Appendix II

Optically stimulated luminescence dating

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History of luminescence dating

In the last 10–15 years, luminescence dating has become a well established method for providing an absolute chronology for the deposition of Quaternary sediments (Duller, 2004, 2008a). It is increasingly being used as the method of choice for dating aeolian sediments and is also being used for analysis of sediments from an ever increasing diversity of depositional environments. The basis of the method is that naturally occurring minerals (including quartz and feldspars) act as natural dose meters, recording the amount of ionizing radiation they have absorbed since last exposed to daylight. By stimulating such mineral grains in the laboratory, either by heating them or exposing them to light, a luminescence signal is generated. Luminescence is the emission of light from the grains, and the intensity of this light is dependent upon the radiation dose to which grains have been exposed. This latter quantity is known as the equivalent dose and abbreviated to D_e. When the equivalent dose is divided by the rate at which a sample is exposed to radiation after burial (the dose rate) an age can be calculated.

$$Age\,(a) = \frac{Equivalent\ Dose\,(Gy)}{Dose\ Rate\,(Gy/a)}$$

In the last decade, four major developments have enabled the method to become more reliable. First, in the 1990s a convenient method was developed for optically stimulating a luminescence signal from quartz, using blue light emitting diodes (Bøtter-Jensen *et al.*, 1999). Prior to this, optically stimulated luminescence (OSL) measurements on quartz were difficult to make, requiring large and complex Ar-ion lasers. Consequently, much luminescence research was focussed on the use of another light sensitive signal, the infrared stimulated luminescence (IRSL) signal from feldspars. While many useful ages were generated using this signal, a constant concern is that in some studies this signal has been shown to be unstable over short periods of time. Known as ‘anomalous fading’, this is not entirely understood and it is not clear whether it is a universal phenomenon (e.g. Huntley & Lamothe, 2001; Spooner, 1994) or whether it is restricted to certain types of feldspar (Duller, 1997). The fact that quartz is not prone to anomalous fading shows the importance of the development of a convenient and feasible method of stimulating an OSL signal in quartz.

The second significant development was the single aliquot regenerative (SAR) dose procedure (Murray & Wintle, 2000, 2003; Wintle & Murray, 2006). This is a method for the measurement of the radiation dose to which the sample has been exposed during its period of burial (the equivalent dose, D_e). The method has two major advantages. First, it explicitly tests for changes in the sensitivity of the luminescence signal during the procedure. Second, because it is a single aliquot procedure (Duller, 1991), all the measurements necessary to derive a value of D_e are made on a single subsample of the material being dated. This makes it possible to test the similarity of replicate measurements made on the same material.

The third development has been in the analysis of replicate measurements of D_e from a sample in order to test the reliability of the age. One of the assumptions of luminescence dating is that, at the time when the grains were deposited, the luminescence signal from mineral grains would have been close to zero. The luminescence signal is sensitive to light and exposure to more than a few tens of seconds of daylight is sufficient to reduce it to near zero. For aeolian materials this is a reasonable assumption, supported by studies of modern aeolian sediments, from which ages as young as a few decades have been obtained. For other depositional environments the assumption is more problematic. For instance, in fluvially deposited sediments, some grains may be transported at the base of the water column, thus restricting their exposure to daylight, while others may rise to the top of the water column or they may be temporarily deposited on bars where exposure to daylight can occur. For aeolian sediment all grains would have had zero D_e at the time of deposition and, assuming the sediment remained buried, the D_e of all grains will have increased together. For the fluvial sediment, at deposition some grains will have had a D_e of zero, while others will have retained a signal from their previous period of burial, thus giving D_e values significantly above zero (Olley *et al.*, 1998). The ability to make replicate measurements of the D_e from a sample makes it possible to test explicitly whether or not all the grains within a sediment have the same value of D_e.

The fourth development was a system capable of making measurements on single mineral grains (Duller *et al.*, 1999; Bøtter-Jensen *et al.*, 2000). Where sediments are likely to consist of grains that had their luminescence signals reset to different extents at the time of deposition, this may be detected by making standard measurements looking at many hundreds or thousands of mineral grains simultaneously. However, a more detailed analysis can be obtained using measurements on single mineral grains. Using standard equipment such measurements are prohibitively time consuming. Duller *et al.* (1999) described an automated system that used a focussed laser beam to measure sand-sized

(~200µm diameter) grains individually (Fig. 1). Using the SAR protocol, this enables a value of D_e to be determined for each mineral grain. This approach makes it feasible not only to identify when samples contain a mixture of grains with different values of D_e, but also to use statistical methods to determine the D_e appropriate for the depositional event of interest (Duller & Murray, 2000). This has opened up the possibility of dating complex materials, such as glaciofluvial sediments (Glasser *et al*. 2006, Duller, 2006), that could not be dated confidently using methods based on the analysis of many hundreds or thousands of grains simultaneously.

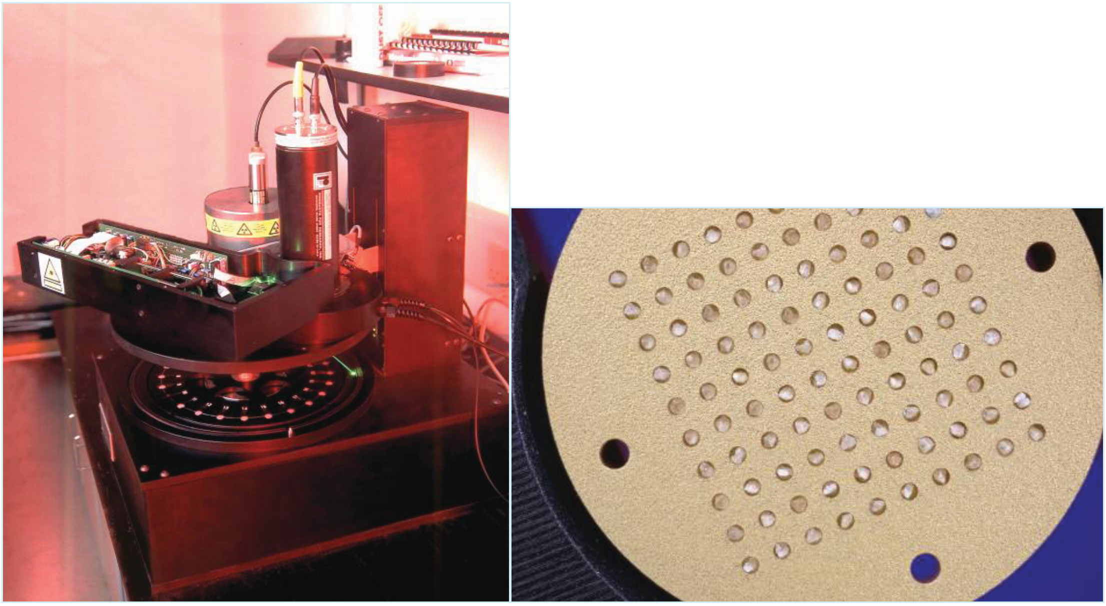

Figure 1: Left: Automated system for measurement optically stimulated luminescence from single mineral grains. Right: A 9.7 mm diameter aluminium disc in which 100 quartz grains are loaded for analysis (images taken from Duller, 2004).

Table 1: Dosimetry measurements derived from (a) in situ gamma spectrometry and (b) laboratory based GM beta counting and thick source alpha counting (TSAC), and total dose rate assuming a 10% water content. The contribution from cosmic rays has been calculated based on the thickness of overburden and is included in the Total Dose rate.

	In situ gamma spectrometry			GM – beta counting	TSAC		
Sample	K (%)	U (ppm)	Th (ppm)	Beta dose (Gy/ka)	U (ppm)	Th (ppm)	Total dose (Gy/ka)
78/MA1	0.79±0.03	2.39±0.08	6.02±0.21	0.84 ± 0.04	2.82±0.23	6.40±0.76	1.49 ± 0.09
78/MA2	0.29±0.02	1.69±0.08	2.32±0.12	0.55 ± 0.01	2.11±0.09	1.91±0.27	0.93 ± 0.09
78/NO1	0.38±0.02	1.73±0.08	2.51±0.12	0.78 ± 0.01	2.02±0.17	3.73±0.56	1.08 ± 0.06
78/NO2	0.31±0.02	1.82±0.11	2.47±0.14	0.58 ± 0.01	2.12±0.14	2.77±0.46	0.93 ± 0.06
78/NO3	0.39±0.02	1.94±0.10	3.05±0.17	1.03 ± 0.01	2.34±0.20	5.86±0.67	1.33 ± 0.06
78/NO4	-	-	-	1.06 ± 0.02	2.30±0.25	7.86±0.84	1.66 ± 0.08
78/RN1	0.20±0.01	1.40±0.08	1.98±0.11	0.43 ± 0.01	1.64±0.08	1.54±0.24	0.75 ± 0.08
78/RN2	-	-	-	0.71 ± 0.03	2.22±0.10	2.87±0.33	1.17 ± 0.09
78/RR1	0.38±0.02	0.94±0.05	2.58±0.13	0.44 ± 0.02	1.34±0.10	2.30±0.31	0.78 ± 0.08

Methods

Nine samples were collected for OSL analysis, from Marfield Quarry (78/MA1, 78/MA2; see Chapter 2.6.1, Plate 2.5), Nosterfield Quarry (78/NO1, 78/NO2, 78/NO3, 78/NO4; see Chapter 2.6.2, Figs 2.49–2.50), Ripon North (78/RN1; see Chapter 2.6.3, Fig. 2.54), Norton Mills (78/RN2; see Chapter 2.8.1, Fig. 2.67) and Ripon South (78/RR1; see Chapter 2.6.4, Fig. 2.59). The samples from Marfield and Nosterfield were of glaciofluvial origin, although the Nosterfield fan deposits were clearly laid down in the open rather than subglacially. The samples from Ripon South, Ripon North and Norton Mills were from Holocene fluvial deposits.

Sample collection and dosimetry

All nine samples were collected either by inserting an opaque plastic tube into the section or, more commonly, by placing sediment directly into a black plastic bag with the whole procedure shielded from daylight under an opaque tarpaulin (Fig. 2). Many of the samples were collected from gravel-rich sediments that could potentially have a heterogeneous dose rate. For seven of the nine samples, measurements of the radiation dose rate were therefore made *in situ* using a portable gamma spectrometer (Table 1).

Figure 2: Collecting material for OSL dating at Ripon South (Brown & Potter's quarry).

In addition, the dose rate to samples was assessed using laboratory-based measurements of thick-source alpha counting (TSAC) and GM-beta counting (Table 1). These were undertaken on the samples after they were dried and finely milled to homogenize them. The best estimate of the dose rate to coarse quartz grains within the sample would come from combining the gamma dose rate measured using the portable gamma spectrometer and the GM-beta counting, since this would cope with heterogeneity in the dose rate. For the two samples for which it was not possible to obtain field-based measurements using the gamma spectrometer, the gamma dose rate was calculated using a combination of the beta and alpha counting measurements (Table 1). For the purposes of this table, an average water content of 10±2% was assumed during burial.

Laboratory separation of quartz grains

In the laboratory, the OSL samples were prepared under subdued red lighting to avoid inadvertent removal of any of the luminescence signal. Sand-sized quartz grains were separated from the sediments using a standard procedure following Wintle (1997). It consisted of a combination of 20 vols H_2O_2 to remove organic material, 10% v.v. HCl to remove carbonates, dry sieving and finally density separation using sodium polytungstate solutions at 2.62 and 2.70 $g.cm^{-3}$. Material with a density between these values was then placed in 40% hydrofluoric acid for 40 minutes. This procedure removes remaining feldspar grains as well as the outer ~10µm skin of the quartz grains, which is affected by alpha radiation.

Luminescence measurements

Prior to measurement of the nine samples studied here, the calibration of the beta source and the reproducibility of the SAR procedure on the single-grain system was checked. This was undertaken using 300 grains of quartz that had previously been annealed at 450°C and given a gamma dose of 5 Gy at Risø National Laboratory (Pers. Comm. Dr. A.S. Murray). The dose in these grains was measured using the SAR procedure (preheat 220°C for 10 seconds, cut heat at 160°C for 0 seconds, and a test dose of 0.7 Gy). For a typical grain, Fig. 3a shows the decay in the luminescence signal during one OSL measurement with the laser in the single grain system. The laser is a 10 mW $NdYVO_4$ solid state laser emitting at 532 nm, but because the beam is focussed onto one grain at a time, the power density is very high (~50 $W.cm^{-2}$). This leads to a rapid decay in the OSL signal, as expected from quartz grains (e.g. Duller *et al.*, 2000). By pooling measurements of the regeneration doses and test doses from this grain, its response to radiation can be characterized (Fig. 3b).

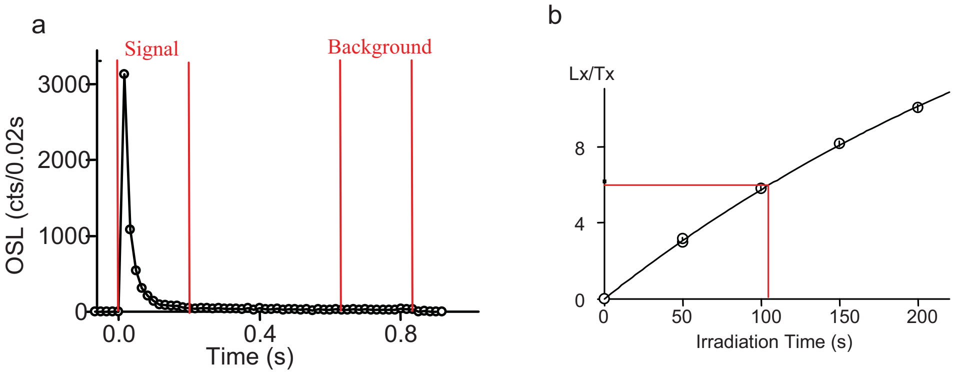

Figure 3: (a) OSL decay curve for a single grain of quartz used for calibrating the single grain system. The parts of the curve integrated to calculate the signal and the background are shown. (b) The SAR growth curve for the same grain of quartz as a function of the irradiation time in the luminescence reader. The D_e for this grain is 109.8 ± 4.7 seconds, which equates to 5.24 ± 0.22 Gy. (Pos 9, grain 50, record 456)

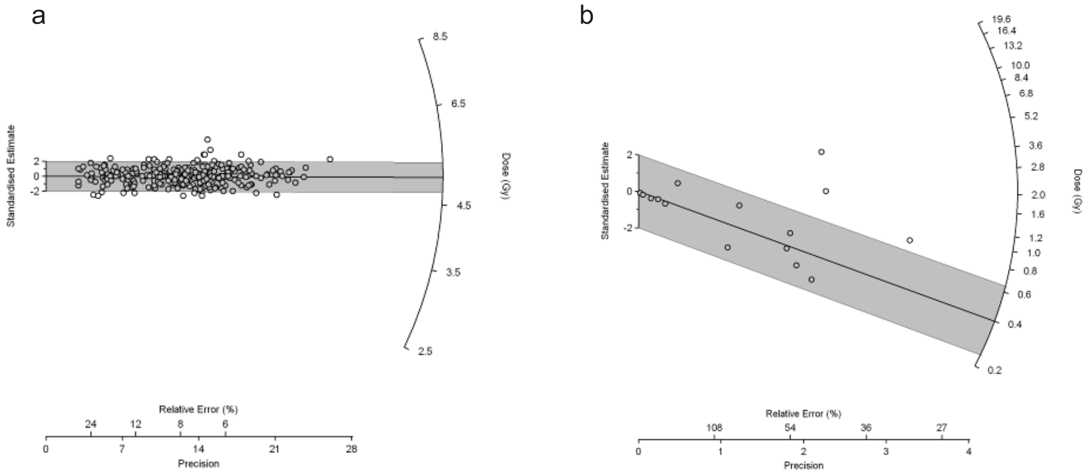

Figure 4: (a) Radial plot showing the doses calculated for 300 individual grains of quartz that had been annealed and given a gamma dose of 5 Gy. (C020804). (b) Radial plot of the grains from sample RR1 from which the signal originated from quartz.

The quartz used for this calibration process has been specially sensitized prior to its use. Thus all 300 analysed grains yielded signals that were sufficiently bright and reproducible to be used to generate D_e values. Figure 4a combines together these 300 D_e values from the sensitized quartz, one for each grain, on a radial plot (Galbraith, 1990). On the diagram, each point represents the D_e obtained for a single grain. The more precisely the D_e value is known, the further the point is plotted to the right of the diagram (the x-axis is the precision). The y-axis is the number of standard deviations that the D_e for a grain is, away from a chosen value. For Figure 4a, the chosen value is 5.0 Gy. The result of such a plot is that grains with the same D_e will plot on a straight line originating from the origin. The value of the D_e can be read from the radial axis on the extreme right-hand side of the plot. As expected for an artificially irradiated sample, the D_e values all cluster tightly to form a single band, consistent with the known dose of 5 Gy. For materials that were incompletely bleached at the time of deposition, the distribution of D_e values may be far more complex (e.g. Roberts *et al*., 1998; Duller, 2006, 2008a).

Results

For each of the nine samples studied here, between 900 and 2000 grains were measured (Table 2) using the single grain system described above. Previous studies have found that many grains of quartz do not yield any detectable OSL signal (Duller *et al*., 2000), with only between 5–10% of grains contributing luminescence. For the samples here, the response to the test dose (11.9 Gy) following the measurement of the natural signal in the SAR sequence was used to assess whether a grain had sufficient signal to be used. A grain was said to have a 'detectable' OSL signal if the intensity in the initial 0.2 s of optical stimulation is above the background signal (measured in the last 0.2 s of optical stimulation: Fig. 3a) by three times the variability of the background signal. Between 9 and 44 grains for each sample passed this criterion, equivalent to 0.9–2.0% of grains, much lower than has typically been found in other studies.

Table 2: The number of grains measured for each sample, those from which a detectable OSL signal can be observed, and the number of those grains which passed the IR OSL depletion ratio test and other criteria (primarily the recycling ratio). The numbers in brackets are the data expressed as a percentage of the total number of grains measured.

Sample	Grains measured	Grains with 'detectable' OSL signal	Grains passing IR OSL depletion ratio test and other criteria
78/MA1	1000	16 (1.6%)	3 (0.3%)
78/MA2	1000	12 (1.2%)	0 (0.0%)
78/NO1	1000	9 (0.9%)	1 (0.1%)
78/NO2	1200	26 (2.2%)	1 (0.1%)
78/NO3	2000	24 (1.2%)	5 (0.3%)
78/NO4	900	19 (2.1%)	2 (0.2%)
78/RN1	1000	16 (1.6%)	6 (0.6%)
78/RN2	1000	17 (1.7%)	12 (1.2%)
78/RR1	2000	44 (2.2%)	20 (1.0%)

A second criterion that is applied to single grain measurements is to test whether the grains are sensitive to optical stimulation using infrared (IR) wavelengths (830Δ30 nm). The aim of this test is to exclude any grains with a luminescence signal that does not originate from quartz. The test, known as the IR OSL depletion ratio (Duller, 2003), exploits the observation that quartz is not sensitive to IR radiation, while feldspar is. For samples 78/MA1-MA2, 78/NO1-NO4 and 78/RN1-RN2, this test reveals that for almost all of the grains from which a detectable luminescence signal was observed, the signal appears to originate from a non-quartz mineral. Given the thorough preparation procedure that was followed, these are likely to be small inclusions of feldspars and other minerals in quartz grains (e.g. Fragoulis & Readhead, 1991). The occasional occurrence of inclusions like this is not uncommon in quartz and has been observed in previous single-grain studies (e.g. Jacobs *et al*., 2003). What is unusual in these samples is that these inclusions seem to be the dominant source of OSL, and the quartz grains themselves yield negligible OSL.

Standard criteria as described in Jacobs *et al*. (2003) were also applied to each grain in this current study. However, it was the IR OSL depletion ratio test that caused the majority of grains to be rejected.

Sample 78/RR1 has a marginally higher proportion of grains that can be detected, with approximately half of those that are detectable also passing the IR OSL depletion ratio test, which suggests that the signals originate from quartz grains. Statistical analysis of this small data set would be problematic, but the data are broadly consistent with a Medieval age for this fluvial deposit (Fig. 4b), as deduced from the discovery of a leather shoe within the sequence nearby (see Chapters 3 & 4).

Conclusions

Given the success of single grain optically stimulated luminescence in dating glacigenic deposits from other areas, such as Chile and Scotland (Glasser *et al*., 2006; Duller, 2006), the results obtained here are disappointing. It is common experience that the OSL from quartz originating in different areas may vary significantly in brightness, although the causes of this are not yet understood. The optically stimulated luminescence emission from the quartz measured in these samples from the Swale/Ure catchment is unusually low. This may be related to the hydrothermal source of much of the quartz in the catchment, but at this stage this is only conjecture. Some OSL emissions are observed, but these are almost entirely derived from contaminants within the quartz. Single grain measurements have been useful in demonstrating the nature of this contamination, and avoiding the pitfall of incorrectly using such signals to derive age estimates that would almost certainly be erroneous. The one sample from which a small proportion of quartz grains yield OSL signals (78/RR1) does not have sufficient number of grains, nor sufficiently bright grains, to enable statistical analysis, but the results are consistent with the interpretation of the sediments from other lines of evidence (see Chapters 3, 4 & 5).

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