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Single and multi-grain OSL investigations in the high dose range using coarse quartz

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A R T I C L E   I N F O

A B S T R A C T

There is evidence that optically stimulated luminescence (OSL) dating of quartz using the single-aliquot regenerative-dose (SAR) protocol underestimates the equivalent dose (D_e) for paleodoses above 100–200 Gy. Additionally, 'infinitely' old samples found not to be in laboratory saturation were reported. We present single and multi-grain SAR-OSL investigations for a coarse-grained (180–250 μm) quartz sample extracted from loess collected below the Brunhes/Matuyama transition at the Roksolany site (Ukraine). The sample was dated to more than 1000 ka by electron spin resonance using a multi center approach (Al and Ti signals), confirming that the D_e (~2000 Gy) falls beyond the limit of standard OSL D_e measurement techniques. However, the natural signal measured using multi-grain aliquots of quartz was found to be below the laboratory saturation level. A comparison was made between synthetic dose response curves (DRCs) generated from single-grain and multi-grain aliquot data, respectively; the natural signal was found to be closer to the latoratory saturation level (92%) in the case of the single-grain synthetic DRC than for the multi-grain synthetic DRC where the signal was 86% of the saturation level. This difference could not be attributed to stimulation with different wavelengths, i.e. blue and green light stimulation for multi and single-grain measurements, respectively. By analysing synthetic data obtained by grouping grains according to their brightness, it was observed that brighter grains give a natural signal closer to the laboratory saturation level. This trend was confirmed for multi-grain aliquot data. Based on these findings we infer that variability in the contribution from populations of grains with different levels of brightness may represent a controlling factor in the closeness of the natural signal to laboratory saturation level for infinitely old samples.

1. Introduction

The single-aliquot regenerative-dose (SAR) protocol (Murray and Wintle, 2000) provides the most robust approach currently available for dating of quartz samples. The maximum attainable equivalent dose is limited by the saturation of the optically stimulated luminescence (OSL) signal. An upper limit of $2 \times D_0$ (equivalent to ~85% of saturation) was proposed by Wintle and Murray (2006) for deriving reliable equivalent doses. Above this limit the measurement precision is questionable, as the equivalent doses are expected to be subject to large and asymmetric uncertainties. Various studies carried out over the past decade using quartz from samples with independent age control (e.g. Murray et al., 2007; Buylaert et al., 2008; Lai, 2010; Timar-Gabor et al.,

2011; Constantin et al., 2014) produced evidence of systematic equivalent dose underestimation when the paleodoses are higher than 100–200 Gy. Underestimation in these cases cannot be associated with the closeness of the natural signal to the laboratory saturation level. This raises doubts on the accuracy of the SAR-OSL measurements at large doses.

In a recent study of single-grain quartz OSL dating of samples with independent age control, Thomsen et al. (2016) have tested the effect of applying a D_0 selection criterion on the accuracy of dose estimate. It was shown that by accepting only the grains with D_0 values higher than the average dose of the sample, the accuracy of the dose estimate was increased.

Chapot et al. (2012) compared the natural and laboratory-

constructed dose response curves (DRCs) for a range of samples collected from loess units L1-L6 at the Luochuan section in China. The natural DRC was constructed by plotting the sensitivity corrected natural signals (L_n/T_n) against the expected paleodoses calculated using measured dose rates and independently determined ages. It was found that the two DRCs overlap only in the dose range up to ∼200 Gy, the laboratory dose response curve continuing to grow at higher doses (> 500 Gy), where the natural DRC is in saturation. A similar approach was applied to quartz samples from Costinesti loess profile in Romania (Timar-Gabor and Wintle, 2013) and the results confirm the findings of Chapot et al. (2012). These observations are also consistent with other observations reporting that the natural OSL signal of 'infinitely' old samples from Romanian (Timar-Gabor et al., 2012) and Chinese loess (Buylaert et al., 2007) was not in laboratory saturation.

The present work aims at obtaining more insights into these observations by investigating the degree of correspondence between the natural OSL signal and the SAR laboratory saturation level for an 'infinitely'old sample collected below the Brunhes/Matuyama boundary at Roksolany loess profile (Ukraine). Extended dose response curves are constructed for coarse (180–250 μm) quartz from this sample using both single-grain and multi-grain aliquot approaches and some of the factors controlling the disagreement between natural and laboratory saturation discussed.

2. Experimental details

2.1. Samples

The sample used in this study was collected from the Roksolany loess-paleosol section on the northern Black Sea coast of the Ukraine. It was taken from the base of the profile (∼45 m depth), below the Brunhes/Matuyama (B/M) polarity transition that was previously identified based on paleomagnetism measurements (Tsatskin et al., 1998; Dodonov et al., 2006) (see Fig. S1). Since the investigated sample (coded ROX 1.14) was collected from loess approximately 10 m below the ∼780 ka ago Brunhes/Matuyama polarity transition, an age of ≥800 ka is expected for this sample. Given the measured dose rate of 2.1 ± 0.1 Gy/ka (see Supplementary information on OSL dating and Table S1), ROX 1.14 is expected to have a minimum paleodose of ∼1700 Gy. Electron spin resonance (ESR) dating using Al-hole center signals and Ti signals gave equivalent doses of > 2000 Gy (see Section 3.1), consistent with expectations. In addition to sample ROX 1.14, another three samples (coded ROX 1.1, 1.2 and 1.3) (Fig. S1), were used to perform bleaching corrections for ESR dating of sample ROX 1.14 (see Section 3.1).

Purified quartz (180–250 μm) was extracted from this sample, first by treatment with HCl and H_2O_2, followed by sieving, heavy liquid separation (using densities of 2.62 and 2.75 g/cm³) and finally 40% HF etching for 40 min. The purity of the quartz extract was checked using the conventional IR depletion test (Duller, 2003). It was was further tested by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using a FEIQuanta 3D FEG dual beam microscope. As expected, the chemical composition of the extract is dominated by Si and O; other elements, such as Al, Mg, Na, Fe and K make up less than 0.5%, indicating that any contamination with feldspars or muscovite is negligible (Fig. S2).

2.2. Instrumentation and measurement protocols

Multi-grain luminescence measurements were carried out using two TL/OSL Risø DA-20 readers (Bøtter-Jensen et al., 2010), equipped with a classic and an automated detection and stimulation head (DASH), respectively. In the classic OSL head, blue (470 nm) and infrared (870 nm) stimulation LEDs deliver ∼40 and ∼130 mW/cm² respectively at the sample position. The automated DASH includes blue (470 nm), infrared (850 nm) and green (525 nm) LEDs providing 80,

300 and 40 mW/cm², respectively. The resulting OSL signals were detected using an EMI 9235QA and a PDM 9107Q-AP-TTL-03 (160–630 nm) photomultiplier respectively in combination with 7.5 mm Hoya U-340 filters. A single grain laser attachment (Bøtter-Jensen et al., 2003) was used for single-grain luminescence measurements of quartz. The stimulation source is a 10mWNd:YVO₄ solid-state diode pumped laser emitting at 532 nm, which can be focused sequentially onto a square grid of 100 grain holes in an aluminium sample disc. Prior to measurements, the empty discs were checked for contamination by promptly measuring (no preheat) the response to a beta dose of 70 Gy. Laboratory irradiations were performed using calibrated $^{90}Sr/^{90}Y$ beta sources mounted on the readers.

Green laser stimulation at 125 °C was performed for 0.9 s in the case of single-grain measurements. Blue or green LED stimulations for 40 s at 125 °C were used for stimulating multi-grain aliquots. A preheat of 260 °C for 10 s and a cut-heat of 220 °C were applied prior to the measurement of the main OSL signal and the test dose signal, respectively. For both single and multi-grain aliquot extended dose response curves, a double SAR protocol (Roberts and Wintle, 2001) employing an IR stimulation at 125 °C (for 40 s) prior to blue or green stimulations was used. In all cases, a blue bleach for 40 s at 280 °C was performed at the end of each SAR cycle. Since low sensitivity of the OSL signal from sedimentary quartz is common in single-grain analyses (e.g., Duller et al., 2000; Yoshida et al., 2000; Duller, 2006), a test dose of 97 Gy was given to increase the chances of a detectable test dose response. For the sake of consistency, the same test dose was used for the multi-grain investigations. All multi-grain measurements were performed using 9.8 mm diameter stainless steel discs having the whole surface covered with silicone oil. In the case of the single-grain analyses, the signal was summed over the initial 0.06 s of stimulation, whereas the background was evaluated from the final 0.15 s, i.e. late background subtraction. For the multi-grain-analyses, the signal was summed over the first 0.3 s of the decay curve and the background was assessed from the 1.69–2.30 s interval, i.e. early background subtraction. Different background integrations were used for single- and multi-grain measurements as a matter of routine application; however, the difference in both single- and multi-grain analyses between data obtained using early and late background integration is not significant (< 1.5%). A 1.5% instrumental error was assumed for uncertainty calculation.

Electron spin resonance analyses were carried out using a Bruker EMX + spectrometer. Samples were measured in the X band at 90 K using a variable temperature unit. A high sensitivity cavity (unloaded quality factor of 15000) was used and samples were rotated in the cavity for collecting several spectra using a programmable goniometer. Samples were measured in high purity quartz tubes and specific care was taken that all samples have the same length. The mass of one sample was approximately 200 mg, with variations of 10% that were taken into account by performing mass normalisation. Measurement parameters employed for recording Al-hole ($[AlO_4]^0$) signals were: temperature 90 K, modulation frequency 100 kHz, modulation amplitude of 1G, 3350 G centerfield with a 300 G sweep width, 120 s sweep time, 40 ms conversion time, 40.96 ms time constant. Microwave power was 2 mW and the sample was rotated 3 times in the cavity. For titanium centres ($[TiO_4M^+]$) the following measurement parameters were used: temperature 90 K, modulation frequency 100 kHz, modulation amplitude 1G, 3490 G centerfield with a 220 G sweep width, 22 s sweep time, 10 s conversion time, 20.48 ms time constant. Microwave power was 10 mW and 30 scans were performed. Signals were quantified using peak to peak height from g = 2.018 to g = 1.993 in the case of Al signals as recommended by Toyoda and Falguères (2003) (see Fig. S3a) and widely used in ESR dating studies, and from g = 1.978 to g = 1.913 in the case of Ti respectively, 'option A' in Duval and Guilarte (2015) (see Fig. S3b). Irradiations were performed using a Nordion Gammacell 220 Co-60 gamma irradiator, with a dose rate of 2 Gy/s at the time of irradiation. Based on Monte Carlo simulation for the geometry used in the irradiations, the dose rate to quartz was estimated to

be 94% of the dose rate to water. The errors for all datasets are at one sigma level.

3. Experimental results and discussions

3.1. Electron spin resonance equivalent doses

It is well known that bleaching of ESR signals usually used for dating remains problematic and poorly understood (see Tissoux et al., 2012 as an example). As such, we have derived equivalent doses using both Al and Ti signals. Toyoda et al. (2000) first proposed such a multiple center approach to address this issue, a procedure later re-inforced by Rink et al. (2007) and Duval and Guilarte (2015). Recently, Duval et al. (2017) recommend that such a multiple center approach should become part of the standard dating procedure. In order to test the procedure, but also to obtain data needed for further bleaching corrections for sample ROX 1.14, we have applied the method to a modern analogue, a Holocene sample with a known age obtained by quartz OSL dating. In order to obtain sufficient material to properly constrain the ESR signals dose response curves, a composite modern analogue was prepared by mixing quartz extracts of the same grain size (125–180 μm) from three Holocene samples (ROX 1.1, 1.2 and 1.3) dated by conventional SAR-OSL using 63–90 μm quartz to 4.8 ± 0.4 ka, 3.7 ± 0.3 ka and 8.3 ± 0.7 ka respectively (see Supplementary information on OSL dating and Table S1). The equivalent dose (~15 Gy) of this modern analogue is thus negligible compared to the natural dose (> 1700 Gy) received by sample ROX 1.14. This modern sample was measured in a multiple aliquot standard added dose pro-tocol, and the dose response curves are presented in Fig. S4. Extra-polation resulted in ESR equivalent doses of 553 ± 48 Gy in the case of Al and 572 ± 50 Gy in the case of Ti signals. These significant apparent residual doses confirm that these ESR signals must be corrected for residual dose in order to obtain accurate equivalent doses. Conse-quently, the ESR signals measured for this modern analogue were used for correcting the ESR signals recorded for sample ROX 1.14, measured in a standard multiple aliquot approach (Fig. 1). The corrected equivalent doses for sample ROX 1.14 using 125–180 μm quartz are 2100 ± 300 Gy for Al-hole signals and 2830 ± 50 Gy for Ti signals. Although the agreement is probably not within uncertainty, derived ages of 1000 ± 160 ka for Al signals and 1360 ± 90 ka for Ti signal confirm an age older than the timing of the Brunhes/Matuyama tran-sition for sample ROX 1.14 and gives us confidence that the sample can be considered as 'infinitely' old from the perspective of quartz OSL dating.

Fig. 2. Average (n = 6) SAR dose response curve constructed using multi-grain aliquots of quartz. The sum of two saturating exponential functions was used for data fitting.

3.2. Single aliquot and single grain OSL dose response curves and equivalent doses

Dose response curves (DRCs) were constructed up to 2500 Gy using 6 multi- and 38 single-grain aliquots (100 grains per single-grain ali-quot) of quartz. The individual multi-grain DRCs are given in Fig. S5. The average dose response curve of the six multi-grain aliquots is pre-sented in Fig. 2. The sensitivity corrected (L_x/T_x) laboratory OSL signal is fully saturated by ~1000 Gy, but the natural L_n/T_n only reaches ~86% of the laboratory saturation level. The closeness to saturation of the natural signal was assessed using the $(L_n/T_n)/(L_x/T_x)_{max}$ ratio, where $(L_x/T_x)_{max}$ represents the average value of the data points in the plateau region of the dose response curve. A $(L_n/T_n)/(L_x/T_x)_{max}$ ratio was computed for each dose response curve and then an average was calculated using the six individual values. Since defining the $(L_x/T_x)_{max}$ value can be problematic when the dose response curve is not smooth, averaging the data points in the plateau region is intended to minimise the contribution from such variations. The laboratory dose response for multi-grain aliquots is well represented by the sum of two saturating exponential functions, i.e. $I(D) = I_0 + A*(1 - \exp(-D/D_{01})) + B*(1 -$
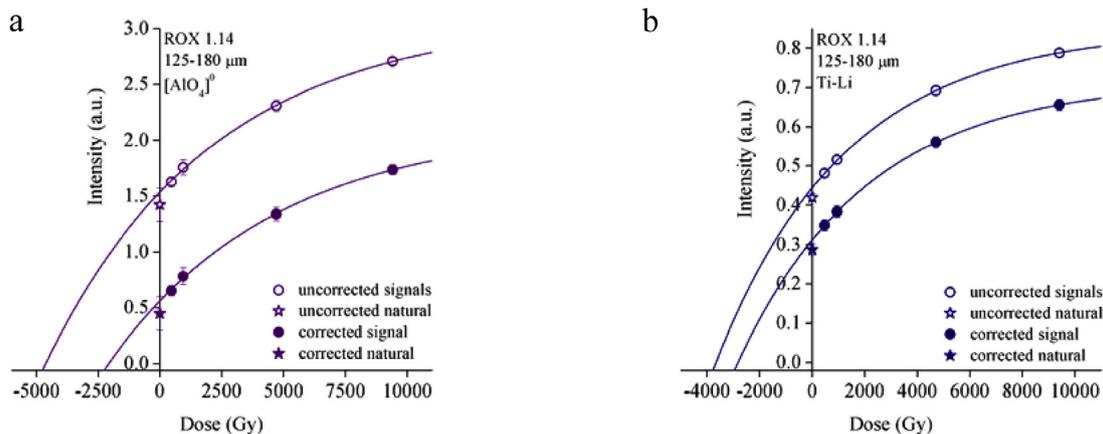

Fig. 1. Dose response curves for Al (a) and Ti (b) paramagnetic centres for ROX 1.14, 125–180 μm quartz. In the case of Al signals each data point represents the average peak to peak intensity derived from 4 measurements, while in the case of Ti-signals measurements were carried out twice. Open symbols represent the signals measured following gamma dose irradiation on top of the natural accrued dose, while filled symbols represent the values obtained after the correction using the natural signals of the modern analogue sample. Dose response curves were fitted with single saturating exponential functions, with saturation parameters of $D_0 = 6770 \pm 1200$ Gy for Al signals and $D_0 = 4920 \pm 90$ Gy for Ti signals.
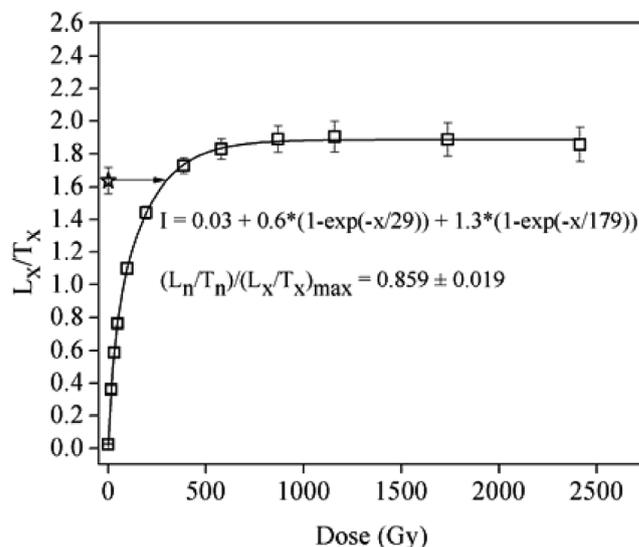
exp(-D/D$_{02}$)), where I is the sensitivity-corrected OSL intensity at dose D, I_0 is a residual luminescence signal, A and B represent the amplitude of the two exponential components and D_{01} and D_{02} are the doses that characterise the curvature of the DRC. Since the natural signal was not found to be in saturation, finite equivalent doses could be derived for multi-grain aliquots of quartz (see Supplementary material on OSL dating). The resulting equivalent dose and corresponding apparent OSL age are given in the supplementary material (Table S1).

In the single grain dataset, less than 10% of the grains were sufficiently bright (i.e. the response to the test dose was known to better than 20%) to allow a dose response curve to be constructed. The dose response curves are highly variable both in shape and in the position of the natural signal relative to the laboratory saturation level. A representative selection of grains classified according to their natural OSL signal intensity is presented in Fig. S6. The single grain datasets are well represented by a single saturating exponential function of the form I (D) = A *(1 – exp((-D – xc)/D$_0$)), where xc is a dose offset. Equivalent doses were determined for 184 grains which passed the rejection criteria used by Thomsen et al. (2016). Both the rejection criteria applied for D$_e$ estimation and the D$_e$ results (Fig. S7) are presented in the supplementary material on OSL dating ("Equivalent doses and OSL ages" section, point b).

3.2.1. Signal intensity variability at individual grain level

Inter-grain OSL intensities for ROX 1.14 are highly variable, the magnitude of the net natural signal ranging from tens of counts to hundred thousand counts recorded in the first 0.06 s of stimulation. The majority of the total OSL signal originates from less than 10% of the measured grains, which is consistent with previously published results for single grains of quartz from sedimentary samples (see Table 1; Jacobs et al., 2003; Duller, 2006).

The grains with natural OSL signals of more than 50 counts recorded in the first 0.06 s of stimulation (353 out of 3,800 measured grains) were classified into five groups based on the intensity of their net natural signal or natural test dose response. The absolute and relative contributions from each group of grains to the total light sum (of the 3,800 measured grains) for both natural and first test dose signal and the number of grains in each group are given in Table 1. More than 70% of the natural and first test dose signals originates from 44 grains which make up ~1.2% of the total measured grains. These grains represent the two most intense groups in Table 1, with 130,000–18,000 and 9,000–2,000 counts recorded in the first 0.06 s of stimulation, respectively. Although numerically dominant, the dimmer grains only make up ~20% of the summed total signal. Besides grouping the grains based on the intensity of their natural signal (as presented in Table 1), other groups were formed based on the intensity of the first test dose signal, e.g. using the grains having more than 50 counts recorded in the first 0.06 s of stimulation of the first test dose signal (data not shown). Irrespective of the grouping criteria, e.g. either by looking at the magnitude of the natural or the magnitude of the first test dose signal, the relative contribution of each group to the total OSL signal is similar.

3.3. Multi and single-grain synthetic dose response curve

A multi-grain synthetic aliquot dose response curve was constructed using the summed OSL signals (summed L$_x$ divided by summed T$_x$) from the six multi-grain dose response curves presented in Fig. S5. The resulting OSL signal and dose response curve are equivalent to that of one large single aliquot containing all the grains from six multi-grain discs. The synthetic dose response curve is displayed in Fig. 3a and it can be seen that the natural signal is at 86% of the laboratory saturation level.

Using single-grain data the individual OSL signals from each measured grain (3,800 in total) were summed, in the attempt to reproduce the single aliquot measurement results. A single-grain aliquot synthetic DRC was constructed using the summed OSL signals from the 3,800 individual grains. The L$_n$/T$_n$ value of this single-grain synthetic DRC is 92% of the laboratory saturation level (Fig. 3b).

3.4. Blue versus green light stimulation

One possible explanation for the difference observed between the fraction of laboratory saturation of the natural signal in the case of multi and single-grain synthetic aliquots may be that optical stimulation was carried out at different wavelengths, i.e. 470 nm (blue) and 525 nm (green) for multi and single-grain measurements, respectively (Thomas et al., 2005). Singarayer and Bailey (2004) have shown that the bleaching rate of the fast and medium components is wavelength dependent.

To test whether green light stimulation gives rise to a higher (L$_n$/T$_n$)/(L$_x$/T$_x$)$_{max}$ ratio than the ratio obtained using blue light stimulation, three multi-grain aliquots were used to construct extended dose response curves. The measurement protocol described in Section 2.2 for multi-grain DRCs was used, except that the OSL stimulation used green light (525 nm, 40 mW/cm^2) instead of blue light (470 nm, 40 mW/cm^2). The average DRC of the three measured aliquots is given in Fig. S8. An average (L$_n$/T$_n$)/(L$_x$/T$_x$)$_{max}$ ratio was calculated using the individual (L$_n$/T$_n$)/(L$_x$/T$_x$)$_{max}$ values determined for each measured aliquot. Again, the natural signal is only 83% of the laboratory saturation. This value is consistent with that obtained when the luminescence signal from multi-grain aliquots was stimulated with blue light. Therefore it is concluded that stimulation with different wavelengths is not the cause of overestimation of the natural L$_n$/T$_n$ saturated signal by the laboratory DRC in the case of the single-grain synthetic DRCs compared to the multi-grain synthetic DRCs.

3.5. Natural signal saturation level as function of brightness

3.5.1. Single grain data

Since the luminescence signal from a multi-grain aliquot is the sum of the signals from all individual grains making up the aliquot, the difference in the closeness of the natural signal to saturation when comparing single-grain to multi-grain synthetic aliquot DRCs may be the result of a different relative contribution from populations of grains

Table 1

Classification of the individual grains into five groups based on the intensity of their net natural signal (counts collected in the first 0.06 s of stimulation). The absolute and relative contributions of each group to the total light sum are given. Note that no grains were found in 9,000 to 18,000 counts group.

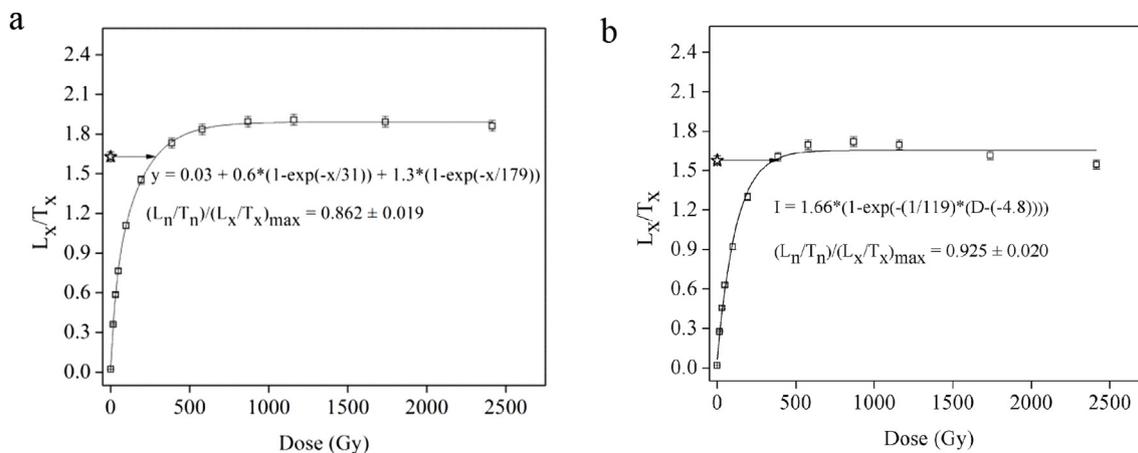|	Sum of all grains	Sum of grains with between:					
		130,000–18,000 counts (Super bright grains)	9,000–2,000 counts	2,000–500 counts	500-200 counts	200-50 counts	130,000–50 counts
Number of grains	3,800	4	40	59	73	177	353
L$_n$ net (counts)	523,408	252,736	166,851	51,056	23,207	17,995	511,845
T$_n$ net (counts)	331,871	136,403	108,803	38,964	15,676	14,710	314,556
% of the total signal for L$_n$	100%	48.3%	31.9%	9.8%	4.4%	3.4%	98%
% of the total signal for T$_n$	100%	41.1%	32.8%	11.7%	4.7%	4.4%	95%

Fig. 3. Synthetic dose response curve constructed using a) the summed OSL signals from 6 multi-grain aliquots and b) the summed OSL signals from 3,800 individual grains of quartz. Data are fitted using a) a sum of two single-saturating exponential functions and b) a single saturating exponential model.

with different characteristics.

Variability in the luminescence brightness of individual grains from a sample plays a major role when a number of individual signals are added as the very bright grains dominate the total light sum. Four super bright grains (with more than 18,000 cts in the first 0.06 s of stimulation of the natural signal) were identified out of the 3,800 grains measured, with one dominant grain displaying 130,000 cts. These super bright grains make up ~50% of the total natural signal, another ~30% contribution coming from the second most bright group, with the natural signal intensity between 2,000–9,000 cts in the 0.06 s of stimulation. With only ~20% contribution from the dimmer grains, the $(L_n/T_n)/(L_x/T_x)_{max}$ ratio corresponding to the total light sum will be dominated by the characteristics of the highly bright grains population.

In order to evaluate the importance of such differential contributions, for each group of grains (as described in section 3.2.1) single-grain synthetic DRCs were constructed by summing the signals from the individual grains. The corresponding sensitivity corrected natural signal was then interpolated onto these synthetic DRCs. Fig. S9 shows a comparison of the single-grain synthetic DRCs for the five groups. The sensitivity corrected natural light level is closer to the laboratory saturation level as the brightness of the grains increases. By plotting the $(L_n/T_n)/(L_x/T_x)_{max}$ ratios as function of the average number of counts collected in the first 0.06 s of stimulation for the natural signal of the grains in each group (Fig. 4, red circles) it can be observed that the ratio increases from 0.81 for the group containing grains with a natural net OSL between 50 and 200 cts collected in the first 0.06 s of stimulation, to 0.98 for the super bright grains group (> 18,000 counts recorded in the first 0.06 s of stimulation). Since the natural signals are expected to show a higher degree of inherent variability due to e.g. microdosimetric effects, the grains were also sorted according to the intensity of the first test dose signal (T_n) which should not be influenced by such issues; the resulting $(L_n/T_n)/(L_x/T_x)_{max}$ ratios for each group of grains are plotted against the average number of counts collected in the first 0.06 s of stimulation in Fig. 4. (black circles). The two datasets are very similar, indicating that signal selection has no significant impact on the observed trend. A potential cause of this trend could be a higher thermal instability of the signal from the dimmer grains, as indicated by a lower L_x/T_x ratio with decreasing brightness of the grains observed for a randomly chosen regenerative dose (see Fig. S10); since the preheat temperature (260 °C) is higher than the cutheat temperature (220 °C), a lower L_x/T_x ratio is expected for the dim grains if they are more thermally unstable than the brighter grains. Further experiments on single grains of quartz (e.g. preheat plateau and isothermal decay experiments) are needed in order to confirm or disprove this hypothesis.
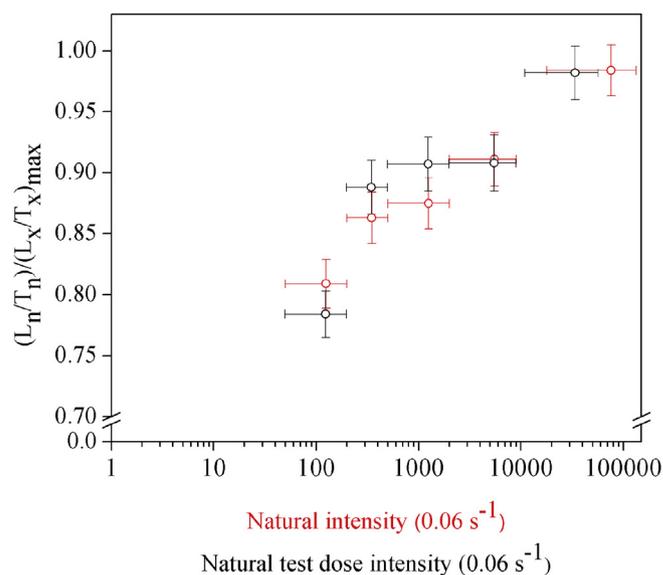

Fig. 4. The ratios $(L_n/T_n)/(L_x/T_x)_{max}$ as function of the average number of counts recorded in the first 0.06 s for the natural signal of the grains in each group are shown as red circles (obtained using the data in Fig. S9). Same data obtained for groups of grains constituted based on the intensity of the first test dose signal is represented with black circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.5.2. Implications for multi-grain aliquots

We now investigate whether the correlation between the closeness to saturation of the natural signal and the brightness of individual grains is reflected in the multi-grain data. Investigations on multi-grain aliquots of quartz from ROX 1.14 were not possible due to insufficient coarse material. To explore the existence of such a dependency in multi-grain aliquots, data for the oldest four samples collected from L2 unit (corresponding to MIS 6) at the Costinesti loess-paleosol section in Romania were re-analysed. This section was previously described by Timar-Gabor and Wintle (2013) and Constantin et al. (2014) and samples CST 22 – CST 25 were previously shown to be in field saturation (Fig. S11). $(L_n/T_n)/(L_x/T_x)_{max}$ ratios were calculated for these samples for 9 to 13 multi-grain aliquots per sample using 63–90 μm quartz. The considered value for $(L_x/T_x)_{max}$ is the value obtained for a regenerative dose of 1000 Gy. Since the dose response curves for these samples were constructed only up to 1000 Gy, $(L_x/T_x)_{max}$ could not be calculated as the average value of the data points in the plateau region;

however, 1000 Gy is a high enough dose for the laboratory signal to be in saturation (see Timar-Gabor et al., 2017).

Despite the reduced number of aliquots measured for each of the these samples (between 9 and 13), an increasing $(L_n/T_n)/(L_x/T_x)_{max}$ ratio can be observed as function of the signal brightness for both natural (Figs. S12a, b, c, d) and first test dose (Figs. S12e, f, g, h) signals. The same procedure was applied for one sample collected from the Dnieper till at Stayky loess-paleosol section in Ukraine (Veres et al., submitted) with similar results (see Fig. S13 and Fig. S14). This indicates that the dependency of the $(L_n/T_n)/(L_x/T_x)_{max}$ ratio on the brightness of the grains observed for the single-grain synthetic aliquots is also detectable at the multi-grain aliquot level. However, it should be noted that for some samples (e.g. CST 25 and STY 1.10) this pattern is slightly perceivable.

4. Conclusions

Single and multi-grain single aliquot regenerative (SAR) OSL investigations were carried out for a coarse-grained (180–250 μm) quartz sample extracted from loess collected below the Brunhes/Matuyama transition at the Roksolany section in Ukraine. The aim was to investigate the consistency of the sensitivity-corrected natural OSL signal and the laboratory SAR saturation level. Electron spin resonance dating of this sample using a multiple center approach (Al and Ti signals) resulted in ages above 1000 ka, confirming that the accrued dose (about 2000 Gy) of the sample falls beyond the limit of standard OSL equivalent dose measurement techniques. However, when multi-grain SAR-OSL extended dose response curves were constructed, the natural signal was found to be 14% below the laboratory saturation level.

It was found that for the single-grain synthetic DRC the natural signal is closer to the laboratory saturation level (92%) than in the case of the multi-grain synthetic DRC (86%). This difference can not be attributed to different stimulation wavelengths, i.e. blue and green light stimulation for multi- and single-grain measurements, respectively.

When groups of grains were synthetically formed based on the intensity of either the natural signal or the first test dose signal, it was observed that the $(L_n/T_n)/(L_x/T_x)_{max}$ ratio increases as function of the signal brightness. Although less clear, a similar trend was observed for multi-grain aliquot data obtained for coarse-grained (63–90 μm) quartz extracts from Costinesti (Romania) and Styky (Ukraine) loess-paleosol sections. It is concluded that variations in the contribution from populations of grains with different levels of brightness can be considered a controlling factor in the closeness of the natural signal to laboratory saturation SAR OSL level for this 'infinitely' old sample.

The results obtained in this study contribute to a better understanding of previously reported cases in which the natural signal of 'infinitely old' quartz samples was found to be below the laboratory saturation level. Further OSL investigations are needed in order to examine whether this finding contributes to the underestimation often reported in literature for quartz samples with expected paleodosesdoses higher than ~200 Gy. A comparative study of the properties of the highly bright and dim quartz grains using different physical methods could definitely bring more information on this issue.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx. doi.org/10.1016/j.radmeas.2018.06.008.

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