

*Kennedyite, a new mineral of the  
pseudobrookite series.*

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*Summary.* A new mineral with the approximate composition of  $\text{Fe}_2\text{MgTi}_3\text{O}_{10}$  and isostructural with pseudobrookite  $\text{Fe}_4\text{Ti}_2\text{O}_{10}$  has been observed in an olivine-augite-alkali-feldspar rock of the Karroo succession from the Mateke Hills area in south-eastern Southern Rhodesia. Chemical analysis and indexed X-ray powder data ( $a$  9.77,  $b$  9.95,  $c$  3.73 Å.) of the mineral are given, and the name kennedyite is proposed. The name karrooite is proposed for the artificial product  $\text{MgTi}_2\text{O}_5$ .

THE Mateke Hills area lies in the south-eastern part of Southern Rhodesia and is characterized by several ring-complexes of late-Karroo age, which are emplaced in an extensive trough of Karroo volcanics with generally thin basal sediments. The Karroo rocks rest unconformably on the paragneisses of the Limpopo valley.

The lower part of the Karroo volcanic succession consists mainly of olivine-rich rocks. These are in part extrusive and may be termed in general limburgites, and in part intrusive as sills, dykes, and plugs. The intrusive rocks are fine- to medium-grained and vary in composition from olivine-dolerites to picritic and shonkinitic types.

The specimens containing the new mineral were collected from what is believed to be an extensive sill at the base of the volcanic succession immediately overlying the Cave Sandstone.

*Petrographic description.* Under the microscope the rock (table I, anal. 1) consists predominantly of broken and abraded olivine phenocrysts from 1 to 5 mm. in length, smaller euhedral or rounded clinopyroxene crystals, often clustered around the margins of the olivines, and rectangular, lath-shaped to fibrous crystals up to 2 mm. in length of the new mineral, set in a ground-mass of an alkali feldspar, which is intergrown with extremely thin apatite needles (fig. 1).

The olivine is partly altered into serpentine along the cracks and contains in addition red-brown patches of another later alteration product. Small grains of magnetite and minute brownish oriented inclusions producing a schiller structure are common. The clinopyroxene, a light

coloured non-pleochroic variety, appears to be free of inclusions and alteration products.

The new mineral is usually opaque, though some of the smaller crystals, particularly along the margins, are commonly translucent and of a dark brown colour. In these, straight extinction has been observed. The mineral is invariably confined to the feldspar matrix, which consists of

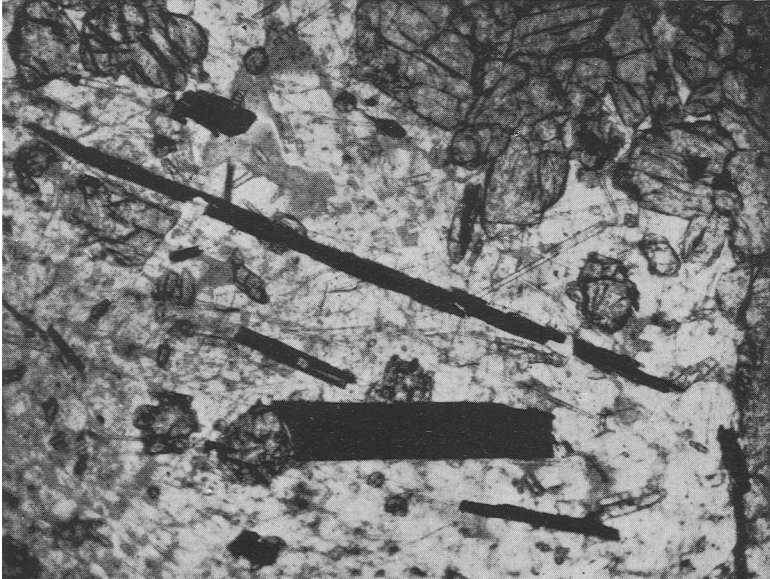


FIG. 1. Kennedyite (opaque) set in a matrix of alkali feldspar with apatite needles. Ordinary light,  $\times 64$ .

irregular laths without apparent twinning but in which characteristic wavy cracks and undulose extinction have been noted.  $2V$  of the feldspar varies from rather small to moderate; some grains are altered to a greenish sericitic substance; chemical and X-ray data suggest a sodapotash feldspar variety, perhaps an anorthoclase.

An examination of polished sections showed the new mineral in well-defined laths. In some grains marginal patches of secondary hematite were observed and with high magnification ( $\times 500$ ) lamellar intergrowths were seen. The lamellae are believed to be exsolved rutile. Pleochroism was not apparent and with crossed nicols only weak steel-grey to purplish-brown anisotropic effects were seen.

*Separation of the mineral.* The rock contains approximately 3 to 4%

of the new mineral and the separation of this was carried out as follows: the rock was crushed and passed through a 120-mesh sieve. The powder was first repeatedly slimed with water in a large beaker using a little detergent in order to lessen the surface tension. After drying, all magnetic particles were removed with a strong hand magnet and the rest was separated using a Frantz-type magnetic separator, applying a forward slope of  $20^\circ$  and a tilt of  $15^\circ$ . The main fraction containing the new mineral was obtained between 0.6 and 0.8 amps. This fraction was further carefully crushed and slimed and separated with Clerici solution. The mineral was again magnetically separated and a fraction between 0.7 and 0.75 amps. was retained for analysis. Examination under a binocular microscope showed only traces of impurities attached to some of the larger grains, which were removed by hand picking.

*Mineralogy and chemistry.* The orthorhombic pseudobrookite series is represented by only one naturally occurring mineral, pseudobrookite,  $\text{Fe}_2\text{TiO}_5$ , which was first observed in cavities in an andesite from Aranyer Berg in Transylvania and subsequently described by Koch in 1878 (Dana, 1892). In recent years several artificial compounds with the pseudobrookite structure have been noted in titaniferous slags and others have been synthesized. Indeed, the first synthetic pseudobrookite corresponding to the above formula was found as a sublimate on bricks in a sulphate furnace and reported by Doss as early as 1892.

The chemical analyses of natural pseudobrookites invariably show an excess of titania over the theoretical amount indicated by the formula  $\text{Fe}_2\text{TiO}_5$  and in addition there is always a small amount of magnesia present. Pauling (1930) made a structural analysis on pseudobrookite crystals from Aranyer Berg and arrived at the same formula,  $\text{Fe}_2\text{TiO}_5$ , as proposed by Doss. He observed, moreover, reflections of rutile in the material examined and the presence of this exsolved mineral phase accounts for the high titania content found in natural pseudobrookites. As for magnesia, no comments were made at the time.

According to Ernst (1943) there is a marked solubility of  $\text{TiO}_2$  in pseudobrookite at high temperatures ( $> 1500^\circ\text{C}$ ). At lower temperatures the solubility is much reduced and highly titaniferous pseudobrookites should therefore not be common in nature. Among the synthetic compounds with the structure of natural pseudobrookite the following end-members have been recognized: tieilite,  $\text{Al}_2\text{TiO}_5$ ; unnamed,  $\text{MgTi}_2\text{O}_5$ ; anosovite,  $\text{Ti}_2\text{TiO}_5$ ; unnamed,  $\text{FeTi}_2\text{O}_5$ .

The solid solution series  $\text{Al}_2\text{TiO}_5$ - $\text{MgTi}_2\text{O}_5$  has been described by Sigurdson and Cole (1949) and the series  $\text{MgTi}_2\text{O}_5$ - $\text{FeTi}_2\text{O}_5$  was noted

by Moore and Sigurdson (1949) in smelting ilmenite ore. Crystals of anosovite,  $Ti_2TiO_5$ , have been observed in titaniferous blast furnace slags and studied by Rusakov and Zhdanov (1951) and the  $Fe_2TiO_5$ - $FeTi_2O_5$  series has been investigated by Akimoto *et al.* (1957).

In his study on the ore paragenesis of Katzenbuckel in Odenwald, Frenzel (1953) was the first to draw attention to the magnesia content of

TABLE I. Chemical composition of kennedyite and of the kennedyite-bearing rock.

	1.	2.	2a.	Norm. of 1.
SiO <sub>2</sub> ...	46.59	—		
TiO <sub>2</sub> ...	2.83	60.33	Ti 3.27	or 11.7
Al <sub>2</sub> O <sub>3</sub> ...	5.89	2.15	Al 0.18	ab 11.5
Fe <sub>2</sub> O <sub>3</sub> ...	3.54	28.77	Fe <sup>3+</sup> 1.56	an 4.7
Cr <sub>2</sub> O <sub>3</sub> ...	0.19	0.37	Cr 0.03	di 16.9
FeO ...	8.31	2.00	Fe <sup>2+</sup> 0.12	hy 18.1
MnO ...	0.16	0.07	Mn 0.00	ol 24.2
MgO ...	21.00	6.45	Mg 0.69	mt 5.1
CaO ...	5.79	tr.		il 5.3
Na <sub>2</sub> O ...	1.37	—		ap 1.0
K <sub>2</sub> O ...	1.97	—		sal
H <sub>2</sub> O + ...	1.76	—		fem
H <sub>2</sub> O - ...	0.10	—		
P <sub>2</sub> O <sub>5</sub> ...	0.46	—		
	<u>99.96</u>	<u>100.14</u>		0.395

1. Specimen F 7168/C888. Anal. O. von Knorring.

2. Kennedyite from spec. F 7168/C888, 29 miles ESE. of Nuanetsi, Southern Rhodesia. Anal. O. von Knorring.

2a. Atomic ratios to 10 oxygen.

natural pseudobrookites. The pseudobrookite from this locality is associated with hematite, occurs in a natronshonkinite and related rocks, and is considered to have formed by oxidation of original titano-magnetite and ilmenite in connexion with fumarolic or hydrothermal activity. In these pseudobrookites Frenzel has observed variations in the optical properties, which are believed to be related to temperature-controlled changes in the chemical composition of the pseudobrookites.

The chemical composition of the new mineral (table I, anal. 2) is distinctly different from previously analysed pseudobrookites and especially from the accepted composition of pseudobrookite as defined by the formula  $Fe_2TiO_5$ . The name kennedyite has been proposed for this new mineral in honour of Professor W. Q. Kennedy. The chemical composition of kennedyite is close to the intermediate member  $Fe_2MgTi_3O_{10}$  in the series  $Fe_2TiO_5$ - $MgTi_2O_5$ . This composition can be deduced from the pseudobrookite formula written as  $Fe_4Ti_2O_{10}$  by coupled substitution of MgTi for FeFe.

The chemical analysis also shows considerable amounts of aluminium, ferrous iron, and chromium. A qualitative spectrographic analysis of kennedyite gave the following results: major: Ti, Fe; minor: Mg, Al, Cr; trace: Si, Ca, V, Mn, Ni, Ga, Zr.

TABLE II. X-ray powder data for minerals of the pseudobrookite series. The following cell dimensions were obtained for kennedyite: *a*, 9.77, *b*, 9.95, *c*, 3.73 Å.

<i>hkl</i>	Tielite Al <sub>2</sub> TiO <sub>5</sub>		Anosovite Ti <sub>2</sub> TiO <sub>5</sub>		Kennedyite Fe <sub>2</sub> MgTi <sub>3</sub> O <sub>10</sub>		Pseudobrookite Fe <sub>2</sub> TiO <sub>5</sub>		Karooite MgTi <sub>2</sub> O <sub>5</sub>	
	<i>d.</i>	<i>I/I</i> <sub>1</sub>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I/I</i> <sub>1</sub>	<i>d.</i>	<i>I/I</i> <sub>1</sub>
200	4.71 Å.	47	4.78 Å.	m	4.88 Å.	s	4.902 Å.	45	4.9 Å.	12
220	3.35	100	3.46	vs	3.485	vs	3.483	100	3.51	100
101										
121					2.855	vw			2.86	9
230	2.65	70	2.70	vs	2.743	s	2.748	80	2.75	60
301	2.36	20	2.42	m	2.450	m	2.454	20	2.45	20
131			2.37	w	2.403	w	2.402	25	2.42	15
240	2.14	31	2.17	m	2.217	w	2.221	11	2.22	15
321	2.11	30	2.14	vw	2.195	w	2.198	15	2.19	20
331	1.897	52	1.93	s	1.970	m	1.971	25	1.967	30
002	1.792	44	1.85	vs	1.865	s	1.862	30	1.876	60
250			1.81	w	1.843	w			1.846	15
022	1.687	28	1.73	m	1.746	w	1.744	15	1.754	15
060	1.606	27	1.65	s	1.661	w	1.663	15	1.665	15
600	1.578	28	1.62	s	1.631	w	1.632	20	1.634	20
	1.519	6	1.58	vw						
	1.484	36	1.54	vs	1.544	m	1.54	35	1.551	30
			1.53	s	1.529	w			1.535	20
	1.449	8	1.49	vw	1.490	vw	1.49	11		
	1.371	14	1.42	s	1.419	vw	1.42	15	1.424	9
			1.37	w	1.370	vw	1.37	9	1.378	8
	1.305	16	1.35	m	1.350	vw			1.358	15
	1.266	11	1.31	vw	1.312	vw	1.31	5	1.318	8
	1.253	11	1.29	m	1.288	vw	1.30	5		
	1.219	9	1.26	m	1.259	vw	1.26	7	1.265	10
			1.24	m	1.240	vw	1.24	5	1.245	10

For the unnamed end-member MgTi<sub>2</sub>O<sub>5</sub>, being one of the major components in the mineral kennedyite, the name karrooite is proposed.

Kennedyite exhibits a tabular to fibrous habit. The colour is normally black, though smaller grains are translucent and are of a dark brown colour. The crystals are striated longitudinally and have a brilliant metallic lustre. The specific gravity determined by suspension in Clerici solution is 4.07, compared with 4.33 for the pseudobrookite from Thomas Range (Dana, 1946). Table II shows the X-ray powder data of kennedyite in relation to the synthetic end-members of the pseudobrookite series. The values for Al<sub>2</sub>TiO<sub>5</sub> (tielite) and MgTi<sub>2</sub>O<sub>5</sub> (karrooite) are

quoted from Moore and Sigurdson (1949), for anosovite from Zhdanov and Rusakov (1952), and for pseudobrookite from the ASTM X-ray Powder Data File.

In fig. 2 two powder photographs of kennedyite using Fe- $K\alpha$  radiation are shown. The first is on unheated material, the second on ignited (c. 1300° C.) powder. The latter is more clearly defined and shows distinctly an additional line at approximately 4.9 Å., which corresponds to the line at 5.0 Å. given for karrooite. As regards 'impurities' only the strongest line for rutile at approximately 3.2 Å. is discernible.

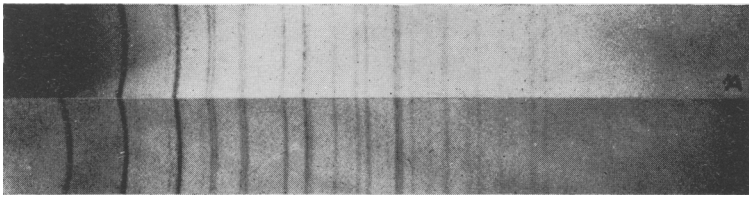


FIG. 2. X-ray powder photographs of kennedyite. 9 cm. camera, Fe- $K\alpha$  radiation. A, unheated material. B, powder heated to 1300° C. for 5 minutes.

With the knowledge of the above synthetic phases iso-structural with pseudobrookite, the excess titania and additional magnesia reported from natural pseudobrookites can be better understood. The composition of kennedyite gives a further indication of numerous possible diadochic replacements that may take place in the pseudobrookite structure.

The end-members corresponding chemically to pseudobrookite can be assigned the general formula  $X_2ZO_5$  (cf. Zhdanov and Rusakov, loc. cit.). The position of  $X$  may be occupied by the following trivalent metals of similar ionic radii (Ahrens' values): Al 0.51 Å., Ti 0.76 Å., V 0.74 Å., Cr 0.63 Å., Fe<sup>+++</sup> 0.64 Å., and Ga 0.62 Å.;  $Z$  is represented by quadrivalent Ti 0.68 Å. For the end-members containing divalent ions the formula  $YZ_2O_5$  can be applied. Here  $Y$  may be one of the following elements: Mg 0.66 Å., Mn 0.80 Å., Fe<sup>++</sup> 0.74 Å., Co 0.72 Å., Ni 0.69 Å., and Zn 0.74 Å. The rock containing kennedyite has a unique chemical composition (table I, anal. 1) and constitutes in itself an interesting petrological problem.

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