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Hellandite: a new type of silicoborate chain

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Abstract

The crystal structure determination of hellandite was made on a specimen from Predazzo, Italy (a = 18.99, b = 4.715, c = 10.30 Å, β = 111.4°, space group $P2/a$), through Patterson and Fourier methods, with data collected on a single crystal diffractometer. The least squares refinement led to a final discrepancy index R = 0.05 for 1480 independent reflexions.

The most interesting features in the crystal structure are the infinite silicoborate chains $[Si_4B_4O_{20}(OH)_2]^{-14}$; two such chains are parallel to c in the (010) plane, with silicon and boron atoms at $y \simeq \frac{1}{2}$, and are related to each other by the glide plane. Iron and aluminum in octahedral coordination and calcium, yttrium, and rare earths in square antiprismatic coordination are all located at $y \simeq 0$ and connect the silicoborate chains. The structural investigation indicated the following formula for hellandite:

$$[Ca_{5.5}(Y,RE)_{5.0}\square_{1.5}]\ (Al_{1.1}Fe^{3+}_{0.9})\ (OH)_4[Si_8B_8O_{40}(OH)_4]$$

The relation between the structures of hellandite on the one hand and melilite and melilite-like minerals on the other hand is stressed. The crystal chemistry of hellandite is clarified, and its close relationship with tadzhikite is discussed.

Introduction

Hellandite is a rare mineral first found in granite pegmatite near Kragerø, Norway. Brögger (1903, 1907, 1922) studied its morphological crystallography, established its monoclinic symmetry, and gave chemical analyses. The paragenesis of the type locality pegmatite was described by Bjørlykke (1937). Two new findings of hellandite were made in recent years by Emiliani and Gandolfi (1965) in Predazzo granite, Italy, and by Miles *et al.* (1971) in Evans-Lou mine, southern Quebec.

The various chemical formulae proposed for hellandite before 1964 were erroneous because they were derived from Brögger's chemical data, which incorrectly identified boron, one of the main constituents of hellandite, as aluminum. Oftedal (1964, 1965) proved that hellandite was a borosilicate and in his 1965 paper proposed for it the formula $Ca_3(Y,RE)_4B_4Si_6O_{27}\cdot 3H_2O$; in the same paper he gave the first X-ray powder pattern of the mineral. Efimov *et al.* (1970) described a mineral from the Turkestan-Alai alkalic province in Tadzhikstan, U.S.S.R., which, although similar to hellandite in chemical composition and X-ray powder pattern, showed substantial chemical differences, and so was classified as a new mineral, tadzhikite, in the hellandite group, with proposed formula $Ca_3RE_2 = (Ti,Al,Fe)B_4Si_4O_{22}$.

The most recent paper on hellandite is a comprehensive study made by Hogarth *et al.* (1972) on samples of hellandite from all three known localities. They obtained unit-cell data, presented two new chemical analyses for the Canadian and Italian hellandites, comparing them with the chemical data for tadzhikite and Norwegian hellandite, and suggested the formula $(Y, Ca)_2(Si, B, Al)_3O_8 \cdot H_2O$.

The various formulae proposed for hellandite, the remarkable differences among hellandites from different sources, the questions on the role played by boron and the place of the mineral in the crystal-chemical classification of silicates, all prompted us to study this interesting borosilicate to elucidate both its crystal structure and crystal chemistry.

Experimental

A small crystal of hellandite (0.1 × 0.15 × 0.3 mm³) from Predazzo, Italy, was used for the crystal structure determination. Oscillation and Weissenberg photographs confirmed the data from Hogarth *et al.* (1972), which indicated a monoclinic unit cell with a = 18.911, b = 4.708, c = 10.276 Å, β = 111°31′, space group $P2/a$ or Pa.

Table 1. Chemical analyses and unit cell contents of hellandite from different sources

	1	2	3		1a	2a	3a
SiO_2	25.57	26.65	24.41	Si	8.0	8.0	8.0
B_2O_3	[14.85]	10.5	8.47	B	[8.0]	5.44	4.79
Al_2O_3	3.04	2.58	4.59	Al	1.12	0.91	1.77
Fe_2O_3	3.77	3.07	2.29	Fe	0.89	0.71	0.56
FeO		0.07					
TiO_2	<0.2	0.39	<0.2	Ti	<0.05	0.09	<0.05
ThO_2	-	1.46	0.57	Th	-	0.10	0.04
MnO	0.70	0.41	0.58	Mn	0.18	0.10	0.15
MgO	-	0.60	-	Mg	-	0.27	-
CaO	15.22	11.51	9.28	Ca	5.10	3.70	3.26
Y_2O_3	18.07	21.68	26.53	Y	3.01	3.46	4.62
RE_2O_3	16.0	15.63	19.19	RE	1.55	1.46	1.98
				O	43.22	38.41	40.17
H_2O^+	[4.50]	3.75	5.3				
H_2O^-		1.89	2.0				
				H_2O	[4.68]	5.60	7.97

1 and 1a: Hellandite from Predazzo, analysis by D.C. Harris (Hogarth et al., 1972). Boron content was calculated assuming eight boron atoms in the unit cell, as indicated by structure analysis. Iron content was recalculated assuming all the iron present as Fe_2O_3. Water content was calculated to give 48 oxygen atoms in the unit cell.

2 and 2a: Hellandite from Norway, analysis by B. Brunn (Oftedal, 1965).

3 and 3a: Hellandite from Canada, analysis by D.C. Harris and D.S. Russell (Hogarth et al., 1972). Iron content was recalculated assuming all the iron present as Fe_2O_3.

Cell parameters of our sample, determined on a single-crystal Philips PW 1100 diffractometer, were $a = 18.99 \pm 0.01$, $b = 4.715 \pm 0.005$, $c = 10.30 \pm 0.01$ Å, $\beta = 111.4° \pm 0.1$. Intensity data were collected by the same diffractometer, using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å), θ–2θ scan, scan width 1.80° and scan speed 2.7°/min. A total of 2458 independent reflections were collected from 2° to 30°; the intensities were corrected for Lorentz and polarization factors, but not for absorption (owing to the very small dimensions of the crystal). 978 reflections were classified as "not observed," having measured structure factors F_{obs} less than three times the corresponding standard deviation, $\sigma(F_{obs})$.

The density of a very small crystal, measured by the heavy liquid method is 3.63 g cm^{-3}.

Structure determination

The crystal structure determination was carried out in space group $P2/a$ using Patterson and Fourier syntheses. The Patterson map indicated that the three heaviest atoms were at $y \simeq 0$. The Fourier synthesis calculated with structure factors phased by the contribution of these atoms, assuming scattering factors $\frac{1}{2}(f_Y + f_{Ca})$, was obviously pseudosymmetric with a'

$= a/2$ and symmetry planes at $y = 0$ and $y = ½$. In this map a maximum was located at $y = ½$, which by its height appeared due to a silicon atom; it was surrounded by eight lower maxima in a cubic coordination at distances corresponding to Si–O bond lengths. The pseudosymmetry was then removed by taking four of these maxima in tetrahedral coordination and discarding the remaining ones. With two subsequent Fourier syntheses another silicon atom, one more heavy atom in the 0,0,0 position, to which the scattering factor of calcium was attributed, and a total of eleven oxygen atoms were located. After one cycle of full-matrix least-squares refinement the value of $R = \Sigma \, ||F_{obs}| - |F_{calc}|| / \Sigma \, |F_{obs}|$ was 0.27. A Fourier synthesis calculated at this point revealed two boron atoms in general positions and two more oxygen atoms in special positions x, 0, y and x, ½, y respectively. Two new cycles of least-squares refinement dropped the R value to 0.092.

All the scattering factors were taken from *International Tables for X-Ray Crystallography* (1962).

Refinement

The refinement of the crystal structure was made together with the assessment of the crystal chemistry of hellandite. The "calcium" atom at 0,0,0, was found in octahedral coordination with an average distance to the oxygen atoms of 1.97 Å. As suggested by the chemical analysis of hellandite from Predazzo (Table 1), Al^{3+} and Fe^{3+} cations were placed in this site with occupancies 0.55 and 0.45, respectively. A more intriguing problem was how to distribute calcium, yttrium, and rare-earth cations among the three available sites. The yttrium and rare-earth cations were considered together, and a scattering curve, referred to as the (Y,RE) curve, was calculated on the basis of the atomic proportions obtained from the chemical analysis (Table 1). In the course of the least-squares refinement, an optimal distribution of (Y,RE) and Ca among the three sites was found, account being taken of the following points: (1) the heights of the peaks in the Fourier syntheses; (2) the values of the thermal parameters obtained in the various refinement cycles for the three [Ca,(Y,RE)] atoms; (3) the total number and the relative proportion of Ca and (Y,RE) cations from the chemical analysis; (4) the average bond distances in the three sites; (5) the electrostatic valence balance.

Three full-matrix least-squares cycles with isotropic temperature factors and unit weights were calculated, the refined parameters including also the occupancies in the three sites among which calcium, yttrium, and rare earths are distributed. After these cycles the R value was reduced to 0.071. Two more block-diagonal least-squares cycles, with anisotropic temperature factors for all the atoms except the boron atoms, and a weighting scheme based on the experimental standard deviations $\sigma(F_{obs})$, derived from the counting statistics, reduced R to the value 0.05.

The final atomic positional and thermal parameters are reported in Table 2, with their estimated standard deviations, and the cation chemistry and occupancy in the $M(1)$, $M(2)$, $M(3)$, and $M(4)$ sites are given in Table 3. Observed and calculated structure factors are on deposit at the Business Office of the Mineralogical Society of America.[1]

Description and discussion of the structure

The cystal structure of hellandite is illustrated in Figure 1 and 2. The most characteristic features are the silicoborate chains parallel to c, which lie in the (010) plane. Two such chains are in the unit cell; both have silicon and boron atoms at $y \simeq ½$ and are related to each other by the glide plane. The repeat unit in the chain is made up by two "condensed" five-member rings of tetrahedra. All the largest cations, iron and aluminum in octahedral coordination, and calcium, yttrium, and rare earths in square antiprismatic coordination, are located at $y \simeq 0$ and connect the silicoborate chains.

The interatomic distances and bond angles were calculated using the System X-RAY 70 of J. M. Stewart, University of Maryland, College Park, Maryland, and are reported in Tables 4 and 5 together with the Si–O–B and B–O–B angles in the five-member rings.[2]

[1] To obtain a copy of the structure factors, order Document AM-76-033 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

[2] In Tables 4 and 5 and Fig. 3 the atoms of the different units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	x	y	$1+z$
ii	atom at	x	y	$-1+z$
iii	atom at	x	$-1+y$	z
iv	atom at	x	$-y$	z
v	atom at	$-x$	$1-y$	$-z$
vi	atom at	$-x$	$-y$	$1-z$
vii	atom at	$-x$	$-y$	$-z$
viii	atom at	$½-x$	y	$2-z$
ix	atom at	$½-x$	y	$1-z$
x	atom at	$½-x$	$-1+y$	$1-z$
xi	atom at	x	$1+y$	z
xii	atom at	$½-x$	$-1-y$	$-1-z$

Table 2. Final atomic positional and thermal parameters

Atom	x	y	z	B eq.	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(1)	0.0	0.0	0.0	1.29	89(7)	1771(130)	325(26)	-17(30)	90(11)	2(57)
M(2)	0.04179(4)	0.01878(14)	0.35996(7)	0.94	63(2)	1333(27)	239(6)	-32(8)	75(3)	-33(15)
M(3)	0.24771(8)	0.00225(37)	0.65957(16)	0.93	65(4)	1238(72)	230(16)	8(17)	64(6)	-7(33)
M(4)	0.15428(6)	-0.03944(26)	0.92862(12)	1.02	49(3)	1466(50)	329(12)	44(12)	89(5)	109(23)
O(1)	0.0408(4)	0.2436(14)	0.5635(7)	1.36	107(22)	1531(304)	310(71)	-33(69)	60(31)	-251(127)
O(2)	0.1757(4)	0.3127(14)	0.7556(7)	1.50	75(19)	1770(310)	453(76)	51(67)	30(33)	-42(132)
O(3)	0.0698(4)	-0.3003(15)	0.7357(7)	1.63	94(21)	2167(332)	461(76)	124(71)	93(33)	-157(136)
O(4)	0.1312(4)	-0.3268(14)	0.5404(7)	1.42	129(22)	1478(294)	452(75)	11(68)	173(34)	169(128)
O(5)	0.0373(4)	0.1926(13)	0.8669(7)	1.37	96(21)	1723(285)	375(71)	53(70)	110(31)	64(133)
O(6)	0.2457(4)	-0.2345(14)	0.8605(7)	1.46	111(22)	1463(289)	432(76)	73(68)	100(34)	-41(128)
O(7)	0.1665(4)	0.2219(13)	0.4475(6)	1.22	92(20)	1406(275)	326(70)	41(64)	65(30)	86(122)
O(8)	0.1303(4)	0.6744(15)	0.3085(7)	1.89	202(27)	1670(318)	298(72)	105(76)	39(35)	-174(131)
O(9)	0.1872(4)	0.3281(15)	0.1633(8)	1.96	99(22)	1891(328)	927(99)	171(72)	234(38)	517(155)
O(10)	0.0848(4)	0.7286(15)	0.0388(7)	1.62	86(21)	2265(334)	364(72)	107(71)	36(31)	284(139)
O(11)	0.0526(4)	0.2484(15)	0.1576(7)	1.68	118(22)	2047(329)	307(72)	-143(74)	84(32)	161(131)
O(12)	0.25	0.3267(21)	0.0	1.64	190(35)	1741(481)	373(118)	0(100)	37(51)	0(180)
O(13)	0.25	0.6515(20)	0.5	1.31	82(32)	1336(444)	549(109)	0(100)	37(47)	0(180)
Si(1)	0.0999(1)	0.4851(6)	0.6468(6)	1.10	79(6)	1387(106)	336(23)	21(24)	98(9)	53(46)
Si(2)	0.1112(1)	0.4966(6)	0.1616(3)	1.31	81(7)	1727(113)	382(27)	43(30)	93(11)	93(54)
B(1)	0.1708(5)	0.5344(18)	0.4510(9)	B = 0.25(4)						
B(2)	0.2544(4)	0.4527(17)	0.1375(8)	B = 0.18(4)						
H	0.047	0.04	0.92	B = 4						

The values of x, y, z are given in fractional coordinates, the anisotropic thermal parameters ($\times 10^5$) are of the form: $\exp -(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})$. Estimated standard deviations are in parentheses. The hydrogen positional parameters were found by a difference Fourier synthesis; its thermal parameter was estimated by peak height.

Table 3. Estimated bond valences (V. U.); cation chemistry and occupancy of *M*(1), *M*(2), *M*(3), *M*(4) sites are also given

Site	Cation chemistry	Occupancy	Site	Cation chemistry	Occupancy
M(1)	$Al_{1.1}Fe_{0.9}$	1.0	M(3)	$Ca_{0.875}(Y,RE)_{0.125}$	0.86
M(2)	(Y,RE)	0.87	M(4)	$Ca_{0.625}(Y,RE)_{0.375}$	0.89

	M(1)	M(2)	M(3)	M(4)	Si(1)	Si(2)	B(1)	B(2)	Σc_v	Anion chemistry
O(1)		0.38(x2)			1.07				1.83	O^{2-}
O(2)			0.23	0.22	0.93			0.70	2.08	O^{2-}
O(3)		0.36		0.28	1.08				1.72 [1.86]	O^{2-}
O(4)		0.25	0.18		0.93		0.71		2.07	O^{2-}
O(5)	0.49	0.30		0.30					1.09 [0.95]	OH^-
O(6)			0.26	0.25 0.32				0.82	1.65	$O^{2-}_{0.5}OH^-_{0.5}$
O(7)		0.34	0.22 0.25				0.83		1.64	$O^{2-}_{0.5}OH^-_{0.5}$
O(8)		0.28	0.16			0.95	0.70		2.09	O^{2-}
O(9)			0.26	0.12		0.97		0.74	2.09	O^{2-}
O(10)	0.50			0.32		1.03			1.85	O^{2-}
O(11)	0.52	0.34				1.04			1.90	O^{2-}
O(12)			0.27(x2)					0.76(x2)	2.06	O^{2-}
O(13)				0.27(x2)			0.74(x2)		2.02	O^{2-}

Σc_v = sum of bond valences reaching the anions.
In brackets the values corrected for hydrogen bonding.

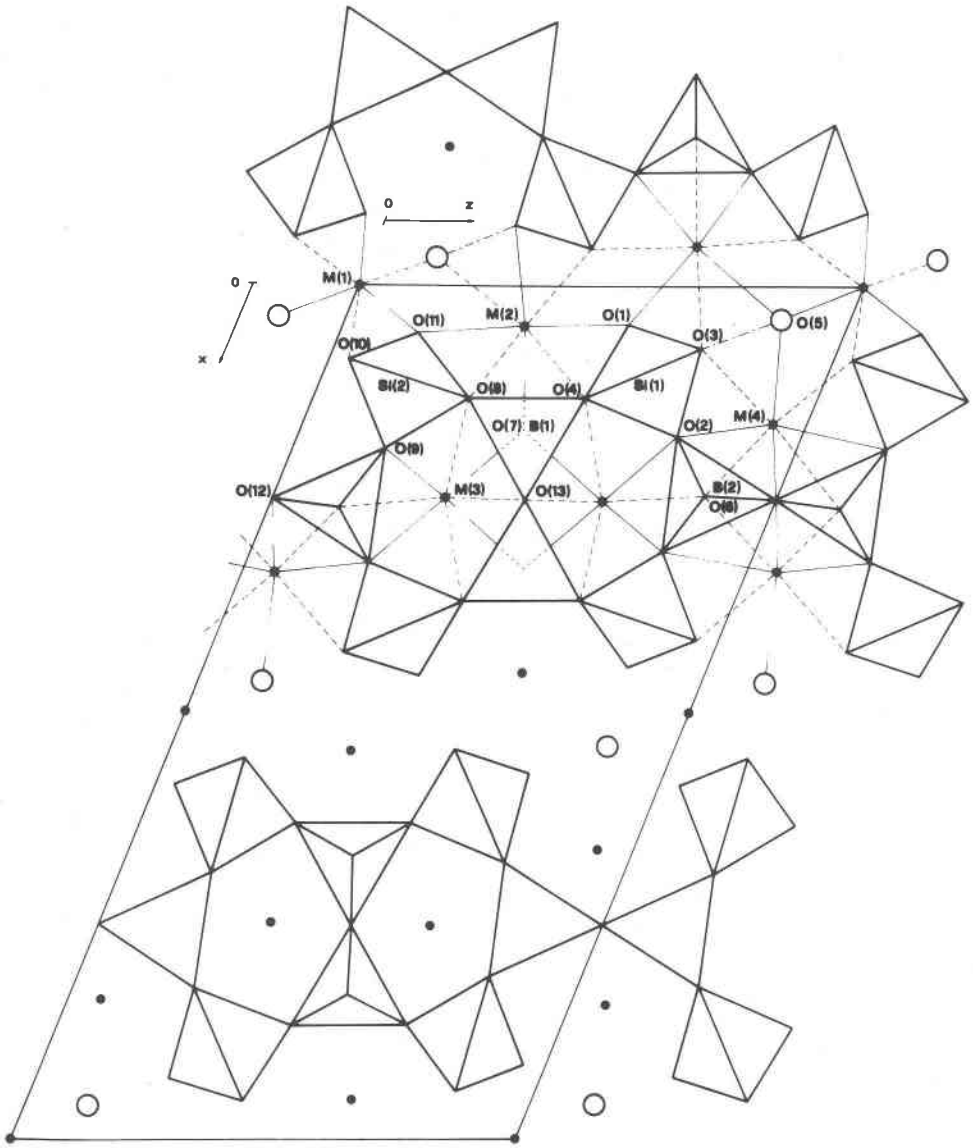

Fig. 1. Crystal structure of hellandite as seen along [010]; dashed lines indicate that the bond is associated with an oxygen atom translated one unit in the [010] direction; dot-dashed lines indicate hydrogen bond; open circles indicate hydroxyl ions.

From the values of the bond lengths and on the basis of the cation distribution and occupancies found in the refinement process, the bond valence sums were calculated following the method of Donnay and Allmann (1970), with the aim of testing the soundness of the structure and determining the position of hydroxyl ions. The bond-valence sums, reported in Table 3, clearly show that O(5) is a hydroxyl ion and also indicate substantial deviations from the ideal value 2 for the valence sums relative to O(3), O(6), and O(7). As regards O(3), the relatively short O(3) . . . O(5) distance (2.921 Å) clearly indicates that O(3) is linked in a hydrogen bond with the O(5) hydroxyl ion. A difference Fourier synthesis showed a well-defined peak assigned to hydrogen in the expected position; its coordinates are given in Table 2. The hydrogen-bond valence strength was estimated by the procedure of Donnay and Allmann (1970) from the distance between the hydrogen-bonded atoms; the correspondingly corrected valence sums for O(3) and O(5) atoms are given in brackets in Table 3. The chemical composition of the investigated specimen (Table 1) suggests the presence of more hydroxyl ions than those placed in the four

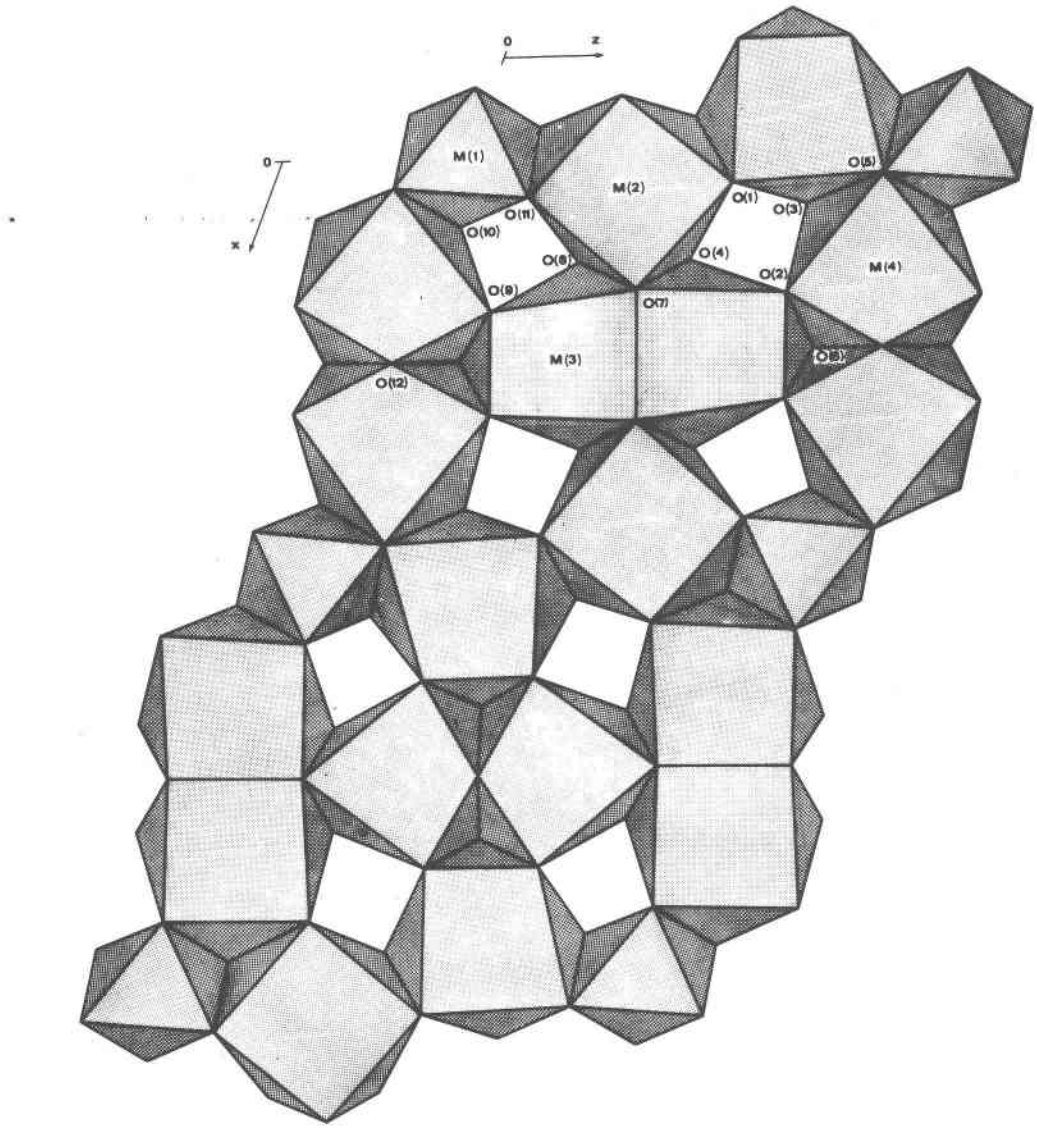

Fig. 2. Layer of octahedra and square antiprisms in the structure of hellandite, as seen along [010].

O(5) positions in the unit cell. The valence sums of bonds for O(6) and O(7) suggest the stoichiometry $O^{2-}_{0.5}(OH)^{-}_{0.5}$ for these positions. The questions of the partial occupancies inside the square antiprisms deserves some attention at this point, as it is linked, in our opinion, to the substitution oxygen–hydroxyl ions in the O(6) and O(7) positions. In fact, the sum of occupancies in the three polyhedra which surround each O(6) and O(7) site is nearly 2.5. Thus when all three polyhedra are fully occupied, an oxygen atom is placed at the anion position, whereas when only two of the polyhedra are occupied, a hydroxyl ion is placed in that position, with the hydrogen atom displaced toward the empty site. The partial occupancy of O(6) and O(7) sites by hydroxyl ions and the disordered position of hydrogen atoms prevent the location of these hydrogen atoms in the difference Fourier synthesis.

The results of the structural investigation can be summarized in the following formula for hellandite:

$$[Ca_{5.5}(Y,RE)_{5.0}\square_{1.5}]\,(Al_{1.1}Fe^{3+}_{0.9})\,(OH)_4\,[Si_8B_8O_{40}(OH)_4].$$

The presence of borosilicate chains with composition $[Si_4B_4O_{20}(OH)_2]^{14-}$ places hellandite among the chain silicates according to the classification of Zoltai (1960), with a sharing coefficient of 1.625 [2.5 according to the modified definition by Coda (1969)].

The structure of hellandite appears closely related to the structures of melilite and melilite-like minerals, a group which comprises more than twenty natural and synthetic compounds. The structure of one mineral of the group, meliphanite, $Ca(Na,Ca)BeSi_2O_6F$, space group $I\bar{4}$, a = 10.516, c = 9.887 Å (Dal Negro *et al.*, 1967) is shown in Figures 4 and 5, to stress the similarities as well as the differences with the structure of hellandite. Comparing Figures 2 and 5, we see that whereas in Figure 5 the square empty spaces, over which the silicon tetrahedra are placed, are regularly disposed so to permit a continuous tetrahedral sheet to match with a calcium and sodium polyhedra sheet, this does not happen in the case of hellandite (Fig. 2) because of the insertion of (Al,Fe) octahedra. In this situation, matching is possible with a sheet of parallel tetrahedral chains which can be easily recognized as clipped from the continuous tetrahedral sheet in melilite and melilite-like minerals.

Table 4. Interatomic distances (Å) and angles (°), with (in parentheses) their e.s.d.'s, of silicon and boron tetrahedra

Si(1)-O(1)	1.609(7)	O(1)-Si(1)-O(2)	106.0(4)	O(1)-O(2)	2.624(8)
-O(2)	1.676(6)	O(1)-Si(1)-O(3)^{xi}	115.3(4)	O(1)-O(3)^{xi}	2.713(10)
-O(3)^{xi}	1.603(9)	O(1)-Si(1)-O(4)^{xi}	111.7(4)	O(1)-O(4)^{xi}	2.721(10)
-O(4)^{xi}	1.678(8)	O(2)-Si(1)-O(3)^{xi}	108.8(4)	O(2)-O(3)^{xi}	2.667(10)
		O(2)-Si(1)-O(4)^{xi}	105.7(4)	O(2)-O(4)^{xi}	2.674(9)
average value	1.641	O(3)^{xi}-Si(1)-O(4)^{xi}	108.9(4)	O(3)^{xi}-O(4)^{xi}	2.670(12)
Si(2)-O(8)	1.650(7)	O(8)-Si(2)-O(9)	109.7(4)	O(8)-O(9)	2.692(12)
-O(9)	1.642(8)	O(8)-Si(2)-O(10)	106.1(4)	O(8)-O(10)	2.603(10)
-O(10)	1.608(7)	O(8)-Si(2)-O(11)	108.2(4)	O(8)-O(11)	2.638(9)
-O(11)	1.605(8)	O(9)-Si(2)-O(10)	111.0(4)	O(9)-O(10)	2.678(9)
		O(9)-Si(2)-O(11)	104.2(4)	O(9)-O(11)	2.563(11)
average value	1.626	O(10)-Si(2)-O(11)	117.5(3)	O(10)-O(11)	2.747(10)
B(1)-O(7)	1.476(11)	O(7)-B(1)-O(8)	113.7(6)	O(7)-O(8)	2.521(9)
-O(8)	1.535(10)	O(7)-B(1)-O(13)	114.4(7)	O(7)-O(13)	2.506(10)
-O(13)	1.506(9)	O(7)-B(1)-O(4)^{xi}	114.0(7)	O(7)-O(4)^{xi}	2.522(10)
-O(4)^{xi}	1.531(13)	O(8)-B(1)-O(13)	104.6(7)	O(8)-O(13)	2.407(6)
		O(8)-B(1)-O(4)^{xi}	102.0(6)	O(8)-O(4)^{xi}	2.382(11)
average value	1.512	O(13)-B(1)-O(4)^{xi}	106.9(6)	O(13)-O(4)^{xi}	2.440(8)
B(2)-O(9)	1.514(12)	O(9)-B(2)-O(12)	104.5(6)	O(9)-O(12)	2.390(9)
-O(12)	1.509(10)	O(9)-B(2)-O(6)^{xii}	112.3(7)	O(9)-O(6)^{xii}	2.483(10)
-O(6)^{xii}	1.475(11)	O(9)-B(2)-O(2)^{ix}	105.8(6)	O(9)-O(2)^{ix}	2.428(9)
-O(2)^{ix}	1.530(9)	O(12)-B(2)-O(6)^{xii}	113.9(7)	O(12)-O(6)^{xii}	2.502(11)
		O(12)-B(2)-O(2)^{ix}	104.0(7)	O(12)-O(2)^{ix}	2.395(8)
average value	1.507	O(6)^{xii}-B(2)-O(2)^{ix}	115.2(6)	O(6)^{xii}-O(2)^{ix}	2.538(9)

Si(1)^{iv}-O(4)-B(1)^{iv}	122.4(5)	B(1)-O(13)-B(1)^{ix}	137.1(8)
B(1)-O(8)-Si(2)	121.6(5)	Si(2)-O(9)-B(2)	127.1(6)
B(2)^{ix}-O(2)-Si(1)	125.3(5)		

Table 5. Interatomic distances (Å) and angles (°), with (in parentheses) their e.s.d.'s, of octahedron and square antiprisms

M(1)-O(5)^{ii}	1.979(8)	M(3)-O(2)	2.445(8)
-O(10)^{v}	1.980(7)	-O(4)	2.613(6)
-O(11)	1.954(6)	-O(6)	2.364(8)
average value	1.971	-O(7)	2.400(6)
		-O(13)^{iv}	2.343(7)
M(2)-O(1)	2.355(7)	-O(7)^{ix}	2.500(8)
-O(4)	2.586(6)	-O(9)^{ix}	2.360(7)
-O(7)	2.405(6)	-O(8)^{x}	2.703(8)
-O(8)^{iv}	2.529(8)	average value	2.466
-O(1)^{vi}	2.348(8)		
-O(3)^{vi}	2.388(7)	M(4)-O(2)	2.574(8)
-O(5)^{vi}	2.479(6)	-O(3)	2.389(6)
average value	2.439	-O(5)	2.346(7)
		-O(6)	2.289(8)
		-O(9)^{i}	2.852(8)
		-O(12)^{i}	2.419(7)
		-O(10)^{iii}	2.306(8)
		-O(6)^{viii}	2.482(6)
		average value	2.457

Details of the hellandite structure

Bond distances and angles in silicon and boron tetrahedra and the edge lengths are given in Table 4. Bond distances in the (Al,Fe) octahedron and in the square antiprisms are given in Table 5, and their edge lengths are given in Figure 3, where the polyhedra are represented with the corresponding Schlegel diagrams.

The mean bond length, (Al,Fe)–O, is 1.971 Å. The bond distances Fe^{3+}–O and Al–O calculated from the Shannon and Prewitt (1969) effective ionic radii for octahedral coordination are 2.00 and 1.89 Å, respectively. The three shortest edges among the six crystallographically independent edges of the octahedron lie on the same face: two of them are shared with *M*(2) and *M*(3) polyhedra with distances 2.643 and 2.751 Å, respectively.

The cation chemistry and occupancy inside *M*(2), *M*(3), and *M*(4) polyhedra are given in Table 2. The mean bond distances *M*(2)–O, *M*(3)–O and *M*(4)–O are 2.439, 2.466, and 2.457 Å, respectively. As can be seen from Figure 3, the shortest edges within each polyhedron are shared edges.

The silicon tetrahedra in hellandite are isolated and are connected through two diborate groups, each of ideal composition $B_2O_6(OH)$, to form infinite chains. The mean bond length in the four nonbridging Si–O bonds (1.606 Å) is shorter than the mean bond length in the four bridging Si–O bonds (1.661 Å). This happens also in the boron tetrahedra where B(2)–O(7) and B(2)–O(6) have bond lengths (1.475 Å) much shorter than those corresponding to the six bridging B–O bonds (mean value 1.521 Å). Whereas silicon tetrahedra do not share edges, boron tetrahedra share the edges of the face parallel to the (010) plane with square antiprisms; the faces are thus narrowed, and tetrahedra are distorted toward an elongated trigonal pyramid.

Crystal chemistry of hellandite and tadzhikite

The three reliable chemical analyses of hellandite are reported in Table 1, with the unit cell contents calculated on the basis of eight silicon atoms in the unit cell. The analysis of the Norwegian hellandite (Oftedal, 1965) was made on altered material, and Hogarth *et al.* (1972) observed that single-crystal photographs of the Canadian hellandite were "poor with highly diffused spots probably due to poor crystallinity." Thus the only analysis made on material of good crystallinity was the microprobe analysis of the Italian hellandite given by Hogarth *et al.* (1972). The corresponding formula

$$[Ca_{5.10}Mn_{0.18}Y_{3.00}RE_{1.56}\square_{2.16}]\ (Al_{1.12}Fe^{3+}_{0.89})\ (OH)_4\ [Si_8B_8O_{38.26}(OH)_{5.74}]$$

compares very well with that derived from the structure analysis; the calculated density 3.645 g cm^{-3} matches with the observed value 3.63 g cm^{-3}. The crystal-chemical formulas of the Canadian and Norwegian hellandites can be written:

$$[Ca_{3.26}Mn_{0.15}Y_{4.63}RE_{1.97}Th_{0.04}\square_{1.95}]\ (Al_{1.44}Fe^{3+}_{0.56})(OH)_4\ [Si_8 = Al_{0.33}B_{4.75}\square_{2.88})O_{32.14}(OH)_{11.86}]$$

and

$$[Ca_{3.70}Mn_{0.10}Y_{3.46}RE_{1.46}Th_{0.10}\square_{3.18}]\ (Al_{0.91}Fe^{3+}_{0.69}Fe^{2}_{0.02}Ti_{0.09}Mg_{0.27})(OH)_4\ [Si_8(B_{5.44}\square_{2.56})O_{28.82}(OH)_{15.18}]$$ respectively.

In these formulas all the water content is calculated as hydroxyl ions. While this is surely correct for hellandite from Predazzo, as it is indicated by the crystal-structure determination, it is not proved for Canadian and Norwegian hellandites, in which some water molecules could substitute for hydroxyl ions. In deriving the crystal-chemical formulas, the unit cell contents in water molecules were assumed so as to have a total of forty-eight oxygen atoms as suggested by the crystal structure. Whereas the calcu-

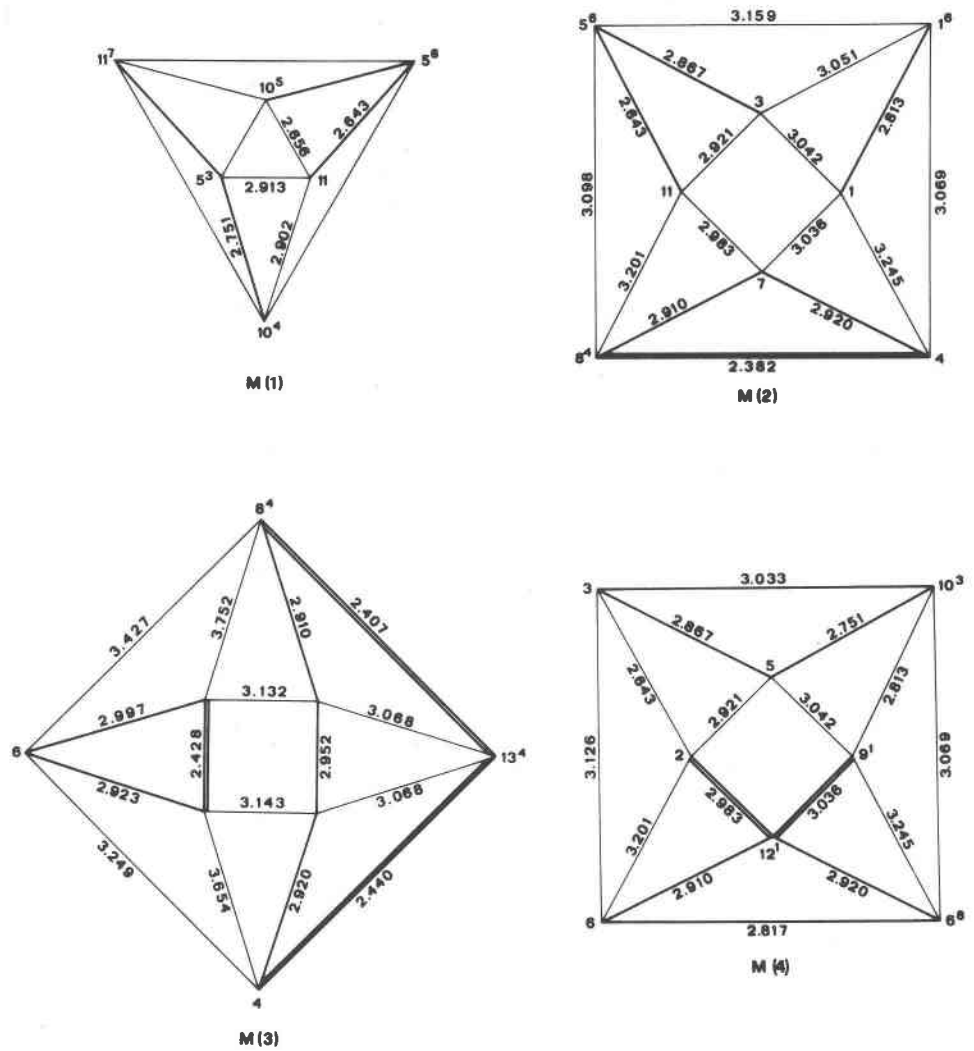

Fig. 3. Coordination octahedra and square antiprisms in hellandite, described by Schlegel diagrams; edges shared with large polyhedra are drawn bold, edges shared with tetrahedra are drawn with a double line.

lated content matches well with the observed one for Canadian hellandite (7.93 and 7.97 water molecules, respectively), the calculated content differs substantially from the observed one of Norwegian hellandite (9.59 molecules as compared with 5.60). However, much higher water contents, in good agreement with the crystal-chemical formula, were reported by Brögger (1903, 1907) for the same material.

The crystal chemistry of tadzhikite appears closely related to that of hellandite. Two morphological types of tadzhikite were identified: tadzhikite I was found as spherulites or aggregates of bent flakes, with monoclinic symmetry and density 3.86 g cm^{-3}, and tadzhikite II was found as flattened prismatic crystals with probably triclinic symmetry but a metrically monoclinic unit cell with dimensions $a = 17.93$, $b = 4.71$, $c = 10.39$ Å, $\beta = 100°45'$. On this basis tadzhikite was considered different from hellandite, not only because of the chemical composition (Efimov *et al.*, 1970) but also because of the unit cell dimensions. However, the latter does not appear correct, because another metrically monoclinic unit cell can be selected with dimensions $a = 18.97$, $b = 4.71$, $c = 10.39$ Å, $\beta = 111.8°$, agreeing well with those of hellandite (transformation matrix from the cell given by Efimov *et al.* (1970) to the preceding one: [101/010/00$\bar{1}$]). Table 6 gives the chemical composition for the two types of tadzhikite, together with the empirical unit-cell contents. The data of this table and the structural work on hellandite suggest two possible

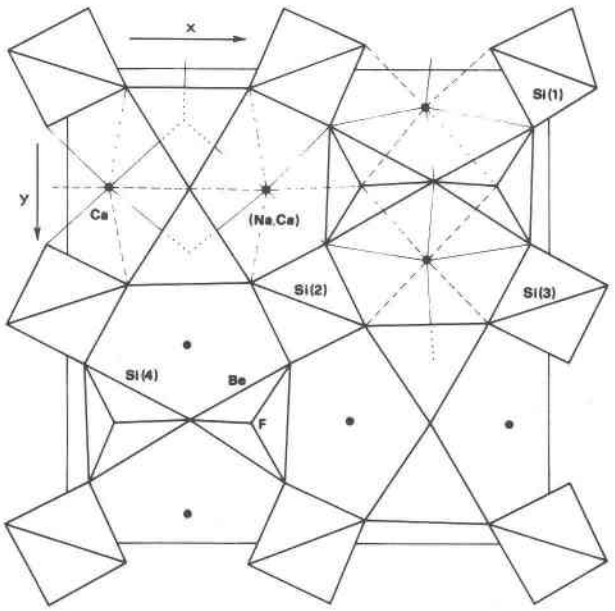

Fig. 4. Crystal structure of meliphanite, as seen along [001].

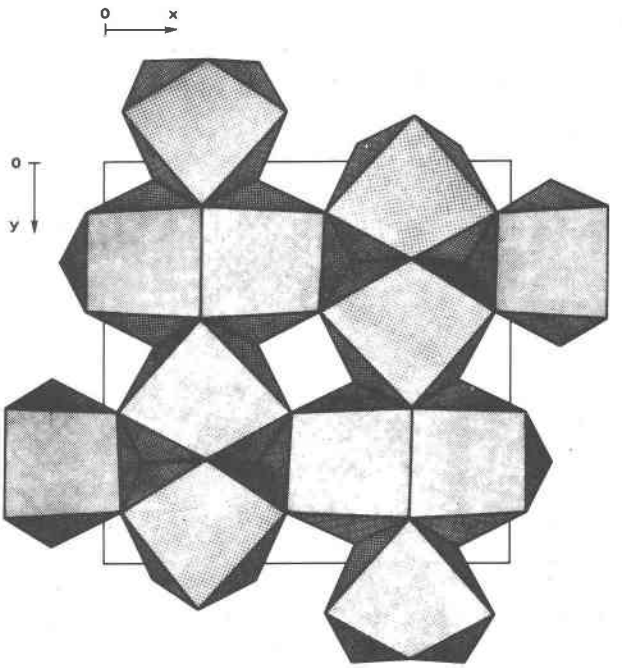

Fig. 5. Layer of octahedra and square antiprisms in the structure of meliphanite, as seen along [001].

Table 6. Chemical analyses and unit cell contents of tadzhikite I and tadzhikite II

	I	II		Ia		IIa	
SiO_2	24.70	23.35	Si	8.24		7.52	
BeO	-	0.20	Be	-	15.54	0.15	15.71
B_2O_3	12.70	14.47	B	7.30		8.04	
TiO_2	6.53	3.72	Ti	1.64		0.90	
Al_2O_3	-	2.30	Al	-	1.97	0.87	1.77
Fe_2O_3	1.32	3.12	Fe	0.33		0.75	
ThO_2	0.50	0.50	Th	0.04		0.04	
Nb_2O_5	0.75	-	Nb	0.11		-	
MnO	0.89	0.40	Mn	0.25		0.11	
MgO	0.42	-	Mg	0.21	12.42	-	11.39
CaO	18.31	18.06	Ca	6.54		6.23	
RE_2O_3	32.43	34.07	RE	4.52		4.26	
SrO	0.04	0.04	Sr	-		-	
NaO	1.17	-	Na	0.75		-	
			O	45.72		44.29	

Analyst: M.E. Kazakova in Efimov et al. (1970).

crystal-chemical formulations, which in the case of tadzhikite II can be expressed as follows:

$$Ca_7(Y,RE)_5(Al,Ti)_2(OH)_4\ Si_8B_8O_{44}$$

and

$$Ca_7(Y,RE)_5(Al,Ti)_2O_2\ Si_8B_8O_{44}.$$

According to the first formulation, a substantial water content should appear in the chemical analysis, contrasting with the anhydrous nature of tadzhikite claimed by Efimov *et al.* (1970). Possibly fluorine substitutes for hydroxyl ions in the structure, and for some reason its presence remained undetected. The second formulation, which is in agreement with the chemical analysis, can be rationalized by admitting a square pyramidal coordination of oxygen atoms around the titanium cation, a coordination already found in minerals (Woodrow, 1964; Moore and Louisnathan, 1967), and synthetic phases (Mumme and Wadsley, 1968). The ordering of titanium cations would also explain the change to triclinic symmetry indicated for this mineral by Efimov *et al.* (1970). More chemical and structural work on tadzhikite thus seems desirable.

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