THE AMERICAN MINERALOGIST, VOL. 46, SEPTEMBER-OCTOBER, 1961

OBSERVATIONS ON THE THERMAL BEHAVIOR OF BRANNERITE

HANS H. ADLER, *U. S. Atomic Energy Commission, Washington, D. C.*

AND

JOSEPH A. PUIG, *Grumman Aircraft Engineering Corp.,*
Bethpage, L. I., N. Y.

ABSTRACT

Five specimens of brannerite were examined by differential thermal analysis. The thermal curves indicate loss of water at relatively low temperatures and recrystallization above 550° C., accompanied by two exothermic reactions. Experiments involving preheating of brannerite from Cordoba, Spain, suggest that initial recrystallization is a three-stage process involving both loss and gain of energy. Thermal curves of brannerite are sufficiently different to distinguish material from various localities.

INTRODUCTION

Certain radioactive minerals presumably undergo changes in structure due to internal alpha bombardment, resulting in lattice disorder. The amorphous condition arising from this transformation is commonly referred to as the metamict state. Although metamict characteristics are not peculiar to all radioactive minerals, the condition is generally prevalent in uraniferous and thoriferous multiple oxides of titanium, columbium, and tantalum, as well as in certain other minerals such as allanite and zircon which contain minor amounts of uranium and thorium as vicarious constituents.

The metamict state is characterized by optical isotropism, hence *x*-ray diffraction and optical characteristics are not an aid in identification of the natural mineral. The metamict nature of the mineral may, however, be detected by *x*-ray study. Although recrystallization of metamict minerals is frequently brought about by the application of heat, it has been suggested that, in some cases, the original crystal structure may not be reconstituted. Several investigators have, therefore, resorted to differential thermal analysis to facilitate identification of these minerals.

The differential thermal method of analysis has been employed with particular success in the differentiation and identification of clay minerals and has been generally applied to the study of a large number of individual minerals and mineral groups which yield thermic reactions. Kerr and Holland (1951) have applied the differential thermal technique to metamict minerals in their study of davidite and other multiple oxides; Orcel and Levy (1953) have applied it to betafite; and Kulp, Volchok, and Holland (1952) have shown its usefulness in determining the ages of metamict minerals.

This paper describes briefly some observations on the thermal behavior of brannerite, a metamict multiple oxide of uranium and titanium which normally contains minor amounts of calcium, rare earths, thorium, and iron.

APPLICATION AND TECHNIQUE

DTA reactions usually involve oxidation, the loss of adsorbed and lattice water, inversion, recrystallization, melting, and sublimation, and occur in many instances at different temperatures and rates for various minerals owing to diverse compositions and chemical bond strengths. Many minerals undergo more than one transformation in the course of heating. The peaks that have been observed for metamict minerals are related as a rule to two principal reactions: the loss of water and the transition from the metamict to the crystalline state. The latter involves exothermic reactions accompanied by loss of energy which has accumulated in the lattice as a result of atomic displacements caused by alpha irradiation.

Thermic reactions are usually represented graphically by plotting the magnitude and rate of evolution or absorption of heat energy as a function of temperature. Characteristic reaction peaks often suffice for the identification of a mineral, the amplitude and shape of the thermal peak reflecting the rate of the reaction, and the area under the thermal peak approximating proportionality to the energy exchange involved in the reaction. Thermal peaks due to the recrystallization of metamict minerals contain areas that are assumed to be proportional to lattice disorganization caused by bond breakage.

The apparatus used in this study is a modification of the portable differential thermal analyzer originally described by Hendricks, Goldrich, and Nelson (1946). The thermocouples are chromel-alumel and the crucibles are iron-nickel alloy. Energy differences were measured on a galvanometer, and crucible temperature was recorded from a pyrometer. Primary voltage fluctuations were stabilized by a constant voltage transformer, while the rate of heating was maintained at approximately 10 to 13 degrees Centigrade per minute by means of a manually adjustable variable transformer. The instrument is provided with a sensitivity selector which permits relative sensitivity factors of 1, 3, and 9. The thermal curves shown were obtained at highest sensitivity. When desirable, the variable transformer could be regulated to heat sample material at a fairly constant temperature over prolonged periods of time. The pyrometer was calibrated after the method of Barshad (1952) by using inversion and melting-point temperatures of several inorganic salts, and reference points were established at 160° C. and 212° C. with silver nitrate and at 314° C. with sodium nitrate. The inversion temperature of quartz (573° C.) and reaction temperatures of kaolinite (600° C. and 980° C.) proved useful in establishing additional reference points.

The samples were prepared for analysis by grinding to pass a 100-mesh sieve. Thermal analyses were made in air at atmospheric pressure. Alumina (90 mesh) was used as the inert standard. Material for thermal analysis was carefully selected under binocular and petrographic microscopes to exclude obvious impurities. *X*-ray determinations using copper radiation were obtained on all samples before and after heating, and identification was made by comparison with diffraction patterns obtained from type material available at the U. S. Geological Survey's *x*-ray laboratory in Washington, D. C.

Parker, Hathaway, and Blackmon (1956) discuss the disadvantages inherent in the routine use of portable equipment similar to that employed in this study. Although the curves obtained during this investigation may not be strictly comparable with those obtained using standard differential thermal analysis equipment, the use of controlled heating rate and temperature reference points should minimize any differences and avoid the principal disadvantages cited by Parker *et al.* The thermal curves may be considered valid inasmuch as reproducible experimental conditions were maintained. The utilization of this instrument under controlled conditions enhances its application to more rigid studies of the nature of thermal reactions.

Specimen Description

Prior to 1950 brannerite was, for all practical purposes, a mineralogical curiosity. It had been reported (George, 1949) in a pegmatite deposit near Fuenteovejuna, Cordoba, Spain, as more or less distinct crystals and in a placer gravel in Kelley Gulch, Custer County, Idaho. It was first discovered in significant quantity at Crockers Well, South Australia, and in the Blind River district, Canada, where it constitutes an important fraction of the uranium ores.

The specimens used for this study originated near the following localities:

(1) Fuenteovejuna, Corboda, Spain
(2) Crockers Well, South Australia
(3) Bou Azzer, French Morocco
(4) Florence, Montana
(5) Elk City, Idaho

All five specimens in the unheated state are metamict as determined by *x*-ray powder patterns.

Brannerite from a pegmatite at Fuenteovejuna, Cordoba, Spain, was originally considered to be uraninite pseudomorphous after beryl; however, identification as brannerite was subsequently established by chemical analysis. Chemical determinations reported by George (1949) show a uranium content of about 51 per cent and indicate that the mineral is primarily an oxide of titanium and uranium. The unheated material is massive, jet black, with vitreous luster, and shows conchoidal fracture. Surfaces of several fragments examined are partially coated with thin layers of light-brown alteration products, and small flakes of muscovite occur superficially; however, no other extraneous substances were observed.

In transmitted sodium light the index of refraction of the Cordoba brannerite is 2.21±0.03. The specific gravity is approximately 5.17. Fragments of the unheated mineral are optically isotropic. On heating to 960° C. the refractive index is increased to 2.39±0.03, due to loss of water as well as recrystallization from the amorphous state.

Brannerite from Crockers Well, South Australia, occurs as irregular masses and scattered crystals in fracture zones in syenitic rock. The mineral appears olive green to red brown and is coated with yellow to red-brown alteration products. Fresh mineral surfaces show a greasy or resinous luster and irregular to semiconchoidal fracture.

In transmitted light thin splinters of the mineral are pale yellow to brown and isotropic, whereas larger fragments seem opaque. The index of refraction in sodium light is close to 1.95, and the specific gravity is 4.13. After heating to 960° C. refractive indices of 2.2 to 2.3 in sodium light were obtained for various fragments. Alteration may account for the relatively low index and specific gravity of the unheated material. The low index is, furthermore, consistent with high water content indicated by the large endothermic peak between 100° and 300° C. (Fig. 1). The area under the dehydration curve, as determined by trapezoidal integration, is 3.9 times greater than the area of the corresponding peak of the Cordoba mineral, suggesting an increment in water content of this magnitude. This agrees well with the ratio of 4.2 shown by chemical analyses of samples of the Crockers Well (9.95% H_2O by weight) and Cordoba (2.35% H_2O) minerals in Table 2.

A polished surface of the Crockers Well material shows very minor included matter which is seemingly inert, or the amount is insufficient to produce a detectable thermal reaction. The *x*-ray diffraction pattern obtained on unheated brannerite fragments contains a few lines that are not characteristic of heated brannerite but agree most closely with lines produced by thorite and rutile.

Brannerite at Bou Azzer, French Morocco, is disseminated in metallic sulfide veins. It appears black with a vitreous luster and fractures conchoidally. In transmitted light the fragments are opaque to transparent brown and are isotropic at the thin edges. In sodium light the index of refraction is 2.22±0.03.

At Florence, Montana, brannerite is found as small, subrounded detrital grains in heavy sands consisting largely of rutile, ilmenite, and garnet. The brannerite is green to red brown. A few of the brannerite grains are subhedral crystals. The fragments appear opaque in transmitted light but have transparent isotropic edges. The index of refraction in sodium light is 2.26±0.03.

TABLE 1. VARIATION IN INDICES OF REFRACTION OF BRANNERITE

	S. Australia	Spain	Fr. Morocco	Montana	Idaho
Unheated	1.95±0.03	2.21±0.03	2.22±0.03	2.26±0.03	2.26±0.03
Heated to 350° C.	2.06±0.03	2.28±0.03	2.23±0.03	2.30±0.03	2.30±0.03
Heated to 960° C.	2.2 to 2.3	2.39±0.03	2.39±0.03	2.39±0.03	2.39±0.03

Brannerite occurs as rounded black pebbles in a placer deposit near Elk City, Idaho, together with ilmenite, rutile, garnet, and magnetite. Davidite, betafite, and euxenite were also identified in the gravel. The brannerite pebbles show no crystal faces. In sodium light the refractive index of the unheated brannerite is 2.26±0.03.

Refractive indices of the five brannerite specimens obtained on unheated fragments as well as material heated to 350° and 960° C. are included in Table 1. The index of refraction increases slightly with loss of water (350° C.), and a further increase takes place after heating to 960° C. presumably as a result of recrystallization of the mineral.

DISCUSSION OF THERMAL CURVES

All five brannerite specimens failed to yield *x*-ray diffraction powder patterns before heating; however, all produced similar characteristic lines after heating to high temperatures. The detectable energy changes produced are shown by the thermal curves in Fig. 1, which are characteristic of each specimen but show marked dissimilarities. Although each curve contains two exothermic peaks, there are major differences in peak position, shape, area and amplitude which can not reasonably be attributed to variations in particle size, but may reflect varying degrees of lattice disorganization as well as compositional variance.

The endothermic peak between 100° and 300° C. is due to release of water, and the area under the dehydration peak should be roughly indicative of the amount of low-temperature water which these specimens contain. The Idaho material may have lost much of its water below 100° C. Both the South Australia and Montana brannerite have a relatively high water content, which may be due to alteration and may account for the resinous appearance and green to red-brown color of the specimens.

The thermal curve of the Cordoba brannerite shows two exothermal

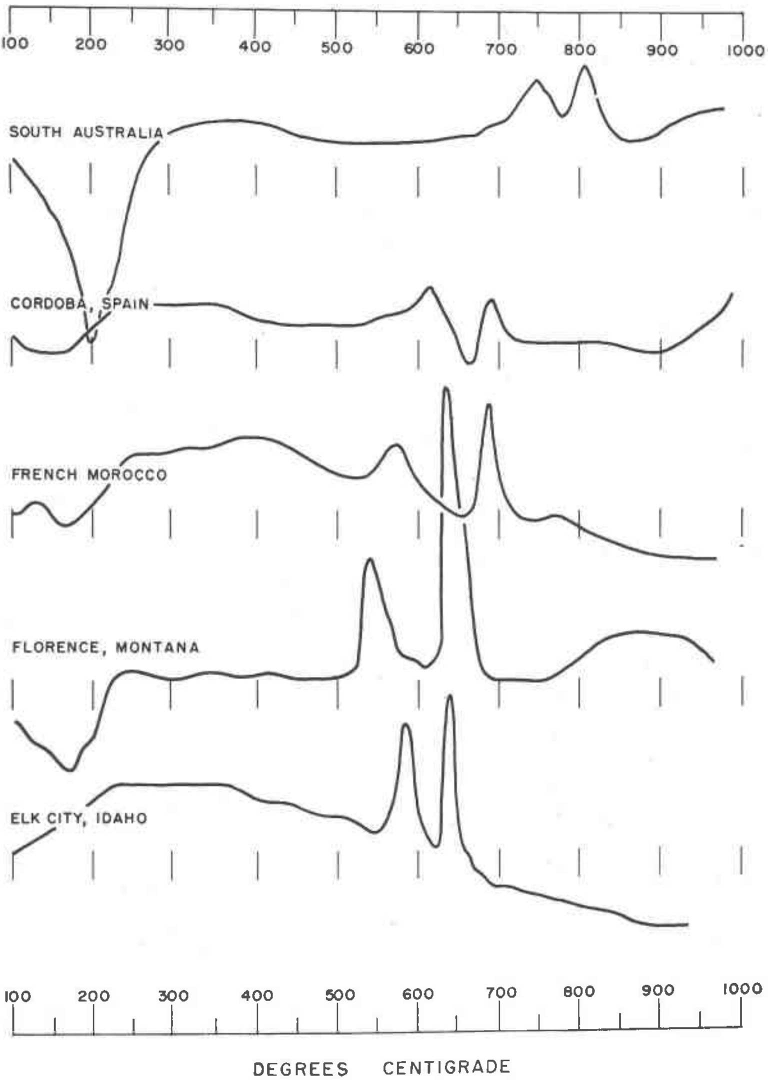

FIG. 1. Thermal curves of brannerite.

peaks, the significance of which has been established to some extent. After heating the sample to 660° C. no *x*-ray lines are obtained, indicating the persistence of an essentially random structure. On heating to 740° C. broad and somewhat diffuse lines are obtained, suggestive of initial reorientation. The *x*-ray pattern, however, is not typical of heated brannerite although several lines coincide. The resultant material, referred to as Phase I, has not been identified. Further heating to 980° C. is accompanied by a marked change in the *x*-ray pattern and a concomitant increase in the sharpness of the lines, which are typical of recrystallized brannerite. Preheating the Cordoba material at 550° C. for 9 hours produces no pattern, but subsequent heating to about 900° C. produces an *x*-ray pattern which is identified as Phase I; however, the lines appear sharper than in the pattern obtained after heating directly to 740° C., indicating less random orientation. Although substantial exothermic reactions accompany the changes in atomic reorientation yielding Phase I, the only reflection of modification to the brannerite structure is the sharp exothermic rise in the thermal curve above 900° C. This transition requires further investigation. The existence of several crystalline phases emphasizes, of course, the importance of controlled heating before *x*-ray analysis, as either structure could possibly result from heating this brannerite in the Bunsen flame.

Brannerite from South Australia heated to 840° C. yields an *x*-ray pattern which is identical to that obtained from the Cordoba material heated to 980° C. Brannerite specimens from Idaho, Montana, and French Morocco heated to above 900° C. also yield similar *x*-ray patterns. The thermal curves, on the other hand, show characteristic variances which uniquely identify the specimens from each locality. In all cases the exothermal doublet is related to energy liberated during recrystallization.

Further study of the thermal behavior of Cordoba brannerite has revealed an interesting phenomenon that is evidently associated with the transformation to Phase I. Curves 1, 2, 3, and 4 in Fig. 2 show the effects of preheating the mineral at 550° C. for about 3, 5, 7, and 9 hours, respectively. The Cordoba curve in Fig. 1 shows an initial exothermic peak at about 610° C., the amplitude of which exceeds that of the high-temperature peak at 690° C. On preheating for prolonged periods, the amplitude of the peak at 610° C. diminishes with a corresponding increase in the amplitude of the peak at 690° C. Also, the combined area under both peaks of the curve in Fig. 1 is smaller than the area under curve 4 in Fig. 2, suggesting that the lattice has gained energy as recrystallization proceeds. There is a suggestion of energy absorption in the endothermic peak at 665° C. which is not apparent in the South Australia, Montana or

Idaho brannerite curves, but does appear in the curve obtained on the French Morocco mineral. Most of this energy increment is presumably gained from furnace heat inasmuch as the energy loss of the first reaction (610° C.) is considerably less than the energy gain reflected in the second exothermic peak (690° C.). The reaction at 610° C. is ascribed to initial reorientation of atomic groups within the lattice, which results ap-

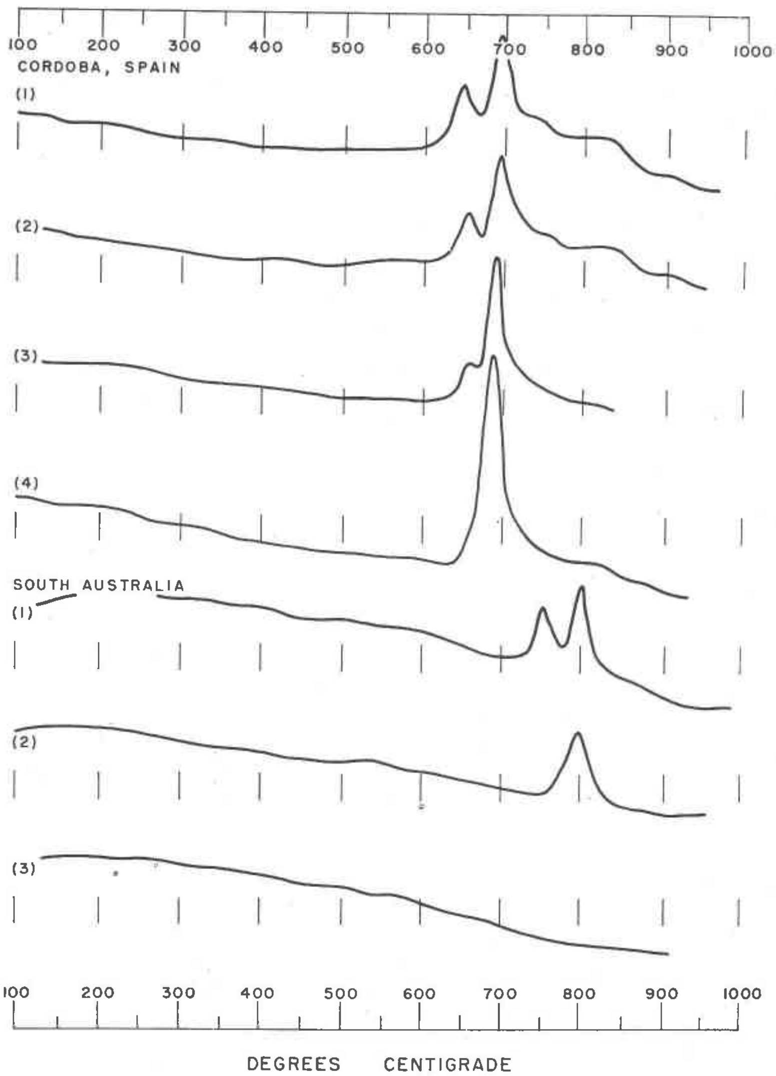

FIG. 2. Progressive heating curves of brannerite.

parently in no detectable lattice order. The accompanying energy changes evidently enable recrystallization to proceed to a more stable and ordered state at 690° C. Hence, recrystallization of the Cordoba mineral to Phase I is seemingly a three-stage process involving both loss and gain of energy, although evolution of heat is largely reflected in the thermal curve (Fig. 1).

Similar effects were not observed after preheating brannerite from South Australia. The writers believe, however, that the temperature and time variants used may not have been sufficient to obtain ample resolution and intermediate results. Curves 1, 2, and 3 in Fig. 2 were obtained respectively on material preheated at 685° C. for 1 hour, at 705° C. for 3 hours, and at 770° C. for 6 hours. It is also conceivable that the state of lattice disorder may differ for the Cordoba and South Australia specimens inasmuch as they are compositionally different (see Table 2). This may account for the difference in thermal behavior, *i.e.*, the higher exothermic reaction temperatures of the South Australia brannerite and the results obtained during preheating experiments.

Table 2. Chemical Analyses of Brannerite, in Weight Per Cent
(after Frondel, 1958)

	1	2
CaO	2.74	—
PbO	2.34	2.79
FeO	3.11	—
UO_2	—	—
UO_3	—	31.83
U_3O_8	51.76	—
ThO_2	1.20	12.81
Ce_2O_3	1.10	1.43
$(Y, Er)_2O_3$		3.71
TiO_2	32.45	35.13
H_2O	2.35	9.95
Rem*	~.16	1.69
Total	97.21	99.34

1. Cordoba, Spain.
2. Crockers Well, Australia.
* Additional minor constituents are reported in the reference cited.

The results of the present study also suggest that differences in amplitude of thermal peaks obtained on specimens of a single species of metamict multiple oxide may be due partially to a natural exchange of energy at temperatures too low to produce recrystallization. The reactions may

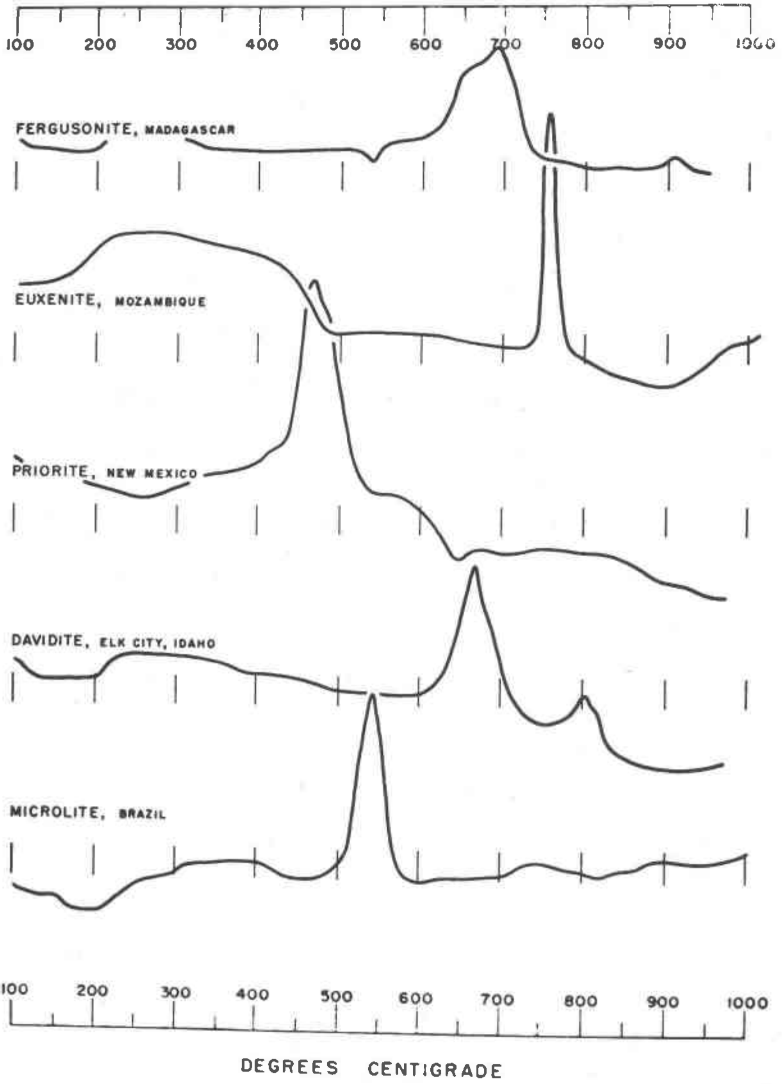

FIG. 3. Thermal curves of various multiple oxides of columbium, tantalum, and titanium.

have been effected by heat of disintegration of radioactive elements contained in the mineral and, in certain cases, by renewed igneous or hydrothermal activity.

Attempts to relate differences in the thermal curves to compositional variations in brannerite have been unsuccessful owing to the lack of adequate analytical data. Published analyses (Pabst, 1954; Frondel, 1958) of Crockers Well and Cordoba brannerite shown in Table 2 do not distinguish between UO_2 and UO_3 content. The distinction may be important inasmuch as disruption of the lattice structure, and subsequent reorganization, may be partially related to oxidation-induced changes in the size and valence of the uranium ion.

Thermal curves of several other multiple oxides of uranium and thorium are shown in Fig. 3. These compare favorably with curves obtained by Kerr and Holland (1951) and Kulp, Volchok, and Holland (1952).

REFERENCES

BARSHAD, I. (1952), Temperature and heat of reaction calibration of the differential thermal analysis apparatus: *Am. Mineral.*, **37,** 667–694.

FRONDEL, C. (1958), Systematic mineralogy of uranium and thorium: *U. S. Geol. Survey Bull.* **1064,** p. 333.

GEORGE, D. (1949), Mineralogy of uranium and thorium bearing minerals: *U. S. Atomic Energy Comm. RMO*-**563,** p. 78.

HENDRICKS, S. B., GOLDRICH, S. S., AND NELSON, R. A. (1946), A portable differential thermal analysis unit for bauxite exploration: *Econ. Geol.*, **41,** 64–76.

KERR, P. F., AND HOLLAND, H. D. (1951), Differential thermal analyses of davidite: *Am. Mineral.*, **36,** 563–572.

KULP, J. L., VOLCHOK, H. L., AND HOLLAND, H. S. (1952), Age from metamict minerals: *Am. Mineral.*, **37,** 709–718.

ORCEL, J., AND LEVY, C. (1953), Analyse thermique de la betafite, mineral métamicte: *France, Acad. Sci., Comptes Rendus*, **236,** 1, 1177–1179.

PABST, A. (1954), Brannerite from California: *Am. Mineral.*, **39,** 109–117.

PARKER, C. J., HATHAWAY, J. C., AND BLACKMON, P. D. (1956), Some curves from a portable differential thermal analysis unit: *U. S. Geol. Survey Bull.* **1021-G,** 237–251.

Manuscript received December 1, 1960.