

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)° and $2 V_{\text{calc}} = 32^\circ$ (589 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 \AA ,” 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 $[\text{Si}_6\text{O}_{17}]^\circ$. 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