Iron-rich kornerupine from Port Shepstone, Natal.¹

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Occurrence.—A very interesting kornerupine-bearing rock was sent by Mr. W. H. Cross during 1938 to the Geological Survey for identification. The material, of which about 800 grams were available for study, was stated to have been found in the Port Shepstone district. The occurrence has, however, not been visited by the writer.

The hand-specimens examined were all somewhat weathered. Macroscopically these consisted of an intergrowth of grey, columnar crystals of kornerupine, up to 5 centimetres in length, and adhering iron-stained quartz. Shiny 'books' of biotite occur both in the kornerupine and the quartz, while small patches and specks of dark brown tourmaline and bluish grandidierite were observed enclosed in the kornerupine. 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.

Physical properties.—Cleavage, prismatic, distinct. H. $6\frac{1}{2}$, sp.gr. 3.445. Fuses at 6 to a black, moderately magnetic globule. Colour, greyish in hand-specimen, light yellow in powder. Moderately magnetic. The mineral is fairly friable owing to advanced and incipient alteration along cracks, and contains fairly abundant inclusions.

The specific gravity was obtained by matching the crushed mineral with a heavy liquid until neither sinking nor floating occurred, and measuring the specific gravity of the liquid immediately. The result given is the mean of several determinations, which range from 3.438 to 3.446, and is corrected for water at maximum density.

Crystallographic properties.—The following faces were observed on crystal fragments: a(100), b(010), and m(110). These gave poor reflections on the goniometer. The measurements obtained were in accordance

¹ Published by permission of the Hon. The Minister of Mines, Union of South Africa. with orthorhombic symmetry, the mean of a large number of determinations yielding the result (100):(110) = 40° 30' (accuracy $\pm 15'$), corresponding to the axial ratio a:b = 0.854:1.

Optical properties.—Fragments oriented on the goniometer were sectioned and the following optical properties noted under the petrographic microscope:

 $\alpha = c, \gamma = b.$ 2V α 48° (±4°), Mallard's method. r < v.

Pleochroism, α and β colourless or nearly so, γ light amber (yellow with some brown and green).

Refractive indices were measured on conoscopically oriented grains or cleavage fragments in sodium-light:

 α 1.682, β 1.696, γ 1.699 (all ± 0.002).

As a check on the accuracy of these indices the optic axial angle was calculated. This gave $2V_{\alpha} \pm 50^{\circ}$. No appreciable variation from the above properties was noted in the material available for examination.

Below is listed in tabular form the principal properties of kornerupine from the various localities known.

TABLE I. Physical, optical, and crystallographic properties of kornerupine.

	Н.	Sp. gr.	α.	β.	γ.	2Vα.	a:b:c.
I.	6]	3.445	1.682	1.696	1.699	48°	0-854:1
II.	6 1	3.27	1.6650	1.6766	1.6770	19 1 0*	0.860:1* —
III.		3.28	_				0.865:1:0.423
IV.	7	3.345	1.6711	1.6826	1.6840	28°48′	0.862:1:0.435
V.	6 1	3.273			—	19° *	0.854:1

I. Port Shepstone, Natal. Analysis I (table II) by C. J. van der Walt, Division of Chemical Services, Pretoria.

II. Itrongay, Madagascar. Analysis II by F. Raoult in A. Lacroix, Minéralogie de Madagascar, 1922, vol. 1, p. 396.

- III. Waldheim, Saxony (var. prismatine). B. Gossner and F. Mussgnug, Neues Jahrb. Min., Abt. A, 1928, Beil.-Bd. 58, p. 227. [M.A. 4-109.]
- IV. Waldheim, Saxony (var. prismatine). J. Uhlig, Zeits. Kryst. Min., 1910, vol. 47, p. 215.
 - V. Fiskernæs, Greenland. J. Lorenzen, Meddelelser om Grønland, 1884, vol. 7, p. 19.

* These figures were calculated by the writer from relevant data.

Chemistry.—The kornerupine for chemical analysis was crushed and cleaned by separation with heavy liquids. The resultant product was found on microscopic examination to be of fair purity, the total impurities (consisting of ilmenite with some grandidierite, quartz, &c.) being estimated at less than 1%.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30.90
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46 ·79
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	_
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19.46
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$H_{2}O$	1.30
100.29 100.16 100.93 99.75 1	00.47

TABLE II. Chemical analyses of kornerupine.

I-V, localities and references at foot of Table I.

Various attempts have been made in the past to find a formula that adequately expresses the variations in the composition of kornerupine, and the following general expressions have been put forward:

(1)	J. Lorenzen (1884)	•••	•••		MgAl ₂ SiO ₆ .
(2)	J. Uhlig (1910)		•••		H ₃ NaMg ₆ Al ₁₂ Si ₇ O ₄₀ .
(3)	B. Gossner & F. Muss	gnug (1	.928)		4MgSiO ₃ .3Al ₂ O ₃ .
(4)	A. Lacroix (1922)		•••	• • •	$(SiO_4)_7Mg_8(Al,B)_{12}O_{12}$

Only the analyses by van der Walt and Raoult show the presence of boron. Since, however, the Fiskernæs and Waldheim materials closely resemble minerals analysed by these workers, it must be assumed that boron is a constant constituent of kornerupine. It may further be observed: (i) Lorenzen apparently did not analyse for alkalis and gave all his iron as Fe_2O_3 ; (ii) the comparatively high molecular percentage of silica in the analysis of Gossner and Mussgnug is probably due to an admixture of quartz in the analysed material, since the presence of this mineral is recorded by these writers.

In an attempt to deduce a suitable expression for the composition of kornerupine, reliance must therefore be placed chiefly on the analyses by Raoult and van der Walt.

Inspection of table II shows that the kornerupine from Port Shepstone differs from that of other localities chiefly in having a higher ferric iron and lower magnesia content. The Waldheim prismatine also has a low percentage of magnesia, but this deficiency is balanced by a higher content of ferrous iron and sodium. As there would thus appear to be room for doubt as to whether the iron in the Port Shepstone mineral is chiefly ferric and not ferrous the following report by Mr. van der Walt is appended.

'I have carried out the iron determination three times and obtained results that show satisfactory agreement. There is, however, a possibility that the mineral is not completely decomposed by HF and H_2SO_4 .'

The question as to whether the water must be regarded as constitutional or absorbed cannot be answered with certainty. In view, however, of the small amounts usually present (in one case practically negligible) it was decided to disregard the water in an attempt to arrive at a general formula.

The lattice constants for prismatine were determined by Gossner and Mussgnug. These are a 13.86, b 16.02, c 6.78 Å. Kornerupine from Fiskernæs gave c 6.8 Å. As the axial ratio a:b of kornerupine from Itrongay and Port Shepstone agrees closely with that of Waldheim and Fiskernæs (see table I) it can be assumed that the unit cells of the various varieties of kornerupine are of nearly equal dimensions. These constants and the density enable the unit-cell contents of the Itrongay and Port Shepstone material to be calculated.

A	Po tomic ratio	ort Shepst	one. olume × 3-4	Itrongay. Atomic ratio \times unit-cell volume \times 3-27				
	Mol. ratios.	Atomic ratios.	Metal atoms.	Oxygen.	Mol. ratios.	Atomic ratios.	Metal atoms.	Oxygen.
SiO ₂	0.4915	0.4915	15.64	31.28	0.5177	0.5177	15-45	30.90
B ₂ O ₃	0.0503	0.1006	3.20	4.80	0.0516	0.1032	3.08	4.62
Al ₂ O ₃	0.4017	0.8034	25.56	38.34	0.3746	0.7492	22.35	$33 \cdot 52$
Fe ₂ O ₃	0.0730	0.1460	4.65	6.98	0.0127	0.0254	0.76	1.14
FeO	0.0185	0.0185	0.59	0.59	0.0102	0.0102	0.30	0.30
MnO	0.0011	0.0011	0.04	0.04		<u> </u>	_	
MgO	0.2704	0.2704	8.60	8.60	0.5584	0.5584	16.65	16.65
CaO		_			0.0091	0.0091	0.27	0.27
Na ₂ O	0.0113	0.0226	0.72	0.36	0.0219	0.0438	1.31	0.66
K2Ō			_		0.0008	0.0016	0.05	0.03
Total o	xygen ato:	ms		90.99				88.09

TABLE III. Empirical unit-cell contents of kornerupine.

Inspection of tables III and IV shows that the number of oxygen atoms to the unit cell of kornerupine is constant within the limits of experimental error, but that the number of metal atoms varies. It is thus not possible to deduce a general formula for the series which is based on the grouping together of structurally equivalent atoms. A satisfactory formula can, however, be computed on a purely chemical basis. This can be written as $(R''_2, R''_3, R'_6)_3(Si_3, B_4)O_{15}$.

		Po	Itrongay.				
Si	 	15.5	15-5 (16	15.7	15.7	16
в	 	3.2	$\begin{pmatrix} 0.5 \\ 2.7 \end{pmatrix}$	25	3.1	0·3) 2·8	25
Al	 •••	25.3	$\left\{\begin{array}{c} 22\cdot3\\3\cdot0\end{array}\right\}$	20	22.8	22·2) 0·6	
Fe'''	 	4.6	4.6		0.8	0.8	
Fe''	 •••	0.6	0-6	17.4	0.3	0.3	20.3
Mg	 	8.5	8.5	11.4	17.0	17-0 (200
Ca	 •••	_			0.3	0-3	
Na	 	0.7	0.7)		1.3	1.3	
Total	 	58.4	,		61.3	•	

TABLE IV. Unit-cell contents on basis of 90(0).

TABLE V. Molecular proportions of kornerupine.

				Port Shepstone.		Itrongay.
SiO ₂	• • •		4915	(S: P.)0 190	5177	$(Si = 4c_1)O_1 = 198$
B ₂ O ₃			502·6	$(SI_3, D_4)O_6 = 189$	515.5	(513, 00:/08 - 100
Al ₁ O ₃	•••		4017		3746	
Fe ₂ O ₃			730-2		126-5	
FeO	•••		185-1		101-6	
MnO			11-3	$(A1 M_{\pi} + h_{\pi})(A) = 109$	_	$(Al_{6}, \&c.)O_{9} \approx 196$
MgO			2704	$(Al_{6}, Mg_{9}, \alpha c.) O_{9} = 192$	5584	
CaO					90.95	
Na ₂ O			112.9		219.4	1
K,Ō		•••	—)		8.49	

In the case of the analysis by van der Walt the TiO_2 was calculated as ilmenite and the P_2O_5 disregarded.

A calculation of the unit-cell contents in terms of the above group yielded a satisfactory approximation to the whole number 6, the actual figures obtained being 6.1 and 5.9 for the Port Shepstone and Itrongay minerals respectively. The unit cell would thus contain 90 oxygen atoms. Particular formulae were deduced from the general formula as follows:

Port Shepstone	•••	•••	Al ₂₅ Fe ^{''} ₅ Mg ₈ Fe ^{''} Si ₁₅ B ₄ O ₉₀ .
Itrongay		•••	Al ₂₃ Fe"'Mg ₁₇ Na ₂ Si ₁₅ B ₄ O ₉₀ .

New analyses of kornerupine from Waldheim and Fiskernæs would be of great use in determining the full range of the kornerupine series. The prismatine from Waldheim alone apparently varies considerably in composition, and it would be worth while making a fractional separation of the cleaned material in heavy liquids and determining the optical and chemical properties of fractions differing by say 0-005 in specific gravity.

KORNERUPINE FROM NATAL

Microscopic characters of the rock.—In thin section under the microscope quartz, biotite, and tourmaline can be seen to be interstitial to kornerupine (figs. 1 and 2). These minerals usually show no tendency toward crystal form, especially the tourmaline which is frequently present in vein- and net-like structures. On the other hand, kornerupine frequently shows good crystal outlines. Grandidierite is present as light



FIG. 1.

FIG. 2.

FIG. 1. Kornerupine (k) showing crystal outlines; with quartz (q) and biotite (b). \times 22.

Fig. 2. Kornerupine (k) with grandidierite (g) and tourmaline (t). $\times 22$.

bluish, pleochroic patches and blebs enclosed in kornerupine. It has, however, been possible to obtain rod-like crystals of this mineral suitable for measurement on the goniometer. Ilmenite occurs disseminated throughout the rock as small, rounded or irregular blebs. In addition to these minerals and small amounts of alteration products (chiefly iron oxides and a fine-grained mineral resembling sericite), very small amounts of graphite and garnet are also present.

The following properties were determined for the minerals:

Tourmaline.— ω 1.659(±0.004). Pleochroism, ω deep red-brown, ϵ light straw-yellow. The refractive indices indicate that the mineral is composed of nearly equal parts of dravite and schorlite.

Biotite.— β 1.635(±0.004), 2V α 14°(±2°). Pleochroism, α light yellow, β and γ dark reddish-brown.

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Grandidierite.— $\alpha 1.597, \beta 1.630, \gamma 1.632$ (all ± 0.004). Cleavages, a(100), b(010). Pleochroism, α light greenish-blue, β colourless, γ light greenish-blue. $\alpha = a, \gamma = b$. $2V\alpha 29^{\circ}(\pm 3^{\circ}), r < v$ strong. A qualitative chemical analysis showed the mineral to be chiefly a boro-silicate of aluminium and iron.

Garnet.— $n 1.804(\pm 0.004)$.

Summary.—Kornerupine, which differs from previously described material chiefly in having a higher ferric iron and lower magnesia content, is found in the Port Shepstone district, Union of South Africa. An analysis of this material shows that the composition of kornerupine varies between wider limits than hitherto known. From this and other analyses the general formula is deduced as $(R''_2, R''_3, R'_6)_3(Si_3, B_4)O_{15}$.