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A theoretical model for a new dating protocol for quartz based on thermally transferred OSL (TT-OSL)

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Abstract

Recently a new dating procedure has been suggested, which is based on the thermally transferred optically stimulated luminescence (TT-OSL) signal that is measured after irradiated quartz is optically bleached and then preheated. Experimentally the TT-OSL signal was measured after a high temperature preheat (260 °C for 10 s) following an optical bleach at 125 °C for 270 s to deplete the fast and medium OSL components. The TT-OSL signal was measured for 90 s at 125 °C in order to avoid the effect of re-trapping of electrons in the 110 °C trap of quartz. The luminescence sensitivity changes were monitored by the OSL response to a test dose. In this paper, we use a modified version of a comprehensive model to simulate the complete experimental sequence of the new protocol, and to fit the experimental dose–response graphs of the OSL, TT-OSL and basic-TT-OSL signals for doses up to 4000 Gy. Two possible mechanisms for the production of the TT-OSL signals in this quartz are discussed, namely the double transfer mechanism suggested for the recuperation effect, and a single transfer mechanism in which the TT-OSL signal is due to the thermal transfer of charge from a “source trap” into the fast OSL trap of quartz. The results of the simulation indicate that the latter mechanism is more likely to be responsible for the observed TT-OSL dose growth in fine-grained quartz extracted from Chinese loess. © 2008 Elsevier Ltd. All rights reserved.

Keywords: OSL; Thermally transferred OSL; Quartz; Dose–response curves; Quartz dating

1. Introduction—the new dating procedure

Although the fast component of the optically stimulated luminescence (OSL) signal in quartz has been established as the basis of an accurate and precise luminescence dating method (Wintle and Murray, 2006), its use is limited by the saturation of the measured OSL signal. However, another OSL signal has been proposed as the basis of a new OSL dating procedure (Wang et al., 2006a), namely the thermally transferred OSL (TT-OSL) that is measured after irradiated quartz is optically bleached and then preheated (Wang et al., 2006b). Using the TT-OSL signal, the dating range for fine-grained quartz extracted from Chinese loess can be extended by almost an order of magnitude (Wang et al., 2006a).

Wang et al. (2006a) used a TT-OSL signal obtained after a high temperature preheat (260 °C for 10 s) following an

optical bleach at 125 °C for 270 s to deplete the fast and medium OSL components. The TT-OSL signal was measured for 90 s at 125 °C in order to avoid the effect of re-trapping of electrons in the 110 °C TL trap. The luminescence sensitivity related to this TT-OSL measurement was determined by the OSL response to a subsequent test dose. Wang et al. (2006a) proposed a method that used multiple aliquots to construct the dose–response curve and use these for ED determination.

In this paper, we use the model of Bailey (2001) to predict the OSL and TT-OSL signals that would be obtained when using this method, and we compare directly the experimental results with this model output.

Table 1 is an outline of the stages involved in our simulation of the new TT-OSL dating procedure of Wang et al. (2006a). Specifically steps 1–4 are a simulation of the “natural” quartz sample, as proposed by Bailey (2001), and the rest of the steps are a simulation of the sequence of steps in the protocol of Wang et al. (2006a). Firstly no regenerative dose is delivered, which is equivalent to $D_i = 0$ in step 5. The preheat in step 6

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Table 1
Steps in the simulation of the TT-OSL protocol

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—200 Gy at 220 °C at 0.01 Gy/s
5	Regenerative dose D_i at 20 °C and at 1 Gy/s
6	Preheat to 260 °C for 10 s
7	Blue stimulation at 125 °C for 270 s
8	Preheat to 260 °C for 10 s
9	Blue stimulation at 125 °C for 90 s (L_{TT-OSL})
10	Test dose = 7.8 Gy
11	Preheat to 220 °C for 20 s
12	Blue stimulation at 125 °C for 90 s (T_{TT-OSL})
13	Anneal to 300 °C for 10 s
14	Blue stimulation at 125 °C for 90 s
15	Preheating at 260 °C for 10 s
16	Blue stimulation at 125 °C for 90 s (L_{BT-OSL})
17	Test dose = 7.8 Gy
18	Preheat to 220 °C for 20 s
19	Blue stimulation at 125 °C for 90 s (T_{BT-OSL})

Repeat the above steps for different regenerative doses D_i in step 5, with D_i in the range 0–4000 Gy.

removes electrons in unstable traps, while the same preheat in step 8 thermally induces the TT-OSL signal. During the optical stimulation in step 7 the OSL signal (L_{OSL}) is measured, while the TT-OSL signal (L_{TT-OSL}) is measured in step 9. The test-dose OSL response (T_{TT-OSL}) is measured in steps 10–12. The annealing in step 13 thermally transfers the remaining charge that can give rise to the recuperated OSL signal; this signal is removed by optical stimulation in step 14. The preheat in step 15 thermally induces the basic transfer OSL (BT-OSL) signal (L_{BT-OSL}) which is measured in step 16. Finally, in steps 17–19 the test-dose OSL response (T_{BT-OSL}) is obtained. The above sequence gives the data required to calculate the corrected natural signal $[L_{TT-OSL}/T_{TT-OSL}] - [L_{BT-OSL}/T_{BT-OSL}]$. Steps 5–19 are then repeated once for each of 15 aliquots using one regenerative dose (D_i in step 5) in the range 0–4000 Gy.

2. The numerical model

A modified version of the original Bailey (2001) model is used in the present simulation and is shown schematically in Fig. 1. The original model consists of five electron traps and four hole centers. Level 1 in the model represents a shallow electron trapping level, which gives rise to a TL peak at ~ 100 °C with a heating rate of 5 K/s. The corresponding OSL signal plays only a minor role in the current simulations, since OSL measurements are carried out at 125 °C. Level 2 represents a generic “230 °C TL” trap, typically found in many quartz samples. Levels 3 and 4 are usually termed the fast and medium OSL components and they yield TL peaks at ~ 330 °C as well as giving rise to OSL signals. The photostimulation rates for these levels are discussed in some detail in the original paper by Bailey (2001). The model does not contain any of the slow OSL components which are known to be present in quartz, and which were incorporated in later versions of the model (Bailey, 2004). Level 5 is a deep, thermally disconnected,

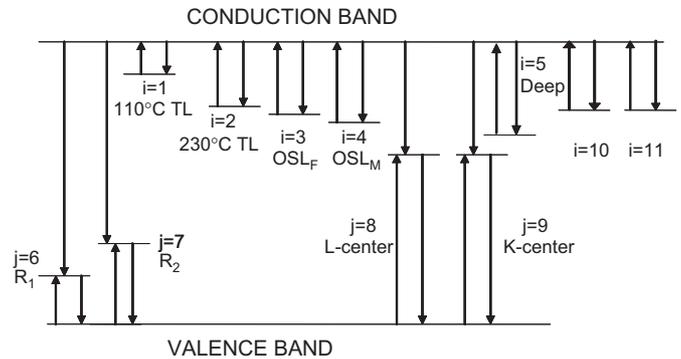


Fig. 1. The modified Bailey (2001) model used in simulating the procedure shown in Table 1. Electron levels added as levels 10 and 11.

electron center. The original Bailey (2001) model contains also four hole trapping centers which act as recombination centers for optically or thermally released electrons. Levels 6 and 7 are thermally unstable, non-radiative recombination centers (“hole reservoirs”). Level 8 is a thermally stable, radiative recombination center termed the “luminescence center” (L). Level 9 is a thermally stable, non-radiative recombination center termed a “killer” center (K).

The modified version of the model contains two additional levels, 10 and 11 in Fig. 1. These levels play a crucial role in the production of the TT-OSL signals and BT-OSL signal which are observed experimentally by Wang et al. (2006a, b). It is assumed that electrons are thermally transferred into the empty fast component trap (level 3) from level 10, which represents a slightly less thermally stable trap with high dose saturation. This trap (level 10) is assumed to be emptied optically in nature by only long sunlight exposure. Thus level 10 is believed to represent the source trap for the charge giving rise to the TT-OSL signal. On the other hand, it is thought that the electrons giving rise to the BT-OSL signal are derived from light insensitive traps which are more thermally stable than either level 3 or level 10. Level 11 is believed to contribute to most of the BT-OSL signal.

The computer code is written in *Mathematica*, and was tested for consistency by successfully reproducing several of the simulation results in Bailey (2001). The parameters are as defined by Bailey (2001); N_i are the concentrations of electron traps or hole centers (cm^{-3}), n_i are the concentrations of trapped electrons or holes (cm^{-3}), s_i are the frequency factors (s^{-1}), E_i are the electron trap depths below the conduction band or hole trap depths above the valence band (eV), A_i are the valence band to trap transition probability coefficients ($\text{cm}^3 \text{s}^{-1}$) and B_i are the conduction band to hole trap transition probability coefficients ($\text{cm}^3 \text{s}^{-1}$). Other parameters related to the photoionization cross-sections of the optically sensitive traps are the photo-ejection constant θ_{oi} (s^{-1}) at $T = \infty$, the thermal assistance energy E_i^{th} (eV) and P representing the photon stimulation flux (Bailey, 2001). The functions n_c and n_v represent the instantaneous concentrations of electrons and holes in the conduction and valence band correspondingly.

Table 2
The parameters used in the present simulation

	N_i (cm ⁻³)	E_i (eV)	s_i (s ⁻¹)	A_i (cm ³ s ⁻¹)	B_i (cm ³ s ⁻¹)	θ_{oi} (s ⁻¹)	E_i^{th} (eV)
1	1.5e7	0.97	5e12	1e-8		0.75	1
2	1e7	1.55	5e14	1e-8		0	0
3	4e7	1.73	6.5e13	5e-9		6	0.1
4	2.5e8	1.8	1.5e13	5e-10		4.5	0.13
5	5e10	2	1e10	1e-10		0	0
6	3e8	1.43	5e13	5e-7	5e-9	0	0
7	1e10	1.75	5e14	1e-9	5e-10	0	0
8	3e10	5	1e13	1e-10	1e-10	0	0
9	1.2e12	5	1e13	1e-14	3e-10	0	0
10	5e9	1.65	6.5e13	1e-11		0.01	0.2
11	4e9	1.6	5e12	6e-12		0	0

The set of equations to be solved during the simulation are:

$$\frac{dn_i}{dt} = n_c(N_i - n_i)A_i - n_i P \theta_{oi} e^{(-E_i^{\text{th}}/k_B T)} - n_i s_i e^{(-E_i/k_B T)} \quad (i = 1, \dots, 5 \text{ and } i = 10, 11), \quad (1)$$

$$\frac{dn_j}{dt} = n_v(N_j - n_j)A_j - n_j s_j e^{(-E_j/k_B T)} - n_c n_j B_j \quad (j = 6, \dots, 9), \quad (2)$$

$$\frac{dn_c}{dt} = R - \sum_{i=1}^5 \left(\frac{dn_i}{dt} \right) - \sum_{i=10}^{11} \left(\frac{dn_i}{dt} \right) - \sum_{j=6}^9 (n_c n_j B_j), \quad (3)$$

$$\frac{dn_v}{dt} = R - \sum_{j=6}^9 \left(\frac{dn_j}{dt} \right) - \sum_{j=6}^9 (n_c n_j B_j). \quad (4)$$

R denotes the pair production rate (cm⁻³ s⁻¹) and the instantaneous luminescence is defined as

$$L = n_c n_8 B_8 \eta(T) \quad (5)$$

with $\eta(T)$ representing the luminescence efficiency, with allowance for thermal quenching (Bailey, 2001).

The parameter values for levels 1, 2 and 5–9 (Table 2) were those of Bailey (2001) and for levels 3 and 4 those of Singarayer and Bailey (2003), with slight modifications as discussed by Pagonis et al. (2007). The E and s values for level 10, the proposed source trap, are taken from Spooner and Questiaux (2000) for a TL peak at $\sim 325^\circ\text{C}$ with a slight modification for the s -value. The photoionization cross-section for level 10 is assigned a value which is almost two orders of magnitude smaller than the value for the fast OSL traps (level 3) and the energy of thermal assistance E_i^{th} for level 10 is at this point chosen arbitrarily, due to the lack of any experimental data in the literature. There was an additional systematic variation of the parameters within a physically acceptable range of values, and by fitting the available experimental data in a consistent manner. A more detailed comparison of the parameters in Table 2 with the original values by Bailey (2001) and their effects on dose–response curves will be presented elsewhere.

It is emphasized that a good fit does not necessarily mean that this is the only correct set of parameters. Nevertheless,

the success of the model lies in the fact that it can provide a mathematical description of the complex mechanism giving rise to the TT-OSL signals, as well as predicting the correct experimental dose–response for these signals.

3. Results of the simulation

Wang et al. (2006a, b) performed all luminescence measurements at 125°C to avoid complications associated with the 110°C TL peak; the stimulation times were 90 or 270 s (as indicated in the various steps of Table 1), and the integrated intensity of the first 5 s of the TT-OSL signal was used, after subtraction of 50% of the signal from the last 10 s of the optical stimulation. This TT-OSL signal is superimposed on a much larger slow component of the OSL signal in quartz. The slow component was characterized by curve fitting and the TT-OSL signal was measured by subtracting the fitted curve from the total signal.

Figs. 2a and b show simulated decay curves for conventional OSL and TT-OSL signals using the parameters in Table 2. No slow component is seen as their trapping levels are not used in this model. The inset in Fig. 2a shows the OSL data on a semilog scale, indicating the presence of the fast and medium OSL components. The inset in Fig. 2b shows the TT-OSL plotted against the OSL for the same dose of 100 Gy, giving a graph that is very close to the line of unit slope on a log–log scale. This indicates that the two components have the same relative proportion in the two signals, but are a factor of 10^3 different in magnitude, similar to the experimental data of Wang et al. (2006b).

Fig. 3 shows a set of experimental data obtained for 4–11 μm quartz extracted from a young sample (IEE209) which had a natural dose of 3 Gy obtained from OSL measurements (Lu et al., 2007). The sensitivity-corrected luminescence L/T was for the first 5 s of the decay curve for the OSL, TT-OSL and BT-OSL signals measured using the new dating procedure. The OSL dose–response curve (Fig. 3a) cannot be fitted by a single saturating exponential function (as would be expected for a signal dominated by the fast OSL component) since it contains a significant contribution from the medium OSL component (inset in Fig. 2a). The data in Fig. 3 are similar to those

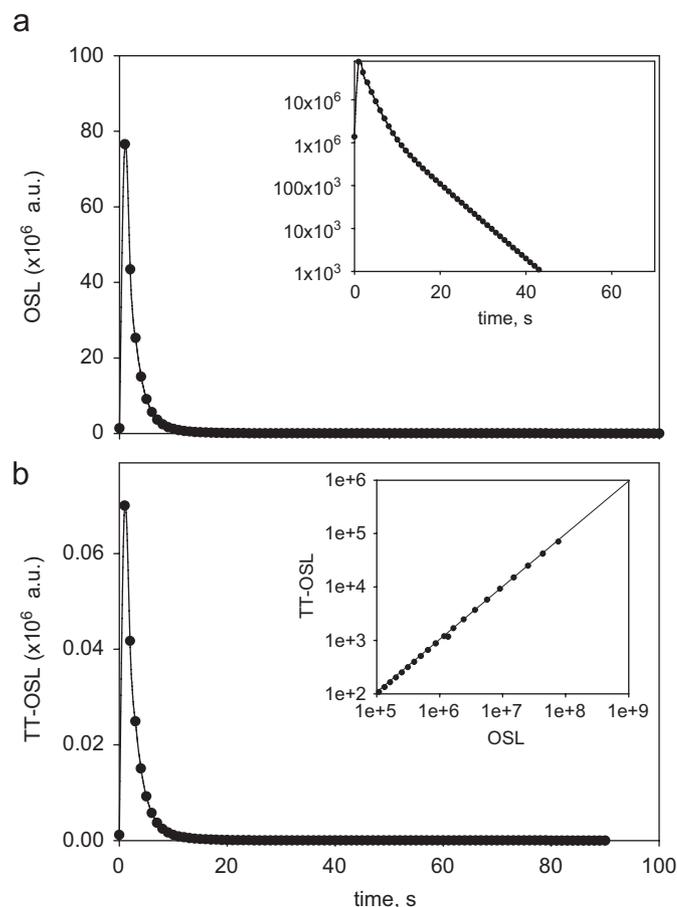


Fig. 2. Simulated OSL and TT-OSL signals using the parameters shown in Table 2. The insets are discussed in the text.

obtained for multiple aliquot measurements made when doses were added in addition to the natural dose and the measurement sequence was run only once (Wang et al., 2006a). The difference between the signals in Fig. 3b is the recuperated OSL (ReOSL) used for calculating the equivalent dose. The solid lines represent the simulation output obtained using the sequence in Table 1 and the parameters in Table 2. Good agreement with the experimental data is obtained for all doses up to ~ 4500 Gy.

4. Discussion and conclusions

Two possible mechanisms could give rise to the experimentally observed TT-OSL signals, namely those involving a double step or a single step charge transfer. The double step mechanism for TT-OSL suggested by Aitken (1998), uses a less optically sensitive “refuge trap”. Aitken and Smith (1988) suggested that this refuge trap was operative during stimulation at room temperature and gave rise to the 110 °C TL peak; this mechanism has been modeled recently (Pagonis et al., 2007).

In the alternative single charge transfer mechanism, the regenerated OSL signals are caused by the thermal transfer of electrons into the empty fast component trap from a less thermally stable trap with high dose saturation. This trap is

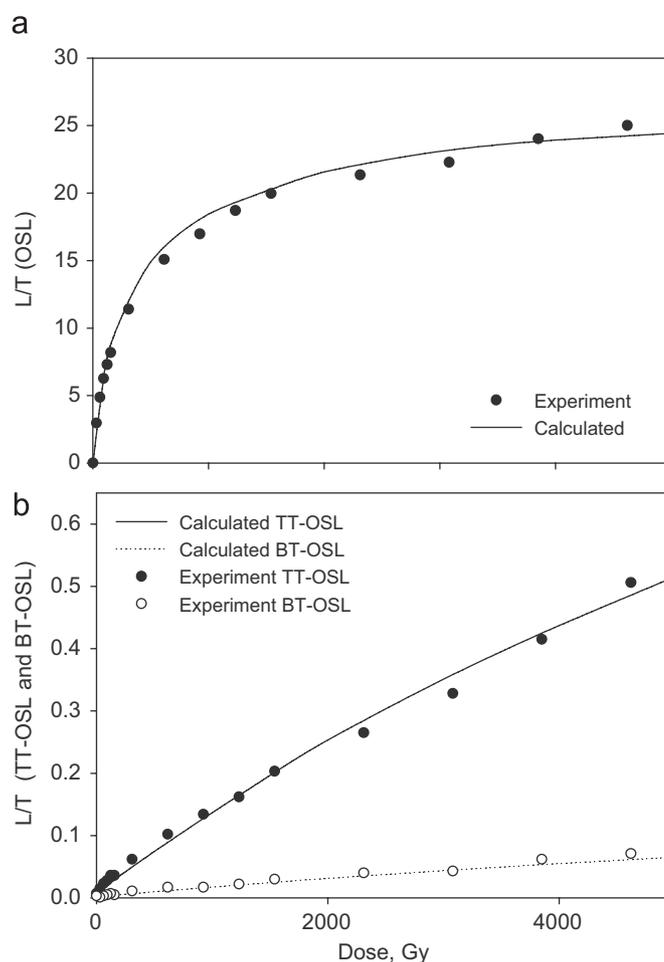


Fig. 3. Experimental and simulated OSL, TT-OSL and BT-OSL dose-response curves.

assumed to be emptied optically only by long sunlight exposure in nature. This has been shown to be the more correct model for stimulation at 125 °C (Adamiec et al., submitted for publication).

The results of the current simulation are also in agreement with a single charge transfer mechanism being responsible for the TT-OSL signals measured by Wang et al. (2006a), rather than the more complex double step mechanism hypothesized by Aitken (1998). More specifically the results of the simulation show that only a small percentage of the charge in this TL trap (~ 2 –10%) transfers into the main fast OSL traps during the 10 s preheat at 260 °C.

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