

STORAGE OF ENERGY IN METAMICT MINERALS*

SHELDON F. KURATH, *Department of Chemistry, University of Wisconsin.*

ABSTRACT

A number of radioactive minerals have been studied by means of differential thermal analysis. The amount of heat evolved in heating under nitrogen and the radioactivity of these minerals have been quantitatively determined.

Metamict minerals are capable of storing appreciable quantities of energy from radioactivity in the form of atomic displacements within the crystal. These minerals which were originally crystalline, have had their crystal structures partially destroyed by the radioactive disintegration of uranium, thorium and their radioactive decay products which are present in the mineral. The fast moving alpha particles and recoiling parent nuclei interact with the atoms present at the lattice sites, displacing them and causing the partial disordering of the crystal structure. Accompanying this rearrangement of the crystal lattice is the storage of energy together with marked changes in the physical and optical properties of the minerals.

If the disordered crystal is annealed by raising the temperature, the original crystal structure is reconstituted with the evolution of heat. Faessler, in making a calorimetric study of the mineral gadolinite, observed the evolution of heat amounting to 89.1 cal./gm. (2). Kerr and Holland (4) also noted the evolution of heat in performing thermal analysis experiments on davidite, fergusonite, priorite and other metamict minerals.

Morehead and Daniels (5), using differential thermal analysis, reported the evolution of heat amounting to 25 cal./gm. for one polycrase mineral. The experimental work described herein is an extension of this work, carried out with improved apparatus, in an attempt to find still larger quantities of stored energy.

DIFFERENTIAL THERMAL ANALYSIS

The theory underlying the use of thermal analysis to determine heats of reaction is discussed by many investigators (5, 9, 10, 13). Two samples are placed in adjacent holes within a metal sample block. One sample is thermally active, (i.e. exhibits an absorption or evolution of heat) the other is thermally inert. Both samples are then heated at a uniform rate. If heat is absorbed by the active sample, by fusion or a polymorphic transition, the temperature will fall below that of the inert material.

* More complete details of this investigation may be obtained from the Ph.D. thesis of Sheldon F. Kurath filed in the library of the University of Wisconsin, 1953.

Such temperature differences, measured with a differential thermocouple, appear as minima in the curve when plotted against the temperature. Similarly the evolution of heat from a chemical reaction or the release of energy stored in the displacement of crystal units will place the active sample at a temperature higher than the inert sample and give a maximum in the curve. Such maxima and minima are shown in the differential thermal analysis (DTA) curves of Fig. 1. The areas under the peaks are proportional to the heat evolved (10).

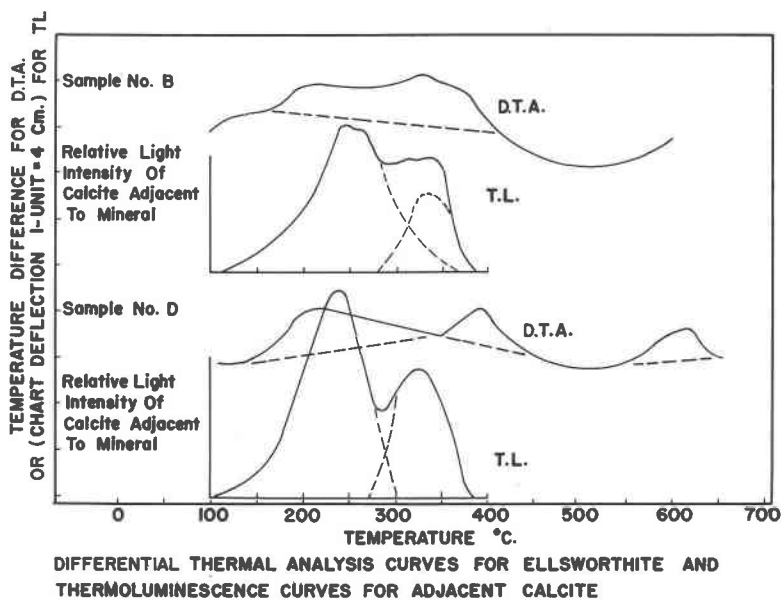


FIG. 1

EXPERIMENTAL

The apparatus used in this investigation is similar to an improved differential thermal analysis apparatus developed by Whitehead and Breger (11). A small stainless steel cylinder 1" by $\frac{7}{8}$ " in diameter contained two holes $\frac{1}{4}$ " in diameter which served as sample holders. One hole is the holder for the thermally active material and the other contains thermally inactive alumina. A thermocouple, placed in a small hole between the two sample holes, serves to measure the mean temperature of the sample holder. The temperature difference between the inert and active samples is measured by means of a chromel—"P"—alumel differential thermocouple. The out put potential from the differential thermocouple is fed in to a Liston Becker Model 14 D.C. amplifier. After amplification,

the potential is recorded on a Brown Model 142 two-pen continuous potentiometric recorder. The differential temperature and the temperature of the sample holder are recorded simultaneously. The sample holder is heated by means of a nichrome wound alundum tube furnace. Both sample holder and furnace were constructed to fit inside of a heavy steel cylinder. The cylinder was made so that it could be evacuated, purged with nitrogen and then operated under nitrogen at reduced pressures.

The most convenient manner in which to evaluate the area under the thermal analysis peaks, is to run heating curves on substances having known melting and inversion points. If the weight of the sample and the heat of fusion are known, the area under the curve can be evaluated in terms of cal./cm.² /gm. as described by other authors (1, 5, 12). The sample weights ranged from 0.1 to 0.01 g. The following materials whose heats of fusion are well known were used for calibration in the present work; Bi, Pb, anhydrous CdCl₂, PbI₂, Zn and Al.

All samples were heated from room temperature up to 700° C. under nitrogen at reduced pressure, (10 mm). Mineral samples which had been annealed for reference material under nitrogen at 700° C. to remove exothermic maxima or peaks in the *DTA* curves were also analyzed thermally. The differential thermal analysis curves of both active and annealed samples were then compared before determining the area under the peaks of the active samples.

Measurements of the radioactivity exhibited by the minerals were also carried out. The apparatus used in radioactivity measurement included a scaling unit model No. 162 made by Nuclear Instruments and Chemical Corporation, and was equipped with a radiation counter type D-33 operated at 1200 volts D. C. and having a mica window with a stopping power of 3.5 mg./cm.². Samples were placed 0.2 mm. from the mica window of the geiger tube. Checks were made with scintillation counters, sensitive only to alpha particles, to convert the readings into alpha ray activity. The alpha activity of these minerals, which are in radioactive equilibrium, was from $\frac{1}{4}$ to $\frac{1}{8}$ of the total activity determined by geiger counting. The alpha activity was estimated by multiplying the geiger count values by the appropriate factor.

RESULTS

The results of thermal analysis experiments and radioactivity measurements are presented in Table 1. The temperatures at which *DTA* peaks were observed are reported along with the heat evolved or absorbed. The radioactivity is reported in terms of alpha counts/min./cm.² emitted from the surface of the sample. Typical differential thermal analysis curves are shown in Fig. 1 for several samples of ellsworthite.

TABLE 1. RADIOACTIVITY AND STORED ENERGY IN METAMICT MINERALS

Sample	Peak temperature °C.	Heat evolved cal./gm.	Radioactivity α counts/min./cm ²
<i>Ellsworthite</i>			
A ^a	none	none	2,170
B ^b	flat	18.6	2,220
C	112-517° C.		
	197	1.8	2,200
	302	5.5	
	405	13.9	
	608	43.1	
		Total	64.3
D ^b	215	5.4	2,280
	395	4.0	
	615	28.3	
		Total	37.7
<i>Fergusonite</i>			
A ^c	680	49.4	1,080
	543	7.8	
		Total	57.2
B ^{d,e}	210-417°	7.2	900
	440	15.2	
		Total	22.4
C ^e	440	4.6	770
D ^{d,e}	none	none	700
E ^f	633	64.9	800
	360	2.2 ^f	
	183	1.9 ^f	
		Total	64.9
F ^g	680	36.6	150
	619	27.3	
	347	1.0 ^f	
	176	1.8 ^f	
		Total	63.9

^a Samples from MacDonald Mine, Bancroft, Ontario, collected by Dr. D. F. Saunders.

^b Examined by x -ray and found to yield no x -ray diffraction pattern.

^c Sample from Dr. J. C. Rabbitt of the U. S. Geological Survey.

^d Examined by x -ray and found to yield no x -ray diffraction pattern.

^e From J. J. Goll Mine, Madawaska, Ontario.

^f Heat was absorbed instead of evolved.

^g From Baringer Hill, Texas, collected in 1902 by Marshall Hanks.

TABLE 1—(continued)

Sample	Peak temperature °C.	Heat evolved cal./gm.	Radioactivity α counts/min./cm. ²
<i>Sammaraskite</i>			
A ^c	640	3.2 ^t	1,000
	510	5.2	
	200	9.4	
	Total	14.6	
B ^c	650	44.2	1,450
<i>Euxenite^a</i>			
	610	32.8	1,900
	395	15.4	
	305	0.9 ^f	
	135	6.0 ^f	
	Total	48.2	
<i>Exchymite-priorite^c</i>	515	46.3	870

Ellsworthite: Experimental data on four samples of ellsworthite ($\text{CaO} \cdot \text{Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$) are given in Table 1. Typical *DTA* curves for samples *B* and *D* are shown in Fig. 1. They indicate evolution of heat at several different temperatures. Although the samples were obtained from the same locality and had similar amounts of radioactivity, they failed to yield the same peak structure in the heating curve. Surprisingly, sample *A* yielded no peak structure even though highly radioactive. The failure of this sample to evolve heat is probably due to the fact that the sample was not heated to a high enough temperature. Other investigators have noted exothermic peaks as high as 980° C. (4), but it was not possible with the present equipment to go above 700° C. In the case of sample *C* the differential thermal analysis yielded four distinct peaks.

All of these samples were imbedded in salmon colored calcite which was found to exhibit a high degree of thermoluminescence. Thermoluminescence glow curves labelled *TL* are presented in Fig. 1 for the calcite adjacent to the ellsworthite for samples *B* and *D* as obtained with a photomultiplier tube.

Fergusonite: Sample *A* was kindly given to us by Dr. J. C. Rabbitt of the U. S. Geological Survey. Three samples, *B*, *C* and *D*, were obtained from the J. J. Goll Mine at Madawaska, Ontario. Samples *E* and *F* were given to us by Mr. Marshall Hanks from a collection which he had made in a pegmatite cerium mine in 1902 at the Baringer Hill of Texas.

The results are given in Table 1. As in the case of ellsworthite, samples *B*, *C* and *D* from the same location yielded different thermal analysis peaks although they all had about the same radioactivity. Sample *D* showed no evolution of heat even though it was highly radioactive and metamict in character as shown by the absence of *x*-ray diffraction patterns. Presumably this sample would have yielded an exothermic heat of reaction at temperatures above 700° C. (2). Samples *E* and *F* gave small endothermic peaks which may be due to dehydration.

Samarskite, Euxenite-Polycrase, Eschynite-Priorite: A limited number of samples of other minerals were also found to evolve heat when their temperatures were raised. Two samples *A* and *B* of samarskite were kindly given to us by Dr. J. C. Rabbitt of the U. S. Geological Survey. The euxenite sample came from the MacDonald Mine at Bancroft, Ontario. The eschynite-priorite sample was given by Dr. J. C. Rabbitt. The results are presented in Table 1. All of these minerals were highly radioactive and evolved large amounts of heat during differential thermal analysis. As in the case of fergusonite, endothermic peaks may be traced to the evolution of water of hydration.

Minerals Indicating No Energy Storage

Two samples of allanite were found to have no stored heat releasable below 700°, even though they had radioactivity counts of 103 and 81 counts/min./cm.² respectively. Two samples of cyrtolite yielded radioactive counts of 525 counts/min./cm.² and gadolinite and zircon had counts of approximately 50 counts/min./cm.². These minerals are found in the metamict state and probably have energy peaks well above 700° C. (4, 6).

Several samples of purple fluorite showed no stored energy although nearly black in color. Uraninite (UO₂) and xenotime similarly exhibited no stored energy. All these minerals had high alpha ray activity. These results support the generalization that highly ionic materials are not found in the metamict state.

DISCUSSION

The majority of the minerals exhibiting energy storage showed complex peak structures in the differential thermal analysis curves. The fact that all of these experiments were carried out in nitrogen, after previous evacuation, precludes air oxidation as a factor in these exothermic peaks. The appearance of a multiple peak structure can be compared with the mineral thorium silicate in which the appearance of several phases was noted (6).

The low-temperature peaks are probably associated with the produc-

tion of crystalline components of the metamict mineral while the other components remain in their amorphous state. Similarly, the peaks which appear at the higher temperature correspond to the conversion of the other materials to their crystalline form or to the reaction of crystalline components with the surrounding isotropic medium to form an entirely crystalline medium.

In some instances, no energy evolution was observed even though the mineral was highly radioactive. There are a number of explanations for this lack of heat evolution. In the case of zircon, gadolinite, and cyrtolite the energy evolution, in all probability, does not take place in the temperature range from room temperature to 700° C. It is known, for example, that gadolinite evolves energy in the neighborhood of 800° C. (4). This limitation to low temperatures probably accounts for the fact that one fergusonite sample which was known to be metamict, failed to evolve heat in these experiments. Other minerals may have been geologically too young to have sufficient radiation damage to detect and in other cases in which heat was not evolved the radioactivity may have been too low to cause appreciable structural damage (e.g. gadolinite, 50 α counts/min./cm²).

The data presented in previous sections may be used to estimate the time necessary for a mineral to become metamict. Making the qualified assumption that all the energy from radioactive decay is spent in disrupting the crystal structure, Pabst (6) estimated that it would take a sample of gadolinite (Ytterby), at least 110,000 years to become metamict.

An alternate approach to estimating the time of metamictization is given in the following paragraph. A sample of powdered fergusonite in a deep layer in a 5.3 cm.² dish gave 3,580 alpha counts per minute. Assuming that the alpha particles have an energy of 5.0 mev with a range of 3.5 cm. in air, that the "atomic number" of fergusonite is 70, that the density is 5.7 g. per cc. and that the "atomic number" and density of air are 7.2 and 1.23×10^{-3} respectively, the range of the alpha particles in fergusonite is given by the relation

$$\text{range} = \frac{3.5 \times 1.23 \times 10^{-3}}{7.2} \left(\frac{70}{7.2} \right)^{1/2} = 22.6 \times 10^{-3} \text{ cm.}$$

It can be shown that 25 per cent of the alpha particles within 2.26×10^{-3} cm. of the sample surface may escape to be counted (3). If all the alpha particles that escape the surface of the sample are counted, the alpha particles that are emitted per year per gram of sample may be estimated at

$$\text{alphas/year/gm.} = \frac{3.580 \times 60 \times 24 \times 365}{0.25 \times 2.26 \times 10^{-3} \times 5.3 \times 5.32} = 1.10 \times 10^{11}.$$

A 5 mev alpha particle will give about 10,000 electron-volts of energy in collisions and the recoil atom will transfer about 60,000 electron volts as collision energy making a total of 70,000 ev. (8). If all of the collision energy of the alpha particle and the recoil atom are stored, then every alpha count should represent an energy storage of about 70,000 ev. The rate of energy storage in the fergusonite sample is, therefore,

$$1.10 \times 10^{11} \times 7 \times 10^4 \times \frac{(1.6 \times 10^{-12})}{(4.18 \times 10^7)} = 2.95 \times 10^{-4} \text{ cal./gm./year}$$

where $1.6 \times 10^{-12} / 4.18 \times 10^7$ is a factor to change electron volts per alpha particle into calories. Since the heat evolved upon thermal analysis was 57.2 cal./gram, a minimum time for this highly radioactive mineral to become metamict may be estimated at

$$\frac{57.2}{2.95 \times 10^{-4}} = 198,000 \text{ years.}$$

This estimate is to be regarded as a minimum value because only part of the collision energy from the disintegration process will appear as stored energy, much of it being dissipated immediately as heat. Many metamict minerals have a considerably lower content of radioactive elements and would require a much longer time than this to become metamict. Moreover, the efficiency of energy storage decreases as the mineral becomes more metamict and the crystal structure becomes more disordered.

According to other views (7, 8), a 5 mev alpha particle and its recoil atom might produce less than 890 interstitial atoms and if each interstitial atom involves the storage of approximately 10 ev, there would be an energy storage of 8,900 ev per alpha particle. This value is considerably less than the 70,000 ev used in the preceding calculation and would lead to a much longer time requirement for metamictization.

The fact that many of the highly radioactive minerals, which have reasonably simple crystal structures, do not store any energy in the crystal structures suggests that there is something about the complicated crystal lattices of the metamict minerals which holds a dislocated ion or atom of the lattice in its abnormal position so that the disorder will not be annealed out at earth temperature.

ACKNOWLEDGMENT

The author is glad to acknowledge the help of Professor Farrington Daniels under whose direction this research was carried out. He is indebted to the Atomic Energy Commission for financial support of the project which provided him with a research assistantship. He wishes to

also thank Dr. Donald F. Saunders, and Dr. John C. Rabbitt who provided some of the metamict minerals.

REFERENCES

1. BARSHAD, I. (1952), Temperature and heat of reaction calibration of the differential thermal analysis apparatus: *Am. Mineral.*, **37**, 667-694.
2. FAESSLER, A. (1942), Untersuchungen zum Problem des metamikten Zustandes: *Zeits. Krist.*, **104**, 81-113.
3. HALLIDAY, D. (1950), Introduction to Nuclear Physics, p. 145, John Wiley and Sons.
4. KERR, PAUL F., AND HOLLAND, H. D. (1951), Differential thermal analysis of davidite: *Am. Mineral.*, **36**, 563-572.
5. MOREHEAD, F., AND DANIELS, F. (1952), Storage of radiation energy in crystalline lithium fluoride and metamict minerals: *J. Phys. Chem.*, **56**, 546-548.
6. PABST, A. (1952), The metamict state: *Am. Mineral.* **37**, 137-157.
7. PELLAS, P. (1954), *Bull. Soc. Franc. Miner. Krist.*, **77**, 447-460.
8. SEITZ, F. (1949), On the disordering of solids by action of fast massive particles: *Disc. of the Faraday Society*, **5**, 271-282.
9. SMOTHER, W. (1951), Bibliography of differential thermal analysis. *University of Arkansas Institute of Science and Technology*.
10. SPELL, S. (1944), Applications of thermal analysis to clays and aluminous materials: *U. S. Dept. of Int., Bur. of Mines, R. I.* **3764**.
11. WHITEHEAD, W. L., AND BREGER, I. A. (1950), Vacuum differential thermal analysis: *Sci.* **111**, 279-281.
12. WITTELS, M. (1951), The differential thermal analyzer as a microcalorimeter: *Am. Mineral.*, **36**, 615-621.
13. WITTELS, M. (1951), Some aspects of mineral calorimetry: *Am. Mineral.*, **36**, 760-767.

Manuscript received June 2, 1956.