

# Clinotobermorite, $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18}\cdot 5\text{H}_2\text{O}$ , a new mineral from Fuka, Okayama Prefecture, Japan

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## Abstract

Clinotobermorite,  $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18}\cdot 5\text{H}_2\text{O}$ , has been found as a vein-forming mineral in gehlenite-spurrite skarns at Fuka, Okayama Prefecture. It is associated with tobermorite, plombierite, apophyllite, and calcite. The clinotobermorite is colourless or white and occurs as tabular or acicular crystals. It is monoclinic with the space group  $Cc$  or  $C2/c$ . The unit cell dimensions are  $a$  11.331,  $b$  7.353,  $c$  22.67 Å,  $\beta$  96.59°. Microtwinning and stacking disorder on (001) are observed. On heating the clinotobermorite at 300°C, the 002 spacing is reduced from 11.3 to 9.3 Å. Its refractive indices are  $\alpha$  1.575,  $\beta$  1.580,  $\gamma$  1.585, and the density 2.58 g/cm<sup>3</sup> (meas.), 2.69 g/cm<sup>3</sup> (calc). The Moh's hardness is 4.5. Calculation of the analytical data on the basis of six tetrahedral cations shows that this mineral has a simplified chemical formula  $\text{Ca}_{5.3}\text{Si}_6(\text{O},\text{OH},\text{F})_{18}\cdot 5\text{H}_2\text{O}$ . The chemical composition and the unit cell are closely related to those of tobermorite. It is most likely that clinotobermorite is a low-temperature polymorph of tobermorite.

**KEYWORDS:** clinotobermorite, new mineral, tobermorite, Okayama Prefecture, Japan.

## Introduction

TOBERMORITE (11.3 Å tobermorite), plombierite (14 Å tobermorite), tacharanite (12.6 Å tobermorite), riversideite (9.3 Å tobermorite) and oyelite (10 Å tobermorite) have been known as tobermorite group minerals (McConnell, 1954; Heller and Taylor, 1956; and Kusachi *et al.*, 1984).

Several calcium silicate hydrate minerals occur in gehlenite-spurrite skarns at Fuka, Okayama. Three members of the tobermorite group minerals have been reported for this locality; these are tobermorite and plombierite (Mitsuda *et al.*, 1972) and oyelite (Kusachi *et al.*, 1984). During a mineralogical study of tobermorite, we found that some samples which were considered to consist of tobermorite crystals show an X-ray powder diffraction pattern distinctly different from that of usual tobermorite. This mineral is not orthorhombic but monoclinic, and has a chemical composition almost identical to that of tobermorite. Our study revealed that it is a monoclinic polymorph of tobermorite.

We have named this new mineral clinotober-

morite. The mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, in May 1990. The type material of clinotobermorite is deposited at the National Science Museum, Tokyo, Japan.

The present paper deals with the mineralogical properties and mode of occurrence of the clinotobermorite found at Fuka. This mineral has been previously reported as 'monoclinic tobermorite' by the authors in an article in Japanese (Henmi and Kusachi, 1989).

## Occurrence

Skarns were formed on both sides of the quartz monzonite dykes that penetrate limestones at Fuka. The skarns consist mainly of gehlenite and spurrite. Some parts of the skarns were retrogressively altered and were cut by numerous veins consisting of such minerals as tobermorite (Mitsuda *et al.*, 1972), oyelite, bultfonteinite, scawtite, xonotlite (Kusachi *et al.*, 1984), afwillite and jennite (Kusachi *et al.*, 1989).

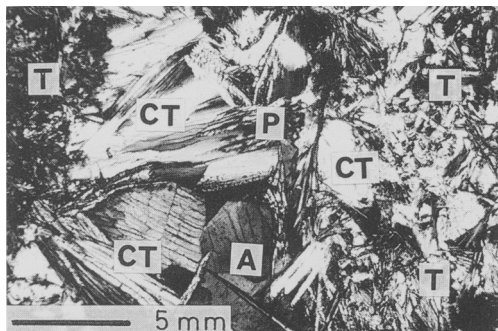


FIG. 1. Photomicrograph of clinotobermorite. Crossed nicols. Abbreviations: T, tobermorite; CT, clinotobermorite; P, plombierite; and A, apophyllite.

Clinotobermorite occurs in veins filling fissures of the contaminated rock which consists mainly of feldspar and pyroxene and may be considered to be a kind of endoskarn. The thickness of the vein varies from one to two centimetres. In these veins, minerals develop from the wall to the

centre of the vein in the following order: calcite, tobermorite, clinotobermorite, plombierite and apophyllite. Fig. 1 shows the occurrence of clinotobermorite in one of these veins.

#### Physical and optical properties

Clinotobermorite occurs as tabular crystals parallel to the *c*-face with up to 5 mm width and as aggregates of acicular crystals parallel to the *b*-axis up to 2 mm in length. The mineral is colourless or white with a vitreous luster in hand specimen and colourless in thin section. Cleavage is perfect on (001) and poor on (100). The mineral is optically biaxial with refractive indices  $\alpha = 1.575$ ,  $\beta = 1.580$  and  $\gamma = 1.585$ . We were unable to obtain its optical axial angles ( $2V$ ) because of well-developed microtwinning. The  $2V$  angle calculated from the refractive indices is  $89.8^\circ$ . Vickers microhardness is 251–174 kg/mm<sup>2</sup> (25 g load) and the Mohs hardness is 4.5. The density measured with heavy liquids is 2.58 g/cm<sup>3</sup>. The calculated density is 2.69 g/cm<sup>3</sup>.

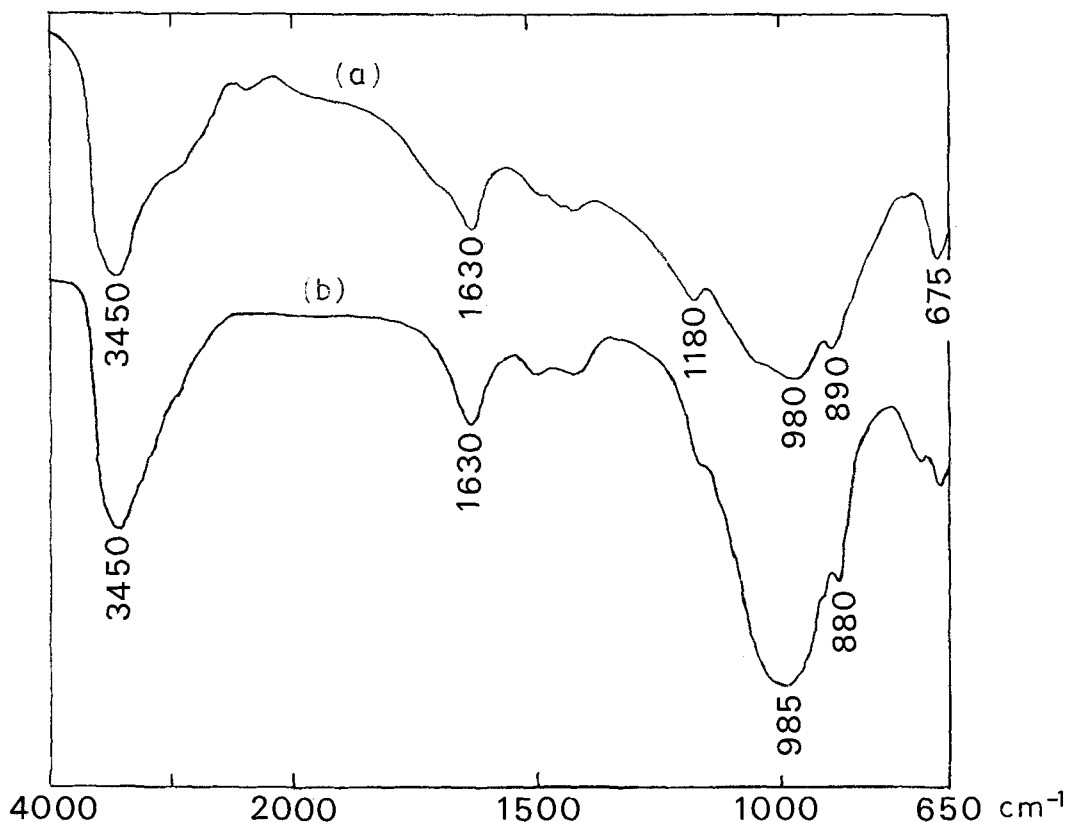


FIG. 2. Infrared spectra for (a) clinotobermorite and (b) tobermorite from Fuka.

Table 1. Chemical analyses of tobermorite group minerals from Fuka.

	clinotobermorite		tobermorite		plombierite	oyelite
	1	1	2	3	1	3
SiO <sub>2</sub>	46.55	48.98	45.12	46.7	43.34	35.3
TiO <sub>2</sub>	0.01	0.03	-	0.0	-	0.0
Al <sub>2</sub> O <sub>3</sub>	0.36	1.03	3.31	2.2	0.39	0.3
B <sub>2</sub> O <sub>3</sub>	0.23	0.03	-	0.0	-	4.8
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.03	0.23	0.0	-	0.0
MnO	0.06	0.03	-	0.0	-	0.0
MgO	0.11	0.04	0.04	0.0	0.00	0.0
CaO	39.04	37.90	35.24	37.3	34.64	41.2
Na <sub>2</sub> O	0.02	0.01	0.24	0.1	0.05	0.1
K <sub>2</sub> O	0.10	0.02	0.23	0.1	0.32	0.0
H <sub>2</sub> O	13.75	11.46	15.52	13.2	19.69	18.7
F	0.18	0.00	-	-	-	-
-O=F	0.08	0.00	-	-	-	-
Total	100.34	99.56	99.93	99.6	99.51*	99.5**

1. Present study.

2. Mitsuda and Taylor (1978).

3. Kusachi et al. (1980 and 1984)

\* includes H<sub>2</sub>O(-) 1.08 %.\*\* includes H<sub>2</sub>O(-) 0.7% and CO<sub>2</sub> 0.4%.

Clinotobermorite loses molecular water on heating at 300 °C in air, resulting in shrinkage of the  $d_{002}$  reflection from 11.3 to 9.3 Å.

The IR spectra of clinotobermorite are measured using the conventional KBr method for the region 4000 to 650 cm<sup>-1</sup>. Fig. 2 shows the spectra of clinotobermorite and tobermorite for comparison. They are very similar. The absorption bands at 3450 cm<sup>-1</sup> are attributed to the OH stretching vibration and the weak bands at 1630 cm<sup>-1</sup> to the OH bending vibration. Numer-

ous bands below 1200 cm<sup>-1</sup> are characteristic of both tobermorite (Mitsuda and Taylor, 1978) and clinotobermorite.

### Chemical composition

The chemical composition of clinotobermorite was obtained using an electron microprobe analyser except for F, B and H<sub>2</sub>O. The concentrations of F, B and H<sub>2</sub>O were determined by

Table 2. Unit cell dimensions of tobermorite group minerals from Fuka.

	clinotobermorite	tobermorite	plombierite	oyelite*
a(Å)	11.331(9)	11.233(3)	11.250(6)	11.25(2)
b(Å)	7.353(7)	7.372(3)	7.344(4)	7.25(2)
c(Å)	22.67(2)	22.56(1)	27.99(1)	20.46(3)
$\beta$ (°)	96.59(7)			

\*Kusachi et al. (1980 and 1984).

Table 3. X-ray powder diffraction data for clinotobermorite and tobermorite from Fuka. The calculated values are based on  $a=11.331$ ,  $b=7.353$ ,  $c=22.67$  Å and  $\beta=96.59^\circ$ . After Henmi and Kusachi (1989).

			clinotobermorite			tobermorite		
h	k	l	d(obs.)	I	d(calc.)	d(obs.)	I	h k l
0	0	2	11.25	100	11.262	11.3	100	0 0 2
0	0	4			5.631	5.63	9	0 0 4
2	0	0	5.60	20	5.628			2 0 0
1	1	-2			5.550			1 1 -2
2	0	-2	5.27	20	5.283	5.45	38	2 0 1
1	1	2			5.264			1 1 2
2	0	2	4.782	10	4.818			2 0 2
0	0	4			3.770			0 0 4
0	0	6	3.745	36	3.754	3.754	7	0 0 6
1	1	-6			3.749			1 1 -6
2	0	-6	3.304	51	3.303	3.642	8	1 1 5
0	0	3			3.302	3.514	30	0 0 3
2	2	2	3.068	45	3.079	3.309	16	2 2 0
2	2	1	3.034	60	3.024			2 2 1
2	2	1	3.012	37	3.012	3.080	92	2 2 0
0	0	6	2.950	25	2.970			0 0 6
3	1	-3			2.944	2.972	70	2 2 2
2	0	3	2.910	23	2.913			2 0 3
0	0	8			2.816	2.806	68b	0 0 8
4	0	0	2.811	41	2.814			4 0 0
4	0	-2			2.807			4 0 -2
2	2	3	2.794	60	2.787			2 2 3
1	1	1			2.781	2.723	6	4 0 2
2	0	-8	2.641	27	2.642			2 0 -8
4	0	-4			2.641	2.513	20	4 0 4
1	1	8	2.495	11	2.502	2.424	9	0 2 7
1	0	8			2.421			1 0 8
2	4	0	2.414	12	2.410			2 4 0
1	1	4			2.409			1 1 4
1	1	3	2.394	20	2.395			1 1 3
1	1	3			2.388			1 1 3
4	0	-1	2.380	15	2.387	2.282	18b	4 0 -1
3	1	6			2.378			3 1 6
0	0	10	2.248	27	2.252	2.250	18	0 0 10
4	2	-1			2.244			4 2 -1
4	2	-3	2.190	13	2.197			4 2 -3
1	3	4			2.185	2.141	18	1 3 4
5	1	1	2.117	8	2.121			5 1 1
4	0	-8			2.115	2.079	13	4 0 -8
4	1	10			2.079			4 1 10
5	1	2	2.075	20b	2.074	2.071	13	5 1 2
					2.073			
			2.005	10b		2.002	24	
			1.917	16b				
			1.875	13				
			1.837	14	1.843	1.836	19	
			1.748	14b			22b	
			1.712	10				
			1.670	17				
			1.647	12b	1.669	21		
			1.604	10				
			1.593	17b	1.618	9		

means of wet chemical analyses for the specimen purified through heavy liquids and hand picking separation. The result is given in Table 1 and is compared with the chemical compositions of tobermorite group minerals from Fuka. According to the formula of tobermorite reported by Megaw and Kelsey (1956), the empirical formula calculated on the basis of  $Si + Al + B = 6$  is  $(Ca_{5.29}Mg_{0.02}K_{0.02})_{5.33} (Si_{5.90}Al_{0.05}B_{0.05})_{6.00} (O_{16.54}OH_{1.39}F_{0.07})_{18.00} \cdot 5.1H_2O$ . This result shows that the ideal structural formula of clinotobermorite is  $Ca_5Si_6(O,OH)_{18} \cdot 5H_2O$ . The chemical composition of clinotobermorite is very close to that of tobermorite. The aluminium content is lower than that of tobermorite and the calcium content is slightly higher. The low aluminium and high calcium contents found in the Fuka clinotobermorite are possible not essential for clinotobermorite in general.

### X-ray studies

Precession and Weissenberg photographs show that clinotobermorite is monoclinic with the possible space group  $Cc$  or  $C2/c$ . The detailed crystallography of this mineral was already reported by Henmi and Kusachi (1989). It is summarised as follows. All the crystals are twinned on the  $c$ -plane or along the  $a$ -axis. The reflections with  $h = 2n$  and  $k = 2n$  show streaks parallel to  $c^*$ . This indicates the presence of stacking disorder on the  $c$ -plane. No single crystals suitable for crystal structure analysis have been found.

The unit cell dimensions of clinotobermorite, refined from the X-ray powder data, are given in Table 2, and are compared with those of the tobermorite group minerals from Fuka. The unit cells of tobermorite group minerals have the  $a$ -

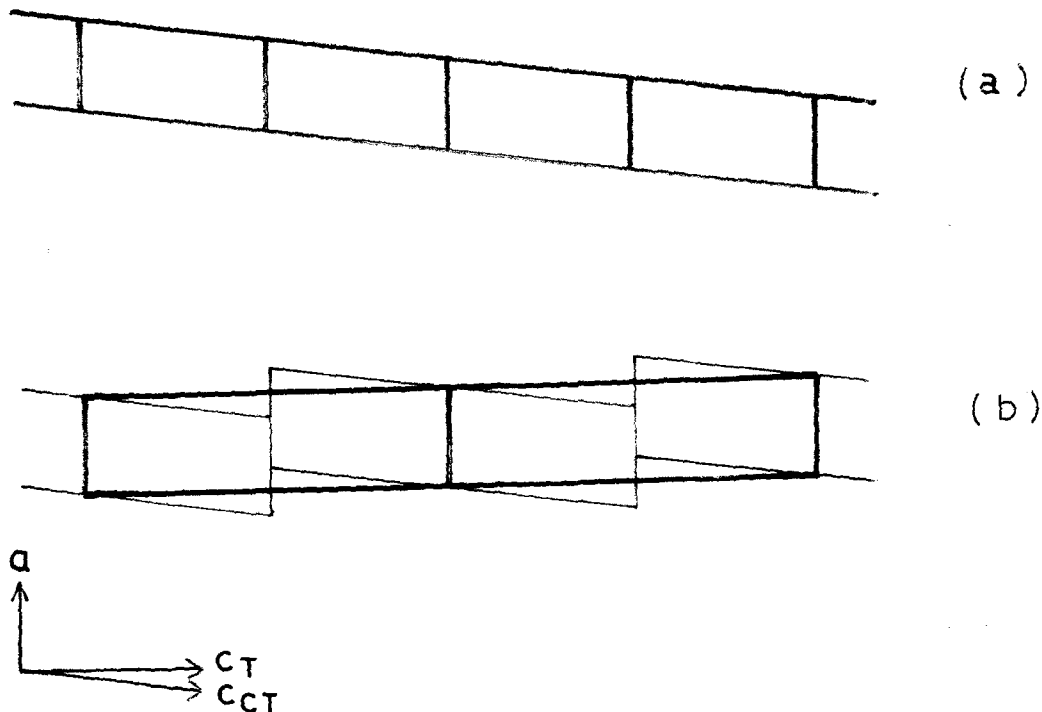


FIG. 3. Schematic diagram showing the geometrical relation of unit cells between clinotobermorite and tobermorite. (a) Clinotobermorite. (b) Stacking of the cells of clinotobermorite on (001) with an alternative displacement of 0 and  $1/2a$  results in the cell of tobermorite with the doubled  $c$ -axis. Thick lines indicate the unit cells. The  $a$ - and  $b$ -axes are in common for both cells.

and  $b$ -axis in common with one another. The unit cell of clinotobermorite is closely related to that of tobermorite. The stacking of the (001) layers of the clinotobermorite with an alternative displacement of 0 and  $1/2a$  results in the cell similar to the tobermorite cell with the doubled  $c$ -axis and the  $a$ - and  $b$ -axes in common (Fig. 3).

The X-ray powder diffraction data of clinotobermorite are listed in Table 3 together with those of tobermorite for comparison (after Henmi and Kusachi, 1989). They are considerably different from each other although there are some similar reflections with odd numbers of  $h$  and  $k$ .

### Discussion

McConnell (1954) reported that tobermorite is orthorhombic with the space group  $C222_1$ . Because of the presence of stacking disorder, the precise structure of tobermorite has not been determined. Megaw and Kelsey (1956) presented essential features of the tobermorite structure and suggested that the true cell is triclinic. Hamid

(1981) determined an average structure of tobermorite in the orthorhombic subcell with  $a$  5.586,  $b$  3.696, and  $c$  22.779 Å and reported one of the possible ordered structures which is monoclinic with the space group  $P2_1$ . The cell of clinotobermorite presented in this paper is different from the monoclinic cell suggested by Hamid (1981). The stacking disorder of clinotobermorite on the (001) plane is similar to that of tobermorite reported by McConnell (1954). The cell dimensions, the relation shown in Fig. 3, and the IR spectra indicate that the crystal structure of clinotobermorite is closely related to that of tobermorite. It is noteworthy, however, that not only the single crystal data but also the powder data of clinotobermorite are distinctly different from those of tobermorite (Table 3).

The relation between the clinotobermorite and tobermorite unit cells (Fig. 3) resembles that between clinopyroxene and orthopyroxene described by Morimoto (1959). Orthopyroxene is also considered to be a twinned clinopyroxene (Ito, 1950). The twinning of clinotobermorite, in

the same scheme as clinopyroxene, results in the cell of tobermorite with the doubled *c*-axis, which is the same as that formed by the alternative glide shown in Fig. 3.

The relation between the clinotobbermorite and tobermorite unit cells is also similar to that between wollastonite-1T and wollastonite-2M reported by Trojer (1968). The stacking disorder in clinotobbermorite may be similar to that in wollastonite, which was reported by Jefferson and Bown (1973), and also to that in foshagite, which was reported by Gard and Taylor (1960).

Although the chemical composition of the Fuka clinotobbermorite falls within the variation range expected for normal tobermorite along with Ca/(Si + Al) ratio (Mitsuda and Taylor, 1978), the high Ca content, exceeding that given by the ideal formula  $\text{Ca}_5\text{H}_2(\text{Si}_3\text{O}_9)_2 \cdot 5\text{H}_2\text{O}$ , is noteworthy together with the lower aluminium content. The chemical formula referred to by Hamid (1981) has smaller Ca content than that of the formula given above,  $\text{Ca}/\text{Si} = 4.5/6$ . The structure model permits the variable content of Ca. Meyer and Jaunarajs (1961) suggest that the Ca/Si ratio of synthetic tobermorite reaches unity. Also, a non-stoichiometric Ca/Si ratio is confirmed for killalaite (Taylor, 1977). Therefore, the variable Ca/Si ratios do not impede a prefix clino being applied to this case.

The mode of occurrence indicates that clinotobbermorite precipitated after tobermorite in fissures. The aluminium content of clinotobbermorite is lower than that in tobermorite, and the symmetry of clinotobbermorite is lower than that of tobermorite. Therefore, it may be inferred that clinotobbermorite is a low-temperature polymorph of tobermorite.

#### Acknowledgements

We would like to express our thanks to Emeritus Prof. Kitinosuke Henmi and Prof. Akira Kawahara of Okayama University for useful discussions. Thanks are also due to Dr. Akira Kato, National Science Museum, Tokyo, for his valuable advice.

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[Manuscript received 5 December 1991]