

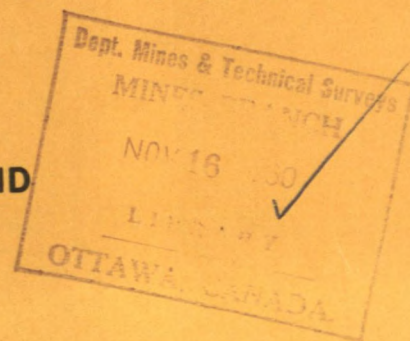


CANADA

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QUEBEC

E. H. NICKEL, B. S. KARPOFF,
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AND



A ZIRCONIUM-BEARING GARNET
FROM OKA, QUEBEC

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DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
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MINERAL SCIENCES DIVISION

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HOLMQUISTITE FROM BARRAUTE, QUEBEC

E. H. NICKEL², B. S. KARPOFF³, J. A. MAXWELL⁴, AND J. F. ROWLAND⁵

ABSTRACT

A new occurrence of the rare lithium amphibole, holmquistite, has been discovered near Barraute, Quebec. It occurs at or near the contact of spodumene pegmatites and hornblende-rich rock. A chemical analysis indicates a composition close to $\text{Li}_2(\text{Mg}, \text{Fe}^{II})_3(\text{Al}, \text{Fe}^{III})_2\text{Si}_8\text{O}_{22}(\text{OH})_2$. The holmquistite is orthorhombic, space group $D_{2h}^{16}-Pnma$, with $a = 18.30$, $b = 17.69$ and $c = 5.30$. The optical and physical properties are similar to those of other holmquistites cited in the literature.

INTRODUCTION

Holmquistite, a comparatively rare lithium amphibole, was first found at Utö, Sweden, and was characterized by A. Osann (1913) and later by N. Sundius (1947). Since its original discovery, holmquistite has been reported from the Hiddenite Mine in South Carolina, U.S.A. (Palache, Davidson & Goranson, 1930), and from two localities in the U.S.S.R.—the Kola peninsula (Ginzburg & Ginzburg, 1950) and the Eastern Sayan mountains (Khvostova, 1958). In the Utö and Kola peninsula occurrences the holmquistite is found at or near the contact of lithium pegmatites with the country rock; in the Eastern Sayans it occurs in quartz-biotite-amphibole schists; and in South Carolina it was found in and around a single cavity in a quartz-biotite gneiss.

Although holmquistite was originally regarded as monoclinic and a member of the glaucophane group, recent work has shown that it is orthorhombic and, hence, structurally related to anthophyllite (Vogt, Bastiansen & Skancke, 1958; Ginzburg, Rogachev & Bondareva, 1958; and Sundius, 1959).

The holmquistite described in the present paper was collected on the property of the Quebec Lithium Corporation near Barraute, Quebec, by

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one of the authors (Boris S. Karpoff). He submitted the samples to the Mines Branch in 1957, where they were identified as holmquistite (Nickel, 1957). Mr. J. F. Rowland of the Physical and Crystal Chemistry Section of the Mines Branch performed the x-ray diffraction work. The chemical analysis was made by Dr. J. A. Maxwell of the Geological Survey of Canada.

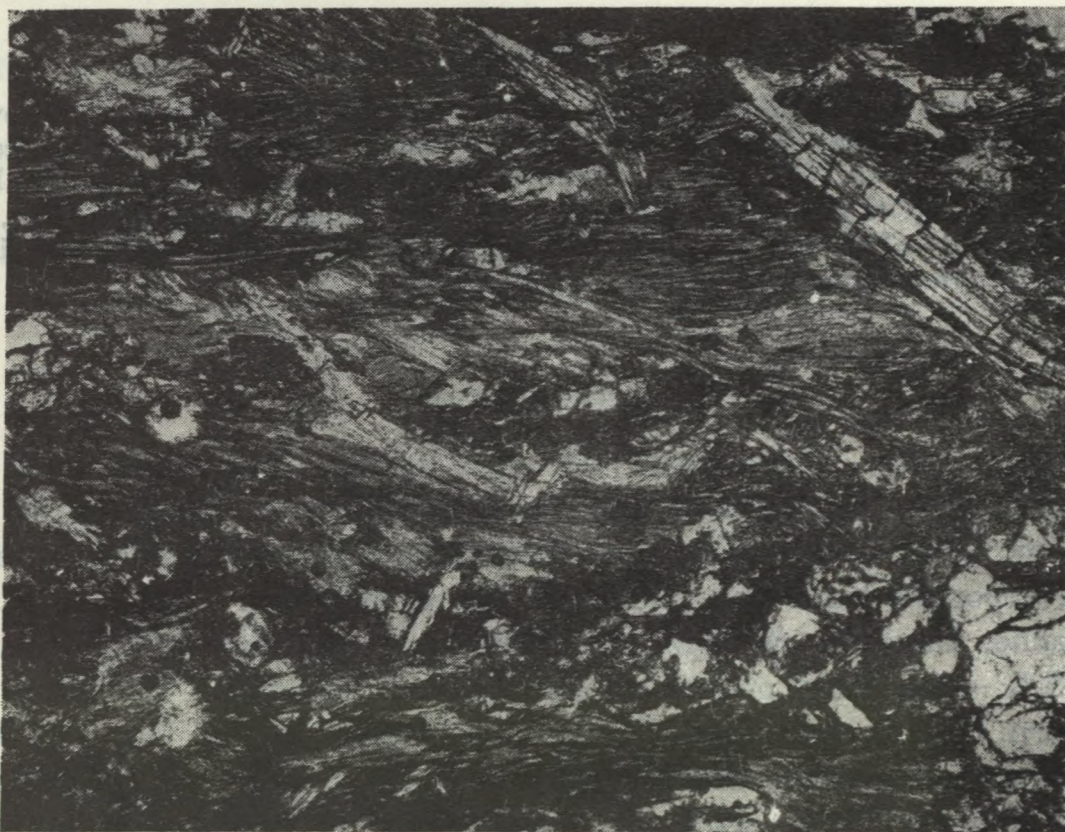


FIG. 1. Photomicrograph of thin section of a holmquistite aggregate in plane polarized light, showing the sub-parallel arrangement of the individual crystals. The equant grains in the section are epidote. $\times 22$.

LOCATION

Barraute is in the Lacorne district of Quebec, midway between Val d'Or and Amos and about 60 miles east of Noranda. The mining property of Quebec Lithium Corporation is located on surveyed lots of ranges VIII, IX and X in the townships of Lacorne and Fiedmont in the Abitibi East county, of the Province of Quebec. At present the mine plant and underground workings extend over lots 52, 53 and 54 of range IX of the mining concession.

GENERAL GEOLOGY

The regional geology has been described by Tremblay (1950). On the property of Quebec Lithium Corporation, the principal rock types are

altered volcanics of basic to intermediate composition, recrystallized sediments consisting largely of quartz-biotite and biotite schists, and a granodiorite body known as the Preissac-Lacorne batholith.

Spodumene-bearing pegmatites occur in the area as long, narrow, dike-like bodies, which cut across the contact between the granodiorite and the volcanics. The major constituents of the pegmatites are spodumene, feldspar and quartz. The minor constituents, which occur sporadically, include mica, beryl, columbite-tantalite, molybdenite, bismuthinite and fluorite.

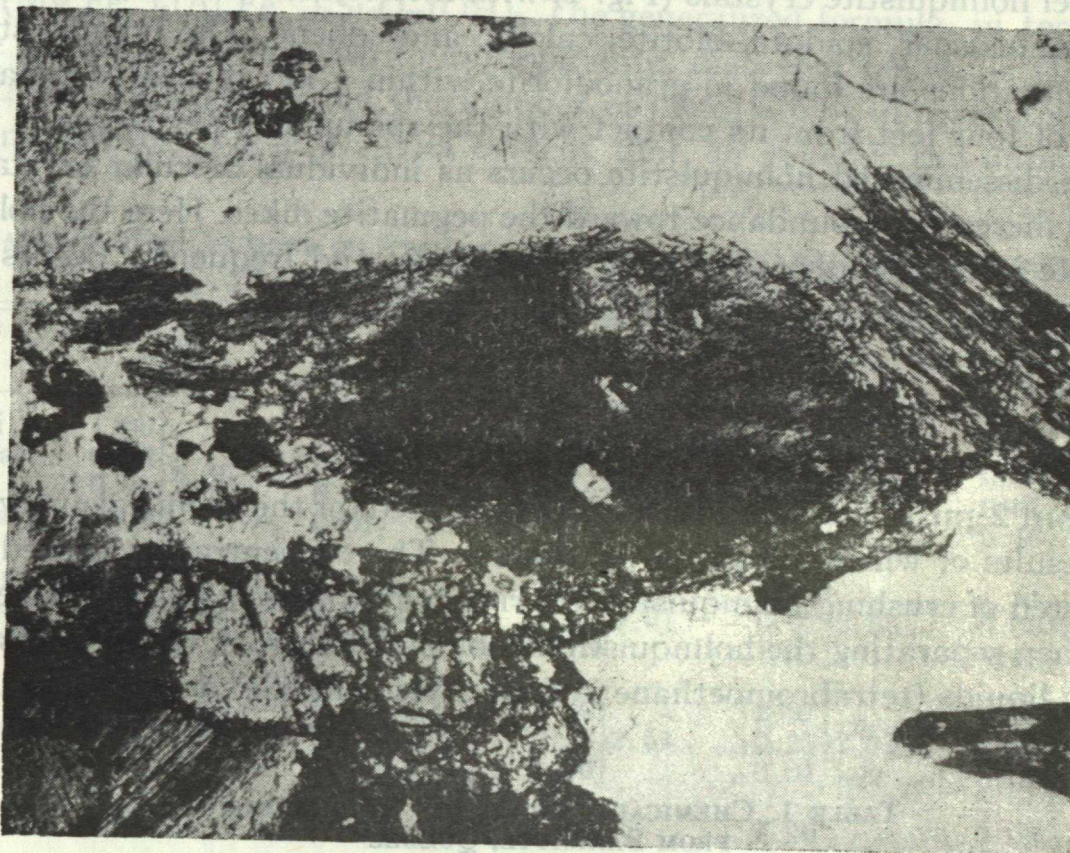


FIG. 2. Photomicrograph of thin section of rock containing disseminated holmquistite. A narrow rim of holmquistite (medium grey) almost completely surrounds the hornblende grain (dark grey) in the centre of the photomicrograph. The fibrous holmquistite at the right of the photomicrograph contains a few hornblende remnants. $\times 45$.

OCCURRENCE OF HOLMQUISTITE

In hand sample the holmquistite is easily recognized by its colour, which varies from light blue to dark violet-blue. It commonly occurs in rather massive aggregates which could be described as columnar, lamellar, or fibrous (sometimes asbestiform, with a felted texture). These masses are usually in the form of pods ranging from $1/32$ to $1/4$ inch in thickness, widening in rare instances to as much as two inches. The holm-

HOLMQUISTITE FROM BARRAUTE

quistite also occurs as disseminations of acicular crystals in sub-parallel arrangement, or in sheaf-like aggregates which are rather lustrous and talcose.

The holmquistite always occurs at or near the contact of the spodumene dikes with hornblende-bearing wallrock. The massive aggregates occur in fractures or joints in the wallrock adjacent to the contact with the pegmatite dikes, and along the margins of the dikes. In thin section these aggregates are seen to consist of an interlaced network of sub-parallel holmquistite crystals (Fig. 1) with interstitial minerals, including quartz, feldspar, epidote, biotite, calcite, and sphene. The holmquistite disseminations are found in granodiorite within a few inches to a maximum of four feet from its contact with the spodumene pegmatite.

The disseminated holmquistite occurs as individual acicular crystals, which increase in abundance toward the pegmatite dikes. Here the holmquistite is closely associated with hornblende, and frequently occurs as narrow rims around hornblende grains (Fig. 2).

CHEMICAL COMPOSITION

About 2 gm. of holmquistite was concentrated for the chemical analysis, the results of which are given in Table 1. The concentration procedure consisted of crushing holmquistite-bearing rock to pass a 65-mesh screen, and then separating the holmquistite from the other rock components by heavy liquids (tetrabromoethane and methylene iodide) and by a Frantz

TABLE 1. CHEMICAL ANALYSIS OF HOLMQUISTITE
FROM BARRAUTE, QUEBEC

SiO ₂	59.73%
Al ₂ O ₃	11.21
Fe ₂ O ₃	2.97
FeO	8.92
MgO	10.16
CaO	0.56
Na ₂ O	0.18
K ₂ O	0.15
Li ₂ O	3.56
H ₂ O ⁺	2.08
H ₂ O ⁻	0.02
TiO ₂	0.17
MnO	0.20
F	0.24
	100.15
Less O ≡ F	0.10
	100.05

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isodynamic separator. Examination of the final concentrate in oil immersion under a petrographic microscope revealed that the sample was quite homogeneous.

The number of metal atoms in the formula of holmquistite (1/4 unit cell) has been calculated from the analysis on the basis of a total of 24 oxygen, hydroxyl and fluorine atoms. These values are shown in Table 2, together with those of other holmquistites. According to these values, the formula of the holmquistite from Barraute, Que., approximates $\text{Li}_2(\text{Mg}, \text{Fe}'')_3(\text{Al}, \text{Fe}''')_2\text{Si}_8\text{O}_{22}(\text{OH})_2$. The generalized formula, in terms of the apparent relationship to anthophyllite, discussed below, is $(\text{Li}, \text{Mg}, \text{Fe}, \text{Al})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. From the number of metal atoms in other analyzed holmquistites (Table 2), it is evident that, in general, the number of

TABLE 2. THE NUMBER OF ATOMS IN THE FORMULA OF VARIOUS HOLMQUISTITES, CALCULATED ON THE BASIS OF 24(O,OH,F)

	Barraute Que. ¹	Utö Sweden ²	South Carolina ³	Kola Peninsula ⁴	Eastern Sayans ⁵
Li	1.90	1.89	1.28	1.32	1.40
Na	0.05	0.13	0.17	0.06	0.33
K	0.03	0.05	0.13	—	0.07
Ca	0.08	0.01	0.19	0.14	0.10
Mg	2.01	2.32	1.86	1.90	1.41
Mn	0.02	0.05	—	0.02	0.08
Fe''	0.99	0.54	1.15	1.01	1.49
Al	1.75	1.13	2.30	2.07	1.20
Fe'''	0.03	0.94	0.18	0.23	0.59
Ti	0.02	—	0.06	0.01	0.03
Si	7.92	7.95	7.38	7.96	7.92
F	0.10	0.09	—	0.06	0.39
OH	1.84	1.98	2.80	1.69	2.49
O	22.06	21.93	21.20	22.25	21.12
Tot.	39.07	39.01	38.70	38.72	38.62

¹This paper.

²Sundius, 1947.

³Palache, Davidson & Goranson, 1930.

⁴Ginzburg, Rogachev & Bondareva, 1958.

⁵Khvostova, 1958.

alkali atoms per formula varies between 1.5 and 2.0 and that of the trivalent atoms (Al''', Fe''') varies between 1.8 and 2.5, while the number of divalent atoms appears to remain constant at 3 per formula. The low silica and high alumina of the holmquistite from South Carolina indicate substitution of some of the silicon atoms by tetrahedral aluminum.

HOLMQUISTITE FROM BARRAUTE

X-RAY DIFFRACTION

Single-crystal x -ray determinations, using precession and Weissenberg cameras, show that holmquistite, like anthophyllite, is orthorhombic with the space group $D_{2h}^{16}-Pnma$. The cell dimensions are listed in Table 3, together with those of anthophyllite and other holmquistites. The holmquistite sample from Utö, Sweden was kindly provided by the Mineralogy Division of the Geological Survey of Canada.

As given in this paper, $a:b:c = 1.0345:1:0.2994$. This is not the standard setting of $c < a < b$ used for the orthorhombic system and which is given in Donnay & Nowacki's "Crystal Data" (1954). It corresponds, however, to the setting used for anthophyllite in petrographic literature. If the $c < a < b$ were used, then $a:b:c = 0.9667:1:0.2895$, and the space group would be $Pmnb$.

The powder pattern measurements of the Barraute holmquistite are listed in Table 4. Direct comparison of the powder patterns of this holmquistite and that of the holmquistite from Utö, Sweden shows that they are identical.

TABLE 3. CELL DIMENSIONS OF HOLMQUISTITE AND ANTHOPHYLLITE

Mineral	Locality	Cell Dimensions (Å)		
		<i>a</i>	<i>b</i>	<i>c</i>
Holmquistite	Barraute, Que. ¹	18.30	17.69	5.30
Holmquistite	Utö, Sweden ¹	18.36	17.71	5.29
Holmquistite	Kola pen. U.S.S.R. ²	18.27	17.71	5.30
Anthophyllite	Falun, Sweden ³	18.56	18.07	5.28

¹This paper.

²Ginzburg, Rogachev, & Bondareva (1958). The value for *b* given in their paper is 17.17 but this is probably a misprint, since their powder pattern can be indexed satisfactorily with a *b* value of 17.71, but not with 17.17.

³Strukturbericht II, p. 532. (The values have been converted from kX to Angstrom units.)

The measured *d*-values listed in Table 4 are very close to those published by Ginzburg, Rogachev & Bondareva (1958). Their indexing, however, omits diffractions which are relatively strong on our single crystal films, but includes those of approximately the same spacing which are relatively weak or not visible. Examples are: 410, 430, 450 and 601 given by them, instead of 040, 231, 251 and 351, respectively, as in this paper. The inclusion of the 610 β line in their indexing is unnecessary, as this diffraction appears with approximately the same relative intensity when the radiation is properly filtered, and is indexed readily as 250. Since the

TABLE 4. X-RAY POWDER DIFFRACTION DATA OF HOLMQUISTITE FROM BARRAUTE, QUE.
 CuK α radiation, $\lambda = 1.5418\text{\AA}$, camera diameter = 114.6 mm.

I_v	d_m	$1/d_m^2$	$1/d_c^2$	hkl	I_s	I_v	d_m	$1/d_m^2$	$1/d_c^2$	hkl	I_s
$\frac{1}{2}$	8.815	.0129	.0128	020	w	2	2.205	.2057	.2042	271	m
10	8.107	.0152	.0151	210	s				.2045	080	mw
1	5.072	.0386	.0386	101	w				.2172	502	ms
1	4.866	.0422	.0388	011	w	4	2.134	.2196	.2191	371	mw
1	4.572	.0478	.0418	111	mw					432	w
			.0476	201	w				.2204	512	s
			.0478	400	mw	2	2.100	.2268	.2253	561	ms
			.0508	211	mw	$\frac{1}{2}$	2.066	.2343	.2331	741	vw
7	4.427	.0510	.0511	040	s	1	2.038	.2408	.2395	821	m
			.0514	121	m				.2400	471	w
1	4.050	.0610	.0604	221	w	1	1.956	.2614	.2582	661	ms
2	3.832	.0681	.0674	131	m				.2618	751	m
5	3.612	.0766	.0763	231	ms	$\frac{1}{2}$	1.919	.2716	.2702	452	w
			.0898	141	w	1	1.856	.2903	.2889	702	w
6	3.339	.0897	.0913	331	mw				.2903	921	w
			.0918	250	ms	3	1.818	.3026	.3018	10.1.0	ms
{ 2	3.212	.0969	.0962	421	m	2	1.800	.3086	.3064	291	m
{ 2	3.176	.0991	.0987	241	w				.3066	851	m
			.0989	440	ms	1	1.766	.3206	.3196	0.10.0	s
	3.000	.1111	.1107	610	s	1	1.742	.3295	.3269	113	—
			.1121	431	mw				.3274	10.3.0	m
			.1231	521	mw	2	1.710	.3420	.3418	861	ms
4	2.797	.1278	.1275	251	s				.3495	033	—
3	2.701	.1371	.1363	630	s	$\frac{1}{2}$	1.689	.3505	.3508	313	—
			.1391	531	mw				.3590	282	w
3	2.643	.1432	.1424	351	s	$\frac{1}{2}$	1.660	.3629	.3604	323	—
1	2.598	.1482	.1487	112	w				.3615	233	—
5	2.538	.1552	.1537	161	s	$\frac{1}{2}$	1.628	.3773	.3764	333	—
2	2.472	.1636	.1545	202	m	2	1.592	.3946	.3926	961	s
			.1633	451	s				.3956	880	s
			.1685	270	ms	4	1.572	.4047	.3986	2.11.0	s
1	2.406	.1727	.1694	302	m				.4036	153	—
			.1726	312	w	$\frac{1}{2}$	1.556	.4130	.4126	253	—
			.1902	551	s	1	1.542	.4206	.4197	443	—
3	2.282	.1920	.1911	800	mw	1	1.522	.4317	.4300	12.0.0	ms
			.1935	412	mw				.4314	613	—
1	2.244	.1986	.1985	461	m	1	1.501	.4438	.4410	623	—

I_v Intensities, estimated visually. d_m Measured spacings, corrected for film shrinkage. $1/d_m^2$ Calculated from measured spacings.
 $1/d_c^2$ Calculated from unit cell determined by single crystal films, Orthorhombic with $a = 18.30$, $b = 17.69$, $c = 5.297\text{\AA}$.
 hkl Indices of calculated spacings. I_s Intensities from single crystal precession films, estimated by eye, Mo/—, adjusted to include multiplicity factor, but other corrections omitted. — Intensity not available.

HOLMQUISTITE FROM BARRAUTE

Swedish and Canadian holmquistites gave similar single crystal patterns, it is unlikely that a composition difference accounts for such intensity variations, and it is probable that these diffractions (and others) have been mis-indexed by Ginzburg, Rogachev & Bondareva.

PHYSICAL AND OPTICAL PROPERTIES

The physical and optical properties of the Barraute holmquistite are given in Table 5, together with those of other holmquistites cited in the literature. The refractive indices of the Barraute holmquistite were determined by the immersion of mounted oriented crystals in calibrated refractive index oils, using sodium light. The $2V$ value was measured on a universal stage. The specific gravity was determined by pycnometer on the 2 gm. sample prepared for analysis.

TABLE 5. PHYSICAL AND OPTICAL PROPERTIES OF HOLMQUISTITE

	Barraute, Que.	Utö, Sweden	S. Carolina, U.S.A.	Kola Pen., U.S.S.R.	E. Sayans, U.S.S.R.
α	1.622	1.640	1.625	1.624	1.642
β	1.642	—	1.645	1.645	—
γ	1.646	1.663	1.654	1.651	1.666
$2V_x$	49°	44°	51°	50°	50–52°
Pleochroism					
α	colourless	greenish- yellow	light yellow	greyish- yellow	yellowish- green
β	violet	violet	violet	violet	—
γ	violet	sky-blue	purplish- violet	bluish- violet	bluish- violet
Birefringence	0.024	0.023	0.029	0.027	0.024
Specific Gravity	3.13	3.09	3.11	3.06	3.12

The optical orientation of holmquistite is the same as that of anthophyllite, namely, $\alpha = a$, $\beta = b$, $\gamma = c$. The theoretical specific gravity of the Barraute holmquistite, calculated from the chemical analysis and unit cell dimensions, is 3.09.

DISCUSSION

The occurrence of the holmquistite at the contact of lithium pegmatites with the country rock at Barraute, as well as at Utö, and in the Kola peninsula, strongly suggests that this mineral has been formed by the reaction of pegmatitic components with the wallrock. This view is supported by the existence of holmquistite rims around hornblende grains, noted above, and suggests a lithium metasomatism of the hornblende. That the lithium is very likely derived from the pegmatite is indicated

not only by the close proximity of holmquistite to the pegmatite veins, but also by the relationship between holmquistite and spodumene. Wherever holmquistite is present in the wallrock, spodumene is absent in the pegmatite immediately adjacent to the holmquistite, and the greater the amount of holmquistite, the wider is the spodumene-free zone. Nowhere have holmquistite and spodumene been observed in mutual contact. Thus it appears that the holmquistite in the wallrock has formed at the expense of spodumene in the veins.

If the stability temperatures of holmquistite and spodumene are similar to those of their lithium-free analogues, hornblende and pyroxene, then the holmquistite assemblage can be regarded as a lower-temperature assemblage than the spodumene pegmatites, since pyroxene is generally regarded as a higher-temperature mineral than hornblende, both in igneous and metamorphic processes. In view of these considerations, it appears that the holmquistite is probably a deuteric mineral resulting from local retrograde lithium metasomatism of hornblende in the wallrock during the late stages of pegmatite emplacement.

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The authors appreciate the assistance rendered by Dr. A. T. Prince, Chief of the Mineral Sciences Division of the Mines Branch, and Dr. N. F. H. Bright, Head of the Physical Chemistry Section of the Mineral Sciences Division, who read the manuscript and made helpful suggestions.

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A ZIRCONIUM-BEARING GARNET FROM OKA, QUEBEC¹E. H. NICKEL²*Mines Branch, Ottawa, Canada*

During a mineralogical investigation in 1956 at the Mines Branch, Ottawa, of some diamond drill cores from the Oka property of Quebec Columbian Limited, a small amount of a zirconium-bearing garnet was observed by the writer (Nickel, 1956). The garnet occurred as anhedral grains up to 5 mm in diameter in rock consisting largely of calcite, nepheline and biotite, with minor amounts of diopside and apatite. The composition of the garnet is given in Table 1. The percentages shown, except for that of zirconium, were determined spectrographically by Dr. W. M. Gray of the Mines Branch.

Recently, in a re-examination of the material, a chemical determination of the zirconium content was made on a 45-mg sample of hand-picked garnet by Miss E. E. Lepine of the Mines Branch, using a colorimetric method. The value obtained, 3.7% ZrO₂, is lower than, but of the same order of magnitude as, the 5% Zr determined spectrographically and somewhat higher than a gravimetric chemical determination made at the time of the 1956 investigation.

TABLE 1. APPROXIMATE COMPOSITION OF ZIRCONIUM-BEARING GARNET

Element	Wt %	Oxide	Wt %
Ca	30	CaO	42
Si	15	SiO ₂	32
Fe	10	Fe ₂ O ₃	14
Ti	3	TiO ₂	5
Mn	2	MnO	2.6
Al	2	Al ₂ O ₃	3.8
Mg	0.6	MgO	1.0
Zr (chem.)	2.7	ZrO ₂	3.7
			104

The garnet is black in colour, and thin splinters are dark brown in transmitted light. Some of the other properties of the mineral are given in Table 2, with those of andradite and kimzeyite listed for comparison.

The gross chemical composition of the garnet indicates that it can be classified as a variety of andradite, and its titanium content suggests that it could further be grouped under schorlomite, the titanium-rich andradite. The zirconium content is considerably below that of kimzeyite,

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a zirconium garnet from Magnet Cove, Ark., recently described by Milton & Blade (1958) and which contains about 20% ZrO₂. Like kimzeyite, however, the Oka garnet is high in calcium and iron and also contains appreciable titanium.

TABLE 2. PHYSICAL AND OPTICAL PROPERTIES OF ZIRCONIUM-BEARING GARNETS AND ANDRADITE

	Zirconium-bearing Garnet, Oka, Que.	Kimzeyite Magnet Cove, Ark.*	Andradite**
Refractive Index	1.94	1.95	1.887
Specific Gravity	3.70	—	3.859
Cell Edge (<i>a</i>)	12.15 Å	12.46 Å	12.05 Å

*Milton & Blade (1958).

(After submission of this communication, Dr. Charles Milton reported (personal communication) that further work on the kimzeyite from Magnet Cove has resulted in the following modifications of his previously published data: refractive index 1.94; specific gravity 4.0, and ZrO₂ content 29.9%.)

**Skinner (1956).

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