

THE SUBSTRUCTURE OF CLINOTOBERMORITE

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The tobermorite group minerals comprises tobermorite and clinotobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot x\text{H}_2\text{O}$), plombierite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$), riversideite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$), okenite ($\text{Ca}_{10}\text{Si}_{18}\text{O}_{46} \cdot 18\text{H}_2\text{O}$), nekoite ($\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7\text{H}_2\text{O}$), oyelite ($\text{Ca}_{10}\text{B}_2\text{Si}_8\text{O}_{29} \cdot 12\text{H}_2\text{O}$), and tacharanite ($\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{33}(\text{OH})_{36}$). This group is defined (STRUNZ, 1970) as being composed of $\text{Ca}(\text{O},\text{OH})_6$ octahedra forming sheets together with wollastonite related Si_3O_9 chains (Dreiereinfachketten) with a periodicity of ca. 7.3 Å. The structure of nekoite (MAMEDOV & BELOV, 1956) consists of tetrahedral sheets and that of okenite (MERLINO, 1983) of sheets and chains, thus at least okenite should only be considered related to the tobermorite group. The structure of tobermorite is strongly disordered, thus only a substructure with $a/2$ and $b/2$ could be refined (HAMID, 1981). TAYLOR (1992) provides strong arguments that also jennite ($\text{Ca}_8(\text{Si}_6\text{O}_{16}(\text{OH})_2)(\text{OH})_8\text{Ca} \cdot 6\text{H}_2\text{O}$) should be considered a member of the tobermorite group. Most of these minerals are known to form during the cement process but also occur in nature as hydrothermal alteration products. The major distinction of the tobermorite phases are the varying water contents lengthening or shortening the interlayer distances and therefore the c-axis of the orthogonal unit cell.

HENMI & KUSACHI (1992) described clinotobermorite from Fuka, Japan as a new mineral, associated with tobermorite, plombierite, apophyllite, calcite.

A sample of natural clinotobermorite, $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18} \cdot 5\text{H}_2\text{O}$, from the Wessels mine, South Africa, provided by R. Dixon, was investigated. It occurs in yellowish-colorless intergrown (001) plates.

The surface structure of the plates was investigated by AFM methods; and the chemical composition was determined by electron microprobe analysis.

Rotation photographs recorded with b as rotation axis indicate that $h, k = \text{even}$, l layers are sharp whereas $h, k = \text{odd}$, l layers are diffuse but still structured with broadened reflection maxima. Subsequently, X-ray single-crystal data were collected on a Siemens P4R diffractometer for structural solution. Only the sharp reflections characteristic of the substructure were considered leading to an I-centered unit cell of $a = 5.593(6)$, $b = 3.645(4)$, $c = 22.46(3)$ Å, $\beta = 96.97(5)^\circ$, $V = 454.42$ Å³. Thus the complete structure has a and b doubled leading to $a = 11.186$, $b = 7.290$ Å.

For the substructure determination 11246 sharp reflections up to $q = 50^\circ$ were collected, followed by data reduction and empirical absorption correction. The substructure was solved and refined from 2598 unique reflections in space group $I2/m$, converging at $R = 8.17\%$ and $wR = 6.49\%$.

The average structure is built by superimposed tetrahedral »Dreiereinfachketten« running along the b-axis (see Fig.). The chains are either connected by Ca layers or loosely linked by disordered Ca and H₂O. As these calcium- water- layers are only partly occupied they allow the tetrahedral chains to develop four different stacking varieties. If the sub- cell structures of tobermorite (HAMID, 1981) and clinotobermorite are compared, there is a difference in stoichiometry. The orthorhombic variant has the composition Ca₉(Si₁₂O₃₀(OH)₆·4H₂O, while the monoclinic variety has Ca₁₀(Si₁₂O₃₂(OH)₄·5H₂O. Thus these two structures should not be regarded polymorphs.

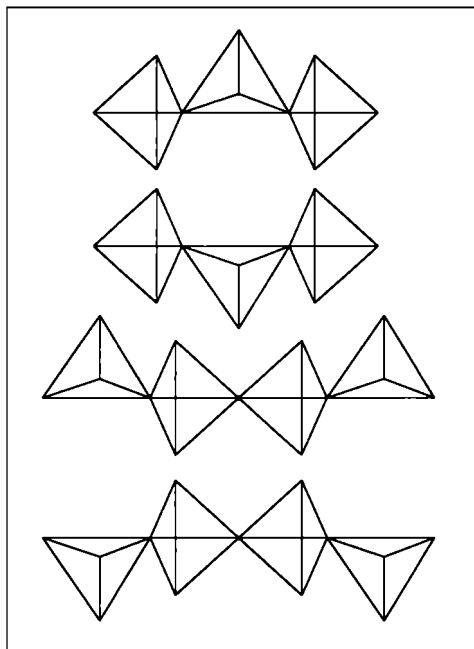


Fig. Four possibilities of chain arrangements observed as superimposed in the substructure.

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