KORNERUPINE FROM LAC STE-MARIE, QUEBEC, CANADA¹

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Abstract

This study of two varieties of kornerupine from the vicinity of Lac Ste-Marie, County of Gatineau, Province of Quebec (Canada) has furnished new data on this rare mineral. The forms observed are (010), (100) and (110). Data deduced from an x-ray powder diagram are given together with unit cell dimensions determined with the Weissenberg x-ray goniometer (a=13.65 and 13.69, b=15.91 and 15.93, c=6.68 and 6.68 kX, for the green and yellow varieties respectively). Two new complete chemical analyses, from which a formula of the type R_{40} (Si, B)₁₈ · O₈₆ can be deduced, are given.

The author has examined the relationships, between the chemical composition, the refractive indices, the axial angle, and the specific gravity of seven analyzed varieties of kornerupine. The relationships between kornerupine and its associated minerals at the Lac Ste-Marie occurrence were studied: kornerupine occurs with quartz, orthoclase, biotite, tourmaline, andalusite, almandite, rutile, zircon, dumortierite, etc. This deposit is found in paragneisses, of the Grenville series, which have been modified by igneous emanations.

INTRODUCTION

First found in Greenland (Lorenzen), kornerupine was later reported from a few localities: in Saxony (Sauer, Uhlig, Gossner and Mussgnug, Harker), in Madagascar (Lacroix, 1912, 1922, 1923, 1939) (Payne), in Antarctica (Mawson), in Ceylon (Hey, Anderson, & Payne), and in South Africa (de Villiers). The chemical composition of the mineral was not accurately known until boron was detected in it by Lacroix and de Gramont (1921) and until as a result of comparative studies published in 1940, Hey, Anderson & Payne showed that much of the iron is present in ferrous condition in the mineral.

The kornerupine here described was discovered in 1949 near Lac Ste-Marie, by Prof. Pierre Mauffette, of the Ecole Polytechnique in Montreal when he was mapping the area for the Quebec Department of Mines. He submitted a specimen of this mineral for identification to the Department of Mines Laboratories. Later, the writer visited Lac Ste-Marie in order to collect specimens, but he had too little time to make a full study of the mode of occurrence of the mineral.

The region is largely underlain by formations of the Grenville series, which are locally made up principally of paragneisses and crystalline limestones. Igneous intrusives of diverse composition cut the Grenville rocks intricately. A contact between the limestone and the paragneisses east of the occurrence, strikes N 50° E and dips 35° E. The kornerupine-

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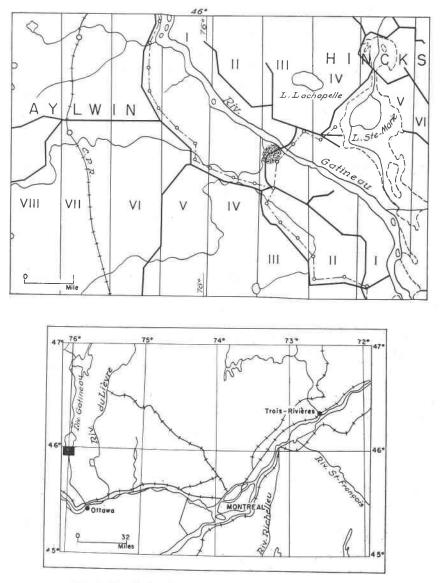


FIG. 1. Sketch showing location of kornerupine bearing rocks near Lac Ste-Marie, Quebec.

bearing rocks crop over a length of about 500 feet and a width of 100 feet.

The deposit is in the Aylwin township, Range III, Lots 15 and 16, and along the road from Kazabazua to Lac Ste-Marie, on the southwest bank of Gatineau river, near Hincks bridge (Fig. 1).

GEOMETRIC CRYSTALLOGRAPHY

Two varieties with somewhat different properties have been studied.

A green kornerupine is found in well defined dark green or black orthorhombic crystals of diverse dimensions which may be as much as two inches long and nearly $\frac{1}{2}$ inch diameter. The faces are very shiny and allow accurate goniometric measurements in spite of the slight irregularities of their surfaces. Faces (110) and (100) tend to be better developed than (010). No (001) face has been found.

The *yellow* variety occurs as fairly well defined greenish-yellow crystals, forming as much as 40 per cent of the rock. The crystals are commonly smaller than those of the green kornerupine, but they show the same crystal faces; however (100) and (010) are in some crystals better developed than (110). The faces are dull and not suitable for good angle measurements.

Forms ²	Measur	ed	Calculated		
Forms*	φ	$\rho = C$	¢	$\rho = C$	
010	0°00′		0°00′	90°00′	
100	90 02 (6)		90 00	90 00	
110	49 17 (4)	-	49 19	90 00	

TABLE 1. KORNERUPINE FROM LAC STE-MARIE (green variety)MEASURED AND CALCULATED ANGLES, Orthorhombic $a:b:c=0.8597:1:0.4198^1 p_0:q_0:r_0=0.4883:0.4198:1$

N.B. Numbers in parentheses indicate the number of measurements.

¹ The values in which axis c enters have been calculated from x-ray diffraction data. ² The author has observed dull and irregular (101) and (201) faces at one end of a small crystal of kornerupine from Natal.

X-RAY CRYSTALLOGRAPHY

Measurements of the unit cell dimensions of the two varieties of the kornerupine from Lac Ste-Marie, as well as of a sample from Natal, South Africa (Table 2) were made with the Weissenberg x-ray goni-

Cell Dimensions -	Lac S	Ste-Marie	Natal	Ceylon ² Hey et al	
kX ¹	Green	Yellow	Inatai	(1941)	
a	13.69	13.65	13.65	13.68	
b	15.93	15.91	15.91	15.95	
С	6.68	6.68	6.68	6.68	

TABLE 2. KORNERUPINE, Orthorhombic, Cmmm?

¹ Using wavelengths FeK α_1 1.93208 kX and FeK α_2 1.93601 kX.

² Given as A but probably really kX units.

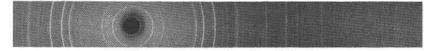


FIG. 2. Kornerupine (yellow variety) X-ray powder pattern, Fe/Mn radiation, Contact print of film from 114.6 mm. diam. camera reduced to $\frac{1}{2}$ size (1° θ =1 mm. on print).

ometer. An x-ray powder photograph was also made of the yellow kornerupine of Lac Ste-Marie (Table 3 and Fig. 2). The unit cell is base centered. Furthermore, after a short immersion in fused Na₂CO₃, crystals exhibit etch patterns indicating the presence of a plane of symmetry perpendicular to the *c* axis. These tests, together with the morphology of the crystals, lead to the belief that kornerupine probably belongs to the dipyramidal class. In this case, the only space group susceptible to accommodate the 86 atoms of oxygen present in the cell would be D_{2n}^{19} — *Cmmm*.

CHEMICAL COMPOSITION

The samples for chemical analyses were prepared from selected crystals which were crushed and screened (-50+70 mesh and -70+100 mesh). The two screen fractions were then processed separately, with

I(Fe)	d(meas)	hkl	d(calc)	I(Fe)	d(meas)	hkl	d(calc)
8	10.4	110	10.36A	-	1 076	∫313	1.985
4	7.94	020	7.96	5	1.976	551	1.978
7	6.83	200	6.82			234	1.870
1	4.06	221	4.09	4	1.864	403	1.862
6	3.99	∫040	3.98			172	1.860
0	3.99	131	3.98	4	1.795	552	1.760
7	3.42	∫400	3.41			712	1.674
1	5.42	041	3.42	8	1 670	661	1.671
9	3.34	002	3.34	0	1.670	004	1.670
10	3.00	202	3.00			820	1.668
4	2.87	421	2.84	6	1 500	∫603	1.590
5	2.69	510	2.69	6	1.590	224	1.589
10	2.61	350	2.61	7	1 522	∫044	1.540
6	2.387	402	2.385		1.533	662	1.532
		531	2.280			882	1.491
5	2.273	600	2.275	9	1.488	{ 590	1.483
		152	2.273	1 I I		083	1.482
5	2.117	203	2.118	6	1.436	∫1.11.0	1.438
8	2.095	∫460	2.093	6	1.450	0.10.2	1.436
	2.095	512	2.095			1.11.1	1.406
6	2 060	∫062	2.077	8	1.406	2.10.2	1.405
6	2.069	550	2.072			354	1.404

TABLE 3. KORNERUPINE (YELLOW VARIETY)—X-RAY POWDER PATTERN Orthorhombic *Cmmm*?; a=13.65, b=15.91, c=6.68kX¹

¹ Using wave-lengths FeKa₁ 1.93208 kX and FeKa₂ 1.93601 kX.

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bromoform, methylene iodide, and Clerici solution (specific gravity: 3.50). The concentrates of kornerupine thus obtained were purified by hand sorting under the binocular microscope. A small quantity of rutile remained as a minor impurity. Kornerupine is very resistant to acids, especially the green variety, and FeO had to be determined by the Carius tube method.

The chemical composition of the two varieties of kornerupine from Lac Ste-Marie compared with other published analyses will be found in Table 4. Several other analyses were not considered, for the boron had

Elements	1	2	3	4	5a	5b	ба	6b	7
SiO ₂	31.09	30.5	29.3	30.5	30.24	30.32	30.18	30.35	29.53
B_2O_3	3.59	2.8	2.5	3.0	3.50	3.51	3.27	3.29	3.5
Al_2O_3	38.17	37.6	40.0	35.8	40.86	40.97	41.95	42.21	40.97
Fe_2O_3	nil	3.3	nil	3.2	0.42	0.42	0.90	0.91	nil
FeO	2.55	4.8	5.0	9.1	8.52	8.52	9.10	9.15	12.22
MgO	22.51	20.7	21.0	17.6	14.87	14.91	12.48	12.56	10.90
CaO	0.51	-	_		0.06	0.06	0.18	0.18	
Na_2O	1.36	trace	0.1	1.6	0.08	0.08	0.13	0.13	0.70
$K_{2}O$	0.08	trace	0.6	trace	0.00	0.00	0.00	0.00	
H_2O+	0.10	-			∫0.97	0.97	1.06	1.07	0 67
H_2O-	0.10				0.00	0.00	0.00	0.00	0.67
${ m TiO}_2$	-				0.19	0.00	0.51	0.00	0.44
P_2O_5	_				0.09	0.09	0.08	0.08	0.12
Cr_2O_3			-		0.06	0.00	0.04	0.00	_
ZrO_2					0.00	0.00	0.05	0.00	
MnO		3			trace	trace	trace	trace	0.08
		Loss:							
		0.2							
Total	99.96	99.9	98.5	100.8	99.86	99.87	99.93	99.93	99.13
Specific	3.27	3.335	3.330	3.37		37		39	3.449
gravity		± 0.005	± 0.003	± 0.010	$\pm 0.$		$\pm 0.$		

TABLE 4. SELECTED CHEMICAL ANALYSES OF KORNERUPINE

 Itrongay, Madagascar (Lacroix, 1922) "corrected in accordance with a new FeO determination" (Hey, 1941), F. Raoult, analyst. Hey, Anderson & Payne note that a new measurement of the density gave 3.29.

2 - Ceylon "normal type" (Hey, Anderson & Payne). M. H. Hey, analyst.

3 -Ceylon "optically pseudo-uniaxial type. (Hey, Anderson & Payne). M. H. Hey, analyst.

4 --- "Prismatine." Waldheim, Saxony. (Hey, Anderson & Payne). M. H. Hey, analyst.

5a-Lac Ste Marie, green variety (new data). H. Boileau, analyst.

5b-Lac Ste Marie, green variety corrected for 0.19% rutile and 0.08% chromite.

6a-Lac Ste Marie, yellow variety (new data). H. Boileau, analyst.

6b—Lac Ste Marie, yellow variety corrected for 0.51% rutile, 0.05% chromite and 0.07% zircon.

7 —Port Shepstone, Natal, South Africa (de Villiers), C. J. van der Walt, analyst; "corrected in accordance with a new FeO and total iron determination" (Hey, Anderson & Payne), M. H. Hey, analyst. not been determined (Lorenzen, Sauer, Uhlig, Gossner and Mussgnug, Lacroix (1912), or for other reasons, Hey, Anderson, and Payne (their analysis No. II).

The analyses of Lac Sainte-Marie kornerupine show about one per cent of water. The role of this water in the mineral is not clear, and accordingly experiments were undertaken to determine if possible how it occurs. Samples were heated in a Chevenard thermobalance (Duval), which allows an accurate recording of the changes of weight with rising temperature. The results with kornerupine were inconclusive as yet.

Three hypotheses concerning the state of the water were considered. These are: a) the kornerupine contains only absorbed water; b) the kornerupine holds one molecule of water; c) all the water found in the analysis is water of constitution.

Analyses 5b and 6b were recalculated to sum 100 on each of those hypotheses and the empirical atomic contents of the unit-cell were calculated. The results are shown in Table 5. Examination of this table shows that the most plausible hypothesis is that kornerupine holds one mole-

	Number of atoms									
Elements	No molecular water		1 molec	1 molecule H ₂ O		Total H ₂ O contents as molecular				
	Green	Yellow	Green	Yellow	Green	Yellow				
Si	15.1	15.2	15.0	15.1	14.9	15.0				
в	3.0	2.8	3.0	2.8	3.0	2.8				
Al	24.3	24.8	23.9	24.7	23.8	24.5				
Fe'''	0.2	0.3	0.2	0.3	0.2	0.3				
Fe''	3.5	3.8	3.5	3.8	3.5	3.8				
Mg	11.1	9.4	11.0	9.3	10.9	9.3				
Ca	0.0	0.0	0.0	0.0	0.0	0.0				
Na	0.1	0.1	0.1	0.1	0.1	0.1				
Р	0.0	0.0	0.0	0.0	0.0	0.0				
H	0.0	0.0	2.0	2.0	3.2	3.4				
0	86.0	85.6	86.1	86.1	86.3	86.3				
Si+B	18.1	18.0	18.0	17.9	17.9	17.8				
Al+Fe'''	24.4	25.2	24.0	25.0	24.0	24.9				
Mg+Fe''	14.6	13.2	14.5	13.1	14.5	13.0				
ΣR	39.1	38.5	40.6	40.2	41.7	41.5				
ΣA	143.3	142.1	144.8	144.3	145.9	145.6				

TABLE 5. EMPIRICAL UNIT-CELL CONTENTS OF LAC STE-MARIE KORNERUPINE

 ΣR : sum of atoms except Si, B and O.

 ΣA : sum of all atoms.

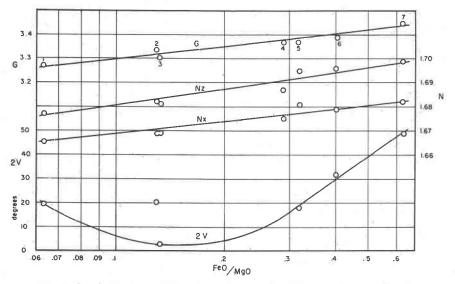


FIG. 3. Graph showing variations in optic properties of kornerupine according to the molecular ratio of FeO to MgO contents.

cule of water of constitution. With this hypothesis the number of oxygen atoms is nearest to 86, as suggested by Hey, Anderson & Payne (1941).

PHYSICAL AND OPTICAL PROPERTIES

Hardness—The hardness of the kornerupine from Lac Ste-Marie is $6\frac{1}{2}$ to 7 for the green variety,¹ and 6 to $6\frac{1}{2}$ + for the yellow.

Specific Gravity— $3.37 \pm .01$ (green) to $3.39 \pm .02$ (yellow). The yellow variety contains microscopic inclusions which makes it difficult to separate a homogeneous grain for determination.

Cleavage—(110) cleavage is imperfect in the green variety, slightly better in the yellow variety.

Fusibility-6.

Optical Properties—The two varieties of Lac Ste-Marie crystals are sufficiently large and clear cut to make it feasible to cut oriented sections from them. The optical properties (Table 6) were determined on such oriented sections. The varieties, the analyses of which are given above, were grouped in this table according to the increasing values of the ratio of molecular FeO to MgO. Figure 3 shows a close relationship between this ratio and the indices of refraction, the axial angle, and the specific gravity. The reason for the deviation of 2V of sample 2 from the curve is not at once apparent.

The yellow kornerupine shows variations from about 28° to about 36° in the value of the axial angle.

¹ Hardness measurements made with the Bierbaum Microcharacter 2100 to 2200.

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No.	Origin	FeO MgO molec- ular	N_X	NY	Nz	$N_Z - N_X$	2V	Pleochroism
1	Madagascar ¹	0.064	1.6650	1.6766	1.6770	0.0120	194°	-
2	Ceylon ¹	0.130	1.669	1.681	1.682	0.013	20 ¹ / ₂ °	X green; Y pale-brownish yellow, Z pale brownish green.
3	Ceylon ¹	0.132	1.669	1.681	1.681	0.012	3°	
45	Saxony ¹	0.291	1.675	1.687	1.687	0.012	-	
5	Lac Ste Marie (green variety)	0.321	1.681	1.694	1.695	0.014	18°	X colorless; Y colorless or pale yellowish-green, Z green.
6	Lac Ste Marie (yellow variety)	0.409	1.679	1.694	1.696	0.017	32°±	X colorless; Y colorless or very pale pink; Z pale green (in thick section, 1 mm).
7	Natal ¹	0.629	1,682	1.696	1.699	0.017	48°	X=Y colorless, Z light amber (yellow with some brown and green).

TABLE 6. COMPARATIVE OPTIC PROPERTIES OF ANALYZED KORNERU	TABLE 6. CO	MPARATIVE OP	TIC PROPERTIES	OF ANALYZED	KORNERUPIN
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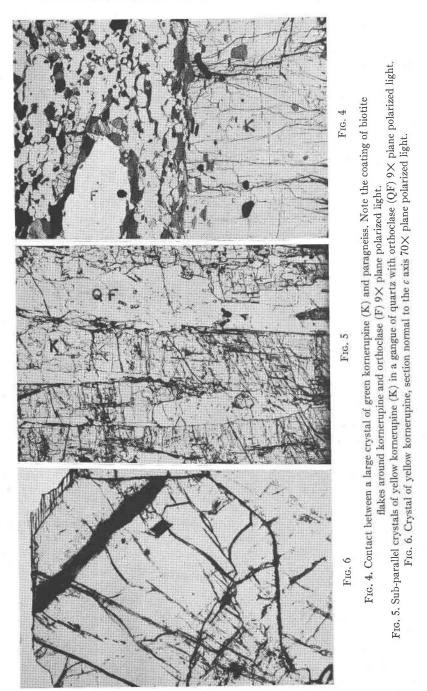
Index values are given for the D line with a precision of ± 0.002 except for sample 4 (± 0.004). ¹ Data from Hey, Anderson & Payne (1941).

Petrography

Green Kornerupine

The green kornerupine occurs in an injected biotite and tourmaline paragneiss, that is rich in orthoclase and relatively poor in quartz. Injected zones are parallel with the foliation and are clearly visible due to their light color against the dark background of the rock; the injected material is made chiefly of orthoclase with occasionally some large crystals of kornerupine; quartz is rare in it, tourmaline rare or absent. Kornerupine is not distributed uniformly through the rock but is found either in the immediate vicinity of the injected zones or in nests which are as much as two inches in diameter and whose limits are marked by numerous biotite flakes, and containing many sub-parallel prisms of kornerupine embedded in orthoclase with a little guartz. The crystals of kornerupine are not always parallel to the foliation. They are generally coated with biotite flakes; in the neighbourhood are also observed large areas of orthoclase with a coating of biotite (Fig. 4). Tourmaline is extremely rare as inclusions in kornerupine; on the other hand inclusions of pyrite, pyrrhotite, and biotite are fairly common; very few inclusions of rutile occur in the green variety, whereas this mineral is rather common in the yellow variety.

One thin section shows an irregular mass of andalusite, which appears to be moulded on the kornerupine. In the same section, a thin rim of quartz surrounds an apparently corroded crystal of kornerupine.



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Tourmaline is small grains with polygonal outlines is uniformly distributed in the apparently non-injected parts of the rock. Biotite defines the foliation, and it contains many inclusions of zircon surrounded by pleochroic halos. A few grains of pyrite and pyrrhotite are also present.

Yellow Kornerupine

The rock containing the yellow variety is probably also a paragneiss, but it may originally have had a different composition from the paragneiss containing the green variety or have undergone a different process of metasomatism. Kornerupine abounds in it and is in some parts one of the main constituents of the rock. The other important minerals in this rock are quartz, and in certain places, almandite. Aggregates of tourmaline are observed in places. This rock contains less feldspar than the rock in which the green variety is found. Here and there, needles of sillimanite are sparsely disseminated. In one section, a few needles of dumortierite were seen in a grain of almandite.

Kornerupine, that is found as elongated crystals (Fig. 5) which define the foliation of the rock, is very rich in various inclusions of quartz, orthoclase, rutile, biotite, pyrite, pyrrhotite, tourmaline (rare), etc. In thin sections normal to the *c*-axis the yellow kornerupine shows good euhedral shape (Fig. 6).

GENETIC CONSIDERATIONS

Little precise information on the geology and petrography of the kornerupine occurrences is found in the mineralogical literature. Some Madagascar kornerupine may have originated in a quartz vein, with a pegmatitic facies. The vein may be interbedded in a cordierite-rich gneiss (Lacroix 1939); in Ceylon kornerupine is found in gravels, together with zircon, garnet, and spinel (Hey, Anderson & Payne); in Natal kornerupine is accompanied by biotite and quartz with little tourmaline and grandidierite ("the nature and texture of the component minerals make it seem likely that the rock is of pegmatitic origin and that contact assimilation of iron and magnesium has played a part in its formation," de Villiers, 1940); in Saxony kornerupine is found in an albitic facies of a "granulite" together with corundum, kyanite, sillimanite, and tourmaline (Harker), etc.

It would therefore appear that kornerupine is a product of metasomatism; furthermore, the presence of boron, unsuspected by the early authors, and the usual association with tourmaline lead to the belief that the proximity of boron-bearing intrusives, such as occur near the deposit of Lac Ste-Marie, is necessary to the formation of kornerupine. For these reasons, and also because of the analogy between kornerupine and tourmaline, it would be worthwhile to investigate possible relation-

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ships between these two minerals. Perhaps, elements that should normally form tourmaline end by forming kornerupine when placed in certain physico-chemical environments which must surely be very unusual in view of the rarity of this mineral.

Acknowledgments

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The author wishes to record his indebtedness to Mr. Fernand Claisse, physicist, for the x-ray work performed and for much kind cooperation, and also to Mr. Henri Boileau, chief-chemist, who carried out the chemical analyses presented here. Hearty thanks are due to his other colleagues of the Department of Mines who took part in this work and whose friendly cooperation was much appreciated. Thanks are also due to Prof. L. G. Berry, of Queen's University, Kingston, for his criticisms of the manuscript.

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