

Geikielite and the ferro-magnesian Titanates.

By T. CROOK, A.R.C.Sc.I., F.G.S., and B. M. JONES, B.A. (Oxon.)
 Assistants in the Scientific and Technical Department of the
 Imperial Institute.

[Read January 23, 1906.]

Communicated by permission of the Director of the Imperial Institute.]

IN connexion with the systematic examination of the minerals of Ceylon, which is being conducted in the Scientific and Technical Department of the Imperial Institute, the authors have recently examined a large quantity of coarse gem-gravel refuse obtained from the Balangoda and Rakwana districts of Ceylon.

The material varies somewhat in character, but zircon generally predominates, while tourmaline, corundum, and pleonaste are fairly abundant. Among other minerals present in noticeable quantities are geikielite, picroilmenite, ordinary ilmenite, rutile, and fergusonite, all of which are generally in the form of rounded or sub-angular pebbles.

This association of the members of the geikielite-ilmenite series seemed to be a matter of some interest, especially on account of the fact that among the specimens examined there occurred varieties having specific gravities intermediate between those of geikielite and picroilmenite.

GEIKIELITE.

Physical characters.—The specimens identified as geikielite are quite similar in their physical characters to those first described by Mr. Allan Dick.¹ They have a dull black appearance on worn surfaces, but freshly fractured surfaces are jet-black and show a somewhat vitreous lustre. The cleavage is rhombohedral, the angles between the cleavage-planes being about $93\frac{1}{2}^{\circ}$. This appears to be a true cleavage and not a parting. None of the specimens shows any trace of twinning. The cleavage-faces when perfectly fresh show a metallic-adamantine lustre, but generally they are dulled by a thin film of titanium dioxide, even in the freshest specimens. It is only when this film is present that the plum-coloured hue described by Mr. Dick can be seen. The fracture is generally uneven, but occasionally sub-conchoidal. The hardness is 6.

The streak is purplish-brown, and not black as stated by P. von

¹ Min. Mag., 1893, vol. x, p. 145.

Sustschinsky.¹ When the powder is finely ground in an agate mortar, its colour is deep purple and quite characteristic. The mineral is opaque, except in thin splinters under the microscope, these being translucent and of a deep reddish-purple colour. The splinters give a uniaxial figure of negative sign, and are non-pleochroic. Geikielite is slightly magnetic, but less so than picroilmenite and much less so than common ilmenite.

Chemical composition.—In the analysis published by Dick, only 3.8 per cent. of iron oxide was recorded. In 1902, Sustschinsky, who examined some geikielite from Ceylon having the same physical characters as that described by Dick, recorded 9 per cent. of iron oxide. The following are the two analyses:—

	Dick.	Sustschinsky.
TiO ₂	67.74	61.32
FeO	3.81	2.03
Fe ₂ O ₃	—	7.75
MgO	28.73	28.95
	<u>100.28</u>	<u>100.05</u>
Specific gravity ...	3.98–4.0	3.976

The results of a considerable number of analyses of the material examined by the present authors confirm the analysis recorded by Sustschinsky. The following are two typical analyses of geikielite poor in iron:—

	I.	Molecular ratios.	II.	Molecular ratios.
TiO ₂	64.78	0.809	64.41	0.805
FeO	5.92	} 0.110 ²	5.44	} 0.114 ²
Fe ₂ O ₃	2.22		2.77	
MgO	27.90	0.697	27.90	0.697
	<u>100.82</u>		<u>100.52</u>	
Specific gravity ...	3.89		3.97	

The specimen used for analysis I is slightly altered and shows leucoxene along the cleavage-cracks; hence the comparatively low specific gravity. The material II was quite fresh, and the specific gravity given

¹ 'Beiträge zur Kenntniss des Geikielith, Ilmenit und Hämatit,' Zeits. Kryst. Min., 1902, vol. xxxvii, p. 57; abstract Min. Mag., vol. xiii, p. 307.

² All the iron is calculated as ferrous oxide.

above may be taken as representing the true value for unaltered geikielite containing 8.2 per cent. of iron oxide.

It seemed unlikely that these specimens could differ chemically from those examined by Mr. Dick, seeing that they were so very similar in all other respects. Accordingly, Mr. Dick kindly permitted his material to be re-examined. The fragments consisted partly of rutile, but this was coarse enough to allow of its separation. A portion of geikielite free from rutile gave the following analysis:—

III.				
TiO ₂	63.77
FeO	6.34
Fe ₂ O ₃	1.93
MgO	28.50
				100.54

From this result it seems probable that the iron oxide was not completely separated from the titanium dioxide in the original analysis.

The method of analysis adopted was fusion of 0.3 to 0.5 gram of the finely powdered mineral with potassium hydrogen sulphate, the solidified cake being dissolved in cold water acidified with sulphuric acid. After diluting to one litre and reducing with a little sodium sulphite, the whole was boiled from six to seven hours, water being added at intervals to replace that lost by evaporation. The precipitated titanium dioxide was filtered off, dried, ignited with a few grains of ammonium carbonate, and weighed. The titanium dioxide thus obtained generally contained about 2 per cent. of iron oxide, and sometimes as much as 7 per cent.; but it rarely contained more than a trace of magnesia. The process of fusion was repeated to separate completely the iron oxide and magnesia. A third fusion was necessary in two cases only. The filtrate from the titanium dioxide was tested with hydrogen peroxide to make sure that all the former was precipitated; then ammonium chloride was added, and the total iron and magnesium determined in the usual way. To determine the ferrous iron, a portion of the powdered mineral weighing about 0.3 gram was decomposed by a mixture of hydrofluoric and dilute sulphuric acids, in the absence of air, and the solution obtained titrated with potassium permanganate.

Geikielite with only 8 per cent. of iron oxide is comparatively rare in the gem-gravels. More commonly, varieties occur which are somewhat richer in iron, containing 10 to 14 per cent. of the oxides. These have a somewhat higher specific gravity, as one would expect. They also

diminish somewhat in transparency, while the streak and colour of the powder deepen in shade as the percentage of iron increases. The following analyses illustrate the varying composition of these specimens:—

	IV.	V. ¹	VI.	VII.	VIII.	IX.	X.
TiO ₂ ...	63.94	64.03	62.49	62.25	61.60	60.87	60.02
FeO ...	10.09	12.14	10.70	11.58	7.79	6.03	5.81
Fe ₂ O ₃ ...	0.25	—	3.54	—	4.95	5.69	6.80
MgO ...	25.79	24.66	23.60	26.03	26.31	27.29	27.79
	<u>100.07</u>	<u>100.83</u>	<u>100.33</u>	<u>99.86</u>	<u>100.65</u>	<u>99.88</u>	<u>100.42</u>
Sp. gr.	4.01	4.11	4.01	3.91	3.90	3.87	3.79

The material of analyses IV and V was fresh; that of VI slightly decomposed along the cleavages; while in VII, VIII, IX and X it showed growths of leucoxene increasing in amount as the specific gravity diminishes.

From these results it is seen that ferric iron may or may not be present, but ferrous iron is always present, and generally in much larger quantity than the ferric. Further, the ferric oxide appears to be sometimes of primary and sometimes of secondary origin. In some instances (as in Nos. VIII, IX, and X) the ferrous iron and magnesia unite with the titanium dioxide, leaving a surplus of ferric oxide. When this is the case, it seems reasonable to explain the presence of ferric oxide as an isomorphous replacement of the geikielite molecule. In other cases, however (as in Nos. I, II, IV, and VI), there is a deficit in the sum of ferrous oxide and magnesia molecules, a deficit which is remedied by reducing (in calculation) such ferric oxide as is present to a ferrous state, and adding this to the sum of existing ferrous oxide and magnesia. In these cases it appears probable that the ferric oxide is secondary and that it has arisen by oxidation from the ferrous state. In still other cases both primary and secondary ferric oxide appear to be present. It is only on this assumption that many of the analytical results can be explained.

It is, however, a noteworthy fact that a specimen may show a considerable amount of the leucoxene decomposition product, though containing no secondary ferric oxide; on the other hand, apparently fresh specimens may contain this secondary ferric oxide.

¹ No. V contained a trace of manganese.

In general, the *specific gravity* increases with the percentage of iron, but within narrow limits the variations are complex and difficult to understand, though the reduction of the specific gravity by the partial decomposition along the cleavages accounts for most peculiarities. Assuming equal molecular volumes for the different members of the geikielite-ilmenite series, and taking the specific gravity of ilmenite (FeTiO_3) as 4.7, the specific gravity of geikielite free from iron (MgTiO_3) should be 3.7. In this connexion the following comparison is of interest as illustrating the relation between specific gravity and composition in some of the least altered specimens:—

	Calculated sp. gr.	Observed sp. gr.
(Mg,Fe)TiO ₃ with 8 per cent. FeO	3.87	3.97
" " 14 " " 	3.96	4.11
" " 27 " " 	4.28	4.30
" " 34 " " 	4.42	4.44

It is probable that neither the calculated nor the observed specific gravities are correct in the second place of decimals, as the specific gravity of ilmenite is uncertain and the specimens are liable to decomposition. But such as the numbers are, they appear to indicate that the molecular volume for the geikielites is somewhat smaller than that for the ilmenites.

Alteration products of geikielite.

Rutile.—The specimens are generally free from visible intergrowths with other minerals. One specimen, however, is associated with rutile as an alteration product. It is sub-angular in shape and weighed about 16 grams; it appears to have been broken from a much larger specimen. Except on the fractured surface, which has the characteristic thin film of titanium dioxide, the specimen is covered with a shell of rutile varying in thickness from one to two millimetres. The surface of contact between the geikielite and the rutile is very irregular, and there can be no doubt that the latter has resulted from the alteration of the former. The specimen is quite free from intergrowth, and the rutile is confined to the external surface.

Leucoxene.—This is white or yellowish-white in colour, opaque, and for the most part apparently amorphous. It is the commonest alteration product of geikielite and is similar in appearance to that familiar on the cleavage-planes of ilmenite. It is generally confined to the cleavage-planes; one specimen was found, however, a portion of which was almost

completely decomposed, and this furnished about a decigram of material which gave the following analysis:—

TiO ₂	81.3
Fe ₂ O ₃	6.4
CaO	3.0
MgO	trace
SiO ₂	4.2
H ₂ O	5.6
				100.5

In this case the leucoxene consists mainly of amorphous titanium dioxide. The ferric oxide is probably present as limonite, while the lime and silica are probably in combination with a portion of the titanium dioxide as sphene.

Sphene.—This occurs as colourless, translucent granules intimately associated with the leucoxene in the cleavage-cracks. These granules show the optical characters of sphene, and their identification as such is confirmed by the above analysis of the leucoxene.

Limonite.—This was observed in the cavities of much decomposed specimens.

PICROILMENITE.

Picroilmenite¹, or magnesian ilmenite, appears to occur in considerable quantities in the Balangoda district. It has a specific gravity of 4.25, when fresh; two specimens gave the following analyses:—

	XI.	XII.
TiO ₂ ...	57.64	56.08
FeO ...	16.57	24.40
Fe ₂ O ₃ ...	10.17	5.43
MgO... ..	15.56	14.18
	99.94	100.09
Specific gravity ...	4.17	4.25

In specimen No. XI, the ferric oxide appears to be partly primary and partly secondary, while in No. XII it is all primary. The mineral is thus very similar in composition to the magnesian ilmenite of

¹ P. Groth, 'Tabell. Übers. d. Mineralien,' 4th edition, 1898, p. 143.

Warwick, New York, analysed by C. F. Rammelsberg in 1858, and by S. L. Penfield and H. W. Foote¹ in 1897.

Notwithstanding its high percentage of iron, it is translucent in very thin splinters under the microscope and shows a deep purple-red colour very similar to that of geikielite. Its streak, and the colour of its powder in the mass, are similar to those of geikielite in tint, but much darker in shade. Its hardness is 6, and, like geikielite, it appears to be about half a degree, on Mohs's scale, harder than ilmenite.

In all its properties it is much more akin to geikielite than to common ilmenite. Its composition generally corresponds to the formula $(\text{Fe}, \text{Mg})\text{TiO}_3$, where $\text{Fe} : \text{Mg} = 1 : 1$; this fact, together with the intermediate character of its general properties, makes it advisable to regard picroilmenite as the middle member of the series of ferro-magnesian titanates. Those members of the series containing less magnesia and more iron oxide than picroilmenite should be classed as ilmenites, while those with more magnesia and less iron should be classed as geikielites.

SUMMARY AND CONCLUSIONS.

1. Up to the present no geikielite has been found containing less than 8 per cent. of iron oxide.

2. For this reason the formula $(\text{Mg}, \text{Fe})\text{TiO}_3$ represents the composition of geikielite more correctly than the formula MgTiO_3 .

3. Picroilmenite is closely related to geikielite in its general properties.

4. It is advisable to divide the ferro-magnesian titanates into ilmenites and geikielites, and to regard picroilmenite as the middle member of the series.

5. It seems likely that, considering the association in the present instance of geikielite and picroilmenite, many specimens commonly classed with the latter may turn out on closer examination to be geikielite.

6. The alteration products of geikielite are similar to those of ilmenite, and include rutile, amorphous titanium dioxide (leucoxene), sphene, and limonite.

¹ Amer. Journ. Sci., 1897, ser. 4, vol. iv, p. 108.
