

CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

No. 8. Davidite from Tuftan, Iveland

By

HENRICH NEUMANN and THOR L. SVERDRUP¹

In 1956 a quantity of gadolinite from the Tuftan pegmatite dyke was sold to an American firm dealing in rare element raw materials. To his surprise the Norwegian exporter received a complaint that the gadolinite was of inferior quality and could not be accepted. A sample of the exported material was sent to this Museum for examination and the bulk of it was found to be a black metamict amorphous mineral, in appearance strikingly like gadolinite. However, by its X-ray powder pattern when heated, and by semiquantitative optical spectrograms the material was identified as davidite. A sample of the same material had found its way into the collections of dr. H. F. Harwood in Wales who sent it to the Atomic Energy Division of the Geological Survey of Great Britain where dr. J. E. T. Horne coincident with us identified it as davidite, and kindly sent us a copy of his report (Mineralogical report No. 621, dated 20th September, 1957).

Mode of occurrence.

The Tuftan pegmatite dyke is situated in the northern part of the pegmatite district of Iveland, north of Kristiansand in southern Norway. (2). It is apparently nearly vertical, strikes about NW, and is more than one hundred meters long. The Tuftan dyke is probably richer in rare minerals than any other granite pegmatite in this country and is one of the very few dykes in Norway worked for rare minerals (thortveitite, gadolinite and euxenite) yielding some feldspar and

¹ Now at Norges Geologiske Undersøkelse.

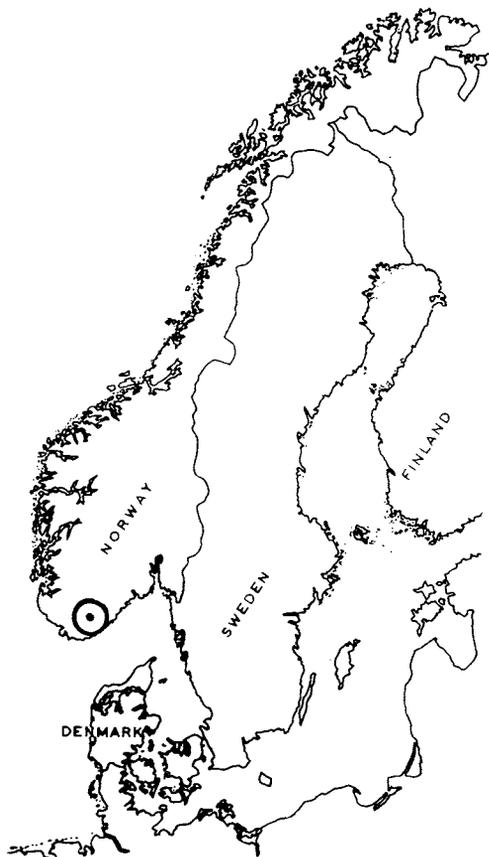


Fig. 1. Key map. The dot with a ring around it indicates the location of Tuftan, Iveland.

quartz as by-products. The following mineral species have been found: microcline, plagioclase, quartz, biotite, muscovite, garnet, allanite, zircon, beryl, gadolinite, thortveitite, euxenite, blomstrandine, davidite, magnetite, ilmenite, rutile, xenotime, pyrite, and molybdenite.

All together about 200 kilograms of davidite have been found in the Tuftan dyke. The davidite occurs as elongated masses with rough semi-linear outlines attaining a length of 20 cms. or even more.

The davidite is always to a greater or lesser degree transected by tiny veinlets or small irregular elongated masses of an intergrowth of ilmenite and rutile with smaller amounts of feldspar, quartz, muscovite, and biotite as illustrated by fig. 2. The structure would seem to indicate that the ilmenite-rutile intergrowth is younger than the

davidite, having replaced the latter along cracks which possibly to some extent follow cleavage directions in the originally crystalline mineral. However, as seen in fig. 2 the ilmenite-rutile intergrowth is full of cracks which only very exceptionally continue into the davidite, and this might be interpreted as an indication that davidite has replaced an older mass of ilmenite and rutile with pre-existing cracks. If so, one would expect the replacement to take place preferentially along these cracks, which is not the case, however; the cracks characteristically stop against a smooth contact line between the ilmenite-rutile intergrowths and the davidite. The formation of these cracks is probably

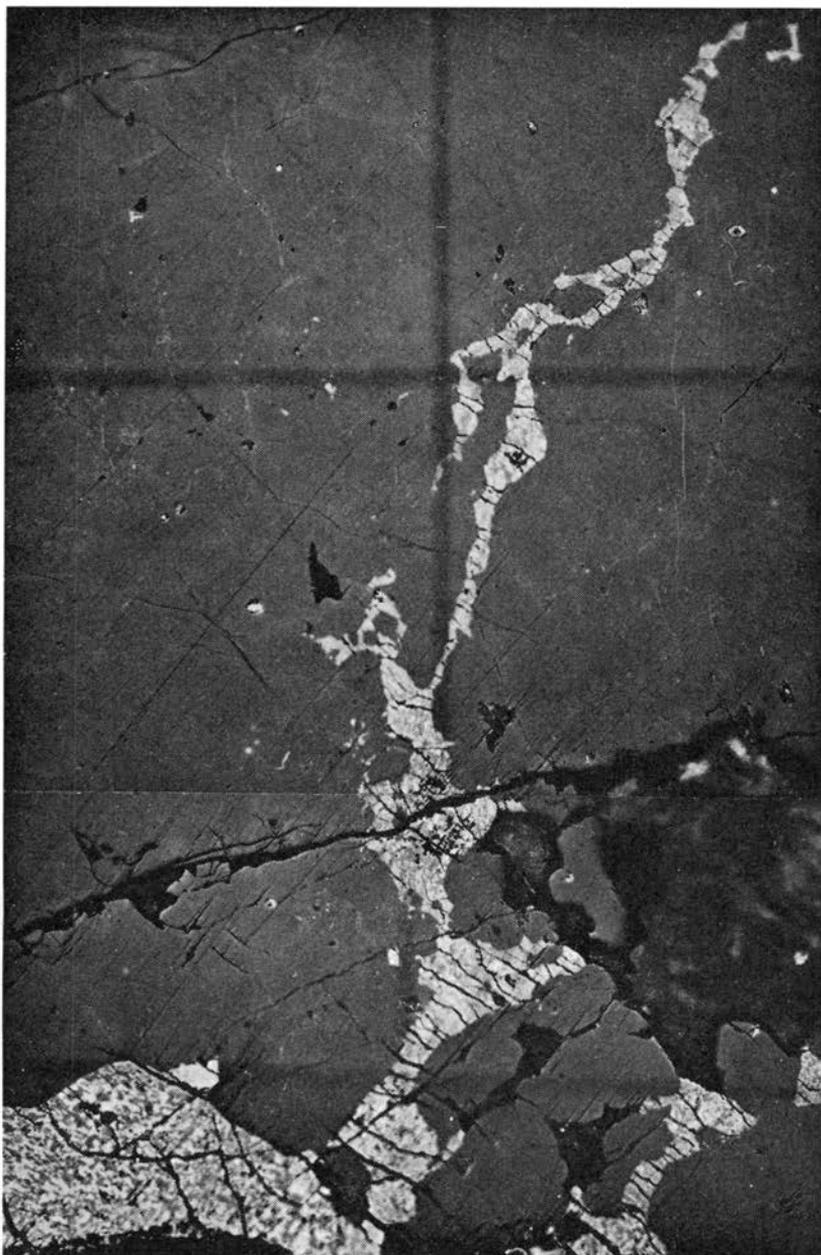


Fig. 2. Polished section of davidite. Dark gray: davidite. Light gray: intergrowth of ilmenite and rutile in veinlets. Very dark gray with internal reflections: silicates. Magnification 70x.

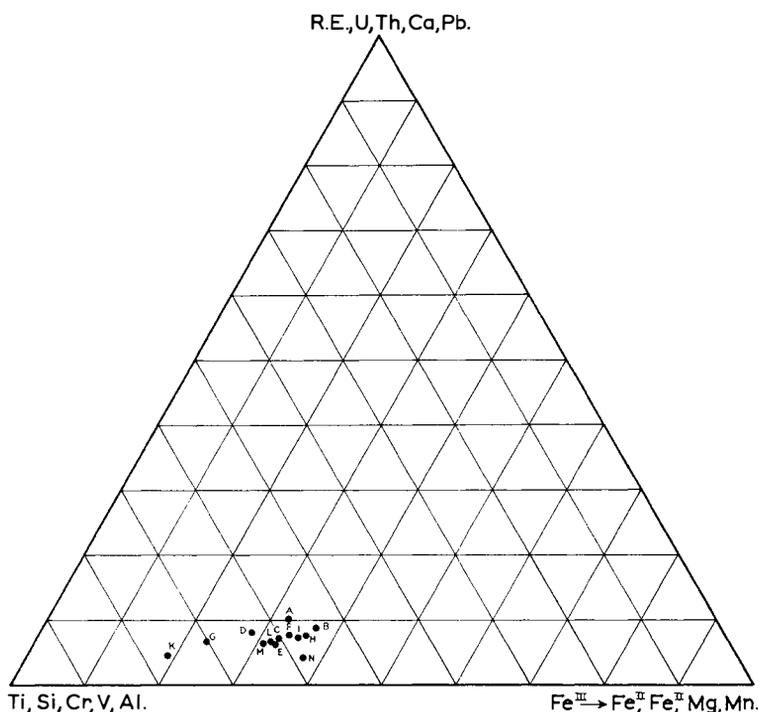


Fig. 3. Chemical composition of davidites plotted on a triangular diagram in atomic percentages. Letters refer to analyses in table 1.

a secondary phenomenon caused by an increased internal pressure during metamictization which cracked the tiny veinlets of ilmenite and rutile without affecting the main massive mass of homogenous davidite. If so these cracks are of no consequence for the interpretation of the age relations between davidite and the ilmenite-rutile veinlets. With proper consideration of the inherent difficulties in deciding relative ages on the basis of structures of this kind it is concluded that in all probability the older davidite was before metamictization replaced by the younger veinlets of ilmenite and rutile.

Physical properties.

The davidite from Tuftan in unweathered splinters is completely black with a shining vitreous luster. It has a subconchoidal fracture with no signs of cleavage directions. The streak or powder colour is

black or very dark gray. Oxidized surfaces often have a brown or reddish colour.

Only five small incomplete crystals of davidite, 2–5 cm. across have been found, and they are not sufficiently well developed to be measured even with a contact goniometer. The crystals may be hexagonal like those described by Bannister and Horne (1) from Mozambique.

The hardness is 6, and the specific gravity of the analyzed material is 4.29.

The mineral is opaque except at the very edges of extremely thin splinters where it is translucent with a clove-brown colour. It takes a good polish and is gray and isotropic in polished sections. Apart from the tiny veinlets of ilmenite and rutile mentioned above it is homogeneous even at the highest magnifications.

Chemical composition.

Splinters of davidite which appeared free from impurities when observed with a binocular lens were crushed and then cleaned further with a Frantz isodynamic separator with scores of runs with varying inclinations and field strengths. Even so the material analyzed was not as perfectly free from inclusions as could be desired, but the amount of impurities was less than 3 %.

The analysis, made by B. Bruun, is quoted as A in table 1. together with published analyses of davidite from other localities for comparison.

The atoms constituting the original davidite structure which later collapsed are obviously in addition to oxygen the major elements of the analyses: titanium, iron, rare earths, and uranium. The other elements found in subordinate amounts either substitute for the major elements or originate from impurities. Lead is supposedly a decay product of uranium and was not present in davidite when it first crystallized.

The analyses of table 1. are arranged in order of decreasing rare earth content. It is easily seen that the uranium content in a general way increases as the content of rare earths decreases² and there can hardly be any doubt that uranium substitutes for the rare earths in

² An exception is analysis K, see comment p. 284. It is very surprising that no rare earth content is reported in analyses M and N. The presence of La is, however, shown by spectrographic analyses (7, p. 154). A reexamination of these davidites would certainly be of interest.

Table 1. Analyses of Daviteite (Weight per cent).

	A ¹	B	C	D	E	F	G	H	I	K	L	M	N
SiO ₂	0.34	0.1	0.2	1.4	1.3	4.6	4.6	0.2	0.9	4.4	0.06	3.29	6.02
TiO ₂	52.1	49.0	50.7	53.0	49.8	54.3	49.8	45.3	47.0	53.6	54.5	54.03	46.72
R.E. ₂ O ₃	17.3 ²	12.8	11.6	11.3	8.8	8.3	8.2	7.6	7.0	6.4	5.6		
ThO ₂											0.07		
Al ₂ O ₃		3.1	1.7		1.1		4.3	2.0	0.7	4.2	0.4	3.53	1.05
ZrO ₂													
Cr ₂ O ₃			0.7	0.4	1.1		0.7	1.3	0.6	1.5	0.17	0.04	
V ₂ O ₅			1.2	1.8	2.7	4.6	0.4	0.6	1.5	6.1	1.4	2.26 ⁴	2.88 ⁴
U ₃ O ₈	1.1 ³										9.8	2.17	6.41
UO ₂		1.5	2.3	4.3	3.6		5.6	7.7	8.8	2.8			
Fe ₂ O ₃	9.5	6.8	29.8	25.3	29.9	13.0	20.7	32.1	31.6	17.6	10.2	12.43	16.53
FeO	17.1	23.9				16.0					16.5	15.61	18.33
PbO	n. d.	0.1	0.5	0.7	0.7	1.1	1.0	1.5	0.9	0.9	0.72		
MnO	1.0											0.25	0.61
Mn ₂ O ₄		0.3											
MgO		0.7				1.5						1.20	0.17
CaO											0.3	4.50	1.71
Na ₂ O											0.15		
K ₂ O													
H ₂ O	1.63			1.2		1.5			1.2		0.05		
Loss on ignition					nil			0.5	nil				
Insoluble			0.3	0.5			3.6			0.9			
Sum	100.07	98.3	99.0	99.9	99.0	100.9	98.9	98.8	99.8	98.4	99.98	100.43	101.54

Text to table 1.

A. Davidite from pegmatite, Tuftan, Iveland, Norway. Analyst B. Bruun.
 B. Davidite from pegmatite, Mt. Pleasant, Australia. Analyst J. D. Hayton (9).
 C. Davidite from pegmatite, Billeroo, Australia. Analyst D. Bowditch. (9).
 D. Davidite from Whip Lode, Radium Hill, Australia. Analyst J. D. Hayton. (9).
 E. Davidite from pegmatite, Broken Hill, Australia. Analyst D. Bowditch. (9).
 F. Davidite from a hydrothermal lode, Olary, Australia. (Type locality). Analyst
 W. T. Cooke. Quoted from (1.). G. Davidite from fractured quartzite, Spring
 Hill, Australia. Analyst D. Bowditch. (9.). H. Davidite from calc-silicate rock,
 Mt. Isa, Australia. Analyst D. Bowditch. (9.). I. Davidite from David Lode,
 Radium Hill, Australia. Analyst J. D. Hayton. (9.). K. Davidite from lodes,
 Mt. Victoria, Australia. Analyst D. Bowditch. (9.). L. Davidite from calc-
 silicate rock, Mavuzi, Tete, Mosambique, Portuguese East Africa. Analysts
 Ryan, W., and Maple, P. J. (1.). M.⁵ Davidite from a schist? (not found in
 situ), Six Kangaroos Lease, midway between Mt. Isa and Cloncurry, Australia.
 Analyst G. T. See. (7.). N.⁵ Davidite from a segregation lens of brown calcite
 in granulite, Dajarra, south of Cloncurry, Australia. Analyst G. T. See. (7.).

¹ A spectrographic analysis by C. D. Harvey of the Atomic Energy Division of the Geological Survey of Great Britain shows the presence, "but of probably only very minor significance", of the following elements in addition to those reported in the analysis: Nb, Sc, Sn, V, Zr, Ca, and Al. I. Oftedal determined the scandium content of the analyzed material of davidite from Tuftan and found ~ 0.05 % Sc_2O_3 .

² O. Joensuu made a differential analysis of the ignited precipitate of rare earths by optical spectrographical methods and found: Y_2O_3 23 %, La_2O_3 22 %, CeO_2 32 %, Pr_6O_{11} 2.4 %, Nd_2O_3 2.8 %, $\text{Sm}_2\text{O}_3 < 0.2$ %, Eu_2O_3 0.4 %, $\text{Gd}_2\text{O}_3 < 0.1$ %, $\text{Tb}_4\text{O}_7 < 0.2$ %, Dy_2O_3 1.6 %, Ho_2O_3 0.55 %, Er_2O_3 2.5 %, Tm_2O_3 1.2 %, Yb_2O_3 9.5 %, Lu_2O_3 1.7 %, ThO_2 1.5 %.

³ U_3O_8 content is determined by Forsvarets Forskningsinstitut. An independent radiometric assay of a different sample by E. F. Bunt of the Atomic Energy Division of the Geological Survey of Great Britain gave 1.1 % e U_3O_8 .

⁴ Vanadium content determined as, and figures given for V_2O_3 .

⁵ Lawrence, L. J., et al. (7.) make selfcontradictory statements in the text of their paper pp. 140–142 and under the table with chemical analyses p. 144. Consequently the locality given here for davidite, analysis M, may actually be the locality of davidite analysis N, and vice versa.

the davidite structure, as it usually does in rare earth minerals. All the davidites with low rare earth contents are, however, somewhat deficient in uranium, which is in all probability a secondary phenomenon due to the fact that uranium is easily oxidized to its sixvalent state and then leached by circulating waters.

The role of H_2O in metamict amorphous minerals is in many cases a controversial matter as it may be either an essential constituent of the original crystalline mineral or it may be adsorbed during or after the metamictization. In the case of davidite the water content is always fairly low. It is given as only 0.05 % in analysis L which appears to be very reliable in every respect, also as far as purity of the analyzed material is concerned which has been a major difficulty in davidite investigations. It seems reasonable, therefore, to conclude that the original, non-metamict davidite was a water-free mineral.

The actual state of oxidation of iron in davidite is hard to ascertain. In seven of the thirteen analyses quoted in table 1. ferrous iron was not determined and in the remaining six the relative amounts of ferrous and ferric iron vary within wide limits. In analyses A and L the atomic proportions $Fe^{2+} : Fe^{3+}$ is close to 2 : 1 which may be incidental or may not. In analysis B the Fe_2O_3 content is so low that it is very tempting to assume that the trivalent iron now found in davidites is formed by later oxidation, and that the iron contained in the original crystalline davidites was divalent, perhaps with some trivalent iron substituting for titanium.

There are several reasons why it would seem a difficult and uncertain task to try to calculate a gross formula for davidite: The analyzed material appears from published descriptions in most cases to have been badly contaminated by other minerals, first of all rutile, ilmenite, magnetite, and hematite. Differential analyses of the rare earths are lacking except for the davidite from Tuftan (see table 1., analysis A, note 2)³. Also davidites have apparently in most or all cases been oxidized after their formation, and uranium may have been removed to a greater or lesser extent by selective leaching.

³ While this paper was in print A. Kvalheim of Statens Råstofflaboratorium analyzed the ignited precipitate of rare earths by X-ray spectrographical methods and found: Y_2O_3 20.6 %, La_2O_3 17.3 %, CeO_2 39.2 %, Pr_2O_3 1.8 %, Nd_2O_3 3.8 %, Sm_2O_3 0.2 %, Eu_2O_3 nil., Gd_2O_3 trace, Tb_2O_3 trace, Dy_2O_3 1.5 %, Ho_2O_3 0.7 %, Er_2O_3 2.3 %, Tm_2O_3 1.0 %, Yb_2O_3 9.9 %, Lu_2O_3 1.7 %, ThO_2 1.4 %.

It is quite surprising, therefore, that a calculation of the analyses seems to indicate a fairly simple gross formula if the following reasonable assumptions are made:

- 1) In lack of better data the molecular proportions of the rare earths are calculated on the assumption that all davidites have the same distribution of rare earths as has the davidite from Tuftan.
- 2) Iron was originally present as Fe^{2+} and was later to a greater or lesser extent oxidized to Fe^{3+} .
- 3) Uranium originally present in its fourvalent state was later to some extent oxidized to sixvalent uranium which was partly or wholly removed by leaching. Davidite would consequently tend to be deficient in uranium, especially those davidites which are low in rare earths and high in uranium.

Atomic percentages were calculated and the cations grouped together as large cations (R. E^{3+} , U^{4+} , Pb (originally U^{4+}), Th^{4+} , Ca^{2+}), middlesized cations (Fe^{2+} , $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, Mg^{2+} , Mn^{2+}) and small cations (Ti^{4+} , Si^{4+} , Al^{3+} , Cr^{3+} , V^{5+}). In fig. 3 the results are plotted on a triangular diagram and in spite of the impurity of many of the analyzed samples the plots crowd together within a fairly small area. Exceptions are analyses G and K of the davidite from Spring Hill and Mt. Victoria and these are both reported (9) to contain numerous inclusions of rutile (and other minerals). If these analyses are corrected for a content of 10–15 % of rutile they will also be within the same small area as the others. If the majority of the plots are slightly «lifted» in the diagram to correct for the supposed deficiency in uranium they will all be quite close to a composition corresponding to a proportion of large ions: middlesized ions: small ions = 1 : 3 : 6, or for the pure rare earths end member $\text{Y}_2 \text{Fe}^{II}_6 \text{Ti}_{12} \text{O}_{33}$ where Y stands for the lanthanons and yttrium. The pure uranium end member may be i. g. $\text{U}_2 \text{Fe}^{II}_6 \text{Ti}_{10} \text{Fe}^{III}_2 \text{O}_{33}$ or $\text{U}_{1\frac{1}{2}} \text{Fe}^{II}_6 \text{Ti}_{12} \text{O}_{33}$ but a further discussion of this problem would seem futile with the data available at present.

A differential analysis of the rare earth content in the Tuftan davidite by O. Joensuu is quoted as note two to table 1., and a graphical representation of this analysis is given in fig. 4. The composition of the rare earths is somewhat unusual as there is a pronounced enrichment of the large as well as the small ions while the content of middlesized ions is exceptionally low. Dixon and Wylie have earlier observed an unusual distribution of the lanthanons in South Australian

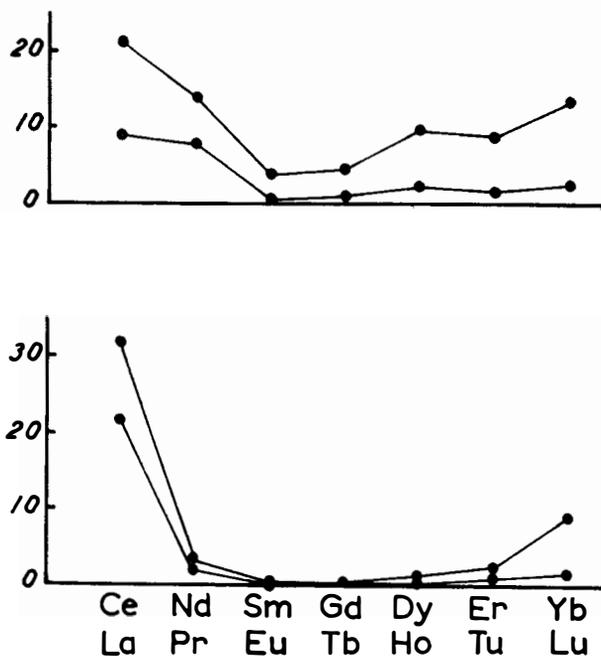


Fig. 4. Distribution of the lanthanons in weight percent of total rare earth oxide contents. Lower curves: davidite, Tuftan. Upper curves: andradite, W. Transbaikal. (8).

davidites (4), and concluded as a probable explanation that "davidite" may not be a well defined mineral, but a complex of more than one mineral species. The authors of the present paper cannot unconditionally accept this explanation, the distribution of the lanthanons in davidite is not in principle any more "abnormal" than for example the distribution of the lanthanons in andradite from skarn in W. Transbaikal examined by SEMENOV and BARINSKII (8), see fig. 4.

Heat-treatment and X-ray pattern.

Unheated metamict davidite gives no X-ray diffractions even with very long exposures. When heated to temperatures between 750°C and 1050°C in air, and to 700°C with a water pressure of 20 000 psi it recrystallizes and gives a characteristic X-ray pattern. The best film was obtained from a run at 1030°C in air for 24 hours and was therefore chosen for measuring the d-values given in Table 2.

d. Å.	I	d. Å.	I	d. Å.	I
3.39	m.	2.47	st.	1.79	m.
3.23	m.	2.41	v. w.	1.69	w.
3.04	w.	2.35	v. w.	1.67	m.
2.88	v. st.	2.23	st.	1.61	v. w.
2.83	w.	2.13	st.	1.59	st.
2.72	v. w.	2.03	v. w.	1.50	w.
2.62	v. w.	1.90	w.	1.43	st.

Table 2. X-ray powder data for davidite from Tuftan, heated in air at 1030°C for 24 hours. Filtered Fe-radiation, camera diameter 9 cm. Intensities visually estimated, v. st. = very strong, st. = strong, m. = medium, w. = weak, v. w. = very weak.

The authors as well as dr. J. E. T. Horne have compared the pattern of davidite from Tuftan with the patterns of davidites from eight different localities. The X-ray diagram of davidite from Tuftan, to quote dr. HORNE (5), "shows a multi-phase pattern in general agreement with those of specimens of davidite, similarly treated", (from other localities). "Perfect agreement is not to be expected in these cases, as minor variations in chemical composition are bound to result in variations in the proportions of the different phases resulting from the heat treatment. The Tuftan pattern agrees as well with the others as they do amongst themselves".

Other Norwegian localities for davidite.

Massive davidite is found in small amounts in a breccia zone in the quarry of Åmot pukverk in the parish of Modum.

Davidite is also found as an impregnation in a crushed and brecciated zone between a pegmatite and the amphibolitic bedrock north of Bringebærkastet on the island of Langøy east of Kragerø.⁴ The narrow brecciated zone is quite strongly radioactive because of the content of davidite.

In both cases davidite was identified in this museum by its characteristic X-ray pattern when heated.

⁴ Viggo Wiik, personal communication.

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Geologisk Museum

University of Oslo, 5th March 1960.

Manuscript received March 10, 1960.

Printed December 1960.