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A radioactive mineral from Mozambique related to davidite.

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EARLY in 1947 a black, opaque, radioactive mineral resembling samarskite in appearance was discovered at Mavuzi in the Tete district of Mozambique, Portuguese East Africa. Two small specimens, one a rough twinned crystal with trigonal symmetry (fig. 3), were sent by A. M. Macgregor, then Director of the Geological Survey of Southern Rhodesia, to the British Museum (Natural History) for investigation, and a chemical analysis by E. Golding (table I, no. 2) followed later in the same year. X-ray photographs of fragments and powder from both specimens were taken, but revealed on development no diffraction spots, lines, or haloes. Only after prolonged heat-treatment could powder lines characteristic of crystalline material be obtained. The metamict nature of the mineral before heat-treatment is not unexpected in view of its chemical composition, optical isotropy, and glassy fracture.

Subsequently, a quantity of larger crystals and also massive material was received by the Geological Survey of Great Britain, making possible a more detailed study of the morphology, the chemical composition, and of the X-ray patterns of the mineral after heat-treatment. It was recognized by Dr. C. F. Davidson that chemically the radioactive mineral from Tete is very similar to davidite from Radium Hill, 20 miles ESE. of Olary, South Australia. The latter occurs as rough cuboidal crystals embedded in late quartz in a hydrothermal lode composed mainly of

¹ Communicated by permission of the Director.

biotite and a titanium-rich iron-ore complex, in part uraniferous.¹ The X-ray powder photographs of the two minerals after heat-treatment in a neutral atmosphere, however, show distinct differences. It is the purpose of this paper to describe the Tete mineral and to compare it with davidite.

The geology of the Tete area was investigated in 1948 by Dr. C. F. Davidson and Dr. J. A. E. Bennett, of the Geological Survey of Great Britain, who state that the dominant rocks are pre-Karoo norites and anorthosites, which were sheared to epidiorite and possibly to saussurite-rock along a number of shear zones. These formed the channels for later mineralizing fluids which altered the sheared rock, producing epidiorite with scapolite and a massive scapolite-calcite or scapolite-dolomite facies. The scapolite-carbonate associations carry the bulk of the radioactive ore, together with rutile, sphene, magnetite, ilmenite, apatite, and molybdenite.

Morphological crystallography (J. E. T. H.).—The mineral usually occurs massive, but sufficient specimens showing crystal faces have been found for some conclusions to be drawn regarding the morphological crystallography. Owing to the roughness of the faces, it has only been possible to make measurements with a contact goniometer, but the mineral appears to belong to the ditrigonal pyramidal class ($3m$) of the trigonal system. The forms have been indexed by adopting an axial ratio $a:c$ of 1:1.37, which corresponds to a polar ratio $p_0:r_0$ of 1.58:1. A table of forms and angles is given below. The conventions followed are those of Dana's

Forms.	Lower.	Upper.	ϕ .	ρ .
Pedions:	\bar{c}	c (0001)	—	0°
Ditrigonal prisms:		h (21 $\bar{3}$ 0)	11°	90
		$-h$ (12 $\bar{3}$ 0)	-11	90
		$-l$ (25 $\bar{7}$ 0)	-14	90
Trigonal pyramid:	$-\bar{n}$	(03 $\bar{3}$ 4)	-30	50
Hexagonal pyramids:		o (11 $\bar{2}$ 1)	0	70
		\bar{p} (22 $\bar{4}$ 1)	0	80
Ditrigonal pyramids:		s (52 $\bar{7}$ 8)	14	51
		t (41 $\bar{5}$ 6)	19	50
		$-u$ (34 $\bar{7}$ 3)	-5	73
		$-\bar{v}$ (34 $\bar{7}$ 2)	-5	78
		$-\bar{w}$ (12 $\bar{3}$ 3)	-11	54
		$-\bar{x}$ (26 $\bar{8}$ 9)	-16	52
		$-\bar{y}$ (13 $\bar{4}$ 4)	-16	55
	$-\bar{z}$ (16 $\bar{7}$ 8)	-22	52	

¹ D. Mawson, Mineral Notes. Trans. Roy. Soc. South Australia, 1916, vol. 40, pp. 262-266; The nature and occurrence of uraniferous mineral deposits in South Australia. Ibid., 1944, vol. 68, pp. 334-357. [M.A. 1-69, 9-250.]

'System of mineralogy', 7th edition (1944, vol. 1, p. 7). A bar over a letter means a form on the lower portion of the crystal; a bar under a letter (figs. 1-4) indicates a face in twinned position.

In habit the crystals are tabular to pyramidal, with ditrigonal pyramids dominant. They are sometimes found in irregular clusters (fig. 2). Twinning occurs by rotation about the axis $[11\bar{2}0]$, as in pyrrargyrite. The hemimorphic character is evident in single individuals and in interpenetrant twins, but well-developed aggregate twins are of apparent holohedral symmetry (figs. 1 A, B, and C). Some of the crystals are very large. For instance, the fragment illustrated in fig. 4 and idealized in fig. 1 B, is 12 inches long and weighs 22 pounds; it is estimated that the original crystal, if fully developed, was 19 inches across and weighed 100 pounds.

The small cuboidal crystals in which davidite occurs at Olary are too rough to be measured, but it is clear that they are quite unlike the Tete mineral in habit. Nevertheless, a cuboidal habit is not necessarily inconsistent with $3m$ symmetry, for assuming an axial ratio of 1:1.37 an aggregate twin of the form $(10\bar{1}1)$ about $[11\bar{2}0]$ is a rhombohedron of rhomb angle $85^{\circ} 40'$.

Physical properties.—The determination of the physical properties of the Tete mineral confirms the preliminary measurements of N. E. Barlow, of the Geological Survey of Southern Rhodesia. It has a subconchoidal fracture with no cleavage, a hardness of 6 (Mohs's scale), and a specific gravity of 4.46. The mineral is opaque, except at the extreme edges of very thin splinters, where it is translucent and clove-brown. Owing to its metamict condition it is isotropic in polished sections. Photoelectric-cell measurements on several polished sections give an average value for reflectivity of 19.5 % in white light, compared with a galena standard, taken as 43.8 % (S. H. U. Bowie, Geological Survey of Great Britain). The colour of fresh surfaces and the streak are grey-black and the lustre submetallic and shining. Slightly oxidized surfaces, such as crystal faces, are usually dark brown, but sometimes reddish. The crushed material is just attracted by a powerful hand-magnet. Tests with the Frantz isodynamic separator show its susceptibility to fall within the ilmenite range and to be rather less than that of haematite. The principal elements, uranium, titanium, and iron, are readily demonstrated by the usual tests. The mineral is attacked with difficulty by hydrochloric and nitric acids.

Chemical analysis.—In view of considerable discrepancies amongst early chemical analyses of this mineral (table I, nos. 2-7) it was decided to obtain a complete analysis of a carefully selected sample. Although hand-specimens may look perfectly pure, polished sections under the

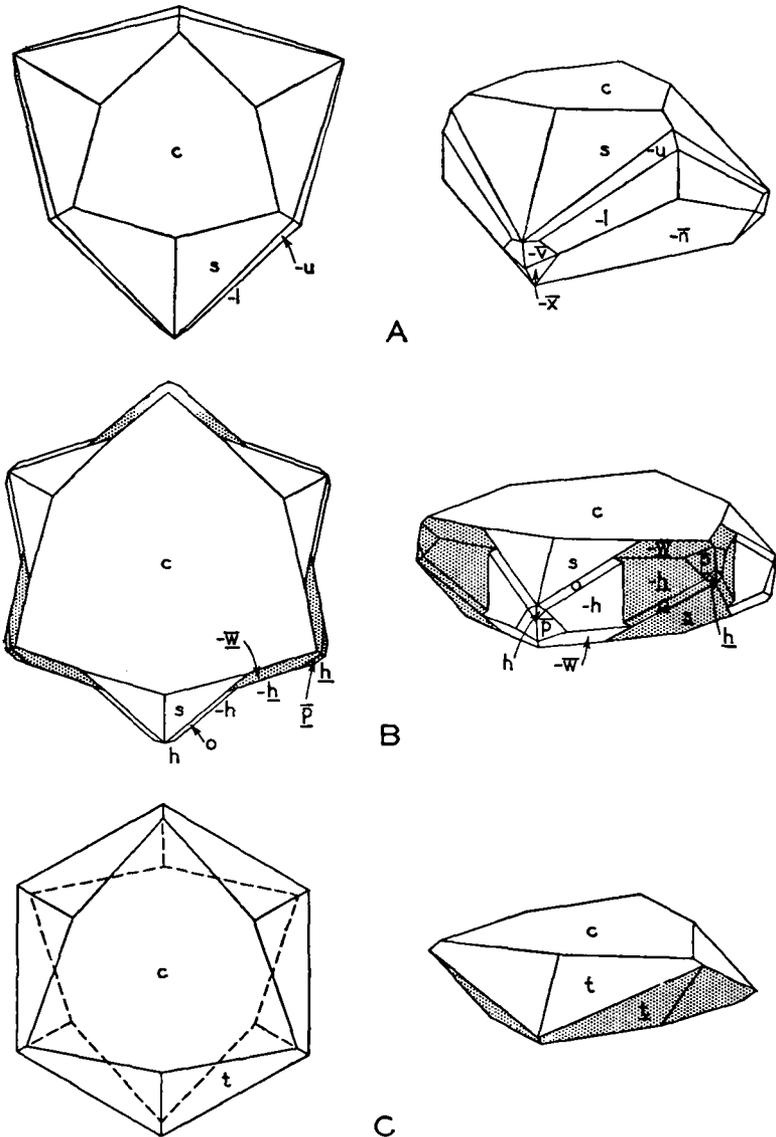


FIG. 1. Idealized drawings of (A) an untwinned crystal; (B) interpenetrant and (C) aggregate rotation twins about $[11\bar{2}0]$. One individual of each twin is stippled. The forms shown are c (0001), h ($21\bar{3}0$), $-\bar{h}$ ($12\bar{3}0$), $-\bar{l}$ ($25\bar{7}0$), $-\bar{n}$ ($03\bar{3}4$), o ($11\bar{2}1$), \bar{p} (2241), s ($52\bar{7}8$), t ($41\bar{5}6$), $-u$ ($34\bar{7}3$), $-\bar{v}$ ($34\bar{7}2$), $-\bar{w}$ (1233), $-\bar{x}$ (2689). The specimens on which the drawings are based are illustrated in figs. 2, 3, and 4.

microscope are usually found to contain small amounts of other minerals. After several trials, however, a polished section was prepared almost

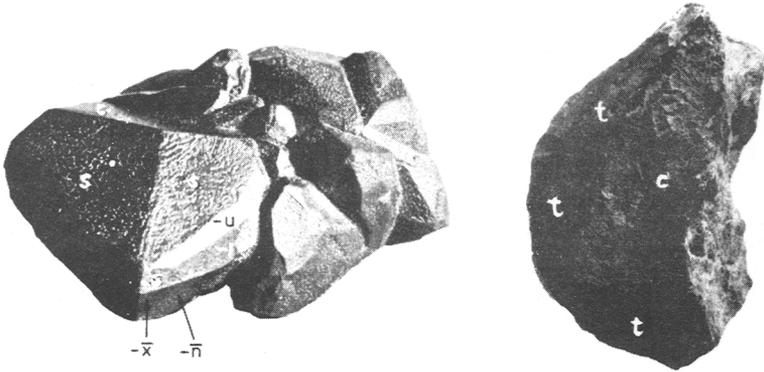


FIG. 2. Radioactive mineral from Tete, Mozambique. $\times \frac{8}{5}$. Cluster of naturally etched crystals of which the largest is untwinned. The forms shown are c (0001), $-l$ (2570), \bar{n} (0334), s (5278), u (3473), $-\bar{v}$ (3472), $-\bar{x}$ (2689). (Cf. fig. 1 A.)

FIG. 3. Radioactive mineral from Tete, Mozambique. $\times \frac{4}{3}$. Portion of an aggregate twin showing apparent holohedral symmetry. The forms shown are c (0001), t (4156). (Cf. fig. 1 C.)

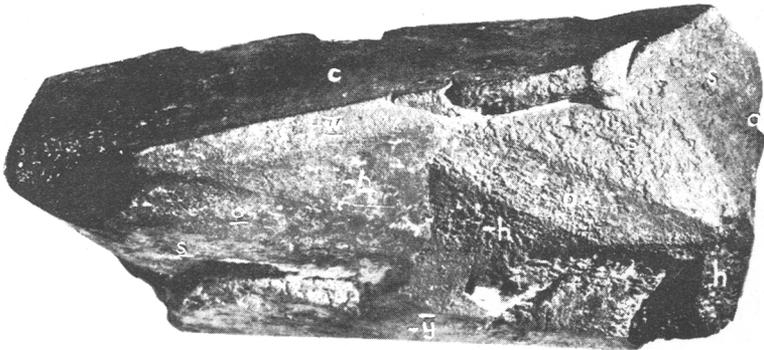


FIG. 4. Radioactive mineral from Tete, Mozambique. $\times \frac{2}{3}$. Portion of a large interpenetrant twin 12 inches long and weighing 22 pounds. The forms shown are c (0001), h (2130), $-h$ (1230), o (1121), s (5278), $-\bar{w}$ (1233), $-\bar{y}$ (1344). (Cf. fig. 1 B.)

entirely free from traces of impurity even at a high magnification; fortunately, the same degree of purity was still found when the section was remounted the other way up. After the bakelite had been carefully

TABLE I. Chemical analyses of the Tete mineral and davidite.

	1.	2.	3.	4.	5.	6.	7.	8.
TiO ₂ ...	54.5	51.00	60.5	36.70	47.40	45.80	51.30	54.3
Fe ₂ O ₃ ...	10.2	13.57	—	—	—	—	—	13.0
Cr ₂ O ₃ ...	0.17	3.23	4.8	3.42	4.62	4.21	4.86	} 4.6
V ₂ O ₅ ...	1.4	—	—	0.25	0.25	0.25	0.25	
U ₃ O ₈ ...	9.8	7.10	7.5	5.50	7.85	8.00	8.02	
FeO ...	16.5	12.37	27.0	21.90	23.20	22.40	24.90	
ZrO ₂ ...	0.4	3.30	—	—	—	—	—	—
(Ce, &c.) ₂ O ₃ ...	5.6	n.d.	—	3.10	3.60	4.52	4.24	8.3
Na ₂ O ...	0.15	1.72	—	—	—	—	—	—
CaO ...	0.3	1.00	—	12.40	5.00	4.60	3.00	1.5
ThO ₂ ...	0.07	—	—	0.12	0.14	0.14	0.12	—
PbO ...	0.72	—	—	—	—	—	—	1.1
H ₂ O +	0.05	1.09	—	—	—	—	—	1.5
Insol. ...	—	—	—	2.90	5.20	3.00	1.40	—
	99.92	99.95	99.8	86.29	97.26	92.92	98.09	100.9

1. Radioactive mineral from Tete, Mozambique; sp. gr. 4.46. The uranium was reported as UO₃ and alkali metals as Na₂O. Also contains SiO₂ 0.06%; MgO, Nb₂O₅, and Ta₂O₅ not found. Analysed by W. Ryan and P. J. Maple, Chemical Research Laboratory, Teddington, Middlesex.

2. Same; sp. gr. 4.48; also contains SiO₂ 0.68, Al₂O₃ 4.24, K₂O 0.32, BaO trace, MnO trace, NiO 0.05, S 0.09, H₂O — 0.19%; analysed by E. Golding, Geological Survey of Southern Rhodesia (private communication, 1947).

3–7. Same; samples containing varying amounts of accessory minerals (see p. 105). MgO and H₂O are present but have not been determined; Nb₂O₅ and Ta₂O₅ both < 0.5%. Analysed by Messrs. Johnson, Matthey & Co., London, 1947, through the courtesy of The British South Africa Company, Limited.

8. Davidite, Olary, South Australia. Also MgO 0.6%, CuO trace; U₃O₈, Cr₂O₃, V₂O₅ 4.6%, mainly uranium oxide; very little ThO₂ in rare-earths; scandium present (according to Sir William Crookes); ZrO₂ absent. Analysed by W. T. Cooke, [Chemical notes on davidite. Trans. Roy. Soc. South Australia, 1916, vol. 40, p. 267. [M.A. 1–79.]

removed from cracks the sample was accordingly submitted to the Chemical Research Laboratory, Teddington, for analysis.

It will be seen that there are few differences between analysis 1 of the Tete mineral and analysis 8 of davidite, the chief being that the Tete mineral has more uranium and less rare-earths. When the figure of UO₃ 9.8%, analysis 1, is re-expressed as U₃O₈ 9.6% with corresponding changes in the FeO/Fe₂O₃ ratio, i.e. with Fe₂O₃ 12.0, FeO 14.9%, the similarity to the composition of davidite becomes more apparent.

An attempt has been made to derive a formula from analysis 1, though in the absence of unit-cell dimensions it must be emphasized that this is strictly provisional. Uranium has been reckoned as U⁶⁺ and vanadium as V³⁺, the Fe³⁺/Fe²⁺ ratio being adjusted accordingly. The rare-earth

oxides have been treated as Ce_2O_3 . The lead is assumed to be radiogenic¹ and has been added to the uranium ratio. The ionic radius of 0.76 Å. for U^{6+} is a mean figure obtained from a paper by Samson and Sillén on the structure of barium uranate,² which gives U-O distances in the distorted UO_6 octahedron as 1.90, 2.12, and 2.22 Å.

	Radius.	Ionic ratios: For 7 anions.	
Si ⁴⁺ ...	0.39 Å.	0.00100	0.004
Ti ⁴⁺ ...	0.64	0.68210	2.382
Cr ⁴⁺ ...	0.64	0.00224	0.008
V ³⁺ ...	0.65	0.01540	0.054
Fe ³⁺ ...	0.67	0.15854	0.553
U ⁶⁺ ...	0.76	0.03750	0.131
Fe ²⁺ ...	0.83	0.19884	0.694
Zr ⁴⁺ ...	0.87	0.00325	0.011
Na ⁺ ...	0.98	0.00484	0.017
Ca ²⁺ ...	1.06	0.00535	0.019
Th ⁴⁺ ...	1.10	0.00027	0.001
Ce ³⁺ , &c.	0.99-1.18	0.03410	0.119
OH ⁻ ...	1.32	0.00555	0.019
O ²⁻ ...	1.32	1.99851	6.981

Grouping similarly sized ions together, it will be seen that the analysis corresponds to the empirical formula $AB_3(O,OH)_7$, where $A = Fe^{2+}$, (Ce^{3+} , &c.), U^{6+} , Ca^{2+} , Na^+ , Zr^{4+} , Th^{4+} , and $B = Ti^{4+}$, Fe^{3+} , V^{3+} , Cr^{3+} . The ideal end-member on this tentative interpretation is thus $FeTi_3O_7$ or $FeO.3TiO_2$. Broadly speaking, replacement of Fe^{2+} by U^{6+} and rare-earths is balanced by replacement of Ti^{4+} by Fe^{3+} and V^{3+} .

The analysis of davidite may be interpreted in a similar way. V_2O_5 and U_3O_8 , reported together in the analysis, have been arbitrarily assigned values of 1.4 and 3.2 % respectively.

	Radius.	Ionic ratios: For 7 anions.	
Ti ⁴⁺ ...	0.64 Å.	0.67960	2.267
V ³⁺ ...	0.65	0.01540	0.051
Fe ³⁺ ...	0.67	0.18600	0.621
U ⁶⁺ ...	0.76	0.01636	0.055
Mg ²⁺ ...	0.78	0.01490	0.050
Fe ²⁺ ...	0.83	0.19948	0.666
Ca ²⁺ ...	1.06	0.02675	0.089
Ce ³⁺ , &c.	0.99-1.18	0.05062	0.167
OH ⁻ ...	1.32	0.08324	0.278
O ²⁻ ...	1.32	2.01552	6.722

¹ On this assumption the age is estimated to be about 565 million years, in agreement with the geological age of the deposit, which is pre-Karoo and probably pre-Cambrian.

² S. Samson and L. G. Sillén, Die Kristallstruktur des Bariumuranates. Nicht-existenz der UO_4 -Gruppe. Arkiv Kemi, Min. Geol., 1948, vol. 25A, no. 21. (M.A. 10-539.)

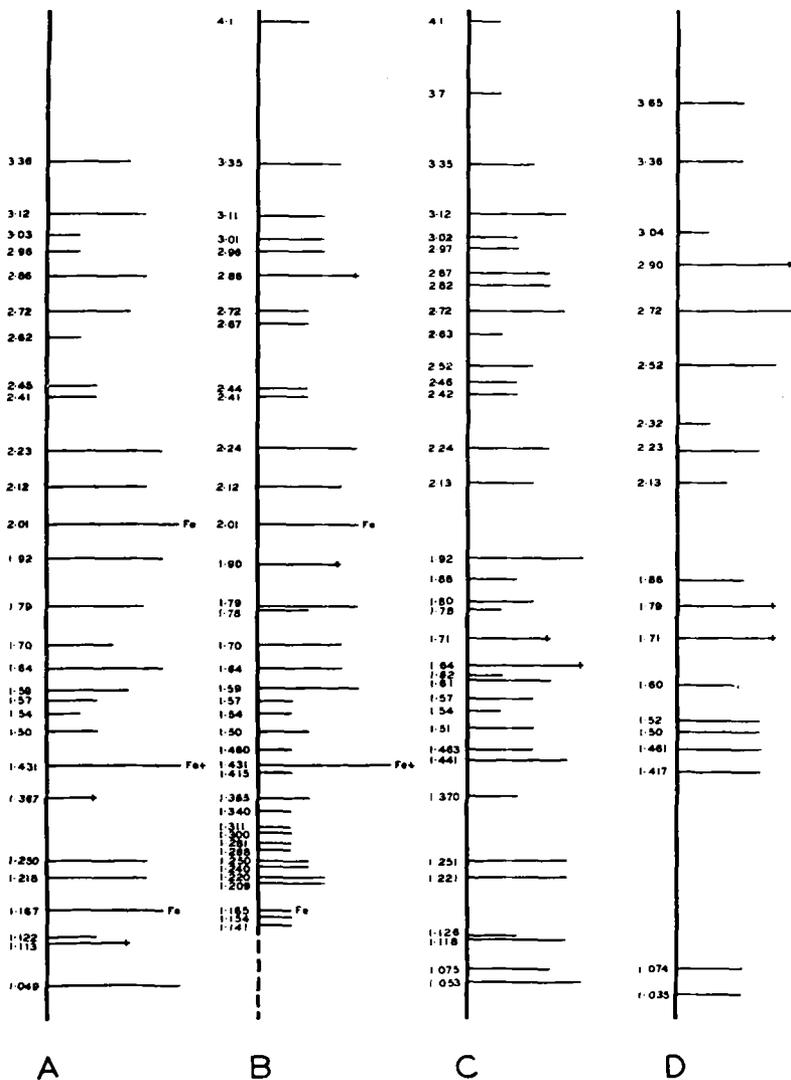


FIG. 5. Spacing-intensity plots of X-ray powder photographs of the Tete mineral after heating: (A) in hydrogen at 1200°C., (B) in nitrogen at 1200°C., (C) in nitrogen at 1000°C., and of davidite (D) in nitrogen at 1000°C.

The d -spacings are plotted on a logarithmic scale and their approximate values in Ångström units are given against each line, the length of which is an indication of the intensity. Lines marked 'Fe' are attributed to α -iron. A cross-bar indicates a broad line on the photograph.

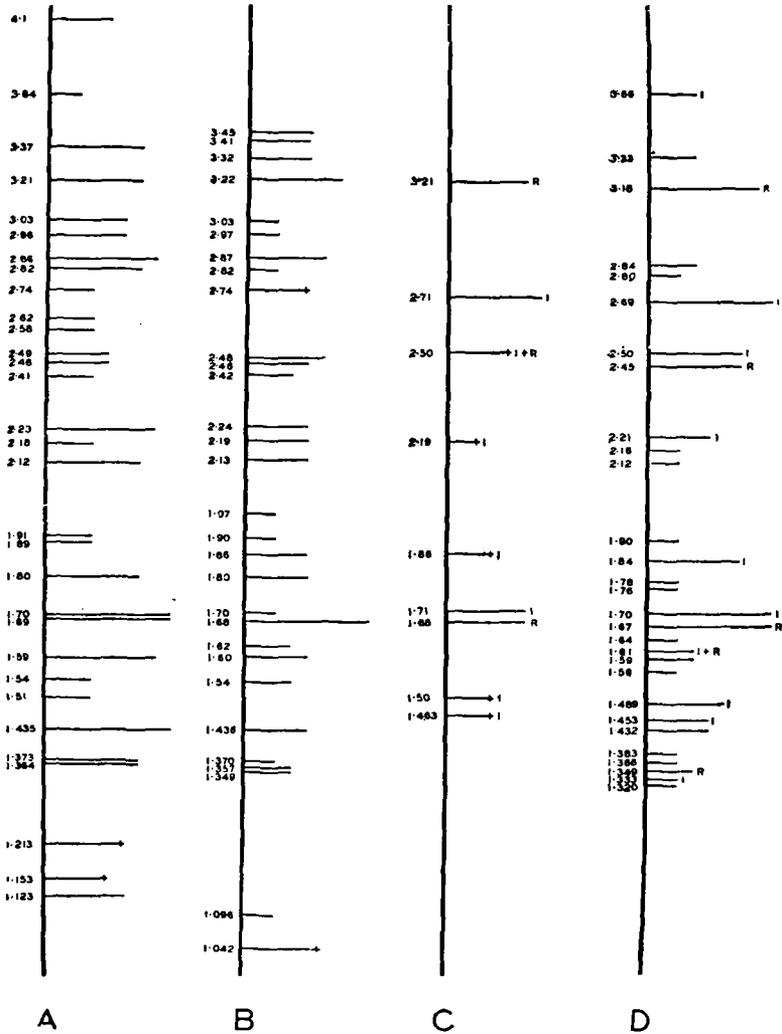


Fig. 6. Spacing-intensity plots of X-ray powder photographs of the Tete mineral (A) and davidite (B) after heating in air at 1000° C., and of sefströmite before (C) and after heating (D) in nitrogen at 1000° C. Lines marked I and R are attributed to ilmenite and rutile respectively.

All the X-ray photographs represented in figs. 5 and 6 were taken in a cylindrical camera, diameter 6 cm. with Co-K α radiation, λ 1.7902 Å.

Thus the available data are not inconsistent with davidite also having a formula of the type $AB_3(O,OH)_7$.

Attempts were made to synthesize the double oxides $FeO.2TiO_2$, $FeO.3TiO_2$, and $FeO.4TiO_2$ by heating the appropriate mixtures of ferrous ammonium sulphate and titanium oxide in nitrogen at $1000^\circ C$. X-ray powder patterns of the products thus obtained, however, show them to be mixtures of ilmenite and rutile in varying proportions, and quite different from the patterns of davidite and the Tete mineral heated under the same conditions.

Heat-treatment and X-ray investigations (F. A. B.).—Both davidite and the chemically similar mineral from Tete, Mozambique, are metamict, but they can be recrystallized by powdering and then heating to a high temperature for several hours. Initially the two minerals were heated for 24 hours at $1000^\circ C$. in air. Powder photographs taken subsequent to cooling, shown diagrammatically in figs. 6 A and B, are similar, and as the chemical analyses then available (table I, nos. 2 and 8) showed no essential differences the mineral from Tete was provisionally identified as davidite. It was soon realized, however, that heating in air would oxidize the ferrous iron content and perhaps result in a misleading similarity of the powder patterns. Heat-treatment in a neutral atmosphere and the subsequent X-ray study of the products will now be summarized.

It was soon discovered that the moisture content of commercial nitrogen is sufficient at high temperatures to oxidize the powdered minerals. This was obviated by passing the gas over heated iron-wool loosely packed into the first four inches of the tubular furnace. The iron-wool plug was renewed before each run and inspected at the end of each run after the furnace had been allowed to cool with the nitrogen stream still passing through. Only when the iron-wool plug retained an untarnished inner end at least one inch long was the run regarded as satisfactory. An additional check on the absence of oxygen in the neighbourhood of the heated samples was afforded by placing powdered ilmenite in the furnace close to and immediately preceding the mineral under investigation, and subsequently examining its X-ray photograph for the lines of pseudobrookite.¹

¹ Ilmenites (B.M. 90156) from Ingelsberg, Salzburg, and (B.M. 37302) from Ilmen Mts., Russia, when heated in air for 24 hours at $1000^\circ C$. yield patterns identical with that of pseudobrookite (B.M. 74455) from Arany, Transylvania, the probable reaction being $2FeTiO_3 + O \rightarrow Fe_2TiO_5 + TiO_2$; no lines due to rutile, anatase, or brookite in addition to those of pseudobrookite, have, however, been detected on powder photographs of oxidized ilmenite.

Figs. 5 c and d show in diagrammatic form the X-ray patterns of powdered specimens of the Tete mineral and of davidite obtained as just described after heating to 1000° C. in a completely neutral atmosphere. They differ from the air-heated patterns represented in figs. 6 A and B, as was to be expected. There are also differences between the two nitrogen-heated patterns (figs. 5 c and d) which cannot be disregarded. It should be emphasized at this point that many samples of the Tete mineral taken from specimens with and without crystal faces have been examined and always yield the same pattern after heat-treatment under the same conditions. This can only be so if the mineral in its metamict condition has a uniform composition throughout and on recrystallization yields either one phase or a mixture of phases always in the same proportions.

It was decided at this stage to raise the temperature of heat-treatment and also to investigate patterns obtained by heating in a reducing as well as a neutral atmosphere. When the Tete mineral was heated to 1200° C. in nitrogen a different pattern was obtained, three lines of which can be attributed to α -iron, showing that the mineral dissociates at the higher temperature (fig. 5 B). X-ray photographs were also taken of the Tete mineral after heating in hydrogen at 800°, 1000°, and 1200° C. respectively. The patterns obtained for all three temperatures are essentially the same (fig. 5 A) excepting that the lines are sharper and more numerous for the higher temperatures, indicating better crystallization; α -iron lines occur in all these photographs. Apart from this identification of α -iron in the Tete mineral after heating in hydrogen or in nitrogen at 1200° C. no other phases have been recognized on any of the X-ray photographs. Rutile, brookite, anatase, haematite, magnetite, ilmenite, and pseudobrookite have been looked for without success. This suggests that the Olary and Tete minerals crystallize as single-phase systems, not mixtures, when heated in nitrogen at 1000° C., but unfortunately it has not proved possible to index the powder photographs, using Bunn's charts.¹

It was natural to hope that as the shapes of the Tete crystals conform to trigonal symmetry it would be possible to index the powder pattern of the recrystallized mineral on the basis of a unit cell with the same symmetry and with an axial ratio simply related to that obtained from rough measurements of interfacial angles, viz. 1:1.37 (page 102). This cannot be done, neither has it proved possible to index any of the powder photographs of the Tete mineral or davidite assuming trigonal, hexa-

¹ C. W. Bunn, *Chemical crystallography*, Oxford, 1945, p. 132. [M.A. 9 217.]

gonal, tetragonal, or cubic symmetry. This may be due to lower symmetry or large unit-cell dimensions; or, of course, to the presence of more than one substance in the recrystallized mineral.

To sum up, there are real, though unexplained, differences in the X-ray powder photographs given by davidite and the Tete mineral after heat-treatment. On this evidence alone, however, it does not seem warrantable to claim that the radioactive mineral from Tete, Mozambique, is a new and distinct species. It should rather be classified as a variety of davidite until unambiguous evidence to the contrary is forthcoming. Davidite itself should be reinstated as a true species, although it may prove difficult ever to decide what its symmetry and crystal structure were before it became metamict.

Sefströmite.—This name¹ was applied (apparently by Sir Douglas Mawson, though not published by him) to a supposed vanadiferous variety of ilmenite occurring with davidite at Radium Hill, near Olary, South Australia. Specimens in the British Museum collection since 1907 (reg. no. 1907,1027 and 1028) yield before heat-treatment lines due to rutile as well as ilmenite (fig. 6 c). After heating in nitrogen to 1000° C. a much stronger and more line-rich pattern (fig. 6 d) was obtained, showing a few weak lines additional to those of rutile and ilmenite. Sefströmite is, therefore, a mixture of one or more metamict minerals, not, however, davidite itself, with rutile and ilmenite.

In conclusion we should like to record our thanks to the Director of the Chemical Research Laboratory, Teddington, for the chemical analysis by Mr. W. Ryan and Miss P. J. Maple, and to Dr. M. H. Hey, who gave us much helpful advice during the progress of the work.

¹ T. Crook, *Min. Mag.*, 1910, vol. 15, p. 281; L. J. Spencer, *tom. cit.*, p. 431.
