

RADIATION DOSIMETRY FROM THE NATURAL  
THERMOLUMINESCENCE OF FOSSIL SHELLS<sup>1</sup>

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ABSTRACT

Absolute radiation dosimetry may be obtained from natural materials using the principles and techniques developed and utilized in medical and radiation physics. The problems peculiar to natural thermoluminescence dosimetry are (1) post-irradiation calibration techniques, (2) dose equivalency factors, and (3) secular equilibrium effects. These problems are illustrated and solutions are suggested by a study of naturally thermoluminescent mollusc shells. The dose equivalence and dose rates measured in these shells agree well with the known radioactivities of these materials and environments. It is suggested, therefore, that the natural radiation dosimetry of post-Pliocene calcites may be used as a basis for relative age and time correlations.

INTRODUCTION

The overwhelming use of thermoluminescence today is for purposes of radiation dosimetry (Attix, 1967). A considerable body of knowledge concerning such absolute dosimetry can be carried over into the interpretation of natural thermoluminescence (Johnson, 1963). Thermoluminescence as it occurs naturally in rocks and minerals, however, differs from the laboratory dosimetry situation in several important respects. This study describes the use, problems, and techniques involved with using natural thermoluminescence as a long-term radiation dosimeter.

Shells of *Ostrea* and *Pecten* were used for this dosimetry evaluation because:

1. These species characteristically secrete calcitic shells with a good thermoluminescence potential (Johnson, 1960).
2. The composition of the shells and environment of deposition is relatively uniform.
3. These species range over a large geologic time span.

The object of this study was to evaluate the basis of natural thermoluminescence dosimetry with respect to the effects of diagenesis, thermal-radiation equilibrium and radiation damage. The usefulness of natural radiation dosimetry as a means of stratigraphic correlation would also be tested.

<sup>1</sup> Presented in part at the NATO-USAF Conference on Applications of Thermoluminescence to Geological Problems, Spoleto, Italy, September, 1966.

## THERMOLUMINESCENCE DOSIMETRY

The thermoluminescence dosimetry systems presently in use rely on the fact that the amount of thermoluminescence accumulated in a given phosphor is proportional to the amount of radiation received by that phosphor. The dose-thermoluminescence characteristics for each batch of phosphor must be determined separately under controlled conditions. Normally this calibration process is done on a representative fraction of the phosphor before it is used as a dosimeter. Occurrences of natural thermoluminescence may be calibrated in a like manner under a given set of laboratory conditions and the equivalent dosimetry specified. However, the calibration in this case is after the fact and not before as in the case of ordinary dosimetry.

In the interpretation of thermoluminescence dosimetry readings, the wavelength or energy dependence effect must be accounted for. Different wavelengths of electromagnetic radiation or different kinetic energies of corpuscular radiation may vary in their efficiency for inducing thermoluminescence. The interpretation of the thermoluminescence must, therefore, relate to the radiation type used during the calibration. Natural radiations are mixed and complicated as compared to the usual calibration radiations, so the energy dependence effect is pronounced for natural thermoluminescence. A third factor involved with natural thermoluminescence dosimetry is the slow rates of irradiation found in nature. In laboratory dosimetry situations, the read-out of the thermoluminescence is accomplished within a short period of time which represents only a small fraction of the storage half-life of the thermoluminescence. In natural thermoluminescence, the read-out may take place many half-lives after initial irradiation. The relative stability of the thermoluminescence with respect to thermal conditions and the irradiation rate, therefore, becomes important (Zeller and Ronca, 1963a; Johnson, 1965).

## EXPERIMENTAL

Sample shells were prepared for calibration by crushing, hand-picking of fragments, grinding, sizing (100–120 mesh), and washing. By using this relatively coarse fraction, the effects of grinding were minimized. Weathered or visibly altered shell material was not used. The decisive criterion for the state of shell preservation was the presence of a characteristic, fibrous crystal habit in the broken shells. Shells not showing this fibrous habit were rejected.

The thermoluminescence measuring system is essentially the research reader described by Kenney, *et al.*, (1963). It utilizes a nonlinear, fast-heat furnace (10–15°C/sec), a 1P21 photo-multiplier, an automatic light sum integrator and a cycle timer. The fast-heat feature has distinct advantages for low-intensity thermoluminescence detection and reproducibility in measurement (Johnson, *et al.*, 1961). A nitrogen atmosphere may be introduced into the sample chamber by flushing the chamber for several minutes with purified nitrogen (50

liters/min) immediately before the reading cycle begins. Measuring precision is approximately 4 percent standard deviation for multiple runs. When signal to background ratios were low, glow-curve peak heights were used. All samples were run in duplicate. A  $^{60}\text{Co}$  source was used for the calibrations. Homogeneous ionization was obtained within the samples by imbedding sample material in a plastic matrix. This procedure insured electronic equilibrium throughout the sample and avoided multiple scattering problems (Johns, 1961, p. 286).

Because of the low levels of thermoluminescence associated with the younger samples, spurious thermoluminescence had to be accounted for. The nitrogen flow system of Aitken, *et al.*, (1967) and Dr. Richard C. McCall (pers. commun.) was adapted for this purpose. Figure 1 shows the effects of nitrogen in suppressing spurious luminescence.

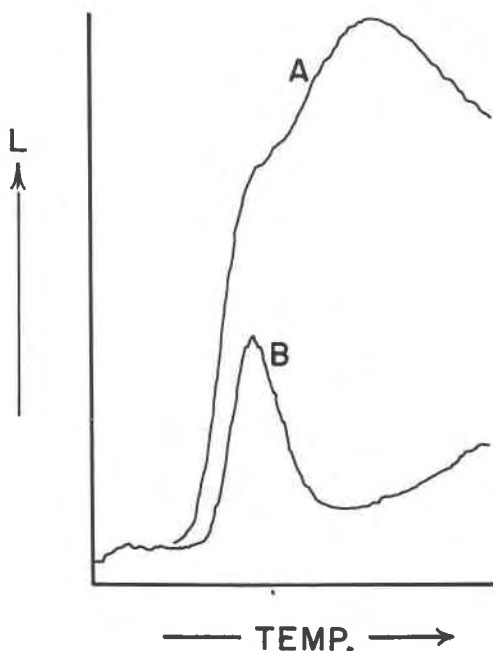


FIG. 1. The effect of  $\text{N}_2$  in suppressing spurious thermoluminescence. Glow curve A shows the natural thermoluminescence of sample 0-21 in air. Glow curve B is the same sample but measured in a  $\text{N}_2$  atmosphere. Note the resolving effect on the  $230^\circ\text{C}$  peak.

Dose calibrations were, in most cases, done by the "method-of-additions" to avoid annealing or optical bleaching of the samples. Basically, with this method the slope of the thermoluminescence/dose curve is determined and used to extrapolate to the natural value (Fig. 2). Where nonlinearity precluded this method, the samples were thermally annealed and reirradiated to the natural thermoluminescence level. Optical bleaching with polychromatic ultraviolet from a high-pressure mercury lamp was not sufficient to completely bleach the natural thermoluminescence. Irradiated samples were annealed at  $100^\circ\text{C}$  for 24 hours to bleach low-temperature peaks.

The uranium content of the samples was determined by a modification of the fluorimet-

ric procedure described by Grimaldi and Levine (1954) and Price *et al.*, (1953). This method consists of extracting the uranium into ethyl acetate from a nitric acid solution which contains  $\text{Al}(\text{NO}_3)_3$  as a salting agent. The ethyl acetate fraction is evaporated to dryness, re-dissolved in dilute  $\text{HNO}_3$ , and diluted to a 5 ml volume. An aliquot of the prepared sample is then fused with a flux and compared fluorimetrically with a known uranium sample which has been similarly fused.

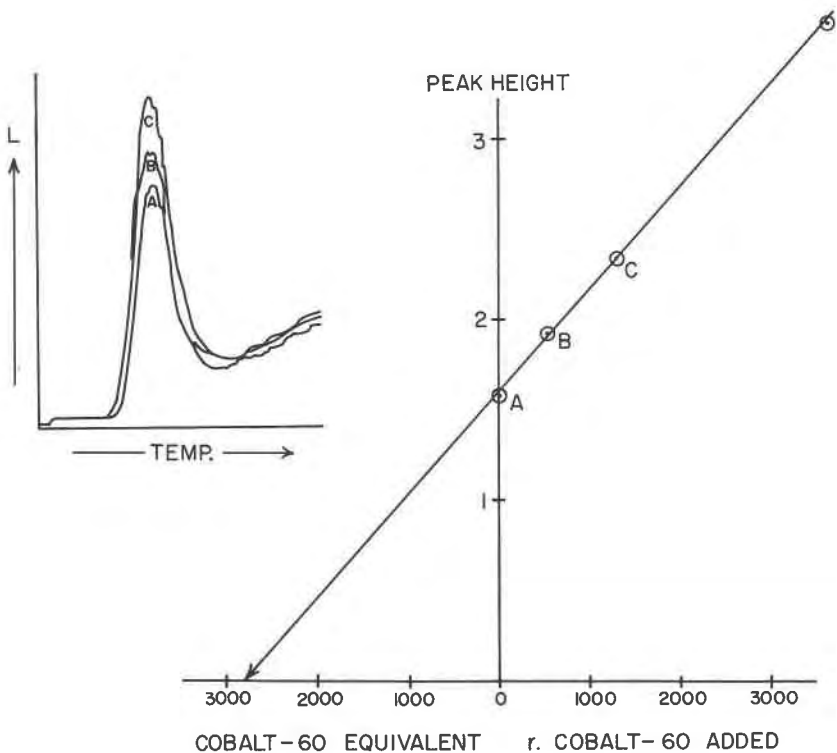


FIG. 2. Natural thermoluminescence calibration by successive additions of radiation dose. *A* is the natural thermoluminescence of sample 0-22, *B* is natural plus 530 R  $^{60}\text{Co}$ , *C* is natural plus 1300 R  $^{60}\text{Co}$ .

The percentage of the uranium recovered in the extraction was determined by measuring the alpha activity of  $^{233}\text{U}$  added as a tracer. The average recovery was  $99 \pm 2$  percent. A Jarrell Ash Ja-2600 Galvanck Morrison Fluorimeter was used for measuring the fluorescence.

The fluorimetric method measures total uranium. Because of the small number of atoms of  $^{234}\text{U}$  and  $^{235}\text{U}$  present, with respect to  $^{238}\text{U}$ , this method measures within 1 percent of the  $^{238}\text{U}$  content of the sample.

The method used to measure the isotopic thorium composition has been described in detail (Blanchard, 1963). A sample of 20–30 grams was dissolved in  $\text{HNO}_3$  and  $^{234}\text{Th}$ , a beta emitter, was added as a tracer to determine the chemical yield. The thorium was concentrated by coprecipitation on ferric hydroxide and mercuric iodate and purified by cation-

exchange techniques. The final effluent containing the "weightless" thorium product was deposited on a 1-inch platinum planchet.

The isotopic composition of the purified throrium product was determined by alpha pulse height analysis and verified by determining the growth and decay of the total thorium alpha activity.

TABLE 1. THERMOLUMINESCENCE RADIATION DOSIMETRY OF CALCITIC MOLLUSCS

Stratigraphic age	Sample	Age	Natural Peak T	Equivalent R Co <sup>60</sup>
Recent	<i>Ostrea</i> sp.	3160 ± 160 (Y-847)	none	
	<i>Ostrea virginica</i>	est. 6000	none	
	<i>Ostrea</i> sp.	2100 ± 300 (X5-384)	none	
	<i>Ostrea</i> sp.	6100 ± 800 (X5-386)	230°C	400 ± 300
	<i>Ostrea edulis</i>	7250 ± 200 (T-291)	230	600 ± 100
	<i>Pecten septemradiatum</i>	8700 ± 200 (T-231)	230	1500 ± 200
	<i>Pecten septemradiatum</i>	9750 ± 250 (T-179)	230	2200 ± 400
Pleistocene (Pamlico fm )	<i>Ostrea</i> sp. (26 specimens)	*est. 7 × 10 <sup>4</sup>	230	ave. 3410
Pliocene	<i>Ostrea</i> sp. (8)		230	ave. 24,600
	<i>Pecta</i> sp. (4)	est. 7 × 10 <sup>6</sup>	230	ave. 16,200
Miocene	<i>Ostrea</i> sp. (4)		230	ave. 53,000
	<i>Pecten</i> sp. (9)	est. 18 × 10 <sup>6</sup>	230	ave. 41,000
	<i>Ostrea</i> sp. (3)		230/300	ave. 277,000
Oligocene	<i>Pecten byramensis</i> (1)	est. 33 × 10 <sup>6</sup>	230	21,000 ± 400
Eocene	<i>Ostrea</i> sp. (3)	est. 50 × 10 <sup>6</sup>	230/300	ave. 305,000
Cretaceous	<i>Ostrea</i> sp. (2)		300	ave. 700,000
	<i>Pecten texanus</i> (1)	est. 1 × 10 <sup>8</sup>		125,000 ± 5000

\* Based on ionium disequilibrium method. See Table 2.

## RESULTS

Table 1 summarizes the dosimetry data for the 73 fossil shells analyzed in this study. In general, it may be seen that the older fossils have the higher dosimetry equivalence. The build-up of thermoluminescence in most cases is linear over the range of doses employed. In some younger shells, however, a supralinear increase of thermoluminescence with dose was observed. In high-dose situations, a sublinear response or leveling off of thermoluminescence build-up was noted. Five specimens were observed to have no thermoluminescence capacity at all.

The thermoluminescent glow curve for a Miocene or younger shell typically consisted of a single isolated peak at 230°C furnace temperature. Higher temperature thermoluminescence, if present, was generally unresolved in these shells. In some Miocene shells, a definite peak or glow

appeared at temperatures greater than 300°C. The Eocene and older shells had predominately greater than 300°C thermoluminescence with a subsidiary 230°C peak. Where only 230°C thermoluminescence was found naturally, the radiation equivalent was generally less than  $5 \times 10^4$ R.

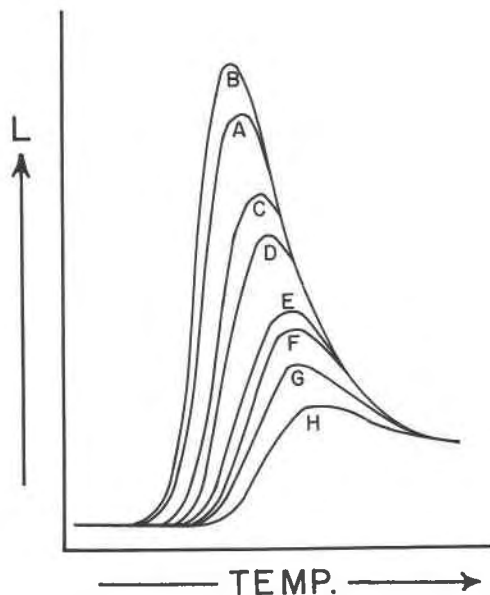


FIG. 3. The relative shift of peak maxima with total thermoluminescence. *A* is the natural  $>300^\circ\text{C}$  thermoluminescence glow curve of Eocene sample 0-6, *B* is natural plus 21,400 R  $^{60}\text{Co}$ , *C-H* are successive stages of annealing at  $175^\circ\text{C}$ .

In shells of Pliocene and older age, a shift of the  $230^\circ\text{C}$  peak position with total thermoluminescence was occasionally observed. Generally, as the amount of thermoluminescence increased, the peak position might shift down temperature by several tens of degree centigrade. In seven cases, mostly in Miocene and older shells, an extreme peak or glow shift was observed during thermoluminescence build-up and/or decay (Fig. 3). In such cases, the shift would be continuous from maximum to minimum thermoluminescence and covered a temperature range of  $150^\circ\text{C}$ . In some of these samples, the  $230^\circ\text{C}$  peak would predominate but show a conspicuous high temperature tail. Thermoluminescence build-up would proceed primarily as an addition to the  $230^\circ\text{C}$  peak. In other cases two subequal peaks ostensibly corresponding to the  $230^\circ\text{C}$  and  $300^\circ\text{C}$  peaks would be seen to build up and meld together. The three Cretaceous shells represented in the collection had distinct and well-resolved  $300^\circ\text{C}$  thermoluminescence with no  $230^\circ\text{C}$  peak.

The grinding and sample preparation treatment used in this study above did not affect the dosimetry evaluations. A real loss of thermoluminescence due to mechanical factors was not observed until the less than 160 mesh fraction was used.

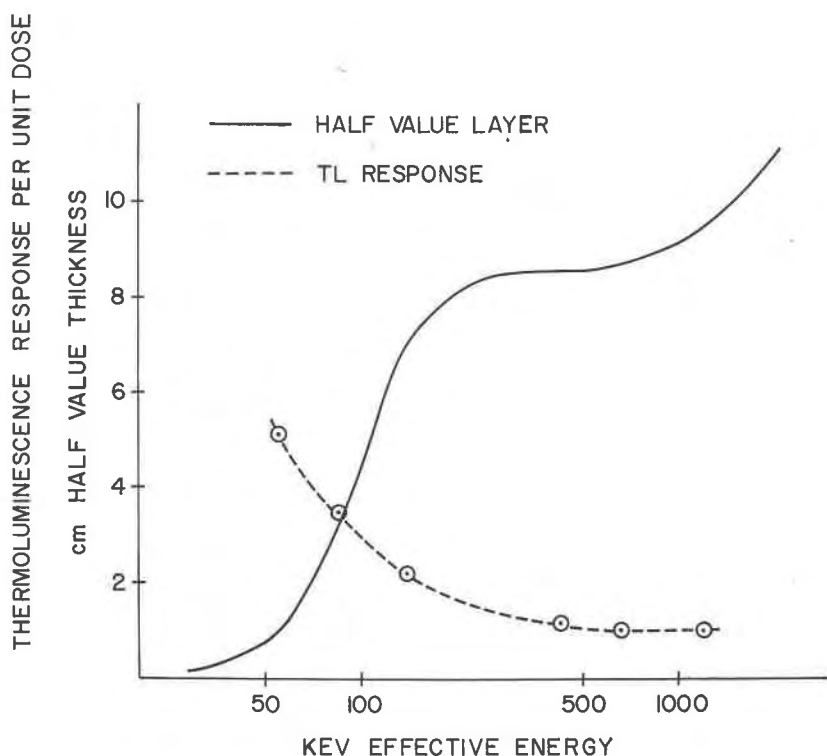


FIG. 4. Half value layers for calcite calculated from data of Johns (1961). Energy dependence of calcite thermoluminescence measured relative to ionization chamber dosimetry.

#### DISCUSSION OF RESULTS

Where applicable, the method-of-additions type of calibration eliminates many of the uncertainties associated with thermal annealing or incomplete optical bleaching. The hazards involved in post-irradiation calibration in changing thermoluminescence response are thus avoided (Zeller and Ronca, 1963b). In supralinear or sublinear thermoluminescence build-up cases, optical bleaching with ultraviolet is superior to thermal bleaching in this respect. Whenever optical bleaching cannot be successfully employed, however, low-temperature natural thermoluminescence can usually be bleached at temperatures sufficiently low to avoid

major crystal modifications. Where spurious thermoluminescence is a problem, a nitrogen atmosphere is necessary to quench the interfering luminescence (Fig. 1).

The radiation dose equivalents expressed in Table 1 are in roentgen units of hard electromagnetic radiation. Figure 4 shows the energy dependence and half-value layers for calcite for other radiation energies that may be used. Although electromagnetic radiation is convenient for laboratory calibrations, it is not characteristic of natural radiation. If the absolute dosimetry of the natural environment is to be calculated, the relative effectiveness of the calibration radiation compared to the

TABLE 2. URANIUM AND ISOTOPIC THORIUM CONTENT OF FOSSIL SHELLS

Stratigraphic Age	$^{238}\text{U}$ , ppm*	$^{230}\text{Th}$ , d/m/g	$^{232}\text{Th}$ , d/m/g	$^{230}\text{Th}/^{238}\text{U}$	$^{230}\text{Th}$ , $^{238}\text{U}$ age (yrs)
Recent	$0.047 \pm 0.002$	Ca.** 0.0023		Ca. 0.065	
Recent	$0.92 \pm 0.03$	Ca. 0.056		Ca. 0.082	
Pleistocene	$0.181 \pm 0.005$	$0.078 \pm 0.007$	$0.021 \pm 0.002$	$0.58 \pm 0.05$	$82,000 \pm 8,000$
Pleistocene	$0.202 \pm 0.008$	$0.071 \pm 0.006$	$0.016 \pm 0.002$	$0.47 \pm 0.05$	$62,000 \pm 6,000$
Pleistocene	$0.092 \pm 0.006$	$0.032 \pm 0.006$	$0.003 \pm 0.002$	$0.47 \pm 0.08$	$62,000 \pm 8,000$
Pliocene	$2.44 \pm 0.09$	$1.66 \pm 0.11$	$0.16 \pm 0.02$	$0.92 \pm 0.07$	>200,000
Pliocene	$1.41 \pm 0.04$	$1.05 \pm 0.03$	$\leq 0.05$	$1.01 \pm 0.04$	Equil.
Pliocene	$1.03 \pm 0.04$				
Pliocene	$1.18 \pm 0.07$				
Miocene	$4.29 \pm 0.21$	$3.08 \pm 0.09$	$\leq 0.23$	$0.97 \pm 0.05$	Equil.
Miocene	$0.40 \pm 0.01$	$0.31 \pm 0.02$	$0.05 \pm 0.02$	$1.03 \pm 0.07$	Equil.
Miocene	$0.150 \pm 0.006$	Ca. 0.111		Assume 1.00	
Miocene	$0.19 \pm 0.01$				
Miocene	$0.48 \pm 0.02$				
Eocene	$2.18 \pm 0.08$				
Cretaceous	$0.15 \pm 0.01$				

\* 1 ppm  $^{238}\text{U}$  = 0.7404 disintegration/minute/gram.

NOTE: errors are 1 standard deviation.

\*\* Ca. = calculated values—insufficient sample for thorium analysis.

natural environmental radiation must be known. Natural radioactivity in crustal rocks is primarily in the form of low-energy alpha particles on an energy-deposited basis. Alpha particles are considerably less effective for inducing thermoluminescence than gamma rays in most phosphors (Morehead and Daniels, 1957). In calcite, the efficiency per rad has been determined at 21 percent that of a roentgen of gamma radiation (Woodley and Johnson, 1967). However, about 15 percent of the total ionizing energy of uranium in secular equilibrium is in a "high efficiency" form for inducing thermoluminescence, *i.e.*, beta, gamma or X-radiation. The net effect of a rad of uranium radiation should, therefore, be about two-thirds that of a roentgen of  $^{60}\text{Co}$ .

Beta particles comparable in energy to average natural betas have been found similar to  $^{60}\text{Co}$  for inducing thermoluminescence in calcite



on a rad exposure basis (Johnson, 1963). To a first approximation, therefore,  $^{40}\text{K}$  radiations are roughly equivalent in thermoluminescence inducing efficiency to  $^{60}\text{Co}$ . The contribution of cosmic radiation is usually several orders of magnitude less than the radionuclide component in most environments and need not generally be considered (Janossy, 1950, p. 298).

#### DOSE RATES

Mollusc shells are notable for the small amounts of radioactive impurities they contain. Blanchard and Oakes (1965) have found that the average uranium and radium content in modern calcitic mollusc shells is  $0.026 \mu\text{g/g}$  and  $0.031 \text{ pg/g}$  respectively. This is two orders of magnitude less than ordinary limestone (Adams, *et al.*, 1959). In fossil calcitic shells, however, the uranium content may range considerably higher than in modern shells but still averages less than limestone. This increase in uranium concentration is probably due to diffusion of uranium from the surrounding sediments. Preliminary data indicates that in well-preserved shells this probably occurs soon after burial (Blanchard, 1963, p. 75). The radium concentration in modern calcitic shells is over twice that supported by the accompanying uranium and the  $^{232}\text{Th}$  content is usually nil (Blanchard, 1963). These conclusions are generally confirmed by the uranium and isotopic thorium analyses made on a representative selection of shells in this study (Table 2).

Within a typical modern calcitic shell then the maximum dose rate due to internal radioactivity would be on the order of  $10^{-3}\text{R }^{60}\text{Co/yr}$  assuming secular equilibrium for the  $^{238}\text{U}$  series and an efficiency factor of one-third (see above). On the basis of Table 2 and previous data (*e.g.*, Blanchard, 1963) the average internal dose rate expected from fossil calcitic shells should be on the order of  $10^{-2}\text{R }^{60}\text{Co/yr}$ .

In modern and relatively young shells, however, the lack of secular equilibrium in the uranium series complicates the dose rate and dose quality problem. The change of radioactivity with time may be calculated using the methods of Urry (1962). Since  $^{226}\text{Ra}$  and its successive daughters account for seventy percent of the decay energy in the  $^{238}\text{U}$  series, its concentration is a good indicator of relative radioactivity and approach to equilibrium (Fig. 5). The reaction  $^{238}\text{U} \rightarrow ^{234}\text{U}$  which is in near equilibrium in these shells would contribute a constant 12 percent to the dose rate. The period of low radioactivity at about  $10^4$  years is due to the deficiency and build-up of  $^{230}\text{Th}$  (ionium) equilibrium. As indicated by  $^{230}\text{Th}/^{238}\text{U}$  ratios, uranium diffusion may increase the internal dose rate of a shell but not necessarily change the pattern of radioactivity described by Figure 5 (Blanchard, 1963, p. 73-75).  $^{235}\text{U}$  comprises less than one

percent of common uranium and therefore may be ignored in this connection. Potassium, the only other important source of natural radioactivity, is likewise not abundant enough in these shells to be significant.

One other possible source of ionizing radiation for the shells in their natural environment is the  $\beta$  and  $\gamma$  fields generated outside the shells in the matrix minerals. Assuming the shells are buried in average shale, these fields may amount to  $0.2R$   $^{60}\text{Co}/\text{yr}$ . In high potassium or highly

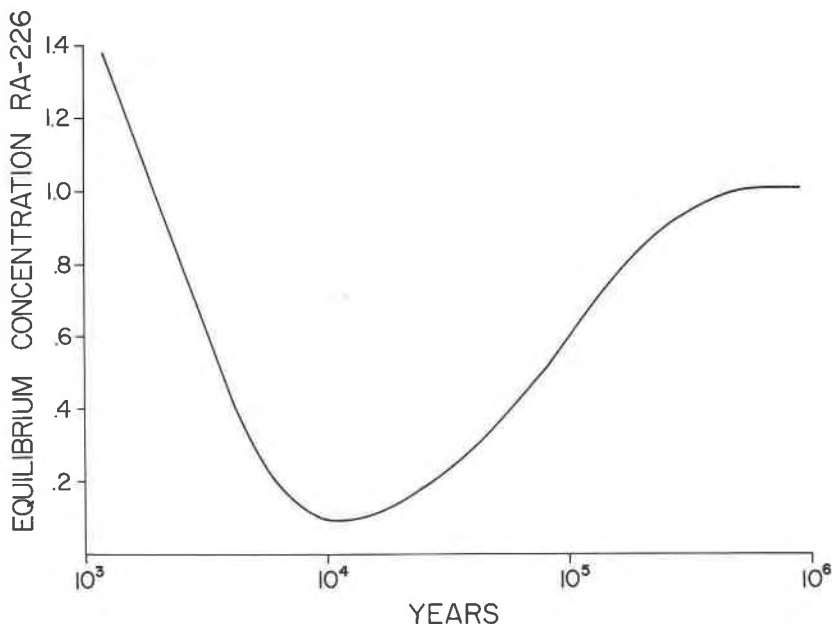


FIG. 5. Calculated concentration of  $^{226}\text{Ra}$  with time assuming (1) no chemical migrations, (2) initial activity ratio  $^{234}\text{U}/^{238}\text{U}$  of 1.15, (3) initial activity ratio  $^{226}\text{Ra}/^{238}\text{U}$  of 2.3 and, (4) no initial  $^{230}\text{Th}$ .

organic muds these fields may be proportionately increased. The buried shells, however, having a finite size would differentially absorb and attenuate the radiation exposure for the bulk of the shell.

The thermoluminescence dosimetry listed in Table 1 refers to the equivalent dosage of  $^{60}\text{Co}$  required under short term laboratory conditions to induce the observed natural thermoluminescence. However, because of the thermal sensitivity of the  $230^\circ\text{C}$  thermoluminescence in calcite, the rate of thermoluminescence build-up is appreciably slowed in the long term by thermal decay. Under a set of simple premises, *i.e.*, (1) linear thermoluminescence build-up potential, (2) first-order isothermal decay, (3) chemical and crystallographic stability, and (4)

constant irradiation rate, the effective dose rate ( $\alpha$ ) is given by (Johnson, 1965):

$$\alpha = \frac{\beta N}{1 - e^{-\beta t}} \quad (1)$$

where  $N$  is the radiation dose equivalent of the natural thermoluminescence and  $\beta$  is the effective isothermal decay constant. In a field situation, the value for  $N$  may be obtained by a dosimetry calibration of the natural thermoluminescence. For the initial stage of dosimetry build-up, *i.e.*,

TABLE 3. AVERAGE DOSE RATES CALCULATED FROM EQUATION (1).  
DOSE RATES IN UNITS OF R  $^{60}\text{Co}/\text{yr}$ .

Age	TL Peak	Number of Samples	Mean Temp. 10°C		Mean Temp. 15°C		Mean Temp. 20°C	
			Average	Range	Average	Range	Average	Range
Recent	230° C	4	0.13	0.07-0.23	0.14	0.07-0.23	0.14	0.07-0.23
Pleistocene (Pamlico fm.)	230° C	21	0.05	0.02-0.09	0.05	0.02-0.09	0.06	0.02-0.10
Pliocene	230° C	11	0.02	0.01-0.04	0.04	0.01-0.07	0.11	0.03-0.18
Miocene	230° C	12	0.03	0.01-0.05	0.08	0.01-0.14	0.21	0.30-0.37

small  $\beta t$ ,  $t$  must be determined independently. However, when the dosimeter is at thermal saturation, *i.e.*,  $\beta t$  is very large,  $t$  has diminishingly small importance:

$$\alpha = \beta N \quad (2)$$

In order to assign the proper value of  $\beta$  to a given situation several factors must be considered. First, the mean and extremes of temperature in the burial environment must be known and, secondly, the thermal activation parameters of the thermoluminescence have to be worked out. For the case of buried shells in a mid-latitude, coastal environment a range of 10-20°C would seem to encompass the effective temperature possibilities. The maximum seasonal temperature would be more important in this regard. Moderate burial, however, would attenuate such seasonal extremes. Although the kinetics and activation parameters are not specifically known for the thermoluminescence of calcitic shells, a close approximation can probably be had by using the data that has been worked out for a calcitic limestone (Johnson, 1965). In fact, the stability of the shell thermoluminescence observed at 100°C during this study tends to warrant this approximation. The assumption of first order kinetics at very low decay rates can also be justified on theoretical grounds (Chen and Halperin, 1965).

Table 3 summarizes various solutions to Eq. (1) for the sample data, assuming (1) the age of the Pamlico shells is  $7 \times 10^4$  years, (2) age of the Pliocene shells averages  $7 \times 10^6$  years, and (3) age of the Miocene shells averages  $18 \times 10^6$  years. Since the  $230^\circ\text{C}$  thermoluminescence is at or near equilibrium for all but the Pamlico and Modern shells the absolute age is not critical in these calculations (Eq. 2). For the age sensitive Pamlico shells the age assigned was based on ionium disequilibrium data (Table 2); age for the Modern shells was taken as the carbon-14 age (Table 1). The premises implicit in Eq. 1 are not strictly satisfied for each sample, e.g., linearity, constant temperature, and crystal stability; however, in aggregate the results should average out some of these disparities. Table 3 therefore gives a reasonable, thermally corrected set of dose rates for the geologic time represented by the fossil collection. Table 3 suggests a long-term dose rate of  $10^{-2}\text{R } ^{60}\text{Co}/\text{yr}$  which agrees with the observed range of radioactivities of the shells themselves (see above). This dose rate, however, is distinctly lower than that expected in ordinary limestone. Apparently, the  $\beta$  and  $\gamma$  field from the surrounding sediments does not contribute significantly to the dose delivered to the bulk shell.

In carbon-14 dated shells, the effective dose rates measured range from 0 to 0.2 roentgens  $^{60}\text{Co}$  per year. These high dose rates may reflect an initial excess of radium in these samples. For shells less than 6000 years old, natural thermoluminescence could not be detected even though the detection threshold in these cases was less than 1000 roentgen. The dose rates for the Pamlico shells do not indicate any period of low radioactivity (Fig. 5). The only clear-cut  $320^\circ\text{C}$  thermoluminescence is associated with Cretaceous shells and this thermoluminescence implies a somewhat lower average dose rate of  $0.005\text{R } ^{60}\text{Co}/\text{yr}$  assuming an age of  $10^8$  years. The accuracy of this dosimetry, however, is compromised by the (1) nonlinear build-up of thermoluminescence, (2) lack of discrete, singular glow-curve peaks, and (3) the probable involvement of long-term radiation-crystallographic damage effects.

#### RADIATION DAMAGE EFFECTS

Within the range of doses used in these experiments, the  $>300^\circ\text{C}$  thermoluminescence was generally not seen within the younger samples. High dose treatments, however, are known to sensitize the thermoluminescence response of some phosphors (Zimmerman, *et al.*, 1967) and some of the glow curves in this study indicate that the same effect is manifest in calcite. Similarly, the appearance of the conspicuous  $300^\circ\text{C}$  thermoluminescence peak in the Miocene and older shells supports the conclusions of Vaz and Zeller (1966) that long-term radiation damage is important in modifying the thermoluminescence potential of carbonates.

## SUMMARY

The methods and problems associated with natural thermoluminescence radiation dosimetry have been examined through a case study of thermoluminescent mollusc shells. The dose rates observed in these shells are consistent with the known levels of radioactivity associated with these samples. The potential of natural thermoluminescence dosimetry as a viable geologic tool is thus substantiated. Absolute dosimetry determinations are contingent on accurate calibrations appropriate thermal corrections and long-term phosphor stability. The most serious uncertainty at present is the dose equivalence factor between natural radiation and the common type of radiation used for calibration. The presence of higher temperature thermoluminescence peaks in older shells suggests that in some cases absolute dosimetry may be determined with less dependence on thermal effects. Because of imperfect knowledge concerning radiation damage, accurate dosimetry in calcitic shells is limited to dosages of less than  $10^5$ r.

An example of stratigraphic correlation on the basis of thermoluminescence dosimetry is provided by this study. Twenty-six specimens of *Ostrea*, collected in localities from Maryland to South Carolina, show a close range of natural thermoluminescence dosimetry,  $3410 \pm 43$  percent R  $^{60}\text{Co}$ . Significantly, all these samples were taken from Pamlico-equivalent formations (Table 1). This range of dosimetry values is sufficiently distinct to differentiate these specimens from the Recent and Pliocene specimens which also are found in this area. The degree to which such correlations may be extended would depend on the differences in age, radioactivity and temperature between stratigraphic sections.

Once valid radiation dosimetry has been obtained from a given sample and the dose-rate (radioactivity) of the environment is known, the irradiation-time for the sample can be calculated (Johnson, 1963). It should be possible to date or correlate in this way Post-Pliocene carbonates such as sea cores, caliche beds, lake marls and cave deposits. Studies are presently underway to explore these possibilities.

## ACKNOWLEDGEMENTS

The help and advice of Dr. Sam Bird in collecting and identifying the fossil material is gratefully acknowledged. This study was supported by the U. S. Atomic Energy Commission through Contract AT (30-1) 2982.

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*Manuscript received January 3, 1967; accepted for publication, June 7, 1967.*