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AGE FROM METAMICT MINERALS*

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ABSTRACT

Various specimens of metamict zircon, samarskite, microlite, fergusonite, pyrochlore, and ellsworthite have been subjected to alpha activity measurement, differential thermal analysis and x-ray diffraction analysis. The ratio of the area under the thermal curve peak, (which is proportional to the lattice disorganization), to the alpha activity increases with the age of the mineral. Furthermore in the case of eleven specimens of samarskite of the same geologic age from the Spruce Pine District it was found that the *DTA* peak area increases with alpha activity over a considerable range. It appears that a new method of age determination is available although much detailed study will be required before accurate geologic dates can be derived.

INTRODUCTION

In an earlier paper, Holland and Kulp (1950), it was suggested on theoretical grounds that metamict minerals might be useful as age indicators. This report presents the experimental results of a preliminary survey of the problem.

The principles involved may be stated rather simply. Internal alpha bombardment of a mineral due to the presence of uranium or thorium series isotopes breaks chemical bonds and disorganizes the lattice. The number of bonds broken depends on the alpha activity, the length of time during which the mineral has undergone bombardment, and the inherent strength of the crystal. The disorganization of the structure may be measured by several methods. Small amounts of lattice disruption can be measured by thermoluminescence techniques (Daniels and Saunders, 1950) and by changes in optical properties. If the concentration of broken bonds is large, measurement of density or of the energy of recrystallization on heating become useful means of determining the amount of lattice disruption. The energy liberated during recrystallization is readily measured by differential thermal analysis. The

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area under the thermal curve peak related to the recrystallization energy, is proportional to the total lattice disorganization due to the alpha bombardment. Until a saturation value is reached, this should be roughly linear with time for a fixed alpha activity. The alpha activity is determined by direct counting procedures. *X*-ray diffraction serves to identify the particular phase (mineral) studied. Complete chemical analysis of each specimen would be desirable to assess the effect of substitution on lattice stability but this was not possible in the present reconnaissance study.

The minerals which have undergone sufficient lattice disruption to be detected by *x*-ray diffraction or thermal analysis are called metamict. The common representatives are the isodesmic multiple oxides of the type $A_mB_nO_{2mn}$, where $A=$ U, Th, rare earths, Ca, Na, etc., and $B=$ Nb, Ta, Ti, etc. These include pyrochlore-microlite, fergusonite, euxenite-polycrase, eschynite-priorite, samarskite, betafite. Uraninite and thorianite are commonly non-metamict probably due to the simplicity of crystal structure. Zircon is also found in the metamict state.

One of the major problems in this investigation was to procure a sufficient number of samples from enough different localities to demonstrate definite age relations. Another difficulty was presented by the uncertainty in the geologic age of many of the specimens due to the absence or inadequacy of uranium-lead ratio data.

The ultimate "age curve" for a particular mineral structure which can become metamict will be a plot of the ratio of energy of recrystallization to present alpha activity against time.

The authors wish to acknowledge the kind cooperation of Dr. Frederick Pough, Director, American Museum of Natural History and Frank A. Taylor, acting Director U. S. Nat. Museum, who helped us augment the specimens of the Columbia University Mineralogical Collection provided through the kindness of Prof. Paul F. Kerr. The assistance of Mr. Edward Lyden in the laboratory was most helpful.

The measurement of the alpha activity of these specimens was done by the scintillation counting of thin sources. The technique is described in detail elsewhere (Kulp, Holland and Volchok 1951). The differential thermal analysis apparatus and procedure is the same as that previously described (Kulp and Kerr, 1949). The *x*-ray diffraction patterns were taken at 40 KV, 20 m.a. in a straumanis camera using copper radiation.

Results

A. Zircon

Table 1 summarizes the data obtained on the specimens of zircon which were studied. The "probable geological age" was obtained from

TABLE 1. DATA ON ZIRCON SPECIMENS

GROUP 1. NON METAMICT BY *X*-RAY DIFFRACTION AND DTA CRITERIA

Locality	Probable Geologic Age in M. Y.	Activity α/mg/min.
Miask, Urals.	350±100	0.1
Ilmen Mts., U.S.S.R.	350±100	0.1
Espailly, France.	300±100	0.40± .05
Ceylon (1).	600±100	1.03± .05
Deer Hill, N.Y.	400±100	1.4 ±0.1
Henderson, N. C.	300±100	2.9 ±0.1
Renfrew Co., Ontario.	1000±200	3.5 ±0.2*
St. Peters Dome, Colo.	800±100	3.7 ±0.2*
Brudinelle, Ont.	600±200	4.0 ±0.2*
Walhalla, S. C.	250± 50	11.2 ±0.4*

GROUP 2. METAMICT

Locality	Probable Geologic Age M.Y.	Activity α/mg/min.	Area/Activity (Arbitrary Units)
Walhalla, S. C.	250± 50	11.2±0.4	0
Norwich, Mass.	250± 50	100 ±5	3
Hybla, Ont. (1)	300±100	662 ±2	1
Hybla, Ont. (2)	300±100	28.4±0.2	6
Madagascar	350± 50	15.2±0.2	6.5
Bedford, N. Y. (1)	375± 50	32 ±2	7
Bedford, N. Y. (2)	375± 50	16.0±0.5	7.5
Minas Geras, Brazil	500±100	52 ±1	13
Ceylon (2)	600±100	15.8±0.1	15
Arendal, Norway	1000±200	50 ±2	3.5

* Slight broadening of high angle lines.

the best U-Pb or U-He age data available. The specimens in Group 1 were not metamict by *x*-ray or thermal criteria. None of this group give any thermal reaction although several show slight broadening of the high angle *x*-ray lines, indicative of incipient metamictization. This line broadening appeared only in specimens with alpha activity greater than 3α/mg/min. and an age greater than 200 m.y. Group 2 comprises metamict minerals including border line case (Walhalla) included for comparison. The ratio of area under the thermal peak (which is related to the heat of recrystallization, and thus to the number of bonds broken) to the alpha activity should be related to age for clean zircons of similar composition. It can be seen that the ratio does increase with age. There are only two anomalous specimens, Hybla (1) and Arendal, Norway

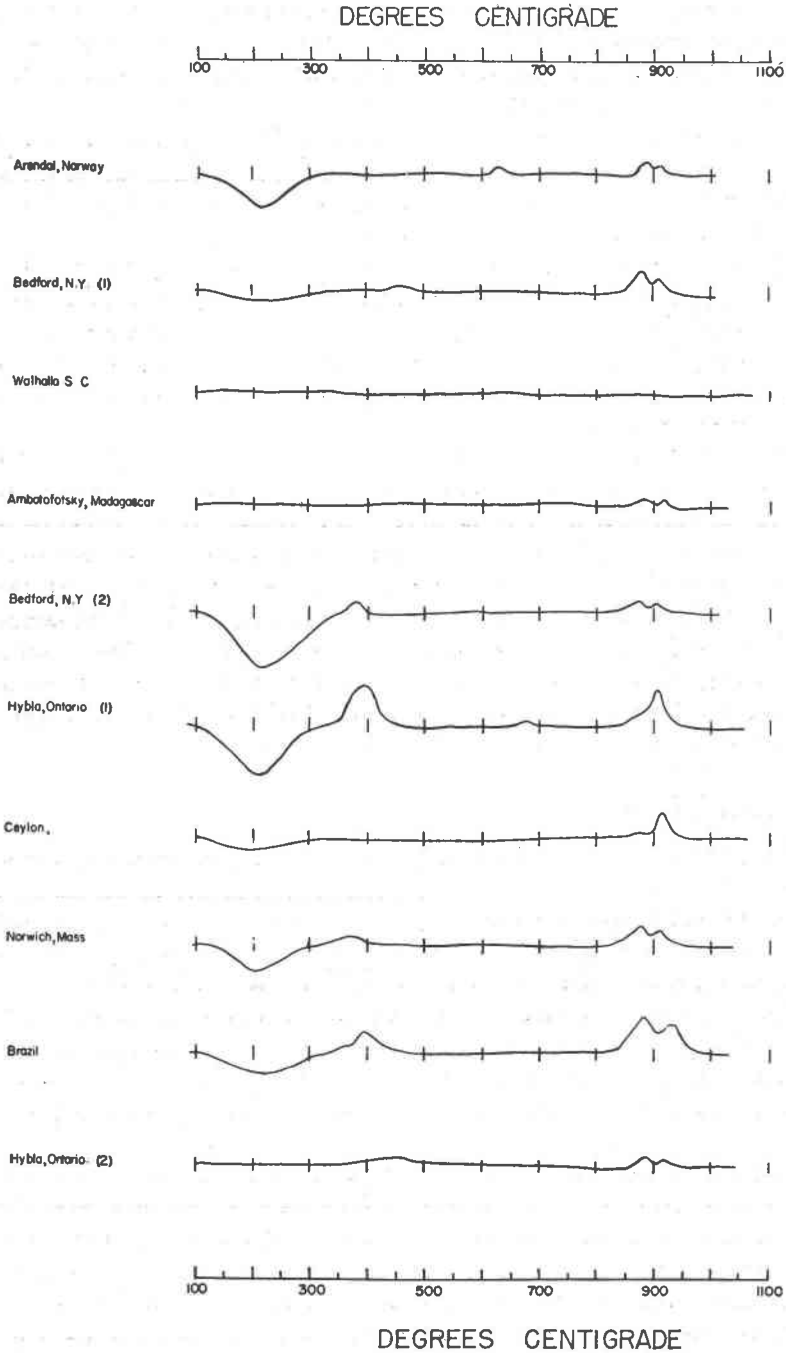
DEGREES CENTIGRADE
100
300
500
700
900
1100
Arendal, Norway
Bedford, N.Y. (1)
Walhalla S. C.
Ambatofotsky, Madagascar
Bedford, N.Y. (2)
Hybla, Ontario (1)
Ceylon.
Norwich, Mass.
Brazil
Hybla, Ontario (2)
100
300
500
700
900
1100
DEGREES CENTIGRADE

FIG. 1

both of which obviously contain at least one other radioactive constituent from an examination of the thermal curve. The foreign constituent apparently contains a large proportion of the alpha active elements so that the ratio is much smaller than expected.

The consistency of the ratios of the two Bedford specimens indicates the probable error for uncontaminated samples of identical chemical composition and the same age with the present technique. It is believed that this precision can be improved by a factor of ten.

Figure 1 shows the thermal curves of the Group 2 specimens. The characteristic thermal curve for metamict zircon appears to consist of a doublet at temperatures of 890 to 910° C. Thus the recrystallization of this mineral is a two-stage process. It will be noted that the relative energy for the two processes varies among the specimens. At present this remains unexplained.

The *x*-ray diffraction patterns of unheated zircons from Hybla with different alpha activities are shown in Plate 1 (*A* and *B*). That Hybla (2) is not considerably less metamict than Hybla (1) is undoubtedly due to the fact that most of the measured alpha activity is derived from a mineral other than zircon in Hybla (1). This is consistent with the interpretation of the area/activity ratio and the extra peak in the thermal curve of Hybla (1) described above. Patterns *C* and *D* of Plate 1 show the change in crystallinity as a result of heating metamict zircons to successively higher temperatures. Note that heating at 1000° for 15 min. is inadequate to completely recrystallize the zircon.

B. Samarskite

Figures 2 and 3 show the thermal curves for the samarskite specimens. The characteristic thermal curve of samarskite appears to consist of a single exothermic peak at 700–710° C. Specimens 2-7, 2-8, 2-9, 2-10 and 2-11 (Fig. 2) show clean *x*-ray (Plate 1 pattern F) diffraction patterns of samarskite after heating, indicative of no foreign constituents.

The relationship of probable geologic age of these samarskite specimens to the area/activity ratio is given in Table 2. A general increase in ratio with age appears, but the Ilmen Mts. specimen is anomalous, and the number of specimens is too small to permit drawing any firm conclusion.

Figure 3 shows thermal curves of samarskite specimens from the Spruce Pine District. Most of these specimens show evidence of peaks due to other minerals. The consistent peak at 450–500° is probably due to priorite while those at 750 may be due to euxenite or eschynite, (Kerr and Holland 1951). The eleven specimens from the one district provide an opportunity to test the metamict age method in another way. Since these are all of the same age, although varying considerably in

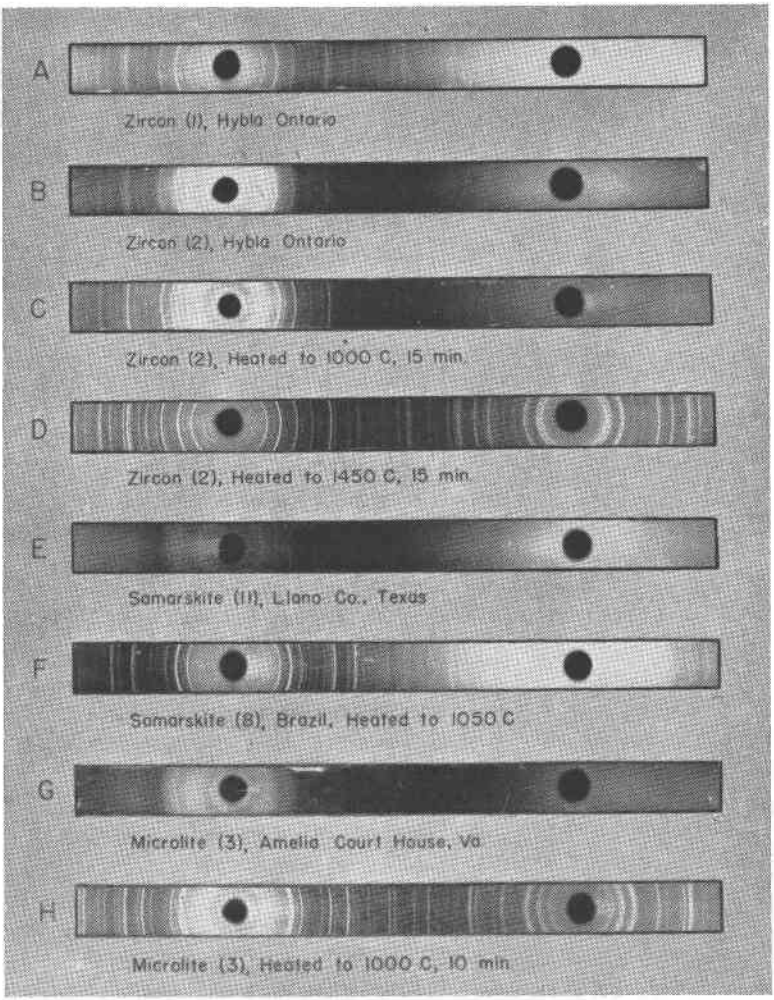

PLATE 1

TABLE 2. AGE RELATIONSHIPS OF SAMARSKITE SPECIMENS

Locality	Probable Geologic Age	$\frac{\text{DTA area in cm.}^2}{\alpha/\text{mg./min.}}\times 1000$
Spruce Pine, N. C.	250 ± 50	15
Canyon City, Colo.	350 ± 100	18
Minas Gerais, Brazil	500 ± 100	21
Llano, Texas	1000 ± 200	33
Ilmen Mts., U.S.S.R.	350 ± 100	35

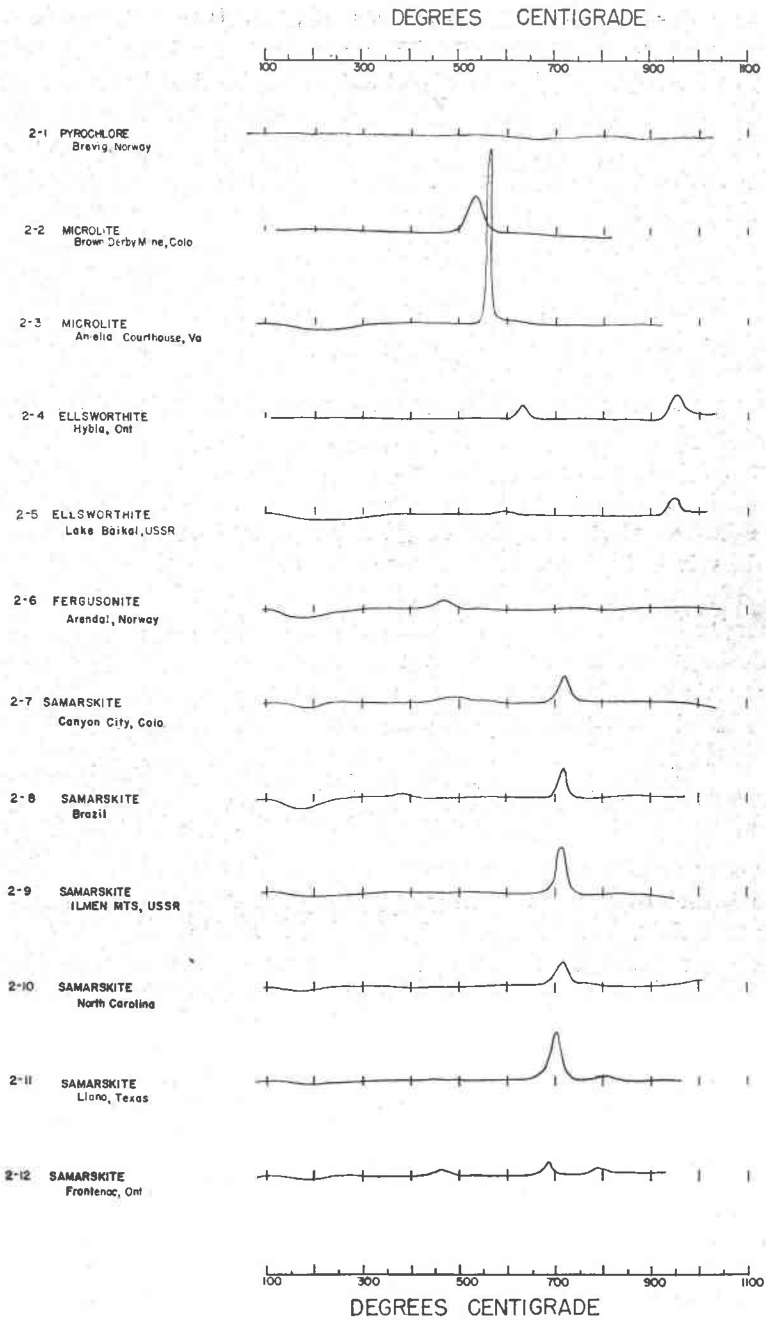
DEGREES CENTIGRADE
100
300
500
700
900
1100
2-1 PYROCHLORE
Brevig, Norway
2-2 MICROLITE
Brown Derby Mine, Colo
2-3 MICROLITE
Amelia Courthouse, Va
2-4 ELLSWORTHITE
Hybla, Ont
2-5 ELLSWORTHITE
Lake Baikal, USSR
2-6 FERGUSONITE
Arendal, Norway
2-7 SAMARSKITE
Canyon City, Colo
2-8 SAMARSKITE
Brazil
2-9 SAMARSKITE
ILMEN MTS, USSR
2-10 SAMARSKITE
North Carolina
2-11 SAMARSKITE
Llano, Texas
2-12 SAMARSKITE
Frontenac, Ont
100
300
500
700
900
1100
DEGREES CENTIGRADE

FIG. 2

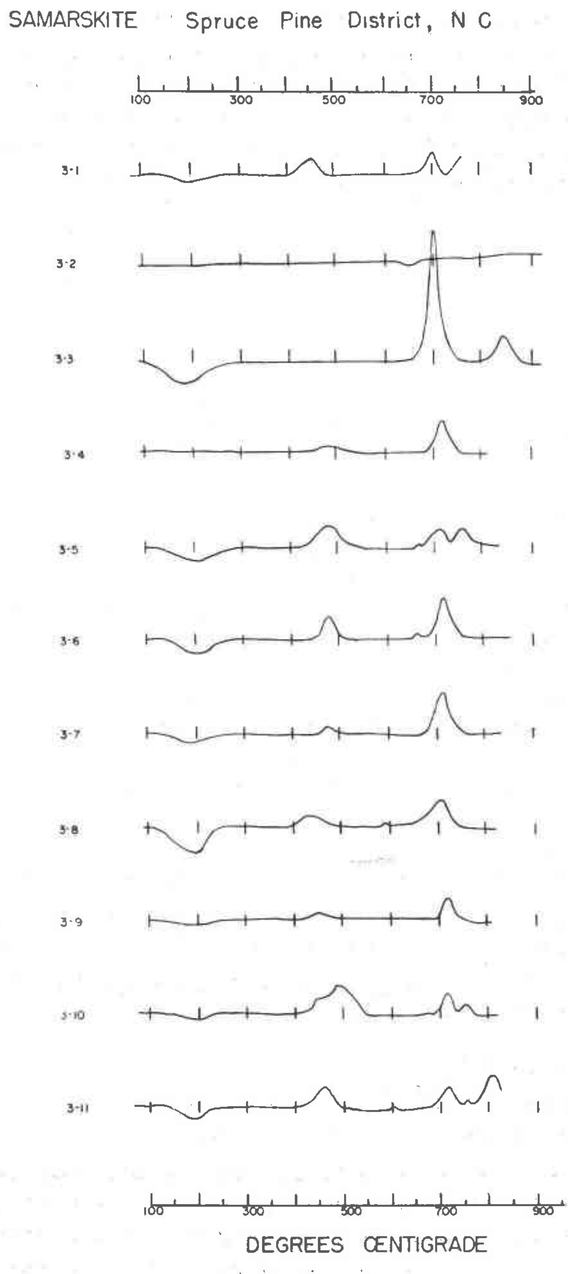
SAMARSKITE Spruce Pine District, N C
100
300
500
700
900
3-1
3-2
3-3
3-4
3-5
3-6
3-7
3-8
3-9
3-10
3-11
100
300
500
700
900
DEGREES CENTIGRADE

FIG. 3

activity, the plot of thermal peak area to activity should be a simple relationship. Figure 4 is a plot of this data over a four fold range in activity. Two important observations can be made. (1) There is a simple linear relationship between area and activity for specimens of the same locality, and (2) for this level of activity in the mineral samarskite, at an age of about 300 m.y., the rate of lattice destruction has not started

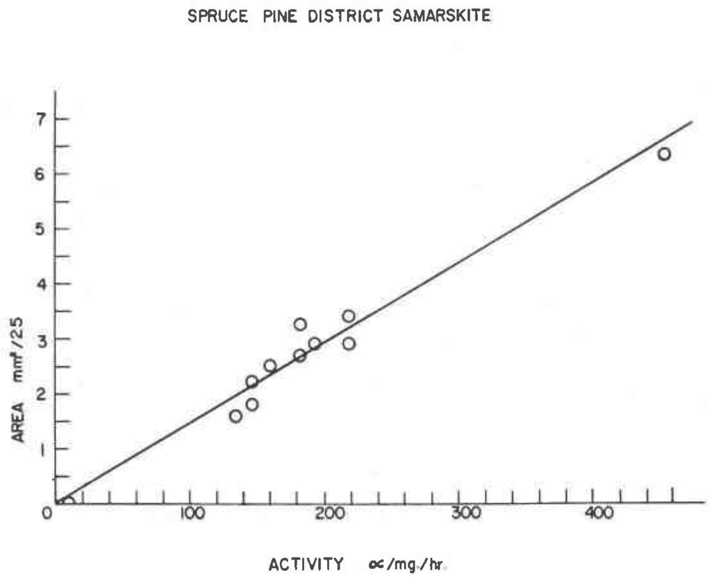

FIG. 4

to level off. If such saturation were reached it would only be possible to estimate a minimum age. That the data for these specimens follow the curve as closely as they do suggests that most of the activity is present in the samarskite. A corollary would be that priorite and exuenite yield greater lattice disruption per alpha than samarskite.

C. Other Minerals

A few specimens of other minerals which have been reported to occur in the metamict state were studied. Figure 2 shows thermal curves for pyrochlore, microlite, ellsworthite (?) and an impure samarskite (2-12). Only the pyrochlore and microlite were identified with certainty by the *x*-ray diffraction method. Note from Plate 1, G & H that metamict microlite from Amelia Courthouse, of similar age and greater activity than the samarskite from North Carolina, still retains most intense diffraction lines of crystalline microlite. This suggests that the structure of minerals in the pyrochlore-microlite series is more stable than that of samarskite. That the pyrochlore specimen gave no observable thermal peak is not surprising in view of its lower activity.

The difference in the sharpness of the peaks in the microlite specimens from Brown Derby and Amelia Courthouse is probably related to crystallite size which in turn is affected by the rate of formation of the mineral and the type and extent of substitution. Many of the multiple oxide minerals containing radioactive constituents show very sharp exothermic peaks indicative of a narrow range in crystallite size (Kerr & Holland, 1951); however samarskite appears to be an exception to this. The shape of the peaks is also affected by the rate of heating but these curves are comparable because a constant heating rate was employed.

Ellsworthite appears to be characterized by a single exothermic peak at about 950° C.

CONCLUSIONS

(1) A preliminary study of the relationship of alpha activity, degree of lattice destruction and age of metamict minerals suggests that if the first two of these factors may be measured, the age may be estimated.

(2) *DTA* can be used to measure the amount of lattice disorganization if the number of chemical bonds broken per gram is sufficiently great.

(3) For a set of specimens of a given age, the lattice disruption increases directly as the alpha activity providing the age is not too great.

(4) If more detailed work is carried out in which all of the mineral phases present in each sample, the crystallite size, and the nature of the substitution in each phase are quantitatively determined, it should be quite possible to arrive at reasonably accurate ages for rocks containing metamict minerals. To do this it must be possible to obtain unweathered samples. Also it must be assumed that temperature effects since the early history of the rock have been negligible.

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