

NEW DATA ON HELLANDITE

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ABSTRACT

Hellandite is known from pegmatite near Wakefield Lake, Canada, Kragerø, Norway, and from granite near Predazzo, Italy. In each of these occurrences it is associated with a niobium oxide, allanite and various yttrium-bearing minerals. The Canadian mineral was formed from a pegmatite fluid rich in Ca, Y and B during an intermediate stage of the pegmatite-forming process. Hellandite is monoclinic $-P2/a$ with $a = 18.82-18.91$, $b = 4.69-4.71$, $c = 10.25-10.28\text{\AA}$, with Italian hellandite having larger cell constants (related to more calcium in the formula) than that from Canada and Norway, and $\beta = 111^{\circ}26' - 111^{\circ}36'$. The most probable cell formula is $4[(\text{Ca},\text{Y})_2(\text{Si},\text{B},\text{Al})_3\text{O}_8 \cdot \text{H}_2\text{O}]$ although the ordering of boron and the rôle of water are uncertain. Physical properties of Canadian hellandite are consistent with those reported in the literature for hellandite from Italy and Norway but the optic sign tends to be negative ($2V_x \sim 90^{\circ}$) and x -ray investigation has established $b = X$. In differential thermal treatment, hellandite changes to an apatite structure at 860°C .

INTRODUCTION

Hellandite, from the Lindvikskollen pegmatite dyke, near Kragerø, southern Norway was described by Brøgger (1903, 1907, 1922). The paragenesis of the Lindvikskollen pegmatite, with the rare earth minerals allanite, thorite, yttrian titanite, euxenite, hellandite, was described by Bjørlykke (1937). A somewhat different mineral association was noted by Emiliani & Gandolfi (1965) and Gandolfi (1966) for Predazzo granite, northern Italy, where coexisting rare earth minerals included allanite, thorite, fergusonite, ancylite and hellandite. Hellandite was collected from the Evans-Lou mine, southern Quebec in 1968 (Miles, Hogarth & Russell 1971; Hogarth 1971).

Other data on hellandite are reported as follows: morphological crystallography (Brøgger 1903, 1907, 1922), physical and optical properties (Brøgger 1907; Winchell & Winchell 1927; Emiliani & Gandolfi 1965), x -ray diffraction patterns (Ofteidal 1965; Emiliani & Gandolfi 1965; Semenov 1963), chemical composition (Brøgger 1903, 1907; Semenov & Barinskii 1958; Ofteidal 1964, 1965).

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Recently Efimov *et al.* (1970) have described tadjhikite, alleged to be an anhydrous, Ce-Nd member of the hellandite group.

The following chemical formulae have been proposed :

$\text{Ca}_2\text{Y}_3\text{R}_3^{3+}(\text{SiO}_4)_4(\text{OH})_6$	(Brøgger 1907)
$\text{Ca}_2\text{Y}_3\text{R}_3^{3+}(\text{SiO}_4)_4(\text{O},\text{OH})_4$	(Betekhtin 1950)
$(\text{Ca},\text{Y})_{<3}\text{R}^{3+}(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$	(Strunz 1957)
$\text{Ca}_2\text{Y}_2\text{Al}_2\text{Si}_3\text{O}_{14} \cdot 4\text{H}_2\text{O}$	(Semenov 1963)
$\text{Ca}_3\text{Y}_4\text{B}_4\text{Si}_6\text{O}_{27} \cdot 3\text{H}_2\text{O}$	(Ofstedal 1965)
$\text{Ca}^3\text{R}_4^{3+}\text{B}_4[\text{O}(\text{OH})_2\text{Si}_2\text{O}_7]_3$	(Strunz 1970)
$\text{Ca}_3\text{RE}_2(\text{Ti},\text{Al},\text{Fe})\text{B}_4\text{Si}_4\text{O}_{22}$	(Efimov <i>et al.</i> 1970, "tadjhikite")

HELLANDITE FROM THE WAKEFIELD LAKE REGION

The abandoned Evans-Lou quarry near Wakefield Lake, Quebec, exposes a pegmatite dyke that contains fergusonite, kainosite (cenosite), tenerite (type of Vormea *et al.* 1966), xenotime, wakefieldite and hellandite. The pegmatite cuts Precambrian metamorphic rocks and is zoned with a quartz core, giant perthite-quartz zone, perthite-plagioclase-quartz zone and graphic granite (on the periphery). Rare earth minerals are mainly concentrated in the giant perthite-quartz zone. Further details of the pegmatite are given by Miles, Hogarth & Russell (1971).

Hellandite has been found in some quantity on the dump. It was identified by comparison of x-ray patterns with those of Norwegian hellandite supplied by the University of Oslo and the Geological Survey of Canada. The largest fragments weighed 5.38 and 6.62 kg. These were red-brown and noticeably zoned in hand specimen but other specimens were black, grey, green, yellow and cream. The lustre varied from vitreous (black variety) to dull. Commonly hellandite occurred in quartz, was spotted with chlorite, veined by red kainosite and stained white by "tenerite". Less common alteration products were hematite, calcite, thorumite, doverite and, perhaps, wakefieldite.

During the summer of 1970, 10 metres of water were drained from the pit and hellandite appeared abundantly on the hanging wall (west) side of the pegmatite. Hellandite was found in greyish quartz-rich portions of the giant perthite-quartz zone close to, and mostly within 1 metre of, the barren white quartz core. Commonly hellandite, quartz and microcline are brecciated and cemented with a new generation of quartz.

At one location in the pit, comparatively unaltered crystals measured up to 0.55 m long and 0.10 m wide. Crystals and crystal fragments in breccia, 0.3 m long, were not rare in other parts of the pit.

Fergusonite is a common associate of hellandite. Other primary minerals sometimes seen near hellandite are yttrian spessartine, allanite, uraninite, specularite, muscovite, pyrrhotite and chalcopyrite.

During alteration hellandite is bleached from black to pale yellow and becomes soft. Finally it is transformed into a grey, pulverulent or even clay-like mass. However, as seen through the microscope, the alteration proceeds in an interesting manner. Inclusions are swept away along fractures and turbid hellandite becomes clear to within 0.05 to 0.20 mm of the crevice (Fig. 1). Brown iron oxide is concentrated close to the crevice. Some open fractures are sealed with prismatic kinosite and many cavities are lined with flaky "tengerite".

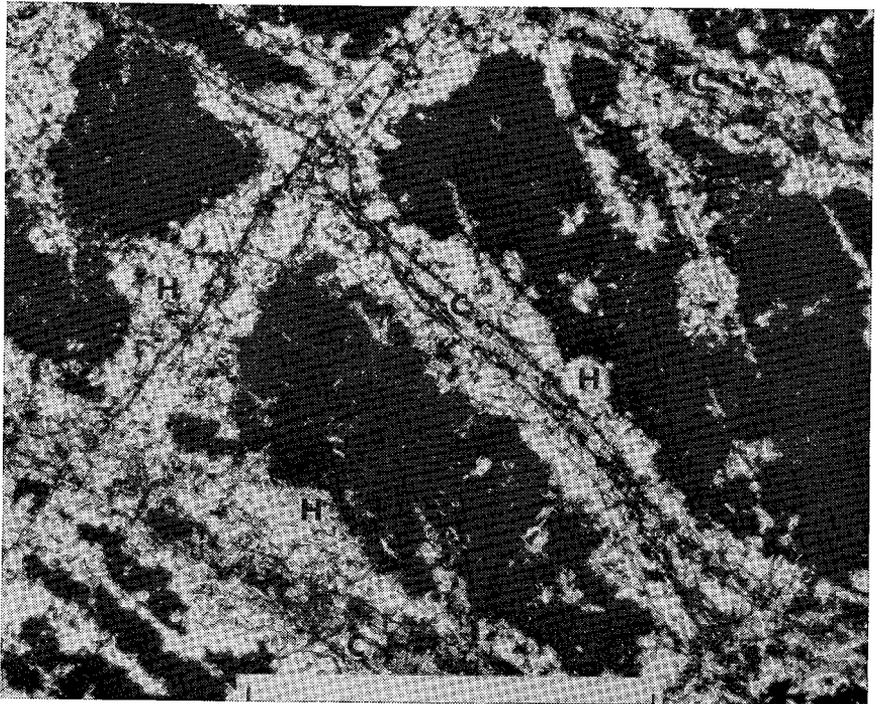


FIG 1. Photomicrograph. Crossed polars. Dark grey, fine-grained kinosite (C) in the central portion of the veinlets surrounded by lighter grey, optically continuous hellandite (H). Dark intervening portions are mainly hematite and chlorite. Bar scale 1 mm. (53 \times).

X-RAY CRYSTALLOGRAPHY

Over twenty crystal fragments of the Quebec hellandite were studied by Weissenberg and precession methods. The single crystal photographs of all of these fragments were poor with highly diffused reflection spots probably due to poor crystallinity. The best photographs, obtained from fragments showing vitreous luster, gave $a = 18.79 \pm 0.05 \text{ \AA}$, $b = 4.67 \pm 0.02 \text{ \AA}$, $c = 10.21 \pm 0.03 \text{ \AA}$, $\beta = 111^\circ 28' \pm 5'$. Systematic extinctions were consistent with the space groups $P2/a$, Pa or $P2$. The non-centro symmetric space groups $P2$ and Pa may be eliminated on morphological considerations (Brøgger 1903, 1907). Single crystal photographs of hellandite from Predazzo, Italy were identical to those of hellandite from Quebec except that the reflection spots were much sharper and gave slightly larger cell parameters. Several attempts on the hellandite from Kragerø, Norway, failed to produce usable single crystal photographs.

X-ray powder diffraction photographs of hellandite from the three localities were virtually identical by sight. Both the Norwegian and Italian minerals gave sharply defined diffraction lines whereas the Quebec mineral gave poor, diffused lines and strong background. Carefully prepared powder photographs with metallic silicon as internal standard, were measured and the lines were indexed by comparison with d -values calculated from the cell parameters obtained from single crystal work. Single crystal photographs were used as a guide in indexing and indices of the strong reflections only were used. The cell parameters were then refined by the least squares method. The refined values for hellandite from the three localities are compared with the cell parameters of tadjhikite in Table 1.

TABLE 1. CELL PARAMETERS OF HELLANDITE
(E.S.D. in parentheses)

	Hellandite Canada (EL—215)	Hellandite Italy (No. 19)	Hellandite Norway (Yellow brown)	Tadjhikite U.S.S.R. (Efimov <i>et al.</i> 1970)
a	18.824(4) Å	18.911(4)	18.845(5)	17.93
b	4.696(1) Å	4.708(1)	4.687(1)	4.71
c	10.248(2) Å	10.276(2)	10.269(3)	10.39
β	111°26'(1)	111°31'(1)	111°36'(1)	100°45'
V	843.20 Å ³	851.28	843.31	862

TABLE 2. X-RAY POWDER DIFFRACTION PATTERNS OF HELLANDITE
(114.6 mm camera, Si internal standard)

<i>hkl</i>	Hellandite ¹ Canada (CoK _α radiation)			Hellandite ² Italy (CuK _α radiation)			Hellandite ³ Norway (CuK _α radiation)		
	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i>
200							8.77	8.761	30
201				5.56	5.542	20	5.51	5.521	30
202				5.06	5.047	20	5.04	5.044	10
010	4.70	4.696	80	4.71	4.708	80	4.69	4.687	80
210	4.14	4.139	10	4.15	4.151	20	4.13	4.133	10
401	3.522	3.522	10	3.539	3.535	10	3.517	3.520	30
212	3.433	3.433	50	3.446	3.443	70	3.436	3.433	70
012				3.349	3.354	10	3.344	3.345	5
410	3.205	3.203	40	3.214	3.214	60	3.198	3.200	70
601				3.145	3.145	10			
412	3.067	3.065	40	3.075	3.076	60	3.068	3.067	60
212	2.893	2.889	50	2.899	2.896	60	2.884	2.886	60
411	2.819	2.818	60	2.829	2.827	80	2.812	2.815	100
013		2.633			2.639			2.633	
043	2.635	2.636	100	2.642	2.644	100	2.635	2.639	80
611	2.606	2.605	50	2.618	2.615	50	2.603	2.605	80
204	2.546	2.549	10	2.557	2.558	10	2.552	2.554	10
610	2.476	2.480	10	2.490	2.489	10	2.483	2.479	10
004	2.385	2.385	10	2.393	2.391	10	2.388	2.387	20
802	2.342	2.341	20	2.352	2.352	20	2.345	2.344	40
121				2.294	2.292	10			
314	2.245	2.247	10	2.255	2.253	10	2.247	2.250	10
710	2.208	2.209	10	2.218	2.218	10	2.209	2.208	20
313	2.169	2.167	30	2.176	2.173	30	2.165	2.166	40
014		2.126			2.131			2.127	
222	2.127	2.128	10	2.134	2.133	10	2.127	2.125	10
812	2.095	2.094	20	2.098	2.104	10	2.093	2.097	10
422				2.035	2.037	10	2.029	2.029	5
421	1.953	1.954	30	1.962	1.959	20	1.951	1.951	30
322		1.887			1.892			1.884	
023	1.887	1.889	40	1.891	1.893	50	1.885	1.887	40
10.01					1.856			1.848	
10.03				1.854	1.854	5	1.849	1.849	5
805	1.802	1.801	10	1.809	1.808	5	1.807	1.806	10
802	1.760	1.761	10	1.772	1.767	10			
10.00	1.752	1.752	20	1.760	1.760	10	1.755	1.752	30
414		1.707			1.711			1.706	
406	1.707	1.708	20	1.711	1.713	10	1.706	1.711	10
822				1.664	1.664	5	1.657	1.657	5
10.10	1.6417	1.6416	20	1.6477	1.6483	20	1.6402	1.6412	20
416	1.6053	1.6051	20	1.6099	1.6094	10	1.6085	1.6076	10
622	1.5919	1.5909	20	1.5966	1.5957	10	1.5888	1.5891	10
030				1.5694	1.5692	5	1.5655	1.5624	5
825				1.4337	1.4337	5	1.4301	1.4304	5
033	1.4042	1.4044	20	1.4077	1.4078	10	1.4026	1.4025	20

¹ EL—215.

² No. 19. Specimen supplied by G. Gandolfi.

³ Yellow-brown specimen supplied by P.C. Saebo.

The indexed powder patterns of hellandite are given in Table 2. The powder pattern of the Norwegian hellandite agrees well with that reported by Oftedal (1965) except that more lines were recorded in this work. However, the d -values in the low angle region reported here on the Italian hellandite are significantly smaller than the values reported by Emiliani & Gandolfi (1965).

CHEMICAL ANALYSIS

After a semiquantitative spectrochemical analysis, conducted at the Geological Survey of Canada under the direction of W. H. Champ, metallic constituents (Ca, rare earths, Mn, Ti, Si, Al, Fe) in a hellandite fragment from EL-109 were determined by microprobe analysis with data processed according to the computer program of Rucklidge (1967). Standards were Fe metal, Mn metal, Al_2O_3 and analysed kainosite from the Bicraft mine (Pouliot, Maxwell & Robinson 1964). In order to avoid decomposition of the specimen the beam was broadened to 20 μm and the specimen current reduced to 0.035 microamperes.

The remaining constituents (Th, U, V, B and H_2O) were determined from a split portion (4 g.) of the original sample under the direction of D. S. Russell at the National Research Council. After the fragments were ground and Y_2O_3 removed, Th, U and V were tested by optical emission. Total water was determined by the Penfield method, H_2O^- by weight loss at 110°C, and H_2O^+ by difference. Boron was determined by titration.

Sample 19 of Gandolfi (1966) was received as 10 sandsized grains and all constituents were determined by the electron microprobe from 3 grains mounted in a polished section. Standards were those used for EL-109. The results of the two new analyses are compared with an analysis of Norwegian hellandite (Oftedal 1965) in Table 3 and lanthanide compositions are graphically compared in Fig. 2.

CHEMICAL AND STRUCTURAL CONSIDERATIONS

The simplest formula that can be derived from the 4 analyses of Table 3 is $(\text{Y,Ca})_2(\text{Si,B,Al})_3\text{O}_8 \cdot \text{H}_2\text{O}$ or $\text{X}_2\text{Z}_3\text{O}_8 \cdot \text{H}_2\text{O}$. Cation content of X and Z are listed in Table 4. On the basis of a rational formula iron seems best included in Z but, because iron is present in small amount in EL-109, Mössbauer spectra did not give decisive results on the role of this element.

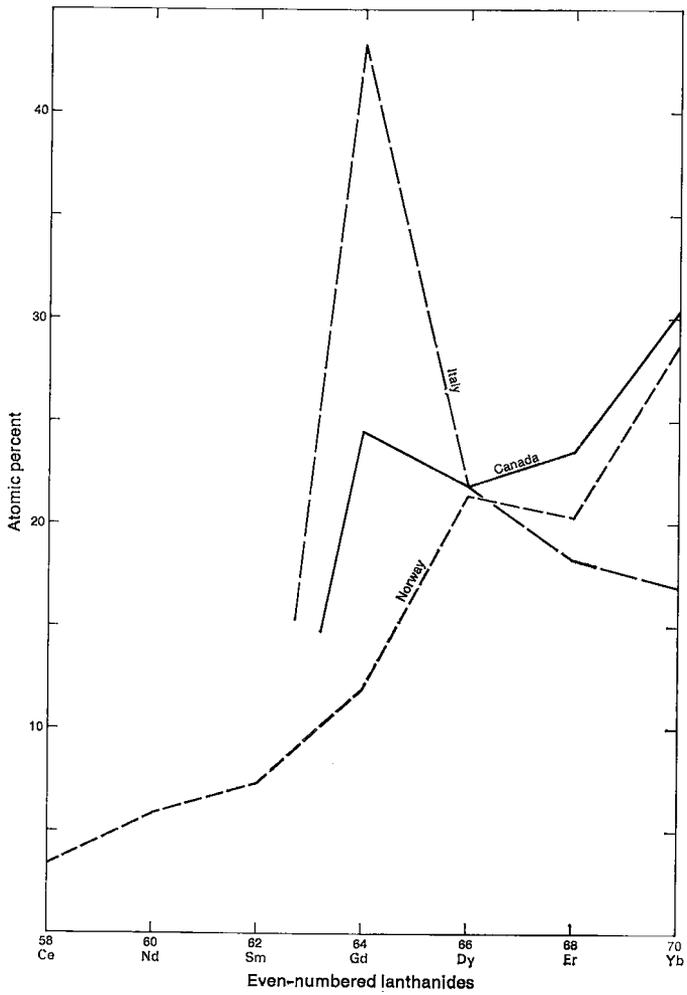


FIG. 2. Lanthanide composition of hellandite.

TABLE 3. ANALYSES OF HELLANDITE

	Norway ¹ (altered, brownish white)	Canada ² (EL-109)	Italy ³ (No. 19)	U.S.S.R. ⁴ ("tadzhikite", No. 2)
CaO	11.51%	9.28%	15.22%	18.06%
Y ₂ O ₃	21.68	26.53	18.07	} 34.07
La ₂ O ₃	0.08			
Ce ₂ O ₃	0.39			
Pr ₂ O ₃	0.04			
Nd ₂ O ₃	0.73			
Sm ₂ O ₃	0.89			
Eu ₂ O ₃	< 0.04			
Gd ₂ O ₃	1.66	4.48	6.60	
Tb ₂ O ₃	0.37			
Dy ₂ O ₃	2.84	4.12	3.35	
Ho ₂ O ₃	0.73			
Er ₂ O ₃	2.75	4.64	2.91	
Tm ₂ O ₃	0.45			
Yb ₂ O ₃	4.05	5.95	2.67	
Lu ₂ O ₃	0.61			
MnO	0.41	0.58	0.70	0.40
MgO	0.60			Tr.
TiO ₂	0.39	< 0.2	< 0.2	3.72
ThO ₂	1.46	0.57		0.50
SrO ₂				0.04
BeO				0.20
V ₂ O ₅		< 0.05		
U ₃ O ₈		< 0.2		
SiO ₂	26.65	24.41	25.57	23.35
Al ₂ O ₃	2.58	4.59	3.04	2.30
B ₂ O ₃	10.5	8.47	not determined	14.47
FeO	0.07	2.06	3.39	not found
Fe ₂ O ₃	3.07			3.12
H ₂ O+	3.75	5.3	not determined	
		101.0	80.82	
H ₂ O—	1.85	2.0	not determined	
	100.1			100.11

Analysts :

¹ R. Bruun in Oftedal (1965).² D.C. Harris and D.S. Russell ; total iron calculated as FeO.³ D.C. Harris ; total iron calculated as FeO ; Specimen supplied by G. Gandolfi.⁴ M.E. Kazakova in Efimov *et al.* (1970).

Data for the 3 hellandite specimens of Table 4 suggest 1 atom of *B* per 8 oxygens and the formula $X_2Z_2BO_8 \cdot H_2O$. However this formula cannot be reconciled with the compositions of tadzhikite given by Efimov *et al.* (1970). Conversely, because of a variable Ca : RE ratio, the compositions of hellandite cannot be easily adjusted to the tadzhikite formula — $Ca_3RE_2(Ti,Al,Fe)B_4Si_4O_{22}$ — proposed by the Russian authors. It should be noted that tadzhikite is an anhydrous mineral but x-ray data suggest an isostructural relationship with hellandite.

The rôle of water is uncertain but the best evidence suggests 1 unit of H_2O per formula unit of $X_2Z_2O_8$. The analysis of Norwegian hellandite by Oftedal (1965) suggests 0.78 H_2O but if, instead, the value of 4.86% H_2O + (Brøgger 1907, p. 432) be substituted with Oftedal's data, this hellandite contains 1.01 H_2O per formula unit. Canadian hellandite contains approximately 1 unit of H_2O + in its formula. Infrared analyses of samples EL-109 and EL-312 show a weak absorption maximum at 1640 cm^{-1} , indicating some H_2O , but hydroxyl could neither be definitely established nor precluded. It is, of course, possible that the mineral con-

TABLE 4. FORMULAE OF HELLANDITE

		Norway ¹	Canada ¹	Italy ²	U.S.S.R. ³ ("tadzhikite")
X	Ca	0.78	0.64	1.02	1.12
	RE	1.06	1.30	0.93	0.79
	Mn	0.02	0.03	0.05	0.02
	Mg	0.06			
	Ti	0.02			0.16
	Th	0.02	0.01		0.01
Z	Si	1.70	1.56	1.61	1.36
	Al	0.19	0.35	0.23	0.16
	B	1.13	0.97	[0.98]	1.49
	Fe	0.15	0.11	0.18	0.14

$X_{1.96} Z_{3.17} O_8 \cdot 0.78 H_2O$ Norway

$X_{1.98} Z_{2.99} O_8 \cdot 1.13 H_2O$ Canada

$X_{2.11} Z_{3.15} O_3$ U.S.S.R.

¹ Formula based on 8 oxygens.

² Formula based on X = 2; B by difference assuming Z = 3.

³ Formula based on 8 oxygens. Atomic weight rare earths (RE) = 125.8.

tains hydroxyl and has the formula $X_2BSi_2O_7(OH)_2$, suggesting a relationship of hellandite with such sorosilicates as woehlerite — $Ca_2Na(Zr,Nb)Si_2O_7(O,F)_2$. However, the x-ray pattern has no apparent similarity to patterns of minerals of the woehlerite group. The justification of linking hellandite with woehlerite, as was done by Brøgger (1907) and Strunz (1970), seems very tenuous.

The unit cell parameter, a , seems to vary directly with the amount of calcium in the formula (Fig. 3). This is easily explained by the larger radius of Ca^{2+} (0.99Å) than Y^{3+} (0.89Å) and ions of the heavy lanthanides (average 0.89Å; values from Handbook of Chemistry and Physics). The fact that the b and c parameters are comparatively unaffected by Ca content would seem to indicate that the calcium ions are preferentially concentrated along the a direction.

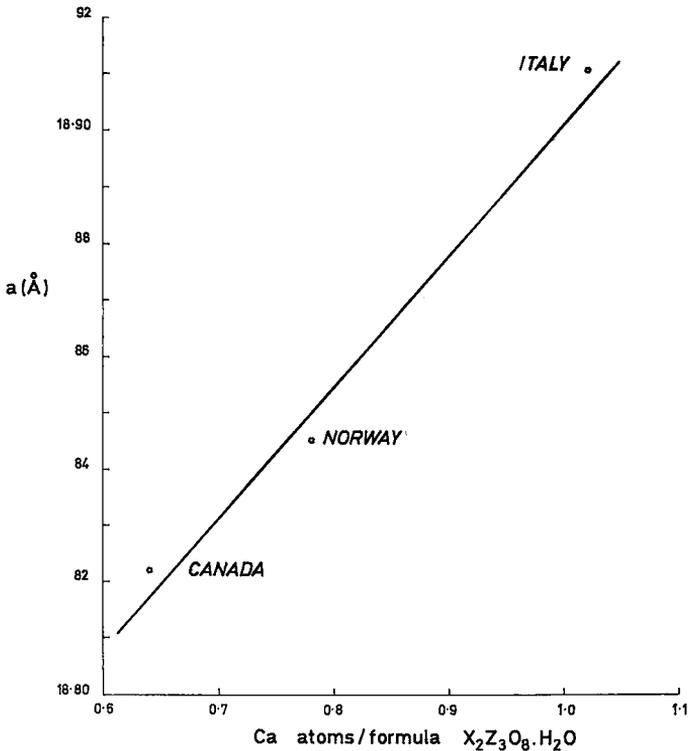


FIG. 3. Relationship of the cell parameter a with Ca in hellandite.

PROPERTIES OF HELLANDITE

Properties of hellandite are listed in Table 5. Specific gravities of Canadian hellandite were measured with a Berman balance. Each value is an average of determinations on three or more fragments. The specific gravities varied from 2.95 ± 0.01 for yellow pulverulent hellandite to 3.55 ± 0.03 for black hellandite. The calculated density of EL-109 ($M.W. = 401.3$, $Z = 4$, cell vol. = 843.2 \AA^3) is 3.161 g/cc .

Crystals normally do not show well developed faces. Some are flattened along $b\{010\}$, with flattening roughly parallel to the contact of the pegmatite zones. Cleavage is poorly developed parallel $a\{100\}$ and $b\{010\}$. An altered crystal, $23 \times 4 \times 2\frac{1}{2}$ centimeters, gave contact goniometric measurements suggesting elongation parallel to c and the forms $a\{100\}$, $b\{010\}$, $c\{001\}$ ($\rho = 20^\circ$), $e\{201\}$ ($\rho = 37^\circ$), $r\{203\}$ ($\rho = 01^\circ$).

Optical properties are quoted for Na_D . The mean refractive index of EL-109 calculated with the rule of Gladstone and Dale is 1.644 ($G = 3.27$; specific refractive energies of Larsen & Berman 1934 and Jaffe 1956; values for Gd_2O_3 , Dy_2O_3 , Er_2O_3 and Yb_2O_3 assumed 0.141; all iron assumed Fe^{3+}). X is normal to the second most important cleavage, shown by x -ray goniometry to be (010). An oriented thin section, parallel to this cleavage, was cut from specimen EL-312. The extinction angles ($Z\Lambda c$) were measured against the other cleavage, by x -ray (100). Optic angles were measured on the flat stage using the method of Kamb (1958, pp. 1052-1060) with one value checked against a measurement on the universal stage (80° U-stage, 79° flat stage).

In thin section hellandite is clear to cloudy and normally colourless. "Red hellandite" is apparently pigmented by fine inclusions of hematite but in this variety, hellandite itself is pale yellow to colourless.

Hellandite veinlets were noticeably zoned across their width accounting for the variation extinction and optic angles recorded for EL-312. In an oriented thin section of red hellandite (EL-348), extinction angles varied from $Z\Lambda c = 44^\circ$ ($2V_x \sim 70^\circ$) in the core to $Z\Lambda c = 53^\circ$ ($2V_x \sim 80^\circ$) on the rim of the veinlet. Weak crossed dispersion was observed in some sections.

Hardness was determined on sawn surfaces. On one specimen (EL-312) the hardness on a plane cut $\perp c$ appeared superior to that of topaz but less than that of corundum. Surfaces cut \parallel (010) and (100) could easily be scratched by quartz. The anisotropy of hardness needs further investigation; it may be due to impurities in the specimen.

TABLE 5. PHYSICAL PROPERTIES OF HELLANDITE

	EL-109	EL-215	EL-312	Norway (Brøgger 1907)	Italy (Emiliani & Gandolfi 1965)
Macroscopic appearance	greenish yellow, dull; formless	yellow; rough unidentified forms	black vitreous tabular (010)	brown to red crystals	yellow grains
α	1.652 \pm 0.002	1.656 \pm 0.002		1.65 (Winchell & Winchell 1927)	\sim 1.72
β	1.657 \pm 0.001	1.662 \pm 0.002	1.712 \pm 0.003	1.75 (Ofstedal 1965)	
γ	1.662 \pm 0.001	1.668 \pm 0.002		100°	1.73
$2V_x$	85°	87°	81° rim of veinlet 72° intermediate zone 79° centre of veinlet		48°-86°
$Z\Delta c$			+44° rim of veinlet +42° intermediate zone +35° centre of veinlet	+6° - +43½°	
Orientation			$X = b$	$X = b$	
D meas.	3.27 \pm 0.01	3.3	3.55 \pm 0.03	3.35-3.70	> 3.3
H	4½	4½	6½	1½-5½	
Cleavage	not observed	100 distinct (parting?)	100 distinct (parting?) 010 less distinct	100 distinct on nut brown material	$\perp X$
Twinning (in thin section)	not observed	not observed	100, polysynthetic (rare)	100, polysynthetic	common, plane containing X

HEAT TREATMENT

Differential thermal analysis (argon ignition) of Canadian hellandite (EL-109) produced endothermic peaks at 174, 405, 479, and 568°C (Fig. 4). A separate run on a second ground fragment from the same crystal showed that the last 3 peaks vary greatly in intensity from one specimen to the next. A cooling curve did not show any corresponding exothermic peaks and a chilled sample (heated to 600°C in nitrogen) gave a hellandite x-ray pattern, somewhat sharper and with a smaller cell size, than unheated hellandite. It is thought that the DTA peaks may represent dehydration and expulsion of boron (endothermic effects) combined with crystallization (exothermic effects). Thermogravimetric analysis (Fig. 5) suggests that a large proportion of the weight loss occurs in two stages: 100-300°C (curve inflection at 130°C) and 400-600°C (curve inflection at 450°C). Possibly these two stages correspond to DTA endotherms at 174 and 479°C and indicate two types of "water" or decomposition and separation of boron. With regard to the latter it should be noted that the weight loss (12.16%) exceeds the amount of analysed water (7.14%).

A major endothermic peak occurs at 860°C and the DTA product (argon ignition, 1100°C maximum temperature) gives an x-ray pattern with the apatite structure ($a = 9.29$, $c = 6.79\text{\AA}$). This peak is therefore believed to represent the phase transition hellandite \rightarrow britholite (+ glass?)

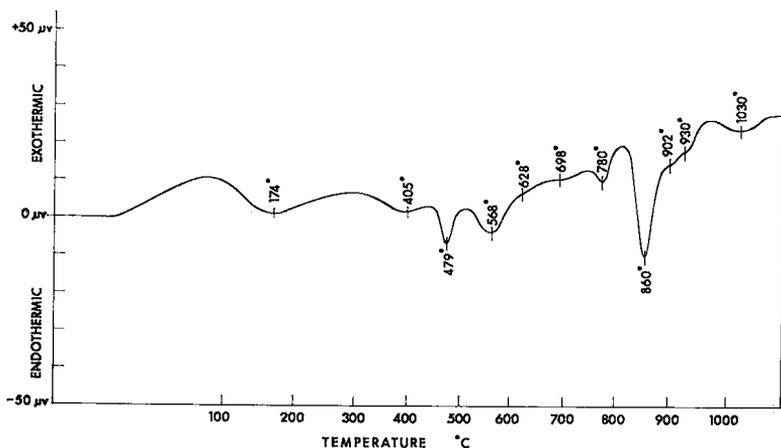


FIG. 4. Reconstructed DTA curve for specimen EL-109, Argon ignition, heating rate 12°C/min, Full scale deflection 100 microvolts.

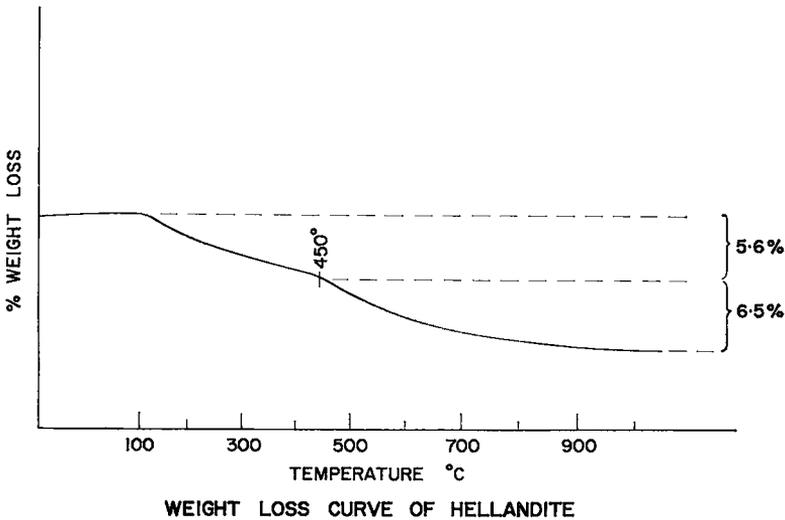


FIG. 5. Reconstructed TGA curve for specimen EL-109. Argon ignition. Heating rate 6°C/min.

+ B_2O_3 ?). In addition, weak x-ray lines were registered at 4.40 and 3.26Å, lines also superimposed on the "apatite" pattern of ignited spencite from Cardiff township, Ontario (Jaffe & Molinski 1962, footnote p. 12). Specimens heated in air to 950°C (EL-109 and Norwegian hellandite) also show the apatite structure.

GENESIS

Figure 6 shows the association of primary rare earth minerals at the Evans-Lou mine. Passing from the perthite-plagioclase-quartz zone into the giant perthite-quartz zone we progressively encounter the following assemblages: apatite — fergusonite — titanite, titanite — fergusonite — allanite and titanite — allanite — spessartine, all lying on the Ca-RE-Fe plane. Near the quartz core there is a strong enrichment in boron, and hellandite appears along with fergusonite, some spessartine and rare allanite. The sequence is shown by the arrow on the diagram. All these phases are associated with quartz-rich portions of the pegmatite, with quartz becoming notably enriched in the direction of the arrow. It should be noted that, if crystallization of the pegmatite proceeded from the walls inward, the arrow also indicates a time sequence. Euxenite and tourmaline are also seen but not in association with hellandite. The fact that

euxenite and black tourmaline are found with hellandite at the Lindvikskollen pegmatite (Brøgger 1907, Bjørlykke 1937) suggests that, at the stage that these minerals were formed, the Norwegian pegmatite fluid was comparatively poor in rare earths but rich in iron. This hypothesis is strengthened by the tenor of these elements in hellandite itself: Norway 32.3% RE, 2.2% Fe; Canada 37.7% RE, 1.6% Fe (values after Table 3, this paper).

At the Evans-Lou mine hellandite, quartz and feldspar have been fractured and cemented by a second generation of quartz. Most hematite is late and postdates both hellandite and second-generation quartz.

The scarcity of hellandite in nature can, at least in part, be ascribed to an unusual composition of the pegmatite fluid: strongly enriched in calcium, boron and yttrian rare earths. Sodium and iron, if present in large amounts, would result in growth of tourmaline which would remove boron from the system.

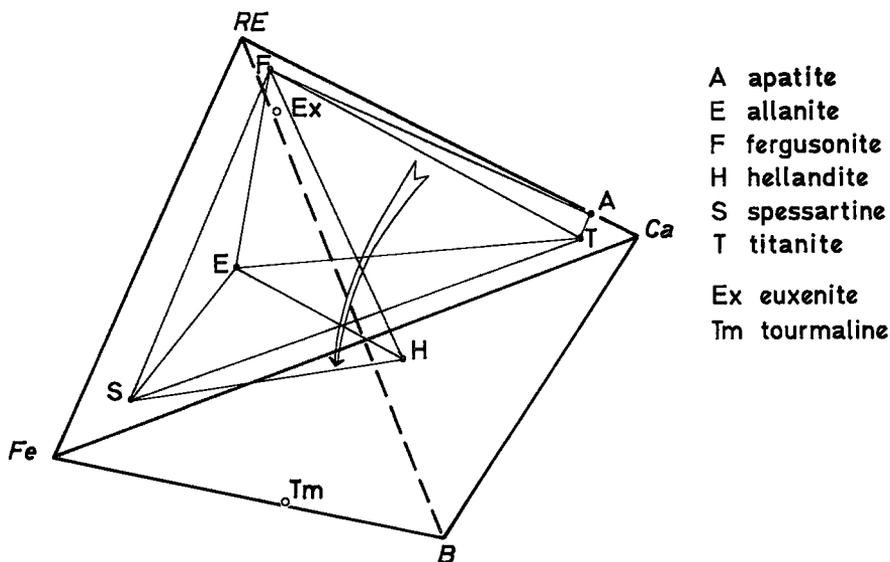


FIG. 6. Phase diagram showing yttrium-rich phases in the system Ca, RE, Fe, B. SiO_2 in excess. Arrow indicates sequence passing from the exterior of the pegmatite dyke inwards. Plots are approximately positioned by partial chemical analyses and optical properties.

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