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Thermoluminescence emission from quartz at 480 nm as a high-dose radiation marker

P.G. Hunter[1,2], N.A. Spooner[1,2] and B.W. Smith[2]

[1] Institute for Photonics & Advanced Sensing and the School of Physical Sciences, University of Adelaide, Adelaide, South Australia 5005

[2] Defence Science and Technology Group, Edinburgh, South Australia 5111

Abstract

In this study we investigate the creation of high dose markers in the TL of quartz when irradiated with doses up to and exceeding 8 kGy, with a view to using the characteristics as a potential tool for retrospective dosimetry. Supralinear growth of the 210 °C and 350 °C 480 nm TL peaks was confirmed at high doses, as observed by others. Both peaks decrease abruptly at doses over 16 kGy, which we tentatively attribute to depletion of the 480 nm luminescence centres. Test doses applied after measurement of the high-dose TL showed that the 350 °C TL peak retained the sensitisation to dose, whereas the 210 °C TL peak did not. The 350 °C TL peak retains a significant marker of prior radiation exposure even after a one-hour annealing at 400 °C. Kinetic analysis on a quartz sample has shown that at high doses the 210 °C and 350 °C TL peaks have fundamentally the same E and s values as found for low-dose samples. The 12.0ka lifetime of the 210 °C peak makes it suitable for retrospective dosimetry.

Key words

Retrospective dosimetry; Quartz TL; High Dose TL; Quartz TL Sensitization

1. Introduction

Nuclear accidents or the operation of nuclear facilities can result in absorbed doses to the surroundings which are much higher than seen in typical samples analysed for TL dating applications. In this study we investigate the creation of high dose markers in the TL of quartz, and the potential use of quartz TL for retrospective measurements of doses up to and exceeding 8 kGy.

There are few studies characterising the TL of quartz above the common 'saturation' dose levels typically seen for dating, of approximately 300 Gy. None specifically addresses the potential for retrospective dosimetry applications, but several have noted that quartz TL continues to grow and that there appears to be sensitisation after delivery of very high doses.

The TL peak temperatures measured depend on both the heating rate employed and the thermal lag in the experimental apparatus. For clarity, in the discussion below we refer to the '210 °C' and '350 °C' peaks, which are the approximate peak temperatures measured when using a heating rate of 1K/s.

Durrani et al. (1977) and Sawakuchi and Okuno (2004) both used Brazilian quartz without any pre-treatment to investigate the TL response to very high doses (using proton and γ irradiation). They found a range of TL peaks, including the 210 °C and 350 °C peaks reported in this study.

David et al. (1978) reported sensitisation of quartz by 'pre-gamma exposure' where high doses of gamma irradiation sensitised the 400-480 nm blue TL emission of quartz.

Durrani et al. (1977) and Sawakuchi and Okuno (2004) both reported sensitisation of over an order of magnitude for both 210 °C and 350 °C TL peaks and Sawakuchi and Okuno (2004) reported rapid desensitisation of the 210 °C TL for doses exceeding 16 kGy (but not the 350 °C TL). Importantly, David et al. (1978) found that heating the samples up to 600 °C did not destroy the sensitisation of the 350 °C TL peak.

In another study Spooner (1987) observed supra-linear growth of the 350 °C/480 nm TL peak for laboratory administered γ doses of 300-4000 Gy, using quartz from the same origin as the current study. Huntley and Prescott (2001) using a different sedimentary sample, found significant growth in 350 °C/380 nm TL emission beyond 700 Gy. Chawla et al. (1998) have also shown sensitisation of blue TL emission for doses above 300 Gy, and suggested a possible link to the growth of an ESR centre. Woda et al. (2002) extracted quartz from volcanic rocks for TL and ESR analysis. They reported that the 480 nm blue emission at 350 °C displayed saturating characteristics for doses to 300 Gy before abruptly sensitising over 1 kGy and saturating again at 16 kGy. In this paper we progress these studies by undertaking a detailed characterisation of the TL properties of highly dosed quartz.

2. Experimental Methods

We selected well-studied quartz grains extracted from sand collected at a depth of 1 metre from the lunette bordering the western side of Lake Woods, located at 17°37.169' S, 133°02.889' E in the Northern Territory, Australia. The unprocessed sample was carbonate free and red in colour due to an iron oxide coating, with a moisture content in the range of 0.02-0.007g/g. Particles <20 μm were removed using dispersion with NaOH solution and decantation, and the remaining material sieved for the 90-125 μm fraction. The para- and diamagnetic material fraction was removed by magnetic separation using a Franz magnetic separator. The remaining material was etched for 40 minutes at 20 °C with 40% HF to remove the outer 6-8 μm layer of the quartz grains and to remove the

remaining non-quartz minerals. All measurements in this study started with this unbleached sedimentary quartz which had a natural dose of 16.9 Gy (Hutton et al., 1984)

For all but the kinetic measurements the quartz grains were loaded into 12 mm stainless steel cups, prepared by having the central 7 mm portion masked and sprayed using silicon oil to ensure there was no loss of grains. The aliquots comprised monolayers with mass ~8-10 mg. Results were subsequently mass normalised.

The test aliquots were β irradiated using 1.5 GBq $^{90}Sr/^{90}Y$ plaque sources with dose rates of 0.105 Gy/s and 0.063 Gy/s, contained within Risø reader models TL/OSL DA-20 and TL DA-15. All TL measurements were preceded by evacuation of the heating chamber to ~0.07 T before flooding with dry, high purity (N5) nitrogen to ensure no spurious TL emissions were present. A heating rate of 1 K/s was used throughout this study, except when it was varied for kinetic analysis. The measurement conditions for each specific experiment are provided below.

The TL emission spectrum was investigated using a 3D TL Fourier transform spectrometer (Prescott et al., 1988). This instrument allows the entire spectrum from 740 - 250 nm wavelength to be obtained simultaneously. Correction for the quantum efficiency of the PMT was undertaken during deconvolution calculations of the raw data.

The conventional TL measurements were made using a Risø TL DA-20 reader with an EMI model 9235QB bialkali PMT and 3 mm thick Schott glass BG39 filter (420-560 nm bandpass) to suppress unwanted TL emissions and incandescence. A Schott ND4 neutral

density filter (which attenuates the intensity by 75%) was used when PMT saturation was possible.

3. Results

3.1.3D TL Spectra

Aliquots of quartz from Lake Woods were irradiated with doses ranging from 8 Gy-16 kGy in addition to the natural dose (16.9 Gy). TL data collection commenced at 50 °C and extended at a heating rate of 1 K/s to a maximum of 400 °C where incandescence begins to dominate the emission spectrum.

The results are illustrated in Figure 1 which shows the TL emission as a function of temperature and wavelength/energy.

As the dose increases there is a strong blue emission at 480 nm, seen first in the 210 °C TL range, but then very prominently at 315-350 °C. In the following studies we refer to this compound peak as two peaks that we designate ‘315 °C and ‘350 °C. Note also that the 315-350 °C TL is visible at much lower intensity in the natural spectrum (N+8 Gy is shown here), where it emits more strongly in the red.

The 480 nm emission dominates all other TL emissions at doses exceeding 300 Gy. Martini et al. (2012) reported that the “blue” TL emission from a ground quartz crystal was composed of two components, one at 2.53 eV (480 nm) and another at 2.80 eV (440 nm). However, we only observed the 2.53 eV TL emission from our sample.

3.2.First Glow Response

A series of sets of four aliquots with added doses ranging from 1 Gy to 64 kGy were measured in the Risø TL DA-20 reader. This was the first heating of the aliquots and is conventionally called the 'first glow'. The aliquots were mass normalised and the results for each irradiation point averaged over the four measurements.

The counts for the 210 °C was derived by use of the Glow Fit program (Puchalska and Bilski, 2006) assuming first order kinetics and with the parameters (temperature of maximum, maximum and width of peak) optimised to fit the observed glow curve. The 350 °C TL peak has been described as intermediate order by (Hornyak et al., 1992), so the assumption of first order may not be valid. However, that approximation should have minimal effect on the peak counts reported here. The peak counts were measured for each of the 210 °C, and 350 °C peaks and plotted against the added dose (β Gy) in Figure 2 (note the logarithmic scales).

The 210 °C peak initially shows steady linear growth due to the added dose from a low level as the natural (geological) signal has faded due to relatively low thermal stability. It then shows an abrupt sensitisation, with a supralinear increase of two orders of magnitude, for doses exceeding 300 Gy. It saturates at around 8 kGy and then decreases abruptly for dose exceeding 16 kGy. By observation, the 315-350 °C peak starts at a higher level due to the natural component. It grows steadily for doses of several hundred Gy where there is evidence of saturation, followed by sensitisation of the 350 °C peak and supralinear growth beyond 1 kGy. It peaks at about 10 kGy and then follows the 210 °C peak into a rapid decline beyond 16 kGy. The 315 °C peak appears to saturate at 300 Gy and is obscured at doses exceeding 500 Gy.

We do not address the cause of the TL sensitisation in this paper except to note that both the 210 ° and 350 °C TL peaks appear to sensitise at the same dose and by approximately

the same degree, suggesting a potential link to the 480 nm luminescence centre. Note that that in the following section we demonstrate a difference in persistence of this sensitisation between the two peaks. The fact that both the TL peaks decline together for doses exceeding 16 kGy dose suggests depletion of the 480 nm luminescence centres.

3.3. Second Glow Response to a 100 Gy Test Dose

The persistence of the sensitivity enhancement seen at high doses in the first glow was investigated by applying a 100 Gy test dose after the first glow and measuring the TL under identical conditions (the 'second glow' measurement). This test dose shows if the prior exposure to high dose has caused an enduring increase in TL sensitivity. The results are shown in Figure 3.

For aliquots given an initial dose of up to approximately 300 Gy the test dose gave a constant value for all TL peaks. However, above that level the 350 °C TL peak was sensitised by over two orders of magnitude (between 300 Gy and 8 kGy) before remaining constant to our maximum pre-applied dose of 64 kGy. The 210 °C TL peak was enhanced slightly, but by much less than the 350 °C peak. These differences in enduring sensitivity implies that different sensitisation/desensitisation mechanisms are at play for the 210 °C and 350 °C TL peaks.

3.4. The Effect of Annealing on Dose Sensitivity

The results above were further extended by investigating the effect of a prolonged annealing at 400 °C (rather than the previous quick heat to this temperature during the TL measurements). An aliquot of quartz was given a 4 kGy dose and glowed out (1st glow)

followed by a 100 Gy test dose and glowed out (2^{nd} glow). This was followed by heating to 400 °C for 1 hour (annealing) before repeating the irradiate/glow process for doses of 100 Gy (3^{rd} glow), 4 kGy (4^{th} glow), 100 Gy (5^{th} glow) and concluding with a reheat for background measurement, which has been subtracted for all the results shown Figure 4.

These results show that the 350 °C TL peak sensitisation to dose has remained despite the annealing. The 4^{th} glow peak count corresponds to within 2% of the value expected for a single dose of 8 kGy, showing that the annealing has not interrupted the progression of the sensitisation.

The drop in the 350 °C test peak between 2^{nd} and 3^{rd} glows is consistent with measurements by Chawla et al. (1998) who found a loss of 25% total sensitivity after ~3 days of heating at 200 °C.

Figure 4 also shows that the 210 °C TL peak sensitisation has been lost after the 1^{st} glow (although it returns once the sample is again given a high dose). The 80 °C TL peak (commonly appearing at 100 °C when higher heating rates are applied) is roughly consistent throughout, noting that it may have faded more significantly during the long irradiation times for the 1^{st} and 4^{th} glow.

3.5.Kinetic Analysis of the 480 nm Peaks after a High Radiation Dose

The kinetic parameters for the 480 nm TL emission were investigated using the variation of heating rates (Hoogenstraaten) method.

The experiments were attempted initially with sample cups, but it was found that stainless steel discs gave more reproducible results with consistent thermal transfer which is

critical for these measurements. For inter-aliquot consistency, near-identical 9.7 mm stainless-steel discs were carefully selected within the range 0.2815-0.2820 g. Each disc was masked, and the central 5 mm area sprayed with silicon oil for adhesion of the sample grains. The total mass for each disc was nearly the same at between 0.2861 and 0.2863 g (with around 4.5 mg of grains).

These aliquots were irradiated with a 4 kGy β dose and the TL measured in a Risø TL DA-20 reader with heating rates of 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02 and 0.01 K/s. The temperature where the '210 °C' and '350 °C' peaks occurred was recorded for each heating rate. The experimental results are plotted in Figure 5 where the plot slope is equal to the trap depth (E in eV) and the pre-exponential factor (s) is calculated from

$s = E/k_s * \exp(-y\ intercept)$ seconds^{-1} (1)

where y intercept is the y axis intercept of the plot.

The lifetime (τ) at 20 °C is calculated from

$\tau = s^{-1} * \exp(E/k_s * T)$ seconds (2)

where T_m= temperature of TL peak maximum (K), β = heating rate (K/s), T= temperature (K), k_s=k/e=8.617*10^{-5} K^{-1}, k=Boltzmann's constant, e=electron volt.

The calculated results are E = 1.57 ± 0.04 eV, s = (2.73 ± 2.53) * 10^{15} s^{-1} for a lifetime of 12.0+16.8/-3.9 ka at 20 °C for the 210 °C peak and E = 1.44 ± 0.05 eV, s = (3.02±2.90) *10^{10} s^{-1}for a lifetime of 6.2 + 6.8/-2.9 Ma at 20 °C for the 350 °C TL peak.

The values of E and s are broadly consistent with the results reported for the 210 °C peak (Veronese et al., 2004) and the 350 °C peak (Hornyak et al., 1992) for quartz samples which had received a much lower dose (i.e. unsensitised). Pagonis et al. (2006) suggested that thermal quenching in quartz could influence kinetic parameters obtained by the

variation of heating rate method but this is not observed to be the case in practice. For example, Spooner and Questiaux (2000) did not observe detectable effects on kinetics parameters resulting from thermal quenching, obtaining consistent results for the 350 °C peak using the isothermal decay and peak shift methods and the peak shift method for even the 315 °C peak, which is known to exhibit strong thermal quenching. In this study, the peak integral estimates for the various heating rates were constant for heating rates in the range 0.01-1 K/s and decreased at higher heating rates, indicating the results were not significantly affected by thermal quenching. Also, note that for both the 210 °C and 350 °C peaks the results for β= 10 K/s, 5 K/s and 2 K/s were not used in the kinetic calculations as thermal lag became significant (as shown by the deviation from a straight line on the plot).

3.6.Isothermal Fading

A series of aliquots were β irradiated with a 4 kGy dose and stored in groups of four for varying periods at either 20 °C (room temperature- RT) or 100 °C (elevated temperature- ET). At the end of each storage period the TL of the four aliquots was measured, peak counts for the 210 °C and 350 °C peaks recorded, each group of four averaged and the results plotted in Figure 6.

None of the 350 °C (room temperature), 350 °C (elevated temperature) and 210 °C (room temperature) results displayed any loss of counts, indicating no fading took place over the two-month storage. At elevated temperatures the 210 °C peak showed fading which was broadly consistent with that calculated from the measured kinetic parameters (lifetime of 90 ±9 hours at 100 °C compared with a calculated lifetime of 166 +29/-24 hours). Hence, we conclude that neither of the peaks display anomalous fading.

4. Conclusion

Whilst the detailed measurements in this study were made on quartz from a single source, the observations are generally consistent with earlier work giving confidence that the results can be extended to quartz in general. It should also be noted that the laboratory β doses were administered at a dose rate of ~0.1 Gy/s which is around ten orders of magnitude greater than the environmental dose rate.

The 480 nm TL emission from quartz at both 210 °C and 350 °C is sensitised by radiation doses greater than about 300 Gy. The emission continues to increase until a dose of about 8 kGy. The 350 °C TL sensitisation persists for subsequent low-dose irradiations after the initial TL has been zeroed, even after a prolonged annealing. In contrast, the 210 °C TL sensitisation is eliminated by heating.

The 210 °C TL peak, with a lifetime of 12.0 ka at 20 °C and no indication of anomalous fading, appears to be the most suitable signal for use in retrospective dosimetry as it is reset for each irradiate/heat cycle with minimal sensitivity change. In contrast, the 350 °C TL peak has a sensitivity enhancement that accumulates over multiple irradiate/heat cycles.

Kinetic and anomalous fading tests on the TL emission give confidence that the observed sensitisation as sufficient stability to be used as a marker of prior exposure to very large radiation doses. A comparison of the 210 °C and 350 °C sensitivities may also yield information on doses received in prior irradiate/heat cycles. These two TL peaks de-sensitise to dose when irradiation exceeds 16 kGy. The reduction in both at the same time suggests this could be due the depletion of 480 nm recombination centres at high doses.

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Figure captions

Figure 1.

TL emissions from the quartz sample as a function of temperature and emission energy, showing the changes with increasing radiation dose: Natural + 8 Gy (a), Natural + 1 kGy (b), Natural + 4 kGy (c), Natural + 16 kGy (d).

Figure 2.

The first glow TL emission as a function of dose, showing sensitisation of all three peaks. The standard error is contained within the symbols.

Figure 3.

The second glow TL emission ('sensitivity') after a 100 Gy test dose, plotted as a function of added dose prior to the first glow. The standard error is contained within the symbols.

Figure 4.

TL glow curves measured before and after a 400 °C annealing. Test regime: 1st glow after 4 kGy, 2nd glow after 100 Gy, anneal 1 hour @ 400 °C, 3rd glow after 100 Gy, 4th glow after 4 kGy, 5th glow after 100 Gy.

Figure 5.

The kinetic analysis of the sensitised TL emission at 210 °C (a) and 350 °C (b). The standard error is contained within the symbols.

Figure 6.

Isothermal fading of the TL emissions at 20 °C (RT) or 100 °C (ET). The standard error is contained within the symbols.

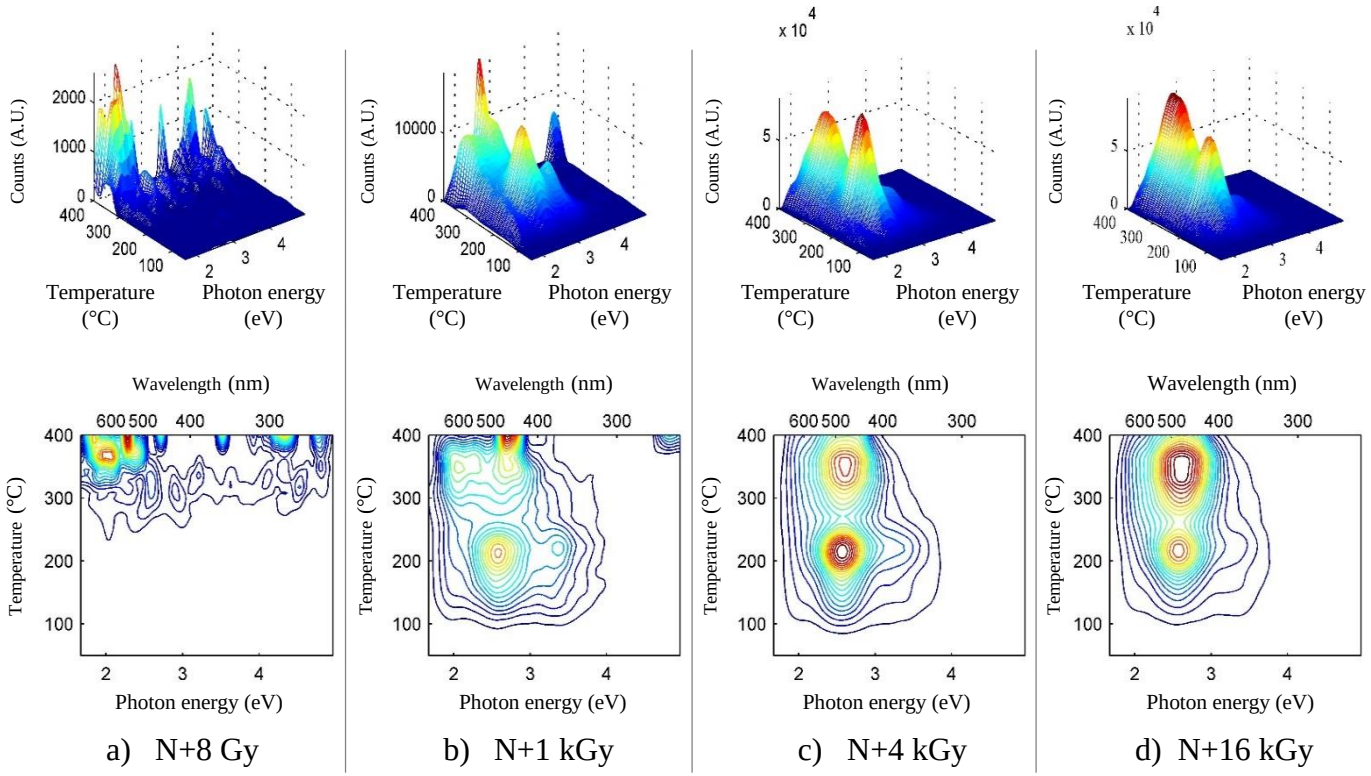
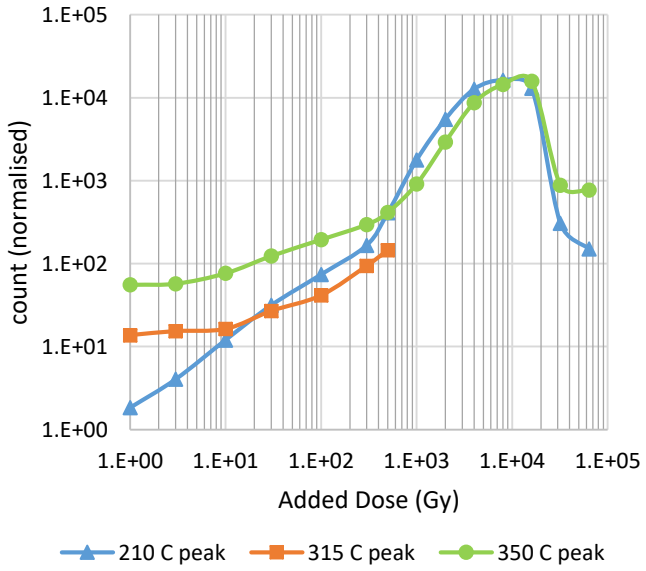

Counts (A.U.)
Temperature (°C)
Photon energy (eV)
x 10^4
Wavelength (nm)
Temperature (°C)
Photon energy (eV)
a) N+8 Gy
b) N+1 kGy
c) N+4 kGy
d) N+16 kGy

Figure 1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1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
count (normalised)
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
Added Dose (Gy)
210 C peak
315 C peak
350 C peak

Figure 2

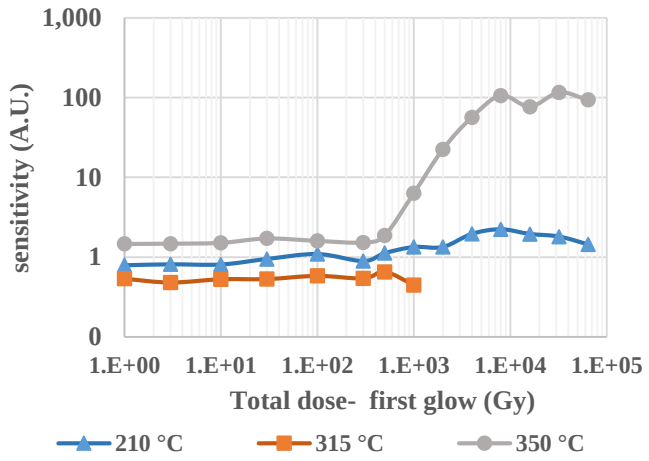

1,000
100
10
1
0
sensitivity (A.U.)
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
Total dose- first glow (Gy)
210 °C
315 °C
350 °C

Figure 3

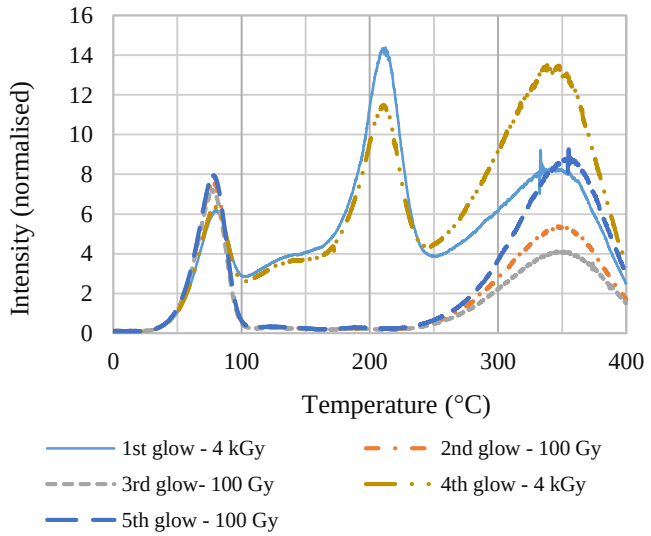
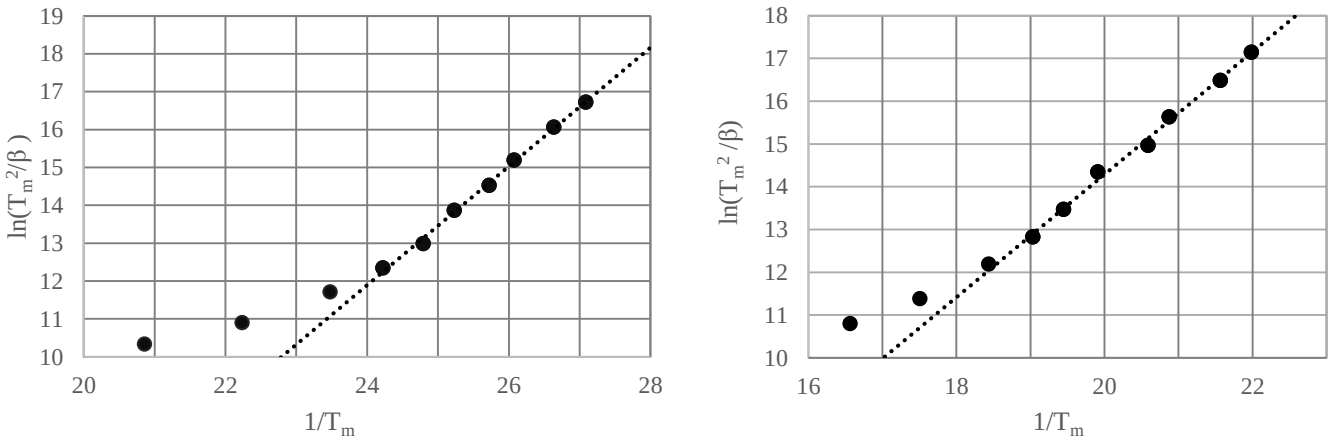

16
14
12
10
8
6
4
2
0
Intensity (normalised)
0
100
200
300
400
Temperature (°C)
1st glow - 4 kGy
2nd glow - 100 Gy
3rd glow- 100 Gy
4th glow - 4 kGy
5th glow - 100 Gy

Figure 4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18
17
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22
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26
28
1/T_m
18
17
16
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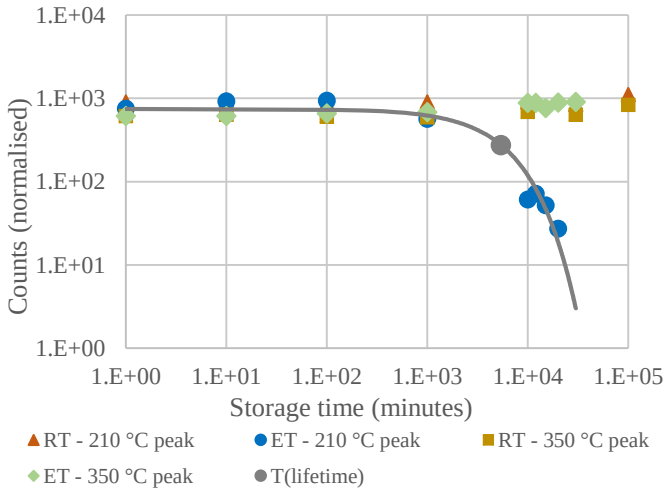
16
18
20
22
1/T_m

Figure 5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1.E+03
1.E+02
1.E+01
1.E+00
Counts (normalised)
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
Storage time (minutes)
RT - 210 °C peak
ET - 210 °C peak
RT - 350 °C peak
ET - 350 °C peak
T(lifetime)

Figure 6