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Competition between long time excitation and fading of thermoluminescence (TL) and optically stimulated luminescence (OSL)

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ABSTRACT

In the present work, we consider the filling and thermal emptying of traps and centers in a simple one-trap-one-recombination-center model in a small system such as a quartz grain in nature, when both the excitation and thermal release of electrons are very slow. Due to the nature of the very slow process, Monte Carlo simulations appear to be a very appropriate method. However, in parallel, we have applied an approximate analytical method and found practically the same results although the Monte Carlo results showed some small fluctuations due to the statistical nature of the procedure. This is in line with the experimental results which are also expected to have statistical fluctuations. The main result found is that after a long enough time, measured in hundreds or thousands years or more, the filling of the trap reaches a plateau which, depending on the parameters, may be very significantly smaller than the concentration of the trap in question. This equilibrium value is the same if we start from very low, e.g. zero concentration or very high, above the equilibrium value. This plateau level depends strongly on the relevant parameters. However, comparing simulations with activation energies of 1.2 eV and 1.3 eV shows strong dependence of the plateau level on the energy. Similarly, we can expect strong dependence on the temperature at which the sample is held. The results reached here and shown in Figs. 1–4 are based on the simplest OTOR model, but similar results of approaching a plateau level which are not due to the saturation of traps may occur in more complex systems as is demonstrated by simulations based on the Bailey model for quartz which includes several traps and centers.

1. Introduction

In two recent papers the slow fading of thermoluminescence (TL) and optically stimulated luminescence (OSL) have been studied using Monte-Carlo simulations. The models used were the one-trap-one-recombination-center (OTOR) (Chen and Pagonis, 2015) in which mainly non-exponential fading was predicted and a more complex model with additional deep trap (Chen and Pagonis, 2020) where fading was shown to be mainly exponential. The fading involved was considered to be the thermal fading from basically rather stable, deep traps, like those found in archaeological or geological samples. However, if the time scale is of hundreds or thousands years or more, a very slow thermal decay can be expected. In these papers by Chen and Pagonis (2015, 2020), it is suggested that since the thermal release of electrons in a small grain (e.g. of quartz from pottery) from traps is very slow, of the order of one electron per day or less, the natural way of dealing with the decay is by using a Monte-Carlo method rather than solving the relevant set of differential equations governing the process at constant temperature.

One should remember, however, that with archaeological and geological samples, the scenario is different than having a preliminary fast excitation and a very long fading. Actually, for hundreds or thousands (or more) years it is irradiated very slowly and in parallel, electrons are escaping thermally very slowly from the traps into the conduction band, from which they can either retrap or perform recombination with holes in centers. One can expect that after a certain (long) period of time, the concentration of trapped electrons will reach a plateau which, depending on the trapping parameters and rate of excitation, may be significantly lower than real saturation of the traps. The number of electrons trapped during the archaeological or geological periods may be translated into the TL or OSL intensities during the readout, thermal or optical, or to the ESR signal.

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In a paper by Autzen et al. (2018), the question of how many electron-hole pairs are produced in a quartz grain under natural irradiation is discussed. By using the previously developed radiation transport model-Geant4, they report values of ~80000 electron-hole pairs generated per Gray for quartz grains of ~50 μm. A typical dose rate in nature may be ~2Gy/ka, which would mean ~160 pairs produced per year or ~0.4 per day in the grain.

In this paper, we consider the filling of traps under these conditions of very slow excitation and very slow release of trapped electrons. We follow the process by using a Monte Carlo simulation as well as an approximate analytical procedure.

In the present work, we have also further investigated this effect by using the comprehensive phenomenological general models by Bailey (2001) and Pagonis et al. (2008). These models have been used effectively to simulate various aspects of luminescence in quartz, and have explained many phenomena observed in luminescence emissions from quartz (Pagonis et al., 2011; Chen and Pagonis, 2011). In the present paper we are interested in the effect of slow irradiation and rather elevated irradiation temperature on the trap filling process for a quartz sample. Relevant previous simulations were carried out by Koul and Patil (2015) and Koul et al. (2016). These authors carried out extensive simulation studies and examined the effect of geological and burial temperatures on the sensitization of luminescence emission in quartz. The results of these simulations suggested that the temperatures prevailing during burial time have appreciable impact on the natural luminescence signals in quartz.

2. The model

The simple model we consider is shown schematically in Fig. 1. It consists of a trap N (cm^{-3}) with instantaneous occupancy of n (cm^{-3}), activation energy E (eV), frequency factor s (s^{-1}) and a center M (cm^{-3}) with instantaneous occupancy of m (cm^{-3}). The recombination probability coefficient is A_m (cm^3s^{-1}) and the retrapping probability coefficient is A_n (cm^3s^{-1}). This is the well known one-trap-one-recombination-center (OTOR) model and it is assumed that holes are trapped first in the center during the excitation and then, electrons from the conduction band may recombine and annihilate them. X ($cm^{-3}s^{-1}$) is the rate of production of electron-hole pairs which, as mentioned above is rather small. It is assumed that the hole is trapped in the center rather quickly during excitation, and the electron either retraps or recombines with a hole in the center instantaneously. Later on, once an electron may be thermally raised into the conduction band, it either recombines with a trapped hole or retraps into an empty trap. Under these assumptions, occurring at the relatively low temperature of excitation, we do not have to consider the concentrations of electrons in the conduction band or holes in the valence band. As a result, we can assume that within the OTOR model, all along the process, we have an equal number of trapped electrons and holes, $n=m$. This version of OTOR in which $n=m$ is sometimes termed "General one trap (GOT)" model (see e.g. Kierstead and Levy, 1991).

In this process, we consider thermally released electrons being captured by traps on one hand and being annihilated by recombination on the other hand. Intuitively, we can expect that after a long enough period of time, the number of electrons entering the trap per unit time will be the same as the net number of electrons captured, and we will get an equilibrium situation. Let us examine this equilibrium and its dependence on the relevant parameters first. Let us consider a period of time Δt which for the sake of the Monte Carlo simulations will be 1 day = 86400 s. Let us define the probability that an electron is thermally raised per second,

$$\gamma = s\exp(-E/kT). \tag{1}$$

This means that the dimensionless probability for an electron to be raised to the conduction band is $\gamma\cdot\Delta t$. To begin with, let us consider the situation at the equilibrium reached after long enough exposure to irradiation. The balance of electrons being trapped during this period of 24 h is,

$$X\frac{A_n(N-n)}{A_n(N-n)+A_m n}+\gamma n\frac{A_n(N-n)}{A_n(N-n)+A_m n}=\gamma n. \tag{2}$$

The first term on the left is the ratio of electrons raised by the irradiation in this period of time which end up in the traps. The second term on the left represents those electrons raised thermally from the traps but end up back in the traps due to retrapping. Together, they are equal to the total number of electrons raised thermally from the traps. The equality between the two sides of the equation results from the fact that we assume no accumulation of electrons in the conduction band.

It is important to mention that as pointed out above, we are dealing with a small grain with a volume of $\sim 10^{-7}$ cm^{-3}. For the sake of the Monte Carlo simulation, it is very convenient to consider the number of traps and their occupancy as dimensionless numbers rather than concentrations. If, for example, the concentration of relevant traps is $\sim 10^{14}$ cm^{-3}, from this point on, we'll take the number of traps in the grain as $N=10^7$ and the occupancy n will be the instantaneous number of trapped electrons (as well as trapped holes) in the grain (see also the discussion in the Appendix). Obviously, Eq. (2) will remain the same with this revised definition of N and n. Moving the second term on the left to the other side and rearranging results in

$$X\frac{A_n(N-n)}{A_n(N-n)+A_m n}=\gamma\frac{A_m n^2}{A_n(N-n)+A_m n}. \tag{3}$$

Since the denominators are the same, we get directly a quadratic equation

$$\gamma A_m n^2 + XA_n n - XA_n N = 0. \tag{4}$$

The positive solution of this equation is the equilibrium value n_{eq}

$$n_{eq}=\frac{-XA_n+\sqrt{X^2A_n{}^2+4XA_n\gamma NA_m}}{2\gamma A_m}. \tag{5}$$

The second term in the numerator of Eq. (5) can be written as $XA_n\sqrt{1+4\gamma NA_m/XA_n}$ and for a given set of the parameters and a small enough X, the unity under the square root sign can be dropped. The expression for n_{eq} reduces to

$$n_{eq}\approx\frac{XA_n\left(\sqrt{4\gamma NA_m/(XA_n)}-1\right)}{2\gamma A_m}. \tag{6}$$

Again, for small enough X, the unity can be dropped and one gets

$$n_{eq}\approx\sqrt{\frac{NXA_n}{\gamma A_m}}. \tag{7}$$

Thus, for a given set of parameters, for small enough X, n_{eq} goes like the square root of the value of X.

We will evaluate the equilibrium values found by Eq. (5) to the results of the Monte Carlo simulation and the approximate analytical solution for certain sets of parameters below. It is worth mentioning that within the framework of the OTOR model, this equilibrium value which is expected to be reached after long enough time is independent of the initial filling of the traps. No matter whether we start with empty traps and centers ($n = 0$) or any other value, we expect to get the same equilibrium value. This includes situations with initial values higher than the equilibrium occupancy as demonstrated below. Another important point is that the equilibrium value obviously depends on the given parameters N, A_m and A_n, but also on the variable parameters, X, the rate of production of electron-hole pairs and on the temperature at which the grain is held during the long irradiation through the parameter γ given in Eq. (1).

3. Monte Carlo simulation

As pointed out above, the natural way to deal with this very slow process of excitation is by using a Monte Carlo method. Although an approximate analytical solution is also given (see below), let us describe briefly the Monte Carlo procedure. Suppose that at a certain point in time, there are n trapped electrons. For the next period of time, Δt, we consider the probability that an electron pair is produced and once that has taken place, the probability that the electron gets trapped (rather than recombines). With the mentioned rate of electron-hole production of 0.4 (per Δt), we draw a MATLAB-generated pseudo-random number between zero and 1 and if this number is smaller than 0.4, we draw another such pseudo-random number and check if it is smaller than $A_n(N\text{-}n)/[A_n(N\text{-}n)+A_m n]$. If both conditions are met, we determine that the electron has been trapped and change n into n+1. For the same period of time Δt, we should check if electrons are thermally released into the conduction band. For each of the n trapped electrons we draw a pseudo-random number between zero and 1 and if this number is smaller than γ from Eq. (1), we change n into n-1. However, the raised electron is momentarily in the conduction band and may retrap. We draw one more such pseudo-random number and if it is smaller than $A_n(N\text{-}n)/[A_n(N\text{-}n)+A_m n]$, we determine that the electron has retrapped and change the previous n-1 back to n. Once all the electrons have been tested, we register the final number of electrons in traps, go to the next time interval Δt and repeat the procedure with the final number of electrons as the new initial value. Obviously, within the framework of this model, we assume that the number of trapped holes in centers is the same as the number of trapped electrons all along.

An example of the Monte Carlo results are shown in Fig. 2. The parameters chosen are $N = 10^7$; $n_0 = 10^5$; $A_m = 10^{-8}\text{cm}^3\text{s}^{-1}$; $A_n = 10^{-10}$ cm^3s^{-1}; $E = 1.3$ eV; $s = 10^{-12}$ s^{-1}; T=300 K and $X = 0.4$ per day. The points in Fig. 2 (a) show the number n of trapped electrons as a function of time when we start from empty traps. The same procedure can be repeated when we start with more trapped electrons than the equilibrium reached after a long time. This is shown as the points in curve (b) in Fig. 2. We chose here an initial value of $n_0 = 10^5$. As is seen, the two curves converge into practically the same value. As for the value of the equilibrium, substituting in Eq. (5) one gets $n_{eq} = 5.643 \times 10^4$ and practically the same result with Eqs. (6) and (7). Also, as can be seen in Fig. 2, both (a) and (b) converge toward the same value.

The same procedure has been repeated for the same set of parameters with one change, namely, the activation energy is somewhat smaller, $E = 1.2$ eV. The results are shown in Fig. 3 where the points in curve (a) represent the Monte Carlo results when we start from empty traps and in curve (b) when the procedure starts with $n_0 = 10^4$. Using Eq. (5), we get with this set of parameters $n_{eq} = 8.18 \times 10^3$, which is also the plateau reached in Fig. 3. Note the significant difference in the value of n_{eq} for a rather small change in the activation energy.

To demonstrate further the strong dependence of the results on the activation energy and the temperature, Fig. 4 shows the results of the Monte Carlo simulations with the same set of parameters except for $E = 1.4$ eV and only from $n_0 = 0$ up, for the temperatures 35, 50, 65 and 80 °C. As is seen, here only the 80 °C line reaches the equilibrium after ~2750 years, and the lower-temperature lines are expected to reach equilibrium only after much longer periods of time.

A point should be made about the use of dimensionless numbers for the values of N and n_0. These are pure numbers of the traps and their occupancy in a given grain. Obviously, the Monte Carlo method can deal only with numbers. The connection between these numbers and the dimensional magnitudes one normally uses is described in the Appendix below.

4. Approximate analytical analysis

Using the same terms appearing in Eq. (3) we can write the differential equation governing the filling or emptying the traps,

$$\frac{dn}{dt} = \frac{A_n(N-n)}{A_n(N-n)+A_m n}X - \frac{A_m n^2}{A_n(N-n)+A_m n}\gamma. \tag{8}$$

The first term on the right is the rate of free electron creation multiplied by the fraction of those electrons that end up in the trap. The second term on the right is the rate of the thermal excitation of electrons out of the trap multiplied by the fraction of those electrons that end up recombining in the center.

To simplify the expressions, let us assume that $n << N$,

$$\frac{dn}{dt} = \frac{A_n N}{A_n N + A_m n}X - \frac{A_m n^2}{A_n N + A_m n}\gamma. \tag{9}$$

Note that although we assume that $n << N$ we keep the second term $A_m n$ in the denominator because we may have that A_m is significantly larger than A_n so that $A_m n$ may not be negligible compared to $A_n N$. We can re-write Eq. (9) as

$$\frac{dn}{dt} = \frac{A_n NX - A_m n^2\gamma}{A_n N + A_m n}. \tag{10}$$

Equation (10) shows that the electron concentration n increases when $A_n NX > A_m n^2\gamma$ while n decreases if $A_n NX < A_m n^2\gamma$. This means that, whatever the initial value of n is, n will asymptotically tend toward $n = \sqrt{A_n NX/A_m\gamma}$ as pointed out above in Eq. (7). This is a quasi-steady state of the trap in question.

Reorganizing Eq. (10) leads to

$$\frac{A_n N + A_m n}{A_n NX - A_m n^2\gamma}dn = dt, \tag{11}$$

and we can integrate

$$\int_{n_0}^{n}\frac{A_n N}{A_n NX - A_m n'^2\gamma}dn' + \int_{n_0}^{n}\frac{A_m n}{A_n NX - A_m n'^2\gamma}dn' = t, \tag{12}$$

where n_0 is the initial concentration. n' is a variable of integration. After some algebra, one gets

$$\frac{1}{2}\left[\sqrt{\frac{A_n N}{XA_m\gamma}}\ln\frac{1+\sqrt{\frac{A_m\gamma}{A_n NX}}n}{1-\sqrt{\frac{A_m\gamma}{A_n NX}}n} - \frac{1}{\gamma}\ln\left(1-\frac{A_m\gamma n^2}{A_n NX}\right)\right]_{n_0}^{n} = t. \tag{13}$$

Equation (13) is a transcendental equation which allows us to compute directly the time t at which a given n occurs. This allows plots of n vs. t to be made. Such results are shown in the solid lines of Fig. 2(a and b) and Fig. 3(a and b) for the sets of parameters mentioned in the text. The results of this approximate solution are seen to be very close to the Monte Carlo simulation results.

5. Bailey's model

We have further investigated the phenomena described in the previous sections, by using the comprehensive phenomenological general models by Bailey (2001) and Pagonis et al. (2008). We are interested in the effect of slow irradiation and elevated irradiation temperature on the trap filling process for a quartz sample. Relevant previous simulations were carried out by Koul and Patil (2015) and Koul et al. (2016). The results of these simulations suggested that the temperatures prevailing during burial time have appreciable impact on the natural luminescence signals in quartz.

The model by Bailey (2001) is based on five electron and four hole trapping centers. The electron trapping centers consist of the 110 °C trap, a 230 °C trap, fast and medium OSL traps, and a thermally disconnected trap. These electron traps are designated as Levels 1–5 in the model, respectively. The hole traps in the model consist of thermally unstable non-radiative recombination centers (R_1 and R_2), thermally stable radiative recombination center (L) and thermally stable

non-radiative recombination center. These hole traps are designated as Levels 6–9 in the model, correspondingly. The transport equations describing the traffic of charge with time in various centers and traps of the model are:

$$\frac{dn_i}{dt} = n_c(N_i - n_i)A_i - n_i\lambda_i(P,T) - n_i s_i \exp(-E_i/kT) \quad (i = 1, ..., 5), \tag{14}$$

$$\frac{dn_j}{dt} = n_v(N_j - n_j)A_j - n_j s_j \exp(-E_j/kT) - n_c n_j B_j \quad (j = 6, ..., 9), \tag{15}$$

$$\frac{dn_c}{dt} = X - \sum_{i=1}^{q}\left(\frac{dn_i}{dt}\right) - \sum_{j=q+1}^{q+r}(n_c n_j B_j), \tag{16}$$

$$\frac{dn_v}{dt} = X - \sum_{j=q+1}^{q+r}\left(\frac{dn_j}{dt}\right) - \sum_{j=q+1}^{q+r}(n_c n_j B_j), \tag{17}$$

$$L = n_c n_8 B_8 \eta(T). \tag{18}$$

According to Bailey (2001), the levels 1 to q = 5 are electron traps while levels q+1 to q + r (with r = 4) are hole centers. Apparently due to a print mistake, the last term on the right-hand side of Eq. (17) was missing in Bailey's paper. The correct version has been given later by a number of researchers (see e.g. Friedrich et al., 2016). Equations (14) and (15) represent the variation in the charge population with time, for electronic and hole trapping centers respectively. Similarly equations (16) and (17) represent the change in the charge population with time in the conduction and valence bands, respectively, and Eq. (18) describes the luminescence signal produced by recombination at the luminescence center L. The various parameters described in the above equations are: N_i, the total concentrations of the i-th electron traps (cm^{-3}); n_i, the instantaneous concentrations of trapped electrons (cm^{-3}); s_i, the frequency factors (s^{-1}); E_i, the electron trap depths below the conduction band (eV); N_j the j-th total concentration of hole traps (cm^{-3}); n_j, the instantaneous concentrations of trapped holes (cm^{-3}); E_j, the hole depths above the valence band (eV); k, Boltzmann's constant ($eV{\cdot}K^{-1}$); T, the absolute temperature (K); A_i, the conduction band to electron trap transition probabilities (cm^3s^{-1}); A_j, the valence band to hole trap transition probabilities (cm^3s^{-1}); B_j, the conduction band to hole trap transition probabilities (cm^3s^{-1}); λ_i, the optical de-trapping rates (s^{-1}); t, the time (s); η, the luminescence efficiency factor which describes thermal quenching effects; β, the constant heating rate (Ks^{-1}) and X, the ionization or pair production rate ($cm^{-3}s^{-1}$). The optimum values assigned to these parameters for different centers and traps of the model are listed in Table 1 of Bailey (2001), as model variant Qtz-A1. The simulation procedures used in this paper for the natural quartz sample are identical to the ones used in Bailey (2001), and are listed as steps 1–4 in the present Table 1. The slow natural irradiation during the geological and burial time spans was performed by using a very low dose rate of 2 mGy/year or 6.34×10^{-11} Gy·s^{-1}, close to the dose rate one would expect in nature. These simulation procedures of the natural sample are of course a simplification, and the actual natural processes are much more complex. However, the simulations provide a useful insight into the effect of the slow dose rate and of burial temperature of the quartz

Table 1
The simulation steps using the comprehensive quartz model by Bailey (2001). Steps 1–4 are a simulation of a "natural'' quartz sample similar to Bailey (2001) procedure but at a lower burial temperature, a lower dose rate and over a longer time than he used. The results of these simulations are shown in Fig. 5.

1	Geological dose irradiation of 1000 Gy at 1 Gy/s.
2	Geological time – heat to 350 °C.
3	Illuminate for 100 s at 200 °C.
4	Burial dose D at burial temperature T = 10 °C at a very low natural dose rate of 6.34×10^{-11} Gy/s, for a burial period of 60,000 years. Record the trap filling of levels 2. and levels 3 in the model during the burial period of 60,000 years.
5	Repeat the simulations steps 1–4 above for other burial temperatures T = 20–60 °C.

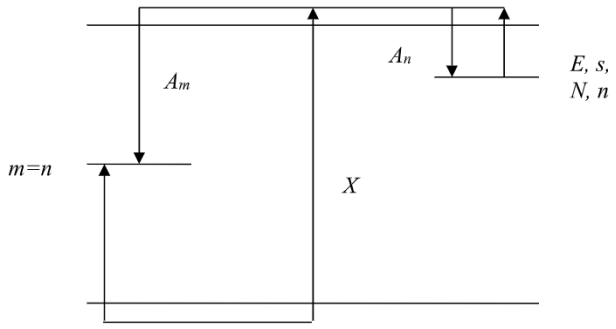

Fig. 1. Transitions taking place during excitation and fading in the basic one trap one recombination center system.

sample on the trap filling process. Specifically we examine the trap filling $n_2(t)$ and $n_3(t)$ for levels 2 and 3 in the Bailey (2001) model, which correspond to TL peaks at 230 °C and 300 °C respectively. It is noted that level 3 in the model also represents the source of the fast OSL component in quartz, which is used routinely for luminescence dating applications. The environmental temperatures generally prevailing on the globe in the range 10–60 °C were used to represent the burial temperatures experienced by quartz grains in the simulation. The simulations were carried out using the open access R programs KMS by Peng and Pagonis (2016). These programs provide the code for several published kinetic models of luminescence phenomena in quartz, and contain compact functions to simulate events in the geological history of quartz: crystallization, irradiation, optical illumination, and heating processes. These processes can be simulated easily by creating sequences of compact R functions for several models. The simulations in this paper were carried out using both the Bailey (2001) and the more comprehensive Pagonis et al. (2008) models. The two models produced very similar results in this study, and led to the same conclusions. Graph 5(a) shows the results for level 2 of the Bailey model. This electron trap corresponds to the TL peak

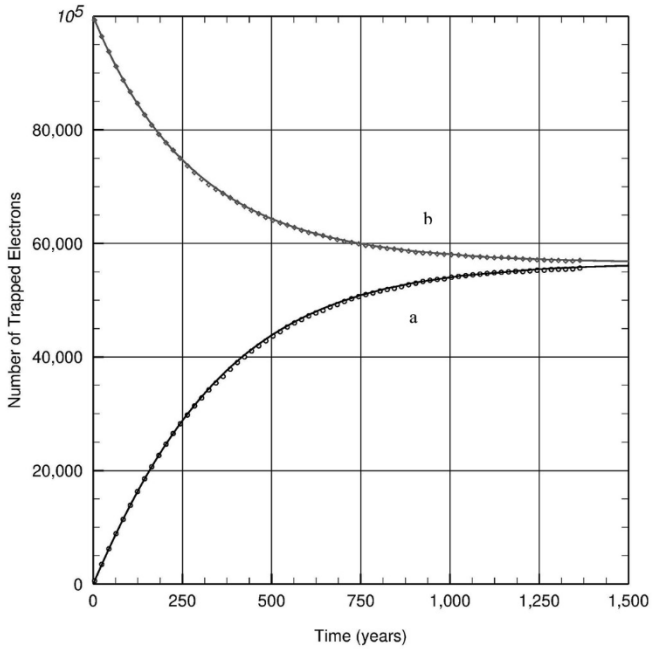

Fig. 2. Simulations of the population of electrons in traps as a function of time. The parameters chosen are $N = 10^7$; $A_m = 10^{-8}$ cm^3s^{-1}; $A_n = 10^{-10}$ cm^3s^{-1}; E = 1.3 eV; $s = 10^{12}$ s^{-1}; T = 300 K. The points represent the results of the Monte Carlo simulation whereas the solid lines are the results of the approximate analytical solution reached by numerical solution of Eq. (13). In curve (a), the initial number of trapped electrons is 0 and in curve (b) it is 10^5.

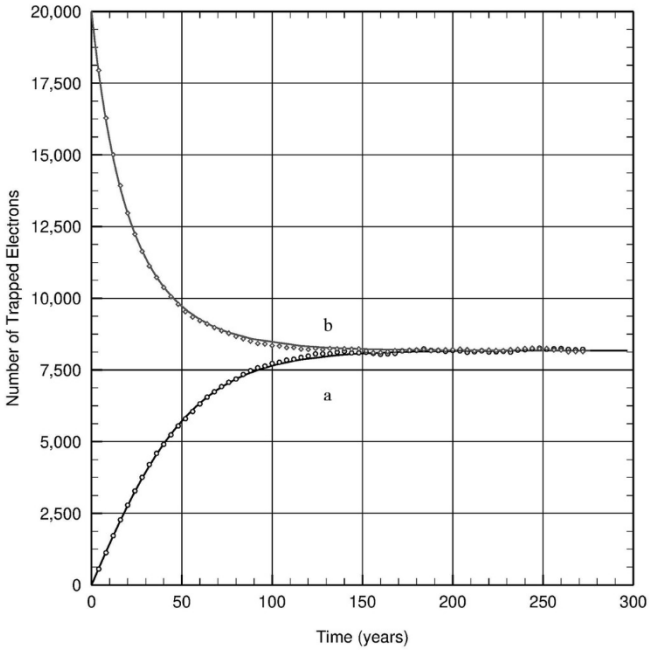

Fig. 3. Similar to Fig. 2, with the same parameters but smaller activation energy $E = 1.2$ eV. Here, the initial number of trapped electrons in curve (b) is 2×10^4.

at ~220 °C and its trap filling during the burial is clearly affected by the burial temperature of the sample. The kinetic parameters for this trap are $E = 1.55$ eV, $s = 5 \times 10^{14}$ s^{-1} which corresponds to a TL peak with a maximum at 220 °C when using a heating rate of 1 K/s. At a burial temperature of 30 °C this trap will have reached equilibrium in nature over a span of 60,000 years. Graph 5(b) shows the corresponding behavior for level 3 of the Bailey model. This deeper electron trap corresponds to the TL peak at ~300 °C, and is also the source of the fast OSL component in quartz. The filling of this trap is affected very little by the burial temperature of the sample. The kinetic parameters for this trap are $E = 1.70$ eV, $s = 5 \times 10^{13}$ s^{-1} and a maximum intensity at 300 °C with a heating rate of 1 K/s. Even at a burial temperature of 50 °C, this trap will not have reached equilibrium in nature over a span of 70,000 years. The conclusion is that the 220 °C TL peak of quartz should be used with caution for dating and thermochronometry, while the 300 °C is much less problematic. These results from the comprehensive multiple level quartz models are consistent with the Monte Carlo simulations in the previous sections, and also with the general practice in thermochronometry and dating applications. We also note the relevant thermochronometry work by Schmidt et al. (2015) who studied the red TL luminescence signals from deep core quartz samples, and found that the TL peaks at ~230 °C and ~300 °C behave in different ways when irradiated in the laboratory, and also when their natural signals are modeled.

6. Discussion

In this work, we report on the competition between very slow excitation of electrons into traps in a small grain and the very slow thermal decay taking place during rather long periods of time which may be the case in archaeological and geological samples in nature. The simulation was performed using the Monte Carlo method which seems to be appropriate here since the electrons are being raised either thermally or by the irradiation at a very slow rate, and can be considered one at a time. However, repeating the calculation analytically with reasonable approximations resulted in very close results as seen in Figs. 2 and 3. It should be noted that the asymptotic equilibrium values of trapped electrons (and holes) were the same for a given set of parameters

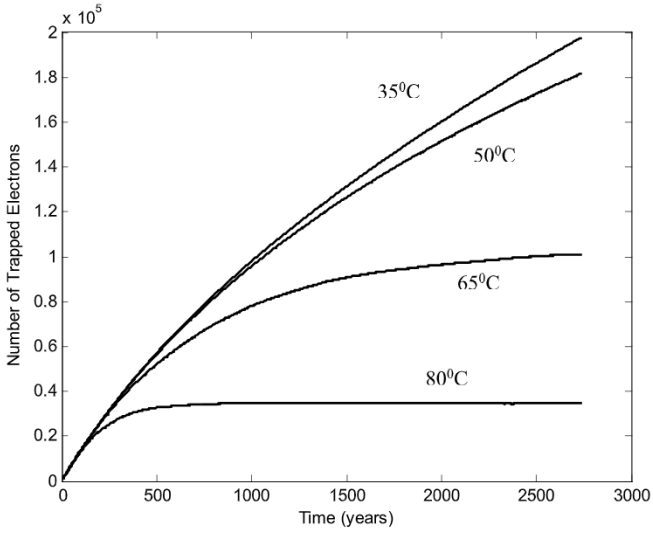

Fig. 4. With the same set of parameters except for the use of $E = 1.4$ eV, the growth of the number of trapped electrons simulated by the same procedure, starting from $n_o = 0$ at different temperatures.

irrespective of whether the initial concentration is smaller (zero in the examples given) or higher than the final equilibrium values. Another point to note is the slight scattering of the Monte Carlo points above and below the analytically reached line. This has to do with the statistical nature of the Monte Carlo simulation but one has to remember that the

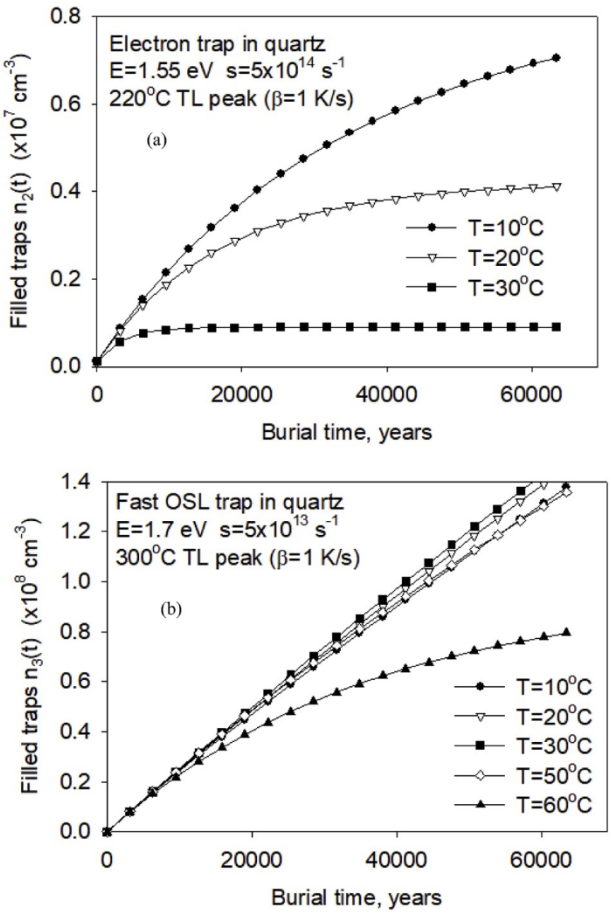

Fig. 5. Simulated results of the occupancy of level 2 (curve a) and level 3 (curve 3) in the Bailey model for quartz. The simulations were performed by the R programs; the parameters are given in the text.

physical processes of excitation and fading are also of statistical nature. In this sense, the Monte Carlo results reflect better the physical situation. Note also that these fluctuations are better visible in Fig. 3 than in Fig. 2, apparently because the equilibrium value (~8000) in Fig. 3 is significantly smaller than in Fig. 2 (~56000). This issue of the statistical nature of the results will be further discussed elsewhere.

We should note that the filling of the traps over very long time has been discussed. The outcome in terms of thermoluminescence (TL) or optically stimulated luminescence may be proportional to the final population. However, more complicated situations may occur, in particular if more traps or centers are involved. Note that if one performs ESR measurements of the trapped electrons (see e.g. Schmidt et al., 2015; Timar-Gabor et al., 2020), similar behavior may be expected. Finally, it should be mentioned that the simulations reached a plateau after a long time which is not the saturation level of the traps. Two papers that bear some resemblance to the present work should be mentioned. Chen et al. (1990) discussed the competition between excitation and bleaching of TL, but the model is different since these authors assume that the bleaching is done optically by the same wavelength of excitation. Also, the time scale discussed there is of minutes. Chen et al. (1991) reported on experimental results of the sensitivity changes of the 100 °C peak in synthetic quartz due to cycles of irradiation followed by high temperature activation. The measured curves resemble the present results, increasing if starting from low sensitivity and decreasing if starting from high sensitivity, and both curves asymptotically approach approximately the same value.

It is interesting to note that, as seen by comparing Figs. 2 and 3, the plateau level reached is strongly dependent on the activation energy which is 1.3 eV in Figs. 3 and 1.2 eV in Fig. 2. Similar strong dependence can be expected with different temperatures. Another important point to remember is that we dealt with the OTOR model which is practically the simplest possible model. Although the mathematics would be more complicated if more traps and/or centers are involved, one can expect that the main result namely that a plateau is reached following a very long period is not the saturation value and that it may depend strongly on the relevant parameter, e.g., the activation energy or the temperature. An example for this has been shown in Fig. 5(a) which has been reached by using the more elaborate Bailey model. It is worth mentioning that Brown et al. (2017) dealt with the balance between irradiation and thermal depletion of traps in a system associated with feldspars. Their theory was based on localized transitions due to tunneling from an excited state to randomly distributed luminescence centers.

In conclusion, if one encounters a TL curve, OSL signal or ESR signal that reaches a plateau level, one should consider the possibility that it is a result of long-time competition between excitation and bleaching rather than real saturation.

As for the simulations of the quartz Bailey model, as pointed out above, one may conclude that for thermochronometry, the peak occurring at 300 °C is much more reliable than that appearing at 220 °C.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

APPENDIX

Let us consider Eq. (8) which is the usual conservation equation for trap population where N and n are concentrations with units of cm^{-3} and X is an ionization rate per unit volume, $cm^{-3}s^{-1}$,

$$\frac{dn}{dt}=\frac{A_n(N-n)}{A_n(N-n)+A_m m}X-\frac{A_m n^2}{A_n(N-n)+A_m n}\gamma. \tag{A1}$$

The Monte Carlo simulation uses integers. Let $\overline{N}$ be the number of traps in the grain and ν be the number of filled traps. N and ν are unitless integers. The grain experiences $\overline{X}$ ionizations per unit time. Thus, $\overline{N}$, ν and $\overline{X}$ are related to N, n and X according to

$$N=\overline{N}/V; \qquad X=\overline{X}/V; \qquad n=\nu/V, \tag{A2}$$

where V is the volume of the grain. Substituting the definitions of Eq. (*A2*) into Eq. (*A1*) and multiplying both sides of the equation by V, we find

$$\frac{d\nu}{dt}=\frac{A_n(\overline{N}-\nu)}{A_n(\overline{N}-\nu)+A_m\nu}\overline{X}-\frac{A_m\nu^2}{A_n(\overline{N}-\nu)+A_m\nu}\gamma. \tag{A3}$$

Equation (*A3*) is the conservation equation analogous to Eq. (*A1*) (Eq. (8) in the text), but for mean trap population ν. In other words, subject to the transformation in Eq. (*A2*), the same conservation equation works for both concentrations N and n and for numbers $\overline{N}$ and ν.

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