5) are placed on the *m* plane, and for better clarity, their further site splitting and positional disorder were forbidden during the refinement. In terms of polytypism (Merlino and Bonaccorsi 2008; Biagioni et al. 2015), paratobermorite is represented by the 2*M* polytype.

Comparison of paratobermorite with other tobermorite-supergroup minerals

Paratobermorite belongs to “tobermorites 11 Å,” as well as tobermorite, kenotobermorite, and clinotobermorite. All known polytypes of these minerals are reported in Table 1.

Based on the structure arrangement, paratobermorite is included in the tobermorite group within the tobermorite supergroup, together with tobermorite and kenotobermorite. The

belonging of paratobermorite to the tobermorite group is justified by the same type of tetrahedral motif in the structure (Figs. 8a and 8b), whereas clinotobermorite (Fig. 8c) and other tobermorite-supergroup members differ from them in this aspect and, thus, do not belong to the tobermorite group (Biagioni et al. 2015).

The peculiar aspects, which characterize paratobermorite as an individual mineral species and distinguish it from tobermorite and other related minerals, are as follows.

The essential building units of the crystal structures of paratobermorite and related minerals are topologically different. The complex Ca-*T*-O layer in the paratobermorite structure is the “complex module of type A” (Fig. 1a), whereas the complex Ca-*T*-O layer in tobermorite is the “complex module of type B” (Fig. 1b). They significantly differ from each other in the mutual arrangement of *T* tetrahedra and Ca polyhedra (see above). From clinotobermorite, paratobermorite significantly differs in the general topological characteristics of the tetrahedral motif (Figs. 8a and 8c). Tobermorite differs from both these minerals in this aspect (Fig. 8b).

In terms of crystal chemistry, paratobermorite differs from all other tobermorite-supergroup minerals in the Al-Si ordering: it is not the only mineral significantly enriched with Al, but it is the first member of the group in which Al-Si ordering is found. The bridging *T*_{3,4} tetrahedra, which connect adjacent complex layers in the whole structure, are occupied by Si and Al atoms in the ratio 1:1 whereas the *T*_{1,2} tetrahedra are occupied by Si (Tables 4 and 5; Figs. 1, 2, and 8). All other structurally studied minerals of the tobermorite-supergroup display Si-Al disorder: in their structures, all *T* tetrahedra are essentially Si-dominant (Merlino et al. 1999, 2000, 2001; Bonaccorsi and Merlino 2005 and references therein). For this reason, the simplified formula of paratobermorite Ca₅AlSi₅O₁₆(OH)·5H₂O = Ca₅(AlSi)Si₄O₁₆(OH)·5H₂O, differs from all other valid minerals of the tobermorite supergroup that have the simplified formulae with only Si in the tetrahedral part (Biagioni et al. 2015; Table 1) and explains the larger value of the *c* parameter in comparison with that of the other members of the tobermorite group.

Paratobermorite differs from all other tobermorite-supergroup minerals in space group and metrics of the unit cell that is a

TABLE 4. Selected interatomic distances (Å) in the structure of paratobermorite

Ca1–O04F1	2.315(7)	Ca3–Ow3	2.05(5)
–O2	2.360(7)	–O7	2.126(12)
–O3	2.405(8)	–Ow2	2.30(5)
–O4	2.423(8)	–Ow4	2.32(7)
–O1	2.505(6)	–O8	2.328(11)
–O9	2.545(11)	–O6	2.720(14)
–O2	2.547(6)	–O5	2.775(14)
Ca2–O4	2.340(8)	Ca4–Ow5	2.04(6)
–O3	2.360(8)	–O9	2.24(2)
–O2	2.451(7)	–Ow1	2.25(3)
–O8	2.461(8)	–O7	2.49(2)
–O1	2.477(7)	–O6	2.85(2)
–O4	2.550(6)	–O5	2.98(2)
–O3	2.612(7)		
T1–O3	1.603(6)	T3–O73	1.634(3)
–O4	1.612(6)	–O6	1.698(9)
–O5	1.615(8)	–O5	1.721(9)
–O7	1.639(8)	–O8	1.728(9)
T2–O2	1.565(6)	T4–O6	1.694(12)
–O1	1.603(6)	–O74	1.705(9)
–O6	1.645(7)	–O5	1.704(12)
–O7	1.649(8)	–O9	1.806(12)

TABLE 5. Bond-valence calculations for paratobormorite

Site	Ca1	Ca2	T1	T2	T3 = Al _{0.35} Si _{0.35}	T4 = Al _{0.15} Si _{0.15}	Ca3 = Ca _{0.25}	Ca4 = Ca _{0.125}	Σ
O1 = O	0.37 0.23	0.25		1.06					1.91
O2 = O	0.33 0.21	0.26		1.16					1.96
O3 = O	0.30	0.33 0.18	1.06						1.87
O4 = O	0.28	0.35 0.21	1.03						1.87
O5 = O			1.02		0.55	0.25	0.03	0.01	1.86
O6 = O				0.95	0.60	0.26	0.03	0.01	1.85
O7 = O			0.96	0.94			0.14	0.03	2.07
O8 = O _{0.25} (OH) _{0.45} (H ₂ O) _{0.3}		0.26			0.55		0.09		0.90
O9 = (OH) _{0.3} (H ₂ O) _{0.7}	0.21					0.19		0.06	0.46
OT3 = O _{0.70}					0.69 ^{κ→}				1.38
OT4 = O _{0.30}						0.25 ^{κ→}			0.50
Ow1 = H ₂ O _{0.50}								0.05 ^{κ→}	0.10
Ow2 = H ₂ O _{0.50}							0.10 ^{κ→}		0.20
Ow3 = H ₂ O _{0.50}							0.18 ^{κ→}		0.36
Ow4 = H ₂ O _{0.50}							0.09 ^{κ→}		0.18
Ow5 = H ₂ O _{0.50}								0.09 ^{κ→}	0.18
Σ	1.93	1.84	4.07	4.11	2.39	0.95	0.66	0.25	

Note: Bond-valence parameters were taken from Gagné and Hawthorne (2015).

consequence of the above-discussed differences in the topology of structure. The crystal data for “tobermorites 11 Å” are summarized in Table 1 and the *ac* projections of the chains of tetrahedra in the unit cells of tobermorite-2*M*, paratobormorite-2*M* and clinotobormorite-2*M* (i.e., monoclinic polytypes with *c* = 22.5–23 Å) are shown in Figure 8.

IMPLICATIONS

Due to the original topological type of its structure, paratobormorite can be considered as a novel microporous material known only as a natural compound. Despite the fact that it has not yet been synthesized, the discovery of paratobormorite at the Bazhenovskoe deposit makes it possible to study its properties. This finding has both scientific and applied value. On one hand, it confirmed the previously predicted (Merlino and Bonaccorsi 2008) existence of a tobermorite-like structure of this topological type. On the other hand, one can expect the presence of paratobormorite as one of the phases in some cement materials (mainly Portland cement), especially materials with a relatively high aluminum content. The upper limit of the substitution of Si for Al in “tobermorites 11 Å” corresponds to the atomic ratio Al:(Al+Si)

of 0.167, which corresponds to the situation of Si-O-Al around all O atoms bridging the wollastonite-type chains. In the case of paratobormorite, this ratio is 0.153, which exceeds the maximum Al:(Al+Si) values of 0.13–0.14 known for synthetic “tobermorites” (Sakiyama et al. 2000). The formation of Al-rich tobermorite-related compounds occurs most probably in some kinds of Al-rich cements containing active SiO₂. Concretes and ceramics prepared from such cements show significant growth of strength with time (El-Didamony et al. 2000; Chervonnyi et al. 2010). The ion-exchange capability is mainly exhibited by Al-substituted tobermorite-related compounds (Bonaccorsi and Merlino 2005). In particular, these compounds show sorption capacity for several transition metals (Al-Wakeel et al. 2001) and a high selectivity for Cs⁺ and Li⁺ (Tsuji et al. 1991 and references therein). Thus, paratobormorite can be considered as a perspective prototype of microporous materials with technologically important properties (cation-exchanger), probably better than ordinary, Al-poor tobermorites.

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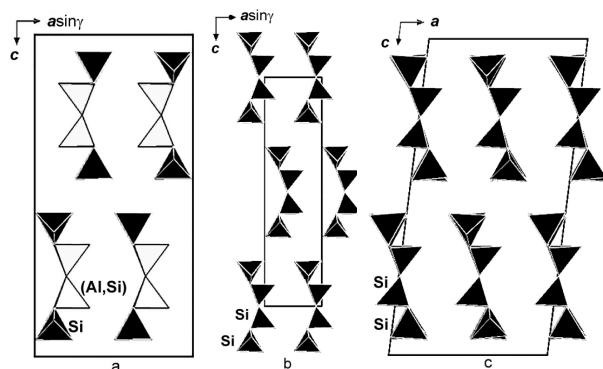


FIGURE 8. Tetrahedral motifs in the structures of 2*M* polytypes of “tobermorites 11 Å.” Paratobormorite (a) for legend see Figure 2; T3- and T4-centered tetrahedra are filled alternatively, and T4 tetrahedra are not shown here for better clarity; tobermorite (b) drawn after Merlino et al. (2001); and clinotobormorite (c) drawn after Merlino et al. (2000). The unit cells are outlined.

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