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THERMOLUMINESCENCE OF CALCITE FROM HIGH GAMMA RADIATION DOSES

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ABSTRACT

Three calcium carbonate samples were subjected to large total doses of both gamma radiation and ultraviolet. Each sample was divided into three portions which were heated prior to irradiation. The individual aliquots were heated at different temperatures prior to the radiation treatment in order to observe the effects of heating. The peak intensity vs. dose curves of the thermoluminescence induced in the samples by gamma rays rise to a maximum at a total dose of about 3×10^6 Roentgens. Increasing the total gamma-ray dose may result in a decrease in light output. Further evidence of trap depopulation is furnished by the sharp rise in peak temperature which takes place at total gamma-ray doses above 3×10^6 R. A defect induced by the gamma radiation in the calcite crystal structure may be responsible for this effect.

Glow-curves are also obtainable from samples which have been illuminated with ultraviolet light. The peak intensities are markedly lower than they are in the gamma irradiated samples. The results obtained from both the gamma-ray and the ultraviolet irradiations suggest that retrapping may be a very important process in the thermoluminescence of calcite.

INTRODUCTION

The application of thermoluminescence to geological problems and archaeologic age determinations has been almost exclusively empirical. Continued progress in the developmet of thermoluminescence as a practical tool requires an understanding of the effects of radiations on geological samples. The behavior of thermoluminescence emission from natural samples subjected to high doses of radiation was studied to learn more about the thermoluminescence processes in these substances. The effect of various heat treatments upon the thermoluminescence emission of crystalline calcium carbonate was also investigated.

Thermoluminescence is the transient luminescent emission produced by various crystals when subjected to a gradually increasing temperature. When the material is subjected to natural or artificial ionizing radiation electrons and holes are formed and the electrons may be raised to the conduction band. They will remain free until they recombine with a hole, either directly or indirectly by first being captured by a luminescent center, or captured by imperfections in the crystal called traps. When the crystal is heated the electrons escape from the traps and recombine with positive holes directly or indirectly by the luminescent centers which, totally or in part, results in the emission of light. Charge trapping in natural samples is the result of the radiations from the decay of radioactive impurities included in the material.

The natural glow-curve (the name commonly given to a curve of

thermoluminescence intensity vs. temperature) of calcite consists of two well defined peaks. One at about 230° C. and the other at about 325° C. Artificial ionizing radiation produces another peak at about 110° C. that is the result of a shallow trap which permits the electron to escape when the sample is kept at room temperature. The traps related to the 230° C. peak may be partially emptied or drained at the earth's normal surface temperatures. The intensity of the peak in any particular sample results from an equilibrium between the rate of electron trapping and the rate of escape of trapped electrons. Measurements of the area of this glow-curve peak has been applied to paleoclimatological problems (Ronca, 1964; Ronca and Zeller, 1965). The traps responsible for the high-temperature glow-curve peak are virtually unaffected by normal room temperatures and therefore the thermoluminescence related to these traps has been used for age determinations (Zeller, 1954).

Experimental

Samples of Iceland spar were obtained from Chihuahua, Mexico, calcite was obtained from Joplin, Missouri, and Lakeside Limestone from Utah. They were ground in an Iler shearing-type pulveriser, and the minus-100 plus-200 mesh fraction retained for glow-curve measurements.

Spectrochemical analyses indicate that the Iceland spar from Mexico contained no impurities in excess of 1 per cent. In this sample the most abundant impurity was magnesium which was between 0.1 and 1 per cent. The Joplin calcite contained 1 to 10 per cent magnesium, about 1 per cent iron, and between 0.1 and 1 per cent manganese. The Lakeside Limestone from Utah contains more than 10 per cent magnesium and between 1 and 10 per cent silicon, aluminum, and iron.

Quantitative measurements of the thermoluminescence of the samples were obtained using a RCA 6810A end sensitive photomultiplier tube. Its output was amplified and recorded simultaneously with the temperature to produce the glow-curve. A regulated power supply maintained constant voltages in the photomultiplier tube. The samples were heated in air. The range covered was of 50° C. to 400° C. and a hot plate was used which consisted of a silver plate, which formed the upper surface of the furnace, heated by a nichrome wire heating element supported on fused alumina rods. Powdered samples were placed in a flat-bottomed depression in the silver plate. One junction of a chromel-alumel thermocouple was embedded in the silver plate, the other junction kept in an ice bath, and the temperature recorded with a strip chart recorder. A Leeds and Northrup control unit was used which automatically compensates for fluctuations in heating rate.

Aliquots of the samples were heated at a programmed constant rate of

temperature rise of 1° C. per sec. The glow-curves of all samples, except the Joplin calcite, were obtained from the same furnace. This was done to avoid shifting the peak temperatures arising from the slightly different heating characteristics of each furnace. The reproducibility of the measurements was tested and found to be within ± 4 per cent when all measurements were made with one furnace.

Samples were exposed to gamma rays from cobalt 60 in a unit that provided a dose of 1.97×10^5 Roentgens per hour. The total doses used ranged from 1.6×10^4 to 10^8 R. The samples were illuminated with ultraviolet light from four General Electric J25T8 low-pressure mercury lamps. Sixty per cent of the output of these lamps is in a narrow wave length region around 2,537 Angstroms. The powdered samples were evenly distributed on quartz plates and illuminated from above and below simultaneously. The lamps were approximately 30 cm apart, and the sample holders were midway between the upper and lower lamps. Filters were not used. Exposure ranged from one minute to 17 hours.

The samples were kept in amber glass bottles and refrigerated at $-4°$ C. after being irradiated with gamma rays or ultraviolet light. This procedure must be followed to avoid optical bleaching and retain low-temperature thermoluminescence.

Each sample was divided into three portions which were heated prior to irradiation; one was heated at 110° C., another at 200° C. and the third at 300° C. Heating for 2 hours at 110° C. did not affect the natural glow-curve peaks. Heating for 2 hours at 200° C. removed the middle-temperature peak without significantly affecting the high-temperature peak. Heating for two and a half hours at 300° C. completely drained all of the traps which account for all of the glow-curve peaks which occur below 400° C.

Results

Figure 1 shows typical glow-curve peaks obtained with the indicated irradiations. The Lakeside Limestone sample was not illuminated with ultraviolet light because of its opacity. It was assumed that the ultraviolet penetration into the grains would be so low the results obtained could not be compared with those from the Iceland spar and Joplin calcite. It is evident that much greater peak intensities are obtained when gamma rays are used as the ionizing agent instead of ultraviolet light. Specifically, when subjected to gamma-ray irradiation the low-temperature peak of Joplin calcite is 10^4 times larger than the highest values obtained by exposure to ultraviolet light and the middle and high-temperature peaks are 10^3 and 10^2 times larger. The same result is obtained with the Iceland spar (Fig. 1B). The gamma induced peaks are 10^3, 10^2 and 5

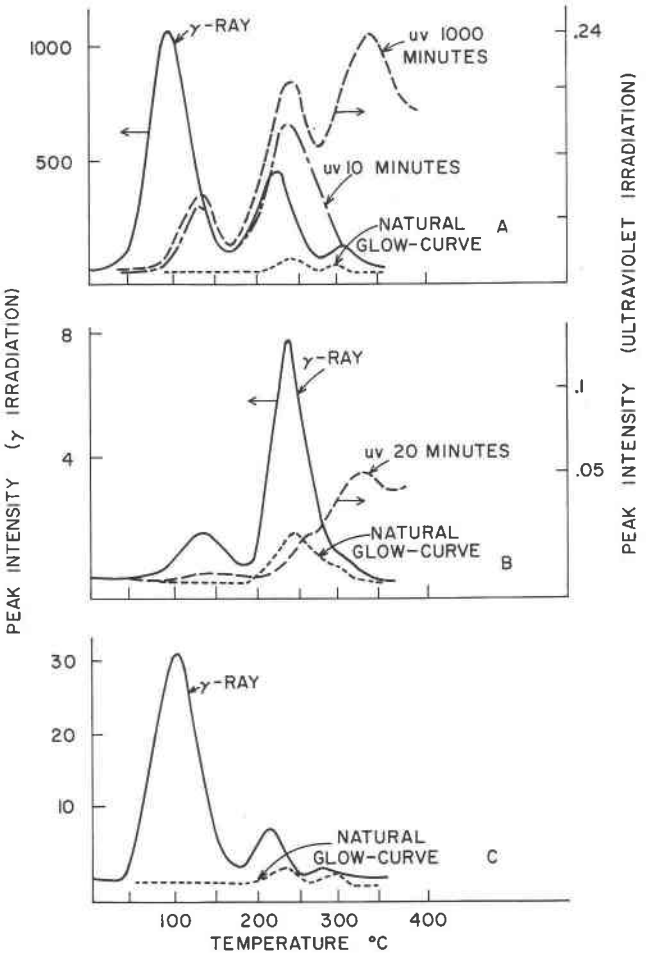

FIG. 1. Glow-curves obtained from natural, gamma-ray irradiated, and ultra-violet illuminated portions of the samples studied. A. Joplin calcite, B. Iceland spar from Mexico, and C. Lakeside Limestone from Utah.

times more intense than the highest peak values reached by the ultra-violet illumination. It should be noted that after exposure to gamma rays the largest peak in the Iceland spar is the 240° C. peak, while in the Joplin calcite it is the 140° C. peak. This tends to confirm the suggestion by Medlin (1963) that the low-temperature peak is associated with the presence of manganese since the Joplin calcite contains 10 times more manganese than the Iceland spar. It should be pointed out that although the peak positions are not precisely the same in all three samples they

fall in a narrow temperature range. It is believed that they are the same peaks and that retrapping may account for all or part of the differences.

Figure 2 shows how the height of the glow peaks depends on the total exposure to ultraviolet light. These curves were obtained with Joplin calcite heated to 300° C. for two and a half hours before exposure to ultraviolet light; the intensity of the high-temperature peak is negligible until the exposure exceeds 200 minutes. One must be careful in analyzing these curves, as there is competition between the charge trapping pro-

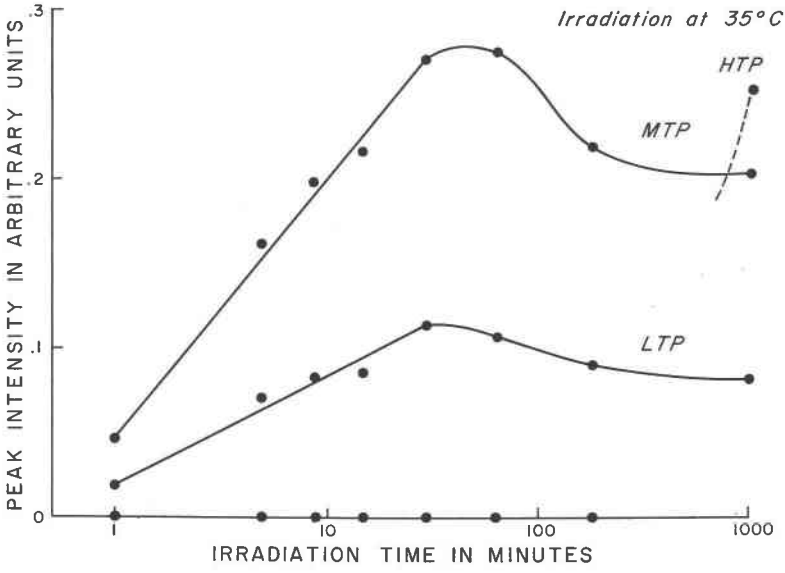

FIG. 2. Peak intensity vs. dose curves for the thermoluminescence produced by exposure to ultraviolet light in the low-temperature peak (LTP), middle-temperature peak (MTP), and high-temperature peak (HTP) of the Joplin calcite portion preheated to 300° C.

cesses and the bleaching processes during the ultraviolet illumination. Specifically, the equilibrium trapped charge concentrations will depend on the bleaching properties of the traps as well as the electron and hole formation or capture rates.

Figure 3 shows the dependence of peak height on total gamma-ray dose. These curves were also obtained with Joplin calcite heated at 300° C. for two and a half hours prior to exposure to gamma rays. Similar curves were obtained from all of the samples originating from all of the localities mentioned, after the same heat treatment and gamma irradiations. However, the Lakeside Limestone did not show the decrease beyond 10^7 R observed in the other samples. It should be noted that in all

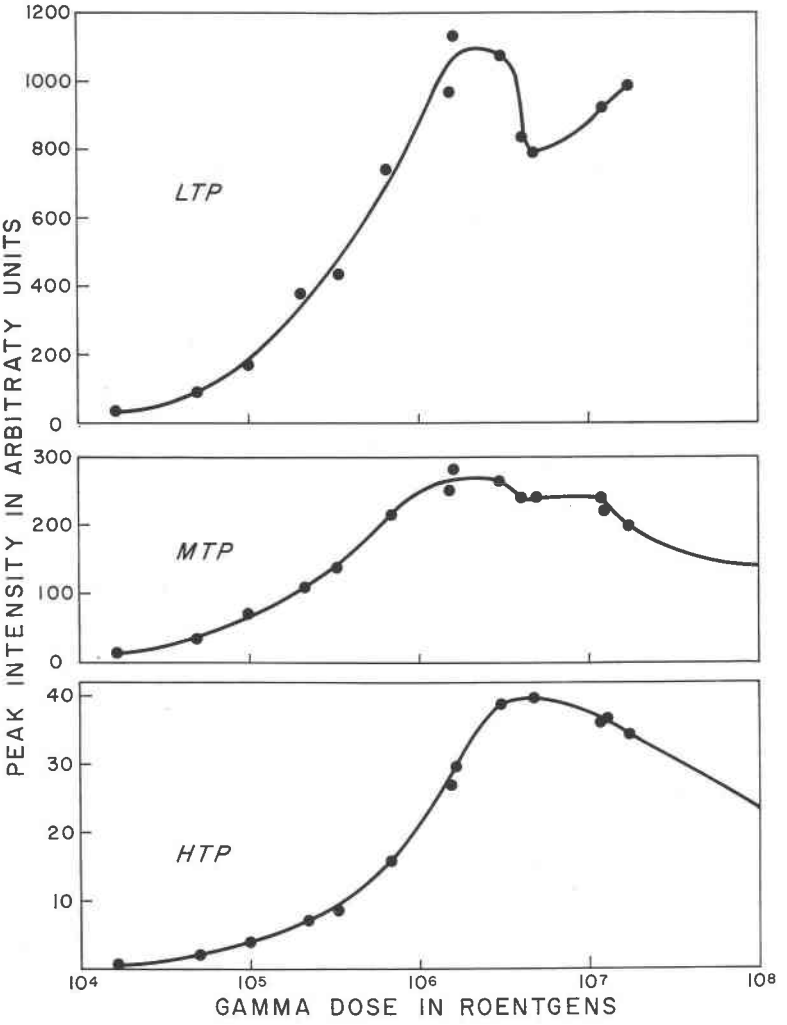

FIG. 3. Peak intensity vs. dose curves for the thermoluminescence produced by exposure to gamma rays in the low-temperature peak (LTP), middle temperature peak (MTP), and high-temperature peak (HTP) of the Joplin calcite portion preheated to 300° C.

cases the glow-curve peak intensity passes through a maximum at about 3×10^6 R.

Figure 4 shows the peak temperature as a function of gamma-ray dose. for the middle-temperature peak of the Lakeside Limestone. The same dependence on dose is observed for the other two peaks. Namely, the peak temperature is independent of dose up to 7×10^5 R, it shifts to lower

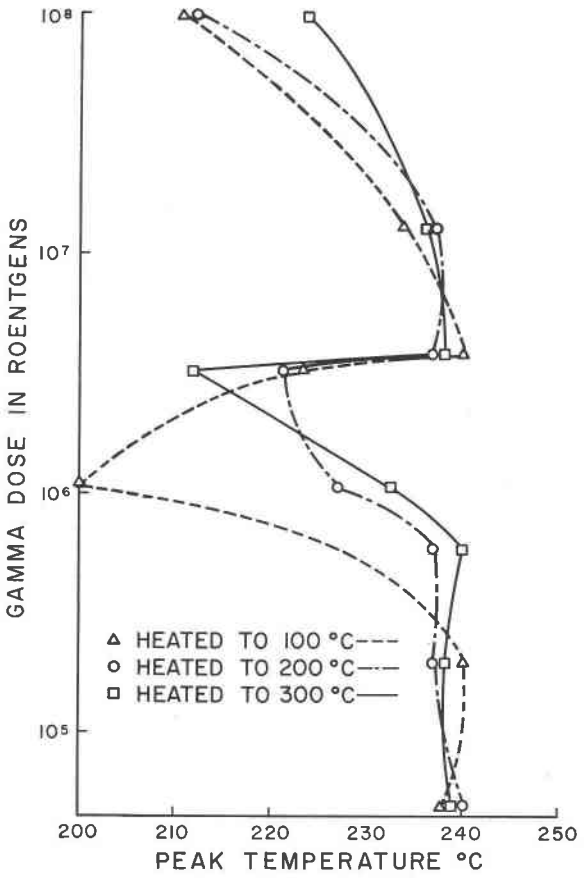

FIG. 4. Peak temperature vs. gamma-ray dose curves for the middle-temperature peak of the Lakeside Limestone. Similar behavior occurs in both the low-temperature and high-temperature peak.

temperatures in the range from 7×10^5 to 3×10^6 R, increases abruptly at 4×10^6 R, and beyond this dose shows a gradual decrease. It is significant that this behavior was observed in all three samples and the inflection points in the glow-curve peak temperature curve occur at the same doses as the inflection points in the peak intensity curves shown in Fig. 3. The same temperature shift, but to a lesser degree, is observed in the Iceland spar sample. The jump to higher temperatures occurring at 4×10^6 R is relatively small in the middle-temperature peak. This peak reaches constant intensity, as a function of increasing dose, up to 10^7 R in all three sample portions. The low-temperature peak in the portion pre-

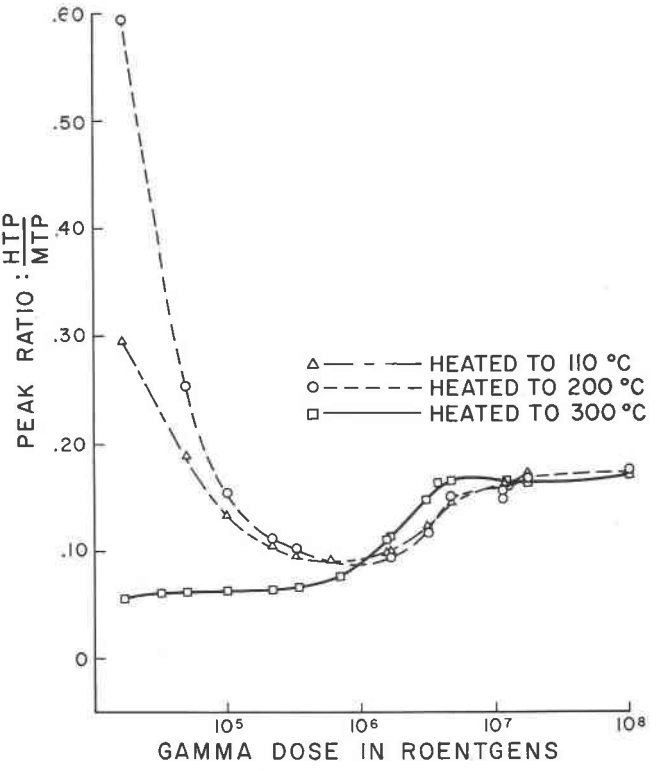

FIG. 5. The high-temperature to middle-temperature peak intensity ratios of the three portions of the Joplin calcite. Curves having the same shape were also obtained for the Lakeside Limestone.

heated at 110° C. shows a maximum in its peak intensity curve at 3×10^6 R. Its peak temperature increases 8° C. at 4×10^6 R.

It is evident that the jump to higher peak temperatures occurs at the same gamma-ray dose as the maxima in peak intensity. This indicates that some process is in operation which produces a relatively large trap depopulation with a relatively small increase in the total dose.

In order to aid in the analysis of this data, curves showing the ratio of the high-temperature peak to the middle-temperature peak height were prepared for all three portions of the Joplin calcite and Lakeside Limestone. The curves corresponding to the Joplin calcite are shown in Figure 5. They clearly show the effects of heat treatment prior to irradiation for doses below 10^6 R. However, at doses above 10^6 R the heat treatment has relatively little effect on the peak ratios. An explanation for these curves will be found in the section below.

Discussion

Previous publications relating to the thermoluminescence of calcite suggest that the three glow peaks are due to three different trapping levels. The data shown in Fig. 1A is consistent with this point of view. When gamma rays are used, the low-temperature traps are populated most rapidly. In the case of the ultraviolet light curves, the population of traps is more likely to occur when electrons are excited from the filled band into the conduction band. However, one must consider that once electrons are in traps they are subject to optical bleaching by absorption of light photons. For example, even though the low-temperature peak trap may be the one most easily filled during the illumination process, its optical absorption properties might make it susceptible to simultaneous bleaching from other wavelength. This explanation applies also to Fig. 1B. Figure 2 which shows the behavior of the glow-curve peaks of the Joplin calcite as a function of the time of exposure to ultraviolet light might appear at first glance to be at variance with this point of view. However, if the low and middle-temperature peak traps are not subjected to optical bleaching, it is probable that the high-temperature peak curve such as shown in this figure would be obtained.

The gamma-ray irradiation data is summarized in Figs. 3, 4 and 5. It was shown in the peak intensity curves presented in Fig. 3 that the peak intensity reaches a maximum at about 3×10^6 R when the samples are irradiated with gamma rays and after exposure for 60 minutes to ultraviolet light (Fig. 2). The maximum coincides with the jump of the peak to higher temperature and appears to be due to the disruption of the equilibrium between the number of electrons entering and leaving the traps. The equilibrium is reached at 3×10^6 R for the gamma dose rate to which the samples were exposed. Beyond this dose the competition for free electrons due to the production of a shallow defect below the low-temperature peak appears to be significant. This hypothesis is also demonstrated in Figure 4 which shows the shift to lower temperatures in the range from 7×10^5 to 3×10^6 R. This would occur if the electron were freed at low temperature and retrapped in the deeper upper levels.

The gradual movement of the peak position towards lower temperatures with increasing gamma-ray dose can be explained by the retrapping of the freed electrons in the level from which they came. Since decay of the trap population is a statistical process of the form

$$N = N_0 e^{-\lambda(E,T)t}$$

it is clear that the electron-hole recombination will be delayed, thus causing the peak to appear at a higher temperature than it would if no retrapping took place. It should be remembered, however, that re-

trapping is highly improbable if the traps are almost all filled and that it increases in probability as the number of filled traps decreases. In this way, retrapping can account for the observed shift to higher temperatures in samples which have a lower proportion of filled traps of a given energy. In the same way, peak temperatures could be expected to fall to its lowest level when the traps reached their maximum filling.

For purposes of discussion we should divide Fig. 5 into two parts relating to doses under 10^6 R, and above 5×10^6 R. Below 10^6 R the data is consistent with the point of view that the peak height depends only on the degree to which the traps present initially in the material are filled when the process of irradiation is started. To illustrate this, consider the curve in Fig. 5 for the portion of Joplin calcite heated for two and a half hours at 300° C. prior to irradiation. This curve indicates that the traps responsible for the middle and high-temperature peaks are filled at the same rate. The curves for the other two portions show that the population of the middle-temperature peak traps relative to the population of the high-temperature peak traps approaches the value obtained when the sample was originally drained completely. The data above 5×10^6 R in Fig. 5 is consistent with the introduction of a defect which gives rise to a trapping level shallower than that which accounts for the low-temperature peak. Inasmuch as the heights of the glow-curve peaks depend strongly on the equilibrium level, the introduction of a shallow trap will tend to remove charges from the peaks at high temperatures and re-distribute them in the lower temperature peaks. This is evident in Fig. 3.

The experimental results can also be explained by assuming that a glow-curve peak may not result from the freeing of electrons from traps of a single energy, but from a distribution of traps ranging from a minimum to maximum energy. By partially draining the traps which cause a specific glow peak and plotting the remaining intensity as a function of peak temperature, a shift to higher temperatures has been observed (Zeller and Ronca, 1963). In addition to the evidence furnished by the decay studies it was found that the peak temperature shifts to lower temperatures with increasing gamma radiation dose. These facts can also be used to support the model of a trap energy distribution rather than a single energy trap. It must be assumed that the electrons freed by gamma rays in the crystal lattice fill the deeper portion of the trap distributions first, and that this filling process continues from the high energy side to the low energy side of the distributions as the gamma-ray dose is increased.

It should be noted that in these samples approximately the same peak intensity maximum is reached for a given peak whether the sample has been thermally drained or not. No matter how much natural thermo-

luminescence the sample had, the same peak intensity level will be reached at about the same dose which was necessary for the drained sample portion, although the peak intensity increases with a lower slope. This can be explained by assuming that as the traps are populated, the physical distance which an electron must move between its point of origin and its nearest trap increases. At the same time the number of holes has increased and the probability of combination with a hole rather than a trap becomes more probable.

The data obtained from these high gamma radiation dose studies has been of substantial value in understanding some of the processes which take place in calcite. At the same time it is clear that thermoluminescence studies alone are not adequate to provide a full explanation of all of the observed phenomena. Work is now in progress in which thermoluminescence studies are being carried on in conjunction with electron spin resonance measurements. It is hoped that these investigations will provide answers to some of the questions which have been raised here.

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