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Thermoluminescence Kinetics of Pyrite (FeS_2)*

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ABSTRACT

Thermoluminescence of pyrite (FeS_2) has been investigated to study the kinetics of single peak glow curves. The material used normally exhibits one large and four small peaks. However a glow curve can be obtained with only the large single peak that is suitable for testing thermoluminescence kinetics. Glow curves from aliquots of a single natural pyrite crystal studied in detail contain two low intensity thermoluminescence (TL) peaks at $\approx 90^{\circ}$ and $\approx 165^{\circ}$ C that are easily "drained" by careful preheating, a single high intensity TL peak at $\approx 250^{\circ}$ C, and two chemiluminescence (CL) peaks at $\approx 350^{\circ}$ and $\approx 430^{\circ}$ C. The CL peaks are largely removable by initially heating the sample chamber under vacuum, pumping through liquid nitrogen traps, and recording glow curves immediately after helium is introduced, procedures which reduce system contaminants that react with pyrite. The shape, the variation of the temperature of the peak maximum (T_{max}) with dose, and the retrapping to recombination cross section ratio (σ) of the large 250° C peak are better described by the general one trap (GOT) kinetic equation, the basic equation from which the 1st and 2nd order kinetic equations are obtained as special cases (see text), than by the 1st or 2nd order equations.

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I Introduction

TL theory, usually called TL kinetics, has been, with few exceptions (Levy, 1984a), concerned with the shape, temperature at peak maximum (T_{max}), and kinetic parameters (s, E, etc.) of single peak glow curves. Unfortunately, it has not been established that even one material exists that exhibits only a single glow peak, especially above room temperature. Over a period of years, twenty or more materials have been studied to determine if they contain a single peak. All clearly show more than one peak with the possible exception of fluorite (Hornyak et al., 1984, 1985).

It is essential to study single peak glow curves to determine if any of the commonly used kinetics, i.e. 1st order, 2nd order, or the general one trap (GOT) equation (from which the other two are derived), actually describe carefully measured glow peak data.

The possibility that one could obtain pyrite glow curves that contain only single glow peaks, suitable for detailed kinetic study, is suggested by the papers of Schwartzmann et al. (1981, 1983). However as described below, after preheating, vacuum baking, etc. the glow curves from natural pyrite contain one quite large TL peak with all other peaks removed or reduced to relatively small intensities. In other words, pyrite glow curves can be obtained that closely approximate single peak glow curves. Such pyrite glow curves have been carefully studied, with particular attention to peak shape, behavior of T_{max} with dose, and the ratio of the retrapping to radiative recombination cross section (σ), to determine which, if any, of the single glow peak kinetic equations best describes the data.

II TL Kinetics

What is here called the general one trap (GOT) kinetic equation was originally discussed by Randall and Wilkins (1945). Apparently, they did not attempt to apply this equation to measured glow peaks. They used it primarily to derive what is currently called the 1st order kinetic equation(s). The GOT equation assumes the following: 1) The system contains one type of electron trap with thermal untrapping energy E and an attempt to escape frequency s. In other words, the thermal untrapping is controlled by the Boltzmann factor $se^{-E/kT}$. 2) N = the concentration (number per unit volume) of traps. 3) At any time t, n = the concentration of occupied traps (trapped charge). 4) Initially, before glow curve measurement, a fraction of the traps are filled, in most cases due to prior exposure to ionizing radiation. n_o = the initial trapped charge concentration. 5) The system contains one type of hole traps that also function as a light emitting recombination center. 6) The trapped electron and hole concentrations are equal which implies that the hole trap concentration is greater or equal to the electron trap concentration. 7) During heating, electrons released at (absolute) temperature T are either retrapped or radiatively recombine with holes in the recombination centers. 8) σ_t = the retrapping cross section, σ_r = the radiative recombination cross section, and $\sigma = \sigma_t/\sigma_r$. The GOT equation describing the trapped charge concentration is

$$-\frac{dn}{dt} = nse^{-E/kT}\left[1 - \frac{\sigma_t(N - n)}{\sigma_r n + \sigma_t(N - n)}\right] \qquad (1)$$

Inasmuch as the emission is due to radiative recombination, the

measured intensity, I, is equal to (or more precisely proportional to) the decrease in the number of trapped charges, i.e.

$$I = -\frac{dn}{dt} \tag{2}$$

The kinetic equations widely used are special cases of (1). First, when no retrapping occurs ($\sigma_t = 0$) and (1) reduces to the 1st order kinetic equation:

$$-\frac{dn}{dt} = nse^{-E/kT} \tag{3}$$

Second, if retrapping occurs and $\sigma_t = \sigma_r$, i.e. $\sigma = 1$, a requirement that is unlikely, (1) reduces to the 2nd order kinetic equation:

$$-\frac{dn}{dt} = n^2(\frac{s}{N})e^{-E/kT} \tag{4}$$

where $s' = s/N$ is often used.

The 1st and 2nd order kinetic equations are often given in analytic form for a linear heating rate β. More specifically, $T = T_o + \beta t$, where T and T_o, the initial temperature, are in degrees Kelvin for all computations. (Data are usually reported in degrees Celsius.) The well known relations for 1st and 2nd order (Randall and Wilkins, 1945; Garlick and Gibson, 1948) are, respectively,

$$I = n_o se^{-E/kT} \exp\{-(s/\beta)\int_{T_o}^{T} e^{-E/kT}\, dT\} \tag{5}$$

and

$$I = n_o^2 \left(\frac{s}{N}\right) e^{-E/kT} \left[1 + (n_o s/N\beta) \int_{T_o}^{T} e^{-E/kT}\, dT \right]^{-2} \qquad (6)$$

Equations (3) and (5) are often called the Randall - Wilkins equation(s), and (4) and (6) are the Garlick - Gibson equation(s). The integrated form of the GOT equation is usually obtained from (1) by computerized numerical methods (Levy, 1984b).

The three kinetic equations (1), (3), and (4) provide information on the temperature of the glow peak maximum (T_{max}) for different values of n_o, i.e. for different doses. As is well known, for 1st order kinetics, T_{max} does not change with irradiation dose (Garlick and Gibson, 1948). For 2nd order kinetics, T_{max} decreases as the irradiation dose increases (Garlick and Gibson, 1948). Computerized numerical computations show that, for GOT kinetics, T_{max} also decreases with increasing dose (Levy, 1984b).

III The Glow Curve Fitting Procedure

As described above, the shape of a single peak glow curve depends upon the kinetic processes occurring, and peak shape can be used to determine which of the three kinetic equations best fit the data. By using well known computational techniques, "best-fit" glow curves for the different kinetics can be calculated for a measured glow curve. Usually, it is immediately apparent which is the best fit.

Two fitting programs, using standard nonlinear least squares fitting procedures, were used in this study. One computes glow curves from the analytic 1st and 2nd order kinetic equations (5) and (6). The second program computes glow curves for GOT kinetics using a differential equation solving routine, IVPAG, from the IMSL Math Library.

Best fit parameters and/or lumped parameters are also determined by the best fit programs. The parameters and lumped parameters that can be determined by fitting to the 1st order equation are s, E, and n_o; from 2nd order $s' = s/N$, E, and n_o; and for GOT $s/(1 - \sigma)$, E, n_o, and $\sigma N/(1 - \sigma)$. That two parameters and two lumped constants can be obtained, not five parameters, by fitting to the GOT equation can be understood by writing (1) as

$$- \frac{dn}{dt} = n\left(\frac{s}{1 - \sigma}\right)e^{- E/kT} \left[\frac{n}{n + \sigma N/(1 - \sigma)}\right] \tag{7}$$

The n_o values, i.e. the initial charge concentrations, are proportional to the peak areas.

IV Experimental Details

A. Equipment and Procedure

Glow curves were obtained by heating samples on a tantalum strip in a helium-filled chamber. The sample temperatures are determined from chromel-alumel thermocouples welded to the bottom of the heating strip. To obtain a precise linear heating rate, the thermocouple output is compared to a linear ramp signal. The TL is measured with a 9635Q EMI Photomultiplier Tube through a red filter, to minimize thermal background radiation. The phototube signal is digitized, and all data is stored in a PDP 11/34 computer.

Unless stated otherwise, all glow curves analyzed result from a four step process. First, a "data" curve was recorded by heating the sample from 40° to 450° C at 2 $C^o s^{-1}$. Each data point results from integrating the signal for 0.4 s. Second, the sample was cooled to below 40° C, and without opening the chamber or changing the atmosphere, a "background" curve was measured. Third, the background curve (the oven glow) was subtracted from the data curve to obtain the TL and/or CL emission. Fourth, the "difference" curve was

normalized to a 5 mg sample mass. Only "normalized" curves are shown below.

B. Samples

All measurements were made on natural pyrite (FeS_2) crystals (from the Rocky Mountain area) that were broken into chips and/or ground into a powder with grain size $\leq$ 0.5 mm. Except for one CL peak -- identified as peak (e) below --, there was no apparent correspondence between peaks occurring in the glow curves of the different crystals. One crystal showed only CL peak (e) even after a dose of $\approx$ 10 kGy. The other crystals all exhibited multipeak glow curves. However, after preheating, vacuum baking, etc. (see below), one of these crystals showed only one large TL peak (peak (c)). Except when noted, powder samples from this particular pyrite crystal were used for the detailed studies described below. Microprobe x-ray spectroscopy showed they contained Ca and P impurities.

C. Chemiluminescence, Surface Color, and Magnetic Effects

1. A typical glow curve for a 2.5×10^3 Gy dose is shown in Fig. 1. All laboratory irradiations were made with a ^{60}Co gamma-ray source. Five peaks, lettered (a) to (e) in order of increasing T_{max}, are apparent. As described below, there is strong evidence to classify peaks (a), (b), and (c) as TL peaks and (d) and (e) as CL peaks.

2. To facilitate a kinetic analysis of the large TL peak (peak (c)), glow curves were recorded with the CL peaks reduced as much as possible. A large peak (e) occurred when glow curve measurements were delayed for $\approx$ 30 minutes after filling the chamber with helium. However, peak (e) was reduced to a negligible level by starting the measurements less than 1 minute after filling the chamber with the inert gas. Peak (d) could not be removed completely.

However, it was reduced 25 to 50% by baking the chamber and sample for ≈ 1.5 hours at ≈ 50° C under vacuum in a system containing liquid nitrogen traps and then allowing the system to cool before introducing helium for the measurements. Therefore peaks (d) and (e) were significantly decreased by procedures which reduced contaminants in the system that can react with pyrite. This is strong evidence that these peaks are chemiluminescence.

3. If conditions allowed peak (e) to appear in a data curve, it would reappear in the normal background curve and interfere with the thermal background curve measurement. However, it could be removed from the background curve by heating the sample at 450° C for ≈ 2 minutes after the data curve measurement. Peak (d) never reappeared in a background curve.

4. After a sample has become discolored and magnetic (see 7 and 8 below), peak (e) cannot be generated by exposing the sample to the atmosphere and reheating under conditions that would produce this peak in a pristine sample. Peak (d) cannot be regenerated by exposing the sample to the atmosphere before heating, even if the surface is not discolored.

5. Measurements on pyrite chips with discolored surfaces indicate that peak (e) can be regenerated by crushing the sample to expose new surface and reheating under conditions that produce this peak. Peak (d) cannot be regenerated in this way.

6. Peak (d) could be regenerated only if the sample was removed from the chamber and irradiated.

7. The pyrite powder was initially silver gray under indoor illumination. When the same powder sample was used repeatedly, the surface color changed from silver to gold, to red, and finally to dark blue. These surface changes have little

effect on the glow curves. Repeated use of the same sample also caused it to become magnetic.

8. The changes in magnetic and surface properties were more pronounced after measurements in which peak (e) appeared than after measurements in which it was suppressed.

9. Electron microprobe x-ray spectroscopy of pyrite chips showed that the Fe/S ratio at the surface increased from 0.5 to 0.8 after a glow curve measurement in which peak (e) occurred and the sample was held at 450° C for 2 minutes.

D. Thermoluminescence Measurements

1. The Peak Shape

A glow curve for a sample which received 1.3×10^4 Gy after all peaks had been removed by heating to 450° C is shown in Fig. 2A. 1) Before recording this glow curve, peaks (a) and (b) were removed by heating to 180° C for 75 seconds. 2) After cooling, the glow curve was measured. 3) Peaks (d) and (e) were suppressed using the procedures described above. 4) The sample was given the same dose and heated to 250° C for 200 seconds to remove peaks (a), (b), and (c). 5) After cooling, the dashed glow curve in Fig. 2B was recorded. The solid curve in 2B is the lower section of the curve in 2A. The data points for peak (c) in Fig. 2 were obtained by subtracting the two curves in 2B (subtracting peak (d)). For clarity, only one-twelfth of the data points are plotted. Also shown in Fig. 2 are best-fit curves from GOT kinetics (solid line), 1st order kinetics (dashed line), and 2nd order kinetics (dash dot line). The GOT kinetic curve clearly fits the data better than the other curves.

2. Dose Dependency Measurements Obtained from Different Samples

To further determine which kinetic equation best fits the data, the dependence of peak (c) on dose -- in particular the behavior of T_{max} -- was determined. Twelve samples were divided into four groups. Each group received a different dose. Samples receiving the same dose, produced somewhat different intensity glow curves. To compare glow curves for different doses, the median height peak (c) glow curve from each group was used to prepare Fig. 3. Four doses were used: natural dose (ND), ND plus 5×10^2, ND plus 2.5×10^3, and ND plus 1.3×10^4 Gy. All curves exhibited peaks (a), (b), (c), and (d) except that (a) and (b) are absent from the ND sample. Peak (e) was always removed. Significantly, the peak (c) T_{max} shifts slightly to lower temperature with increasing dose. The glow curves of Fig. 3 were resolved into individual GOT kinetic peaks using a best-fit procedure. The resulting peak (c) curves are shown in Fig. 4.

3. Dose Dependency Measurements Obtained from a Single Sample

A series of measurements were made using the same sample for all glow curves. This procedure avoids averaging or selecting curves for each dose and determines if the glow curves depend on: 1) cumulative (total) dose, 2) sample surface changes, and 3) magnetic changes. To obtain the glow curves consisting primarily of peak (c), peaks (a) and (b) were thermally removed prior to measurement and peaks (d) and (e) were reduced as much as possible using the procedures given above. First, the glow curve for a selected natural sample was measured. Second, the <u>same</u> sample was given a dose of 5×10^2 Gy, inserted in the chamber and heated to 180° C for 40 seconds. This drains peaks (a) and (b). Third, after cooling, the glow curve was measured. Fourth, the procedure was repeated using doses 2.5×10^3 and 1.3×10^4 Gy.

The results, shown in Fig. 5, again shows that T_{max} shifts to lower temperature with increasing dose.

The data shown in Fig. 5 was fitted to the GOT kinetic equation and the resulting peak (c) curves are given in Fig. 6. Also, the 5 x 10^2 Gy measurement was repeated. As shown in Fig. 7, the resulting glow curve (dashed line) is very similar to the original curve (solid line). It is noteworthy that these curves are similar since, between the original measurement and the repeated measurement, the sample had been heated to 450° C four times and had received a total dose of ≈ 16 kGy.

4. T_{max} and GOT Parameter Values

To objectively determine T_{max} for the glow peaks of Figs. (3)-(7), the polynomial $I = a_2T^2 + a_1T + a_0$ was fitted to each peak with a least squares procedure and the peak temperature computed from $T_{max} = -a_1/2a_2$. The T_{max} values obtained in this way are listed in Table I.

As explained above, the best-fit procedure for GOT kinetics determines the parameters and lumped parameters $s/(1-\sigma)$, E, n_o, and $\sigma N/(1-\sigma)$. For GOT kinetics, σ cannot be determined directly from a fitting procedure. However a maximum value of σ can be determined from the condition $n_o \leq N$ and $\sigma < 1$. For convenience, let the determined lumped parameters $s/(1-\sigma) = C_1$ and $\sigma N/(1-\sigma) = C_2$. Then since $n_o \leq N$, $\sigma n_o/(1-\sigma) \leq C_2$ or $\sigma \leq 1/[1 + (n_o/C_2)]$. Let $1/[1 + (n_o/C_2)] = \sigma_{max}$. Then σ_{max} is the largest value of σ allowed by the best-fit determined constants.

From the lumped parameters $C_1 = s/(1-\sigma)$ and $C_2 = \sigma N/(1-\sigma)$, one obtains $s = C_1(1-\sigma)$ and $\sigma N = C_2(1-\sigma)$. Using $0 \leq \sigma \leq \sigma_{max}$, $C_1(1-\sigma_{max}) \leq s \leq C_1$ and $C_2(1-\sigma_{max}) \leq \sigma N \leq C_2$, or, $n_o/C_2 \leq n_o/\sigma N \leq n_o/C_2(1-\sigma_{max})$. The quantity $n_o/\sigma N$ is proportional to the fraction of traps initially filled, e.g. by irradiation. For small n_o, $n_o/\sigma N$ is small and, as n_o increases,

$n_o/\sigma N$ increases.

The best-fit peak (c) curves obtained from GOT kinetics for the glow curve data in Figs. (3) and (5) is shown in Figs. (4) and (6). Values for σ_{max}, E, and n_o and range of values for s and $n_o/\sigma N$, obtained by the best-fit procedure, are listed in Table II.

5. Low Dose Measurements

As a further test of the GOT equation, glow curves were measured for small doses to determine how $n_o/\sigma N$ depends on dose. As explained above, $n_o/\sigma N$ should increase with dose, i.e. with n_o. For this purpose, glow curves were measured for a ND sample and, using the procedure of Fig. 5, for doses 5 x 10^1 and 1 x 10^2 Gy. The resulting peak (c) T_{max} values are in Table I and the $n_o/\sigma N$ values are in Table II. They change in the expected manner (see below).

6. Measurements on Individual Grains

To determine if the TL of individual grains differed, a sample was irradiated to ≈ 10 kGy and photographed while being heated at the usual rate. The light from peak (c) was yellow, the same color previously observed in the emission from pyrite grains in granite (Schwartzmann et al., 1983). However, only a few grains from each sample were bright enough to appear on the photograph. Glow curves from single grains were obtained using high phototube sensitivity, i.e. high phototube voltage. Most grains exhibited characteristic pyrite glow curves. Some grains emitted exceptionally strong luminescence.

V Discussion and Conclusions

A. Chemiluminescence Results

1. The ≈ 430 °C CL Peak, i.e. Peak (e)

This peak is associated with changes in surface color and magnetic properties of the pyrite. These changes were larger after glow curve measurements producing peak (e) than after measurements where peak (e) was suppressed. Peak (e) could also be associated with a system contaminant since the peak was suppressed by measuring the glow curve immediately after helium was introduced into the chamber. This allowed insufficient time for the contaminant to enter the system. Microprobe analysis showed that heating caused samples to lose sulfur. Presumably a chemical reaction occurs on the surface where pyrite (FeS_2) reacts with the system contaminant to form pyrrhotite ($Fe_{1-x}S$, $0 \leq x \leq 0.2$) (Mellor, 1935). Under certain conditions, enough pyrite reacts to produce the emitted light detected as peak (e). The pyrrhotite forms a surface layer that causes the color changes. The sample also becomes magnetic since, unlike pyrite, pyrrhotite is magnetic.

Other observations mentioned above can also be understood. First, when peak (e) appears, heating to 450° C and cooling immediately does not allow the pyrite → pyrrhotite reaction to reach completion. The sample must be held at 450° C for ≈ 2 minutes to complete the reaction. If not, reheating, e.g. to measure the oven glow, restarts the reaction, and peak (e) is again observed. Second, if the changes in surface and magnetic properties have been completed, peak (e) is not observed when the sample is reheated. Third, if a sample in which the changes in surface and magnetic properties have been completed is subsequently broken into smaller pieces, peak (e) reappears since unreacted pyrite has been exposed.

The proposed reaction for peak (e) requires that this peak should , when not suppressed, appear in the glow curve of <u>any</u> pyrite crystal (not just the crystal used for most of the measurements described above). As explained above, peak (e) appeared in <u>all</u> pyrite crystals measured.

2. The ≈ 350° C CL Peak, i.e. Peak (d)

The nature of the peak (d) has not been determined. Since its intensity is reduced by eliminating system contaminants, the emitted light is, most likely, caused by a chemical reaction between the sample and a contaminant. This peak does not reoccur in samples broken apart or exposed to the atmosphere before reheating. For this CL peak to reappear, samples must be reexposed to radiation.

B. Thermoluminescence Results for the ≈ 250° C Peak, i.e. for Peak (c)

1. Sample-to-Sample Variation and Effects Due to Repeated Use of the Same Sample.

The results obtained by using pristine samples for each glow curve measurement (Fig. 3) and those obtained by using the same sample for each measurement (Fig. 5) are quite similar. Irradiation and heating do not significantly alter the TL properties of the samples even though there are changes in the surface and magnetic properties. This is well illustrated by Fig. (7) which shows two glow curves obtained with the same sample after doses of 5 x 10^2 Gy. However, between the first (solid line) and second measurement (dashed line), the sample was heated to 450° C four times and received a <u>total</u> dose of ≈ 16 kGy. The two curves do not differ significantly. However, the $n_o/\sigma N$ values appear to increase (see Table II). This implies that trap creation may have occurred during irradiation and consequently N increased.

Glow curve intensities differ somewhat for different pristine samples given identical doses. Some of this difference may be due to absorption in the sample; only light from a shallow region near the surface of the grains escapes to the phototube. As mentioned above, all glow curves were normalized

to the same mass. It would have been better to normalize the measurements to total surface area (difficult) or to use uniform grain size samples. Also, some intensity variations can be attributed to the presence of a few grains that are extremely strong emitters whose number will vary randomly.

2. Peak Shape

Fig. 2 shows that GOT kinetics provides the best fit of the single glow peak data. The fit is not perfect, especially at high temperatures where peak (d) was subtracted off. This discrepancy may be due to errors in the subtraction process. For example, CL peak (d) may not be exactly reproducible.

3. Dose Dependence of T_{max}

Table I shows that T_{max} for peak (c) decreases with increasing dose. This result is not an artifact of the fitting procedure since the temperature shifts occur in both the data and the curves obtained by fitting. This shift rules out 1st order kinetics which requires that T_{max} does not change with dose.

The observation that T_{max} depends on dose has been reported previously. For example, a similar shift was seen in the mineral albite (Pasternack et al. 1977) and most recently in the "red emission" from quartz (Miallier et al. 1990; Fain et al. 1990). Such peak shifts are consistent with 2nd order kinetics. The pyrite peak (c) result reported here is unique in the sense that the observed shift -- which rules out 1st order kinetics -- is accompanied by an analysis of the shape of the same peak which rules out 2nd order kinetics.

4. Kinetic Parameters; The Retrapping to Recombination Cross Section Ratio σ

Values of ω_{max} obtained by fitting the GOT equation to the peak (c) curves are given in Table II. The smallest value of σ_{max} obtained is ≈ 0.2 which strongly indicates that σ is not greater than this value. This also indicates that 2nd order kinetics, which requires $\sigma = 1$, does not apply to peak (c).

The quantity $n_o/\sigma N$ is proportional to the fraction of traps filled, e.g. by irradiation, prior to glow curve measurement. Assuming that σ and N remain constant, $n_o/\sigma N$ should increase with dose, i.e. with n_o. Table II shows that $n_o/\sigma N$ tends to increase with dose.

The natural dose, ND, can be readily obtained from a plot of n_o vs dose. This procedure indicates that ND $\approx 7 \times 10^2$ Gy.

The energy for thermal untrapping, E, of peak (c) is 1.4 eV (Table II). However, the GOT fitting program also provides good fits for E values that varied a few tenths of an eV from this value. This causes small, but insignificant changes in the other parameters of Table II.

5. Thermal "Draining" of Peak (c)

If a sample was heated at $\approx 250^o$ C for a short period, prior to measurement, peak (c) decreased. After cooling, in the subsequent recorded glow curve, T_{max} shifted to higher temperature. The shift was roughly proportional to the 250^o C heating period.

VI Summary

1) The shape of the large pyrite glow peak (c), is best described by GOT kinetics -- not 1st or 2nd order kinetics. Also, and most importantly, the peak (c) T_{max} shifts with dose. Thus, peak (c) is not described by 1st order kinetics.

2) The measured peak (c) shapes are best fitted by GOT kinetics with $\sigma \leq 0.2$. Thus, 2nd order kinetics, which requires $\sigma = 1$, is excluded.

3) The same results are obtained if the same sample is subject to a series of doses or if different samples are used for each dose. Samples which were repeatedly irradiated and accumulated large doses did not exhibit obvious radiation damage effects.

4) Plots of peak (c) area, i.e. the measured n_o values, vs dose indicate that the pyrite crystal used for most measurements had received a natural dose, ND, of $\approx 7 \times 10^2$ Gy.

To reiterate, from pyrite glow curves, which normally contain two small and one quite large TL peak and two small chemiluminescent peaks, one can obtain glow curves that are very good approximations to single peak glow curves. The single peak curves exhibit changes in shape and peak temperature expected for GOT kinetics. Furthermore, best fit procedures indicate that GOT kinetics describe the peak shape better than 1st or 2nd order kinetics and that the ratio of the retrapping to recombination cross section, σ, is less than 0.2. In addition, and most significantly, σ is also sufficiently larger than zero to produce glow peaks that do not have 1st order characteristics. In other words, these results indicate that at least one material exhibits all of the properties expected for general one trap (GOT) TL kinetics and that it is likely that other materials will exhibit similar kinetics.

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Figure Captions

Fig. 1. Typical pyrite (FeS_2) glow curve after a 2.5 x 10^3 Gy ^{60}Co irradiation (dose) in addition to the natural dose (ND). The measurement was made on a powder sample from the crystal used for a detailed study of the TL kinetics. Peaks (a), (b), and (c) are thermoluminescence (TL) peaks and (d) and (e) are chemiluminescence (CL) peaks.

Fig. 2. A demonstration that the large pyrite TL peak (c) is "best-fitted" by the GOT TL kinetics (solid line) described in the text. Also shown are the "best-fit" 1st order (dashed line) and 2nd order (dash-dot line) TL kinetic curves. The data points--only 1/12 are shown--were obtained by subtracting the dashed curve from the solid curve shown in (B). Insert A: Glow curve obtained from pyrite irradiated to 1.3 x 10^4 Gy after peaks (a) and (b) were thermally removed. Insert B: Glow curve (dashed line) from pyrite irradiated to 1.3 x 10^4 Gy <u>after</u> peaks (a), (b), and (c) were thermally removed. Also shown is the lower section of the curve in (A).

Fig. 3. Pyrite glow curves obtained by using <u>different</u> samples for each measurement. At each dose level a number of measurements were made and the median curves are shown.

Fig. 4. "Best-fit" GOT kinetic glow curves for peak (c) of each of the curves of Fig. 3.

Fig. 5. Pyrite glow curves for different doses obtained by using the <u>same</u> sample for all measurements. The glow curves were recorded after peaks (a) and (b) were thermally removed. The (a) and (b) peaks do not appear in naturally irradiated, i.e. ND, samples.

Fig. 6. "Best-fit" peak (c) GOT kinetic curves for each of the curves of Fig. 5.

Fig. 7. The 5×10^2 Gy glow curve from Fig. 5 (solid line) and a glow curve (dashed line) from the same sample irradiated to the same dose after it had previously been irradiated to a total of $\approx$ 16 kGy during four successive TL measurements.

TABLE I

TEMPERATURE OF PEAK (c) MAXIMUM (T_{max})(^{o}C)

Dose(Gy)	Data	Fitted Curve	Figs.
(Measurements on Different Samples)			
ND*	255.7	256.0	3,4
ND + $5x10^2$	250.8	250.8	"
ND + $2.5x10^3$	249.0	249.0	"
ND + $1.3x10^4$	246.4	246.7	"
(Measurements on Same Sample)			
ND	250.0	250.0	5,6
$5x10^2$	249.3	248.9	"
**	247.7	247.2	7
$2.5x10^3$	247.8	247.3	5,6
$1.3x10^4$	246.0	246.0	"
(Low Dose Measurements on Same Sample)			
ND	252.4	252.9	---
$5x10^1$	249.8	248.9	---
$1x10^2$	249.7	249.7	---

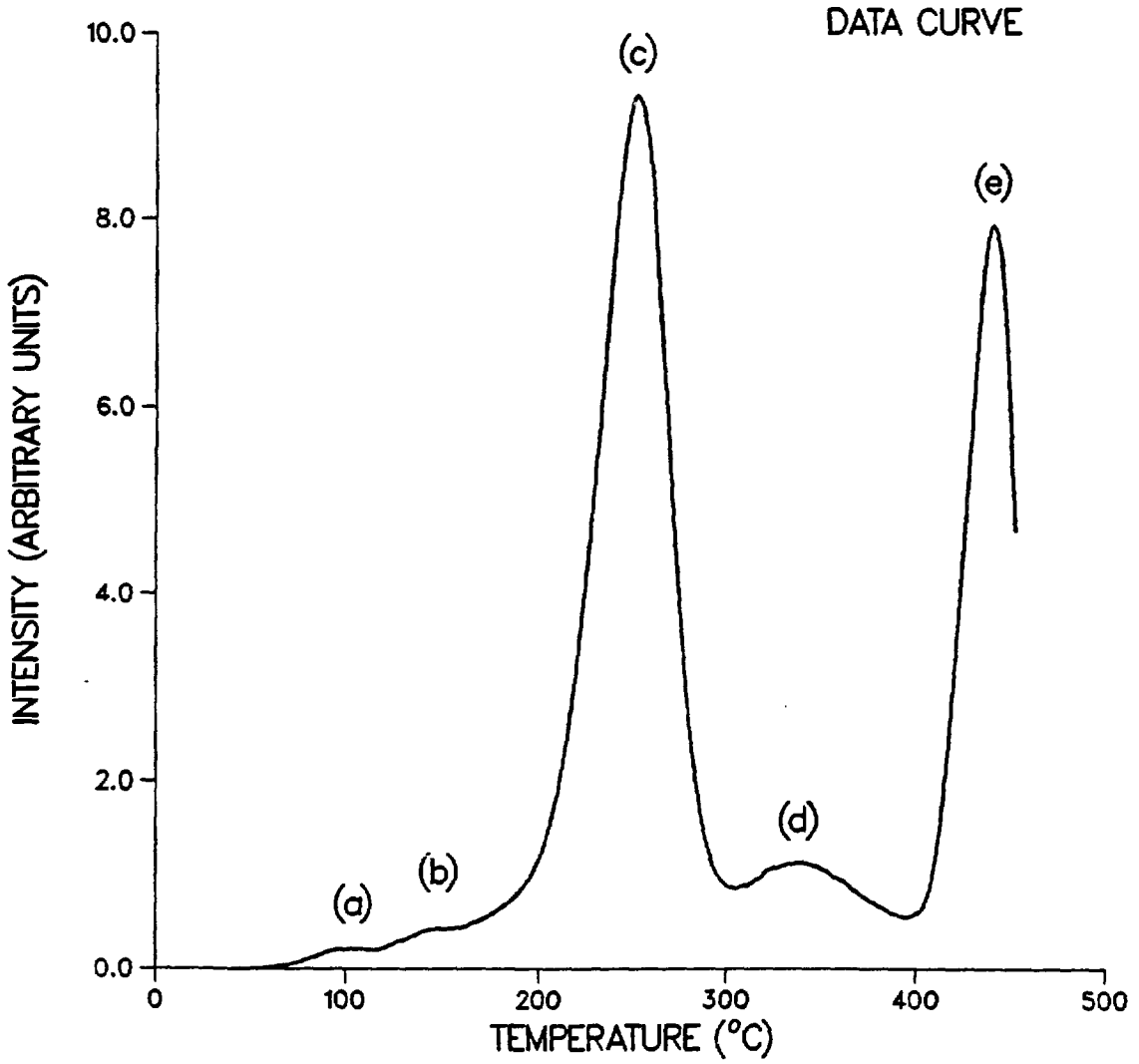
* Natural Dose

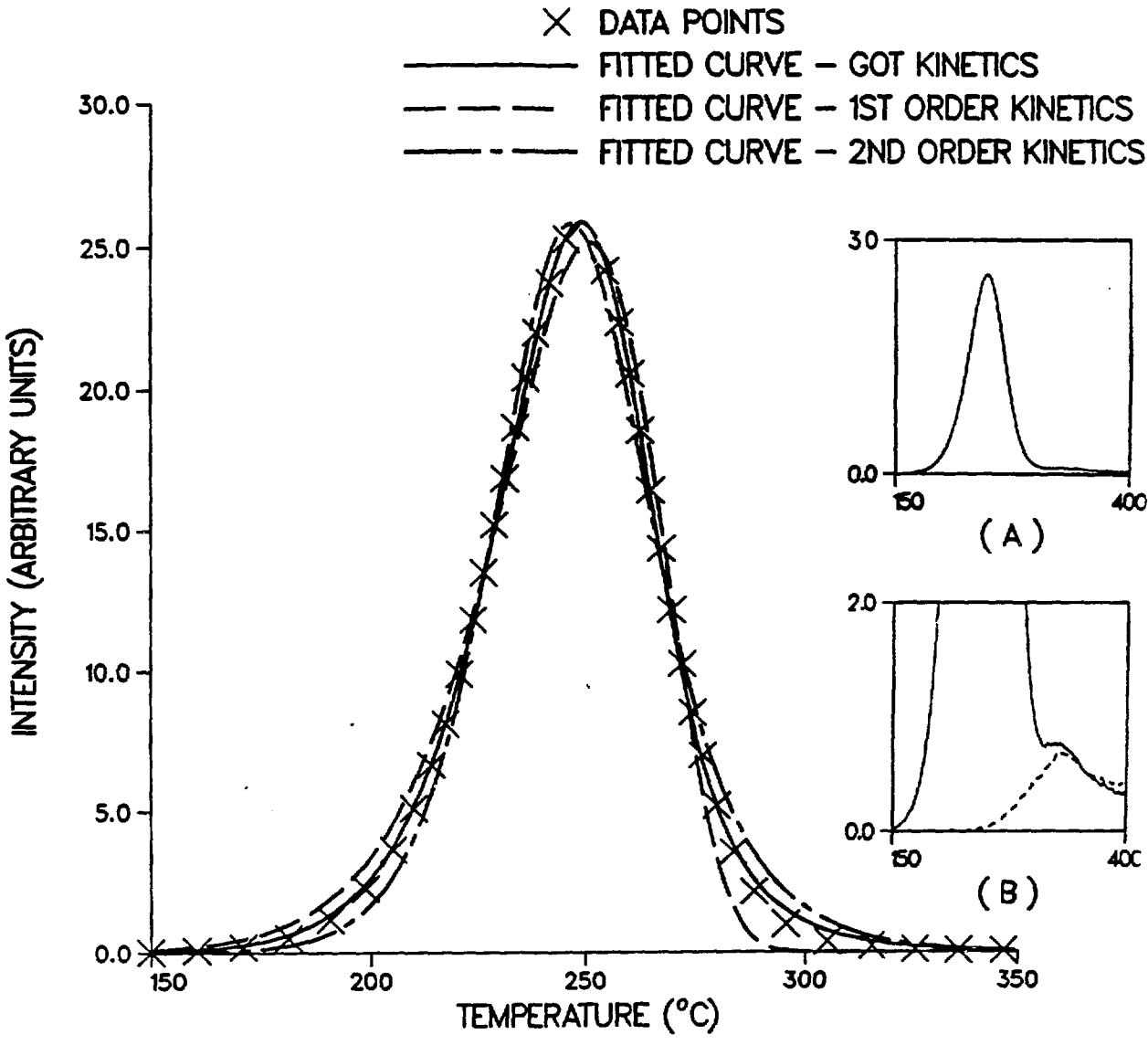
** Measurement repeated after additional irradiation and heating.

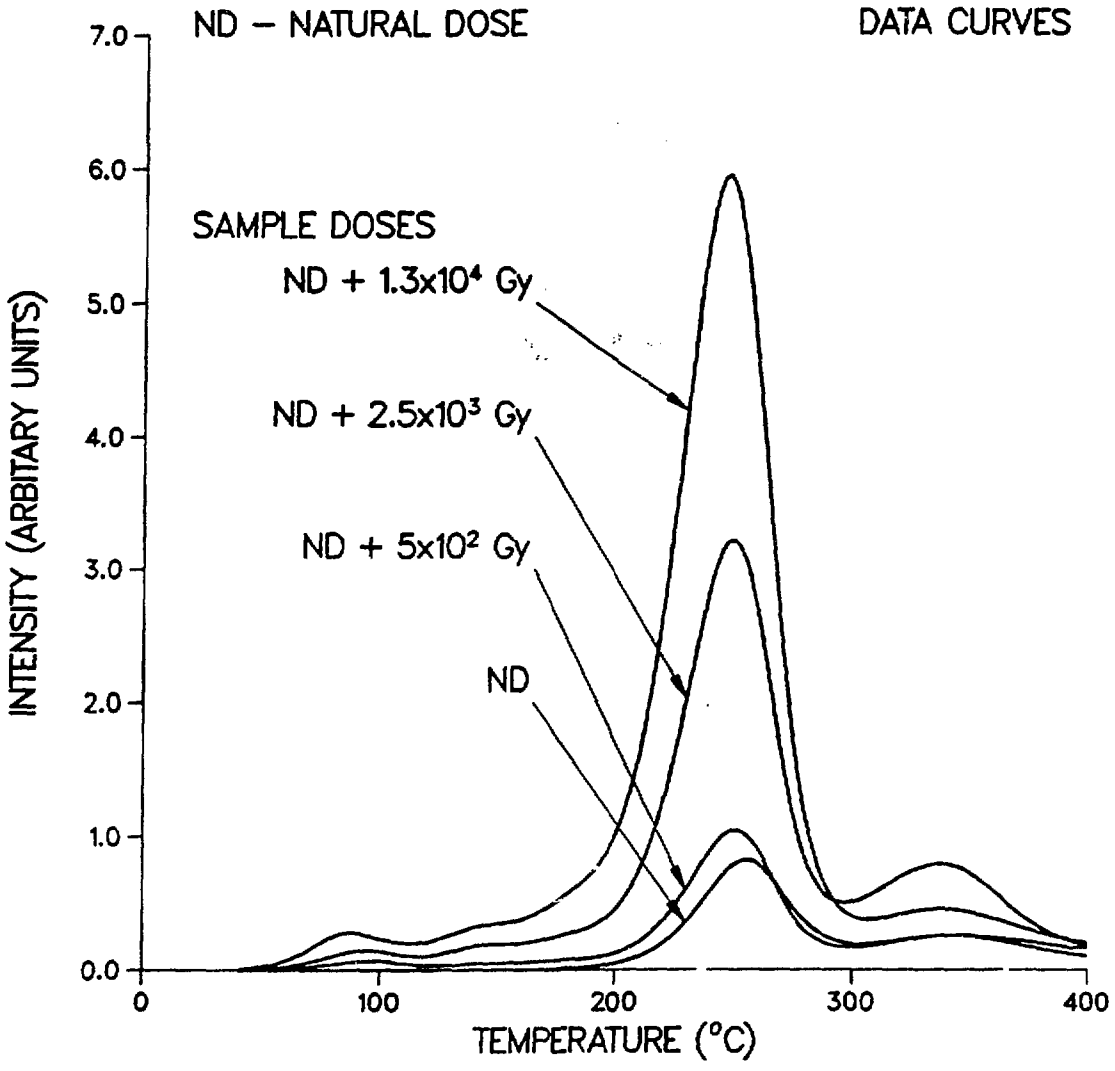
TABLE II
PEAK (c) GOT KINETIC PARAMETERS*

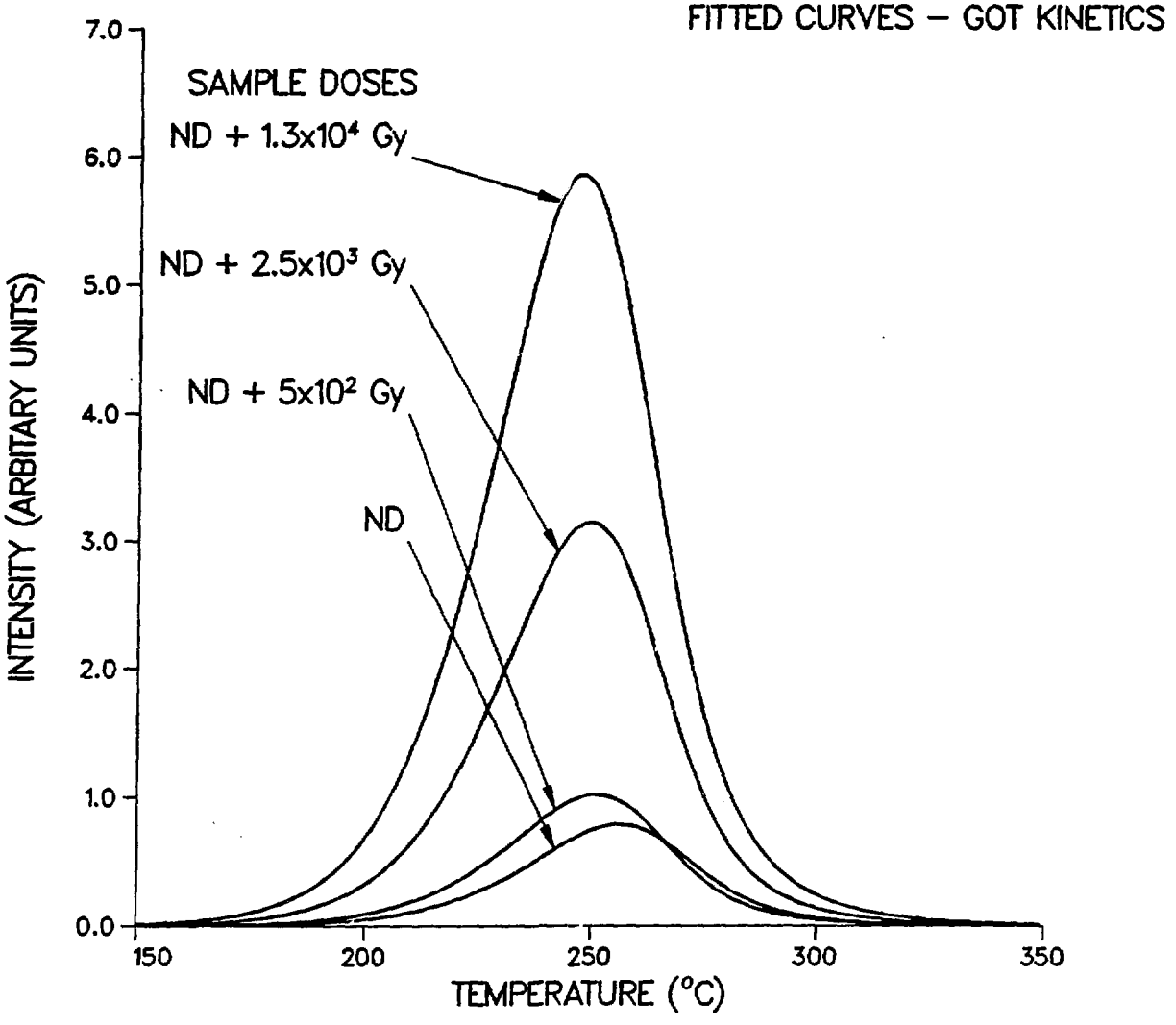
Dose (Gy)	σ_{max}	s (s^{-1}) $x10^{12}$	E (eV)	n_o[a] $x10^{6}$	$n_o/\sigma N$	Figs.
		(Measurements on Different Samples)				
ND	0.21	4.4-5.5	1.4	5.0	3.7-4.7	3,4
ND + $5x10^2$	0.18	4.2-5.1	1.4	6.2	4.4-5.4	"
ND + $2.5x10^3$	0.19	3.4-4.2	1.4	19	4.3-5.3	"
ND + $1.3x10^4$	0.23	4.6-6.0	1.4	36	3.4-4.4	"
		(Measurements on Same Sample)				
ND	0.11	6.1-6.9	1.4	5.2	8.4-9.4	5,6
$5x10^2$	0.22	7.0-8.9	1.4	4.0	3.5-4.5	"
**	0.31	5.6-8.0	1.4	3.6	2.3-3.3	7
$2.5x10^3$	0.24	6.6-8.7	1.4	12	3.1-4.1	5,6
$1.3x10^4$	0.22	6.6-8.5	1.4	21	3.5-4.5	"
		(Low Dose Measurements on Same Sample)				
ND	0.16	4.2-5.0	1.4	9.0	5.2-6.2	---
$5x10^1$	0.38	3.0-4.9	1.4	1.0	1.7-2.7	---
$1x10^2$	0.33	2.7-4.0	1.4	2.4	2.0-3.0	---

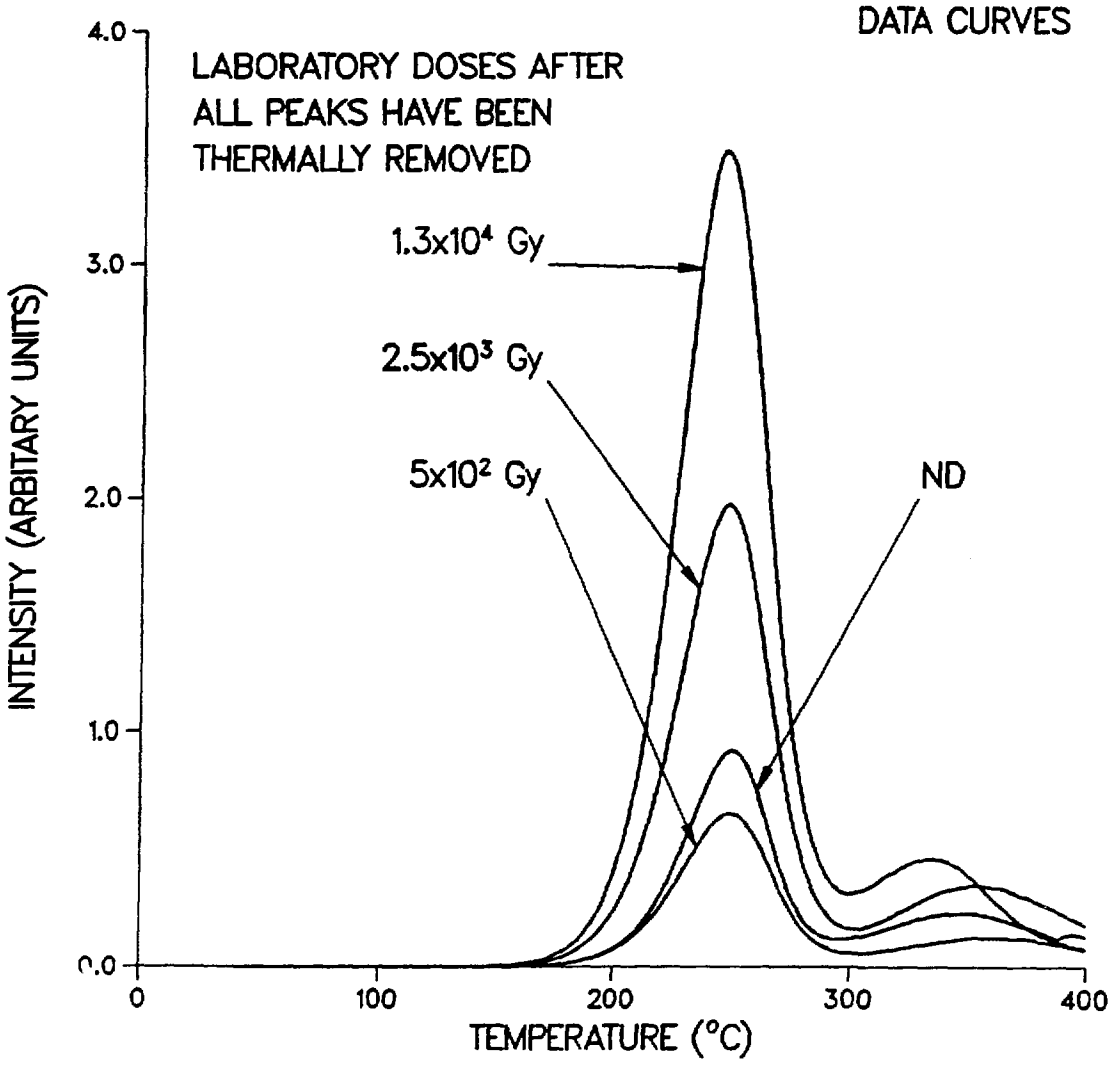
* s and $n_o/\sigma N$ can not be uniquely determined by a fitting procedure using the GOT Equation.
[a] Arbitrary units
** Repeat measurement

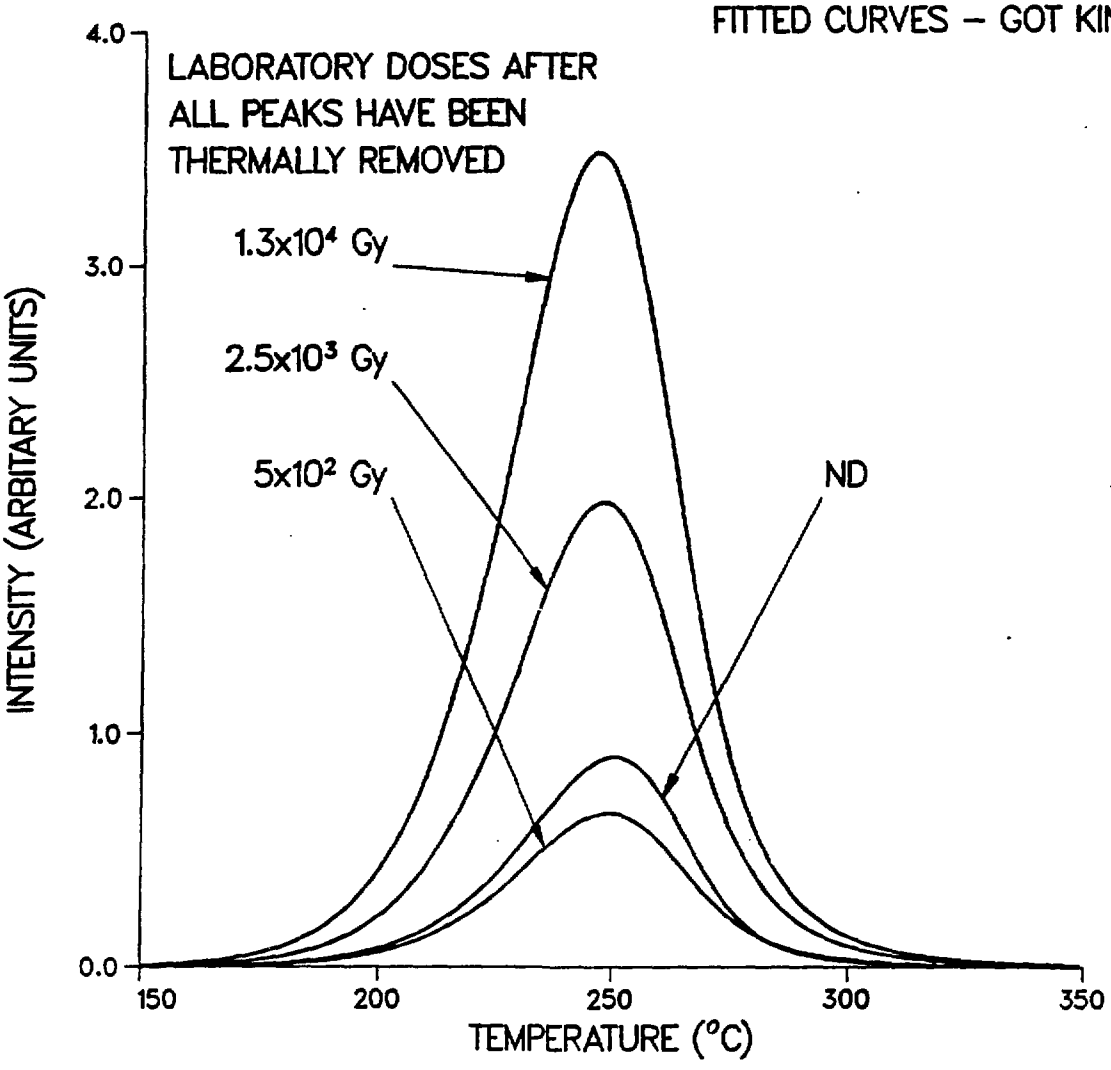

DATA CURVE
(a)
(b)
(c)
(d)
(e)
10.0
8.0
6.0
4.0
2.0
0.0
0
100
200
300
400
500
INTENSITY (ARBITRARY UNITS)
TEMPERATURE (°C)


DATA POINTS
FITTED CURVE – GOT KINETICS
FITTED CURVE – 1ST ORDER KINETICS
FITTED CURVE – 2ND ORDER KINETICS
INTENSITY (ARBITRARY UNITS)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
150
200
250
300
350
TEMPERATURE (°C)
3.0
0.0
150
400
(A)
2.0
0.0
150
400
(B)


ND – NATURAL DOSE
DATA CURVES
SAMPLE DOSES
ND + 1.3x10⁴ Gy
ND + 2.5x10³ Gy
ND + 5x10² Gy
ND
INTENSITY (ARBITARY UNITS)
TEMPERATURE (°C)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0
100
200
300
400


FITTED CURVES – GOT KINETICS
SAMPLE DOSES
ND + 1.3x10⁴ Gy
ND + 2.5x10³ Gy
ND + 5x10² Gy
ND
INTENSITY (ARBITARY UNITS)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
150
200
250
300
350
TEMPERATURE (°C)


DATA CURVES
LABORATORY DOSES AFTER
ALL PEAKS HAVE BEEN
THERMALLY REMOVED
1.3x10⁴ Gy
2.5x10³ Gy
5x10² Gy
ND
INTENSITY (ARBITARY UNITS)
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
TEMPERATURE (°C)


FITTED CURVES – GOT KINETICS
LABORATORY DOSES AFTER
ALL PEAKS HAVE BEEN
THERMALLY REMOVED
1.3x10⁴ Gy
2.5x10³ Gy
5x10² Gy
ND
INTENSITY (ARBITARY UNITS)
4.0
3.0
2.0
1.0
0.0
150
200
250
300
350
TEMPERATURE (°C)

DISCLAIMER