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The Effects of Ultraviolet Light Illumination
on The Thermoluminescence of Calcite*

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ABSTRACT

Measurements of thermoluminescence spectra have been made on samples of natural and gamma-ray irradiated Joplin calcite. A study has been made of the effects on thermoluminescence spectra of illumination with ultraviolet light of various wavelengths. The purpose of this study is to determine the mechanism of charge redistribution between the defect centers responsible for the observed thermoluminescence. Illumination with ultraviolet light is shown to produce changes in the intensity of all glow peaks. Glow peaks which are thermally removed before illumination show increases in intensity upon illumination while peaks which are present before illumination are reduced in intensity. The rate at which changes are produced in the glow peaks depends on the temperature of the sample and wavelength of the light. Wavelengths in the region of 2900 and 2500 Å are particularly effective in producing changes in peak intensities. The effects of illumination are more pronounced in gamma-ray irradiated samples than in natural samples. The above effects may be accounted for in terms of a defect model which assumes the presence of three sets of charge traps and a recombination center in addition to the luminescent center.

INTRODUCTION

Analyses of the light emitted from calcium carbonates when heated above room temperature have been used in a variety of geological studies. Examples are stratigraphic correlation^(1,2), geological age determinations^(3,4), geothermometry⁽⁵⁾, and for the solution of paleoclimatological problems⁽⁶⁾. The material is usually heated linearly, and the resulting curve of luminescence as a function of temperature is called a glow curve or a thermoluminescence spectrum.

Surprising similarities are observed between glow curves obtained from a variety of natural and synthetic crystalline calcium carbonates. Usually there are four glow peaks above room temperature in the glow curve of calcite which has been subjected to ionizing radiation. The peaks occur at about 100, 220, 320, and 350°C at the heating rate used in this investigation and will be referred to as A, B, C, and D throughout this paper. Peak A decays slowly at room temperature, thus it is usually not observed in natural samples. The greatest variations between specimens occur in the region of peak A in the glow curve. Peaks B, and C seem to be common to most specimens, and have been used in paleoclimatological and dating investigations. Peak D is affected by the mechanical treatment of the material⁽⁷⁾. Other peaks have been observed at still higher temperatures but are not considered in this work⁽⁸⁾.

The glow peaks have been attributed to the thermal release of charges from traps. Kinetic models have been proposed to describe the emptying of the traps. These models are applicable to geological problems^(6,12). Also studies have been conducted on the glow peaks

emission spectra⁽⁹⁾, color centers^(8,10), and the properties of sensitizing centers in calcite⁽¹¹⁾. However, nothing is known about the detailed nature of the traps.

Certain features of the experimental glow curves, for example the shifts in temperature of peak maxima, depend on the degree to which a particular trap is populated with charge. This has led to the suggestion that the different glow peaks are not due to a single trap, but due to multiplicity of traps with different depths⁽¹²⁾. An alternative possibility, proposed earlier⁽¹³⁾ and supported by this work, is that a considerable amount of retrapping occurs, i.e. that charges released from one trap are redistributed, not only between luminescent centers, but between all the charge traps. In cases where redistribution of charge occurs in this way during measurement of glow curves, the measured intensities do not reflect the original population of the traps. The original populations can only be calculated if the mechanism of charge redistribution is known.

The purpose of this investigation was to determine charge redistribution kinetics by the selective emptying of traps. This was done by illuminating the samples with ultraviolet light of different wavelengths and determining the effects on the glow curves. Glow curves were determined after bleaching with different wavelength light but with a constant total number of photons at each wavelength. A number of bleaching experiments were also done with the light wavelength fixed and varying the total flux. Some bleaching experiments were done at elevated temperatures where the traps responsible for some of the peaks remain almost entirely depopulated.

Optical absorption measurements were made to determine whether the absorption spectrum changed as the trap population was altered.

EXPERIMENTAL

A natural calcite crystal from Joplin, Missouri was ground and sieved. The minus-100 plus-200 mesh fraction retained for the thermoluminescence measurements. Spectrochemical analysis indicate that this calcite contains 1 to 10 percent magnesium, about 1 percent iron, less than 0.1 percent vanadium, copper, and silicon, and between 0.1 and 1 percent manganese. The gamma-induced thermoluminescence of the same material had been reported in an earlier paper⁽¹³⁾. The thermoluminescence measurements reported here were made as follows. An RCA 6810A end-sensitive photomultiplier tube was used to measure the light output from the samples. Aliquots of the sample were placed in a flat-bottomed depression in the silver plate which formed the upper surface of the furnace. One junction of the chromel-alumel thermocouple was embedded in the silver plate, the other junction kept in an ice bath, and the temperature recorded using a strip chart recorder. The photomultiplier output was amplified and recorded simultaneously with the temperature to produce the glow curve. The sample was heated in air from 50°C to 425°C at a heating rate of 1°C per second. The glow curves were obtained immediately after optical bleaching by ultraviolet light. The furnace served as the sample holder in the experiments where monochromatic light was used. The sample was not disturbed throughout the bleaching and heating procedure.

The optical bleaching data on the glow curve peaks was obtained by illuminating the sample with ultraviolet light of different wavelengths

at room temperature. A Bausch and Lomb grating monochromator with an Osram HBO 200 mercury lamp was used. The width of the entrance and exit slits was set to obtain a band pass of 50Å.

The light intensity in the range from 2380 Å to 4000 Å was measured with an Eppley thermopile and a microvoltmeter. By varying the time of illumination, it was possible to expose the sample to a constant number of incident photons at any wavelength. The required illumination time was obtained from the formula

$$K = \frac{\mu}{eV} \times t$$

where K is a constant, μ is the thermopile output in microvolts, eV is the photon energy in electron volts, and t is the time of illumination in minutes.

The light from the monochromator was directed either on the thermopile or on the sample with a pivoted front-surfaced mirror placed in front of the monochromator. The bleaching was studied using the following experimental procedure: (1) An aliquot of the sample was spread evenly into a depression in the silver upper surface of the furnace. (2) At each wavelength, after determining the light intensity with the thermopile, the sample was illuminated for the time required to obtain a constant total photon flux. (3) The furnace was transferred to the thermoluminescence measuring apparatus and the glow-curve obtained. The procedure was repeated at different wavelengths.

Optical bleaching of samples at temperatures above room temperature was done using a Hanovia type SH mercury lamp with a Corning 7-54 filter. This provided illumination in the 2537 Å region. A copper plate with a chromel-alumel thermocouple soldered to it served as a sample

holder. A hot plate kept the sample at the desired temperature.

In order to study the effects of ultraviolet light illumination on the color centers of calcite, absorption measurements were made on sawed and polished pieces of Joplin calcite 2 mm thick. The crystal was sawed parallel to one of the cleavage faces. The absorption measurements were performed with a Cary recording spectrophotometer at room temperature. A BH 6 mercury lamp and a 2537 Å interference filter were used for the bleaching of the sample.

RESULTS

Illumination with monochromatic ultraviolet light produced marked changes in the population of the trapping centers responsible for the glow curve peaks that occur above room temperature. Figures 1 and 2 present the results of the bleaching experiment at different wavelengths of illumination. Peaks below 150°C were not detected in the untreated natural sample and the gamma-ray irradiated sample was heated at 100°C for 15 minutes to allow thermal bleaching of the low-temperature peak before the sample was illuminated with ultraviolet light. The height of the glow peaks prior to optical bleaching were approximately equal to the values shown in the long wavelength side of the Figures 1 and 2. It is evident in these figures that the peaks that were present before illumination, namely peaks B, C and D, are diminished in intensity, and that the intensity of peak A is increased. It should be noted that the height of peaks B and C have the same dependence on light wavelength and that the minima at 2900Å

and 2500Å in curves for B and C correspond to the maxima in the curves for peak A.

Since peak A decays to one half of its original value in about 3 hours at room temperature, its intensity after illumination at wavelengths where the lamp output is low, and irradiation times correspondingly lengthy, will be affected by thermal decay. In order to correct in Figs. 1 and 2 for the decay of peak A while the sample is being illuminated, data such as that shown in Figure 3 was obtained. This figure shows the decrease in intensity of peak A as a function of time for the gamma-ray irradiated sample when illuminated with 3150Å light. Similar data was obtained to correct the peak A in Fig. 1. The illumination time was increased and the light intensity was reduced with neutral density filters placed in front of the lamp. In order to ascertain that the observed decrease in the peak height was due to thermal effects and not to dose rate dependency, an additional set of measurements, shown in Figure 3, was obtained by illuminating the samples with the same dose of 3150Å light at the intensity corresponding to the 14 minute exposure and the samples allowed to rest in the dark after illumination for increasing lengths of time.

Figure 4 shows the decrease in size, as a function of integrated photon flux, of those peaks that were populated before illumination was started and the simultaneous growth of the peak that was absent. These curves were obtained by exposing natural calcite samples to ultraviolet light without any previous treatment. The curves for all three peaks are very similar in shape for both wavelengths of illumination. As expected from Figs. 1 and 2, bleaching with 2357Å light produces the greatest changes in the peaks. All curves tend to saturate as the bleaching time is increased.

In order to study the bleaching effects of ultraviolet light on the natural samples without having the trapping centers responsible for peak B populated, a portion of the sample was heated at 270°C for 30 minutes and then illuminated with 2537Å light. Figure 5 shows the decrease in intensity of peak D, and the simultaneous growth of peaks A and B as a function of dose. All curves in the figure tend to a nearly constant level after peak A has reached an intensity one eighth of that reached in the previous figure after similar exposure.

Figure 6 shows the effects of 2537Å light on the glow peaks of the samples which have been drained of all natural thermoluminescence by heating at 350°C for 24 hours. Peaks A and B increase linearly but the height of peak A at the largest dose is about one seventieth of that obtained by illumination on the untreated natural sample (Fig. 4). The intensities of peak D in the figure do not show any great change. It has been shown that this peak can be induced by mechanical treatment such as crushing⁽⁷⁾. Since the peak is only slightly affected by bleaching, it will be neglected in the remainder of the discussion.

The data obtained by illuminating untreated natural samples with filtered ultraviolet light in the region around 2537Å at temperatures above room temperature is shown in Figure 7. The samples were illuminated for 20 minutes at increasing temperatures of illumination. At room temperature, peaks B and D are reduced while peak A increases. Increasing the temperature of illumination causes a decrease in the population of the traps corresponding to peak A and the depopulation of the other two peak traps is significantly reduced. At the temperature at which traps A are not able to maintain a carrier population, the intensity of peaks B and D

approaches the level obtained before ultraviolet treatment. At higher temperatures, the intensity of peak B decreases rapidly.

The results of the absorption measurements are presented in Figure 8. Two absorption bands are evident at about 3300Å and 2550Å in the spectrum of the natural sample (curve A). The band at 2550Å is not well resolved, probably due to polarization effects in the spectrophotometer. The absorption spectrum corresponds to that which has been reported for poor quality crystals by Medlin⁽⁸⁾, who has also discussed the differences that can arise due to orientation of the specimen with respect to the axis of polarization of the light. After illumination for 240 hours with 2537Å light, the absorption spectrum is reduced (curve B), with the greatest effect in the 2550Å band.

DISCUSSION

Before discussing the results in any detail, mention must be made of the errors which arise in the measurement of a peak height in a glow curve. Consecutive points on most curves in the figures represent measurements on fresh samples and errors arise in the preparation of aliquots of the sample, its distribution in the sample holder, and the positioning of the sample holder in the optical bleaching apparatus and in the thermoluminescence apparatus. Even with great care, an uncertainty of about 5% must be expected. However, although some of the detailed structure may not be real, the general trends represented by the curves drawn in the figures should be reliable.

A number of things are evident from the results: 1) Subjecting samples of Joplin calcite to ultraviolet light illumination produces marked changes in observed size of the glow peaks. This can result from either changes in the occupancy of charge traps or changes in the probability that the carriers will produce luminescence when they are released thermally from the traps. The changes produced are relatively greater in the gamma-ray irradiated than in the natural samples. 2) The effect of ultraviolet light illumination is wavelength dependent. The curves for A and the changes which occur in curves for B and C in Figures 1 and 2 resemble optical absorption spectra. Light in the region of $2900\text{\AA}$ and $2500\text{\AA}$ seems to have the greatest effect on the intensity of the peaks. The bleaching effect shows a general increase in the region of shorter wavelengths where the optical absorption is increasing. The rapid decrease in the effect at very short wavelengths is probably related to strong interband absorption. This would limit any bleaching effects to thin layers on the surface of the material. 3) Curves showing peak heights with increasing dose, for fixed wavelength (Figures 4 and 5) show that above certain dose the effect apparently reaches constant levels. These levels depend on the wavelength of illumination. For a sample heated to 350°C the effect of optical bleaching is different. In this case, illumination produces a linear increase in heights of peaks A and B and the peaks are very small in comparison with samples which had not been heated. 4) The effect of the illumination is to reduce peak heights when the peaks would be present in the unexposed sample, and to increase peaks which had been removed by thermal bleaching (see for example peak B in Figures 5 and 6). 5) The curves

of Figure 7 for illumination at elevated temperatures show two effects. The first is a reduction in peak heights at temperatures near those at which the peaks are removed thermally, and secondly there is a reduction in peak intensity due to the illumination. The latter reduction occurs only in the region near room temperature where peak A has not been thermally removed.

It is possible to present a model for the behavior of the trapping centers in calcite which accounts for the above effects. This model is not unique and it requires a number of assumptions. First the assumption is made that each of the major glow peaks A, B, and C results from the thermal emptying of one of three different sets of charge traps, and that the charge involved, probably an electron⁽⁸⁾, is the same for all traps. Secondly it is assumed that, in addition to the luminescent recombination center, there is another defect center R which is capable of being ionized, providing a free electron and a positively charged recombination center. A variety of such centers is probably present in most natural materials.

Electrons released from these centers (R) by ultraviolet light illumination may become trapped at any of the traps, A, B, and C, may recombine with positive holes at the centers R, or may recombine at the luminescent centers. In the same way, during the measurement of a glow curve, electrons leaving the traps may either be retrapped at deeper traps, may recombine with positive holes at the centers R (without emitting light), or may recombine at a luminescent center (with the emission of light).

The effectiveness of illumination in producing peak A is greatly dependent on the heat treatment to which the sample has been subjected

before illumination. This can be seen in Figures 4, 5 and 6 by comparing values of intensity of peak A for the same dose of ultraviolet illumination in the following three cases: A natural sample, one heated to 270°C and one heated to beyond 350°C. This effect is probably related to the decreases in optical absorption which occur when samples are heated⁽⁸⁾.

In the same way, the relatively much larger peak A which appears after illumination in the sample which had been gamma-ray irradiated (see Figures 1 and 2) is due to increased optical absorption due to irradiation.

A number of results suggest that charged radiationless recombination centers R, not the trapping centers, are responsible for the impurity related optical absorption in the ultraviolet. Heating the sample reduces the amount of absorption but produces little change in the shape of the absorption spectrum. The changes in shape of the absorption spectrum are smaller than would be expected if the charged trapping centers themselves were responsible for the absorption system. In addition, in contrast to the findings of Medlin⁽⁸⁾, ultraviolet illumination reduces the optical absorption, but increases the population of traps responsible for peak A. On heating the sample, the reductions in optical absorption which occurs when charges are released from trapping centers are attributed to the return of these charges to the centers R.

The effect of illumination can be described as follows: charges released from R populate the trapping centers responsible for peak A. These trapping centers have the largest concentration in comparison to the other trapping centers and may, in addition, have large trapping cross-sections. The charge population of traps B and C are relatively unaffected but, when the glow curve is measured, the peak heights in the regions B and C suffer

an apparent reduction due to an increased number of non-radiative recombinations which occur at R, and possibly also a reduction in the number of available luminescent recombination centers as a result of the production and emptying of peak A. As shown in Figure 7, it is only when the sample is illuminated at temperatures at which traps responsible for peak A are capable of retaining charge, that a reduction occurs in the heights of peaks B and C.

The constant levels reached upon long illumination shown in Figures 4 and 5 are related to the saturation which occurs in the intensity of peak A. It could be due to the thermal instability of A at room temperature limiting the population of A to a fixed level after long periods of illumination. The maximum population level of A depends on the light intensity, the wavelength of illumination and the amount of optical absorption. As expected, the level of saturation of A is lower for 3100 Å than 2500 Å, and is lower in the sample which has been heated to 270°C.

In conclusion, ultraviolet light illumination has been shown to affect the intensities of glow peaks in natural and gamma-ray irradiated Joplin calcite in a way which depends on the wavelength of illumination and on the temperature of the sample. The general behavior of the glow peaks can be accounted for by assuming the presence of an optically active center R, which upon illumination provides charges which populate traps responsible for peaks in the region of 100°C and which, when charged, may affect glow peak intensities by providing a radiationless recombination center.

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Figure Captions

Figure 1. The figure shows the heights of the various peaks in Joplin calcite after illumination with constant numbers of photons of various wavelengths. The peak heights which were observed before illumination have the values 0, 23.6, and 10.3 for peaks A, B, and C + D respectively.

Figure 2. Peak heights of the various peaks in gamma-ray irradiated Joplin calcite after illumination with constant number of photons of various wavelengths. In this case, peaks C and D could be separately resolved. The peak heights which were observed before illumination have the values, 0, 198, 16, and 19 for peaks A, B, C, and D respectively.

Figure 3. The intensity of peak A as a function of time of illumination for a constant total number of photons incident on the specimen. To obtain values represented by the open circles, the intensity of illumination was successively reduced in order to give the exposure time shown in the diagram. The values represented by the filled circles each correspond to a 14 minute illumination time and then a varying time delay before measurement of the glow peak height

Figure 4. The variation of peak heights A, B, and C + D as a function of the total number of photons incident on the specimen. The solid and the dashed lines correspond to wavelengths 2537 $\text{\AA}$ and 3100 $\text{\AA}$ respectively.

Figure 5. The intensities of the glow peaks as a function of total number of photons incident on specimens which had prior to illumination been heated at a temperature at which glow peaks A and B are thermally unstable. Note that this figure has a smaller scale on the ordinate than Figure 4.

Figure 6. Peak heights A, B, and D plotted as a function of total number of photons incident on samples which had previously been heated to a temperature at which all peaks are thermally unstable. Note the much smaller scale in the ordinate on this figure than in Figures 4 and 5. The intensity of peak C was not measurable. The intensities for peak D are not a function of the illumination, but arise from mechanical disturbance of the sample.

Figure 7. The figure shows peak heights for constant illumination dose as a function of the temperature at which the sample was kept during the illumination. The intensities of the peaks before illumination were 0, 23.6, and 10.3 for peaks A, B, and C + D respectively.

Figure 8. Curve A shows the optical absorption in natural Joplin calcite. Curve B shows the same sample after illumination for 240 hours with a BH 6 lamp and 2537 Å⁰ filter. The difference between curves A and B is also plotted in the diagram.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8