Are *n*-alkane biomarkers in loess-paleosol sequences contaminated by post-depositional organic matter? A case study from Germany using a comparative ^{14}C and OSL dating approach
-Supplementary Data-

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Abstract

This supplement provides additional details on the luminescence dating of the quartz fine grain separates of the Gleina section.

1. Preface

The luminescence measurements were performed in 2011 and 2012 in the luminescence laboratories in Bayreuth and Heidelberg, Germany in the framework of the project "Saxony Loess" funded by the DFG (FA 239/13-2 and FU 417/7-2). The project ended in 2012 and the here reported OSL quartz age results had not been re-

calculated using newer conversion factors to (1) avoid numerical inconsistencies with so far reported data and because (2) it does not affecting the overall conclusion of our work.

2. Materials and Methods

2.1. Sample Collection

Samples for luminescence dating were collected during nighttime using a red headlamp ($\lambda = 640 \ \Delta \ 20\,\mathrm{nm}$). After carefully cleaning the wall and removing the daylight affected layer the samples were directly collected into opaque bags.

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Samples for dose rate determination were taken from the surrounding 30 cm of the OSL samples.

2.2. Sample Preparation

The samples were first wet sieved (200 μm, 90 μm, 63 μm). The fraction $< 63\,\mu m$ was treated with H_2O_2 (10 %) and HCl (10 %) to remove any organic material and carbonates respectively. The fine grain fraction (4-11 μm) was subsequently separated by settling applying the Stokes' law. To obtain the quartz fraction the samples were further etched for six or nine days in three day pretreated[1] H_2SiF_6 (34 %) and subsequently washed in HCl (10 %) and rinsed in water (Fuchs et al., 2005; Berger et al., 1980). The purity of the quartz extracts was tested by IR stimulation (IRSL/blue OSL ratio < 1%). The sample preparation was carried out under subdued red light ($\lambda = 640 \Delta 20\,nm$) conditions.

2.3. Instrumentation

Luminescence measurements were carried out on Risø DA-15/DA-20 TL/OSL readers in Heidelberg and Bayreuth. Each machine was fitted with an EMI 9235QB15 UV sensitive photomultiplier tube. For luminescence detection in the ultraviolet (UV) band a 7.5 mm Hoya U-340 (290–370 nm) filter was used. Luminescence were stimulated with blue (LED, $\lambda = 470 \Delta 30\,nm$) and infrared light (LED, $\lambda = 870 \Delta 40\,nm$). The $^{90}Sr/^{90}Y$ β-sources deliver between $2.7\,Gy\ min^{-1}$ and $9.1\,Gy\ min^{-1}$ (calibrated for fine grain quartz). All measurements were performed on aluminum discs. For each aliquot ca. 2 mg of sample material per disc ($\sim 1.2 \times 10^6$ grains/disc, based on MC simulations using the function `calc_AliquotSize`() from the **R** package *Luminescence*, version 0.5.1, R Luminescence Developer Team 2015) was used.

For artificial bleaching (1) a Dr. Hönle SOL2 solar lamp (cooled cooper-plate; UVILEX glass-filter) for the combined preheat and dose recovery tests and (2) a self-designed bleaching unit (Osram Duluxstar 24W/827) for the a-value estimation were used.

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[1]The pre-treatment was done to remove traces of free HF (cf. e.g. Syers et al., 1968).

2.4. Protocol Parameters and D_e determination

For luminescence measurements a standard single-aliquot regenerative dose (SAR) protocol (Murray and Wintle, 2000) was applied. The measurements were performed at elevated temperatures (125 °C) using preheat temperatures of 220 °C and 240 °C held for 10 s. A cutheat of 160 °C was used for all measurements. The preheat temperatures were deduced (1) from combined dose-recovery and preheat tests and (2) from preheat plateau tests (e.g., Wintle and Murray, 2006) on two samples (BT838 and BT842). For the combined preheat and dose recovery tests the samples were artificially bleached for 4 h. The subsequent given β-dose was chosen to fit the range of the expected natural D_e. For both tests, temperatures between 180 °C up to 300 °C were investigated in 20 K steps. Three aliquots per temperature step were measured.

For data analysis the luminescence software Analyst 3.24b (Duller, 2007) was used. The rejection criteria such as recycling ratio, palaeodose error and test dose error were set to 10 %. The threshold of the recuperation rate was 5 %.

For D_e determination the mean and the standard error from 12 aliquots per sample were calculated using the first 0.2 s of the shine-down curve (40 s in total) for signal integration after subtracting the background from the last 4 s. To ensure an easy-to-bleach fast-component (e.g., Bailey et al., 1997) domination of the natural quartz signal, for two samples the continuous wave (CW) signal curves were transformed to pseudo linearly modulated (pLM) curves (e.g., Bulur, 2000). The CW to pLM transformation and the component separation of the pLM-OSL curves were carried out using the statistical programming language **R** (R Development Core Team, 2012) and the **R** package 'Luminescence' (Kreutzer et al., 2012b; R Luminescence Developer Team, 2013, used version: 0.2.4). The components (fast, medium, slow) of the fitted first-order kinetic function were identified by their photoionisation cross-section (e.g., Singarayer and Bailey, 2003; Jain et al., 2003).

2.5. Dosimetry

For the dose rate calculation the U and Th concentrations were determined using thick-source α-counting (e.g., Zöller and Pernicka, 1989) and ICP-MS for K respectively. The dose rate was calculated using the conversion factors from Adamiec and Aitken (1998). The cosmic dose rate was calculated according to Prescott and Hutton (1994). The α-effectiveness (a-value) for every sample was deduced following the procedure suggested by Mauz et al. (2006) and Lai et al. (2008) using an external mono energetic ^{241}Am α-source (Littlemore Alpha Irradiation Type 721/B, $3.7\,$MeV, $1.25\,$Gy min^{-1}, $< 10^{-2}\,$mbar) after artificial bleaching for $6\,$h. The a-values were calculated as mean and standard error of the mean out of up to 12 aliquots per sample.

A water content of $20 \pm 5\,\%$ was assumed for all samples based on our field experience in the Saxonian Loess Region.

3. Results and discussion

3.1. OSL characteristics

The results of the combined preheat and dose recovery tests after artificial bleaching for sample BT838 and BT842 are shown in Fig. S1. The mean and the standard deviation of three aliquots per preheat temperature are shown. Within a $10\,\%$ error all preheat temperatures between $180\,°$C and $280\,°$C are applicable. Nevertheless, the given dose was best reproduced for temperatures of $220\,°$C and $240\,°$C.

Similar sample behavior were found for the preheat plateau tests (Fig. S2) on natural aliquots. The mean and the standard deviation of three aliquots per preheat temperature are shown. Between $200\,°$C and $280\,°$C both samples show a preheat plateau, indicating that the chosen protocol parameters are suitable for D_e determination.

To obtain the natural D_e of the samples, dose response curves were constructed. Typical dose response and shine-down curves (inset) are shown in Fig. S3 for sample BT838 (a) from the upper part and sample BT844 (b) from the lower
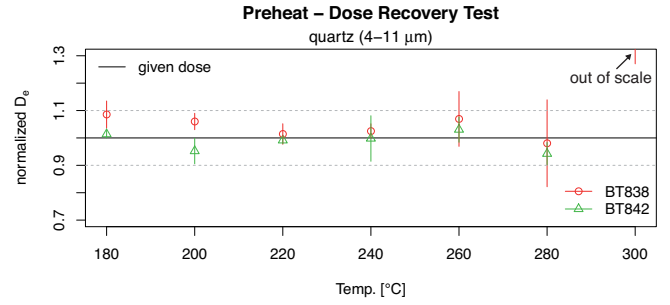

Figure S 1: Dose recovery test for different preheat temperatures on two samples (BT838 and BT842). Three aliquots were measured per preheat temperature. The mean and the standard deviation of each measurement are shown.

part of the profile. The shine-down curves showing bright and fast decaying luminescence signals in the UV band. The dose response curves were best fitted with an exponential plus linear function (EXP+LIN) with sufficient recycling ratios even at higher doses (Fig. S3b). Our results indicate no signal saturation at least up to ca. $300\,$Gy for the fine grain quartz separates.

For the purpose of component separation of the natural luminescence signal the pLM curves (Sec. 2.4 this supplement) were best fitted with a 3-component function (equation: Kitis and Pagonis, 2008). The results for sample BT838 and BT844 are shown in Fig. S4. Both investigated samples show a dominant easy-to-bleach fast-decaying signal component (component 1, red curve) suggesting that the latent luminescence signal was most probably reset during transport.

D_e distributions for sample BT838 and BT844 are shown in Fig. S5. For all samples the scatter in the D_e distribution was narrow (c_v ca. $5\,\%$) and in accordance within errors of the measured aliquots. These results indicate that the chosen number of aliquots was sufficient to obtain the true D_e.

3.2. Dosimetry

Results of the nuclide concentration and dose rate ($\dot{D}$) values are given in Tab. S1. The obtained $\dot{D}$ values range from 3.1 ± 0.2 Gy ka^{-1} (BT836) to 3.5 ± 0.2 Gy ka^{-1} (BT842). These

a)

Preheat – Plateau Test
BT838 (4–11 µm) quartz

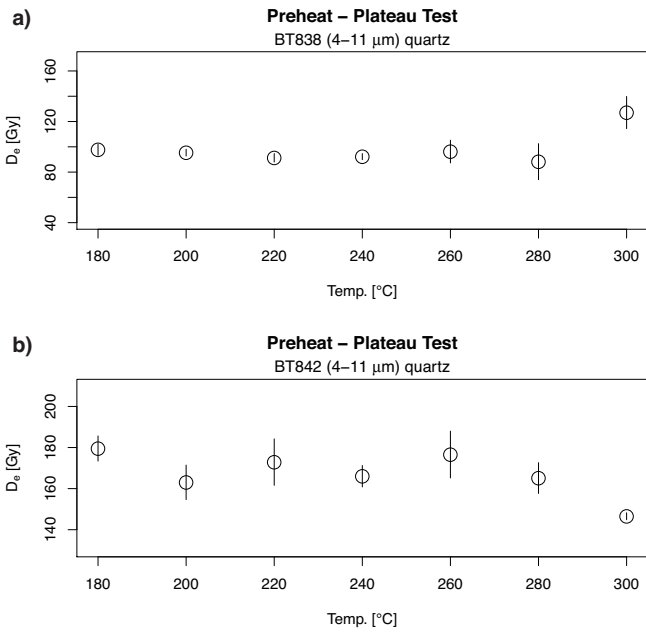b)

Preheat – Plateau Test
BT842 (4–11 µm) quartz

Figure S 2: Preheat plateau tests for different preheat temperatures for sample BT838 (a) and BT842 (b). Three aliquots were measured per preheat temperature. The mean and the standard deviation of each measurement are shown.

a)

Dose response curve: BT838

quartz | 4–11 µm | fit: EXP+LIN

b)

Dose response curve: BT844
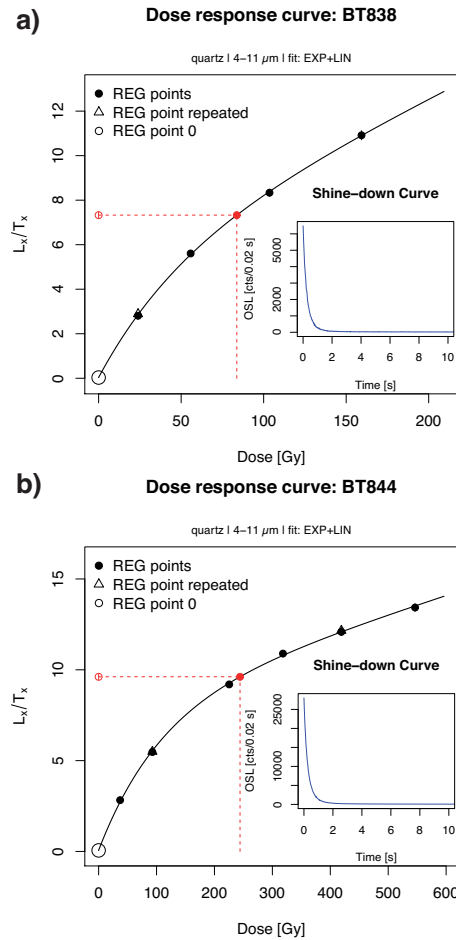
quartz | 4–11 µm | fit: EXP+LIN

Figure S 3: Typical dose response and shine-down curves (insets, only the first 10 s are shown) of sample BT838 (a) and BT844 (b). The growth curves were fitted with an exponential plus linear function. For sample BT844 seven regenerations points and two recycling points (at ca. 100 Gy and ca. 400 Gy) were used.

values are typical for the Saxonian Loess Region (Kreutzer et al., 2012a) and consistent within errors. The obtained a-values vary from 0.025 (BT836) to 0.051 (BT837, BT840) but are consistent with values obtained for fine grain quartz in other studies (e.g., Mauz et al., 2006; Lai et al., 2008).
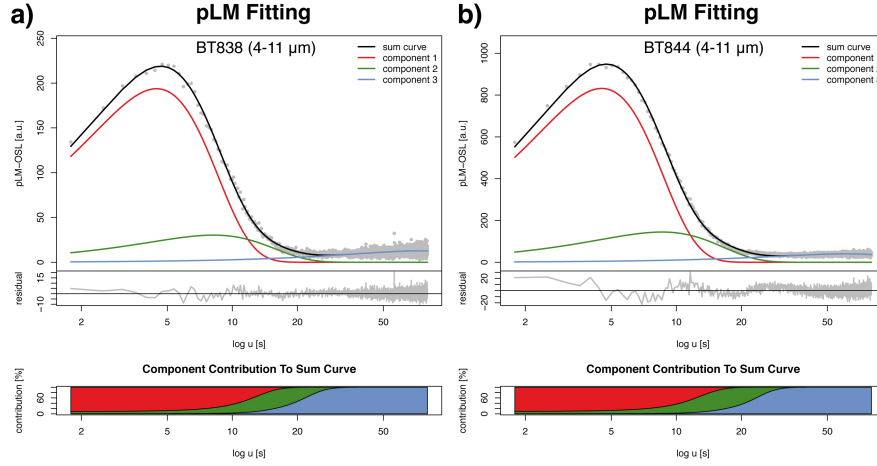
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Figure S 4: Typical natural pLM fitting data of sample BT838 (a) and BT844 (b) are shown on a log x-axis. Note: On the x-axis the transformed variable u in s is shown instead the real stimulation time t. In the lower part of the figure the component to sum curve contribution is given.
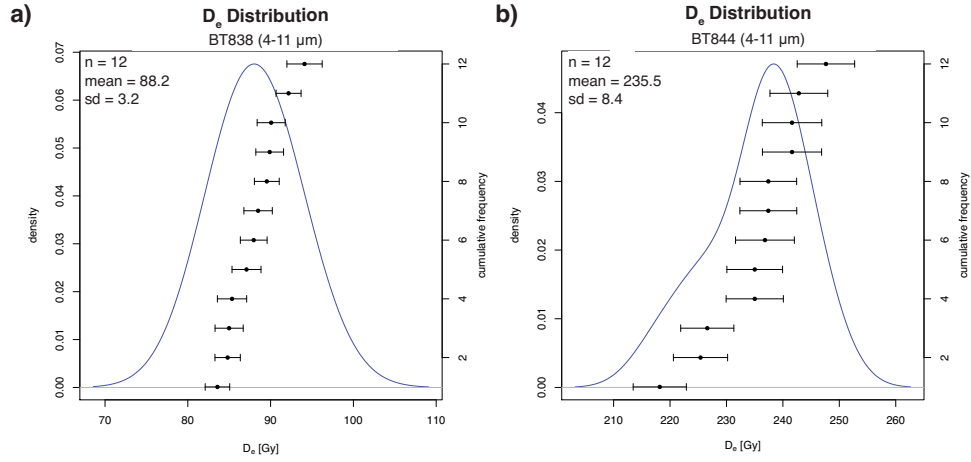

Figure S 5: Typical D_e distributions. Shown are sample BT838 (a) and BT844 (b). Details see main text.

Table S 1: Nuclide concentration and dose rate ($\dot{D}$) values (quartz, 4-11 µm)

Sample	U (ppm)	Th (ppm)	K (%)	a-value	$\dot{D}_{cosm.}$ (Gy ka^{-1})	$\dot{D}_{total}$ (Gy ka^{-1})
BT835	2.39 ± 0.28	11.32 ± 0.93	1.82 ± 0.09	0.042 ± 0.001	0.17 ± 0.01	3.29 ± 0.18
BT836	3.39 ± 0.28	8.48 ± 0.93	1.75 ± 0.09	0.025 ± 0.001	0.17 ± 0.01	3.10 ± 0.17
BT837	3.73 ± 0.28	9.24 ± 0.93	1.61 ± 0.08	0.051 ± 0.001	0.15 ± 0.01	3.38 ± 0.19
BT838	3.92 ± 0.22	8.62 ± 0.71	1.59 ± 0.08	0.031 ± 0.001	0.14 ± 0.01	3.15 ± 0.17
BT839	3.43 ± 0.21	8.58 ± 0.70	1.84 ± 0.09	0.039 ± 0.001	0.13 ± 0.01	3.29 ± 0.18
BT840	3.46 ± 0.26	8.53 ± 0.85	1.84 ± 0.09	0.051 ± 0.002	0.12 ± 0.01	3.41 ± 0.19
BT842	3.85 ± 0.39	9.69 ± 1.30	1.90 ± 0.10	0.040 ± 0.001	0.11 ± 0.01	3.54 ± 0.20
BT844	3.60 ± 0.26	8.51 ± 0.86	1.81 ± 0.09	0.034 ± 0.001	0.11 ± 0.01	3.23 ± 0.18

Note: A water content of $20 \pm 5\%$ was assumed.

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