Component-resolved thermal stability and recuperation study of the LM-OSL curves of four sedimentary quartz samples

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Abstract

Thermal stability as well as recuperation stands among the crucial general characteristics of different OSL components in quartz. Through a series of thermal stability and recuperation experiments, in conjunction with curve fitting studies, a component resolved analysis is carried out, studying these two aspects for the OSL components identified in quartz samples collected from sites around Istanbul. A thermally unstable ultra-fast component is reported, which is almost totally removed by heating up to 250–280 °C. Most slow and medium components show a stability temperature region between 200 and 350 °C, whereas the thermal stability of the final slow component is limited up to almost 300 °C. No detectable recuperation occurs for the first five components reported. The greatest recuperation occurred in the sixth component, despite the fact that it was less than 1%.

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1. Introduction

In order to develop a more robust protocol for OSL single aliquot dating, it is essential to thoroughly understand the general characteristics of different OSL components in quartz. Thermal stability and recuperation are among the crucial factors. If the natural or regenerated OSL signal contains a significant contribution from thermally unstable component, then external thermal treatment is required in order to use the appropriate and thermally stable component. Otherwise, the signal measured would not yield the real expected age. Experiments, which studied the thermal stability of the fast OSL component, were carried out by several authors (Murray and Wintle, 1999; Li and Chen, 2001). However, the best way to determine the thermal stability of the various components of the quartz OSL signal is to study using linear modulated OSL (LM-OSL) measurements following pulse annealing. The process consists of heating the sample to a particular temperature followed by an immediate cooling (Wintle and Murray, 2006). Such experiments were performed by Bulur et al. (2000), Li and Chen (2001), Singarayer and Bailey (2003) and Jain et al. (2003). Works by both Singarayer and Bailey (2003) and Jain et al. (2003) reported an ultra-fast component, which is much less thermally stable than the others, being removed almost completely by heating to 250–280 °C. Therefore, the use of a 10 s pre-heat applied at temperatures between 160 and 260 °C, often used during the procedure of single aliquot regenerative (SAR) protocol (Wintle and Murray, 1998), could effectively remove the ultra-fast component. Most of the medium and slow components showed a remarkable thermal stability over a temperature region ranging from 200 up to 350 °C, with little signal loss when heated to 350 °C. Interestingly, both studies reported the presence of a slow component (S3 of Jain et al., 2003; S2 of Singarayer and Bailey, 2003), much less thermally stable, which was reduced to 50% by heating to 260 °C.
A crucial test regarding the applicability of the conventional SAR dose protocol (Murray and Wintle, 2000) comes from the measurement of the zero dose point in OSL dating. The zero dose regenerative cycle is incorporated in order to monitor the response to 0 Gy dose, i.e. in order to test whether the regenerated growth curve passes through the origin. Theoretically, after an aliquot has been optically bleached, either in nature or in the laboratory, one would not expect a detectable signal when the OSL is measured again. However, transfer of charge from deeper traps may result from irradiations, optical stimulation and pre-heating (Aitken, 1998). In that case, the signal measured could be well above zero, and is termed recuperation. Murray and Wintle (2000) suggested that the recuperation value, expressed as a percentage of the natural OSL signal, should not exceed 5%.

Non-zero response to 0 Gy dose, could be attributed either to electrons trapped during previous dose or to electrons that were transferred to an optically insensitive but thermally shallow trap by the preceding optical stimulation (Wintle and Murray, 2006). Jain et al. (2003) performed LM-OSL measurements on a number of quartz samples, after heating them to 280°C. All samples studied showed significant recuperation (3–12%) for the medium and slow components, whereas only about a quarter of them showed any recuperation in the fast component. Furthermore, the fast components yielded a recuperation value less than 0.5%. Strong recuperation was reported for the combined signal from medium and slow components by Tsukamoto et al. (2003), while performing CW-OSL measurements. Their quartz sample, collected from tephra-rich loess, was proved useless for optical dating for a combination of reasons, including strong recuperation.

The present study reports a component resolved analysis of the behavior of the two different aspects mentioned above, namely thermal stability and recuperation, for the optically stimulated luminescence signal resulting from quartz samples collected from sites around Istanbul. In a recent paper, Kiyak et al. (2007) studied the dose response of each component and performed a component resolved analysis regarding their thermal activation.

2. Experimental procedure

The materials used in the present work were four sedimentary quartz samples collected from four different sites around the Istanbul area, i.e. Şile, Altinkum, Ataköy and Pendik (laboratory reference SIL, ALT, ATK and PDK, respectively) (Kiyak and Canel, 2006). This region is one of the most energetic earthquake zones in the world and is noted for earthquakes with destructive magnitudes. However, while very little is known of the chronology of the neotectonic activity, luminescence dating techniques and the studies on local quartz will provide valuable data that would be of interest to people working on OSL dating.

The samples were taken from a depth of 5–10 cm below the earth’s surface and subjected to wet sieving, and grains of dimensions 90–180 μm were obtained. The sample grains were treated with HCl (10%), H₂O₂ (10%), HF (40%) and a final treatment with HCl (10%). The sample grains were mounted on stainless-steel disks using silicon spray. All aliquots were checked with infrared (IR) stimulation to ensure the absence of any feldspar contamination. The measurements were performed with the automated Riso TL/OSL reader (model TL/OSL-DA-15), using an internal 90Sr–90Y beta source of dose rate 0.1 Gy/s. Blue light emitting diodes (LEDs) (470 nm, 40 mW/cm²) were used for stimulation and the OSL signal was detected through U-340 filters.

All measurements were carried out using the LM-OSL technique, firstly proposed by Bulur (1996). Using the LM-OSL technique, the structure of the signal in terms of the number of components present and their kinetics, may be recorded with greater clarity. Stimulation power is increasingly being used in a variety of diagnostic studies and could potentially be a very useful tool. The measurement protocols for thermal stability and recuperation studies used, are presented in Tables 1 and 2, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
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<tbody>
<tr>
<td>1</td>
<td>Heating to 650°C (TL to 650°C at 5°C/s) to remove all observable signals</td>
</tr>
<tr>
<td>2</td>
<td>Irradiation with 10 Gy</td>
</tr>
<tr>
<td>3</td>
<td>Pre-heat at 100°C</td>
</tr>
<tr>
<td>4</td>
<td>LM-OSL measurement at 125°C for 3600 s</td>
</tr>
<tr>
<td>5</td>
<td>Repeat steps 1–4 for different pre-heat temperatures (125, 200, 250, 300, 350, 200, 400, 450, 500, 200, 550, 600, 200°C). The repeated pre-heat at 200°C was inserted in order to monitor changes in sensitivity</td>
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### Table 2

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
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<tbody>
<tr>
<td>1</td>
<td>Heating to 650°C to remove all observable signals</td>
</tr>
<tr>
<td>2</td>
<td>Irradiation with 25.24 Gy</td>
</tr>
<tr>
<td>3</td>
<td>Pre-heat at 200°C for 10 s</td>
</tr>
<tr>
<td>4</td>
<td>LM-OSL measurement at 125°C for 7200 s (from 0-40 mW/cm², LM-OSL1)</td>
</tr>
<tr>
<td>5</td>
<td>Pre-heat at 220°C for 10 s</td>
</tr>
<tr>
<td>6</td>
<td>LM-OSL measurement at 125°C for 7200 s (from 0-40 mW/cm², LM-OSL2)</td>
</tr>
<tr>
<td>7</td>
<td>The cycle is repeated changing the pre-heat temperature in step 5, for temperatures 240, 260, 280 and 300°C</td>
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</table>

### Protocol A

1. Heating to 650°C to remove all observable signals
2. Irradiation with 25.24 Gy
3. Pre-heat at 200°C for 10 s
4. LM-OSL measurement at 125°C for 7200 s (from 0-40 mW/cm², LM-OSL1)
5. Pre-heat at 220°C for 10 s
6. LM-OSL measurement at 125°C for 7200 s (from 0-40 mW/cm², LM-OSL2)
7. The cycle is repeated changing the pre-heat temperature in step 5, for temperatures 240, 260, 280 and 300°C
3. Method of analysis

A heating procedure is always necessary before any OSL measurement to empty light-sensitive shallow traps, filled by laboratory irradiations. However, this thermal treatment can cause sensitivity change due to the charge transfer from thermally unstable traps to the optically sensitive trap. If the natural or regenerated OSL signal contains a significant contribution from a thermally unstable component, then appropriate thermal treatment is required before each OSL measurement. The sensitisation of each component can also vary for the different components due to the thermal treatment and this could affect the accuracy of dose estimation using an SAR protocol (Jain et al., 2003). The best way to determine the thermal stability of the various components is to make LM-OSL measurements following pulse annealing.

In this study all LM-OSL curves were deconvoluted assuming first order kinetics. The first order kinetics assumption is based on a direct extrapolation from the experience gained from the thermoluminescence (TL) studies of the quartz glow curves, where no higher order kinetics glow peaks exist. The first order kinetics LM-OSL equation obtained by Bulur (1996), further transformed by Polymeris et al. (2006) to contain parameters directly estimated by the measurement procedure, is used in the form below:

\[ I(t) = \frac{I_m}{t_m} \exp\left(-\frac{t^2}{2t_m^2}\right), \]  

(1)

where \( I_m \) and \( t_m \) are the values of OSL intensity and time at the maximum of the LM-OSL peak and \( t \) the time of the stimulation. This LM-OSL equation was used for deconvolution of all experimental data. Curve fitting was performed by MINUIT program (James and Roos, 1977), whereas the goodness of fit was tested by the figure of merit (FOM) of Balian and Eddy (1977), given by

\[ \text{FOM} = \sum |Y_{\text{Exper}} - Y_{\text{Fit}}| / A, \]  

(2)

where \( Y_{\text{Exper}} \) is the experimental glow-curve, \( Y_{\text{Fit}} \) is the fitted glow-curve and \( A \) is the area of the fitted glow-curve. The background was simulated to an equation of the form

\[ bg = z_d \cdot \left( C + \frac{t}{P} \right), \]  

(3)

where \( z_d \) is the zero dose OSL signal after blue stimulation and \( P \) the total stimulation time. The parameter \( z_d \) is evaluated experimentally, by measuring the background OSL signal of non-irradiated samples. \( C \) is a constant, unique for each quartz sample, estimated to be 0.204 in the case of the ALT sample, 0.171 in the case of the ATK sample, 0.167 in the case of the PDK sample and 0.158 for the SIL quartz sample.

4. Results and discussion

LM-OSL curves were fitted to the sum of six components of first order kinetics. Curve shapes and deconvolution examples

![Fig. 1. Normalized thermal stability behavior of components 2–6 for the SIL quartz sample. C2 (Solid circles), C3 (solid triangles), C4 (solid squares), C5 (solid diamonds) and C6 (Crosses). Normalization with respect to the first cycle.](image1)

![Fig. 2. Behavior of the first component (a) and the second component (b) of the LM-OSL curve as a function of the pre-heat temperature; ALT (Solid circles), ATK (solid triangles), PDK (solid squares) and SIL (solid diamonds); normalized with respect to the lower pre-heat temperature of 100°C. The sensitivity of the first component drops rapidly with increasing temperature and is removed completely by heating to 250°C. The sensitivity of the second component shows a decrease for temperatures between 150 and 200°C, followed by a wide temperature stability region for 250–400°C, and completely removed by heating to 500°C.](image2)
Pre-Heat Temperature (°C)

Normalized OSL response

Fig. 3. Normalized behavior of the third component (a) and the fourth component (b) of the LM-OSL curve as a function of the pre-heat temperature; ALT (solid circles), ATK (solid triangles), PDK (solid squares) and SIL (solid diamonds). Normalization with respect to the lower pre-heat temperature of 100°C. Both components, C₃ and C₄, show similar trends, namely a plateau at lower temperatures and a decreasing pattern at higher temperatures.

Fig. 4. Normalized behavior of the fifth component (a) and the sixth component (b) of the LM-OSL curve as a function of the pre-heat temperature; ALT (solid circles), ATK (solid triangles), PDK (solid squares) and SIL (solid diamonds). Normalization with respect to the lower pre-heat temperature of 100°C. The fifth component in (a) shows a rapid and continuous drop for temperatures above 250°C, whereas the sixth component in (b) exhibits a remarkable stability for pre-heat temperatures up to 350°C and afterwards gradually decreases.

4.1. Stability

The measurement at the pre-heat temperature of 200°C was performed in four cycles; cycle 1 after the measurement at 150°C, cycle 2 after the measurement at 350°C, cycle 3 after the measurement at 500°C and finally cycle 4 after the measurement at 600°C, in order to monitor any sensitivity changes. However, no significant sensitivity changes were observed. The higher sensitivity changes, up to 30%, were observed for the case of components C₃, C₄ and C₅ of SIL quartz sample. The respective sensitivity change as a function of the measurement cycle is shown in Fig. 1. In the case of the ALT quartz sample, the sensitivity change was less than 20%, while for the other two samples, was of the order of 10%.

Pulse annealing curves were obtained by plotting the normalized OSL sensitivity vs pre-heating temperature. The effect of the latter on the sensitivity of the first component for all four quartz samples is shown in Fig. 2a. It is established that the sensitivity of this component drops rapidly as the pre-heat temperature increases. In fact, this is the most thermally unstable component, as it can be removed completely by heating to 250°C. This is similar to the stability of the ultra-fast component reported by Jain et al. (2003).

The pulse annealing curves of the second component for all quartz samples are shown in Fig. 2b. The behavior of this component is interesting because its sensitivity shows a decrease
for temperatures between 150 and 200 °C, and a wide temperature stability region for 250–400 °C. This component could be completely removed by heating to 500 °C. This behavior could be explained due to the fact that, at the lower pre-heat temperatures of 100 and 150 °C, the 110 °C glow peak of quartz is not completely erased. Therefore, at least part of this specific TL glow peak is present at the measurement temperature of 125 °C. Since the second component is closely related to the 110 °C glow peak, its response at these low pre-heat temperatures is enhanced. Therefore, the behavior of this component, presented in Fig. 2b, is a result of the normalization, namely the LM-OSL is normalized to a value that has increased sensitivity. Under these circumstances, it is safe to conclude that the real stability of the second component is extended up to 400 °C.

Components 3 and 4 show similar trends, namely a plateau at lower temperatures and a decreasing sensitivity pattern at higher temperatures. The effect of the pre-heat temperature on their sensitivities is shown in Fig. 3a and b, respectively. Sensitivity of both components decreases substantially as the pre-heat temperature increases. However, this decrease becomes sharp for pre-heat temperatures higher than 350 °C, with little signal loss when heated to that specific temperature.

The fifth component is obtained with higher fitting uncertainties than the other components, mainly due to its low intensity. Nevertheless, its behavior, presented in Fig. 4a, shows a rapid and continuous drop for temperatures above 250 °C.

The pulse annealing curves of the sixth component for all quartz samples are shown in Fig. 4b. The behavior of this

Fig. 5. (a) LM-OSL curves measured for 7200 s deconvoluted into their individual components on the logarithmic x-axis. Left-hand side figure LM-OSL 1 and right-hand side figure LM-OSL 2. (b) LM-OSL curves deconvoluted into their individual components on the linear x-axis.
component is of great interest, since it exhibits a remarkable stability for pre-heat temperatures up to 350 °C and then decreases. The components show thermal patterns similar to those of components A, B, C and D reported by Bulur et al. (2000), as well as to those of the fast, medium and slow components reported by Jain et al. (2003).

4.2. Recuperation

Examples of LM-OSL curve shapes of the recuperated signal, analyzed into their individual components, are shown in Fig. 5a and b. In order to obtain a better resolution for the component C6 in the experimental data the LM-OSL signal were extended to 7200 s. We observed that the time maximum positions, \( t_m \), for the component C6 were slightly higher than those measured for 3600 s (Kiyak et al., 2007). The \( t_m \) value for the component C6 was increased from about 3800 to 5700 s (ALT), 5560 s (ATK), 6200 s (PDK) and 5509 s (SIL). The \( t_m \) positions for the other components were similar to the previously measured ones for 3600 s. In these figures the crucial role of the background signal, especially in the case of the right-hand side figure corresponding to the LM-OSL 2 (where the recuperation is expected), is obvious. Step 4 yields the normalized response as a function of the pre-heat temperature for both protocols. For the PDK quartz sample, this normalized response of all components is presented in Fig. 6. The behavior of all other quartz samples is similar for both protocols.

From these data and this figure, it can be inferred that there is not any recuperation signal for the components 1–5. However, these components were included in the deconvolution of the LM-OSL 2. Based on the obtained values of the components 1–5 the recuperation is estimated to be less than 0.1%. The practically zero recuperation of the components 1–5, for all quartz samples could be attributed to a couple of reasons, namely, (i) the extremely high heating temperature of 650 °C in the first steps of both protocols, (ii) the relatively low test dose used.

The situation is different for the sixth component. The recuperation signal expressed as the ratio of the \( (\text{LM-OSL 2}/\text{LM-OSL 1}) \times 100 \) is shown in Fig. 7 for the four quartz samples. The left-hand side of this figure corresponds to measurements according to protocol A, whereas the right-hand side of the figure corresponds to measurements according to protocol B. In both cases a recuperated signal has survived after the first LM-OSL measurement, which decreases as the pre-heat temperature increases. However in the case of protocol A, which

Fig. 6. Normalized response of all components of quartz samples, as a function of pre-heat temperature according to the protocol A (a) and B (b).

Fig. 7. Recuperated LM-OSL signal, for the sixth component, expressed as percentage of the initial signal (step 4), according to the protocol A (in the left) and B (in the right).
incorporates heating, the recuperated signal decreases rapidly as the pre-heat temperature increases. In the case of protocol B, which incorporates blue light bleaching, the recuperated signal decreases very slowly. However, in both cases, recuperation does not exceed 1%.

These results partly contradict the respective ones reported by Jain et al. (2003). Although they also reported no detectable recuperation of the fast and medium components, they concluded that significant recuperation occurs in the slow components, ranging from 10% to 80% depending on the component. This is not the case for any of the components of the four quartz samples of Turkish origin.

5. Conclusions

A series of thermal stability and recuperation experiments, in conjunction with curve fitting studies, yielded the presence of six LM-OSL components, when quartz is stimulated at 470 nm. In general, the six OSL components identified in all four quartz samples studied, display different thermal stability behavior. In accordance with Jain et al. (2003) as well as with Singarayer and Bailey (2003), we report the presence of a thermally unstable fast component, which is almost totally removed by heating up to 250 °C. Interestingly, another slow component is identified, much less thermally stable, and reduced to less than 50% of its initial intensity by heating to 275 °C. The presence of these two components may result in under-estimated dose by SAR. Although a high temperature pre-heat treatment removes these components, sensitivity change and significant recuperation due to medium and slow components may lead to incorrect age estimation. Therefore an optimum temperature for pre-heat and cutheat treatments should be carefully defined. The medium, as well as most slow components, show an extended thermal stability pattern over the temperature region between 200 and 350 °C. All these results also supported those reported by Jain et al. (2003), as well as those by Singarayer and Bailey (2003). No detectable recuperation occurs for the first five components reported. The greatest recuperation occurred in the sixth component, despite the fact that it was less than 1%.

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