Quartz OSL: Effects of thermal treatment and their relevance to laboratory dating procedures

A.G. Wintle\textsuperscript{a,}\textsuperscript{*}, A.S. Murray\textsuperscript{b}

\textsuperscript{a}Institute of Geography and Earth Sciences, University of Wales, Aberystwyth SY23 3DB, UK
\textsuperscript{b}The Nordic Laboratory for Luminescence Dating, Department of Earth Sciences, Aarhus University, Risø National Laboratory, DK-4000 Roskilde, Denmark

Received 18 October 1999; received in revised form 3 January 2000; accepted 27 January 2000

Abstract

In dating procedures, whether single or multiple aliquot, OSL signals are obtained after samples have been heated in the laboratory with preheat procedures as short as a few seconds or as long as several hours. The OSL signals may be obtained whilst stimulating at a variety of temperatures. These thermal treatments will affect both the trapped electron population(s) in the material and the recombination centres (or trapped hole populations). Several effects may occur simultaneously. Experimental evidence is presented which is used to select the most appropriate thermal treatments in laboratory dating procedures. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The possibility of being able to observe a luminescence signal from quartz whilst exposing it to light from a less energetic region of the visible spectrum has been exploited in the dating of sediments and the determination of past exposure of heated materials to ionizing radiation (Aitken, 1998). The first measurements of optically stimulated luminescence (OSL) were made using an argon ion laser (514.5 nm) (Huntley et al., 1985). Subsequent studies have used more convenient and cheaper light sources such as filtered halogen lamps (Botter-Jensen and Duller, 1992), green light emitting diodes (LEDs) (Galloway et al., 1997) and most recently blue LEDs (Botter-Jensen et al., 1999a, b). Reviews of equipment have been published by Botter-Jensen (1997) and Botter-Jensen and Murray (1999) and of dating procedures by Wintle (1997).

1.1. The OSL decay curve

OSL is usually measured during optical stimulation at continuous power and results in an OSL signal that decays with time, but not according to a single exponential. An exponential decay would be expected if a single electron trap were present, and the luminescence efficiency remained constant during stimulation (Aitken, 1998, p. 26; McKeever, 1994). However, during measurement of the main OSL signal, electrons can be transferred into the main OSL trap (e.g. from the 110°C thermoluminescence (TL) trap) (McKeever, 1991; Morris and McKeever, 1993). At the same time, electron movement from deep traps can alter the number of recombination centres available, and even in first order decay, there may be more than one OSL trap present. Hence, simple exponential decay should not be expected. Such charge transfer processes can
give rise to a combination of first and second order effects and many of these processes have been modelled numerically (McKeever et al., 1996; Bøtter-Jensen et al., 1995; McKeever and Chen, 1997; Franklin, 1998).

1.2. The luminescence centre

The OSL emission at room temperature is centred on about 365 nm (3.35 eV) and has a FWHM of 70 nm, as measured by stimulation using the 647 nm line from a krypton laser (Huntley et al., 1991). This emission spectrum is thought to originate with the same centres as those used by various quartz TL peaks. Franklin et al. (1995) have shown that at least four of the TL peaks, namely at 95–110°C, 150–180°C, 200–220°C and 305–325°C have emission peaks in the same region, 376, 392, 410 and 430 nm, respectively (Fig. 1). Franklin et al. (1995) concluded that this “family” of traps use the same luminescence centre, which they access via the conduction band. From their data, it appears as though the emission peak is shifted to longer wavelengths as the temperature of the quartz is increased (see Section 3.1). However, no OSL emission spectra have been recorded at elevated temperatures in order to confirm this behaviour. Temperature dependence of the emission wavelength can be explained in terms of changes in the occupation of higher vibrational states in the configuration coordinate model (Franklin, 1998).

The most likely radiative recombination centre for this emission is [H$_3$O$_4$]$^+$; these centres are silicon vacancies that are occupied by three hydrogen atoms and a trapped hole. Studies on synthetic hydrothermal quartz by Yang and McKeever (1990) have shown that electrons giving rise to the 100°C TL peak recombine at two possible centres. One is the [H$_3$O$_4$]$^+$ centre that emits at 380 nm at room temperature and the other, emitting at 470 nm, is the [AlO$_4$]$^-$ centre, in which an aluminium atom replaces a silicon atom. Emission at 482 ± 4 nm has been observed at 375°C for several samples of sedimentary quartz that have been bleached with yellow light (>475 nm) to remove the 325°C TL peak (Scholefield et al., 1994). For the same samples, the 110°C TL peak emission was reported as 376 ± 2 nm.

Following an initial discussion of the relationship between the OSL and the 325°C TL peak (Section 2), this paper will discuss effects due to: A changing the temperature of OSL measurement (Section 3), viz. shift of the emission peak (L) Section 3.1, thermal quenching (L) Section 3.2, the effect of the 110°C TL trap (E) Section 3.3, thermal assistance (E) Section 3.4; and B thermal pretreatment (Section 4), viz. relative efficiency of recombination centres (L), including radiation quenching Section 4.1, thermal transfer (E) Section 4.2, depopulation of traps (E) Section 4.3. E refers to the electron trap population giving rise to the OSL signal and L refers to the luminescence centres used in OSL production.

2. The relationship between OSL and the 325°C TL signal

The 325°C TL peak in quartz has been shown to bleach rapidly compared with other TL peaks located between room temperature and 500°C (Spooner et al., 1988). It has been termed the ‘rapidly bleaching peak’ (RBP) by Franklin and Hornyak (1990) and has been shown to be selectively bleached by wavelengths longer than 475 nm (Prescott and Fox, 1990; Prescott and Mojarrabi, 1993).

The similarity in the bleaching behaviour of the OSL signal and the 325°C TL peak has often been noted (Smith et al., 1986, 1990a; Kaylor et al., 1995; Huntley et al., 1996). Further studies by Spooner (1994), Wintle and Murray (1997, 1998) and Murray and Wintle (1999) provide four strong pieces of evidence for the electron traps being the same for both luminescence signals:

1. Spooner (1994) demonstrated “quantitative equivalence of the total light sums of the OSL signal and the 325°C TL peak”. He compared the light sums at different temperatures, measuring the OSL at temperatures from room temperature to 250°C and comparing it with the area of the 325°C TL peak.
which he moved from 215 to 340 °C by changing the heating rate from 0.002 to 10 K/s. The data overlap in spite of the considerable effects of thermal quenching on both signals.

2. Spooner (1994) was able to “measure and confirm the concordance of the bleaching response spectra”. He used narrow wave bands (10 nm FWHM) from 400 to 900 nm at room temperature. There was no OSL loss for bleaching wavelengths greater than 695 nm and “progressively greater bleaching efficiency of shorter wavelengths, in accordance with the previous findings for quartz TL”. The energy required to reduce the OSL by a fixed amount (50%) at each wavelength >400 nm was similar to that required to completely bleach the 325 °C TL peak (Spooner et al., 1988). This implies that the TL peak is easier to bleach than the OSL at these wavelengths; for shorter wavelengths the bleaching rates were shown to be similar (Spooner, 1994).

3. Wintle and Murray (1997) showed that the 325 °C TL signal was removed in response to a given blue-plus-green light exposure in direct proportion to the integrated OSL signal resulting from that light exposure.

4. Wintle and Murray (1998) showed that as the temperature was increased from 280 to 330 °C, the OSL was rapidly reduced to <1% of the initial value. This would be expected for an electron trap that gives rise to a TL peak that occurs at about 325 °C when using a heating rate of about 5 K/s. More extensive isothermal decay studies by Murray and Wintle (1999) gave a trap depth (E) of 1.66 ± 0.03 eV and a pre-exponential factor (s) of 1 × 10¹³ s⁻¹ for the major component of the OSL signal. These values are indistinguishable from those determined for the 325 °C TL peak by Wintle (1975), of 1.69 eV and 1 × 10¹⁴ s⁻¹ for a different quartz sample.

It is now possible to draw conclusions concerning the thermal stability of the OSL signal. A lifetime at 20 °C of 110 × 10⁶ yr is predicted using the E and s values from Murray and Wintle (1999). This is comparable with the 30 × 10⁶ yr lifetime derived by Wintle (1975) for the 325 °C TL peak.

3. Changing the temperature of OSL measurement

3.1. Shift of the emission peak

As mentioned in Section 1.2 a shift to longer wavelengths with increasing sample temperature is found in the TL emission. The implication of this effect is that OSL measurements made at increasingly higher temperatures will also be affected. For stimulation with either blue diodes or the filtered green lamp, the detection filter used in the Risø system is a Hoya U-340 (Bøtter-Jensen et al., 1999a). The transmission characteristics of this filter drop rapidly for wavelengths above 360 nm, reaching 10% by 380 nm (Fig. 1). Hence the OSL signal at elevated temperature will be reduced compared with that measured at room temperature, as the amount of light transmitted by the filter is substantially reduced.

3.2. Thermal quenching

In addition to the shift of the OSL peak emission, there is also a reduction in the luminescence efficiency of the centre that occurs as the sample temperature is increased above room temperature (Spooner, 1994). This effect is known as thermal quenching (Chen and McKeever, 1997, p. 74). For the 325 °C TL signal of heated quartz, the activation energy (0.64 eV) and pre-exponential constant (K = 2.8 × 10⁷) for the relevant Arrhenius equation were characterized by Wintle (1975). Both Huntley et al. (1996) and Murray and Wintle (1998) were able to fit their OSL data from sedimentary quartz using similar parameters. Murray and Wintle (1998) measured the integrated OSL signal whilst holding the samples at temperatures from 30 to 500 °C. The data showed a strong decrease in the OSL intensity from 75 to 225 °C (Fig. 2). They were fitted for a single thermal quenching process and gave the parameters W = 0.61 ± 0.02 eV and K = 2.0 × 10⁷ ± 1.2 × 10⁷, very similar to the values derived by Wintle (1975) for the 325 °C TL peak.

3.3. The effect of the 110 °C TL trap

Smith et al. (1986) were the first to show that some fraction of the charge associated with the 110 °C TL

![Fig. 2. Integrated OSL signals (0–100 s) as a function of stimulation temperature. Solid line fitted to L = L₀/(1 + exp(-W/kT)) giving W = 0.636 (±0.013 eV) and K = 3.4 × 10⁷ (±0.9 × 10⁷) for thermal quenching (redrawn from Fig. 4 of Murray and Wintle, 1998).](image-url)
peak could be transferred (by heating, or storage at room temperature) into the OSL trap, so called “recuperation” (Aitken, 1992). The phenomenon of photo-transferred TL has been reported (Bailiff et al., 1977; Murray, 1996; Alexander et al., 1997; Wintle and Murray, 1997) in which optical stimulation transfers charge into the 110°C TL peak. Bailey (1997) and Wintle and Murray (1997) have also reported optical detrapping of charge from the 110°C TL peak. Thus charge can move backwards and forwards between the 110°C TL peak trap and the OSL trap.

In Fig. 3a, the OSL signal obtained as a function of stimulation time is shown for a naturally irradiated sand (WIDG8 De=58 ± 6 Gy). The measurement was carried out at temperatures ranging from 25 to 175°C. It can be seen that there is an initial increase in the signal and a steepening of the initial part of the decay curve as the temperature was increased. Similar results (also shown on a linear/log plot) were presented by Spooner (1994). This behaviour is consistent with the second-order effects to be expected from interaction with the 110°C TL trap.

On a log/linear plot (Fig. 3b), the OSL decay is seen not to be characterised by a single exponential, as shown for the data set used in Fig. 3a. Smith and Rhodes (1994) observed that the OSL decay measured at 220°C was also non-exponential, even though the 110°C TL trap is unavailable at these temperatures. They concluded that there was more than one exponential decay and deconvolved the decay curve into three components — named “fast”, “medium” and “slow” with respect to their rate of decay under visible stimulation. Bailey et al. (1997) took this study further; using the Risø blue-plus-green lamp, they deconvolved three signals with half-lives of about 2, 8 and 800 s for three different sedimentary sands when stimulated at 160°C. The relative proportions of each signal varied, but the fast component was consistently larger than either of the others. McKeever et al. (1997a) presented OSL decay curves for sedimentary quartz held at temperatures from room temperature to 200°C, which had been normalized to the same initial OSL intensity. They compared the experimental data with the results of numerical models. Wintle and Murray (1998) also demonstrated the effect of the 110°C TL peak trap, with a change in shape of the decay curves occurring between measurements at 75 and 110°C. Bøtter-Jensen et al. (1999a) used linearly modulated OSL to identify unambiguously the OSL component arising from the 110°C TL trap. The conclusion drawn by Wintle and Murray (1998) was that quartz OSL dating measurements should be made at, or above 100°C, to remove the effect of re-trapping in the 110°C TL peak trap.

3.4. Thermal assistance

Another temperature sensitive phenomenon can be seen superimposed on the fast component of the optical decay curve (Fig. 3). This thermal assistance of the excitation process was first quantified by Spooner (1994) who observed optical stimulation as a function of temperature from about 100 to 500 K. The activation energy for thermal assistance was obtained at six different stimulation wavelengths and the energy systematically varied with wavelength. Huntley et al. (1996) reported a similar dependence of activation energy on wavelength. In studies of the initial OSL signal of a sedimentary quartz, Murray and Wintle (1998) were able to obtain the thermal assistance energy for experiments using their filtered light source, after correcting for thermal quenching. The thermal assistance was interpreted by Spooner (1994) as an increased rate of trap emptying. It is a further argument for making OSL measurements at an elevated temperature.

3.5. Conclusion with regard to temperature of stimulation

From the above data, it can be seen that measuring the OSL at, or about, 125°C gives a rapidly decaying
luminescence signal, optimized for initial intensity. The raised temperature will prevent retrapping in the 110°C trap and so increase the rate of decay, and remove at least some second order effects. Thermal assistance will also increase the rate of trap depletion, compared with measurements made at room temperature. However, thermal quenching and the shift of the emission peak result in decreased OSL as the temperature is raised beyond this point.

4. Effects of thermal pretreatment

4.1. Relative efficiency of recombination centres

A variety of heat treatments have been applied immediately prior to OSL measurement with the intention of removing possibly unstable OSL signals relating to charge from shallower, optically-sensitive traps (Godfrey-Smith, 1994). The choice of preheat (time and temperature) has been contentious. Short duration preheats (e.g. 220°C for 5 min as originally suggested by Smith et al., 1986) have been claimed to give ages which are in agreement with TL ages and independent age control (Smith et al., 1990a). Smith et al. (1990b) also suggested using longer preheats at lower temperatures, with 160°C for 16 h being adopted by Stokes (1992). Roberts et al. (1993, 1994) demonstrated that for a limited number of samples the latter preheat causes underestimation of the equivalent dose by 10–40%. This claim was vigorously rebuffed by Stokes (1996a, b) in a similar intercomparison using a larger data set. However, none of these experiments allowed for the sensitivity changes known to be brought about by such thermal pretreatment. It is likely that some of these differences were related to the lack of equalization of sensitivities for the naturally and laboratory irradiated samples (Wintle and Murray, 1999). More recently, Huntley et al. (1996) obtained a satisfactory age using a preheat of 48 h at 160°C, but reported too large an equivalent dose being obtained when a cut heat to 210°C was applied. On kinetic grounds, they also suggested that a preheat of 5 min at 220°C would suffice for samples less than 100 ka.

In early attempts to measure the radiation dose in quartz for use as a retrospective dosimeter, sensitivity changes were found to occur (Botter-Jensen et al., 1993; Jungner and Botter-Jensen, 1994). This led to a procedure that applied a single aliquot regenerative dose approach to several aliquots of the sample, each of which had been given a different laboratory dose. This SARA procedure (Medjahd and Botter-Jensen, 1994, 1997; Murray, 1996; Duller et al., 1999) relied upon the sensitivity change between the initial OSL measurement and that of the regeneration doses being proportional, i.e. there was no dose dependence. Although this procedure can be applied to samples showing pronounced sensitivity change, it is not a true single-aliquot procedure and it is inapplicable when the natural signal is close to the saturation level. It is also difficult to use when the aliquots vary considerably in their OSL intensity, as often occurs with partially bleached sediments.

Changes in luminescence sensitivity can be observed for laboratory-irradiated material when it is held at elevated temperatures for short times, as in the case of preheating applied in both single- and multiple-aliquot dating runs. As it is likely that these changes are governed by an Arrhenius equation, these changes would also occur at ambient temperature, in the time since deposition. To obtain a meaningful value of $D_e$, it is thus necessary either to equalize the luminescence sensitivities of naturally and laboratory irradiated samples (a hit-or-miss procedure, as outlined above) or to be able to measure the appropriate luminescence efficiency for each OSL measurement and afterwards make the necessary corrections for the $D_e$ determination. It is also very important to be able to monitor the sensitivity in laboratory experiments that involve thermal treatment, e.g. isothermal decay measurements.

Murray et al. (1997) suggested that sufficiently stringent preheat conditions could be identified by obtaining the same value of $D_e$ for preheats above a certain temperature. They employed an additive-dose single-aliquot procedure to obtain $D_e$ and, using a 10 s preheat, measured different aliquots at temperatures from 160 to 300°C. Their samples were from Australia where ambient temperatures are high and thus might be expected to naturally activate the process of sensitization more completely than, for example, in high latitude environments. For samples with ages of several tens of thousands of years, a constant value of $D_e$ was not reached until preheat temperatures of 280 and 300°C were employed. Murray et al. (1997) reported overestimation in $D_e$ by up to a factor of five when preheats of 10 s at a temperature of 220°C were used on a 30 ka sand. They interpreted this effect as being the result of thermal transfer, but sensitivity changes have since been shown to be entirely responsible (Wintle and Murray, 1999).

The disadvantage of using such high temperature preheats (>280°C) is the significant thermal release of electrons from the main OSL trap, resulting in lower signals. According to the isothermal decay study of Murray and Wintle (1999), the main signal decays by about 0.8% per s at 280°C, with depletion at 300°C being 3% per s and at 320°C being 8% per s. These values, derived using a trap depth of 1.66 eV and a pre-exponential factor of $10^{13}$ s⁻¹, probably have uncertainties of at least one order of magnitude, because of uncertainties in $E$ and $s$ (see Section 4.3). The same sample shows a TL peak at about 310°C for
a heating rate of 5 K/s (Wintle and Murray, 1998). However it should also be remembered that the apparent position of the peak will be affected by thermal quenching (see Section 3.2).

Several attempts have been made to use the 110°C TL peak for normalization in multiple-aliquot additive-dose procedures (e.g. Roberts et al., 1994; Stoneham and Stokes, 1991; Stokes, 1994). Since the OSL signal and the 110°C TL peak use the same luminescence centre (see above) it might be assumed that there is a linear relationship between the two signals that can be used as a correction factor. If this were the case, the 110°C TL response to the subsequent regeneration dose would be an appropriate TL signal to use to correct for sensitivity changes, as suggested by Murray and Roberts (1998) in a single-aliquot regenerative procedure. However, these authors showed that, when the measurement cycle was repeated, the plot of OSL sensitivity (OSL signal divided by its regenerative dose) versus 110°C TL sensitivity (subsequent TL signal divided by the dose giving rise to it) was linear but did not go through the origin, i.e. the two signals did not vary in direct proportion. Nevertheless, this approach can be applied to estimate $D_e$ using a single regenerative dose (chosen to be similar to the expected natural dose to minimize the effect of the non-linearity), if the effect of the intercept is taken into account. The same procedure was also applied to single quartz grains (Murray and Roberts, 1997). Folz and Mercier (1999) have since modified this approach to use a range of regeneration doses. A possible reason for the OSL and TL signals not being in direct proportion to each other is a different non-luminescent recombination competition mechanism for the two luminescence signals (Murray and Mejdahl, 1999; Murray and Wintle, 1998).

4.1.1. Luminescence sensitivity
Changes in luminescence sensitivity as a function of previous treatment can be determined by observing the luminescence response to a test dose. This can either be the response of the 110°C TL peak as discussed in the previous section, or, for samples that have had the charge from their OSL trap(s) removed, the OSL response.

Wintle and Murray (1998), following earlier suggestions by Aitken and Smith (1988) and Stoneham and Stokes (1991), used the 110°C TL peak to monitor for OSL sensitivity change. They demonstrated that the responses to the same preheats were different for two aliquots of sample that were identical, except that one had experienced a natural irradiation over the last 30,000 years, whereas the other had been optically bleached and then given a laboratory dose (Fig. 4). These data clearly showed the reason why a measurement procedure that does not allow for sensitivity change would give different values of $D_e$ as a function of preheat temperature. The natural sensitivity was enhanced by up to 30%, whereas an optically bleached sample given an equivalent irradiation produced a much larger (up to 300%) sensitivity enhancement. In a further study of the same sample, Wintle and Murray (1999) showed that, when samples were held for up to 12 h at temperatures ranging from 160 to 280°C,
the maximum level of enhancement attained was independent of the preheat temperature. However, the rate at which this maximum level was reached increased with increasing temperature (Fig. 5a). Analysis of the data for this sample suggested that the sensitivity change was dominated by a component with a lifetime of about 40 ka at 20°C. Hence the natural luminescence response in Fig. 4 is almost fully sensitized.

This 110°C TL peak behaviour can be compared with the response of the OSL (Fig. 5b). To obtain these data, aliquots of the same sample had been optically bleached at 125°C to erase the geologically derived OSL signal and then preheated for up to 22 h. This showed a similar pattern of sensitization to that of the 110°C TL, although the magnitude of sensitization was less than for the laboratory-irradiated sample (Fig. 5b), as also found for the 110°C TL response for this unirradiated sample (Fig. 5a). From the 110°C TL data presented by Wintle and Murray (1999), it is clear that the absolute response in these experiments depends upon three factors, namely whether or not dose has been given to the sample, whether that was done in nature or in the laboratory, and how the signal was zeroed prior to the dose being delivered.

It is thus vital in any dating procedure that the luminescence sensitivity is monitored for each OSL measurement, as was predicted by computer modelling (McKeever et al., 1997b). From Fig. 5b it can also be seen that the preheats discussed in the previous section, namely 220°C for 5 min or 160°C for 16 h, would give rise to a similar degree of enhancement (~20%) for an optically bleached sample (the zero dose point on a regenerative growth curve).

OSL sensitivity can best be monitored using the OSL response to a small test dose given after every OSL measurement. Such a procedure is applicable to both single-aliquot and multiple-aliquot regenerative-dose procedures. Murray and Roberts (1998) suggested such a single aliquot approach using only a single regenerative dose and Roberts et al. (1998) used this procedure for single grains. Murray and Mejdahl (1999) tested this procedure using multiple grain aliquots. Further studies on single grains and small single aliquots (60–100 grains) have been reported by Olley et al. (1999) in their study of fluvial sediments from New South Wales, Australia.

### 4.1.2. Radiation quenching

A related change in the relative efficiency of different recombination centres has been reported by Huntley et al. (1996) for very old samples for which the OSL signal is in saturation. Godfrey-Smith (1991) reported a reduction in the OSL signal of quartz from a 500 ka dune sand when large irradiations were applied to the natural sample. This “dose inversion”, or radiation quenching (Huntley et al., 1996), was interpreted as being the result of the production of competing recombination centres that are either non-radiative, or emit outside the detection region; the effect has long been known in predose work using the 110°C TL peak (Aitken, 1985). When irradiated samples were stored at 150°C, the OSL increased back to the level of the natural within about 4 h, suggesting that the new centres produced by the irradiation are thermally unstable, and hence play no role in the natural OSL measurement. Huntley et al. (1996) also reported that when they used simple heating to 210°C followed by rapid cooling as the preheat in a dating study of a 122 ka sample, they obtained an equivalent dose that was a factor of two too large. They attributed this to radiation quenching; however, from the preceding section it can be seen that sensitivity enhancement would have occurred at ambient temperature during the 122 ka, and that the short preheat was probably inadequate to equalize the sensitivities for the natural and irradiated aliquots.

### 4.2. Thermal transfer of charge as a function of preheat temperature

A phenomenon that has been reported by several authors is an increase in OSL signal as a function of preheat temperature for laboratory irradiated samples. It has been argued that this type of behaviour can be explained in terms of the existence of a light-insensitive trap that is sufficiently thermally stable that it is not emptied during the period of burial. However, such a trap may be less thermally stable than the OSL traps; in this case, preheating causes charge to be released and then retrapped in the OSL traps. Rhodes (1988) found that the rise observed in the region from 250 to 280°C (just before the main electron trap is emptied) was larger for laboratory irradiated samples than for the naturally irradiated material. In his experiment,
two sets of samples were held for 5 min at different elevated temperatures.

More precise measurements of the effect can be made by observing the initial part of the OSL signal and using a single aliquot which is preheated to a temperature, and then immediately cooled before the OSL is measured. This preheat/short-shine sequence is then repeated in short steps of 10°C from 160 to 500°C. Fig. 6 shows the results obtained by Wintle and Murray (1998) for the natural and regenerated OSL signals of a 30 ka aeolian sample from Australia. Taken at face value, the data indicate thermal transfer occurring for the laboratory irradiated aliquot between 160 and 270°C, with thermal decay for both aliquots occurring from 270 to 300°C. However, if the 110°C TL peak measurements from Fig. 4 are used to correct the data set in Fig. 6, it is seen that the evidence for thermal transfer disappears (Fig. 7). A data set similar to that in Fig. 5 was obtained by Li et al. (1999); however, they did not measure the sensitivity changes that occurred during their experiments and it is likely that thermal transfer was not in fact responsible for their observations, but sensitivity changes. Roberts et al. (1998, 1999) and Murray and Roberts (1998) also report negligible thermal transfer when using the measured sensitivity correction for small aliquots of Australian sedimentary quartz.

In summary, if a quartz crystal starts with all electron traps empty, and then receives a dose, electrons will be stored in both the 325°C TL/OSL trap, and light-insensitive traps; the latter can then be partially or completely emptied by preheating. During preheating, some charge may get transferred to the OSL trap, but from the preheat plateau evidence discussed above, this must be a small fraction of the charge already present in the OSL trap.

It may appear from the above arguments that charge transfer is no longer thought to be an important process, but this is not so. Electron traps are not usually empty at deposition, and shallow light-insensitive traps will, in general, contain a significant electron population. Even charge transfer from these traps is usually not important (otherwise wide preheat plateaus would not be observed), except in the case of very young samples, e.g. a 5-year old sample (Murray and Roberts, 1998). Three more recent studies (Bailey et al., 2000; Murray and Clemmensen, 2000; Hilgers et al., 2000) have also recently reported significant increases in $D_e$ with preheat temperature for modern or young aeolian sands, and this is best explained by thermal transfer from the 250 to 300°C region of the glow curve. Hilgers et al. (2000) went further, and bleached two samples ($D_e$ values of 0.2 and 15 Gy, respectively) with blue light. They then measured $D_e$ as a function of preheat temperature for these samples. In both cases they found that $D_e$ was consistent with a zero dose for 10 s preheats below about 220°C, but increased with preheats above 220°C. It seems likely that thermal transfer is of importance, but only in young samples, and it can probably be avoided by reducing the preheat temperature.

4.3. Depopulation of traps

Holding samples at elevated temperatures for some period also results in the thermal evicition of charge from the OSL trap. In his study of quartz that had been annealed at high temperatures, Rhodes (1990) obtained isothermal decay curves for OSL signals; measurements were made on laboratory-irradiated samples, but after the aliquots had been given a preheat of 5 min at 220°C. In 1996 Huntley et al. carried out isothermal decay measurements on a 800 ka dune sand that had a natural dose of about 350 Gy based on its inferred age and measured dose rate. This dose should cause the OSL signal to be in, or close to, saturation. Rhodes (1990) and Smith et al. (1990a) concluded from the exponential nature of the decay under thermal stimulation that the OSL signal was derived from a single electron trap. On the other hand, Huntley et al. (1996) concluded that 99% of their OSL signal resulted from three electron traps, the deepest of these accounting for about half of the OSL signal.

The experiments carried out by Wintle and Murray (1999) showed how changes in recombination probability would occur during the storage experiments used to produce thermal depopulation of the electron traps (Fig. 5b). Murray and Wintle (1999) used the 110°C TL peak response to monitor the resulting sensitivity change during their experiments on the isothermal decay of both natural and laboratory irradiated samples. They were thus able to derive isothermal
decay curves that had been corrected for sensitivity change and could compare them with the uncorrected data sets. Instead of using the integrated OSL signal, they used the initial part of the OSL signal, thus allowing a decay curve to be obtained for a single aliquot. The uncorrected data for the laboratory-irradiated samples showed initial increases in OSL with storage at elevated (160–280°C) temperature. Fig. 8a shows the uncorrected data for the natural and laboratory irradiated aliquots held at 220°C. The increase seen in the first 0.1 h was removed by applying the 110°C TL peak correction (Fig. 8b). The isothermal decay curves for this initial part of the natural OSL signal could be fitted with a single exponential decay (apart from a residual, more slowly decaying signal making up about 1% of the total initial signal). For the natural signal, the analysis of the corrected data gave a lower trap depth, 1.59 ± 0.05 eV, compared with 1.81 ± 0.05 eV for the uncorrected data (Murray and Wintle, 1999).

For samples that had been either optically bleached or heated to 500°C before irradiation, Murray and Wintle (1999) reported an additional component with a smaller trap depth (about 1.1–1.3 eV) and slightly higher values (about 1.7 eV) for the stable component equivalent to that in the natural OSL. Using these values they concluded that any of the three commonly used preheat treatments (160°C for 16 h, 220°C for 5 min or 280°C for 10 s) would remove the unstable charge associated with the shallower traps.

Since these analyses were obtained after correction for sensitivity change and the data are fitted with an exponential for each storage temperature, and since the slopes of each plot are then used to obtain values of \( E \) for each component, it might be asked how significant is the existence of the more unstable component? According to their prediction, Murray and Wintle (1999) calculated the lifetime to be about 380 yr at 20°C, and thus it would contribute insignificantly to the natural OSL signal. However, they also predicted that it would have lifetimes of 2 h, 130 s and 7 s at temperatures of 160, 220 and 280°C, respectively (although it must be recognized that there are uncertainties of more than one order of magnitude associated with these predictions). Thus, when comparing the natural OSL and regenerated signals, each having been given a 10 s preheat, it would be expected that \( D_E \) would be seen to show an increase as the preheat temperature is increased up to 280°C. It is interesting that this behaviour is not observed in the temperature region from 160 to 300°C (10 s preheats) for the SAR procedure (Murray and Wintle, 2000) (see Section 5).

However, there is some evidence for an unstable OSL signal when preheating laboratory irradiated samples at temperatures below 160°C. Li et al. (1999) observed the OSL measured at a stimulation temperature of 50°C in a pulse anneal sequence similar to that of Wintle and Murray (1998). Above 160°C, their data also showed the effects of larger sensitivity changes for the laboratory irradiated samples. Below 160°C, a rapid decrease in OSL was seen as the sample temperature was increased in 10°C steps above 100°C, using a heating rate of 2 K/s. By plotting the % reduction in OSL for each 10°C increment, they were able to demonstrate that the peak rate of emptying for this unstable component was around 120°C. However, their data were not corrected for sensitivity changes; an initial decrease in sensitivity would also explain their data.

4.4. Conclusions for dating

From the data presented in this section, it is clear that the luminescence efficiency must be monitored in some way. At present, the most efficient manner appears to be through the use of the OSL response to a test dose given after the main OSL measurement. For this to be feasible, each OSL signal must be zeroed by the stimulation prior to the delivery of the radiation dose (either a regeneration dose or a test dose). This monitoring measurement can be applied in either multiple- or single-aliquot regenerative procedures.
Because the sensitivity changes are usually strongly temperature dependent, it would be circumspect to make several measurements of $D_e$ using different preheat temperatures and see if a plateau in $D_e$ values is obtained. This is most easily accomplished using a single-aliquot procedure.

5. Dating protocols

Murray et al. (1997) suggested that single-aliquot runs should be made using a range of preheat temperatures. For the additive dose procedure, this resulted in values of $D_e$ that decreased as the preheat temperature was increased until a region of constant $D_e$ was reached. The change in $D_e$ with temperature was interpreted at the time as the result of apparent thermal transfer, but it now appears to have been the result of not making allowance for thermally-induced changes in luminescence sensitivity (Wintle and Murray, 1999).

Fig. 9. (a) Initial (0.1 s) natural OSL signal and subsequent regenerated signals plotted against the equivalent OSL signal (all measured at 125°C) obtained in response to a test dose ($T_d$) given after the previous OSL signal had been zeroed by stimulation for 100 s at 125°C. A regenerative dose (4.5 Gy for 972001 and 6.5 Gy for 952607) was repeated 15 times. These results are for two samples from Iron Age pottery (redrawn from Fig. 1a of Murray and Wintle, 2000). (b) Similar data set, but net OSL measurements (for 100 s at 125°C) were used for both the regenerated and test responses. The regenerative dose (20 Gy) was repeated 14 times and the test dose was 0.2 Gy. The sample is an aeolian sand from Deaf Adder Gorge in the Northern Territory of Australia, with an age of 24–30 ka (redrawn from Fig. 2e of Murray and Roberts, 1998).
(260°C for 10 s) was used for all grains. For the rock shelter at Jinmium in northern Australia, this approach has resulted in the identification of grains that have significantly different values of $D_e$ (Roberts et al., 1999) and has led to the employment of new statistical procedures to handle the $D_e$ data set (Galbraith et al., 1999). In addition, full growth curve reconstruction has been performed on several grains from Jinmium (Roberts et al., 1999), as well as in attempts to push back the age-limit for optical dating using grains which appear to have a high saturation value (Yoshida et al., 2000).

The SAR protocol has also been adopted for retrospective dosimetry measurements on quartz from house bricks (Banerjee et al., 1999).

6. Conclusions

The intensity and decay curve shape of the OSL signal obtained from quartz is affected by the application of heat, both during the OSL measurement and by thermal treatment prior to measurement.

Changing the temperature of the OSL measurement affects both the luminescence centre and the trapped electron populations. Increasing the stimulation temperature from 25 to 125°C will

1. Probably cause the peak OSL emission wavelength to increase from 365 to about 380 nm (this is implied from TL spectral measurements),
2. result in a decrease of about 10% in luminescence efficiency as a proportion of the centres become non-radiative. As the temperature is increased above 125°C, the effect of this thermal quenching process is to reduce the OSL signal very rapidly to a negligible level,
3. prevent electrons being captured by the 110°C TL trap, and thus prevent the delay in electron/hole recombination that occurs for stimulation below 100°C. It permits shorter stimulation times to be used in a dating procedure,
4. give a larger initial OSL signal, since the effect of thermal assistance outweighs the combined effects of the shift in peak emission and thermal quenching.

Evaluation of the above effects suggests that OSL measurements should be made at, or about, 125°C.

The application of any preheat following delivery of a radiation dose has two major effects, viz.; it changes the relative efficiency of recombination centres and also results in the depopulation of electron traps.

In early attempts to develop a single aliquot dating procedure using additive doses, Murray et al. (1997) found that for 10 s preheats at temperatures below 250°C, the equivalent dose was severely overestimated for a 30 ka aeolian sand from Australia (WIDG8).

They attributed this result to thermal transfer that had occurred in nature and they suggested applying more stringent preheats to cause all such charge (due to both natural and laboratory irradiation) to be transferred. For WIDG8 this condition was apparently found for preheat temperatures above 280°C. Unfortunately, these preheat conditions caused significant depopulation of the electron trap(s) responsible for the stable OSL signal.

However, using the response of the 110°C TL peak to a small test dose, Wintle and Murray (1999) demonstrated that luminescence sensitivity changes occurred during pulse annealing experiments on WIDG8. Since these changes were different for the natural and laboratory irradiated aliquots, they concluded that this sample had been subject to a considerable degree of sensitization in the natural environment. Once the appropriate sensitivity correction was applied, the same value of $D_e$ was obtained for 10 s preheats as low as 160°C (Wintle and Murray, 1999). This result suggests that thermal transfer is much less significant than was previously supposed. It has been shown to be negligible for a wide range of samples (see review by Murray and Olley, 1999), the main exceptions being very young samples, which may exhibit thermal transfer effects above about 250°C.

Although the luminescence sensitivity can be measured using the 110°C TL peak, a more appropriate and convenient measurement uses the OSL response to a test dose. This has led to the development of the latest form of the SAR protocol (Murray and Wintle, 2000), in which a sensitivity-corrected growth curve is generated for a single aliquot, after measurement of the sensitivity-corrected natural OSL signal. Using a range of preheat conditions for a number of separate aliquots provides a test of the strength of the sensitivity correction. The same approach has been extended to single grains of quartz (e.g. Yoshida et al., 2000), using a modified form of the preheat plateau test to check that single-grain $D_e$ values are independent of preheat temperature (e.g. Roberts et al., 1999).

Acknowledgements

The authors wish to thank Dr R.G. Roberts for a helpful review of the manuscript and for providing the Australian quartz WIDG8, without which we could not have accomplished so much.

References


Baili/C128raw, Anglesey, North Wales as determined by OSL dating of quartz, Quaternary Geochronology (Quaternary Science Reviews) 20.


Baili/C128raw, Anglesey, North Wales as determined by OSL dating of quartz, Quaternary Geochronology (Quaternary Science Reviews) 20.

