DIFFERENTIAL THERMAL ANALYSES OF DAVIDITE

PAUL F. KERR AND H. D. HOLLAND,
Columbia University, New York, N. Y.

ABSTRACT

A specimen of a black radioactive mineral from Mozambique of a type recently described by Bannister and Horne (1950) has been examined by means of differential thermal analysis and *x*-ray diffraction. It is believed to correspond in essential features to the davidite from Olary, South Australia, as described by Mawson. The principal metallic elements in the Mozambique mineral are titanium, iron, uranium and chromium. Experimental data further confirm Mawson's original description of davidite as a distinct mineral species. The application of differential analysis to the study of metamict minerals is also suggested.

INTRODUCTION

Davidite was described by Mawson (1906) as a black radioactive mineral occurring in a quartz-ilmenite-biotite lode south of Olary, South Australia. Later Crook and Blake (1910) concluded that davidite consisted of a mixture of ilmenite, magnetite, carnotite, possibly a little rutile and a silico-titanate of rare earths which might have been tscheffkinite, a conclusion with which Mawson (1916) failed to agree.

In July 1948 two specimens of a similar black radioactive mineral from Mavuzi, Tete district, Mozambique, Portuguese East Africa, were separately submitted to the mineralogical laboratory of Columbia University. These were massive in character, but contained chemical constituents suggestive of the constituents of crystals described as davidite by Mawson. The Mozambique mineral was found to yield thermal curves with significant exothermic reactions at about 680° C and 800° C. The mineral is judged to be metamict since unheated material fails to yield *x*-ray diffraction patterns while the patterns from heated samples* are reproducible and distinctive. On polished surfaces the unheated material is isotropic.

Through the kindness of Professor Sir Douglas Mawson, of Adelaide, and Dr. C. F. Davidson of the Geological Survey of Great Britain, an opportunity has been offered to examine a specimen from Olary which contains small black grains of the type described by Mawson. This material yields a distinctive thermal curve with exothermic reactions corresponding to the reactions observed for the material from Mozambique and corresponds in *x*-ray diffraction effects.

Since this work was initiated, *x*-ray, chemical and crystallographic data on the Mozambique occurrence have been published by Bannister

* Heated to 1000° C in air.

and Horne (1950). Data at hand are given for purposes of confirmation and to call attention to the possible application of differential thermal analysis to the study of metamict minerals.

Acknowledgments

This study has been aided by Dr. Anton Gray, Chief Geologist of the Kennecott Copper Corporation, who supplied the original mineral from Mozambique and arranged for assistance in the laboratory examination. Appreciation is also expressed for the assistance of Dr. C. F. Davidson of the Geological Survey of Great Britain in providing a specimen of davidite from Olary. We are also indebted to Dr. P. M. Merritt, of Raw Materials Operations, A.E.C., for a second specimen from Mozambique. Mr. E. F. X. Lyden and Miss Jeanne Hutchinson, of Columbia University, have assisted in the *x*-ray diffraction measurements. Dr. D. L. Everhart of the Raw Materials Operations, A.E.C., has kindly offered suggestions in connection with the manuscript.

Mineral from Mozambique

The mineral from Mozambique is black with a vitreous to submetallic luster and a streak varying from brown to black. It is quite brittle and has a conchoidal fracture. The hardness is about 6, and the specific gravity is near 4.48. On the basis of measurement with a contact goniometer, Bannister and Horne (1950, p. 102) report that the mineral is hexagonal, ditrigonal pyramidal.

The hand specimen shows a platy cleavage but no crystal form was identified. Certain faces, however, suggest that the crystals are large, as illustrated by Bannister and Horne.

Small fragments of unheated material, minus 200 mesh, are often translucent to transparent, the transmitted light being a reddish brown, but both small and large fragments may be opaque. The mineral, when examined by means of polarized reflected light on a polished surface at a magnification of about 180, shows minute anisotropic inclusions, but the main mass is isotropic. The massive mineral appears to be essentially homogeneous as examined on a polished surface. Aside from gangue, impurities are estimated to account for a comparatively small amount of the mass examined.

A radiogram of the polished surface as illustrated in Fig. 1 shows some banding. The unexposed spots mark the position of minor nonradioactive inclusions.

Chemical determinations indicate that the mineral is primarily an oxide of titanium, iron, and uranium. Analyses shown in Table 1 have been reported by Bannister and Horne (1950, 1–7), Cooke (1916, 8) and

Ledoux and Co. (9–10). As pointed out by Bannister and Horne considerable chemical variation exists from sample to sample.

A partial spectrographic analysis of one of the mineral specimens indicates that columbium, bismuth, lead and aluminum are present in undetermined amounts. Scandium and neodymium may also be present. The portion of the mineral not indicated in the above chemical analyses may include these elements.

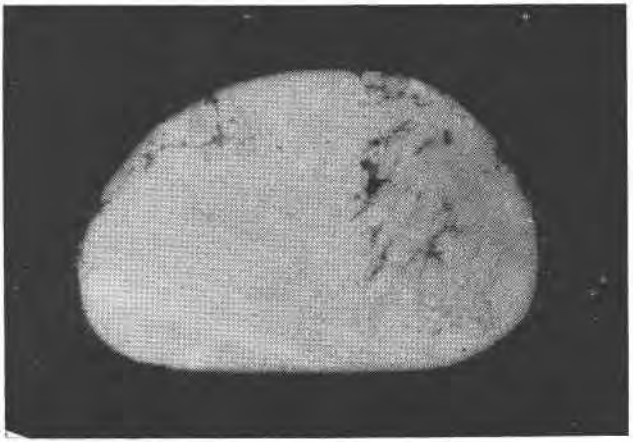

FIG. 1. Radiogram of a polished surface of davidite from Mozambique ($\times 1\frac{1}{2}$). Dark areas represent non-radioactive impurities.

TABLE 1. CHEMICAL ANALYSES

	1	2	3	4	5	6	7	8	9	10
TiO_2	54.5	51.00	60.5	36.70	47.40	45.80	51.30	54.3	49.22	47.91
Fe_2O_3	10.2	13.57	—	—	—	—	—	13.0	8.58	15.73
Cr_2O_3	0.17	3.23	4.8	3.42	4.62	4.21	4.86	}	2.97	—
V_2O_5	1.4	—	—	0.25	0.25	0.25	0.25	4.6	0.91	—
U_3O_8	9.8	7.10	7.5	5.50	7.85	8.00	8.02	}	9.19	5.26
FeO	16.5	12.37	27.0	21.90	23.20	22.40	24.90	16.0	17.96	10.36
ZrO_2	0.4	3.30	—	—	—	—	—	—	—	—
$(Ce, etc.)_2O_3$	5.6	n.d.	—	3.10	3.60	4.52	4.24	8.3	n.d.	7.15
Na_2O	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_2O	0.05	1.09	—	—	—	—	—	1.5	—	—
Insol.	—	—	—	2.90	5.20	3.00	1.40	—	—	—
Total	99.92	99.95	99.8	86.29	97.26	92.92	98.09	100.9	Partial	Partial

The mineral is not noticeably soluble in hot hydrochloric, nitric, or sulfuric acids, or a combination of the first two. In hot concentrated hydrofluoric acid it dissolves fairly rapidly, and a light green alteration product coats the surface. After short periods of immersion, a complicated etch pattern becomes visible.

Without prior heating, the mineral fails to yield an *x*-ray pattern with iron radiation even after exposure of 24 hours, but it gives a distinct and reproducible pattern after being heated to 1000° C, a common behavior for metamict minerals.

Characteristic thermal curves were obtained on apparatus described by Kerr and Kulp (1948). The curves exhibit satisfactory reproducibility (Fig. 2, curves 1, 2) at least in the upper temperature ranges. Exothermic peaks are developed at about 680° C, possibly due to oxidation, and there is a slight indication of a reaction in the vicinity of 900° C. *X*-ray patterns of samples after heating to 710° C give no distinct lines even after extended exposure, but patterns of samples heated to 830° C and 1020° C give groups of lines which are identical. The reversibility of the reactions may be indicated by recording the cooling curves. Since no peaks appear in the cooling curves to correspond to the reaction peaks of the heating curves, the reactions may be considered irreversible.

Thermal curves and *x*-ray patterns of the mineral have been compared with corresponding data for several well-known rare earth minerals (Figs. 3, 4). These curves are only exploratory but they indicate the possible utility of the method in the study of metamict minerals. As far as these comparisons go, the only mineral studied which approximates the thermal history of the Mozambique mineral is davidite. A comparison of the *x*-ray patterns of most of the minerals tested by thermal analysis confirms this evidence since davidite is the only mineral of the group found to have a pattern after heating which corresponds to that obtained from the heated Mozambique mineral. The strongest lines of the pattern from heated davidite are shown in Table 2 with the strongest lines of the pattern from one of the Mozambique specimens (Davidite 1).

Davidite

As indicated above, davidite was described by Mawson (1906) as a black mineral occurring in cube-like crystals. A study by Crook and Blake (1910) purported to show that the mineral described by Mawson was not a unique mineral species but rather a mixture of ilmenite impregnated with magnetite, carnotite, possibly a little rutile, and a titanosilicate of rare earths which might have been tscheffkinite. In a later paper Mawson (1916) pointed out that the material which formed the basis of the report by Crook and Blake contained no typical davidite that

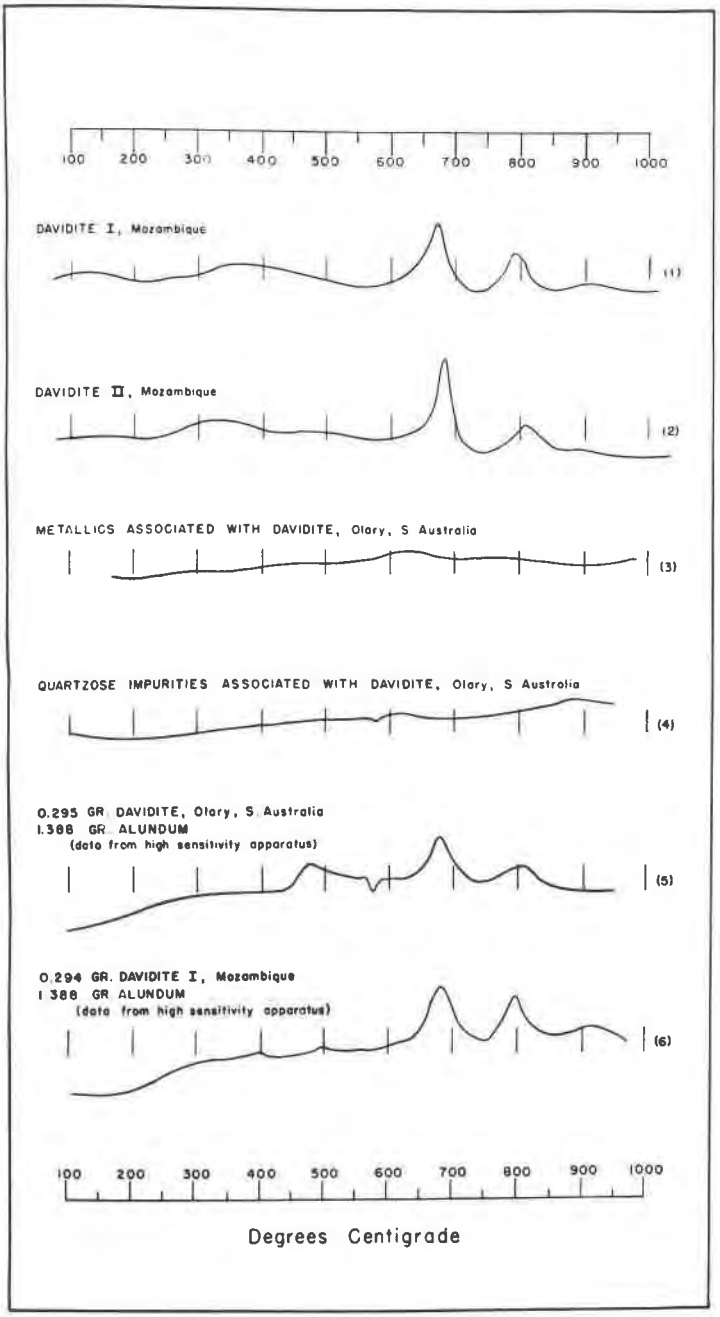

FIG. 2. Thermal curves of davidite specimens.

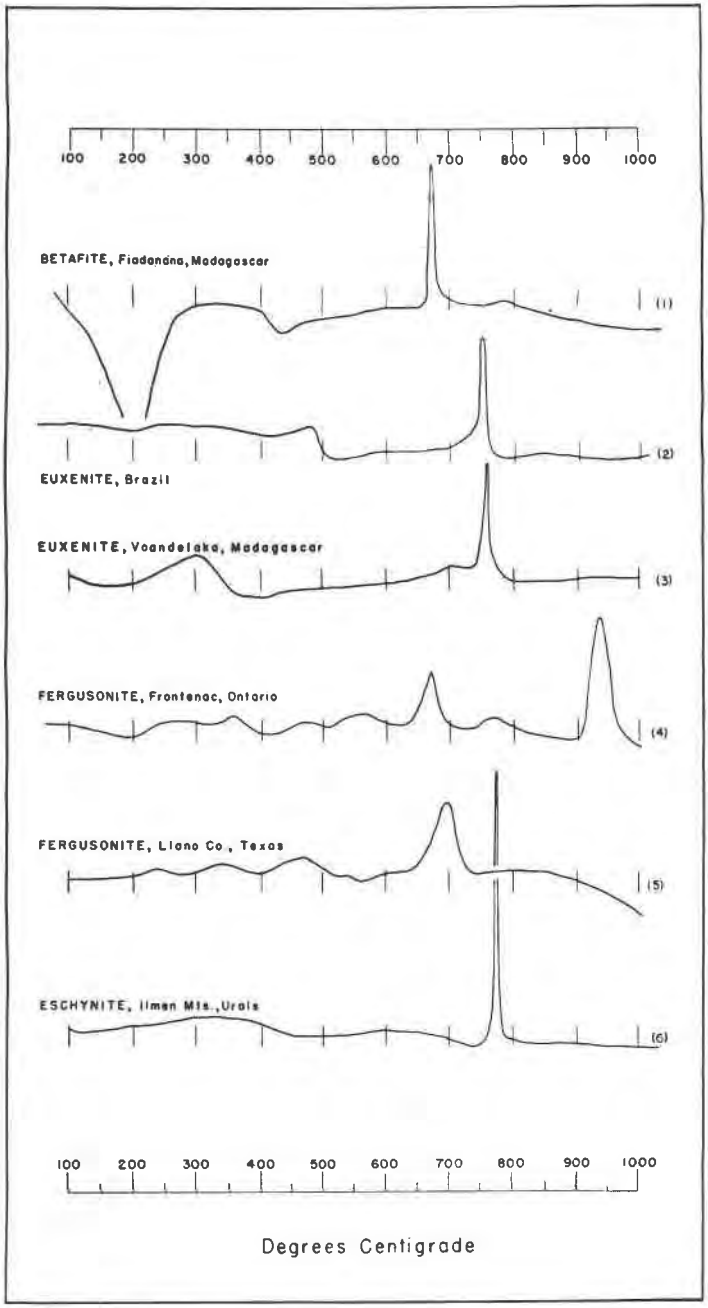

FIG. 3. Thermal curves of betafite, euxenite, fergusonite and eschynite.

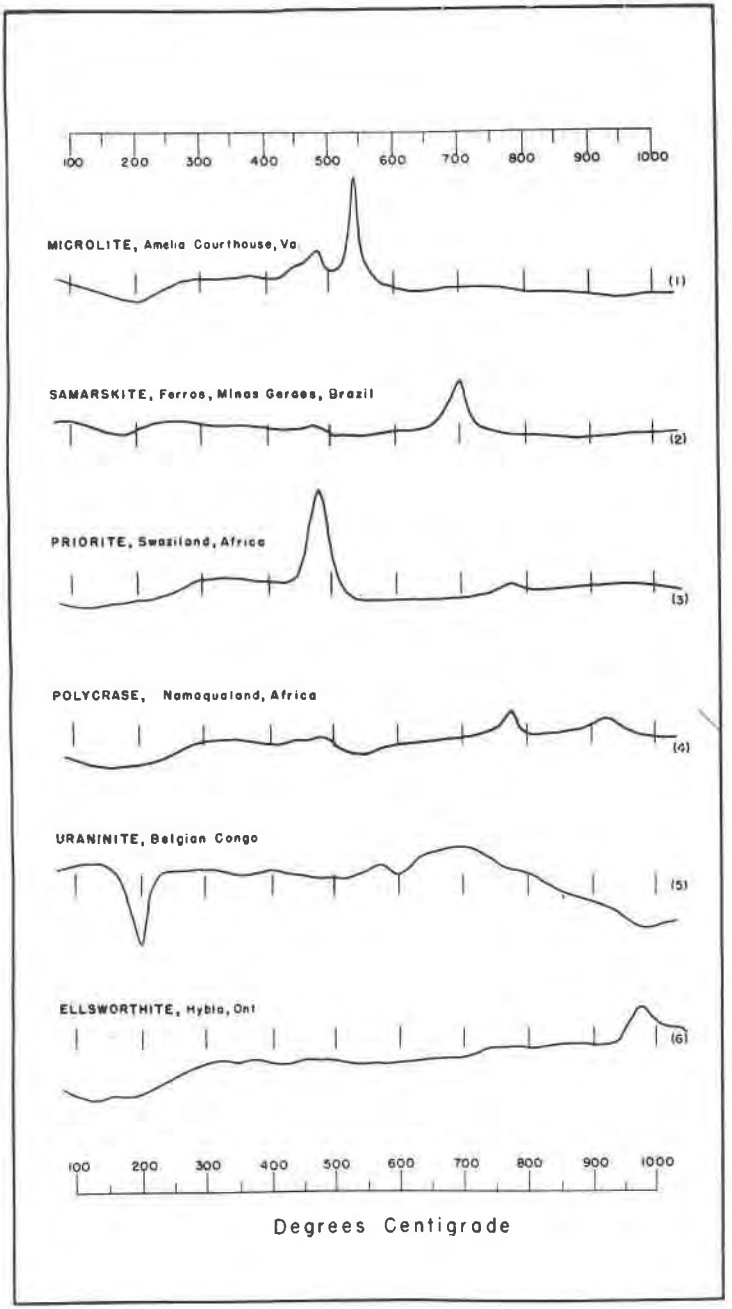

FIG. 4. Thermal curves of microlite, samarskite, priorite, polycrase, uraninite and ellsworthite.

TABLE 2. *X*-RAY DIFFRACTION DATA ON DAVIDITE
(After heating at 1000° C)
Cu—radiation; Ni—filter

Davidite, Mozambique				Davidite, Olary, S. Australia	
Specimen 2		Specimen 1			
d	*Est. I*	*d*	*Est. I*	*d*	*Est. I*
—		6.71	(2)	—	
—		5.16	(1)	—	
—		4.47	(2)	—	
—		4.15	(6)	—	
3.38	(7)	3.40	(9)	3.42	(6)
3.22	(7)	3.23	(8)	3.25	(6)
3.06	(6)	3.05	(8)	3.08	(3)
—		—	—	3.03*	
—		—	—	2.91*	
2.86	(9)	2.87	(10)	2.86	(10)
—		—	—	2.77*	
2.62	(3)	2.62	(3)	2.65	(2)
2.47	(8)	2.48	(8)	2.49	(7)
2.41	(1)	2.42	(3)	2.44	(3)
2.23	(6)	2.25	(8)	2.26	(7)
2.17	(1)	2.19	(3)	2.20	(4)
2.12	(4)			2.15	(1)
2.10	(4)	2.10	(2)	2.09	(1)
		2.03	(1)	2.04	(4)
1.95	(1)	1.96	(2)	1.97	(1)
1.90	(2)	1.91	(4)	1.92	(2)
1.83	(1)	1.84	(2)	1.85	(2)
1.79	(4)	1.80	(6)	1.81	(8)
1.76	(1)	1.78	(1)	1.78	(2)
1.69	(10)	1.70	(9)	1.71	(8)
				1.69	(8)
1.64	(1)			1.65	(1)
1.62	(1)			v. faint	
1.59	(9)	1.60	(5)	1.60	(9)
1.56	(1)	1.57	(1)	1.58	(2)
1.54	(1)	1.55	(1)	1.55	(2)
1.50	(2)	1.51	(3)	1.51	(1)
1.43	(9)	1.44	(7)	1.44	(9)
1.37	(1)	1.38	(4)	†	
1.12	(1)	1.12		†	
1.06	(1)	1.07	(2)	†	
0.90	(1)	0.90	(3)	†	
0.88	(1)	0.89	(2)	†	
0.86	(1)	0.86	(3)	†	
0.83	(1)	0.83	(3)		
		0.82	(1)		

* Impurities.
† Present but faint.

could be observed with the naked eye. Since in other parts of the lode davidite occurs in the form of rough crystals, which are microscopically homogeneous, Mawson felt that the conclusions reached by Crook and Blake were not valid.

W. T. Cooke (1916) analyzed Mawson's material. The result of his analysis is shown in Table 1, together with the analyses of specimens from Mozambique. Material from Olary was secured from Mr. Hugh Ford, of New York. From *x*-ray data it is reasonable to assume that a large part of this sample may be composed of a mixture of ilmenite, magnetite and rutile, although the patterns are rather poor for such a mixture. The thermal curves of the material are inconclusive but could represent such a mixture.

One of the original specimens from which davidite was described was secured through the courtesy of Prof. Mawson and Dr. Davidson. The mineral occurs in bright grains embedded in part in a quartzose matrix and in part in a dark metallic mass. Carnotite coats the surface and mica is present in places. The metallic constituents, the quartz-bearing portion, and the davidite were separated as carefully as possible, and each part was subjected to thermal and *x*-ray analysis.

The metallic constituents associated with the bright black grains yield a somewhat indefinite thermal curve (Fig. 2, Curve 3). The low, broad peaks in the upper range are difficult to interpret. However, it is possible that these peaks are caused by small amounts of the material composing the bright black grains in a mixture with thermally inert minerals.

The light-colored portion of the gangue associated with the davidite gives the *x*-ray pattern of quartz while an admixture of the mineral with an inert material gives a thermal curve (Fig. 2, Curve 4) indicating an endothermic peak at about 573° C.

The bright black grains of the specimen were also subjected to both thermal and *x*-ray analysis. For the former procedure, the sample was mixed with alundum to increase its bulk and was heated in high-sensitivity thermal apparatus (Kulp and Kerr, 1949). The curve obtained is shown in Fig. 2, Curve 5. There are exothermic peaks at 680° C and 810° C, a broad exothermic peak at 435° C, and a small, sharp endothermic peak at 575° C. The endothermic peak is possibly due to quartz, but the remaining peaks seem significant of the dark mineral. These curves show that the black grains differ from the metallics with which they are associated. *X*-ray patterns of the grains confirm this conclusion. The unheated material fails to give an *x*-ray pattern with iron radiation after an eleven-hour exposure, but a pattern is obtained from material heated to 1000° C. The latter agrees in no respect with the pattern of the associated metallics.

X-ray diffraction measurements of the selected material from Olary and the two specimens from Mozambique are given in Table 2. The measurements are in approximate agreement with Bannister and Horne's measurements for material heated in air. Both, however, show the effects of impurities. Certain lines shown by the Olary material are missing in the patterns of the Mozambique specimens. This may be due to differences in exposure or to the presence of slight impurities in the Mozambique pattern causing additional lines. The agreement, however, is believed sufficient to justify the conclusion that the three patterns are representative of materials which are structurally the same.

These data support Mawson's contention that Crook and Blake (1910) based their observations not on the mineral which was originally used in describing the mineral davidite but on material of a different sort.

Conclusions

(1) Davidite as described by Mawson is probably a distinct mineral and the specimen identified by Crook and Blake as a mixture appears to have been a different material.

(2) In general features, material from Mozambique corresponds to davidite as described by Mawson. The similarity in the properties of the two specimens lends support to the conclusion that davidite is a distinct mineral.

(3) It would appear that differential thermal analysis may be applicable to the identification of metamict minerals.

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