Bleaching of the post-IR IRSL signal from individual grains of K-feldspar:
Smedley, R. K.; Duller, G. A. T.; Roberts, H. M.

Published in:
Radiation Measurements

DOI:
10.1016/j.radmeas.2015.06.003

Publication date:
2015

Citation for published version (APA):
Smedley, R. K., Duller, G. A. T., & Roberts, H. M. (2015). Bleaching of the post-IR IRSL signal from individual grains of K-feldspar: implications for single-grain dating. Radiation Measurements, 79, 33-42. https://doi.org/10.1016/j.radmeas.2015.06.003
Bleaching of the post-IR IRSL signal from individual grains of K-feldspar: Implications for single-grain dating

R.K. Smedley*, G.A.T. Duller, H.M. Roberts

Department of Geography and Earth Sciences, Aberystwyth University, Ceredigion, SY23 3DB, UK

Article info

Article history:
Received 12 June 2013
Received in revised form 18 May 2015
Accepted 5 June 2015
Available online 9 June 2015

Keywords:
Feldspar
Luminescence
Single grains
Infrared stimulated luminescence
pIRIR
Residual D<sub>e</sub> values
Bleaching rate

ABSTRACT

Post-IR IRSL (pIRIR) signals from K-feldspar grains measured at elevated temperatures are increasingly being used for dating sediments. Unfortunately the pIRIR signal from K-feldspars bleaches more slowly than other signals (e.g. OSL from quartz) upon exposure to daylight, leading to concerns about residual signals remaining at deposition. However, earlier studies have not assessed whether the pIRIR signal bleaches at the same rate in all feldspar grains. In this study laboratory bleaching experiments have been conducted and for the first time the results show that the rate at which the pIRIR signal from individual K-feldspar grains bleach varies. To determine whether grain-to-grain variability in bleaching rate has a dominant control on equivalent dose (D<sub>e</sub>) distributions determined using single grains, analysis was undertaken on three samples with independent age control from different depositional environments (two aeolian and one glaciofluvial). The D<sub>e</sub> value determined from each grain was compared with the rate at which the pIRIR<sub>225</sub> signal from the grain bleaches. The bleaching rate of each grain was assessed by giving a 52 Gy dose and measuring the residual D<sub>e</sub> after bleaching for an hour in a solar simulator. There is no clear relationship between the rate at which the pIRIR<sub>225</sub> signal of an individual grain bleaches and the magnitude of its D<sub>e</sub>. It is concluded that variability in the bleaching rate of the pIRIR<sub>225</sub> signal from one grain to another does not appear to be a dominant control on single grain D<sub>e</sub> distributions.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Optically stimulated luminescence (OSL) dating of single grains is beneficial in certain depositional environments (e.g. glaciofluvial settings) to detect the partial bleaching of sedimentary grains (Duller, 2008). A major challenge for single-grain measurements using quartz is that commonly only 5% or fewer of the grains emit a detectable OSL signal (Duller, 2006) detected as few as 0.5% of quartz grains in glaciofluvial sediments from Chile. In contrast to quartz, a larger proportion of K-feldspar grains are reported to emit a detectable OSL signal and the signals are also typically brighter (e.g. Duller et al., 2003). However, a major drawback for luminescence dating of feldspars is that the infrared stimulated luminescence signal measured at 50 °C (IR<sub>50</sub>) is prone to anomalous fading over time, which some workers claim to be a ubiquitous phenomenon (e.g. Huntley and Lamotte, 2001). Currently there are two single aliquot regenerative dose (SAR) protocols commonly used for K-feldspar dating, (1) IR<sub>50</sub> measurements, (e.g. Wallinga et al., 2000), and (2) post-IR IRSL measurements typically performed at 225 °C or 290 °C, giving rise to the pIRIR<sub>225</sub> and pIRIR<sub>290</sub> signals (e.g. Thomsen et al., 2008, 2011). Since the development of pIRIR measurement protocols, they have been
that the pIRIR290 signal bleaches more slowly than the pIRIR225 of feldspars and quartz, con-

Although the pIRIR signal may be more stable over time than the IR50 signal, several studies of coarse-grain K-feldspar using multiple grains have obtained bleaching curves which show that the pIRIR signal bleaches more slowly in response to optical stimulation than the IR50 signal (e.g. Buylaert et al., 2012, 2013; Kars et al., 2014; Murray et al., 2012), which in turn bleaches more slowly than the quartz OSL signal (Godfrey-Smith et al., Kars et al., 2014; Murray et al., 2012), which in turn bleaches more slowly than the quartz OSL signal (Godfrey-Smith et al., 1988). More recently, Colarossi et al. (in press) have directly compared the bleaching rates using multiple grain measurements of feldspars and quartz, confirming previous findings, and showing that the pIRIR290 signal bleaches more slowly than the pIRIR225 signal. Equivalent dose (D$_e$) values for the pIRIR signal measured for modern analogues, or the residual D$_e$ values remaining after laboratory bleaching of coarse-grained K-feldspar (Table 1) have been published for different pIRIR signals measured at different temperatures (e.g. Li et al., 2014). The smallest residual D$_e$ values reported for multiple grains (<1 Gy) are measured using procedures with the lowest preheat and pIRIR stimulation temperatures (e.g. pIRIR250 and pIRIR10 protocols). It has therefore been suggested that lower temperature pIRIR protocols may be more appropriate for dating young sediments (e.g. Madsen et al., 2011; Reimann et al., 2011; Reimann and Tsukamoto, 2012). However, the model proposed by Jain and Ankjaergaard (2011) suggests that higher temperature pIRIR protocols access signals that are more stable over geological time. Thus, the pIRIR225 and pIRIR290 signals have the potential to provide more accurate and precise single-grain K-feldspar ages by further minimising the influence of fading beyond that of the pIRIR signals measured at lower temperatures.

Feldspars form a solid-solution series, ranging from anorthite (CaAl$_2$Si$_2$O$_8$), to albite (NaAlSi$_3$O$_8$), to orthoclase (KAlSi$_3$O$_8$). Density separation is routinely used for luminescence dating of sedimentary grains to isolate the K-feldspar fraction. However, geochemical measurements have demonstrated that density-separated K-feldspar fractions can be composed of different types of feldspar grains, which are chemically variable (e.g. Smedley et al., 2012). Thus far, bleaching curves have not been reported for single grains of K-feldspar. Investigating the grain-to-grain variability of bleaching rates of feldspars is important for single-grain dating as it has been suggested that the TL signal from different types of museum specimen feldspars bleaches at different rates in response to sunlight bleaching (e.g. Robertson et al., 1991). However, it has also been reported that the IRSL signal of different types of museum specimen feldspars bleaches at similar rates in response to a range of monochromatic wavelengths from 400 to 1065 nm (e.g. Spooner, 1994; Bailiff and Pooilon, 1991). Thus, it is not clear whether the pIRIR signals from individual grains of K-feldspar in the density-separated fraction, composed of grains that have different internal K-contents, will bleach at different rates or not. The aim of this study is to investigate the bleaching of the pIRIR225 and pIRIR290 signals from single grains of K-feldspar and to examine whether any difference in bleaching rate may influence the D$_e$ determined. Three samples of density-separated K-feldspars extracted from different depositional environments with independent age control are used for these investigations.

2. Equipment and measurement protocols

All luminescence measurements were performed using a Risø TL/OSL DA-15 automated single-grain system equipped with an infrared laser (830 nm) fitted with an RG-780 filter (3 mm thick) to remove any shorter wavelengths (Bøtter-Jensen et al., 2003; Duller et al., 2003), and a blue detection filter pack containing a BG-39 (2 mm), a GG-400 (2 mm) and a Corning 7–59 (2.5 mm) filter placed in front of the photomultiplier tube. The inclusion of the GG-400 filter is to ensure removal of the thermally unstable UV emission centred on 290 nm seen during IR stimulation of feldspars (e.g. Balascu and Lamothe, 1992; Clarke and Rendell, 1997). The system was equipped with a $^{88}$Sr/$^{90}$Y beta source delivering -0.04 Gy/s.

Single aliquot regenerative dose (SAR) pIRIR225 and pIRIR290 protocols were used for dose-recovery and residual dose experiments (Table 2). A high temperature bleach was used at the end of each SAR cycle (step 9, Table 2) to remove any remaining charge arising from the test-dose and prevent charge transfer from the T$_{2}$.

| Table 1 | A summary table of published pIRIR residual D$_e$ values obtained for coarse-grained K-feldspar from multiple-grain aliquots in various studies, and one single-grain study (* Reimann et al., 2012). |
|---|---|
| Reference | Depositional environment | Bleaching method | Protocol Residual |
| Reimann and Tsukamoto (2012) | Coastal | 17 h SOL2 bleach | pIRIR150 0.4 Gy |
| | | 1 week of daylight exposure | pIRIR150 0.7 Gy |
| Madsen et al. (2011) | Beach | Modern analogue | pIRIR150 0.05 ± 0.01 Gy to 2.66 ± 0.06 Gy |
| Reimann et al. (2011) | Coastal | 4 h SOL2 bleach | pIRIR180 < 1 Gy |
| Reimann et al. (2012)* | Coastal | Modern analogue | pIRIR180 0.6 ± 0.03 Gy |
| | | 4 h SOL2 bleach | pIRIR180 0.9 ± 0.04 Gy |
| | | pIRIR225 2 Gy |
| Thomsen et al. (2008) | Beach sand | Modern analogue | pIRIR225 1.4 ± 0.1 Gy |
| Buylaert et al. (2009) | Beach sand | Modern analogue | pIRIR225 < 3 Gy |
| Alappat et al. (2010) | Deltaic core | 4 h SOL2 bleach | pIRIR225 < 2 Gy |
| Thiel et al. (2012) | Shallow marine | Modern analogue | pIRIR200 5.2 ± 2 Gy |
| Buylaert et al. (2012) | Coastal | Modern analogue | pIRIR200 5.2 ± 2 Gy |
| Reimann et al. (2011) | Coastal | 4 h SOL2 bleach | pIRIR200 6.4 ± 1.2 Gy |
| Alexander and Murray (2012) | Glacioluvial | 5 h SOL2 bleach | pIRIR200 12 ± 0.6 Gy |

* In this experiment the distance of each aliquot from the SOL2 light source was ~40 cm.
measurement through to the subsequent \( t_s \) measurement which may affect the accuracy of the dose determinations. The IRSL signal was summed over the first 0.3 s of stimulation and the background calculated from the final 0.6 s. Regenerative doses of 0, 24, 48, 96 Gy and 0, 2, 4, 8, 20 and 40 Gy were used for dose-recovery and residual-dose experiments, respectively. A second 0 Gy dose was repeated after the largest regenerative dose as a second test for recuperation, which was then followed by a dose of 48 Gy (dose-recovery tests) or 8 Gy (residual-dose tests) used for recycling ratio tests.

Four rejection criteria were applied throughout the analyses unless otherwise specified; (1) whether the response to the test dose was less than three times the standard deviation of the background, (2) whether the uncertainty in the luminescence measurement of the test dose was greater than 10%, (3) whether the recycling ratio was outside the range 0.9–1.1, taking into account the uncertainties on the individual recycling ratios, and (4) whether recuperation was greater than 0.5% of the response from the largest regenerative doses, which were 96 Gy and 40 Gy for dose-recovery and residual dose experiments, respectively. Following the method of Thomsen et al. (2005) the instrument reproducibility of the single-grain measurement system was assessed for the protocols used in this study, giving values of 4.6% and 4.5% (per stimulation when the signal is summed over the initial 0.3 s) for the pIRIR225 and pIRIR290 measurements, respectively (Smedley and Duller, 2013). These instrument reproducibility values were incorporated into the \( D_e \) calculations.

### 3. Sample descriptions

Three samples of density-separated K-feldspar grains were used in this study. Sample TC01 was collected from an inland dune field in eastern Argentina and has a multiple grain quartz OSL age (20 ± 5 years) indicating very recent deposition. Sample GDNZ13 was taken from a Late Glacial dune sand from North Island, New Zealand and is overlain by the Kawakawa tephra, which has been dated by radiocarbon to 25.36 ± 0.16 cal. ka BP (Vandergoes et al., 2013). Sample LBA12F4-2 was extracted from glaciogenic sediments in Patagonia, directly linked to a moraine ridge dated to 25.2 ± 0.4 ka using cosmogenic isotope dating (\(^{10}\)Be) of moraine boulders (Kaplan et al., 2011).

Prior to measurement the samples were all treated with a 10% v/v dilution of 37% HCl and with 20 vols H\(_2\)O\(_2\) to remove carbonates and organics, respectively. Dry sieving isolated the 180–212 µm diameter grains, and density-separation with sodium polytungstate provided the <2.58 g cm\(^{-3}\) (K-feldspar-dominated) fractions. The K-feldspar grains were not etched in hydrofluoric acid because of concern about non-isotopic removal of the surface (Duller, 1992). Details of the calculation of the alpha dose-rates for these samples are described in the caption of Table 3. Finally, the K-feldspar grains were mounted into 10 × 10 grids of 300 µm diameter holes in a 9.8 mm diameter aluminium single-grain disc for analysis.

Dose-rates were calculated for the K-feldspar dominated fractions of all three samples using thick source alpha and beta counting on Daybreak and Riso GM-25-5 measurement systems, respectively (Table 3). The K-content of each feldspar separate was measured using a Riso GM-25-5 beta counter to analyse 0.1 g sub-samples of the separated material; this gave values of 6.5% K (TC01), 6.2% K (GDNZ13), and 3.9% K (LBA12F4-2). To calculate the internal dose rate arising from K within the feldspar grains a value of 10 ± 2% was used following the work of Smedley et al. (2012) and Smedley (2014) who showed that the K-content of the majority of grains from these samples which emitted detectable pIRIR signals was 10 ± 2%.

### 4. Determination of \( D_e \) remaining in a recently-deposited sample

The recently-deposited dune sand sample, TC01, was used to assess the residual \( D_e \) values for the pIRIR225 and pIRIR290 signals, using the protocols outlined in Table 2. Two hundred grains were measured using each signal but after applying the rejection criteria only 14 and 10 grains provided residual \( D_e \) values for the pIRIR225 and pIRIR290 signals, respectively. These single-grain residual \( D_e \) values are presented as histograms to show the populations of grains measured using the pIRIR225 (Fig. 1a) and pIRIR290 (Fig. 1b) signals. Although there was variation between the residual \( D_e \) values measured for individual grains, 12 of the 14 grains (86%) measured using the pIRIR225 protocol and 6 of the 10 grains (60%) measured using the pIRIR290 protocol gave residual \( D_e \) values of <2 Gy. The central age model (CAM) \( D_e \) values were calculated from the pIRIR225 and pIRIR290 single-grain populations, giving values of 1.0 ± 0.3 Gy and 1.7 ± 0.4 Gy, respectively.

Multiple-grain dating using the OSL signal from quartz gave a luminescence age for sample TC01 of 20 ± 5 years. For comparison, luminescence ages determined from single grains were also calculated using the CAM \( D_e \) values of the pIRIR225 (CAM \( D_e \) value of 1.0 ± 0.3 Gy) and pIRIR290 (CAM \( D_e \) value of 1.7 ± 0.4 Gy) signals, and the dose-rate in Table 3. The ages calculated for sample TC01 using the pIRIR225 and pIRIR290 signals for single-grains of K-feldspar were 325 ± 100 years and 550 ± 130 years, respectively.

The CAM \( D_e \) value calculated for the pIRIR225 signal from the recently-deposited dune-sand sample (1.0 ± 0.3 Gy) is comparable to the published residual \( D_e \) values of <1 Gy for other samples using the pIRIR290 signal shown in Table 1. However, the CAM \( D_e \) value (1.7 ± 0.4 Gy) calculated in this study using the pIRIR290 signal was larger than 1 Gy. When a synthetic aliquot is derived by summing the signal emitted from all the grains on the single-grain disc, the mean \( D_e \) values calculated from two synthetic aliquots per signal were 1.4 Gy (pIRIR225 signal) and 2.6 Gy (pIRIR290 signal). These \( D_e \) values are consistent with the smallest residual dose values published for the pIRIR signals from multiple-grain aliquots of K-feldspar (Table 1), but slightly larger than the values derived from measurements using single grains.

### Table 3

| Sample  | Grain size (µm) | Water content (%) | K (%)  | U (ppm)  | Th (ppm)  | Cosmic dose-rate (Gy/ka) | Dose-rate (Gy/ka) |
|---------|----------------|-------------------|--------|----------|----------|-------------------------|------------------|
| TC01    | 180–250        | 5 ± 2             | 1.72 ± 0.08 | 1.89 ± 0.19 | 4.38 ± 0.61 | 0.18 ± 0.02 | 3.08 ± 0.17 |
| GDNZ13  | 180–212        | 30 ± 5            | 1.02 ± 0.07 | 2.26 ± 0.19 | 5.25 ± 0.61 | 0.14 ± 0.02 | 2.23 ± 0.14 |
| LBA12F4-2 | 180–212     | 5 ± 2             | 2.35 ± 0.11 | 1.99 ± 0.24 | 6.37 ± 0.80 | 0.09 ± 0.02 | 3.75 ± 0.46 |
Dose-recovery experiments were performed on a suite of 200 fresh grains from sample TC01 using both the pIRIR225 and pIRIR290 signals to assess the suitability of each measurement protocol. A 52 Gy dose was added to the small natural dose as measured above and the resultant De was assessed using the pIRIR protocols outlined in Table 2. The CAM De for the pIRIR225 and pIRIR290 signals gave residual-subtracted dose-recovery ratios of 0.98 ± 0.02 and 0.97 ± 0.04, and overdispersion values of 9.6 ± 0.4% (n = 37 grains) and 17.9 ± 0.4% (n = 45 grains), respectively, demonstrating the appropriateness of both of these protocols for determining De values.

5. Measurement of De remaining after laboratory bleaching

The measurements from the naturally-bleached sample, TC01 (Section 4), demonstrate the degree of variation in residual De values expected in a well-bleached environment. However, single-grain dating is typically used to analyse sediments in environments where the opportunities for bleaching are limited (Duller, 2008). Thus, an investigation of the residual De values observed in response to different bleaching times was conducted to assess the grain-to-grain variability in the rate of bleaching of the pIRIR signal.

5.1. Experimental design

Eight hundred grains that had previously been analysed to determine the natural De value (400 grains from sample TC01, and 400 grains from sample GDNZ13) were used for these experiments to assess the residual De values measured following different laboratory bleaching durations. For each sample, half of the 400 grains were measured using a pIRIR225 protocol, and the other half were measured using the pIRIR290 protocol. Prior to these measurements, the grains were given a 52 Gy dose and then bleached at a distance of ~50 cm from the bulb of a SOL2 solar simulator for different periods of time. Lx/Tx measurements were performed after each bleaching interval and interpolated on to a dose-response curve previously constructed for each individual grain. Replicate measurements were performed on the same grains after different intervals of 1, 4, 8, and 20 h to monitor the depletion of the pIRIR signals for individual grains.

5.2. Laboratory bleaching of an Argentinean dune sand

The CAM was applied to residual De values obtained from single grains of TC01 which passed the rejection criteria (Section 2) for the pIRIR225 (Fig. 2, closed diamonds; n = 15 grains) and pIRIR290 (Fig. 2, open circles; n = 19 grains) signal, measured after the different laboratory bleaching times. The pIRIR225 and pIRIR290 CAM De values determined for the naturally-bleached grains of TC01 (Section 4) are also marked as dashed lines in Fig. 2 for comparison. Neither the pIRIR290 nor the pIRIR225 signal deplete to the natural residual De value, even after a prolonged 20 h bleach in the SOL2, which is equivalent to ~5 ½ days of natural sunlight exposure. Instead, the pIRIR225 and pIRIR290 CAM De values reduced to only 5.0% and 6.6% of the 52 Gy given doses, respectively. The pIRIR225 signal is shown in Fig. 2 to bleach more rapidly after 1 h of bleaching (5.6 ± 0.8 Gy residual De; 11% of the given dose) than the pIRIR290 signal (9.2 ± 1.0 Gy residual De; 18% of the given dose). However, beyond 4 h of bleaching, the residual De values for both signals are similar to one another, and after 20 h both the pIRIR225 and pIRIR290 signals gave a CAM De value ~5% of the 52 Gy given dose.

The bleaching rate of the pIRIR225 signal from single grains of sample TC01 is shown in Fig. 3, and demonstrates that different grains bleach at different rates. Three grains that bleach at different rates (fast, moderate, slow) are highlighted in Fig. 3a (denoted grains a, b and c). Grain (a) bleaches rapidly to a residual De value of 2.4 ± 1.0 Gy (4.6% of the given dose) after 1 h of bleaching and remains at ~2 Gy for the prolonged bleaching times. Grain (b) has a moderate bleaching rate, reaching a residual De value of 7.6 ± 0.8 Gy (15% of the given dose) after 1 h of bleaching and reduces to a value of 2.1 ± 0.3 Gy (4.1% of the given dose) after the prolonged 20 h bleach. Grain (c) bleaches the slowest, giving a residual De value of 15.4 ± 2.0 Gy (29.6% of the given dose) after 1 h of bleaching with a
SOL2 but reaches a value of $3.5 \pm 0.6$ Gy (6.6% of the given dose) after a 20 h bleach. Although the bleaching rates of individual grains varies, all three of the grains (a, b and c) have residual $D_e$ values of $\leq 10\%$ of the given dose after 20 h of bleaching. The implication of this is that for samples from environments where grains are exposed to long periods of sunlight, the variability in residual $D_e$ value from one grain to another at deposition will be small, and hence would be expected to contribute little to scatter in $D_e$ distributions determined from single grains. Whilst the variability in $D_e$ from one grain to another may be small, the average residual $D_e$ remaining even after 20 h in the SOL2 (Fig 3e) is $2.7 \pm 0.3$ Gy, which would be significant when dating young samples.

The residual $D_e$ values of grains (a), (b) and (c) relative to the rest of the single-grain population are also shown as histograms in Fig. 3, representing the different bleaching times used, namely 1 h (Fig. 3b), 4 h (Fig. 3c), 8 h (Fig. 3d) and 20 h (Fig. 3e). The single-grain population has a large range of residual $D_e$ values after the shorter, 1 h bleach ($2-15.5$ Gy) and a smaller range in residual $D_e$ values after the 20 h bleach ($0-5.5$ Gy). Moreover, there is an identifiable population of grains that bleach more rapidly (e.g. grain a). After a short 1 h bleach $\sim 20\%$ and $\sim 50\%$ of the grains bleach to $\leq 5\%$ and $\leq 10\%$ of the given dose, respectively. The grain-to-grain variability of bleaching of the pIRIR signal demonstrates that a population of grains (e.g. grain a) bleaches more rapidly in response to optical stimulation than others (e.g. grains b and c); these rapidly-bleaching grains may be preferable for single-grain analysis of the pIRIR signal from partially-bleached sediments as they might be expected to have the smallest residual $D_e$ values upon deposition.

5.3. Laboratory bleaching of a New Zealand dune sand

The same experiment as that discussed in Sections 5.1 and 5.2 was undertaken for the Late Glacial dune sand sample from New Zealand, GDNZ13. The CAM $D_e$ values calculated from the single-grain populations of sample GDNZ13 measured after the different SOL2 bleaching times are presented in Fig. 4a for the pIRIR$_{225}$ ($n=45$ accepted grains; closed diamonds) and pIRIR$_{290}$ ($n=38$ accepted grains; open circles) signals. The CAM pIRIR$_{225}$ $D_e$ of GDNZ13 is $6.5 \pm 0.5$ Gy (12.6% of the given dose) after 1 h and $3.7 \pm 0.3$ Gy (7.1% of the given dose) after 20 h of bleaching (Fig. 4a). However, the pIRIR$_{290}$ signal of GDNZ13 bleaches comparatively slowly giving a residual $D_e$ value of $12.4 \pm 1.1$ Gy (23.8% of the given dose) after 1 h and $5.3 \pm 0.5$ Gy (10.2% of the given dose) after 20 h in the SOL2.

The distribution of $D_e$ values for individual grains of sample GDNZ13 measured using the pIRIR$_{225}$ signal was similar to that seen for sample TC01 in Fig. 3 (b–d). Histograms of the residual $D_e$ values of the single-grain population measured for GDNZ13 are presented in Fig. 4 for 1 h (Fig. 4b), 4 h (Fig. 4c), 8 h (Fig. 4d) and 20 h (Fig. 4e) bleaching with the SOL2; highlighted on each graph is the CAM $D_e$ value calculated for each bleaching time (dashed line). Although the data are not shown here, the grain-to-grain variability in bleaching was larger for the pIRIR$_{290}$ signal in comparison to the pIRIR$_{225}$ signal for this sample. No grains bleached to residual levels $\leq 5\%$ of the given dose after a 1 h SOL2 bleach using the pIRIR$_{290}$ signal for GDNZ13, however, 11% of the grains did bleach to $\leq 10\%$ of the given dose after a 1 h bleach. The pIRIR$_{225}$ and pIRIR$_{290}$ data from GDNZ13 and TC01 demonstrates that different grains bleach at different rates.

5.4. Dependence of residual $D_e$ on prior dose

Sohbati et al. (2012) measured the dose-dependence of pIRIR$_{225}$ residual $D_e$ values using multiple-grain aliquots of K-feldspar for samples from southeast Spain. Larger residual $D_e$ values were obtained following a 4 h SOL2 bleach for the samples with the larger natural $D_e$ values (up to $-1000$ Gy). The dataset was extrapolated to derive an estimate for the residual $D_e$ value at deposition of
0.98 ± 0.8 Gy, which is similar to the residual De value determined for the recently-deposited aeolian dune sand sample, TC01, in this study (Section 4). In the current study, the impact of prior dose on the residual De of individual grains was assessed using given doses of different magnitudes prior to bleaching. One hundred grains of sample GDNZ13 that had been previously analysed to determine a natural De value (similar to the grains in Sections 5.2 and 5.3) were given a 52 Gy beta dose, bleached for 8 h in the SOL2 and the Lx/Tx ratios were measured. This procedure was repeated twice more following given doses of 102 Gy and 202 Gy, and the Lx/Tx values were interpolated onto a dose-response curve constructed for each individual grain to determine the residual De values.

The residual De values obtained for the pIRIR225 signal of sample GDNZ13 are shown in Fig. 5a as a function of the given dose (i.e. 52 Gy, 102 Gy and 202 Gy). The CAM residual De value (Fig 5b, dashed lines) increased with increased given dose prior to bleaching in the SOL2, and is comparable to the residual De values measured by Sohbat et al. (2012). In the present study, the residual De values after different given doses for grains characterised by a fast, moderate or slow bleaching are highlighted in Fig. 5a (denoted grains x, y and z) for the pIRIR225 signal of sample GDNZ13. Fig 5a shows that all three of the grains (x, y and z) give larger residual De values with larger given doses prior to bleaching. In the natural environment the dose each grain has received prior to the event being dated is unknown and so any variability in the rate at which the pIRIR225 signal of the different grains bleaches can further complicate single-grain dose-distributions.

6. Grain-to-grain variability in bleaching rates of the pIRIR signal

Thus far, this study has demonstrated that the pIRIR signal of individual grains of K-feldspar have the potential to bleach at different rates in response to light. Previous studies have suggested that slow bleaching rates of the pIRIR signal may restrict the use of the pIRIR signal for dating of K-feldspar in partially-bleached environments (e.g. Blombin et al., 2012; Trauerstein et al., 2012). However, the influence that grain-to-grain variability in bleaching rates of the pIRIR signal has on single-grain De distributions has not yet been investigated for natural sedimentary samples.

The observation that the pIRIR signal of different grains bleaches at different rates suggests that dating of partially-bleached sediments may be optimised by trying to preferentially select for analysis those grains that bleach most rapidly. To test this idea, the bleaching rates of individual grains of K-feldspar were assessed by measuring the residual De values after a short 1 h bleach in order to force the largest divergence in behaviour between the more- and less-rapidly bleaching grains in the dataset (e.g. Fig. 3b). These short laboratory bleaching tests involved (1) a given dose of 52 Gy, followed by (2) a 1 h bleach in the SOL2 solar simulator, and (3) single-grain Lx/Tx measurements, which are then interpolated onto the original dose-response curves constructed for dating. The residual De values measured during these bleaching tests give an indication of the relative bleaching rates of the individual grains that form the single-grain De distribution.

Short bleaching tests were performed using the pIRIR225 and pIRIR290 signals on a further suite of single grains of K-feldspar extracted from sample GDNZ13. The single-grain data were first ranked from the smallest to the largest by the residual De values, and then the cumulative percentage of grains (y-axis) were plotted against the residual De values as a percentage of the 52 Gy given dose (x-axis). Fig. 6a compares the bleaching rates measured for sample GDNZ13 using the pIRIR225 and pIRIR290 signals. There was more variability in the single-grain residual De values measured after a 1 h SOL2 bleach using the pIRIR290 signal in comparison to the pIRIR225 signal; ~80% of the grains reduced to residual De values of ≤31% of the given dose (i.e. ≤17 Gy) for the pIRIR290 signal whilst for the pIRIR225 signal the same proportion of grains had residual De values of ≤19% of the given dose (i.e. ≤10 Gy). This reinforces the view that the pIRIR290 signal bleaches slower than the pIRIR225 signal and this is reflected by the larger and more variable single-grain residual De values.
To assess whether the grain-to-grain variability in bleaching rate of the pIRIR225 signal is a dominant control on the single-grain $D_e$ distributions, the residual $D_e$ values for the pIRIR225 signal after the 1 h bleach in the SOL2 solar simulator were compared to the single-grain $D_e$ values for three sedimentary samples from different depositional environments. The three samples tested were from different depositional settings and are constrained by independent age control (Section 3). Sample TC01 is a recently-deposited aeolian dune sand, sample GDNZ13 is a Late Glacial aeolian sand, and sample LBA12F4-2 is a glaciofluvial sample deposited during the Last Glacial period. The short laboratory bleaching tests were performed for all three samples after the measurement of the pIRIR225 signal to determine the natural $D_e$ values. Fig. 6b compares the bleaching rates measured for the three different samples and demonstrates that there was little difference between the samples in the behaviour of the pIRIR225 signal. After the 1 h bleach in the SOL2 solar simulator, the typical behaviour shown by all three samples is that the measured $D_e$ values of ~80% of all the grains reduced to ~20% of the given dose (i.e. ~10.4 Gy) (Fig. 6b). The bleaching tests and the $D_e$ values were assessed using exactly the same grains to permit direct comparison between the inferred bleaching rates and the natural $D_e$ values (Fig. 7). If bleaching rates were a dominant control on the single-grain $D_e$ distribution then there would be a relationship between the residual $D_e$ values measured after the short laboratory bleaching tests and the natural $D_e$ values. The results in Fig. 7 for samples TC01 (a), GDNZ13 (c), and LBA12F4-2 (e) shows that there is no direct relationship between the inferred bleaching rates and the $D_e$ values for single grains from...
any of the three samples.

The individual grains included in Fig. 7 were also ranked from smallest to largest according to the size of the residual $D_e$ value measured after the short 1 h bleaching tests and binned into five groups (0–2.6 Gy, 2.7–5.2 Gy, 5.3–7.8 Gy, 7.9–10.4 Gy and >10.4 Gy). The number of grains included in each bin is shown in the histograms in Fig. 7 (b, d and f). The CAM $D_e$ value was calculated for each bin of all three samples (Fig. 7b, d and f). MAM $D_e$ values were also calculated for each bin of the glaciofluvial sample LBA12F4-2 (Fig. 7f) as the large overdispersion value calculated for single-grain $D_e$ values of this sample (71.6 ± 0.1%; $n = 260$ grains) suggested that it was partially bleached upon deposition. Since these samples have independent age control, expected $D_e$ values could be calculated using the dose-rates (Table 3). The CAM and/or
If bleaching rates are a dominant control on the single-grain $D_e$ distributions then the bins containing the grains with the pIRIR$_{225}$ signals that bleach most rapidly in response to exposure to the SOL2 solar simulator should give rise to the lowest CAM and MAM natural $D_e$ values. For sample TC01 (Fig. 7b) the CAM $D_e$ values calculated using the grains with the most rapidly-bleaching pIRIR$_{225}$ signal (230 ± 30 years) do not give ages in agreement with the OSL age obtained from quartz (20 ± 5 years). The results for sample GDNZ13 (Fig. 7d) show lower CAM natural $D_e$ values for the binned grains that gave the lowest residual $D_e$ values, but the bin representing residual $D_e$ values of 0–2.6 Gy contains only one grain, and the difference between the CAM $D_e$ value calculated for the 2.7–5.2 Gy bin and the bins >5.2 Gy is small.

The opportunity for bleaching in the natural environment is likely to be less in a glaciofluvial setting in comparison to an aeolian setting, and so differences in bleaching behaviour of individual grains (e.g. Fig. 3e) is likely to have a larger influence in a glaciofluvial setting. Fig. 7f presents the CAM and MAM natural $D_e$ values calculated for the binned grains for the glaciofluvial sample L1-H1171.2. The results show no trend between the CAM or MAM $D_e$ values and the inferred bleaching rate of the grains. It is concluded that although differences are observed in the inferred bleaching rates of the pIRIR$_{225}$ signals of single grains, these variable bleaching rates are not a dominant control on the single-grain $D_e$ distribution of these samples. Note that the bleaching rates of individual grains are not related to the extent of bleaching in the natural environment and so the two factors will likely impact samples taken from different depositional settings to different extents. Presumably for samples from well-bleached settings (e.g. aeolian) where the opportunity for resetting of the pIRIR signal is high, other factors such as internal geochemistry (K, Rb, U or Th), external microdosimetry and anomalous fading are a more dominant control on single-grain $D_e$ distributions. This is in contrast to environments where the opportunity for bleaching is low (e.g. glaciofluvial or fluvial) and the extent of bleaching in the natural environment is the dominant control on the $D_e$ distribution; this highlights why single-grain analysis is important for providing accurate ages for sedimentary samples taken from poorly-bleached settings.

7. Conclusions

A naturally-bleached dune sand from Argentina (TC01) that gave an age of 20 ± 5 years using the OSL signal of quartz, gave ages of 325 ± 100 years and 550 ± 130 years using single-grain measurements of the pIRIR$_{225}$ and pIRIR$_{590}$ signals, respectively. Laboratory measurements of residual $D_e$ values after bleaching in a solar simulator were then used to investigate the variability in bleaching rates of the pIRIR$_{225}$ and pIRIR$_{590}$ signals for individual grains of K-feldspar from two aeolian dune samples (TC01 and GDNZ13). These bleaching experiments demonstrated that some grains bleach more rapidly than others in response to laboratory bleaching, regardless of the prior dose. Although the pIRIR signals from individual grains bleach at variable rates, this variation appears to have little impact upon the natural $D_e$ values determined for K-feldspar grains from the samples measured in this study (Fig. 7). For the two aeolian samples it is likely that prior to deposition the grains experienced prolonged periods of sunlight bleaching and so all the grains, regardless of the potential rate of bleaching, reached low residual $D_e$ values (c.f. 20 h bleach in Fig. 3a). The extended exposure to sunlight in an aeolian environment reduces the impact of variable bleaching rates on the natural $D_e$ distributions (e.g. Fig. 7b, d). In contrast, the probability that individual grains have experienced prolonged periods of sunlight exposure in a glaciofluvial setting is low. It is likely that some grains experienced shorter exposure to sunlight than other grains and that the difference in bleaching rates would result in variable residuals in natural $D_e$ distributions (e.g. Fig. 3a). However, the glaciofluvial sample shown in this study suggests that the influence that the bleaching rates of individual grains had on the natural $D_e$ distributions (Fig. 7f) was minimal in comparison to other factors, including the variation due to the stochastic nature of the exposure of individual grains to sunlight.

The pIRIR signal from individual grains of K-feldspar bleaches at different rates, but analysis of the samples described here suggests that these differences in rate are not sufficiently great to have any discernible impact upon the $D_e$ distribution obtained using single grains.

Acknowledgements

Financial support for the laboratory work contributing towards this paper was provided by a NERC PhD Studentship to RKS (NE/I1527845/1). Prof. Joanne Bullard (Loughborough University) is thanked for collecting the aeolian dune sand from Argentina (TC01). Aberystwyth Luminescence Research Laboratory (ALRL) benefits from being part of the Climate Change Consortium for Wales (C3W). Two anonymous reviewers are thanked for their comments that helped to improve the manuscript.

References

Alappat, L., Tsukamoto, S., Singh, P., Srikant, D., Ramesh, R., Frechen, M., 2010. Chronology of Cauvery delta sediments from shallow subsurface cores using elevated-temperature post-IR IRSL dating of feldspars. Geochronometria 37, 37–47.
Alexanderson, H., Murray, A.S., 2012. Luminescence signals from modern sediments in a glaciated bay, NW Svalbard. Quat. Geochronol. 10, 250–256.
Baliff, I.K., Poolton, N.R.J., 1991. Studies of charge transfer mechanisms in feldspars. Nucl. Tracks Radiat. Meas. 18, 111–118.
Balescu, S., Lamotte, M., 1992. The blue emission of K-feldspar coarse grains and its potential for overcoming TL age underestimation. Quat. Sci. Rev. 11, 45–51.
Blombin, R., Murray, A.S., Thomsen, K.J., Buytelaert, J.-P., Sobhati, R., Jansson, K.N., Alexanderson, H., 2012. Timing of the deglaciation in southern Patagonia: testing the applicability of K-feldspar IRSL. Quat. Geochronol. 10, 264–272.
Bett-Jensen, L., Andersen, C.E., Duller, G.A.T., Murray, A.S., 2003. Development in radiation, stimulation and observation facilities in luminescence measure-
ments. Radiat. Meas. 37, 535–541.
Buytelaert, J.-P., Murray, A.S., Thomsen, K.J., Jain, M., 2009. Testing the potential of an elevated temperature IRSL signal from K-feldspar. Radiat. Meas. 44, 566–565.
Buytelaert, J.-P., Murray, A.S., Gebhardt, A.C., Sobhati, R., Ohlundorf, C., Thiel, C., Wastegård, S., Zolitschka, B., The PASADO Science Team, 2013. Luminescence dating of the PASADO core 5022-1D from Laguna Potrok Aike (Argentina) using IRSL signals from feldspar. Quat. Sci. Rev. 71, 70–80.
Clarke, M.L., Rendell, H.M., 1997. Infra-red stimulated luminescence spectra of alkali feldspars. Radiat. Meas. 27, 221–236.
Colarossi, D., Duller, G.A.T., Roberts, H.M., Tooth, S., Lyons, R., 2015. Comparison of paired quartz OSL and feldspar post-IR IRSL dose distributions in poorly bleached fluvial sediments from South Africa. Quat. Geochronol. http:// dx.doi.org/10.1016/j.quageo.2015.02.015 (in press).
Duller, G.A.T., 1992. Luminescence Chronology of Raised Marine Terraces Southwest North Island New Zealand (Unpublished PhD thesis). University of Wales, Aberystwyth.
Duller, G.A.T., 2006. Single grain optical dating of glacialic deposits. Quat. Geochronol. 1, 296–304.
Duller, G.A.T., 2008. Single-grain optical dating of Quaternary sediments: why aliquot size matters in luminescence dating. Radiat. Meas. 37, 589–612.
Duller, G.A.T., Better-Jensen, L., Murray, A.S., 2003. Combining infrared- and green-laser stimulation sources in single-grain luminescence measurements of feldspar and quartz. Radiat. Meas. 37, 543–550.
Godfrey-Smith, D.J., Huntley, D.J., Chen, W.-H., 1988. Optical dating studies of quartz and feldspar sediment extracts. Quat. Sci. Rev. 7, 373–380.

Guerin, G., Mercier, N., Adamiec, G., 2011. Dose-rate conversion factors: update. Anc. TL 29, 5–8.

Guerin, G., Mercier, N., Nathan, R., Adamiec, G., Lefrais, Y., 2012. On the use of the infinite matrix assumption and associated concepts: a critical review. Radiat. Meas. 47, 778–785.

Huntley, D.J., Lamotte, M., 2001. Ubiquity of anomalous fading in K-feldspars and the measurement and correction for it in optical dating. Can. J. Earth Sci. 38, 1093–1106.

Jain, M., Ankjærgaard, C., 2011. Towards a non-fading signal in feldspar: insight into charge transport and tunnelling from time-resolved optically stimulated luminescence. Radiat. Meas. 46, 292–309.

Kaplan, M.R., Strelin, J.A., Schaefer, J.M., Denton, G.H., Finkel, R.C., Schwartz, R., Putnam, A.E., Vandergoes, M.J., Goehring, B.M., Travis, S.G., 2011. In-situ cosmogenic $^{10}$Be production rate at Lago Argentino, Patagonia: implications for late-glacial climate chronology. Earth Planet. Sci. Lett. 309, 21–32.

Kars, R.H., Reimann, T., Ankjærgaard, C., Wallinga, J., 2014. Bleaching of the post-IR IRSL signal: new insights for feldspar luminescence dating. Boreas 43, 780–791.

Li, B., Jacobs, Z., Roberts, R.G., Li, S.-H., 2014. Review and assessment of the potential of various luminescence signals from feldspar-rich sediment extracts. Radiat. Meas. 47, 688–695.

Madsen, A.T., Buylaert, J.-P., Murray, A.S., 2011. Luminescence dating of young coastal deposits from New Zealand using feldspar. Geochronometria 38, 378–390.

Murray, A.S., Thomsen, K.J., Masuda, N., Buylaert, J.P., Jain, M., 2012. Identifying well-bleached quartz using the differential bleaching rates of quartz and feldspar luminescence signals. Radiat. Meas. 47, 688–695.

Prescott, J.R., Hutton, J.T. 1994. Cosmic ray contributions to dose rates for luminescence and ESR dating: large depths and long-term time variations. Radiat. Meas. 23, 497–500.

Reimann, T., Tsukamoto, S., 2012. Dating the recent past (<500 years) by post-IR IRSL feldspar — examples from the North Sea and Baltic Sea coast. Quat. Geochronol. 10, 180–187.

Reimann, T., Tsukamoto, S., Naumann, M., Frechen, M., 2011. The potential of using K-rich feldspars for optical dating of young coastal sediments — a test case from Darss-Zingst peninsula (southern Baltic Sea coast). Quat. Geochronol. 6, 207–222.

Reimann, T., Thomsen, K.J., Jain, M., Murray, A.S., Frechen, M., 2012. Single-grain dating of young sediment using the pIRIR signal from feldspar. Quat. Geochronol. 11, 28–41.

Robertson, G.B., Prescott, J.R., Hutton, J.T., 1991. Bleaching of the thermoluminescence of feldspars by sunlight. Nucl. Tracks Radiat. Meas. 18, 101–107.

Smedley, R.K., 2014. Testing the Use of Single Grains of K-feldspar for Luminescence Dating of Proglacial Sediments in Patagonia (Unpublished Ph.D. thesis). Aberystwyth University, UK.

Smedley, R.K., Duller, G.A.T., 2013. Optimising the reproducibility of measurements of the post-IR IRSL signal from single-grains of feldspar for dating. Anc. TL 31, 49–58.

Smedley, R.K., Duller, G.A.T., Pearce, N.J., Roberts, H.M., 2012. Determining the K-content of single-grains of feldspar for luminescence dating. Radiat. Meas. 47, 790–796.

Sohbati, R., Murray, A.S., Buylaert, J.-P., Ortuzio, M., Cunha, P.P., Masana, E., 2012. Luminescence dating of Pleistocene alluvial sediments affected by the Alhama de Murcia fault (eastern Betics, Spain) — a comparison between OSL, IRSL and post-IR IRSL ages. Boreas 41, 250–262.

Spooner, N.A. 1994. The anomalous fading of infrared-stimulated luminescence from feldspars. Radiat. Meas. 23, 625–632.

Thiel, C., Buylaert, J.-P., Murray, A., Elmejdoub, N., Jedou, Y., 2012. A comparison of TT-OSL and post-IR IRSL dating of coastal deposits on Cap Bon peninsula, north-eastern Tunisia. Quat. Geochronol. 10, 209–217.

Thomsen, K.J., Murray, A.S., Better-Jensen, L., 2005. Sources of variability in OSL dose measurements using single grains of quartz. Radiat. Meas. 39, 47–61.

Thomsen, K.J., Murray, A.S., Jain, M., Better-Jensen, L., 2008. Laboratory fading rates of various luminescence signals from feldspar-rich sediment extracts. Radiat. Meas. 43, 1474–1486.

Thomsen, K.J., Murray, A.S., Jain, M., 2011. Stability of IRSL signals from sedimentary K-feldspar samples. Geochronometria 38, 1–13.

Trauerstein, M., Lowick, S., Pressuer, F., Ruler, D., Schlunegger, F., 2012. Exploring fading in single-grain feldspar IRSL measurements. Quat. Geochronol. 10, 327–333.

Vandergoes, M.J., Hogg, A.G., Lowe, D.J., Newnham, R.M., Denton, G.H., Southon, J., Barrell, D.J.A., Wilson, C.J.N., McGlone, M.S., Allan, A.S.R., Almond, P.C., Pletcher, F., Dabell, K., Diefenbacher-Krall, A.C., Blaaue, M., 2013. A revised age for the Kawakawa/Oruanui tephra, a key marker for the Last Glacial Maximum in New Zealand. Quat. Sci. Rev. 74, 195–201.

Wallinga, J., Murray, A., Wintle, A., 2000. The single-aliquot regenerative-dose (SAR) protocol applied to coarse-grain feldspar. Radiat. Meas. 32, 529–533.

Zimmerman, D.W., 1971. Thermoluminescence dating using K-feldspar. Archaeometry 13, 29–52.