

THE USE OF TL GLOW PEAKS AT EQUILIBRIUM IN THE EXAMINATION OF THE THERMAL AND RADIATION HISTORY OF MATERIALS

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Abstract—This paper examines the use of the relative heights of TL glow peaks at equilibrium to obtain information on the thermal and radiation history of materials. The theory of the method is presented for the simple case of peaks obeying first order kinetics and subjected to irradiation at a constant dose rate while being stored at constant or periodically varying temperature. The limitations of the method are shown and special cases in which this method might provide useful information are suggested.

INTRODUCTION

When thermoluminescence (TL) is used for dating materials a few thousand years old, it is usual to employ only the light emitted from a sample of the material over a narrow temperature range from 350 or 400 °C to the temperature at which black-body radiation becomes serious. This involves the rejection of a large part of the total light of thermoluminescent origin and is done because the shallower filled traps may have half-lives which are short at the effective storage temperature compared to the time for which the material has been stored. While this procedure is necessary and satisfactory if nothing is required but a date, and the only measurements available are the natural and artificial glow-curves over the working range described, potentially valuable information is lost. The low-temperature part of the glow-curve can enable us to draw important conclusions concerning the thermal history of the material, the radiation history or both. This has already been shown for a special case by Ronca (1964 and 1968) and by Ronca and Zeller (1965). They used the 230 °C peak, which was found to be at equilibrium height, in glow curves from calcite. From this they were able to estimate the minimum length of time for which Antarctic temperatures had persisted at their present level. It is the purpose of this paper to show that a number of other deductions can be made by a detailed analysis of glow-curve shape and to give the mathe-

matical arguments which enable us to make these deductions quantitative.

PRINCIPLES OF THE METHOD

Before starting the mathematical analysis it will be useful to illustrate the principles involved. Consider material which has been in a constant environment for a very long time; for example, material from well below the surface of the moon. If the environmental temperature had been sufficiently low, all traps should then be filled and the natural glow curve obtained should be identical with that obtained after artificial irradiation to saturation. In most practical cases, however, the environmental temperature will be high enough for some loss of electrons from the shallower traps. Hence, these shallower traps will never reach saturation but instead will reach a dynamic equilibrium, at which the rate of filling of traps is equal to the rate of emptying. The heights of the corresponding peaks at equilibrium then depend upon temperature and dose rate, and if either of these is known the other is fixed. To find it experimentally we need also to know how the half-lives of the peaks observed vary with temperature in the temperature range of interest. This cannot usually be measured directly but can be found by extrapolation of measurements made at higher temperatures. Then the natural glow curve can be compared with the saturation glow curve derived from a short artificial irradiation to

find the proportion of saturation reached by each peak. If several peaks are distinguishable, more complex histories might be deduced.

MATHEMATICAL TREATMENT

In deriving the mathematical equations relevant to the growth of the thermoluminescence under certain conditions of temperature and radiation dose rate, a few simplifying assumptions have had to be made, and these must always be borne in mind. The main assumptions are that no creation or destruction of traps is caused by the radiation, and that the particular phosphor under consideration obeys kinetics of the first order as summarised in the Randall-Wilkins equation (1945).

With these assumptions, the mathematical treatment is a relatively simple one. The net rate of change in the number of trapped electrons is in this case, simply the difference between the number of traps filled by radiation per unit time, and the number drained per unit time by heat at the temperature at which the phosphor is stored.

If the phosphor is stored at temperature T and under irradiation at a dose rate r , and if

N = total number of traps per unit volume

n = number of trapped electrons per unit volume

E = energy depth of the traps

s = frequency factor for the traps

then the rate of filling of traps per unit volume is:

$$\frac{dn}{dt} = \frac{1}{R_0} (N - n)r - sne^{-E/kT} \quad (1)$$

The first term on the right-hand side of equation (1) gives the rate of filling of the $(N - n)$ empty traps by the dissipation of energy in the phosphor by radiation, at a rate r . The constant R_0 will be discussed later. The second term gives the rate of draining of filled traps by thermal excitation at the storage temperature T . The equation refers to one kind of trap or one peak of the glow curve and it is assumed that no recapture of the thermally released electrons occurs, and that therefore the decay of the number of trapped electrons is in accordance with the first order kinetics theory developed by Randall and Wilkins (1945).

Integrating equation (1) and assuming constant r and T and that all the traps were empty at $t = 0$, we obtain

$$n = N \frac{1 - e^{-[1+(sR_0/r)e^{-E/kT}]R/R_0}}{1 + \frac{sR_0}{r} e^{-E/kT}} \quad (2)$$

where $R = rt$ is the total dose received by the phosphor.

In the special case of very low storage temperature or very high dose rate, drainage can be neglected, and equation (2) reduces to

$$n = N(1 - e^{-R/R_0}) \quad (3)$$

R_0 is seen to be the dose at which a fraction $(1 - e^{-1})$, or 63.2% of the total number of traps are filled. We will define this to be the saturation dose for traps of energy E and frequency factor s , for very low T or very high dose rate r .

For artificial irradiations, equation (3) is applicable in all but the case of low temperature peaks. In nature however, the dose rates and temperatures encountered are such as to make the use of equation (2) necessary.

As the dose R becomes large, the number of filled traps reaches the equilibrium value of

$$n_m = \frac{N}{1 + \frac{sR_0}{r} e^{-E/kT}} \quad (4)$$

By analogy with the saturation dose R_0 defined in the case of filling at low T or high r , a saturation dose R_s can be defined, at which the number of filled traps is a fraction $(1 - e^{-1})$ or 63.2% of the equilibrium n_m . From equation (2) it is found that

$$R_s = \frac{R_0}{1 + \frac{sR_0}{r} e^{-E/kT}} \quad (5)$$

The effect of temperature is seen from equations (4) and (5) to be the reduction of the maximum number of electrons that can be stored in the available traps, and the reduction of the saturation dose by the same factor. A dependence of the number of trapped electrons on the dose rate is also introduced. The cause of this is the fact that the process of filling of traps by radiation is competing with the thermal drainage of traps.

The time or dose needed for the number of trapped electrons to approach the equilibrium number n_m is found from equation (2). In terms of the saturation dose R_s , it is found that doses equal to $3R_s$ and $5R_s$ fill 95% and 99% respectively, of the possible n_m traps that can be filled.

Figure 1 shows the variation with dose of the number of trapped electrons. The approach to equilibrium is shown at two temperatures T_1 and T_2 , T_2 being higher than T_1 . The complete saturation of all the traps is also shown on the right-hand

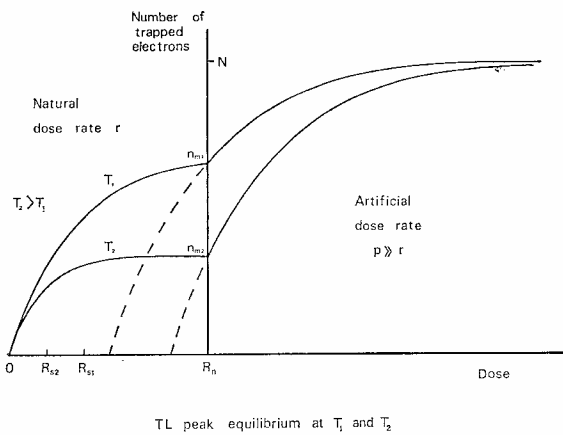
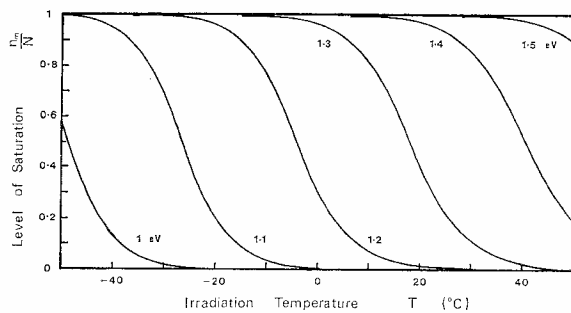


FIG. 1. Growth curves for the number of trapped electrons in traps of a single energy depth. The growth at two storage temperatures ($T_2 > T_1$) is shown. After receiving a natural dose R_{n1} , the sample is irradiated artificially at a dose rate p high enough for thermal drainage to be negligible. This achieves the complete filling of all the N traps.

side, where it is assumed that an artificial dose rate p is used which is very large so that the thermal drainage during irradiation is not significant.

As seen from equation (4) the level at which equilibrium is reached will depend on the particular parameters of the peak and the temperature of storage and dose-rate. Figure 2 shows the maximum fraction of traps which can be filled at various storage temperatures and for different trap depths. Each curve corresponds to a particular trap depth, given in eV. Also shown are some sets of values



Level of saturation reached at irradiation temperature T ($^{\circ}\text{C}$), for $\frac{sR_0}{r} = 3.15 \cdot 10^{22}$ e.g. $s = 10^9 \text{ sec}^{-1}$ $R_0 = 10^6 \text{ rad}$ $r = 1 \text{ rad/yr}$
 $\frac{10^9}{10^6}$ $\frac{10^9}{10^6}$ 0.1
 $\frac{10^8}{10^6}$ $\frac{10^6}{10^6}$ 0.1

FIG. 2. Fraction of traps filled at equilibrium, as a function of storage temperature, for traps of various depths and $sR_0/r = 3.15 \cdot 10^{22}$.

for the frequency factor s , the saturation dose at zero temperature R_0 , and the dose rate r , for which the graph applies. The most striking factor of this graph is the strong dependence of the equilibrium level reached on the storage temperature. Figure 3 gives the storage temperatures for which the fraction of filled traps at equilibrium is 50% (i.e. $n_m/N = 0.5$), for various values of sR_0/r and trap depth E .

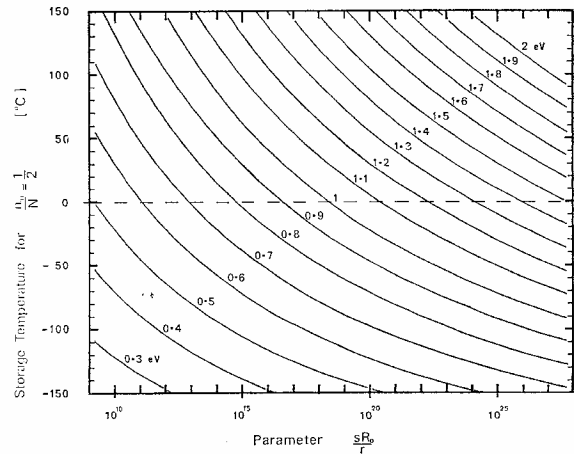


FIG. 3. Storage temperature at which equilibrium is reached after half the number of available traps are filled ($n_m/N = 0.5$). The storage temperature is given as a function of the parameter sR_0/r and for different trap depths.

DETERMINATION OF THE DOSE RATE

Having developed the equations for the growth of thermoluminescence under certain conditions, we now proceed to examine the nature of the information we can derive experimentally.

Let us first examine the method for the determination of the dose rate by the use of peaks at equilibrium at a constant storage temperature which is assumed to be known. This method can be used in cases where the body under examination has been removed from the radiation field in which it existed in its recent history. This is the case for meteorites or lunar samples, when the original radiation field is inadequately known. The process is simple for the case of constant storage temperature. Equation (4) gives the number of electrons trapped under equilibrium conditions. It can also be interpreted in terms of the peak height or area under a peak of the glow curve. In this case, N is the peak height or area when the material

has been artificially irradiated to saturation. Equation (4) can be solved for the dose-rate, r , as shown below.

$$r = \lambda_T \frac{R_0}{\frac{N}{n_m} - 1} \quad (6)$$

where

$$\lambda_T = \frac{\ln 2}{\tau_{1/2}} = s e^{-E/kT} \quad (7)$$

λ_T is the decay constant and $\tau_{1/2}$ the half-life of the peak at the storage temperature, T . The quantities to be determined experimentally are the saturation dose R_0 , the saturation peak height N , the equilibrium peak height n_m , and the decay constant λ_T of the peak at the known storage temperature.

DETERMINATION OF THE STORAGE TEMPERATURE

It is possible, using similar arguments to those for the dose-rate, to obtain experimentally, information regarding the thermal history of the body under consideration. If the dose rate is known and the storage temperature is assumed to be constant then the value of this temperature can be found by solving equation (4):

$$T = \frac{E/k}{-\ln \left[\frac{r}{sR_0} \left(\frac{N}{n_m} - 1 \right) \right]} \quad (8)$$

This expresses T in terms of measurable quantities.

If the dose rate is also unknown, and both this and the storage temperature are assumed to be constant, they can both be determined if two independent peaks are at equilibrium. The storage temperature is given by:

$$T = \frac{\frac{E_a - E_b}{k}}{\ln \left[\frac{sR_0}{\frac{N}{n_m} - 1} \right]_a - \ln \left[\frac{sR_0}{\frac{N}{n_m} - 1} \right]_b} \quad (9)$$

where the quantities in brackets refer to peaks a and b with energies E_a and E_b respectively. The value of T thus obtained can be used in equation (6) for the determination of the dose rate.

PERIODICALLY VARYING STORAGE TEMPERATURE

The case of constant storage temperature is unfortunately very rare in nature. A sample found on the surface of the earth for example, will have been subjected to storage temperature with a significant annual variation and if the sample is of geological age, the storage temperature may have been changing on a much larger time-scale, as major climatic changes occurred.

The problem can be treated in the simple case of periodic temperature variation. Of course with a varying temperature, equilibrium is never reached in the strict meaning of the term. If, however, the amplitude of temperature changes is small compared to the average temperature, or if the half-life of the peak at the maximum temperature reached is long compared to the period of temperature variation, then a quasi-equilibrium is reached and the number of trapped electrons remains almost constant, with very small changes occurring. These changes in the number of electrons can be small enough to be neglected, and are periodic, with the same period as that of the storage temperature.

The rate of thermal drainage is:

$$\frac{dn}{dt} = -n s e^{-E/kT} \quad (10)$$

Neglecting changes in n due to the radiation and integrating over one cycle,

$$\ln \left(\frac{n + \delta n}{n} \right) \approx \frac{\delta n}{n} \approx -s \int_0^{t_p} e^{-E/kT} dt \quad (11)$$

Over the same period t_p , the radiation has filled approximately

$$\delta n' \approx \frac{1}{R_0} (N - n) r t_p \quad (12)$$

traps.

For equilibrium,

$$\delta n + \delta n' = 0 \quad (13)$$

We define a temperature T' , such that

$$e^{-E/kT'} = \frac{1}{t_p} \int_0^{t_p} e^{-E/kT} dt \quad (14)$$

The storage temperature T varies with period t_p , and T' which we will call the Boltzmann-average temperature, is such that over one period, it would drain the same number of traps as the variable storage temperature would drain in the same time.

The equilibrium number of filled traps is then found from equations (11), (12), (13), and (14) to be

$$n_m = \frac{N}{1 + \frac{sR_0}{r} e^{-E/kT'}} \quad (15)$$

This is the same as equation (4) with the storage temperature T substituted by the Boltzmann-average temperature T' .

The Boltzmann-average temperature can be found in simple cases, if not analytically, at least by numerical or graphical methods. The case of an average temperature of 20 °C, which varies sinusoidally between 0 and 40 °C, is shown in Fig. 4. The variation of the Boltzmann factor

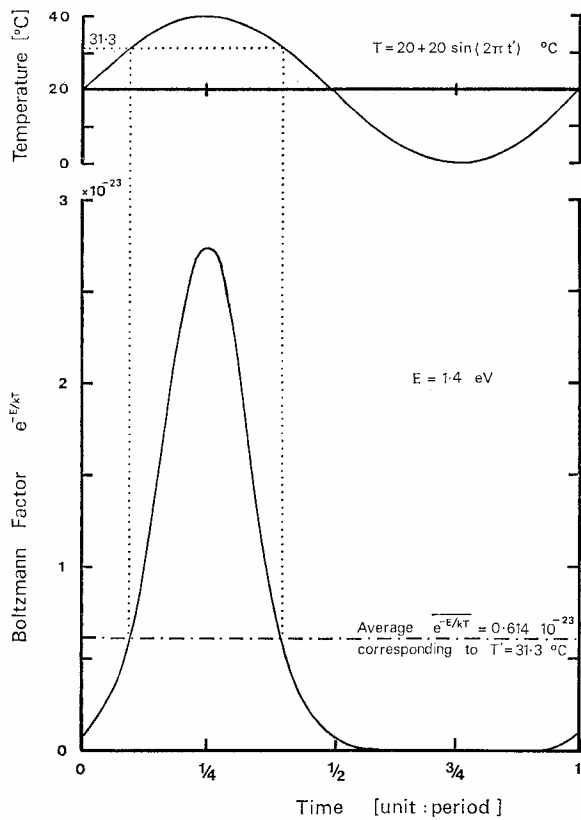


FIG. 4. Variation of the Boltzmann factor for energy of 1.4 eV and storage temperature varying sinusoidally between 0 and 40 °C. The time unit is equal to the period of variation. The average value of the Boltzmann factor over one period is $0.614 \cdot 10^{-23}$, corresponding to a Boltzmann-average temperature $T' = 31.3$ °C.

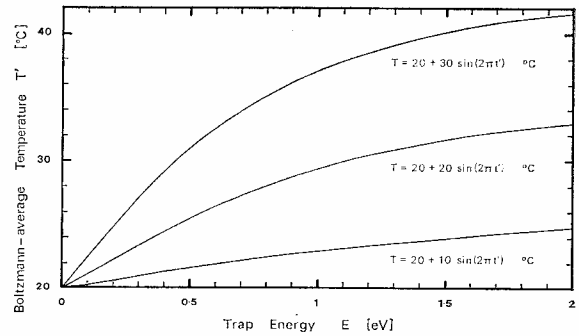


FIG. 5. The Boltzmann-average temperature T' as a function of trap energy depth, for three sinusoidally varying storage temperatures of average values of 20 °C.

with time is shown for a peak of energy 1.4 eV. It must be borne in mind that the product of the Boltzmann factor and the frequency factor s (typically between 10^8 to 10^{13} sec⁻¹), is equal to the fraction of traps emptied per second. The assumption made in the derivation of equation (14), namely that the number of trapped electrons can be considered constant over one cycle, is therefore justified in this case. It is seen from Fig. 4 that drainage can be neglected for half the cycle, and that the Boltzmann-average temperature (31.3 °C) is nearer to the maximum than to the average storage temperature.

Figure 5 shows the Boltzmann-average temperature, for three sinusoidally varying storage temperatures, as a function of trap energy depth. It is found to vary substantially with the energy of the traps, especially for high amplitudes of temperature variation. It is nearer to the maximum temperature for high-energy traps and for large temperature amplitudes. Depending on how high the s factor is, the data of Fig. 5 might be unreliable for trap depths below 1 eV, and long periods of storage temperature variations.

VALIDITY OF THE METHOD

The basic criterion of the validity of the method is whether or not the glow peak or peaks used are at equilibrium. To establish this, two adjacent peaks can be used independently for the determination of T and r . If the results agree, the peaks must be at or very near to equilibrium heights. Two peaks at equilibrium might not however be available or the experimental accuracy might not be good enough to make a comparison of the results

dependable. In this case, the following procedure can be used. Assuming the value of storage temperature found by equation (8) to be correct, the half-life of the peak under consideration at the storage temperature is found by extrapolation of results found from measurements at higher temperatures. Using the high temperature glow, the TL age of the sample is found. If the TL age is longer than 5 or so half-lives of the peak at the storage temperature, the peak can be considered to be at equilibrium height.

A basic assumption made is that the conditions of storage have not been disturbed in the recent history of the material. Evidence of disturbances might be found from comparisons of the results obtained from different peaks. Since the number of peaks observed is limited, so is the number of 'bits' of information that can be obtained by TL about the history of any sample.

CONCLUSIONS

In conclusion, it must be said that the method must be used with caution, and only when a rather high accuracy can be achieved in measuring the various trap parameters needed, such as energy, frequency factor s and half-lives at various temperatures. It must be stressed that the treatment is strictly speaking only valid for phosphors in which first order kinetics determine the rate of decay.

Nevertheless, this line of study might be the only one available for particular cases where the sample under examination has been removed from

the radiation and thermal fields in which it existed, and no knowledge of these is available. Meteorites are a special case, and also lunar material, for which only approximate values for the radiation dose rates exist.

In all cases some knowledge of the thermal history of the material will be helpful in any determination of its thermoluminescent age. If all peaks are a long way from saturation, similar considerations can be applied and, the dose rate being known, the effective storage temperature determined from the peak ratios. Having done this it will also be possible to estimate the rate of loss from the highest observable peak, and if this is significant, make an appropriate correction to the calculated thermoluminescent age of the material. With this in mind, it is hoped that the method may help to improve the accuracy and reliability of dating by thermoluminescence even when it is incapable of producing entirely novel information.

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