Quantum tunneling processes in feldspars: Using thermoluminescence signals in thermochronometry

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ARTICLE INFO

Keywords:
Feldspar
Tunneling model
TL temperature Sensing
TL thermochronometry

ABSTRACT

During the past decade, our understanding of the nature of quantum tunneling processes in luminescence materials has been advanced significantly, by both experimental work and modeling insights into the underlying luminescence mechanism. This paper provides examples of analysis of thermoluminescence (TL) signals in feldspars, based on recent modeling work which showed that the shape of the TL glow curves remains practically unchanged after thermal and/or optical treatment of the samples. Analysis of the experimental TL glow curves in thermally or optically pretreated feldspars shows that these signals can be described as the sum of several Gaussian curves. While the positions and height of these Gaussians depend on the thermal and optical history of the sample, the width of the Gaussians apparently remains the same across the TL glow curve. TL glow curves are analyzed for 10 different samples, and the width of the Gaussian curves is found to be a common property characterizing all samples, at least within experimental error. Specifically it is found that the Gaussian width stays practically unchanged when the irradiated samples undergo thermal treatments for different times and temperatures, or alternatively when they undergo optical bleaching treatments with blue LEDs. The common overall shape of the TL glow curves has important implications for the use of these signals in thermochronometry.

1. Introduction

During the past decade, experimental and modeling studies have established that the main luminescence mechanism in feldspars is quantum mechanical tunneling. From a modeling point of view, the model developed by Jain et al. (2012) has contributed significantly to our understanding of tunneling phenomena resulting from a random distribution of electron-hole pairs. Kitis and Pagonis (2013) quantified the semi-analytical model of Jain et al. (2012) by deriving analytical expressions for different experimental stimulation modes, and these analytical equations have now been used to describe luminescence signals from a variety of feldspars and apatites (Polymeris et al., 2013, 2017; Sfampa et al., 2015). From an experimental point of view, there has been renewed interest in using TL signals from feldspars and other dosimetric materials for temperature sensing (Yukihara et al., 2018), and in thermochronometry applications for much larger geological time scales (Biswas et al., 2018).

Recently Pagonis and Brown (2019) presented new theoretical expressions describing the changes in the TL glow curves in feldspar samples, when they are preheated for various temperatures Tpq in the temperature region 200–300 °C and for various preheat times tpg. These authors showed that the TL glow curves “mirror” the underlying nearest neighbor distance distributions, and that the shape of the TL glow curves for the preheated samples will be close to Gaussian functions, and that the Gaussian width parameter σ stayed practically constant and independent of the preheating conditions. These theoretical predictions were verified by comparison with experimental data on thermally pretreated samples.

Based on their modeling study, Pagonis and Brown (2019) suggested that one could fit TL glow curves in feldspars on an empirical basis, by using symmetric functions like Gaussians. This empirical fitting method is an easy analytical method to extract properties like the full widths at half-maximum (FWHM), the temperature of maximum TL intensity (Tmax), and the half-intensity temperature values T1/2 from experimental data in thermochronometry or temperature sensing applications. The theoretical predictions of Pagonis and Brown (2019) were verified

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https://doi.org/10.1016/j.radmeas.2020.106325
Received 27 October 2019; Received in revised form 23 March 2020; Accepted 27 March 2020
Available online 12 April 2020
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by the extensive experimental data by Pagonis et al. (2019a), on the
dosimetric material MgB$_2$O$_5$:Dy, Na.

In other recent work, Pagonis et al. (2019b) presented Monte Carlo
simulations of tunneling recombination in random distributions of de-
fects. They carried out simulations of continuous wave infrared stimu-
lated luminescence (CW-IRSL), thermoluminescence (TL), iso-thermal
thermoluminescence (iso-TL) and linearly modulated infrared stimu-
lated luminescence (LM-IRSL). They also showed that their Monte Carlo
approach can be applied to truncated distributions of nearest neighbor
distances, which characterize samples that underwent multiple optical
or thermal pretreatments. The accuracy and precision of the Monte
Carlo method were tested by comparing with experimental data from
several feldspar samples.

The overall purpose of this paper is to provide a new look at the
shape of TL glow curves in feldspars which underwent thermal or optical
treatments.

The specific goals of the paper are:

(a) To apply the Monte Carlo method described in Pagonis et al.
(2019b) and Pagonis et al. (2018), to experimental TL glow
curves consisting of several overlapping peaks. Previously
the method has only been applied to single TL peaks in MgB$_2$O$_5$:Dy, Na
and single peaks in preheated feldspar samples.

(b) To analyze experimental TL glow curves in freshly irradiated and
also in pretreated feldspars, as the sum of Gaussian curves. This
empirical method is based on the recently proposed method of
Pagonis and Brown (2019).

(c) To investigate the possibility of a common description of the
shape and behavior of TL signals from freshly irradiated feld-
spars, and also for samples which underwent thermal and optical
treatments.

2. Experimental- Results from the fractional glow technique

The TL measurements for the feldspar samples studied in this paper
were carried out using a Risø TL/OSL reader (model TL/OSL-DA-15),
equipped with a $^{88}$Sr/$^{90}$Y beta particle source, delivering a nominal
dose rate of 0.105 Gy/s. A 9635QA photomultiplier tube with a com-
bination of Pilkington HA-3 heat absorbing and a Corning 7–59 blue
filter (320–440 nm) was used for light detection. All measurements were
performed in a nitrogen atmosphere with low constant heating rates of
1–2 °C/s in order to avoid significant temperature lag, and the samples
were heated up to the maximum temperatures of 500 °C.

The group of 10 feldspar samples used in this paper have been studied
previously in Polymenis et al. (2013), (their Table 1), and consist of
3 sanidine (laboratory code SAM2, SAM3, BAL2), 3 orthoclase
(MRK4, XAN8, VRS4) and 4 microcline feldspars (ELD1, KST4, VRS3,
YRS8). These authors investigated the possibility of using TL for struc-
tural characterization of these ten K-feldspar samples, and found a good
correlation between TL sensitivity and individual K-feldspar structure.
They suggested that these samples are ideal for investigating basic
luminescence signals.

The 10 museum feldspar samples studied in this paper are not chosen
randomly, but were selected on the basis of their geological properties
and specific crystal structure. Specifically the XRD studies of Polymenis
et al. (2013) characterized the parameters of feldspars, by using the probability of the Al-cation to occupy the T1 sites and also by
measuring the volume of the unit cell.

As a first step in the analysis of the complex TL glow curves in these
samples, the well-known fractional glow (FG) technique is applied, with
typical results shown in Fig. 1 for microcline sample ELD1. In the frac-
tional glow technique, the activation energy $E$ of the traps is evaluated
by thermal bleaching of lower temperature peaks, and the sample is
heated and cooled several times. For each cycle one applies the initial
rise method, and the resulting activation energy $E$ is plotted as a function
of the temperature, forming a step-like graph.

![Fractional Glow vs. Temperature](image1)

**Fig. 1.** The fractional glow method applied to microcline sample ELD1,
showing the presence of at least five distinct energy levels, located approxi-
mately at $E = 0.8, 0.95, 1.15, 1.25, 1.40$ eV. These $E$ values are used as initial
starting values for the MC simulations, and for fitting the TL glow curves with
Gaussian functions. Similar results were obtained for the other 9 samples
in this study.

An important part of the FG technique is deciding where exactly the
constant energy “steps” occur in the data. We have used two quantitative
criteria in deciding this:

(a) The “E-steps” must correspond to clear peaks of the TL glow
curve. For example, the TL glow curve in Fig. 1 has peaks at
approximately $T_{max} = 100, 160, 210, 260, 330$ °C.

(b) The “E-steps” must also correspond to at least 3 data points
of almost constant $E$-values in the FG graph.

Based on these two criteria, we interpret the results in Fig. 1 as
showing the presence of at least five distinct energy levels, located
approximately at $E = 0.8, 0.95, 1.15, 1.25, 1.40$ eV. These $E$ values will
be used as initial starting values for the MC simulations, and for fitting the
TL glow curves with Gaussian functions, as described later in this paper.
The optimal $E$ values are obtained by small adjustments to the above
values during the fitting of the TL glow curves. Similar results to Fig. 1
were obtained by applying the fractional glow technique to the other 9
samples in this study.

One can of course argue that the results of Fig. 1 show instead a quad-
continuum of $E$ values, instead of the 5 energy levels chosen above.
However, previous theoretical work on feldspars and on the analysis of
a continuous distribution of energies supports our proposition that in
feldspars one is dealing with 5 discrete levels, instead of a continuous $E$
distribution. Specifically, experimental and theoretical work has shown
that the TL glow curves in feldspars can be described well by a com-
bination of a single value of $E$ and a distribution of frequency factors
$s$, which depend on the distribution of distances between positive and
negative charges. This distribution of frequency factors is contained
implicitly in the original model by Jain et al. (2012), and was given a
specific mathematical form in the recent paper by Pagonis et al. (2019b).

In the authors’ opinion, this combination of factors (single $E$ and dis-
bution of $s$ values), leads to the very broad TL peaks one observes
in feldspars.

3. New simulations of TL glow curves and brief review of the
model and of the Monte Carlo method

In this section new simulations are presented, based on the model
of Jain et al. (2012). This model is based on localized electronic recom-
bination within a system of random distribution of pairs of trapped
electrons and recombination centers, and recombination is assumed to
take place via tunneling from the excited state of the trapped electron and takes place only to the nearest neighbor centers.

Previous simulations by Kitis and Pagonis (2014) showed that the TL glow curves obtained using the model of Jain et al. (2012), are very nearly symmetric for values of the parameter $\rho > 0.01$, with a geometrical symmetry factor $\rho_s = 0.52$. The symmetry factor $\rho_s = \delta/\omega$ is the ratio of the widths $\delta = T_2 T_m$, and $\omega = T_2 T_{}\overline{\omega}$, where $T_2$ and $T_{\overline{\omega}}$ are the temperatures at half maximum intensity on the low and high temperature side of the glow peak, respectively. $T_m$ represents the temperature at maximum intensity. The new simulations presented in Fig. 2 extend these previous simulations by using random variations of the parameters in the model, and by using the MC method described in detail by Pagonis et al. (2019a).

The MC method evaluates the total concentration of remaining electrons $n(I)$ and the TL intensity $I(I)$ simultaneously. In addition, this MC method can also be used for irradiated samples which were exposed to optical and thermal pre-treatments. For such pre-treated samples, one can approximate the nearest neighbor distribution with a truncated distribution function, which extends from a minimum critical radius up to infinity (Pagonis et al., 2019b). This critical radius is treated as an adjustable modeling parameter when fitting experimental data.

Fig. 2 shows the results of the Monte Carlo method, by varying randomly the kinetic parameters $E$, $s$, $\rho$, in a wide range of physically reasonable values. Specifically the activation energy is varied in the range $E = 0.7$–2.0 eV, the frequency factor in the range $s = 10^{10}$–$10^{12}$ s$^{-1}$, and the dimensionless density parameter in the typical experimental range $\rho = 0.002$–0.01 (Pagonis et al., 2019b). The dimensionless density parameter $\rho$ is defined by

$$\rho = \frac{4\pi s / 3}{\alpha^3},$$

where $\alpha$ (m$^{-1}$) is the potential barrier penetration constant, and $\rho$ (m$^{-3}$) represents the actual number density of acceptors per unit volume.

A total of $N = 650$ random variants of the TL glow curves are simulated for different random combinations of $E$, $s$, $\rho$, and these were fitted with a standard Gaussian curve of the form:

$$TL = A \exp \left[ -\frac{(T - T_{\text{max}})^2}{2\sigma^2} \right]$$

where $A$ is the maximum height of the Gaussian, $T_{\text{max}}$ is the location of the maximum TL intensity, and $\sigma$ represents the width of the Gaussian.

The histogram in Fig. 2 shows that the width parameters $\sigma$ of the fitted Gaussian curves are in a rather narrow range of values, with an average $\sigma = (24 \pm 6)$ K (one standard deviation).

From these modeling results, it is concluded that the width parameter of the Gaussians used to fit the TL glow curves will vary within a rather small range of values; this range is practically independent of the values of the parameters $E$, $s$, $\rho$, and therefore the width parameter $\sigma$ can be considered a characteristic of the whole TL glow curve and of the material. This concept of a single value of $\sigma$ characterizing the whole glow curve is used in the next section, to analyze complex experimental TL glow curves in freshly irradiated samples.

It is emphasized that the width of the Gaussian curves in the rest of this paper is not chosen arbitrarily, but is based on previous theoretical considerations and experimental work. Specifically, Pagonis and Brown (2019) presented a comprehensive mathematical study of the effect of thermal and optical treatments on the width of single TL peaks in feldspars. These authors showed quantitatively that the width of individual TL peaks changes very little when feldspars are exposed to various thermal/optical treatments. On the experimental side, the work by Polymenis et al. (2017) and Pagonis et al. (2018, their Figure 10) presented experimental data for the width of the 300°C TL peak of 5 feldspar samples that underwent different thermal treatments. In the latter work, the authors found that the width of the single symmetric TL peak at 300°C was practically constant for the 5 feldspar samples studied. These previous theoretical and experimental studies of the practically unchanging width of the TL peaks in feldspars are consistent with the new simulation results presented in Fig. 2 of the present paper, which shows an almost constant width of the TL peaks.

4. Monte Carlo simulations of complex experimental TL glow curves

In this section we analyze complex TL glow curves by extending the MC method of Pagonis et al. (2019b). While previously this method was used to simulate single TL peaks in preheated samples, in this section the method is extended to describe complex TL glow curves consisting of several closely overlapping peaks. The analysis is based on the following physical assumptions:

(a) Each TL glow curve in a freshly irradiated sample consists of at least 5 constituent glow peaks, each corresponding to a different $E$ value determined by the fractional glow results in Fig. 1. The donor-acceptor pairs for each trap are randomly distributed, and each trap in a freshly irradiated sample is described by its own symmetric nearest neighbor distribution.

(b) There are many more acceptors in the material than donors, so that the material is characterized by a constant acceptor density parameter $\rho$. Electrons from the five traps are likely to be accessing the same recombination center, and all traps are characterized by the same constant parameter $\rho$. 

Fig. 3 shows the results of MC analysis of the TL glow curves for sample BAL21, based on the above assumptions. Specifically, Fig. 3a shows the MC results for a freshly irradiated sample; the complex TL glow curve is analyzed as the sum of 5 individual peaks, located at temperatures of $<100$, 150, 200, 250, 300°C. The parameters in the MC simulation are $E = 0.86$, $1.02$, $1.16$, $1.29$, $1.455$ eV; the frequency factor is $s = 10^{12}$ s$^{-1}$ and $\rho = 0.005$.

The components of Fig. 3a are the result of averaging 10 Monte Carlo runs, with the error bars representing the standard deviations of the 10 runs, in order to indicate the random spread between Monte Carlo runs. The resulting average is close to, but not perfectly symmetric.

Fig. 3b shows the complete sequence of TL glow curves for this sample, obtained by preheating the same sample for 10 s in the range 100–350°C, in steps of 25°C. Good agreement is seen between the MC method shown by the thick gray lines, and the experimental data.

It is important to note that the only adjustable parameter in the MC model is the critical radius $r_c$ for each of the five traps. This parameter describes the truncated distribution of nearest neighbors, which is the result of preheating the sample (Pagonis et al., 2019b). The critical...
radius \( r \) is the only parameter that needs to be adjusted in the model, in order to describe the complete set of TL glow curves in Fig. 3b.

This good agreement between the simulations and the experimental data provides further confidence in applying the empirical deconvolution method proposed by Pagonis and Brown (2019), in which complex TL glow curves are analyzed by the sum of Gaussian functions of the same width. Examples of this deconvolution method are given in the next section.

5. Examples of analyzing TL glow curves as the sum of Gaussian curves

In this section we provide examples analyzing complex TL glow curves as the sum of Gaussian functions. It must be emphasized that the purpose of this type of deconvolution is not to obtain the physical parameters of the model \( (\Delta\alpha, s, \rho' \text{ etc}) \), but rather to obtain the heights, positions and widths of the underlying individual symmetric TL peaks. These relative heights and positions of the peaks are important in thermochronometry studies, since they can be used as indicators of the thermal and optical history of the sample (Pagonis and Brown, 2019).

Figs. 4 and 5 show deconvolution examples for freshly irradiated, and for optically pretreated samples, correspondingly. Fig. 4 shows typical examples for 2 freshly irradiated samples, obtained with a least squares fitting procedure. In this procedure the positions and heights of the Gaussians are treated as independent fitting parameters, and the width of the 5 Gaussians is taken to be the same for all 5 peaks. All TL glow curves for the 10 feldspar samples could be fitted accurately with this procedure, with typical FOM values in the range 2-5%. The average width of the Gaussians for all 10 feldspar samples in this study was \( \sigma = (29 \pm 5) \) K, in reasonable agreement with the value \( \sigma = (24 \pm 6) \) K obtained from the MC simulations in Fig. 2b.

Fig. 5 shows typical examples for microcline sample KST4, which was exposed to blue LED light for times in the range \( t = 1-15,000 \) s,
before measurement of the TL signal. The complete set of TL signals in Fig. 5 are fitted with the same least squares fitting procedure described above, with the width of all Gaussians taken to be the same. All 12 TL glow curves shown in Fig. 5b could be fitted accurately with this procedure. The average width of the Gaussians for all 12 glow curves was \( \sigma = (30 \pm 4) \) K, again in reasonable agreement with the MC simulations in Fig. 2b.

It is noted that two different least squares methods are used in this paper, the Monte Carlo fitting model based on the previous work by Pagonis et al. (2019b), and the empirical Gaussian curve fitting method. The values and the number of the free fitting parameters for these methods, are constrained on the basis of our previous theoretical and experimental studies of these 10 feldspars.

In the first method, the parameters required to model a typical TL glow curve with 5 peaks by using the Monte Carlo method are as follows:

(a) A single dimensionless density \( \rho' \) with typical value of \( \rho' = 0.01 \), is used for all 5 peaks. This value of \( \rho' \) is based on both theoretical and experimental studies, and is allowed to vary by \( \pm 0.005 \).

(b) Five distinct E-values located approximately at \( E = 0.8, 0.95, 1.15, 1.25, 1.40 \) eV and corresponding to 5 broad TL peaks at different temperatures near \( T_{\text{max}} = 160, 160, 210, 260, 330 \) °C. During the fitting process the location of the 5 peaks is allowed to vary only by \( \pm 5 - 10 \) °C. Similarly, the E values are only allowed to change by \( 0.05 \) eV during the MC modeling process.

(c) A single frequency value \( s = 10^{12} \) s\(^{-1} \) is used for all peaks, together with a distribution of nearest neighbor distances \( r \), as required in the model by Jain et al. (2012). This single value of \( s \) becomes mathematically in the model an effective distribution of frequency factors \( \chi_{E} \) defined by:

\[
\chi_{E}(r) = \frac{s}{\exp[(\rho')^{-1}/r]}
\]

This point was discussed in detail in Pagonis et al. (2019b), who derived the mathematical form of this distribution of frequency factors.

(d) Five distinct heights for the 5 TL peaks are varied to achieve the optimum fit to the experimental data.

The Monte Carlo analysis is then based on a total of 12 fitting parameters. For comparison purposes, a similar TL glow curve with 5 peaks for quartz would require a total of 20 fitting parameters, since each TL peak is characterized by 4 parameters. These are the activation energy \( E \) and frequency factor \( s \), plus a kinetic order parameter \( b \), and the corresponding height.

Similarly the Gaussian fitting method used in this paper is restricted in the number of free parameters. This method uses a total of 11 fitting parameters as follows. Each TL peak is characterized by the height and location of the peak (2 \( \times 5 = 10 \)) plus one extra fitting parameter for the assumed common value of the Gaussian widths \( \sigma \). The common parameter \( \sigma \) is assumed to be a characteristic of the whole glow curve.

6. Discussion and conclusions

This paper has presented new experimental TL data for 10 feldspar samples, which were either freshly irradiated (Fig. 3), which had undergone thermal treatment (Fig. 4), or optical treatment (Fig. 5). In all cases the TL glow curves were fitted as the sum of 5–6 independent Gaussian curves of the same width. The results from all 3 types of experiments and from all 10 feldspar samples show that the TL glow curves exhibit common characteristics, and can all be described using a Gaussian width parameter \( \sigma \) with a value around \( \sigma = 30 \) K.

This common behavior of all studied glow curves suggests that the width parameter \( \sigma \) may be a common characteristic of all feldspars, and further experimental work is necessary to verify this possible common behavior.

This common characteristic width parameter \( \sigma \) is of immediate importance for thermochronometry studies, since deconvolution of feldspar TL glow curves with Gaussians provides an easy method to extract the relative heights and positions of the constituent TL peaks in a complex TL glow curve. The position and heights of these peaks maintain a record of the thermal and optical history of the sample (Pagonis and Brown, 2019). Further experimental and modeling work is necessary in order to verify the common behavior of TL in feldspars for other types of samples.

It is noted that there is no direct mathematical relationship between the Gaussian curves and the parameters \( E \) and \( s \). We are not using to Gaussians to derive the values of \( E \), \( s \) as the standard practice for other dosimetric materials. Furthermore, the concept of one specific \( s \)-value does not apply to the TL glow peaks of feldspars. As mentioned above, these broad TL glow curves are a direct consequence of the presence of a distribution of \( s \)-values associated with a single energy value \( E \).

References


