Scottish Universities Environmental Research Centre

Dose Extension of a Sample at the Base of a Sedimentary Sequence in Vietnam

September 2018

A.J. Cresswell[1], D.C.W. Sanderson[1], P.A. Carling[2]

[1] SUERC, East Kilbride, Glasgow
[2] Geography and Environment, University of Southampton

East Kilbride Glasgow G75 0QF Telephone: 01355 223332 Fax: 01355 229898

Summary

Previous optically stimulated luminescence (OSL) dating measurements conducted on samples collected from a sedimentary cover sands sequence in Vietnam indicated basal ages of 14.4 ± 2.1 ka from aliquots yielding finite age estimates. However, some aliquots were beyond the saturation point of the OSL dose response curve (>100Gy, or c. 50 ka). This implies the presence of older material within the deposits. Further investigations have therefore been under taken to investigate luminescence signals associated with deeper traps in these quartzes to extend the range of the dose response.

Investigation using aliquots previously measured for OSL has shown that:

- Thermally transferred OSL (TT-OSL) produces signals at 1% or lower intensities than the OSL signals. For these quartzes the resulting signal intensities are too low to yield precise dose estimates.
- However both the thermoluminescence (TL) during the heating ramp to thermal transfer temperatures (TL-ramp) and isothermal decay (ID) during the thermal transfer period produce large signals whose dose response continues to beyond 500Gy. Since these signals also originate from deep traps following OSL stimulation and grow to high doses they were investigated further.

Using freshly dispensed aliquots of the quartz from the basal sample a new SAR dating run was performed, combined OSL, TL-ramp, I-Decay, and TT-OSL readout. As before TT-OSL intensities were low. However the other signals were measured at dose up to 1 kGy. It was possible to obtain finite dose estimates in the range of 200-250 Gy using TL-ramp and I-Decay signals. These correspond to ages of 100-125ka. This confirms the presence of older material in the basal samples.

Since the basal samples may also be associated with microtektites of even greater age, a short kinetic analysis of the thermal activation energy and frequency factors associated with these signals was undertaken to evaluate their likely stability over a range of environmental temperatures. The outcome suggests thermal mean lives of 10^5-10^6 years at ambient temperatures in the 20-30°C region, with a strong dependence on environmental temperatures. Further work to extend the data sets to other cover sands in the region would potentially be useful.

Contents

Summary i
1. Introduction 1
2. Methods 2
2.1. Sampling and sample preparation 2
2.2. Exploratory analyses 2
2.2.1. Initial exploratory measurements 3
2.2.2. Dependence on transfer temperature and duration 3
2.2.3. Thermal Annealing Investigation 4
2.3. Extended dose single aliquot regeneration (SAR) measurements 4
3. Results 5
3.1. Exploratory measurements 5
3.1.1. Initial exploratory measurements 5
3.1.2. TL ramp and isothermal decay measurements 7
3.1.3. Thermal Annealing Investigations 8
3.1.4. Linearly Modulated OSL (LMOSL) 10
3.1.5. Conclusions of exploratory investigations 10
3.2. Extended dose single aliquot regeneration (SAR) measurements 11
3.2.1. TL ramp data 13
3.2.2. Isothermal decay data 13
3.3. Estimation of trap parameters and thermal stability 16
4. Discussion and conclusions 18
5. References 19

List of figures

Figure 3.1: Dose response curves for un-normalised TT-OSL signals, from the exploratory analysis of aliquots 1 (red) and 2 (blue). 6
Figure 3.2: Dose response curves for the net isothermal decay counts assuming the counts at 0 Gy corresponds to background, from the exploratory analysis of aliquots 1 (red) and 2 (blue). 6
Figure 3.3: Photon counts recorded during the TL ramp and isothermal decay at the hold temperature. 7
Figure 3.4: Isothermal decay for two aliquots (red and blue) at 280°C, normalised to the initial counts (right) with two exponential decay terms fitted. 8
Figure 3.5: Relationships between TT-OSL, isothermal decay and TL ramp photon counts for TL ramps to 280°C (black, sets A and B), 300°C (blue, set C) and 320°C (red, set D). An approximate linear relationship is evident with considerable scatter. . 8
Figure 3.6: Photon counts during the TL ramp and hold for the annealing experiment. 9
Figure 3.7: Dependence of OSL on annealing temperature and time. 9
Figure 3.8: Results of LM-OSL at 125°C, ramping the blue diode power from 0 to 90% over 1000s, following a 5Gy irradiation of two aliquots. 10
Figure 3.9: Dose response curves for two aliquots in each pre-heat group for the TL ramp net counts, with the natural counts shown in open circles on the y-axis. 14
Figure 3.10: Dose response curves for two aliquots in each pre-heat group for the total ID counts, with the natural counts shown in open circles on the y-axis. 14
Figure 3.11: Dose response curves for two aliquots in each pre-heat group for the fast component of the ID counts, with the natural counts shown in open circles on the y-axis. 15
Figure 3.12: Arrhenius plots for the rising edge of the TL ramp signal, and the slopes calculated assuming the temperature reported by the Risø reader is accurate and assuming 10K offsets from this nominal temperature. 17

List of tables

Table 2.1: Exploratory TT-OSL procedure. All steps are common to all sets except step 4. Set A corresponds to the procedure of Adamiec etal (2010).....3
Table 2.2: Exploratory isothermal decay measurements. All steps are common to all sets except step 4. Set A corresponds to set D in the previous experiment. 4
Table 3.1: Results of measurements at 100 Gy showing net counts following late light subtraction for the OSL, TT-OSL and OSL following the test dose, the count rate for the isothermal decay (ID) and the ratio of the TT-OSL to OSL intensity as a percentage. 5
Table 3.2: Effects of different heating regimes following 200 Gy dose showing net counts following late light subtraction for the OSL, TT-OSL and OSL following the test dose, the count rate for the isothermal decay (ID) and the ratio of the TT-OSL to OSL intensity as a percentage.....7
Table 3.3: Protocol for dose extension for this sample, with four pre-heating groups. 11
Table 3.4: Quality parameters for the SAR run. 12
Table 3.5: Equivalent dose estimates for each aliquot using the three methods investigated here. The three means, with appropriate standard errors, are calculated excluding the 280°C pre-heating group and saturated aliquots. 15
Table 3.6: Lifetimes for the trap as a function of energy, associated frequency factor and temperature.....16

1. Introduction

Earlier analysis of small samples from a stratigraphic horizon in Vietnam, overlaying a regionally extensive gravel layer containing tektites and shocked quartz that are evidence for a meteorite impact dated to approximately 700 ka, produced a date for the lowest sample of 14 ± 2 ka, with several aliquots with equivalent doses that correspond to ages significantly in excess of 50 ka using Optically Stimulated Luminescence (OSL) on extracted quartz minerals (Cresswell et.al. 2018). This suggests that these layers are not associated with the impact. However, the significantly older ages for some samples may suggest an earlier deposition with subsequent disturbance introducing the younger material.

The work presented here explores post-OSL thermal treatments that could extend the stored dose measurements beyond the ~100 Gy limit where the OSL measurements saturate. These are then applied to aliquots of retained quartz for the lower sample from the Vietnam profile previously analysed.

2. Methods

2.1. Sampling and sample preparation

The sampling and sample preparation have been described in the earlier report on these materials (Cresswell et.al. 2018).

Exploratory analyses of dose extension methods were conducted on 8 of the 16 aliquots dispensed for the OSL-SAR analysis already conducted on the lower sample of the profile (SUTL2969/1). A further 8 aliquots were dispensed from retained 150-250 µm quartz grains from that work.

2.2. Exploratory analyses

Standard models of luminescence postulate the existence of multiple traps within the band gap between the valence and conduction bands. The traps associated with OSL measurements of quartz fill relatively rapidly, causing the measurements to saturate at 50-100 Gy. It is suggested that deeper traps either fill more slowly or can hold greater charge, and hence do not saturate until much larger doses have been delivered. Accessing the charge stored in these traps thus provides a potential route to determine equivalent doses beyond the point where OSL measurements saturate.

Heating the sample after the OSL measurement is a convenient option for accessing these deeper traps. This could include a Thermal Luminescence (TL) measurement, integrating peak areas for higher temperature components. Heating to a lower temperature may also excite charge from the deep traps, some of which may be transferred to the traps associated with the OSL signals, repopulating these traps which can then be measured with a further OSL measurement, in a process called Thermally Transferred Optically Stimulated Luminescence (TT-OSL). Approaches have also been reported measuring phosphorescence emitted during such heating, a process variously called Isothermal TL (ITL) or Isothermal Decay.

TT-OSL was first reported by Wang etal (2006a,b), also referring to the process as Recuperated OSL (ReOSL), showing a signal that grows to high dose allowing an extension in dating by at least an order of magnitude. The approach developed for fine grains (4-11 µm) was to follow the standard OSL measurement with a 260°C heating held for 10s to transfer charge from the deeper traps to the OSL trap and a further OSL measurement to measure the ReOSL signal. This was followed by a test dose and OSL measurement used to normalise both the OSL and ReOSL signals. It was observed that the intensity of the ReOSL signal is progressively reduced with measurement cycle, and Wang et.al. postulated a second transfer process from even deeper traps that are hard to zero optically referred to as Basic Transfer OSL (BT-OSL), which was measured by annealing the sample to 300°C prior to repeating the measurement cycles. The TT-OSL signal is then the sum of the ReOSL and BT-OSL signals. Adamiec et.al. (2010) studied the process, concluding that a single transfer mechanism best explains the data, and thus removing the need to measure BT-OSL. Methods for removal of the trapped charge at the end of each cycle had been explored by Tsukamoto etal (2008), however both OSL at elevated temperature (280°C) to observe the decay of the signal and heating to 450°C were not ideal resulting in poor

recycling behaviour. The studies of Adamiec etal (2010) suggested that heating the sample to 350°C for 200s was sufficient to remove the charge and produced recycling ratios of 1.01 ± 0.02.

One noted disadvantage with TT-OSL measurements is the small size of the signals reported, typically 0.25-1% of the OSL signal, which would be restrictive in low sensitivity samples (such as the sample investigated here). Also the literature reports TT-OSL largely from fine grain samples, and studies of coarser grained samples are less common with resultant uncertainties about the applicability of the method to these materials. It is noted that there is a phosphorescence signal associated with the transfer heating process, this has been used by Wang etal (2006a,b) and Adamiec etal (2010) to investigate the characteristics of the source traps. Adamiec et.al. (2008) measured both luminescence during the ramp to the transfer temperature and the phosphorescence during the hold at that temperature (referred to as Isothermal TL, IsoTL) and noted that both were linearly proportional to the TT-OSL signal.

2.2.1. **Initial exploratory measurements**

The exploratory measurements started with the procedure reported by Adamiec etal (2010), and included measurements with extended heating duration and higher temperature as summarised in Table 2.1, with two aliquots measured for each set. The natural dose for these samples consisted of any natural signal that had not been removed during the initial SAR measurements, and signals from the approximately 500 Gy total dose administered during the SAR measurements. Step 4 was programmed as an OSL measurement with no stimulation light source, to measure isothermal decay.

Table 2.1: Exploratory TT-OSL procedure. All steps are common to all sets except step 4. Set A corresponds to the procedure of Adamiec etal (2010).

Step	Set A	Set B	Set C	Set D
1	Dose (“natural”, 100Gy, 200Gy, 500Gy, 0Gy)			
2	PH 260°C 10s			
3	OSL 100s at 125°C			
4 - transfer & ID	PH 260°C 10s	PH 260°C 30s	PH 280°C 10s	PH 280°C 30s
5 - TTOSL	OSL 100s at 125°C			
6	TD (5Gy)			
7	PH 220°C 10s			
8	OSL 100s at 125°C			
9	Thermal treatment 350°C 200s			
10	Go to step 1			

.

2.2.2. **Dependence on transfer temperature and duration**

A further experiment on the same samples was conducted with varying the transfer temperature, and extending the duration to 60s to examine the isothermal decay properties. For these measurements the sequence was modified to record the TL during the ramp to the transfer temperature and then proceed immediately to the

isothermal decay measurement without lowering the lift which would cool the disc again. The measurements are summarised in Table 2.2.

Table 2.2: Exploratory isothermal decay measurements. All steps are common to all sets except step 4. Set A corresponds to set D in the previous experiment.

Step	Set A	Set B	Set C	Set D
1	Dose (200Gy)			
2	PH 220°C 10s			
3	OSL 100s at 125°C			
4 - transfer & ID	PH 280°C 30s	PH 280°C 60s	PH 300°C 60s	PH 320°C 60s
5 - TTOSL	OSL 100s at 125°C			
6	TD (5Gy)			
7	PH 220°C 10s			
8	OSL 100s at 125°C			
9	Thermal treatment 350°C 200s			

.

2.2.3. **Thermal Annealing Investigation**

To investigate the effect of thermal annealing, three discs were given a 100 Gy dose. Two aliquots were heated to a temperature T_i (where T_i was progressively raised from 200 to 360°C in 20°C steps), with one aliquot held at this temperature for 10s and the other for 60s. The photon counts during each TL ramp and hold were recorded. After each ramp and hold a short (1s) OSL measurement was conducted at 125°C and 10% power on the LED. The third aliquot did not receive any thermal treatment and acted as a control, with the same OSL readouts.

2.3. **Extended dose single aliquot regeneration (SAR) measurements**

The exploratory analysis is used to define the protocol for measurements to determine equivalent doses for aliquots dispensed from retained quartz.

3. Results

3.1. Exploratory measurements

3.1.1. Initial exploratory measurements

Data for the 100 Gy measurements (Table 3.1) show that the TT-OSL intensity ranges from 0-4% of the OSL intensity, in line with expectations from previous studies, with large uncertainties in the small TT-OSL counts. There is no strong correlation between either the TT-OSL signal and the test dose response nor the ID count rate and test dose response. Thus, the sensitivity measured by the OSL response to a small dose does not provide a means of measuring any sensitivity changes in the thermal responses.

Table 3.1: Results of measurements at 100 Gy showing net counts following late light subtraction for the OSL, TT-OSL and OSL following the test dose, the count rate for the isothermal decay (ID) and the ratio of the TT-OSL to OSL intensity as a percentage.

Set	Aliquot	OSL	TT-OSL	ID cps	TD OSL	TT-OSL : OSL %
A	1	17373 ± 146	354 ± 61	365 ± 6	3077 ± 82	2.0 ± 0.4
	2	11355 ± 121	101 ± 58	228 ± 5	2454 ± 76	0.9 ± 0.5
B	1	5521 ± 92	121 ± 52	139 ± 2	1075 ± 67	2.2 ± 0.9
	2	35451 ± 198	-40 ± 60	203 ± 3	6969 ± 103	-0.1 ± 0.2
C	1	6634 ± 102	250 ± 57	388 ± 6	1086 ± 65	3.8 ± 0.9
	2	42317 ± 216	286 ± 60	464 ± 7	7588 ± 107	0.7 ± 0.1
D	1	8755 ± 112	121 ± 57	275 ± 3	1355 ± 69	1.4 ± 0.7
	2	23100 ± 164	55 ± 56	313 ± 3	4440 ± 88	0.2 ± 0.2

Dose response curves have been produced for the TT-OSL signal and net ID (subtracting the counts for the zero dose measurement as an assumed background), shown in Figures 3.1 and 3.2. The large uncertainties on the small TT-OSL signals are evident, and there is no clear indication of a TT-OSL signal growth with increasing dose. For the isothermal decay, there are clearly increases in counts with dose which will extend beyond 500 Gy, although the trend would indicate a large positive intercept on the y-axis probably indicating that the signal at 0 Gy is not the background value.

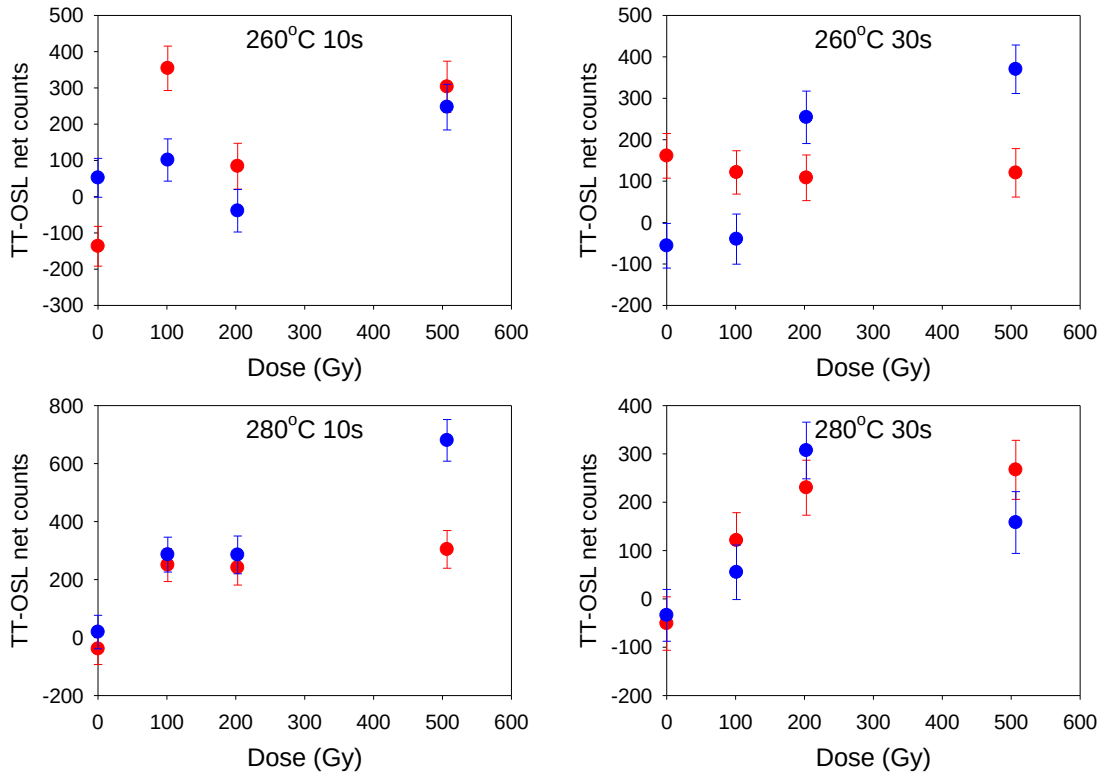

Figure 3.1: Dose response curves for un-normalised TT-OSL signals, from the exploratory analysis of aliquots 1 (red) and 2 (blue).

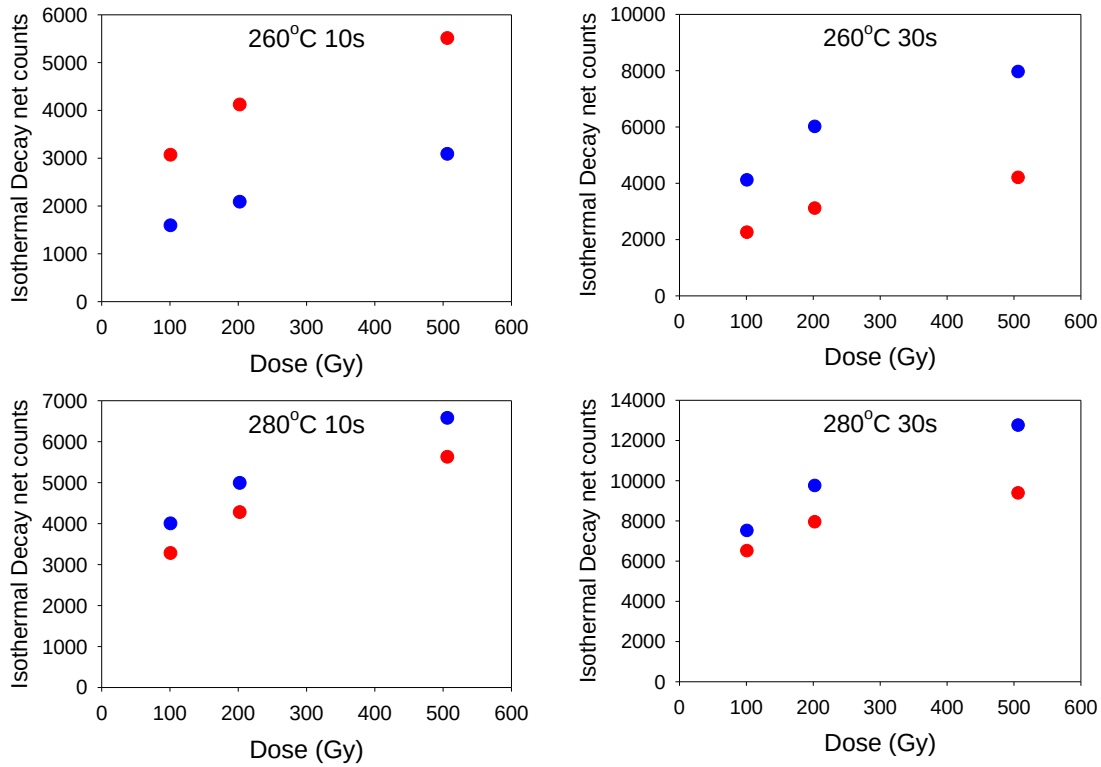

Figure 3.2: Dose response curves for the net isothermal decay counts assuming the counts at 0 Gy corresponds to background, from the exploratory analysis of aliquots 1 (red) and 2 (blue).

3.1.2. **TL ramp and isothermal decay measurements**

The impact of increasing the duration and temperature of the transfer stage is shown in Table 3.2. In all cases the TT-OSL signal is small, but for the 300°C and 320°C heating it is practically zero, and only observed for the brightest of the aliquots (as measured by the OSL) for the 60s heating at 280°C. An isothermal decay signal is observed in all cases. The photon counts observed during the TL ramp and hold are shown in Figure 3.3. The TL ramp above 200°C shows a significant signal, for a peak at 280°C. The isothermal decay over 60s (Figure 3.4) is well fitted by two exponential components. Three measured values (TT-OSL counts, ID net counts following late count subtraction, and the TL ramp counts between 200 and 280°C) show approximate correlation (Figure 3.5), though with considerable scatter and uncertainties for the TT-OSL.

Table 3.2: Effects of different heating regimes following 200 Gy dose showing net counts following late light subtraction for the OSL, TT-OSL and OSL following the test dose, the count rate for the isothermal decay (ID) and the ratio of the TT-OSL to OSL intensity as a percentage.

Set	Aliquot	OSL	TT-OSL	ID cps	TD OSL	TT-OSL : OSL %
A	1	22280 ± 170	287 ± 63	334 ± 9	3413 ± 86	1.3 ± 0.3
	2	10760 ± 120	129 ± 57	189 ± 7	2652 ± 78	1.2 ± 0.5
B	1	6120 ± 100	0 ± 56	67 ± 2	981 ± 65	0 ± 0.4
	2	30310 ± 190	190 ± 60	122 ± 2	7085 ± 103	0.6 ± 0.2
C	1	20230 ± 160	-78 ± 54	105 ± 2	1235 ± 67	-0.4 ± 0.3
	2	38650 ± 210	76 ± 60	115 ± 2	5507 ± 97	0.2 ± 0.2
D	1	11940 ± 130	-10 ± 57	65 ± 2	1254 ± 67	-0.1 ± 0.5
	2	26030 ± 180	141 ± 55	110 ± 2	3353 ± 81	0.5 ± 0.2

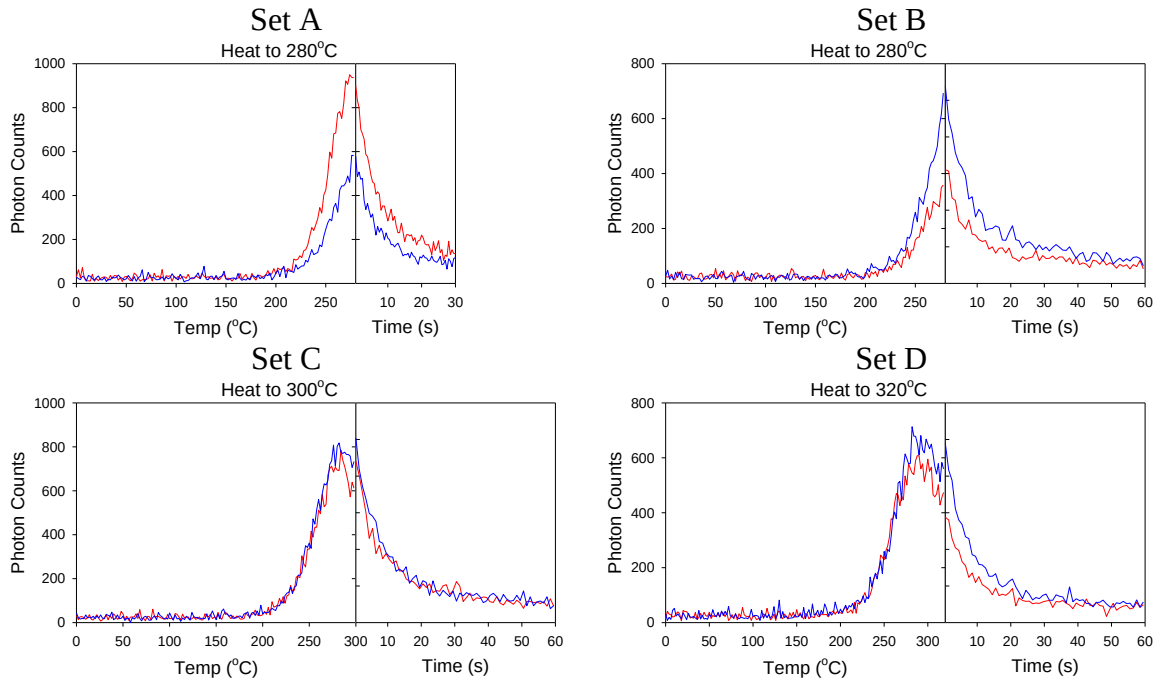

Figure 3.3: Photon counts recorded during the TL ramp and isothermal decay at the hold temperature.

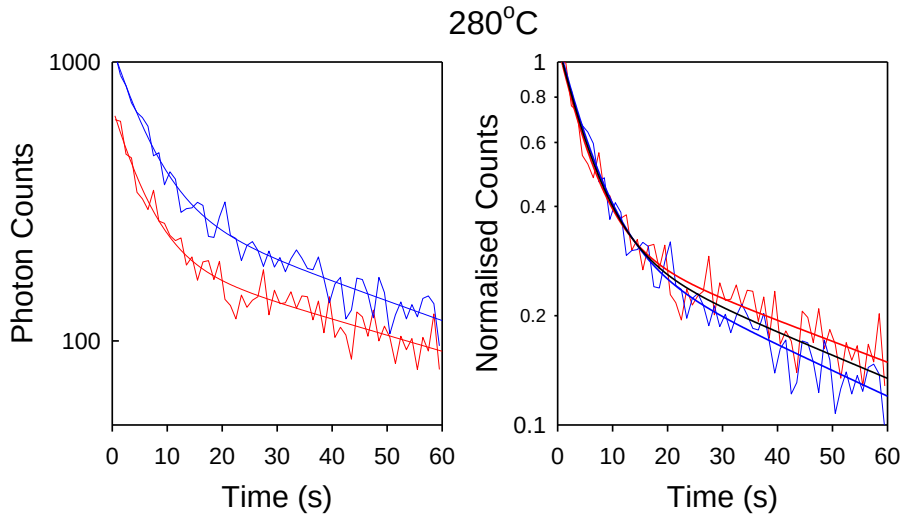

Figure 3.4: Isothermal decay for two aliquots (red and blue) at 280°C, normalised to the initial counts (right) with two exponential decay terms fitted.

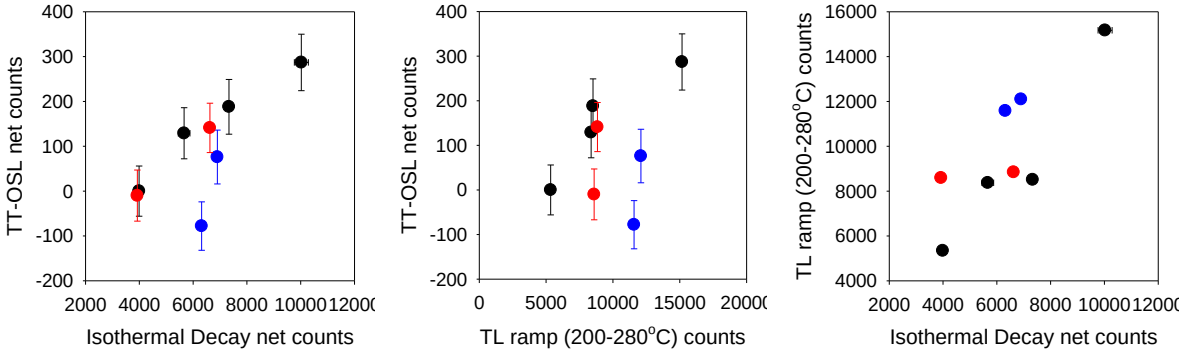

Figure 3.5: Relationships between TT-OSL, isothermal decay and TL ramp photon counts for TL ramps to 280°C (black, sets A and B), 300°C (blue, set C) and 320°C (red, set D). An approximate linear relationship is evident with considerable scatter.

3.1.3. **Thermal Annealing Investigations**

The photon counts recorded during each TL ramp and subsequent hold are shown in Figure 3.6. These show that for the 10s hold a TL measurement with a corresponding isothermal signal is observed from T_i=220°C to T_i=340°C. For the 60s hold the TL measurements are significantly reduced, with no TL observed above T_i=260°C. A plot of the OSL counts normalised to the measurement after the ramp to 200°C (Figure 3.7) shows that for the 10s hold aliquot the OSL signal is constant to T_i=260°C after which is rapidly decreases, falling below the control at 280°C and less than 20% of the initial count at 300°C. The OSL signal for the 60s hold aliquot decreases from T_i=220°C, falling below the control at 240°C and less than 20% at 280°C.

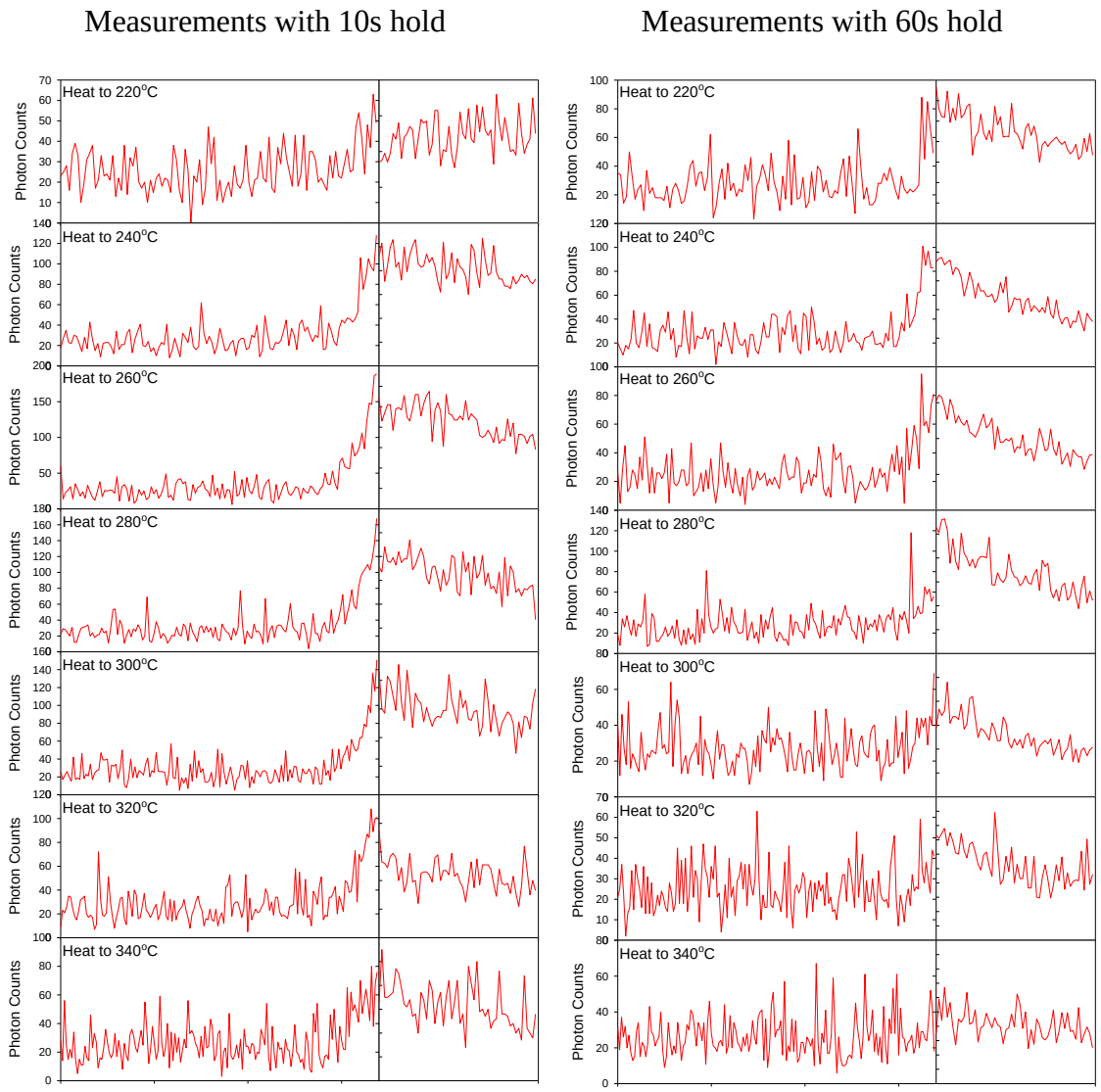

Figure 3.6: Photon counts during the TL ramp and hold for the annealing experiment.

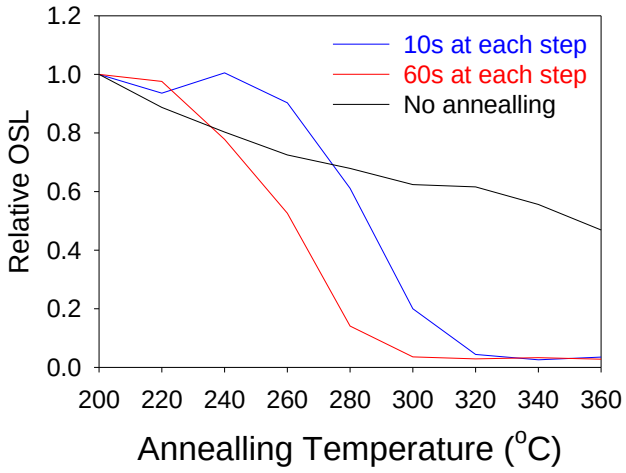

Figure 3.7: Dependence of OSL on annealing temperature and time.

3.1.4. **Linearly Modulated OSL (LMOSL)**

Two aliquots were used to measure LMOSL, the measurements ramped the blue diode power from 0 to 90% over a 1000s period at a readout temperature of 125°C, following a 5 Gy dose. The results are shown in Figure 3.8.

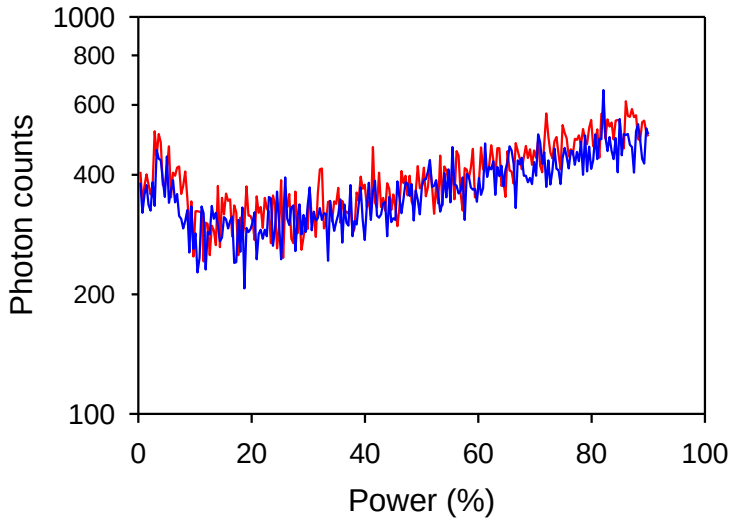

Figure 3.8: Results of LM-OSL at 125°C, ramping the blue diode power from 0 to 90% over 1000s, following a 5Gy irradiation of two aliquots.

3.1.5. **Conclusions of exploratory investigations**

The investigation of quartz aliquots previously measured for OSL SAR dating has shown that the TT-OSL signal from this material is very small, and unsuitable for extending the dose range to investigate the observed saturation of the OSL signals for several of the aliquots initially measured.

Both isothermal decay and the counts recorded during the TL ramp are approximately correlated with the small TT-OSL signal, and both appear promising for dose range extension of this material. The annealing experiment shows that for 10s hold times to temperatures of 260°C there is a transfer of charge from deeper traps sufficient to repopulate the OSL trap partially emptied during the OSL measurement and the thermal emptying of the OSL trap by this treatment, whereas for longer hold times or higher temperatures this thermal treatment removes more charge from the OSL traps than it is able to replenish. This explains the removal of even the small TT-OSL signals with heating above 280°C and holds longer than 10s.

Longer hold times allow the measurement of the isothermal decay and fitting multiple exponentials, however this would be at the expense of a measurable TT-OSL signal. The TL ramp measurement would always be available to complement either an isothermal decay or TT-OSL measurement. For this sample, the OSL signal following a small (5 Gy) test dose does not appear to correlate with any of the thermally produced signals, and is therefore unsuitable for normalizing the data to account for sensitivity changes.

A protocol is therefore proposed for the dose extension of this sample which consists of a preheat (in the standard four groups for OSL measurements) with an OSL measurement, followed by a TL ramp to 260°C and a 60s hold to measure both the TL and ID signals, with a TT-OSL measurement which is expected to be very small. A 50 Gy test dose will then be used with the same set of measurements. A dose response curve will be developed with regenerative doses at 50 Gy, 100 Gy, 200 Gy, 500 Gy and 1000 Gy, with a zero cycle and a repeat of the 50 Gy dose as a recycling test. This is summarized in Table 3.3.

Table 3.3: Protocol for dose extension for this sample, with four pre-heating groups.

Step	Set A	Set B	Set C	Set D
1	Dose (natural, regen doses of 50, 100, 200, 500, 1000Gy, zero, and 50Gy)			
2	PH 220°C 10s	PH 240°C 10s	PH 260°C 10s	PH 280°C 10s
3	OSL 60s at 125°C			
4	TL ramp to 260°C			
5	Isothermal decay for 60s			
6	TT-OSL 60s at 125°C			
7	Test Dose (50 Gy)			
8	PH 220°C 10s	PH 240°C 10s	PH 260°C 10s	PH 280°C 10s
9	OSL 60s at 125°C			
10	TL ramp to 260°C			
11	Isothermal decay for 60s			
12	TT-OSL 60s at 125°C			
13	Thermal treatment 350°C 200s			

3.2. Extended dose single aliquot regeneration (SAR) measurements

A further eight aliquots were dispensed from retained quartz, with two aliquots assigned to each of the four preheating groups. Measurements were conducted using OSL, TT-OSL, TL-ramp (net counts for 200-260°C) and Isothermal Decay (total gross counts and counts for the fast component calculated by fitting the slow component and subtracting from the total). Quality parameters for these measurements for each preheating group are given in Table 3.4.

The measurements following the test dose carried residual signals from the previous doses given, with the exception of the OSL measurement. As such, except for the OSL, these are not suitable for monitoring sensitivity change through the whole cycle and normalising the data. In Table 3.4 the OSL sensitivity and sensitivity change are given for the initial test dose response and across the whole cycle, for the other measurements these are given for the test dose response following the zero cycle, where there is no residual signal from the previous irradiation, and a sensitivity change compared to the first regenerative dose which is also 50 Gy. For OSL the recycling and zero cycle data are for data normalised to the OSL TD response, for all other measurements these are for unnormalised data.

The OSL behaviour is similar to the previous analysis of this sample, with the sensitivity slightly higher than before, reflecting the larger aliquots dispensed for this study. As anticipated, the TT-OSL signals are very small, with considerable

uncertainties in other quality parameters driven largely by the low counts observed. For the TL ramp and the ID signals for the 220°C and 240°C preheats there are reasonable intensities, very small changes in the intensity and good recycling behaviour. For the higher preheat groups the intensities decrease and the recycling ratio degrades and the uncertainties on it increase, this reflects an erosion of the transfer from deep traps that have already been significantly emptied during the preheating prior to the OSL measurements. Both the TL ramp and total ID measurements produce positive zero cycle signals, very large signals for the total ID, which reflect a combination of instrumental backgrounds and potentially residual signals from deep traps that are not completely emptied by the final thermal treatment but still accessible to heating and holding the sample to 260°C. The fitting of the double exponential to the ID curve introduces some significant uncertainties which are reflected in the quality parameters in Table 3.4.

The TL ramp and both ID signals for the lower three preheat temperatures show signals that rise with increasing dose, albeit with a non-zero intercept, with no indication of significant sensitivity changes. Therefore these measurements may be used, without normalisation, for the construction of dose response curves and determination of equivalent doses. The TT-OSL has insufficient signal intensity, and the higher temperature preheat group has eroded the charge stored in the deeper traps making these unsuitable as well.

Table 3.4: Quality parameters for the SAR run.

	Set	OSL	TT-OSL	TL ramp	ID (total)	ID (fast)
Sensitivity (c Gy^{-1})	A	565 ± 128	1.3 ± 0.3	51.5 ± 5.8	434 ± 26	222 ± 8
	B	1709 ± 712	2.3 ± 0.8	30.9 ± 3.1	541 ± 61	215 ± 24
	C	589 ± 98	0.0 ± 2.0	10.2 ± 0.3	276 ± 8	63 ± 3
	D	682 ± 211	3.1 ± 1.8	3.9 ± 0.4	176 ± 6	7 ± 2
Sensitivity change (%/cycle)	A	-5 ± 4	-14 ± 20	1 ± 20	-2 ± 20	1 ± 20
	B	-6 ± 7	-14 ± 20	-2 ± 20	-1 ± 20	1 ± 20
	C	-5 ± 4	-20 ± 22	-3 ± 20	-2 ± 20	-10 ± 21
	D	-7 ± 6	1 ± 23	0 ± 20	-3 ± 20	-16 ± 25
Recycling ratio	A	0.94 ± 0.02	0.01 ± 0.19	0.97 ± 0.02	0.92 ± 0.01	1.06 ± 0.08
	B	0.95 ± 0.03	0.59 ± 0.10	1.03 ± 0.02	0.95 ± 0.01	1.08 ± 0.03
	C	0.98 ± 0.01	0.43 ± 0.12	1.05 ± 0.14	0.87 ± 0.01	0.99 ± 0.28
	D	0.97 ± 0.02	0.35 ± 0.60	1.13 ± 0.46	0.81 ± 0.02	4.00 ± 1.94
Zero cycle (counts)	A	0.003 ± 0.004	-70 ± 10	45 ± 22	3909 ± 21	-130 ± 108
	B	0.001 ± 0.001	2 ± 19	99 ± 22	3991 ± 61	-34 ± 136
	C	-0.001 ± 0.001	96 ± 54	-92 ± 15	3641 ± 139	-85 ± 37
	D	0.002 ± 0.004	36 ± 27	-23 ± 56	3845 ± 39	-99 ± 55
Zero cycle (Gy)	A		-8.4 ± 1.2	0.34 ± 0.17	2.93 ± 0.02	-0.22 ± 0.18
	B		0.1 ± 0.9	1.31 ± 0.29	2.73 ± 0.04	-0.50 ± 2.01
	C		20 ± 11	-3.83 ± 0.62	5.07 ± 0.19	-0.64 ± 0.28
	D		192 ± 144	-2.37 ± 5.75	8.19 ± 0.8	-7.29 ± 4.04

3.2.1. **TL ramp data**

Dose response curves for the TL ramp data are shown in Figure 3.9. These produce good dose responses for all but the 280°C preheating group with the curves saturating at lower dose for increasing pre-heat temperature. The equivalent doses for each aliquot are given in Table 3.5.

3.2.2. **Isothermal decay data**

Dose response curves for the total ID signal are shown in Figure 3.10, with those for the fast component after subtraction of a fitted slow component are shown in Figure 3.11. Again, these produce good dose responses for all but the 280°C preheating group with the curves saturating at lower dose for increasing pre-heat temperature. The equivalent doses for each aliquot are also given in Table 3.5.

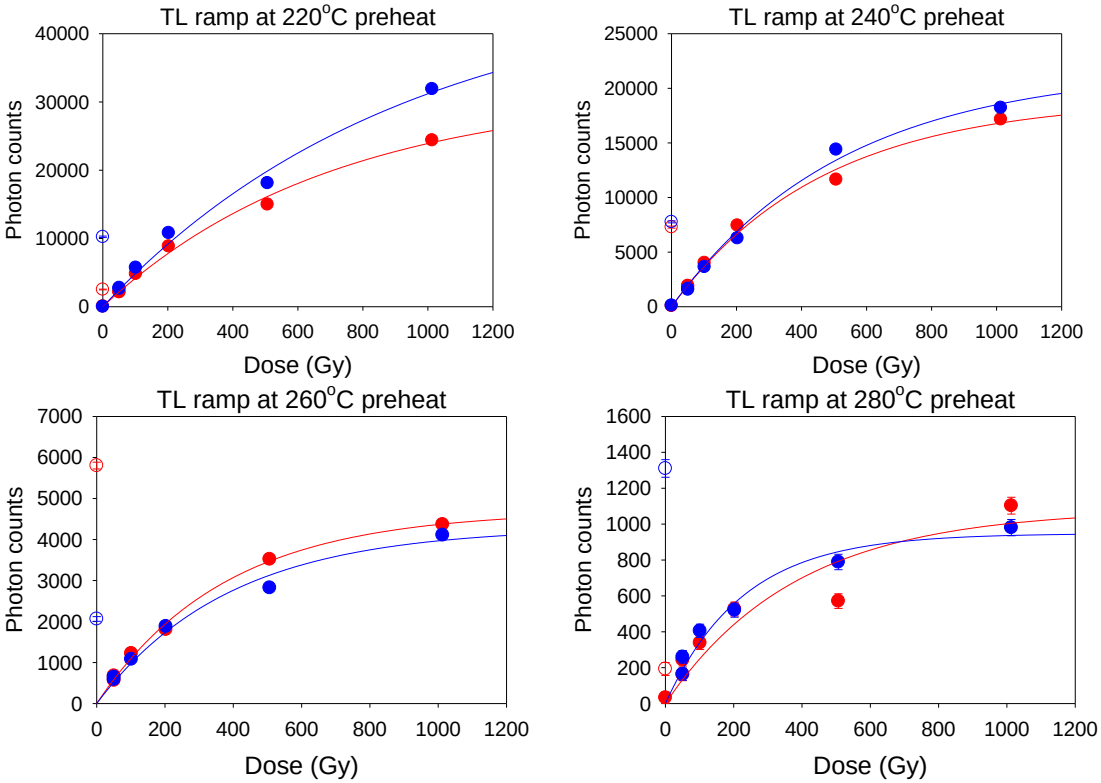

Figure 3.9: Dose response curves for two aliquots in each pre-heat group for the TL ramp net counts, with the natural counts shown in open circles on the y-axis.

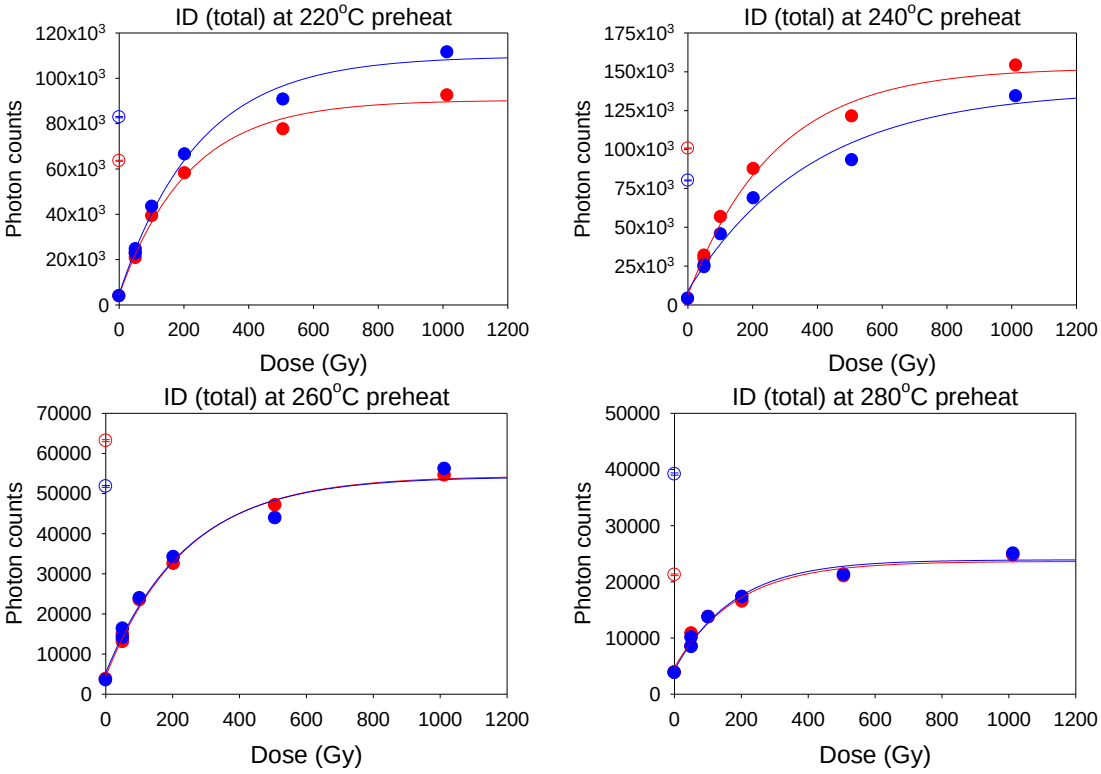

Figure 3.10: Dose response curves for two aliquots in each pre-heat group for the total ID counts, with the natural counts shown in open circles on the y-axis.

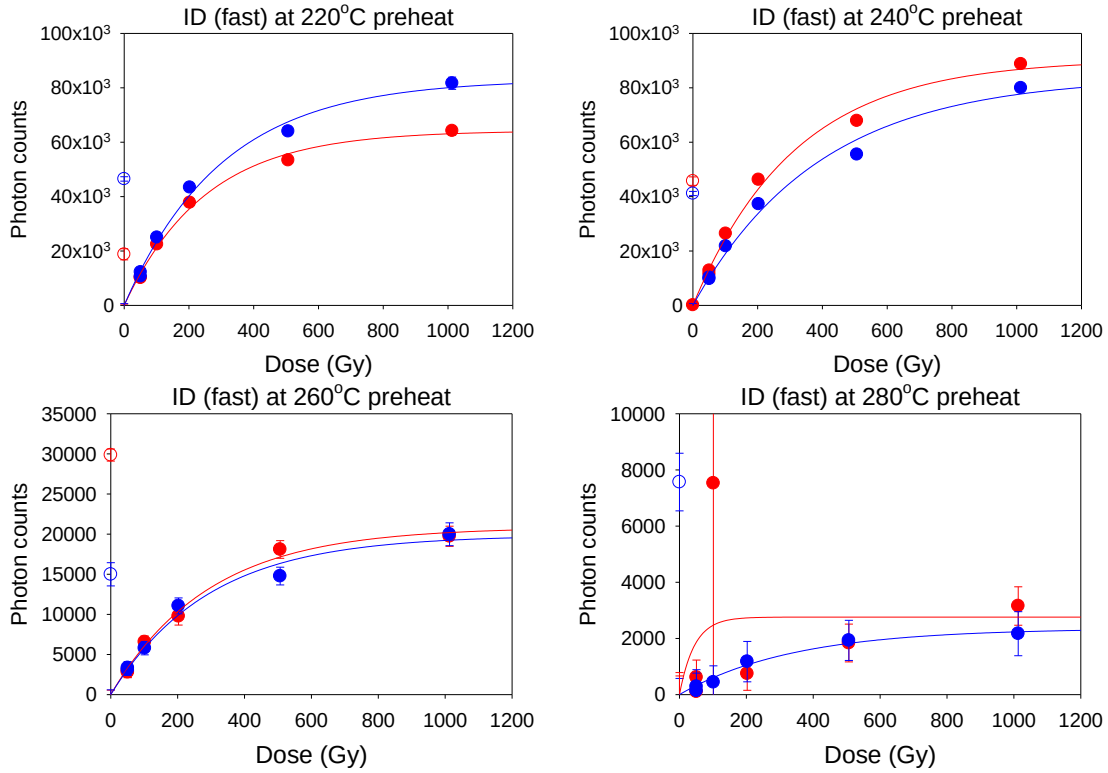

Figure 3.11: Dose response curves for two aliquots in each pre-heat group for the fast component of the ID counts, with the natural counts shown in open circles on the y-axis.

Table 3.5: Equivalent dose estimates for each aliquot using the three methods investigated here. The three means, with appropriate standard errors, are calculated excluding the 280°C pre-heating group and saturated aliquots.

Set / Aliquot	Equivalent Dose (Gy)		
	TL ramp	ID (total)	ID (fast)
A (220°C PH) 1	59 ± 11	289 ± 25	87 ± 13
A (220°C PH) 2	227 ± 69	378 ± 40	248 ± 26
B (240°C PH) 1	226 ± 34	312 ± 29	222 ± 27
B (240°C PH) 2	233 ± 38	366 ± 58	263 ± 44
C (260°C PH) 1	>1000 Gy	>1000 Gy	>1000 Gy
C (260°C PH) 2	254 ± 47	>1000 Gy	411 ± 115
D (280°C PH) 1	75 ± 40	>1000 Gy	-1 ± 13
D (280°C PH) 2	>1000 Gy	>1000 Gy	>1000 Gy
Mean	200 ± 36	336 ± 21	246 ± 52
Weighted mean	98 ± 10	318 ± 16	146 ± 11
Robust mean	229 ± 11	336 ± 9	244 ± 11

3.3. Estimation of trap parameters and thermal stability

The data from the rise of the TL peak during the temperature ramp can be used to estimate the energy level of the associated trap for this signal, and combined with the isothermal decay data the associated frequency factor can also be estimated. The slope an Arrhenius plot for the rising edge of the TL peak gives the energy level, these are plotted in Figure 3.12 for the first three pre-heating groups (for the 280°C preheating group the TL intensity was insufficient). The mean and standard deviation of the slopes for these measurements is 0.96 ± 0.08 eV. This does not include a thermal quenching effect, which following the assessment of Wintle (1975) is taken to be 0.65 eV, giving a level energy of 1.60 ± 0.10 eV. From the slope of the fast component of the isothermal decay the frequency factor is estimated as between 1.2×10^{13} s^{-1} (for E=1.50 eV) and 9.3×10^{14} s^{-1} (for E=1.70 eV). These agree well with the values calculated by Pagonis et.al. (2008) of E=1.65 eV and $s=6.5 \times 10^{13}$ s^{-1}, and the E value calculated by Adamiec et.al. (2010) of 1.46 eV, although the s value calculated here is significantly higher than the 7.6×10^{11} s^{-1} of Adamiec.

The thermal stability of these traps is a function of the trap energy, frequency factor and the temperature. Table 3.6 shows the lifetime expected for E and s values determined here as a function of temperature. It can be seen that for the mean measured energy level (1.6 eV) dose measurements beyond 500ka would require temperatures not to significantly exceed 20°C, and even then a thermal stability correction would be needed. Temperatures below 15°C would lead to dose measurements where a thermal stability correction would have little impact on the age for samples upto 1Ma. It should be noted that the energies and frequencies factors are estimates, and a significantly more rigorous determination of these parameters would be needed to calculate thermal stability and a model of the thermal history of the sample needed to make any corrections based on these parameters.

Table 3.6: Lifetimes for the trap as a function of energy, associated frequency factor and temperature.

E (eV)	s (s^{-1})	Temperature (°C)							
		0	10	15	20	25	30	35	40
1.5	0.12×10^{14}	13Ma	1.4Ma	470ka	170ka	62ka	24ka	9.3ka	3.8ka
1.6	1.1×10^{14}	100Ma	9Ma	2.9Ma	960ka	330ka	120ka	44ka	17ka
1.7	9.3×10^{14}	825Ma	64Ma	19Ma	6Ma	1.9Ma	645ka	225ka	80ka

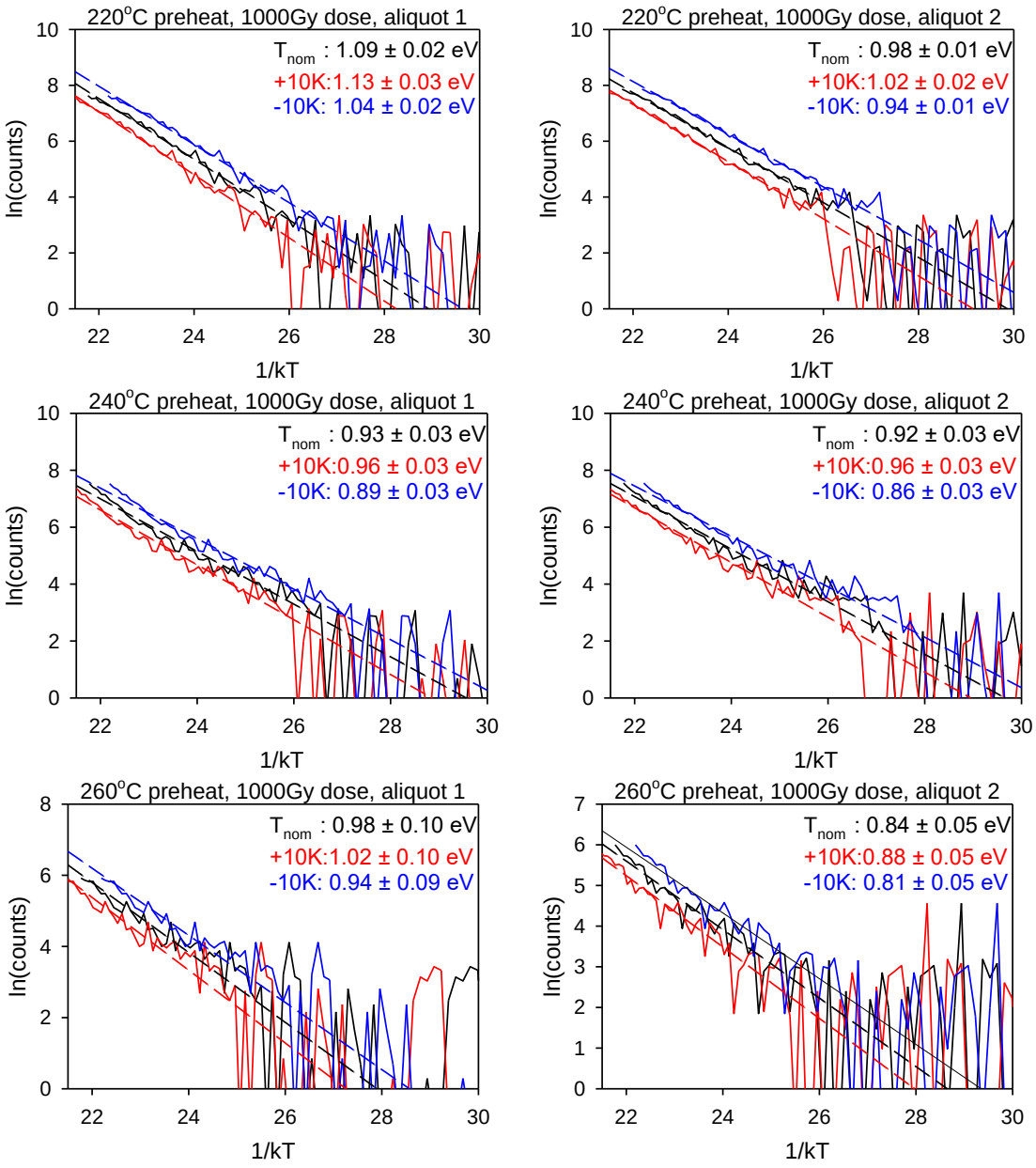

Figure 3.12: Arrhenius plots for the rising edge of the TL ramp signal, and the slopes calculated assuming the temperature reported by the Risø reader is accurate and assuming 10K offsets from this nominal temperature.

4. Discussion and conclusions

The use of thermal treatments to transfer charge from deep traps to the OSL centres has been explored to extend the dose range for a sample from the base of a sedimentary sequence in Vietnam which had previously been dated by SAR OSL to 14.4 ± 2.1 ka, with several aliquots that were saturated (equivalent dose >100 Gy, age > 50 ka). The transferred charge has been measured from the TL signal during the ramp to 260°C and from the isothermal decay while holding at this temperature. The TT-OSL signal was too small to quantify.

This sample contains some aliquots at higher pre-heat temperature, where the thermally transferred signal intensity is lower, which are saturated. The remaining aliquots produce equivalent doses in the range of 200-250 Gy from the TL ramp and fast components of the ID, and 340 ± 20 Gy from the total ID signal. These would correspond to ages of 100-125 ka, or 170 ± 10 ka for the total ID signal, for a dose rate of 1.96 ± 0.15 mGy a^{-1}.

Estimates of the trap parameters suggest that at temperatures typical of Vietnam (~25°C) these signals may show thermal instability with lifetimes of the order of 100 ka to 1 Ma, and as such the ages determined would correspondingly be underestimated by a factor that would require significant additional characterisation of the materials and thermal history to determine.

This work has demonstrated that it is possible to use the TL ramp data and isothermal decay to produce dose response curves that extend beyond 1000Gy. These methods may be affected by thermal instability at ambient temperatures the sample may have experienced in it's history. Nevertheless, the results indicate that there are signals associated with material significantly older than the 14ka determined by SAR analysis, which must be mixed with younger material producing the SAR ages.

5. References

Adamiec, G., Baile, R.M., Wang, X.L., H.M., Wintle, A.G., 2008. The mechanism of thermally transferred optically stimulated luminescence in quartz. J. Phys. D: Appl. Phys. 41 135503.

Adamiec, G., Duller, G.A.T., Roberts, H.M., Wintle, A.G., 2010. Improving the TT-OSL SAR protocol through source trap characterisation. Radiation Measurements 45, 768-777.

Cresswell, A.J., Sanderson, D.C.W., Carling, P.A. 2018. Luminescence Profile Measurements on Samples from Vietnam Submitted by P. Carling. SUERC Technical report.

Pagonis, V., Wintle, A.G., Chen, R., Wang, X.L., 2008. A theoretical model for a new dating protocol for quartz based on thermally transferred OSL (TT-OSL). Radiation Measurements 43, 704-708.

Tsukamoto, S., Duller, G.A.T., Wintle, A.G., 2008. Characteristics of thermally transferred optically stimulated luminescence (TT-OSL) in quartz and its potential for dating sediments. Radiation Measurements 43, 1204-1218.

Wang, X.L., Lu, Y.C., Wintle, A.G., 2006a. Recuperated OSL dating of fine-grained quartz in Chinese loess. Quaternary Geochronology 1, 89-100.

Wang, X.L., Wintle, A.G., Lu, Y.C., 2006b. Thermally transferred luminescence in fine-grained quartz from Chinese loess: basic observations. Radiation Measurements 41, 649-658.

Wintle, A.G., 1975. Thermal quenching of thermoluminescence in quartz. Geophysical Journal of the Royal Astronomical Society 41, 107-113.