FUTURE DIRECTIONS OF LUMINESCENCE DATING OF QUARTZ

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Abstract: Recent developments in our understanding of the limitations of optically stimulated luminescence as a dating tool are presented alongside summaries of results obtained on other luminescence signals measured in sedimentary quartz grains.

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1. INTRODUCTION

Since measurement of the optically stimulated luminescence (OSL) from quartz was first carried out by Huntley et al. (1985), OSL dating has become a popular technique for establishing the depositional age of sediments. Initially, optical stimulation of quartz was achieved using the green light (514 nm) from an argon ion laser, but this was an expensive system to set up. Routine dating of quartz was able to take place once first blue/green light from a filtered lamp and then blue (470 nm) LEDs were available for optical stimulation.

Measurement procedures have been developed in which the equivalent dose ($D_e$) is obtained on single aliquots for quartz (Murray et al., 1997). In single-aliquot regenerative-dose procedures, the natural OSL signal is compared with the OSL signals resulting from doses being given to the same aliquot. In particular, a single-aliquot regenerative-dose (SAR) protocol was developed (Murray and Wintle, 2000) in which there is correction for sensitivity change during the measurement sequence. The ease of use of this protocol and the ability to make multiple $D_e$ determinations with a limited amount of prepared quartz has led to its widespread application in OSL dating. The experimental data and philosophy behind the SAR protocol was reviewed by Wintle and Murray (2006).

Dating sedimentary quartz using the SAR protocol has been carried out on a range of depositional environments and there have been a number of recent reviews; aeolian (Roberts, 2008; Singhvi and Porat, 2008), coastal (Jacobs, 2008), fluvial (Rittenour, 2008), hillslope (Fuchs and Lang, 2009) and even some glacial (Fuchs and Owen, 2008), glaciofluvial (Thrasher et al., 2009) and periglacial (Bateman, 2008) environments. OSL dating of quartz has also been successful in the dating of sediments encasing archaeological material. In particular, extensive studies in southern Africa have been used to date cultural items, such as ochre (Jacobs et al., 2006; Marean et al., 2007) and the remains of shellfish (Marean et al., 2007), and the use of fire for improving the flaking potential of silcrete (Brown et al., 2009). In addition, by applying identical single grain procedures at several sites with two diagnostic stone tool industries, Jacobs et al. (2008a) have been able to date them and calculate the time that elapsed between the end of one industry and the start of the other. It has also been applied to a number of sites in North Africa where distinctive stone tool industries are present (e.g. Barton et al., 2009) and shell beads and ochre have been found (Bouzzougar et al., 2007).

OSL dating of the sediments found at archaeological sites has been greatly aided by the development of instruments that enable measurement of the OSL signals from individual quartz grains (Duller et al., 1999). This has led to a better understanding of the effects of variability in the dose rate in an inhomogeneous sediment unit, e.g. due to the presence of regions of both high and low radioactivity (e.g. Jacobs et al., 2008b). In addition, the ability to use the SAR protocol to measure $D_e$ values for single grains makes it possible to identify those grains that have not had their OSL signal completely zeroed prior to deposition (e.g. Thomsen et al., 2007), or grains which are intrusive. The impact of being able to make OSL studies on single grains has recently been reviewed (Duller, 2008).
In this paper, I would like to review some new approaches that may be used to overcome problems which occur when the fast OSL component is not dominant and to extend the time period over which luminescence dating of quartz can be applied.

2. OSL

This review builds on that published two years ago as part of a special issue of the journal Boreas (Wintle, 2008). In it, I discussed that, although the light sensitivity and thermal stability of the fast OSL component make it ideal for dating Quaternary sediments, the age range is limited owing to saturation as the traps are filled with continuing exposure to radiation in the natural environment. I also discussed analytical methods that have been used to separate the fast component, as it is this signal for which the SAR protocol was developed (Wintle and Murray, 2006).

Although a number of OSL components are seen in any particular quartz, it has so far been impossible to conclusively link any one component to any lattice defect (Preussner et al., 2009). On the other hand, the luminescence centre responsible for the OSL emission at room temperature at 380 nm has been linked to an [AlO$_4$]$^-$ hole trap, based on a direct correspondence between the OSL signal intensity and the aluminium concentration in a synthetic crystal (Martini et al., 2009); the emission peak in that study is similar to the peak at 365 nm observed for sedimentary quartz (Huntley et al., 1991). By necessity, it is this emission that is observed when optical stimulation is at 470 nm.

3. MATHEMATICAL FITTING OF OSL COMPONENTS FOR LIGHT SENSITIVITY

Under constant stimulation power, as usually used in dating measurements, the OSL decay curve can be represented by the sum of a finite number of exponential functions, as first shown by Bailey et al. (1997) and found in more recent studies (e.g. Steffen et al., 2009; Shen and Mauz, 2009; Bailey, 2010; Pawley et al., 2010). Each exponential decay represents one OSL component. If the stimulation intensity is ramped with respect to time (Bulur, 1996), the linearly modulated OSL (LM-OSL) signal that results has a number of peaks (e.g. Bulur et al., 2000; Kiyak et al., 2007; Polymeris et al., 2008; Pawley et al., 2010, 2008). However, it has been pointed out that no better separation of the OSL components can be achieved using LM-OSL than OSL under continuous stimulation (Wallinga et al., 2008; Bos and Wallinga, 2009). Bos and Wallinga (2009) concluded that, from a practical point of view, CW-OSL is to be preferred for routine dating measurements as it is the quickest stimulation mode and gives the highest signal-to-noise ratio; also they conclude that for visualisation of the components, a mathematical transformation of the CW-OSL decay curve to give a pseudo-LM-OSL signal (Bulur, 2000) is helpful.

These mathematical analyses enable the photoionisation cross-sections for the particular wavelength of the stimulation source to be obtained for each type of trap, provided the power provided by the source is known. This enables the light sensitivity of different OSL signals from quartz to be obtained. For studies made with blue LEDs emitting at 470 nm, the values for the fast OSL component are similar; e.g. 2.32±0.16, 2.5±0.3, 2.0, 1.0-1.9, 3.6±0.4, 2.32±0.02×10$^{-17}$ cm$^2$ obtained by Jain et al. (2003), Singarayer and Bailey (2003), Choi et al. (2006a), Steffen et al. (2009), Shen and Mauz (2009) and Pawley et al. (2010), respectively. The similarity (within a factor of 3) of these results suggests that the electron trap giving rise to the fast OSL component may be universally present in quartz, and thus related to a particular, but unknown, defect. When the fast OSL component is weak, it may be because of a low concentration of either this defect or the luminescence centre.

Analysis of the OSL components remaining after the fast OSL component has been removed by bleaching is more uncertain. Jain et al. (2003), Singarayer and Bailey (2003) and Choi et al. (2006a) found a single medium component with a photoionisation cross-section of around 5.7×10$^{-19}$ cm$^2$, Steffen et al. (2009) found a value between 1.4 and 2.0×10$^{-18}$ cm$^2$, whereas Shen and Mauz (2009) and Pawley et al. (2010) reported more than one component with values of photoionisation cross-section that spanned this value. It is not clear whether these discrepancies relate to the difficulty of curve fitting and the precise method of analysis used, rather than the nature of the defects responsible. This problem could also be brought about by the different grains that make up an aliquot having different photoionisation cross-sections (Adamiec, 2005), or apparently different photoionisation cross-sections resulting from differences in light penetration into the crystals. Simulated data suggest that when there are many components, fitting will always result in a small number of exponential components, even if they have no physical meaning.

4. THERMAL STABILITY OF COMPONENTS

Information needs to be provided on the thermal stability of each component. This is achieved by measuring the depletion of the electrons in each OSL trap resulting from heat treatment. This may be made by rapid heating to increasingly high temperatures, termed pulse annealing (see Bulur et al., 2000; Jain et al., 2003; Singarayer and Bailey, 2003; Li and Li, 2006). Following each heating, the OSL is measured and the components separated. The effect of heating on the LM-OSL signal has recently been modelled (Chruścińska, 2009). Kitis et al. (2007) showed that the ultrafast component (seen occasionally) and one of the slow components are less thermally stable than the fast component. Similar measurements have been made for sedimentary quartz with a weak fast component and for the calibration quartz provided by Risø National Laboratory (Steffen et al., 2009). The medium components for these two samples were found to have similar thermal stabilities, considerably less than that for the fast components, as also found by Li and Li (2006), Bailey (2010), and Pawley et al. (2010). However, others report that the medium component is more thermally stable (e.g. Jain et al., 2003; Singarayer and Bailey, 2003). More information on the thermal stability of these less light sensitive traps may also be obtained if TL measurements...
are made after the removal of the various OSL components (e.g. Kitis et al., 2010).

For samples with a weak fast OSL component, the thermal stability of the medium OSL component becomes important as it will contribute to the initial signal that is usually used for dating. It is thus vital to ascertain through experiments whether a medium component is contributing to the OSL signal used for dating and whether it is thermally stable or not. A simple test to see if there is an unstable component is to take the ratio of the OSL decay curves resulting from the natural dose and from a regenerative dose; if the medium component is sufficiently unstable, the ratio will decrease with stimulation time. The instability of the medium OSL component will also be seen if the equivalent dose obtained from the SAR protocol decreases when it is plotted as a function of stimulation time, so called $D_{eq}(t)$ plots (Bailey, 2000a; 2003a,b; Bailey et al., 2003). Other examples from around the world have been presented by Rittenour et al. (2005), Shen and Mauz (2009) and Bailey (2010). If the medium OSL component is less thermally stable, then the most appropriate temperature for the preheat in the SAR protocol can be determined using the ratios of the decay curves obtained in the pulse annealing study (Steffen et al., 2009).

Rather than routinely apply mathematical fitting procedures to every CW-OSL decay curve measured in a SAR protocol, Pawley et al. (2010) suggested using for equivalent dose determination the very first data channel (in their case 0.4 s) and then subtracting the data from the next channel (0.4 to 0.8 s), as had been previously tested for individual grains from very young sediments; this is termed the early background subtraction (EBG) method (Ballarini et al., 2007). The subtraction will remove as much as possible of the medium component, but the quartz needs to have a relatively bright signal to achieve sufficient precision. Pawley et al. (2010) tested this procedure on twelve samples from one site. The values of $D_{eq}$ obtained using the EBG data were within 1% of those for the separated fast component, which in turn were 10% greater than those using the standard procedure (i.e. the initial 0.8 s with background being derived from much later in the decay curve).

5. **EXPERIMENTAL SELECTION OF THE FAST OSL COMPONENT**

As discussed in the previous section, the fitting of mathematical functions to either CW-OSL or LM-OSL signals can allow the fast OSL component to be separated. However, it would be preferable if electrons from the trap giving rise to the fast OSL component obtained under blue (470 nm) stimulation could be stimulated preferentially. Greater separation of the components can be achieved if the wavelength is increased (Singarayer and Bailey, 2004). Green (530 nm) stimulation has been used (Thomsen et al., 2006). To obtain even greater separation, infrared stimulation (~830 nm) has been used, though a higher stimulation temperature is required to cause a reduction in the initial part of the OSL signal (Jain et al., 2005). However, it should be noted that by investigating the LM-OSL curves after IR exposure, Polymeris et al. (2008) concluded that both the medium and fast components were affected by IR exposure at a number of temperatures above room temperature. SAR protocols using stimulation temperatures of 190°C or 150°C have been developed by Bailey (2010) and Fan et al. (2009), respectively. However, use of IR stimulation requires the samples to be relatively bright and complete removal of electrons from the traps during the SAR protocol needs to be achieved using more energetic stimulation (e.g. at 470 nm).

6. **USING OSL SIGNALS OTHER THAN THE FAST COMPONENT**

Since the dose response curves for the fast OSL component always contain a component that saturates at low doses (e.g. Roberts and Duller, 2004), other luminescence signals have also been investigated. There is a slow OSL component that has better growth with dose (e.g. Bailey, 2000b; Singarayer et al., 2000; Rhodes et al., 2006); however, this slow OSL signal is much more slowly bleached in nature and runs the risk of containing a pre depositional signal, resulting in age overestimation. It is also difficult to isolate.

More extensive studies into yet another OSL signal have been successful in providing another SAR protocol for dating older samples. A thermally-transferred OSL (TT-OSL) signal is observed when quartz is heated after it has had a previous light exposure. The optical and thermal behaviour of the TT-OSL signal has been characterised (Wang et al., 2006a, 2006b) and a SAR protocol has been developed (Wang et al., 2007). Subsequently, the SAR procedure for TT-OSL has been modified and made easier to apply by a number of authors (e.g. Tsukamoto et al., 2008; Kim et al., 2009; Porat et al., 2009; Stevens et al., 2009) and the production of the TT-OSL signal has been modelled (Adamiec et al., 2008; Pagonis et al., 2009). The TT-OSL signal is less optically sensitive than the fast OSL signal, but has a similar thermal stability. Its major advantage is the continued growth of the signal to doses of more than ~ 1 kGy. It has been used with success on aeolian deposits, e.g. loess (Wang et al., 2007) back to the Brunhes-Matuyama time-marker horizon at 780 ka and has been tested on sandy near-shore deposits (Athanassas and Zacharias, 2010). Further tests on known age material are required.

7. **USING LUMINESCENCE SIGNALS OTHER THAN OSL**

Another signal investigated for dating is the isothermal TL (ITL) signal, i.e. the phosphorescence observed when quartz is held at a fixed temperature (Choi et al., 2006b; Buylaert et al., 2006; Huot et al., 2006; Jain et al., 2007a, 2007b; Vandenberghe et al., 2009). However, irreversible sensitivity changes during measurement of the natural signal (Buylaert et al., 2006; Huot et al., 2006) make single aliquot procedures impractical and in any case, for some samples there is little extension of the dose range (Vandenberghe et al., 2009; Jain, 2009).

Investigation of the effect of blue light on the ITL led Jain (2009) to conclude that there was a thermally stable
electron trap that was hardly affected by exposure to blue light, but one which was zeroed by exposure to sunlight. It is virtually impossible to separate this component by curve fitting; however, Jain (2009) used a solid state violet (405 nm) laser diode to measure an OSL signal from quartz that had previously been heated to 340°C (to remove thermally unstable, slow OSL components) and then bleached with blue (470 nm) light (to empty the saturating fast OSL component trap). A SAR protocol based on this measurement procedure resulted in a dose response curve with a ten-fold increase in potential dose range.

TL measurements have also been used in a protocol developed for quartz of volcanic origin for which the SAR OSL procedure for violet emission proved problematic (Lai et al., 2006). In volcanic quartz, red ITL emission with a peak at 630 nm is observed (Tsukamoto et al., 2007). However, the red TL signal does not reach zero when exposed to sunlight (Miallier et al., 2006; Lai and Murray, 2006; Ganzawa and Maeda, 2009) and thus a dual-aliquot protocol using the red ITL measured at 260°C was developed to take account of the residual levels (Westaway and Roberts, 2006). This approach has been vital in dating sediments in some key sites in southeast Asia (Morwood et al., 2004; Roberts et al., 2009; Westaway et al., 2007, 2009) and the ages obtained using this procedure have been shown to agree well with independent age evidence (Westaway, 2009).

8. EXTENDING THE TIME RANGE USING OSL MEASUREMENTS

For many quartz samples, the dose response curve of the fast OSL component is best fitted not with a single saturating exponential function, but with an additional linear function. Such behaviour is relatively common for coarse sand sized quartz (e.g. Rhodes et al., 2008; Pawley et al., 2007; Murray et al., 2007, 2008; Porat et al., 2009) but has also been reported for fine sand sized quartz from loess (Buylaert et al., 2008) and for coarse silt sized quartz from loess (Lai, 2006; Lai et al., 2007; Lai, 2010). However, it has been shown that the relative contributions of the exponential and linear functions can be changed by thermal treatment (Lai et al., 2008). Sometimes a second saturating exponential function provides a better fit for large doses than a linear function (Pawley et al., 2010). This results in continuing growth of the dose response curve, implying that larger doses can be measured. However, it must be remembered that the contribution of the saturated function to the dose response curve will reduce the usability of the second function. For twelve samples at one site, Pawley et al. (2010) were able to obtain an age of 438±31 ka, compared with an expected age of 450±23 ka.

However, not all OSL dating studies, even those which use the fast OSL component, have resulted in ages in agreement with independent age estimates beyond 100 ka. Although Watanuki et al. (2005) obtained ages back to 0.6 Ma on Japanese loess using the mathematically-isolated fast OSL component, a similar study by Lai (2010) on Chinese loess resulted in an age of only 107 ka for a sample from beneath the Brunhes/Matuyama boundary at 780 ka. Also, in their study of sand containing the transitional Middle/Early Stone Age assemblage at Kathu Pan, South Africa, Porat et al. (2010) obtained an OSL age of 464±47 ka, compared with the combined U-series-ESR age of $452^{+140}_{-107}$ ka.

Another aspect of the SAR protocol that may cause the dose response curve to change is whether the doses are given using continuous irradiation or whether a stepped irradiation procedure is adopted. Such a procedure was suggested by Bailey (2004) in order to make the laboratory irradiation regime more similar to that in nature. Qin and Zhou (2009) used a stepped irradiation procedure, giving the regenerative dose in ~25 Gy steps with a thermal treatment of 250°C for 10 s between each step. This resulted in better agreement with the known age than when doses up to ten times this were given in a single irradiation. However, this procedure does not overcome the fundamental saturation of the dose response curve (e.g. Nian et al., 2009).

9. CONCLUSIONS

In the last four years, a large number of papers containing OSL ages for quartz grains from a wide range of sedimentary deposits have been published and most of these ages have been obtained using the SAR protocol. There have also been a small number of papers in which OSL ages have been obtained on sediments for which there is independent chronological information. The chronological information is primarily related to the last interglacial, with the fossil soil being found in loess deposits and characteristic marine deposits related to the high sea-level stand. In addition, there are several sites with ages based on uranium-series measurements and in the loess deposits there is the magnetic marker horizon of the Brunhes-Matuyama boundary. The results from OSL dating studies have indicated that at some sites the OSL ages are in agreement, particularly if the fast OSL component can be isolated mathematically and used for analysis instead of the initial signal. However, agreement is not universal, and there appears to be no consensus as to the precise measurement procedure to be applied.

Also, for these older samples, the OSL dose response curve is fitted by two mathematical functions, one of which is a saturating exponential that is already in saturation by the time the natural dose level has been reached. Again, if the growth resulting from the second function is needed to obtain the equivalent dose, its reliability still needs to be proven and guide lines given as to its limitation. It would also be of interest for there to be a mechanism for why the fast OSL component appears to be derived from two sets of traps, one saturating at a dose of few hundred Gy and one with a much higher saturation level.

Meanwhile, TT-OSL appears to be a technique that can be used on samples going back to the Brunhes-Matuyama, but not further owing to it having insufficient thermal stability. Also, it can be applied only to quartz grains that were well bleached at deposition, owing to the source trap being less optically sensitive than the fast OSL trap. A considerable amount of experimental
work and related modelling has given us an understanding of the production of the TT-OSL signal and led to optimisation of the SAR protocol. A number of other signals have been investigated, also with the aim of being able to date further back than the last interglacial. The blue ITL signal is complex, the source of the light-sensitive signal hard to identify and a workable SAR protocol is currently hampered by the inability to monitor sensitivity changes during the measurements. Other signals, e.g. the red ITL, have been used in particular situations where blue signals are too weak for OSL measurements, e.g. in the case of sedimentary quartz derived from volcanic rocks.

In conclusion, I encourage all authors publishing papers containing OSL ages to provide as much detailed information on the data obtained as the journal editor will permit. This will add to the existing data sets obtained during dating runs and in designed experiments. I would also make a plea for studies in which the same samples are used to obtain OSL data that are then analysed by different people using their software; in particular more is needed to be known about the medium component – one or many? Finally, I think that there is more to be learned from the TL runs made after optical stimulation.

REFERENCES


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