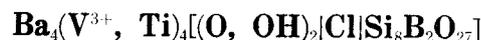


The crystal structure of nagashimalite,



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Abstract

Nagashimalite, $\text{Ba}_4(\text{V}^{3+}_{3.14}\text{Ti}_{0.56})\text{B}_2\text{Si}_8\text{O}_{28}\text{Cl}[(\text{OH})_{0.44}\text{O}_{0.56}]$, a new mineral from the Mogurazawa mine, Gumma Prefecture, is orthorhombic, space group $Pmmn$, with unit cell parameters $a=13.937(3)$, $b=12.122(3)$, $c=7.116(2)$ Å and $Z=2$.

The crystal structure is similar to that of taramellite after Mazzi and Rossi (1965), except for boron and chlorine. It basically consists of a novel borosilicate group $[\text{Si}_8\text{B}_2\text{O}_{27}]$ which is built up of a pair of Si_4O_{12} groups linked together, sharing corners, by a B_2O_7 group. These borosilicate groups are in the structure joined together by sharing of octahedra, parallel to b , formed by oxygen atoms about vanadium atoms. The crystallochemical formula is thus given as $\text{Ba}_4(\text{V}^{3+}, \text{Ti})_4[(\text{O}, \text{OH})_2|\text{Cl}|\text{Si}_8\text{B}_2\text{O}_{27}]$. Mean interatomic distances are: $\text{V}-\text{O}=2.012(5)$, $\text{Si}(1)-\text{O}=1.631(4)$, $\text{Si}(2)-\text{O}=1.617(4)$, and $\text{B}-\text{O}=1.479(5)$ Å. The Ba atoms are thirteen and eleven-coordinated with mean distances of $\text{Ba}(1)^{[13]}-(\text{O}, \text{OH})=3.094(6)$, $\text{Ba}(2)^{[11]}-(\text{O}, \text{Cl})=3.121(8)$, and $\text{Ba}(3)^{[11]}-(\text{O}, \text{Cl})=2.925(8)$ Å.

It appears that the reported taramellite structure would in fact contains boron atoms and belongs to the same borosilicate groups as nagashimalite.

Introduction

Nagashimalite, $\text{Ba}_4(\text{V}^{3+}, \text{Ti})_4[(\text{O}, \text{OH})_2|\text{Cl}|\text{Si}_8\text{B}_2\text{O}_{27}]$, a new mineral found in bedded manganese ore deposits of the Mogurazawa mine, Gumma Prefecture, Japan. The description is given in the preceding article (Matsubara and Kato, 1980).

The X-ray powder pattern suggests an isotypy with taramellite, $\text{Ba}_2(\text{Fe}^{3+}, \text{Ti}, \text{Fe}^{2+})_2[(\text{OH})_2|\text{Si}_4\text{O}_{12}](Z=4)$ (Mazzi and Rossi, 1965). Nagashimalite, however, has a new type $[\text{Si}_8\text{B}_2\text{O}_{27}]$ borosilicate groups.

Experimental

Single crystals were isolated from the type specimen (NSM M-21727) deposited in National Science Museum, Tokyo, Japan, and the size of employed crystal was approximately $0.09 \times 0.13 \times 0.15$ mm.

The precession films of this crystal indicated an orthorhombic unit cell and

systematic absences of $h+k=2n$ for $hk0$ led uniquely to space group $Pnmm$. The refined unit cell parameters were $a=13.937(3)$, $b=12.122(3)$, $c=7.116(2)\text{\AA}$ measured by automated four-circle diffractometer (Syntex P2₁) using monochromatized MoK α radiation ($\lambda=0.71069\text{\AA}$). The ω - 2θ scan technique was used to measure intensities in the limit of $2\theta=75^\circ$. A total of 2621 independent reflections were measured, of which 2241 had intensities greater than $3\sigma(I)$ and were used for the structure refinement. The intensities were corrected for Lorentz and polarization effects and for absorption ($\mu=87.8\text{ cm}^{-1}$).

Refinement of the structure

The X-ray powder diffraction pattern of nagashimalite is very similar to that of taramellite, suggesting its isostructural relation to taramellite studied by Mazzi and Rossi (1965) who proposed the ideal formula as $\text{Ba}_2(\text{Fe}^{3+}, \text{Ti}, \text{Fe}^{2+})_2 [(\text{OH})_2|\text{Si}_4\text{O}_{12}]$ with $Z=4$.

The atomic parameters of taramellite were referred to at the initial stage of the present structure refinement. The atomic scattering factor for each atom

TABLE 1. Atomic coordinates and thermal parameters.

Atom	x	y	z	$\beta_{\text{eq.}}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba(1)	0.25	0.75	0.2392(2)	1.02	11.8	10.9	74.1	0	0	0
Ba(2)	0.25	0.25	0.4730(3)	2.98	23.1	33.1	256.3	0	0	0
Ba(3)	0.4755(1)	0.25	0.0060(1)	0.81	11.5	10.9	44.7	0	-1.8	0
V	0.4995(1)	0.1281(1)	0.5204(2)	0.43	5.8	7.3	20.0	-1.4	-2.7	2.0
Si(1)	0.3665(1)	0.0117(2)	0.2056(3)	0.38	5.2	6.4	18.7	-0.5	-1.1	1.0
Si(2)	0.6444(1)	0.0256(2)	0.2074(3)	0.36	5.2	6.0	16.0	-0.1	0.1	-0.8
B	0.3418(7)	0.75	0.7201(14)	0.28						
O(1)	0.25	-0.0045(6)	0.2229(12)	0.89	5.3	18.6	58.5	0	0	8.6
O(2)	0.75	0.9798(6)	0.2679(11)	0.73	5.2	14.0	47.5	0	0	14.8
O(3)	0.5761(5)	0.25	0.4109(10)	0.65	9.8	7.9	35.6	0	4.3	0
O(4)	0.5706(5)	0.75	0.3585(10)	0.81	6.1	24.1	26.7	0	-1.6	0
O(5)	0.6099(3)	0.9610(4)	0.0182(7)	0.74	12.5	11.3	29.0	-2.9	3.8	-1.4
O(6)	0.4029(3)	0.1211(4)	0.3120(7)	0.65	13.1	6.0	28.7	-1.2	-6.9	-2.0
O(7)	0.4101(3)	0.8929(4)	0.2629(7)	0.60	10.4	7.9	25.8	1.1	-7.1	2.7
O(8)	0.6479(3)	0.1544(4)	0.1489(7)	0.52	9.9	5.9	22.3	-0.5	-2.0	1.9
O(9)	0.5726(3)	0.0050(4)	0.3776(7)	0.58	9.1	9.9	21.6	-0.7	6.3	-0.4
O(10)	0.25	0.75	0.6235(14)	0.67	7.7	19.1	14.2	0	0	0
Cl	0.25	0.25	0.9858(12)	1.80	12.9	27.1	138.6	0	0	0

The anisotropical thermal parameters ($\times 10^4$) are of the form: $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. Standard deviations are in parentheses.

TABLE 2. Interatomic distances and angles.

	Distances(Å) Angles(°)		Distances(Å) Angles(°)		
<i>Si(1) tetrahedron</i>			<i>Si(2) tetrahedron</i>		
Si(1)-O(1)	1.640(1)		Si(2)-O(2)	1.631(3)	
Si(1)-O(5)	1.660(5)		Si(2)-O(5)	1.630(5)	
Si(1)-O(6)	1.609(5)		Si(2)-O(8)	1.616(5)	
Si(1)-O(7)	1.615(5)		Si(2)-O(9)	1.591(4)	
mean	1.631(4)		mean	1.617(4)	
O(1)-O(5)	2.652(7)	107.0(4)	O(2)-O(5)	2.650(7)	108.7(3)
O(1)-O(6)	2.694(6)	112.1(3)	O(2)-O(8)	2.688(7)	111.7(3)
O(1)-O(7)	2.570(6)	104.3(3)	O(2)-O(9)	2.610(5)	108.2(3)
O(5)-O(6)	2.557(7)	103.0(2)	O(5)-O(8)	2.577(7)	105.1(3)
O(5)-O(7)	2.686(7)	110.2(2)	O(5)-O(9)	2.664(7)	111.6(2)
O(6)-O(7)	2.789(6)	119.8(3)	O(8)-O(9)	2.651(6)	111.5(3)
mean	2.658(7)	109.4(3)	mean	2.640(7)	109.5(3)
<i>V octahedron</i>			<i>B tetrahedron</i>		
V-O(3)	1.983(5)		B-O(3)	1.475(7)	
V-O(4)	1.970(5)		B-O(8) × 2	1.494(5)	
V-O(6)	2.005(5)		B-O(10)	1.453(5)	
V-O(7)	2.007(5)		mean	1.479(5)	
V-O(9)	2.073(5)		O(3)-O(8) × 2	2.412(8)	108.7(3)
V-O(9)	2.034(5)		O(3)-O(10)	2.436(7)	112.6(5)
mean	2.012(5)		O(8)-O(8)	2.318(6)	101.7(3)
O(3)-O(4)	2.622(10)	83.1(2)	O(8)-O(10) × 2	2.448(8)	112.3(3)
O(3)-O(6)	2.961(8)	95.9(2)	mean	2.404(7)	108.8(4)
O(3)-O(7)	2.903(7)	93.4(2)	<i>Ba(1) polyhedron</i>		
O(3)-O(9)	2.980(4)	94.5(2)	Ba(1)-O(1) × 2	2.978(7)	
O(4)-O(6)	2.842(8)	91.3(2)	Ba(1)-O(3) × 2	3.474(7)	
O(4)-O(7)	2.910(7)	94.0(2)	Ba(1)-O(7) × 4	2.830(5)	
O(6)-O(9)	2.793(7)	86.4(2)	Ba(1)-O(8) × 4	3.316(5)	
O(6)-O(9)	2.708(7)	84.2(2)	Ba(1)-O(10)	2.734(10)	
O(7)-O(9)	2.852(7)	88.7(2)	mean	3.094(6)	
O(7)-O(9)	2.764(7)	86.3(2)	O(1)-O(7) × 4	2.570(6)	52.5(1)
O(9)-O(9)	2.673(7)	81.2(2)	O(1)-O(8) × 4	3.511(9)	67.6(2)
mean	2.819(7)	89.0(2)	O(3)-O(7) × 4	2.903(8)	53.7(1)
			O(3)-O(10) × 2	2.436(7)	44.2(5)
			O(7)-O(7) × 2	3.465(6)	75.5(1)
			O(7)-O(8) × 4	3.094(7)	59.8(2)
			O(7)-O(10) × 4	3.817(8)	86.6(1)

(cont.)

Distances (Å)		Angles (°)	Distances (Å)		Angles (°)
			O(8)-O(8) × 2	2.846(6)	50.8(2)
			O(8)-O(8) × 2	2.318(6)	40.9(3)
			O(8)-O(8) × 2	3.671(6)	67.2(1)
			mean	3.323(8)	65.6(2)
<i>Ba(2) polyhedron</i>			<i>Ba(3) polyhedron</i>		
Ba(2)-O(1) × 2	3.562(8)		Ba(3)-O(3)	3.204(10)	
Ba(2)-O(2) × 2	3.340(8)		Ba(3)-O(4)	2.672(11)	
Ba(2)-O(4) × 2	2.773(10)		Ba(3)-O(5) × 2	2.826(5)	
Ba(2)-O(6) × 4	2.880(7)		Ba(3)-O(6) × 2	2.865(8)	
Ba(2)-Cl	3.466(4)		Ba(3)-O(7) × 2	3.034(7)	
mean	3.121(8)		Ba(3)-O(8) × 2	2.854(5)	
			Ba(3)-Cl	3.147(17)	
			mean	2.925(8)	
O(1)-O(2) × 2	3.636(11)	63.5(3)	O(3)-O(6) × 2	2.961(7)	58.1(3)
O(1)-O(6) × 4	2.694(6)	48.0(2)	O(3)-O(8) × 2	2.412(8)	46.5(2)
O(2)-O(4) × 4	3.798(7)	76.2(2)	O(4)-O(5) × 2	3.564(7)	80.8(2)
O(2)-O(6) × 4	3.869(8)	76.5(2)	O(4)-O(7) × 2	2.910(7)	60.9(3)
O(4)-O(6) × 4	2.842(8)	60.3(3)	O(5)-O(5) × 2	3.216(6)	53.3(1)
O(6)-O(6) × 2	3.125(6)	65.7(2)	O(5)-O(7) × 2	2.686(7)	42.5(3)
Cl-O(1) × 2	3.517(8)	60.0(2)	O(5)-O(8) × 2	2.577(7)	40.3(2)
Cl-O(6) × 4	3.517(11)	66.6(3)	O(5)-O(6) × 2	2.557(7)	53.4(3)
Cl-O(2) × 2	3.319(7)	58.3(2)	O(5)-O(7) × 2	3.386(7)	70.5(2)
Cl-O(4) × 2	3.501(14)	68.2(4)	O(6)-O(6)	3.125(6)	66.1(3)
mean	3.369(8)	64.7(2)	O(6)-O(8) × 2	3.629(7)	78.8(2)
			O(7)-O(7)	3.465(6)	69.7(2)
			O(7)-O(8) × 2	3.094(7)	63.3(1)
			O(8)-O(8)	2.318(6)	47.9(2)
			Cl-O(4) × 2	3.501(14)	73.4(6)
			Cl-O(5) × 4	3.218(11)	64.9(4)
			Cl-O(6) × 4	3.517(11)	71.4(5)
			mean	3.201(8)	63.9(3)

was taken from International Tables for X-ray Crystallography (1968). The site for vanadium was assigned to be occupied by 86% of V^{3+} and 14% of Ti in accordance with the molecular proportion determined by the chemical analysis. The preliminary structure refinement was carried out by the least-squares program ORFLS (Busing *et al.*, 1963). Three cycles of calculations employing isotropic temperature factors of barium, vanadium, silicon and oxygen atoms

gave $R=0.118$, which was reduced to 0.107 after absorption correction. Three more cycles of least-squares calculations by a full-matrix least-squares program LINUS (Coppens and Hamilton, 1970), adjusting anisotropic temperature factors of each of the above atoms, reduced the R value to 0.080.

To determine the initial positions of boron and chlorine, which were missing in taramellite, a three-dimensional difference Fourier syntheses were made. The difference map revealed the locations of boron and chlorine atoms, and the additional oxygen atoms. Several cycles of full-matrix least-squares calculations, after variation of anisotropic temperature factors of all atoms, reduced the R value to 0.045 for 2241 reflections. In this case, β_{11} for boron atom was negative. Though calculations were repeated after employment of varying isotropic temperature factor of boron atom and anisotropic ones of other atoms, no further reduction of R took place. The final atomic coordinates and thermal parameters are given in Table 1, and interatomic distances and angles in Table 2, respectively. The observed and calculated structure factors are compared in another table*.

Description of the structure and discussion

The crystal structure of nagashimalite is composed of Si_4O_{12} ring silicate groups, VO_6 octahedral chains, double tetrahedra B_2O_7 groups and three non-equivalent barium polyhedra. The projections of the structure along the c - and b -axes are shown in Figs. 1 and 2, respectively.

Si₄O₁₂ ring silicate group: The atomic coordinates of the Si_4O_{12} ring silicate group are very similar to those of taramellite. The Si_4O_{12} ring is formed by connecting two non-equivalent Si_2O_7 sorosilicate groups whose shared oxygen atoms, O(1) and O(2), lie on a mirror plane perpendicular to the a -axis. The ring is nearly parallel to the {010} plane, because Si(1) and Si(2) have similar y coordinates ($\approx 0, 1/2$). The Si(1)-O distances of tetrahedron range from 1.609 to 1.660 with a mean value of 1.631 Å which is slightly shorter than that of 1.64 Å in taramellite. The Si(2)-O distances involving oxygens bonded to vanadium and boron, Si(1)-O(6), Si(1)-O(7), Si(2)-O(9) and Si(2)-O(8), are much shorter than those involving oxygens bonded to another silicon. This may be due to the fact that both V^{3+} and B^{3+} give smaller charge effect to O(6), O(7), O(9) and O(8) than Si^{4+} . The maximum and minimum O-Si-O angles are 119.8° and 103.0°, respectively and they are very close to those of 120° and 101° in taramellite.

V(O, OH)₆ octahedral chain: The atomic coordinates of V(O, OH)_6 octahe-

* A copy of this table is available from the author.

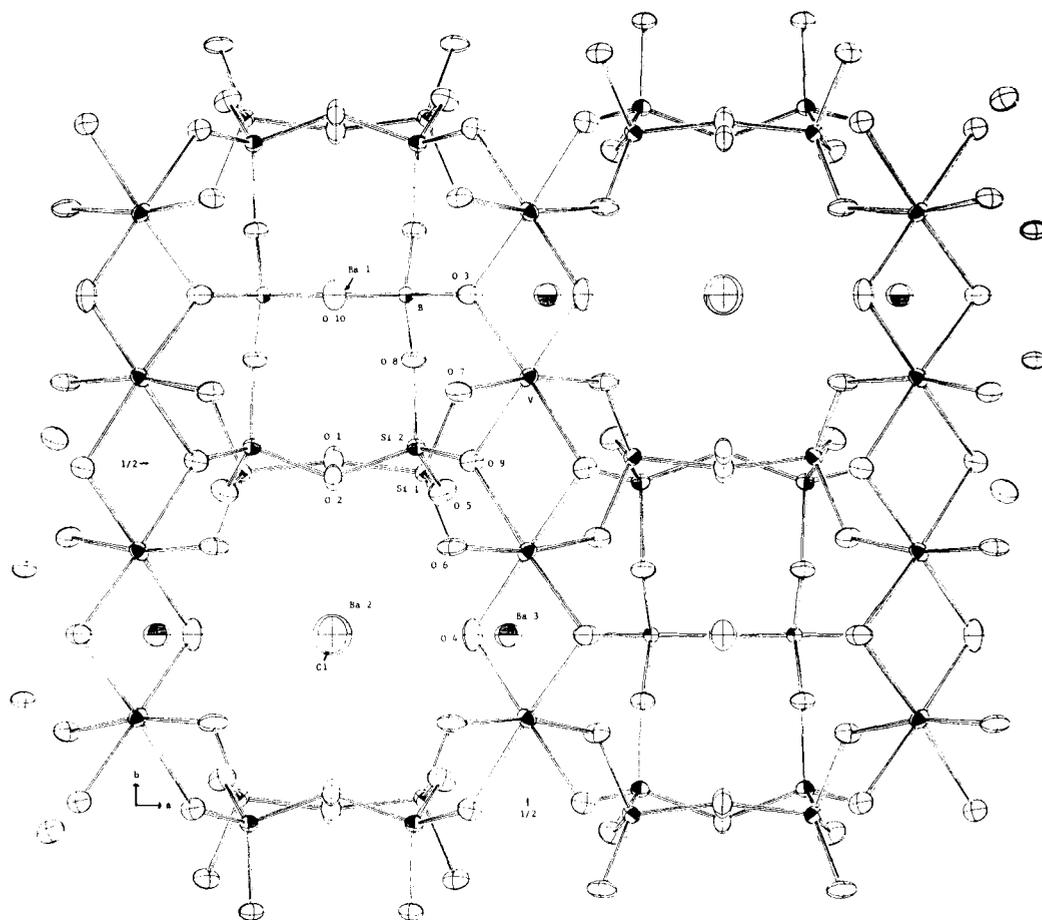


FIG. 1. Projection of the nagashimalite structure along the c -axis.

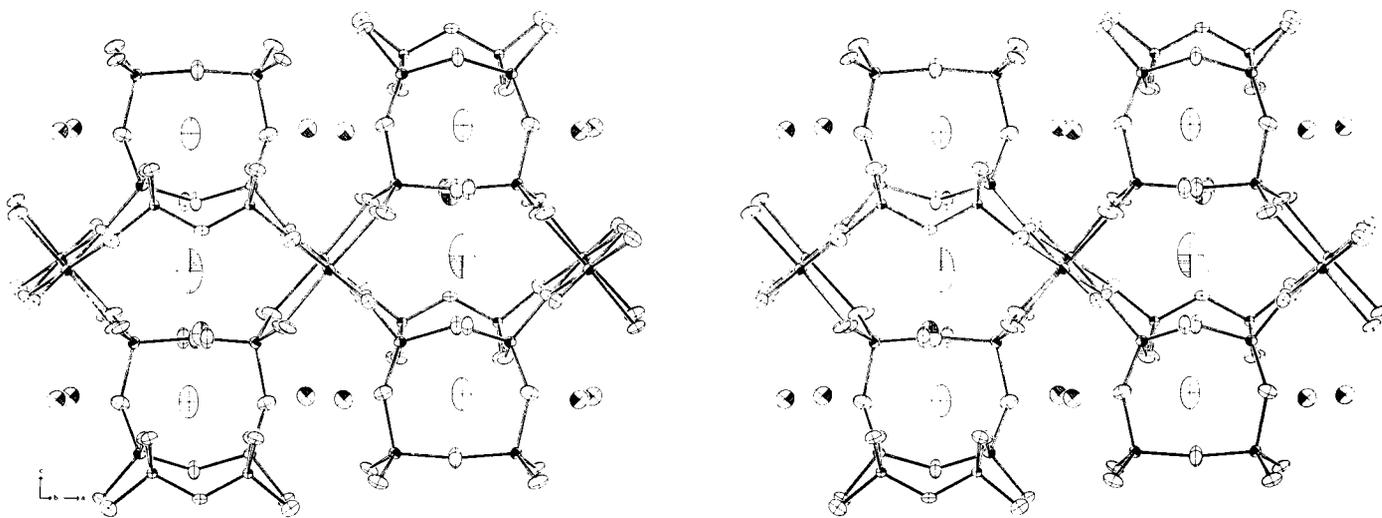


FIG. 2. Stereographic drawing of the nagashimalite structure viewed along *b*.

TABLE 3. V^{3+} -O distances(\AA) of octahedral coordination.

Max.	Minim.	Mean	Mineral	Authors
2.10	1.94	2.03	montroseite	Howard & Mrose (1955)
2.04	1.96	2.00	nolanite	Hanson (1958)
2.04	1.99	2.01	chernykhite	Rozhdestvenskaya & Frank-Kamenetskii (1974)
2.073	1.970	2.012	nagashimalite	This study

dron are quite similar to those of $(\text{Ti, Fe})\text{O}_6$ octahedron in taramellite. The V -(O, OH) distances of octahedron range from 1.970 to 2.073 \AA with a mean value 2.012 \AA , which is very close to those of such V^{3+} -bearing minerals as montroseite, nolanite and chernykhite (Table 3). The $V(\text{O, OH})_6$ octahedral chain is formed by sharing two opposite edges, O(3)-O(4) and O(9)-O(9'), of each octahedron and elongated parallel to the b -axis. The position of hydrogen could not be determined in a difference Fourier map. However, seeing from the calculated electrostatic valency balance (Table 5), a preferential incorporation of (OH) to O(4) site is very likely. The allowance of entrance may be also suggested from the evidence that O(4) is uniquely connected with $V(\text{O, OH})_6$ octahedron without any actual effect to the other polyhedra, except for Ba(2) and Ba(3), which are somewhat remotely located to O(4), however. The prismatic habit parallel to b of nagashimalite corresponds to the direction of this chain. Also each octahedron shares two edges, O(6)-O(9) and O(7)-O(9'), and one apex, O(3), with Si_4O_{12} ring and B_2O_7 group, respectively. The linkage of them forms an open but rigid framework structure, which might be responsible for the uncleavable nature of nagashimalite.

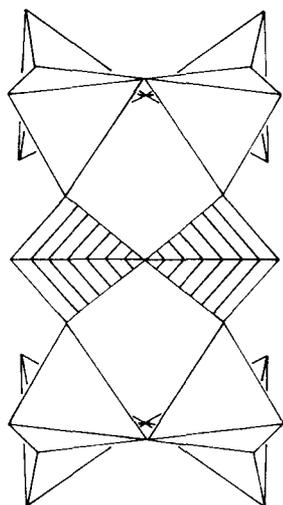


FIG. 3. The configuration of $[\text{Si}_8\text{B}_2\text{O}_{27}]$ borosilicate group of tetrahedra projected down the c -axis, borate tetrahedron being ruled.

TABLE 4. B-O distances (Å), O-B-O angles (°) and Si-O-B angles (°) in borosilicates.

Borosilicate	B-O distances			O-B-O angles			Si-O-B angles			Authors
	Max.	Minim.	Mean	Max.	Minim.	Mean	Max.	Minim.	Mean	
reedmergnerite	1.478	1.443	1.465	113.45	105.57	109.43	135.4	124.9		Appleman & Clark (1965)
howlite	1.52	1.43	1.47	117	102	109	135	127		Finney <i>et al.</i> (1970)
datolite	1.496	1.464	1.480	111.9	106.9	109.5	127.5	122.4	124.3	Foit <i>et al.</i> (1973)
danburite	1.498	1.456	1.474	111.2	102.5	108.3	132.4	126.3	128.9	Phillips <i>et al.</i> (1974)
searlesite	1.492	1.454	1.472	113.58	106.13	109.43	142.6	130.2		Ghose & Wan (1976)
garrelsite	1.496	1.441	1.475	114.28	106.34	109.44	128.4	123.1	126.0	Ghose <i>et al.</i> (1976)
nagashimalite	1.494	1.453	1.479	112.6	101.7	108.8			122.5	This study

B₂O₇ group: Each boron atom is situated within a tetrahedral group consisting of four oxygen atoms. The BO₄ tetrahedron shares the two oxygen atoms, O(8) and O(8'), with one apex of two Si₄O₁₂ rings and one oxygen, O(3), with V(O, OH)₆ octahedral chain. That is, two Si₄O₁₂ rings are joined by B₂O₇ double tetrahedra with sharing four equivalent oxygen atoms, O(8). This mineral can therefore be described as a new type borosilicate characterized by the Si₈B₂O₂₇ group of tetrahedron as shown in Fig. 3. Thus the ideal crystallochemical formula is given as Ba₁V₃³⁺[⁶⁻O(OH)|Cl|Si₈B₂¹⁻O₂₇]. The B-O distances of tetrahedron range from 1.453 to 1.494 Å with a mean value of 1.479 Å and the O-B-O angles range from 101.7° to 112.6° with a mean value of 108.8°. These values are very closely in accordance with those of BO₄ tetrahedral groups in other borosilicates. The B-O distances, O-B-O angles and Si-O-B angles in borosilicates are listed in Table 4. Though Mazzi and Rossi (1965) did not refer to the existence of boron, recently Pabst (priv. comm.) recognized the presence of about 4.3 wt.% of B₂O₃ in Ti-dominant taramellite from California. Since Mazzi and Rossi (1965) realized the structural identity of toprototypic taramellite from Candoglia, Italy, with the Californian Ti-dominant taramellite, it is highly probable that the original taramellite with Fe³⁺ as the dominant octahedral cation (Tacconi, 1908) contains boron as its essential constituent as well.

Ba polyhedra: The atomic coordinates of barium atoms are nearly equal to those of taramellite. The Ba(1) atom is thirteen-coordinated, the Ba-(O, OH) distances ranging from 2.734 to 3.474 Å with a mean value 3.094 Å. The six oxygen atoms, O(7)×4 and O(1)×2, at relatively shorter distances from a distorted hexagon and lie on nearly one plane parallel to {001}. If other six oxygen atoms, O(8)×4 and O(3)×2, at longer distances (over 2.98 Å) are not considered, the polyhedron about Ba(1) can be regarded as a hexagonal pyramid having, at a shortest distance, O(10) at the apex.

The Ba(2) atom is eleven-coordinated, the Ba-(O, Cl) distances ranging from 2.773 to 3.562 Å with a mean value 3.121 Å. The Cl⁻¹ anions occupy the channels along the *b*-axis within the Si₄O₁₂ rings. The Ba(2)-Cl distances (3.466 Å) is much shorter than Ba(2)-O(1) distances (3.562 Å) in this Ba(2)O₁₀Cl polyhedron. If the bonds longer than 2.89 Å are neglected, Ba(2)O₆ polyhedron can be considered as a distorted trigonal prism. The Ba(3) atom is also eleven-coordinated. The Ba(3)-O, Cl distances range from 2.672 to 3.204 Å with a mean value 2.925 Å. The Ba(3)-Cl distance (3.147 Å) is shorter than Ba(3)-O(3) one (3.204 Å) in this Ba(3)O₁₀Cl polyhedron. If the bonds longer than 2.87 Å are not considered, the polyhedron about Ba(3) may be regarded as a fairly distorted trigonal prism with an additional O(4) atom.

TABLE 5. Electrostatic valence balance.

	Si 1	Si 2	B	V	Ba 1	Ba 2	Ba 3	Σ
O 1	0.95($\times 2$)				0.18 ($\times 2$)	0.06 ($\times 2$)		2.14
O 2		0.98($\times 2$)				0.09 ($\times 2$)		2.05
O 3			0.76	0.58($\times 2$)	0.08 ($\times 2$)		0.12	2.12
O 4				0.55($\times 2$)		0.26 ($\times 2$)	0.31	1.71
O 5	0.91	0.98					0.23 ($\times 2$)	2.12
O 6	1.03			0.53		0.21 ($\times 4$)	0.22 ($\times 2$)	1.99
O 7	1.03			0.53	0.23 ($\times 4$)		0.16 ($\times 2$)	1.95
O 8		1.02	0.72		0.10 ($\times 4$)		0.22 ($\times 2$)	2.06
O 9		1.10		0.48+0.44				2.02
O 10			0.81($\times 2$)		0.28			1.90
Σ	3.92	4.08	3.10	3.11	2.16	1.66	2.09	

Electrostatic valency balance: The empirical bond strength calculated from the universal curves presented by Brown and Shannon (1973) is listed in Table 5. The V is made up of 86% V^{3+} and 14% Ti^{4+} , and the curve for V^{3+} was simulated by that for Fe^{3+} . The curve for Ba is calculated from the data for pellyite by Meagher (1976). The sum of bond strength surrounding anion and cations, respectively, demonstrates fairly reasonable valence except for Ba(2). The existence of hydrogen bonding to O(4) is supported from the result of the present calculation.

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Postscript

After the refereeing of manuscript, the crystal structure of taramellite has been described by Mazzi and Rossi (*Amer. Miner.*, **65**, 123-128 (1980)), who propose the same structure framework as that of nagashimalite, verifying the author's expectation.