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THERMOLUMINESCENCE OF FLUORITE AND AGE OF DEPOSITION

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ABSTRACT

Measurements of natural and radiation-activated thermoluminescence, radioactivity, and strontium and yttrium content are presented for 35 samples of fluorite ranging in age from Precambrian to late Tertiary. No "fluorite-type" glow curve of natural thermoluminescence could be recognized. No specific correlation was found between thermoluminescence and strontium and yttrium content. In addition to draining electron traps, heating modifies the traps so that it is not possible by irradiation to duplicate exactly the natural glow curve. The temperatures at which glow-curve peaks appear in irradiated fluorite are independent of the energy of the activating photons.

Of the several parameters determined from the data, geologic age of deposition correlates roughly with the dose of gamma radiation required to "reproduce," in the de-activated fluorite, the middle-temperature portion of the natural thermoluminescence glow curve. Thermoluminescence cannot be used, at present, as a reliable guide to age of fluorite mineralization.

INTRODUCTION

Thermoluminescence is the emission of visible light when a material is heated at temperatures below incandescence. If an insulating crystalline substance is subjected to ionizing radiation, energy is transferred to the crystal and may be manifested in the dissociation of some electrons from their original atoms; these excited electrons may then become permanently or semipermanently trapped in various types of lattice defects. The lifetime of this excited state depends on the energy of the trap and on the temperature at which the substance is maintained. If the substance is heated, a trapped electron may return to a lower energy level and emit a photon of light. The rate of return of electrons is temperature-controlled so that maxima of emitted light occur at specific temperatures, the several maxima which are present each representing a certain energy of trapped electrons. Measurement of the intensity of the emitted light as a function of temperature makes it possible to construct a glow curve for the substance. Normally, a glow curve consists of several peaks between room temperature and incandescence.

Thermoluminescent characteristics of minerals and rocks are known to be related to such factors as origin, composition, radioactivity, age, temperature and pressure environment during and after formation, and geologic history of the materials; as yet, however, thermoluminescence as a tool in geologic interpretation is severely limited. This paper reports the results of investigations into relationships between thermoluminescence (natural and radiation-activated), radioactivity, and geologic age of deposition of fluorite.

Methods

Each sample of fluorite was crushed and sieved, and fifty milligrams in the size range 40 to 60 mesh were used for determination of natural thermoluminescence. The fluorite passing the 60-mesh sieve was further ground to a fine powder and was used for radioanalysis and trace element determinations. The grains retained on the 40-mesh sieve were heated to 600 degrees centigrade and maintained at that temperature for about 15 minutes, to remove all natural thermoluminescence. This material was recrushed and sieved, and samples consisting of 50 milligrams of this heat-treated material were used for determination of radiation-activated thermoluminescence.

Radiation-activated thermoluminescence was induced in the heat-treated samples by means of a source of electromagnetic radiation of 1.33 and 1.17 Mev energy gamma photons resulting from the radioactive decay of Co-60. The time of irradiation varied from a fraction of a minute to several hours, depending upon the dose desired, and the actual dose received by the specimen was determined from a calibration curve based upon the original activity and the half-life of Co-60.

After preparation, a sample was distributed evenly over the bottom of a sample holder, and the various components of the heating and light-measuring apparatus were positioned. As the temperature was raised, at a linear rate of 100 degrees centigrade per minute, the intensity of the emitted light was read at intervals of 10 degrees from the galvanometer of a Photovolt Electronic Photometer (Model 514-M); data recorded in this manner were used to construct glow curves for the samples. The glow curve consists of the intensity of emitted light plotted on a vertical scale against temperature on the horizontal scale.

Each of the fluorite samples was analyzed for alpha, gamma, and gross (alpha and beta) radiation. The radioanalyses were recalculated to micro-microcuries per gram by comparison with a uranium oxide standard (Table 1). *X*-ray spectrochemical methods were used in analyzing for strontium and yttrium, the most abundant and widespread minor elements in fluorite (Table 1).

Results

Sample locations, geologic age, approximate absolute age, radioactivity, and spectrochemical analyses for the samples are given in Table 1. Thermoluminescence data is summarized in Figs. 1 and 2.

Natural Thermoluminescence (Fig. 1). All of the 35 samples studied showed natural thermoluminescence, but with variations in maximum intensity, temperature of maxima, and number of peaks. The most

TABLE 1. SAMPLE LOCATIONS, AGE, RADIOANALYSIS, AND MINOR ELEMENTS

Sample	Radioactivity (μμc./gm.)			Minor Elements		Age $\times 10^6$ Years
	Alpha-Beta	Alpha	Gamma	Y	Sr	
Jamestown district, Colo. (post-early Tertiary[1])						~50
J-1	96	2.0	bkg.	55	140	
J-2	581	3.9	11.3	46	230	
J-3	1,480	2.6	21.9	96	800	
J-4	bkg.	bkg.	bkg.	520	2,500	
J-5	127	1.1	4.0	125	230	
J-6	1,880	17.3	84.1	50	1,150	
J-7	1,434	14.3	67.4	100	800	
J-8	2,914	4.3	11.8	86	1,200	
Northgate district, Colo. (post-Oligocene White River gr.[2])						~20
N-1	11.3	bkg.	bkg.	130	17	
N-2	60.2	1.1	3.7	240	18	
N-3	16.3	bkg.	2.3	50	9	
N-4	44.7	bkg.	bkg.	130	17	
N-5	bkg.	0.2	bkg.	n.d.	22	
N-6	21.9	0.5	2.7	14	37	
N-7	430	8.2	4.7	n.d.	120	
N-8	27.4	2.1	bkg.	37	19	
Wagon Wheel Gap, Colo. (probable Quarternary)						~5
W-1	31.2	0.27	3.1	155	70	
W-2	214	11.3	40.6	20	66	
W-3	26.4	bkg.	bkg.	25	50	
W-4	0.2	bkg.	bkg.	44	86	
Zuni Mountains, N. M. (post Permian, pre-Quarternary[3])						<230
Z-1	48.6	1.2	1.7	530	n.d.	
Z-2	37.3	0.4	20.4	620	10	
Z-3	4.3	bkg.	bkg.	750	n.d.	
Z-4	17.5	bkg.	bkg.	195	n.d.	
Z-5	91	1.3	11.4	640	8	
Lake George, Colo. (late Precambrian)						~600
LG-1	3.7	bkg.	bkg.	1,250	10	
LG-2	423	6.1	114.4	740	7	
South Platte, Colo. (late Precambrian)						~600
SP-1	31.3	bkg.	4.3	1,900	31	
Thomas Range district, Utah (probable Pliocene[4])						~5
T-1	8,120	54.1	243	n.d.	15	
T-2	5,340	29.6	173	n.d.	15	
Browns Canyon, Colo. (post-Oligocene or Miocene, pre-Pliocene[5])						~12
B-2				66	58	
B-4	17.1	bkg.	bkg.	26	140	
Poncha Springs, Colo. (late Tertiary or Quarternary)						~12
P-2	bkg.	bkg.	bkg.	50–500	100	
Rosiclare, Illinois (post-Carboniferous)						<280
R-3	151	4.7	5.3	15	10	
Amelia C.H., Va. (Precambrian)						>600
A-1	351	4.7	15.6	500	50	

[1] Goddard, 1946
[2] Steven, 1954
[3] Rothrock, *et al.*, 1946
[4] Staatz and Carr, 1964
[5] Van Alstine, oral comm.

strongly thermoluminescent fluorite showed a maximum intensity of emitted light about 260 times greater than the most weakly thermoluminescent. Most of the fluorite samples showed a low-temperature peak or inflection at about 155 ± 10 degrees. The most pronounced peak or

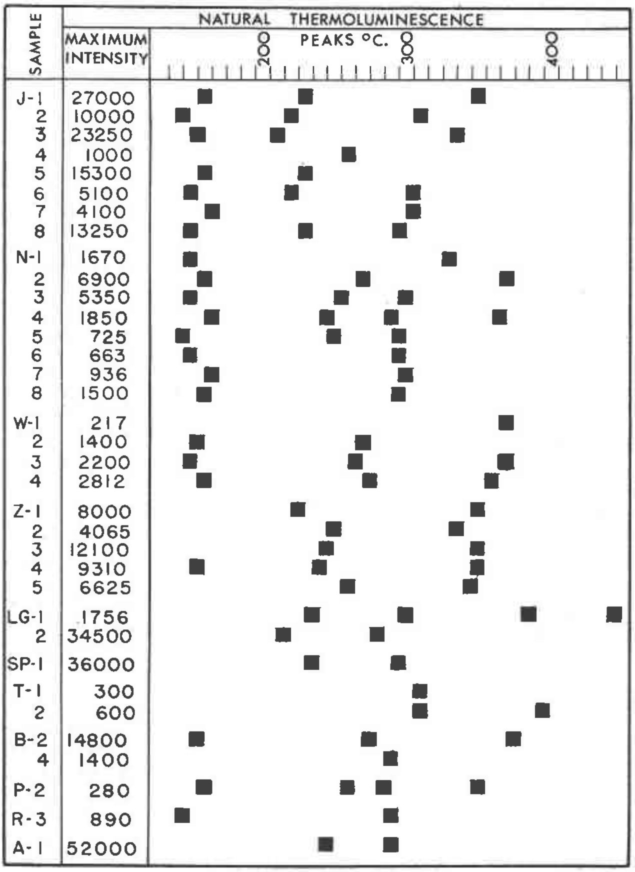

Fig. 1. Maximum intensity (arbitrary units) and peak temperatures from glow curves of natural thermoluminescence.

peaks generally occurred at various temperatures in the middle-temperature range from 210 to 270 degrees. In the higher-temperature range, many of the samples showed a peak between 290 and 375 degrees, and one sample showed a peak at 445 degrees. Intensity ratios for low-, middle-, and high-temperature peaks varied considerably from sample to sample. Among natural fluorites, no "fluorite-type" glow curve could be recognized; maximum intensity of thermoluminescence, the temperature at which peaks occur, the number of peaks, and the intensity ratios of the peaks vary widely. No specific correlation could be found between glow-curve characteristics and content of the predominant trace elements yttrium and strontium, perhaps because the configuration of a glow

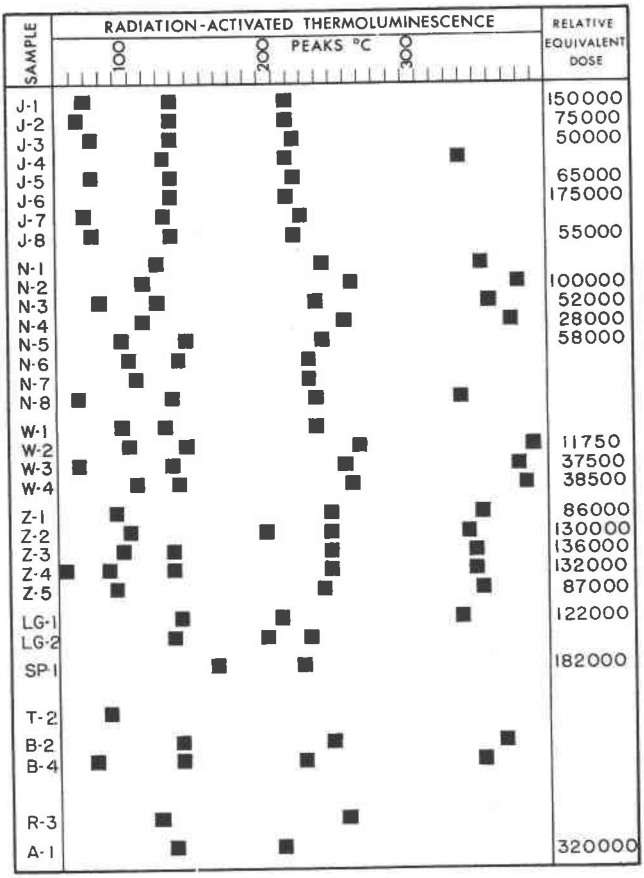

FIG. 2. Peak temperatures and relative equivalent dose from glow curves of radiation-activated thermoluminescence.

curve is controlled by undetected, less abundant trace elements or by the thermal history and pressure conditions.

From preliminary work on pure and rare earth doped synthetic crystals of CaF_2 and from conclusions reached by Moore (1965) on synthetic CaF_2, it seems entirely possible that there is a theoretical "fluorite-type" glow curve which can be closely approximated using pure synthetic CaF_2, but which is rarely if ever closely approximated in the natural glow curves of fluorite. Single crystals of pure synthetic fluorite display very weak thermoluminescence; gamma-irradiation drastically increases the intensity of thermoluminescence without significantly shifting the temperatures at which peaks appear. Apparently, gamma-radiation is not important in causing structural damage within the lattice. This is further supported by the observation that in natural fluorite a very large dose of gamma-radiation does not shift the temperatures at which glow-curve peaks appear. The presence of trace amounts of transition elements in synthetic CaF_2 modifies the type glow curve. Most natural fluorites contain significant amounts of several different solid solution impurities which perhaps results in masking a type glow curve. In addition, alpha-activity (which is measurable in almost all fluorites) not only activates thermoluminescence, but perhaps also causes structural damage resulting in new traps which in turn modify the glow-curve configuration. Again, the type glow curve is masked. Further work along these lines is in progress.

Radiation-Induced Thermoluminescence (*Fig. 2*). All the samples showed artificially-activated thermoluminescence, but with varying characteristics. The temperatures at which peaks occurred were approximately 80 ± 10, 105 ± 10, 135 ± 10, between 190 and 260, and 355 ± 20 degrees. The 80, 105, 135, and 355 degree peaks, when present, were rather uniformly at the specified temperatures. Within the range 190 to 270 degrees, a peak or peaks occurred at various temperatures, depending on the individual sample. Glow curves of heat-treated and irradiated fluorites conform more closely to a "fluorite-type" glow curve than do natural thermoluminescent glow curves.

The intensities of the lower-temperature maxima for each sample depend upon the radiation dose received, and on the temperature maintained and the length of the time between irradiation and heating. As the elapsed time increases, the intensities of low-temperature peaks are reduced as a result of draining of the low-energy (low-temperature) electron traps. The intensities of the moderate- and high-temperature peaks for each sample are dependent on the radiation dose received (Fig. 3B). In general, as the radiation dose is increased the intensity of the various peaks increases, though not necessarily at the same rate (Fig. 3C). Eventually a saturation dose is reached and further increase of the radiation dose does not measurably increase the intensity of the thermoluminescence.

In addition to the method of irradiation described above, one sample was also irradiated with unfiltered x-rays produced by a tungsten tube operated at 60 kilovolts and 35 milliamperes. The glow curve obtained

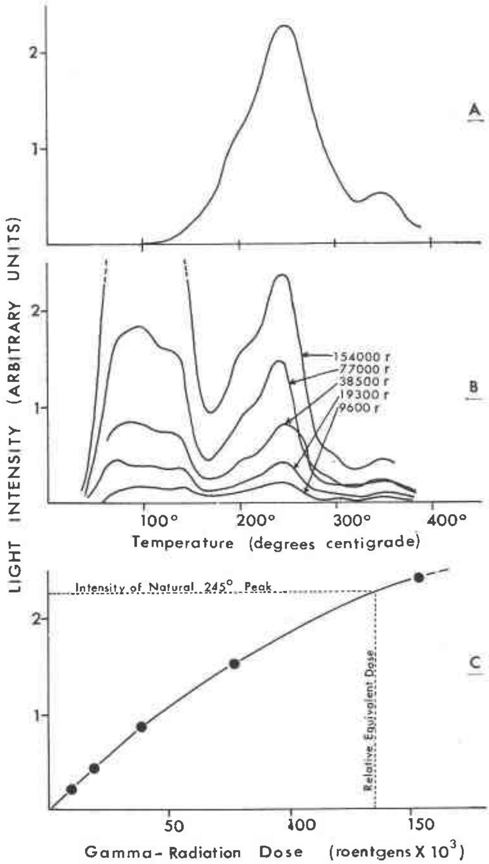

FIG. 3. Natural and radiation-activated glow curves and calibration curve for sample Z-3. A, natural glow curve; B, radiation-activated glow curves representing five different doses of radiation; C, calibration curve based upon the 245 degree glow-curve peak. The natural glow curve is "duplicated" by a dose of approximately 136,000 roentgens.

from this specimen showed the same peaks and general shape as the curve obtained from the sample irradiated by gamma rays from the Co-60 irradiator.

Comparison of Natural and Radiation-Induced Thermoluminescence. By comparison of the natural glow curve with the corresponding artificially-activated glow curves the samples were grouped into three categories:

(1) Those fluorites for which the natural thermoluminescence was very nearly duplicated by exposure to a suitable dose of gamma radiation. In this group the low-temperature peaks produced by irradiation were not found in the natural glow curves, because of drain-

ing of the low-energy traps under natural conditions (Fig. 3). (2) Those samples in which at least one peak on the natural glow curve was matched or nearly matched (in temperature) by a peak on the artificially-activated glow curve. In these samples the matching peak is commonly within the temperature range 225 to 260 degrees. (3) Those samples for which no match was found between natural and artificially-activated thermoluminescence.

Even neglecting the low-temperature peaks, it was not possible by the methods used in this study to duplicate exactly the natural glow curve. The discrepancy is either a small difference in peak temperature, or the shape of the glow curves is different, the artificially-activated specimens generally yielding glow curves with less dispersion to the peak. Apparently, heating the fluorite not only drains the filled electron traps, but also modifies the "depth" of traps, either slightly or greatly.

Thermoluminescence and Geologic Age. It has been noted that older rocks and minerals generally show stronger thermoluminescence than younger ones (Daniels *et al.*, 1953). Parks and Saunders (1951) stated that thermoluminescent intensity of fluorite per unit of radioactivity bears a direct relationship to geologic age of deposition. Zeller, *et al.* (1957) reported that for calcite the radiation dose required to duplicate certain natural thermoluminescent glow-curve peaks (relative equivalent dose) divided by alpha activity of the sample is a linear function of geologic age of deposition. Zeller (1959) suggested that data on the intensity of very low-temperature thermoluminescence and on the natural radioactivity of carbonate rocks from Antarctica might together be useful in determining the length of time which the rocks have been subjected to low temperatures (also see Zeller and Pearn, 1960; Ronca, 1964). Angino (1959) reported that the ratio of thermoluminescence intensity of pressed samples to unpressed samples of Tertiary and Quarternary limestones is related to the age of the rocks. Komovskiy and Lozhnikova (1959) reported that the intensities of thermoluminescence of certain granites are related to the relative ages of the rocks. Thermoluminescence radiation dosimetry has been used with some success by Johnson (1963) to calculate the age of dikes cutting carbonate rocks.

The natural thermoluminescence of a mineral at a specific temperature is believed to be a function of

(1) the number and kinds of crystalline defects, (2) the amount of high-energy radiation received by the material, (3) the temperature at which the material has been maintained, and (4) various factors related to the experimental technique (Lewis, *et al.*, 1959, p. 1125).

If the number and kinds of crystalline defects are neither altered by heating to remove natural thermoluminescence nor by subsequent crushing, if the material was non-thermoluminescent immediately after crystallization, and if natural thermoluminescence has not been modified by natural heating or pressure, then the amount of radiation energy required to reproduce a natural peak should be a function of the radioactivity which the sample has "felt" (the radioactivity of the sample and environment) times the time interval involved (geologic age). As a first approximation, dividing the amount of radiation required to duplicate the natural glow curve by the radioactivity of the sample should yield a parameter related to the age of formation of the sample. Data collected in this study are now considered in terms of this and other theses.

A graph of maximum intensity of thermoluminescence plotted against geologic age shows that older fluorites do tend to show stronger thermoluminescence, but this tendency is so poorly defined that it cannot be considered as a usable relationship. Geologic age plotted against maximum intensity of thermoluminescence divided by alpha, beta, and gamma activities, and against relative equivalent dose (defined below) divided by alpha, beta, and gamma activities yield nearly random distributions of points. Figure 4 shows the relative equivalent dose for moderate-temperature peaks plotted against geologic age. The relative equivalent dose (as used here) is the gamma-radiation dose required to reproduce as nearly as possible the middle-temperature portion of the natural glow curve (Fig. 3). Because of the dissimilar appearance of some of the corresponding natural and radiation-induced glow curves, it was possible to determine relative equivalent dose for only 21 of the 35 samples studied. Because of incomplete knowledge of geologic age, possible variations in the position of points along the horizontal axis are indicated by an arrow (Fig. 4). The points on this graph fall within a linear zone indicating a rough correlation between geologic age and relative equivalent dose.

Saturation of thermoluminescence sets the maximum age that might be determinable by a thermoluminescence technique. Furthermore, because saturation is asymptotically approached, the likelihood of considerable error increases rapidly as saturation is approached. Among the samples for which a relative equivalent dose could be determined, the estimated degree of saturation ranged from 20 to 85% with one sample (A-1) reaching 100%. For this completely saturated fluorite, the relative equivalent dose must be considered a minimum, and in Fig. 4 the point corresponding to this sample may be higher on the vertical scale (note vertical arrow). As would be expected, the geologically older fluorites and the more highly radioactive samples do generally show a higher degree of approach to saturation.

Summary and Conclusions

1. All of the fluorite samples which were tested showed natural thermoluminescence, but with variations, from sample to sample, in number and

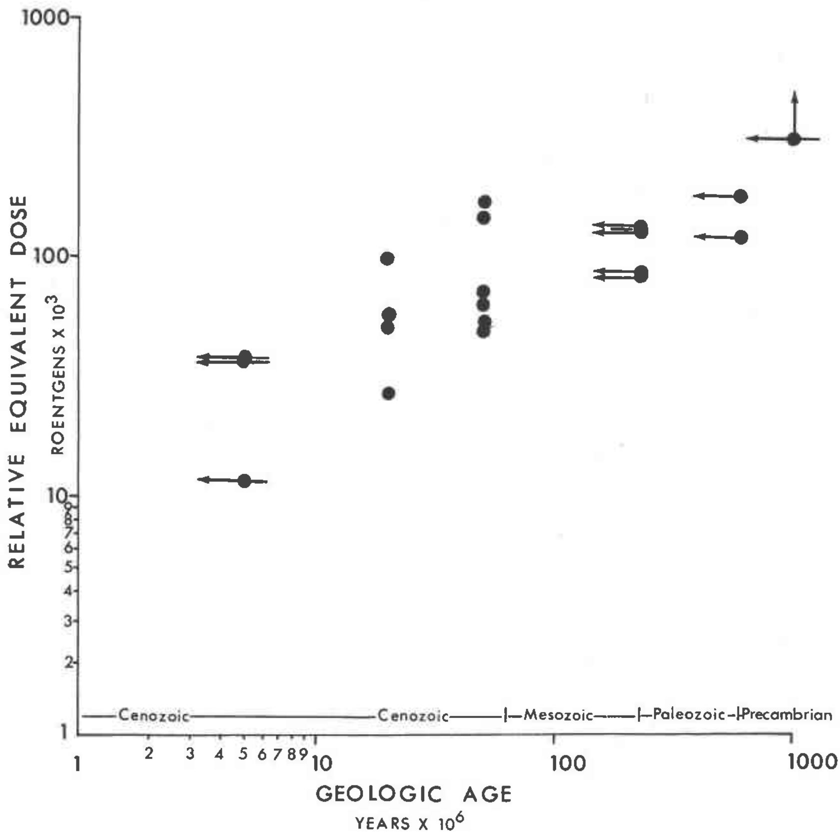

FIG. 4. Relative equivalent dose plotted against geologic age of fluorite mineralization. Logarithmic scales. Horizontal arrows indicate direction of possible error in geologic ages. Vertical arrow indicates saturation (the position of the point could be higher).

temperature of glow-curve peaks and in intensities and intensity ratios of the peaks. For natural CaF_2, there is no "fluorite-type" glow curve. Similarities in the form of the glow curves were noted, however, for different samples from the same fluorite district. No definite correlation was found between thermoluminescence and predominant trace elements (strontium and yttrium), probably because the glow-curve configuration is influenced more strongly by temperature and pressure conditions during and after crystallization or by less abundant trace elements.

2. Gamma-radiation reactivates thermoluminescence in deactivated (heated) fluorite, but the glow curve which is obtained is not identical with that of the natural fluorite. Apparently, heating not only drains traps, but modifies them, slightly in some instances, greatly in others.

Glow curves from reactivated fluorites conform more closely to a "fluorite-type" glow curve. The temperatures at which radiation-activated glow-curve peaks occur are independent of the energy of the activating photons.

3. Relative equivalent dose (the gamma-radiation dose required to reproduce as nearly as possible a certain part of the natural glow curve) shows a rough correlation with geologic age. Neither maximum intensity, maximum intensity of thermoluminescence divided by radioactivity, nor relative equivalent dose divided by radioactivity, seem to be related to age. This anomalous unimportance of radioactivity of the samples may be due to errors in extremely low-level radiation counting or may be because the sample analyzed is not representative of the quantity and kinds of radiation which the sample actually absorbed in nature. Data from this study, and a review of the literature on thermoluminescence of other minerals, show that thermoluminescence cannot, as yet, be used as a reliable indicator of geologic age.

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