

A Barium-bearing Tobermorite from Heguri, Chiba Prefecture, Japan

By

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Abstract—Tobermorite from Heguri, Chiba Prefecture, occurs as veinlets cutting a basic tuff of Mineoka Group of Eocene age, suffering the metamorphism of zeolite facies. One of the most barium-rich analyses yields the empirical formula $(\text{Ca}_{4.42}\text{Ba}_{0.05}(\text{Na}_2)_{0.05}(\text{K}_2)_{0.04})_{\Sigma 4.56}(\text{Si}_{5.34}\text{Al}_{0.66})_{\Sigma 6.00}\text{O}_{14.52}(\text{OH})_{3.49} \cdot 3.20\text{H}_2\text{O}$ on the basis of $\text{Si} + \text{Al} = 6$, specifying the material to be a barium-bearing aluminian tobermorite.

The sharp X-ray powder diffraction pattern is explained by a C-centered orthorhombic cell with a 11.255, b 7.375, c 22.760 Å, $Z=4$, though nearly all the diffractions can be indexed by a subcell with $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$, and $c' = c$.

The compositional variation of natural tobermorites is found to be approximately covered within the range from $\text{Ca}_5\text{Al}_{0.5}\text{Si}_{5.5}\text{O}_{15.5}(\text{OH})_{2.5} \cdot 4\text{H}_2\text{O}$ to $\text{Ca}_4\text{AlSi}_5\text{O}_{13}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$, demonstrating a linear reciprocal relation between the total number of non-tetrahedral cations and aluminum.

Introduction

Tobermorite is a stable member in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ under lower temperature and pressure condition, and natural and synthetic materials are known to contain such minor to subordinate components as Na, K, Mg, Fe^{2+} , Al, Fe^{3+} and Ti, to which Ba has been added by the present material.

The X-ray powder diffraction pattern of the present material is very sharp and the indices have no violation to the extinction rule for the space group $C222_1$, which is assigned to tobermorite. Most of indices are occupied by those with h and $k=2n$, suggesting the presence of a subcell, which corresponds to the body-centered subcell of HAMID (1981), and the diffractions characteristic to the true cell are indicated.

The material is also characterized by higher Al_2O_3 content, presenting a clue to discuss the compositional variation. After the reference to the crystal structure involving cationic vacant sites reflected by the variable Ca/Si ratio from 4/6 to 5/6 in natural materials (HAMID, 1981), a quantitative reciprocal relation is found between non-tetrahedral cations and aluminum substituting silicon, starting from an approximate formula $\text{Ca}_5\text{Al}_{0.5}\text{Si}_{5.5}\text{O}_{15.5}(\text{OH})_{2.5} \cdot 4\text{H}_2\text{O}$ to $\text{Ca}_4\text{AlSi}_5\text{O}_{13}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$.

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Location and Description of the Studied Material

Mineoka Group forms the basement of Tertiary and Quaternary deposits covering Boso Peninsula, and consists dominantly of mudstone and intercalating basic pyroclastic rocks, basic lava flows, and minor arenaceous and siliceous rocks and limestone, in which the latest Eocene fossils are found (SUZUKI *et al.*, 1984). Also, there are many small ultrabasic and basic rock bodies involved within the formation. The distribution of this group forms a narrow zone elongated along E-W direction in the southern part of the peninsula, and at the west end is the tobermorite locality (Fig. 1), where some basic pyroclastic rocks and mudstone are associated with serpentinite and gabbro pegmatites. The studied material was from one of the exposures of basic tuff. It is a light grey green hard rock with a homogeneous feature owing to the fine grain size of components. It is intersected by white veinlets reaching 20 millimeters in maximum width, which consists of porcelain-like compact aggregate of tobermorite with a small amount of thomsonite prisms of millimeter order. The veinlets are rather stiff and pulverized with difficulty unless soaked by such an organic medium as acetone or ethyl alcohol. Under the tinocular, tobermorite aggregate is of high purity allowing the preparation of material for wet chemical analysis after a simple hand-picking. The hardness of aggregate is about 5 in Mohs' scale and the density measured by Berman microbalance is $2.42(1) \text{ g/cm}^3$, which is close to the calculated

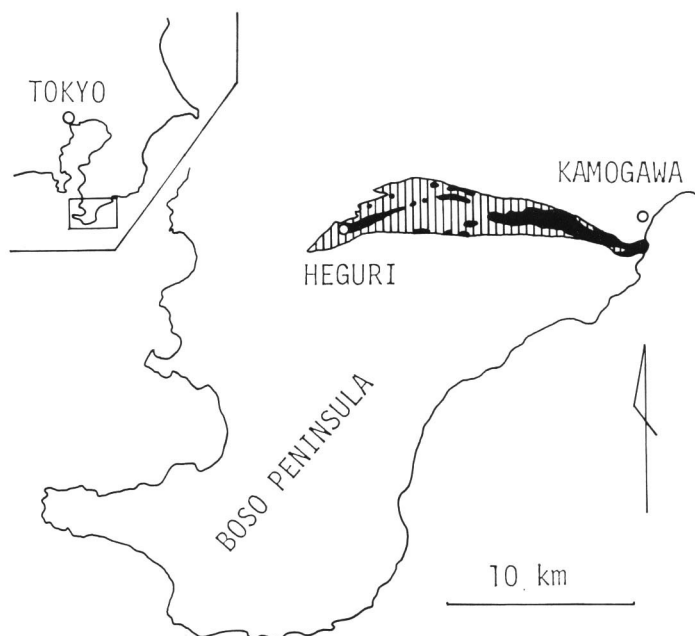


Fig. 1. Index map of the tobermorite locality. Black: ultrabasic and basic rocks. Striated: sedimentary and pyroclastic rocks of the Mineoka Group.

value, 2.52 g/cm³, using the most barium-rich analysis given in Table 1.

In thin section, tobermorite veinlet consists of aggregate of very fine granular to somewhat elongated grains locally forming parallel aggregate and comprises thomsonite prisms and fragments of wallrock. The wallrock is composed of rather angular to subround grains of prehnite, a birefringent chlorite, tobermorite, analcime, pectolite and minor sphene cemented by a less birefringent chlorite. In wallrock fragments trapped within the veinlet pectolite is more abundant. Tobermorite is colourless and the extinction is parallel with positive and negative elongation. Refractive index is 1.546(2) with very low birefringence. Besides the hard basic tuff, wallrock of the veinlet, there is another basic tuff in nearby exposure. It is also grey in colour and inclusive of visible dark grey green clots of chlorite and of minute fractures developed parallel to the bedding plane. This is the host rock of veinlets including xonotlite described by KATO and MATSUBARA (1975) accompanied by barium-free tobermorite as later stated.

Near the exposure is an abandoned quarry where mudstone, basic pyroclastic and volcanic rocks, serpentinite and gabbro pegmatite are found, and the veinlets of the following minerals are developed in them besides tobermorite. They are prehnite, pectolite, xonotlite, thomsonite, natrolite, analcime, hydrogrossular, apophyllite, gyrolite, calcite, aragonite and serpentine minerals. Among them, analcime is also found in the mudstone veined by gyrolite as the essential constituents, suggesting the metamorphic origin. If so, it is very probable that tobermorite in the basic pyroclastic rock is also a metamorphic mineral.

Chemical Composition

The chemical composition of a piece of tobermorite veinlet was surveyed by energy dispersive X-ray spectrochemical analysis using the instrument of Link Co. Ltd. A

Table 1. Chemical analysis of the most barium-rich tobermorite Heguri, Chiba Prefecture, Japan.

	wt. %	recast to 100%	cation number (Si+Al=6)
SiO ₂	43.87	43.50	5.34
Al ₂ O ₃	4.58	4.54	0.66
CaO	33.88	33.59	4.42
BaO	1.70	1.70	0.08
Na ₂ O	0.45	0.45	0.11
K ₂ O	0.52	0.52	0.08
H ₂ O ⁺	12.17	12.07	9.89
H ₂ O ⁻	3.68	3.68	3.65
Total	100.85	100.00	

Empirical formula (basis: Si+Al=6):



Table 2. Cation contents of barium-bearing tobermorite in a single veinlet including the described material.

No.	Ca	Ba	Na	K	Si	Al
1	4.45	0.05	0.00	0.08	5.38	0.62
2*	4.42	0.08	0.11	0.08	5.34	0.66
3	4.37	0.07	0.04	0.05	5.28	0.72
4	4.36	0.07	0.07	0.07	5.25	0.75
5	4.33	0.07	0.08	0.07	5.31	0.69
6	4.50	0.06	0.04	0.04	5.38	0.62
7	4.53	0.06	0.05	0.06	5.33	0.67
8	4.46	0.07	0.04	0.04	5.34	0.66

* This corresponds to the complete analysis in Table 1.

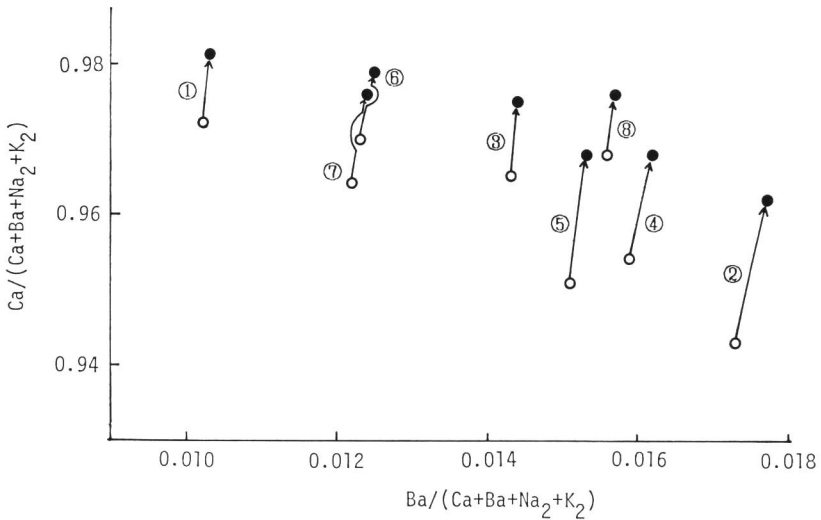


Fig. 2. $\text{Ca}/(\text{Ca}+\text{Ba}+\text{Na}_2+\text{K}_2)$ – $\text{Ba}/(\text{Ca}+\text{Ba}+\text{Na}_2+\text{K}_2)$ diagram of tobermorite from Heguri. Closed circles are for the above values and open ones for the values $\text{Ca}/(\text{Ca}+\text{Ba}+\text{Na}+\text{K})$ – $\text{Ba}/(\text{Ca}+\text{Ba}+\text{Na}+\text{K})$. Note the near linear alignment of closed circles.

separate wet chemical analysis for $\text{H}_2\text{O}(\pm)$ was combined with the most barium-rich one as given in Table 1. Besides this analysis, seven points were analysed to know the compositional variation within a single veinlet as in Table 2, in which the cationic contents are calculated on the same basis as above one, $\text{Si}+\text{Al}=6$. Among the analysed components, barium is evidently in reciprocal relation to calcium to indicate a vicarious substitution. In Fig. 2, the plots using two parameters, $\text{Ca}/(\text{Ca}+\text{Ba}+\text{Na}_2+\text{K}_2)$ and $\text{Ba}/(\text{Ca}+\text{Ba}+\text{Na}_2+\text{K}_2)$, are demonstrated to manifest the more convergent distribution of points than the usage of calculation basis for alkalis as $\text{Na}+\text{K}$ instead of Na_2+K_2 .

The X-ray spectrochemical survey using the same machine was also made on the

Table 3. X-ray powder diffraction pattern of synthetic and the present tobermorites.

1.			2.			
I	d(Å)	hkl	I	d _{obs.}	d _{calc.}	hkl
80	11.3	002	90	11.38	11.38	002
4	5.67	200	5	5.683	5.689	004
					5.625	200
25	5.48	201	25	5.460	5.464	201
6	3.78	006	8	3.795	3.793	006
8	3.64	021	5	3.645	3.639	021
20	3.53	205	30	3.539	3.538	205
18	3.31	023	15	3.316	3.311	023
100	3.08	220	100	3.078	3.083	220
65	2.98	222	75	2.976	2.976	222
40	2.82	400	8	2.846	2.846	008
		207	60	2.812	2.815	207
					2.814	400
10	2.738	402	3	2.731	2.732	402
			3	2.710	2.711	224
12	2.526	404	10b	2.522	2.522	404
			2	2.505	2.509	316
10	2.434	027	14	2.439	2.438	027
8	2.297	209	10	2.308	2.307	209
			17	2.276	2.276	0.0.10
14	2.264	406				
16	2.146	423		2.144	2.144	423
				2.135	2.135	1.1.10
10	2.080	228	12	2.087	2.091	228
		029			2.086	029
20	2.001	425	18b	2.005	2.007	425
		408			2.001	408
40	1.840	427	35b	1.843	1.843	427
		040			1.844	040
6	1.822	603				
<2	1.795	0.2.11				
4	1.738	605	1	1.734	1.734	605
20	1.673	429	18	1.672	1.672	2.0.13
					1.672	620
2	1.571	4.0.12				
		0.2.13				
8	1.541	440	8	1.543	1.542	440
					1.542	247
			2	1.524	1.523	2.2.13
2	1.510	609				
6	1.440	628	1	1.462	1.461	445
		249	4	1.438	1.438	2.2.14
4	1.412	800	3	1.406	1.407	800
			3	1.403	1.404	801
4	1.399	802	3	1.396	1.396	802
			3	1.392	1.393	447
4	1.375	4.2.13	3	1.379	1.379	4.2.13
			3	1.377	1.377	0.4.11
2	1.286	807	2	1.290	1.291	807
		6.0.13				
2	1.263	645	2	1.255	1.256	4.2.15
$a=11.27$			$a=11.255$			
$b=7.35$			$b=7.375$			
$c=22.74 \text{ \AA}$			$c=22.760 \text{ \AA}$			

1. Synthetic tobermorite. JCPDS CARD No. 19-1364.

2. Tobermorite. Heguri, Chiba Prefecture, Japan. Cu/Ni radiation. Diffractometer method.

associated thomsonite and on the tobermorite found in the nearby exposure accompanied by xonotlite to know the distribution of barium. As the result, barium content was under the detection limit in both of them, or lower than 0.1 % BaO if present.

X-Ray Powder Study

The present tobermorite has a good crystallinity, giving a very sharp diffraction peaks in the powder diffractometer diagram. They were indexed in terms of *C*-centered orthorhombic cell with $a=11.255$, $b=7.375$, $c=22.760$ Å after the reference to the data for synthetic material appeared in JCPDS Card No. 19-1364 (Table 3). No violation of the extinction rule for the space group $C222_1$ was found. The obtained cell is comparable with *a*- and *b*-halved body-centered orthorhombic cell of HAMID (1981), and the presence of this subcell is suggested by the full occupation of even numbers for *h* and *k* in the determined (hkl), except for (1.1.10) and (316). The former is closely accompanied by (423), forming a broad peak near 2.14 Å. This broadening may serve to the indication of the non-halved *a* and *b* unless their halvings take place separately. The latter is so-called shoulder type peak near (404), which has a stronger intensity than (316) near 2.52 Å. Owing to the less outstanding situation, this peak was not picked up as the characteristics of non-halved cell edges.

The X-ray powder diffraction pattern of the barium-free material from nearby exposure is essentially identical with that of barium-bearing one in all aspects including the non-halved nature of two cell edges. The unit cell parameters, *a* 11.248, *b* 7.372, *c* 22.740 Å are very slightly smaller than those of barium-bearing one.

Compositional Variation in Tobermorites

There are two significant compositional variations in tobermorites. One is the variable Ca/Si ratio from 4/6 to 5/6 in natural materials and to 6/6 if synthetic ones are taken into consideration (HAMID, 1981). According to his structural study on natural tobermorite, it involves vacant cationic sites capable of accounting for the ratio variation. The other is the variable aluminum content substituting silicon from 2.402 wt. % Al₂O₃ in the material from Pier, Tobermory, Scotland (HEDDLE, 1880) to 6.35 wt. % in the material from Prà da la Stua, Italy (GOTTARDI and PASSAGLIA, 1966). In both of them the charge balance coming from the substitution needs consideration. As to the former, HAMID (1981) indicates a sympathetic increase of OH substituting non-bridging O atom in the Si₃O₉ chain by designating the ideal formulae Ca₄Si₆O₁₆(OH)₂·2H₂O and Ca₅Si₆O₁₈·2H₂O but he did not mention the role of aluminum to the charge balance and the lower content of H₂O.

Six chemical analyses of natural tobermorites including the present one are subjected to the examination to know the quantitative relation of components. As the result, a clear reciprocal relation is found between the contents of non-tetrahedral cations and aluminum (Fig. 3). In Table 4 all the referred analyses are shown together

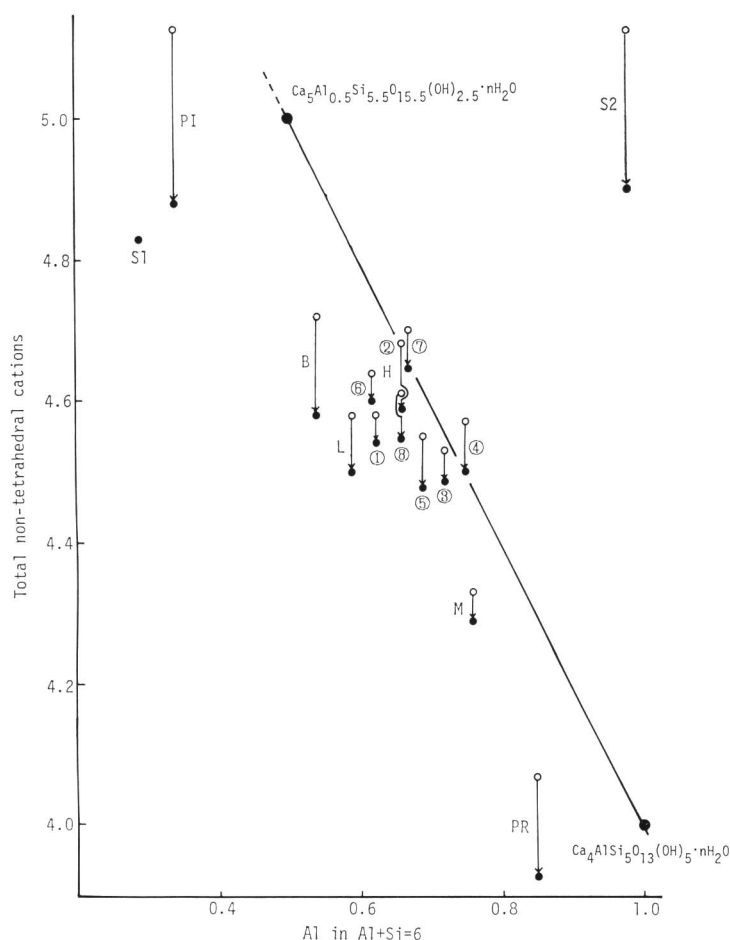


Fig. 3. Total non-tetrahedral cations-Al content diagram in the empirical formulae of analysed tobermorites and the synthetic analogues with the basis $\text{Si} + \text{Al} = 6$. The same symbols as Fig. 2 are used. Abbreviations S1: Synthetic. JCPDS Card No. 19-1364. S2: Synthetic. MITSUDA (1970). PI: Pier, Tobermory. HEDDLE (1880). B: Bloody Bay, Tobermory. HEDDLE (1880). L: Loch Eynort. CLARINGBULL and HEY (1952). H: Heguri (①-⑧) (② corresponds to the chemical analysis in Table 1 and the others to Table 2). M: Monte Biaena, Trento, Italy. GOTTARDI and PASSAGLIA (1967). PR: Prà da la Stua, Trento, Italy. GOTTARDI and PASSAGLIA (1966).

with their empirical formulae calculated on the same basis as here employed, $\text{Si} + \text{Al} = 6$. The range of natural materials is approximately from $\text{Ca}_5\text{Al}_{0.5}\text{Si}_{5.5}\text{O}_{15.5}(\text{OH})_{2.5}\cdot 4\text{H}_2\text{O}$ (Pier) to $\text{Ca}_4\text{AlSi}_5\text{O}_{13}(\text{OH})_5\cdot 4\text{H}_2\text{O}$ (Prà da la Stua), where Ca includes minor Na, K, Mg, Fe^{2+} , Fe^{3+} and Ti. In Fig. 3, the plots for the chemical analyses of the present tobermorite appeared in Table 2 are made to indicate the extension of compositional variation in a single specimen.

Table 4. Chemical analyses of natural and synthetic tobermorites.

	1.	2.	3.	4.	5.	6.	7.	8.
SiO ₂	46.508	46.62	46.17	43.87	45.45	45.39	45.68	41.21
Al ₂ O ₃	2.402	3.895	4.27	4.58	5.63	6.35	2.00	6.82
Fe ₂ O ₃	1.139	0.664			0.55	0.13	0.11	0.86
TiO ₂						0.10		
FeO	1.853	1.080	0.15					
MgO	0.474				0.50	4.38	0.53	
CaO	33.404	33.978	35.15	33.88	33.30	24.53	36.24	35.88
BaO				1.70				
Na ₂ O	0.356	0.891	0.56	0.45	0.22	1.25		0.92
K ₂ O	1.445	0.572	0.25	0.52	0.27	0.71		1.55
H ₂ O	12.606	12.109	13.47	15.85 ¹⁾	14.50 ²⁾	17.94 ³⁾	15.22	12.72 ⁴⁾
Total	100.187	99.809	100.02	100.85	100.42	100.78	99.78	99.96

Empirical formulae: (basis: Si+Al=6)

1. (Ca_{4.35}Fe_{0.19}²⁺Fe_{0.10}³⁺Mg_{0.08}(K₂)_{0.11}(Na₂)_{0.04})_{Σ4.88}Si_{5.66}Al_{0.34}O_{15.52}(OH)_{2.48}·3.88H₂O
2. (Ca_{4.27}Fe_{0.11}²⁺(Na₂)_{0.10}(K₂)_{0.04}Fe_{0.08}³⁺)_{Σ4.58}Si_{5.46}Al_{0.54}O_{14.68}(OH)_{3.32}·3.07H₂O
3. (Ca_{4.41}Fe_{0.01}²⁺(Na₂)_{0.06}(K₂)_{0.02})_{Σ4.50}Si_{5.41}Al_{0.59}O_{14.41}(OH)_{3.59}·3.46H₂O
4. (Ca_{4.42}Ba_{0.08}(Na₂)_{0.05}(K₂)_{0.04})_{Σ4.59}Si_{5.34}Al_{0.66}O_{14.52}(OH)_{3.48}·3.20H₂O(excluding H₂O⁻)
5. (Ca_{4.11}Mg_{0.09}Fe_{0.05}³⁺(Na₂)_{0.02}(K₂)_{0.02})_{Σ4.26}Si_{5.24}Al_{0.76}O_{13.87}(OH)_{4.13}·2.81H₂O(excluding H₂O⁻)
6. (Ca_{2.08}Mg_{0.74}(Na₂)_{0.14}(K₂)_{0.05}Fe_{0.01}³⁺Ti_{0.02})_{Σ3.04}Si_{5.15}Al_{0.85}O_{13.08}(OH)_{4.02}·3.93H₂O
(excluding H₂O⁻)
7. (Ca_{4.85}Mg_{0.10}Fe_{0.01}³⁺)_{Σ4.86}Si_{5.71}Al_{0.29}O_{15.04}(OH)_{2.36}·5.16H₂O
8. (Ca_{4.68}(K₂)_{0.12}(Na₂)_{0.11}Fe_{0.03}³⁺)_{Σ4.96}Si_{4.02}Al_{0.95}O_{15.08}(OH)_{2.02}·3.71H₂O

Localities:

1. Pier, Tobermory, Soctland. HEDDLE (1880).
2. Bloody Bay, Tobermory, Scotland. HEDDLE (1880).
3. Loch Eynort, Scotland. CLARINGBULL and HEY (1952).
4. Heguri, Chiba Prefecture, Japan. The present study. ¹⁾ includes H₂O⁻ 3.68%.
5. Monte Biaena, Trento, Italy. GOTTARDI and PASSAGLIA (1967). ²⁾ includes H₂O⁻ 1.81%.
6. Prà da la Stua, Trento, Italy. GOTTARDI and PASSAGLIA (1966). ³⁾ includes H₂O⁻ 1.06%.
7. Synthetic material. JCPDS Card No. 19-1364.
8. Synthetic material. MITSUDA (1970). ⁴⁾ ignition loss.

It is worthy of note that the chemical composition of an artificial tobermorite prepared from clinoptilolite by MITSUDA (1970) is obviously out of the trend demonstrated in Fig. 3, suggesting the possible presence of another variation trend in tobermorite. In relation to this evidence, it is also of note that a high aluminian synthetic tobermorite appeared in JCPDS Card No. 19-52 is not orthorhombic but monoclinic in symmetry, coming from a distortion of unit cell in the different manner from the monoclinic cell for an ordered tobermorite (HAMID, 1981). The ideal formula of high aluminian material is indicated as Ca₅AlSi₅O₁₇(OH)·5H₂O in the card, which is out of balance and may be read Ca₅AlSi₅O₁₅(OH)₃·4H₂O, since this is very close to the empirical formula of artificial material of MITSUDA (1970). If this material is not orthorhombic but monoclinic in symmetry, it is very natural that the variation trend of a crystallographically different material from the natural ones is distinct from them.

The limit of substitution of aluminum for silicon in synthetic tobermorites is 10% in Al: (Al+Si) ratio (KALOUSEK, 1957) or 15% in the same ratio (DIAMOND *et al.*, 1966), the latter being close to 14.1% of the material from Prà da la Stua (GOTTARDI and PASSAGLIA, 1966) and to 16.7% of the ideal formula $\text{Ca}_4\text{AlSi}_5\text{O}_{13}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$. The Al: Si ratio in this formula can be crystallochemically connected with the unit form of chain structure, $\text{Si}_3(\text{O}, \text{OH})_8$, for, an Al-substituted unit has the form $\text{AlSi}_5(\text{O}, \text{OH})_{15}$ therein and the ratio 1: 5 is very smoothly acceptable to the form. That is, the limit of substitution of Al for Si in $\text{Si}_6(\text{O}, \text{OH})_{15}$ is 1 Al per 2 $\text{Si}_3(\text{O}, \text{OH})_8$. Beyond this point, aluminum plays a role to cut off the chain, forming an isolated tetrahedron of SiO_4 to constitute hydrogarnet (MEYER and JAUNARAJ, 1961). However, it is necessary to note that the formula $\text{Ca}_4\text{AlSi}_5\text{O}_{13}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$ requires the presence of extra (OH) substituting oxygen atom in the $\text{Si}_3(\text{O}, \text{OH})_8$ chain as compared with the maximum value, 4, designated by HAMID (1981), though the expectation of extra (OH) is not unreasonable.

As just mentioned, the trend of compositional variation of tobermorite seems to be different between natural and some synthetic materials. DIAMOND *et al.* (1966) demonstrated the increase of *c*-spacing due to the increase of aluminum content substituting silicon along with synthetic tobermorites. However, the X-ray powder diffraction pattern of the material from Prà da la Stua (GOTTARDI and PASSAGLIA, 1966) cannot be explained by longer *c*-spacing but by a shorter unit cell edges due to the smaller *d*-values of corresponding diffractions with the present ones. If the crystal structure of HAMID (1981) is referred to, the trend of elongation of chain is parallel to *b*-axis and the substitution of aluminum for silicon in the chain is indirectly responsible for the increase of *c*-spacing. But, if the number of vacant sites of cations increases, the effect is considered to give rise directly to the shortening of it, since the cationic sites are arranged on a plane perpendicular to *c*-axis and that one of them is exclusively responsible for the vacant sites. Therefore, the diagram of DIAMOND *et al.* (1966) dealing with the relation between Al: (Al+Si) and *c*-spacing needs the reference to the variable content of the non-tetrahedral cations.

The present discussion is based on the structure model of HAMID (1981) and the informations on the existence of double chain tobermorite (WIEKER, 1968; WINKLER *et al.*, 1979) are not referred to, according to the good coincidence of the crystallographic data of HAMID (1981) with the present one.

Amendments to the Previous Work

The description on xonotlite from the same locality (KATO and MATSUBARA, 1975) referred briefly to the occurrence of a strontium-bearing tobermorite in association with it. However, the restudy of tobermorite accompanied by xonotlite informed that the mineral is free from this element and the material from which the referred analysis was derived is actually the same material as here examined, and that the strontium appeared in the chemical analysis was actually barium after the X-ray spec-

trochemical study. Also, the tobermorite accompanied by xonotlite was found to have a slightly smaller unit cell than the present barium-bearing one. Therefore, the $H_2O(\pm)$ content appeared in the previous work of the first and second authors (1975) was directly referred to the present case.

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References

- CLARINGBULL, G. F. & M. H. HEY, 1952. A re-examination of tobermorite. *Miner. Mag.*, **29**: 960–962.
- DIAMOND, S., J. L. WHITE & W. L. DOLCH, 1966. Effects of isomorphous substitution in hydrothermally-synthesized tobermorite. *Amer. Mineral.*, **51**: 388–401.
- GOTTARDI, G. & E. PASSAGLIA, 1966. Tobermorite «non espandibile» di Prà da la Stua (Trento). *Per. Mineral.*, **35**: 197–204.
- & ———, 1967. Tobermorite «non espandibile» e gyrolite del Monte Biaena (Trento). *Ibid.*, **36**: 1079–1083.
- HAMID, S. A., 1981. The crystal structure of 11 Å natural tobermorite $Ca_{2.25}[Si_3O_{7.5}(OH)_{1.5}] \cdot 1H_2O$. *Zeit. Krist.*, **154**: 189–198.
- HEDDLE, M. F., 1880. Preliminary notice of substances which may prove to be new minerals. *Miner. Mag.*, **4**: 117–123.
- KALOUSEK, G. L., 1975. Crystal chemistry of the hydrous calcium silicates: I. Substitution of aluminum in the lattice of tobermorite. *Jour. Amer. Ceram. Soc.*, **40**: 124–132.
- KATO, A. & S. MATSUBARA, 1975. Xonotlite from Heguri, Chiba Prefecture, Japan. *Bull. Natn. Sci. Mus. Ser. C*, **1**: 61–67.
- MEYER, J. W. & K. L. JAUNARAJ, 1961. Synthesis and crystal chemistry of gyrolite and reyerite. *Amer. Mineral.*, **46**: 913–933.
- MITSUDA, T., 1970. Synthesis of tobermorite from zeolite. *Miner. Jour.*, **6**: 143–158.
- SUZUKI, Y., K. KNODO & T. SAITO, 1984. Latest Eocene planktonic foraminifers from the Mineoka Group, Boso Peninsula. *Jour. Geol. Soc. Japan*, **90**: 497–499. (In Japanese.)
- WIEKER, W., 1968. Silikatanionenstruktur des 14 Å Tobermorits von Crestmore und seiner Entwässerungsprodukte. *Zeit. anorg. allg. Chemie*, **360**: 307–316.
- WINKLER, A. & W. WIEKER, 1979. Über Synthese, Aufbau und thermisches Verhalten von 11 Å Tobermorit. *Ibid.*, **451**: 45–56.