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Bleaching studies on Al-hole ([AlO$_4$/h]$^0$) electron spin resonance (ESR) signal in sedimentary quartz

A. Timar-Gabor$^{a,b,*}$, A. Chruścińska$^c$, K. Benzid$^b$, K.E. Fitzsimmons$^d$, R. Begy$^{a,b}$, M. Bailey$^e$

$^a$ Faculty of Environmental Science and Engineering, Babeș-Bolyai University, Cluj-Napoca, Romania
$^b$ Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeș-Bolyai University, Cluj-Napoca, Romania
$^c$ Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland
$^d$ Research Group for Terrestrial Palaeoclimates, Max Planck Institute for Chemistry, Mainz, Germany
$^e$ Risø High Dose Reference Laboratory, Technical University of Denmark, DTU Risø Campus, Roskilde, Denmark

**ABSTRACT**

Electron spin resonance (ESR) dating of sediments using quartz is most commonly used for older sediments (>100 ka), since large residuals render the ESR signal unsuitable for dating young sediments. The multiple-centre approach (utilising both Ti and [AlO$_4$/h]$^0$ signals) is usually used to test the resetting of the signals used for ESR dating. Here we work towards a better understanding of, and correction for, the residual signal in ESR samples of sedimentary quartz. We undertook multiple-centre ESR measurements using quartz [AlO$_4$/h]$^0$ and Ti signals on young aeolian samples of different grain sizes which have been independently dated using optically stimulated luminescence (OSL). Our results demonstrate that [AlO$_4$/h]$^0$ signal yields residuals indicating equivalent doses of about 500 Gy, substantially older than expected for the known OSL equivalent doses in the range of 8–37 Gy. The decay of [AlO$_4$/h]$^0$ signal as function of bleaching time can be represented by an exponential function. We investigate the dependence of the residual magnitude of the ESR signal as a function of the previous given dose and observe an exponential increase in the residual signal with dose. Such observations are consistent with the results of luminescence process modelling conducted for a model comprising two luminescence centres and several traps, one of which is a so-called deep disconnected trap that cannot be emptied during optical stimulation. We propose that bleaching occurs through an electron-hole recombination process with electrons released from optically sensitive traps. In addition to our new insights into the bleaching mechanisms of the [AlO$_4$/h]$^0$ ESR signal, we discuss the implications for the procedures used for performing residual dose corrections in ESR dating. We recommend that modern analogues be used in addition to laboratory-bleached samples when performing residual dose corrections.

**1. Introduction**

The main quartz electron spin resonance (ESR) signals used for dating sediments derive from defects related to the Al and Ti centres. Two major challenges confront researchers in this field: firstly, the accurate quantification of residual contained within the signal is as yet poorly constrained; and secondly, the physical mechanism for the bleaching of [AlO$_4$/h]$^0$ signal, and consequently understanding the nature of the signal which is being used for dating, is inadequately understood. This leads to potential flaws in the fundamental assumptions used.

Although sunlight exposure does bleach the ESR intensity of the [AlO$_4$/h]$^0$ centre, this is not complete and the signal is reset only to a non-bleachable residual level (Toyoda et al., 2000; Duval et al., 2017).

To determine an equivalent dose for sedimentary quartz using the [AlO$_4$/h]$^0$ centre, it is important that its ESR signal was either zeroed by light at the time of interest, or its initial value can be inferred. Given the substantial contribution of residual signals to the measured signal of interest in sedimentary quartz, the residual ESR signal needs to be determined, and then subtracted, from the measured ESR intensities prior to equivalent dose determination (Voinchet et al., 2003).

The most widely accepted approach to address this is using a multiple-centre approach (Toyoda et al., 2000). ESR ages are considered accurate only if the equivalent dose ($D_e$) estimates based on Al and Ti paramagnetic signals agree (Rink et al., 2007). The multiple-centre protocol has since been adopted as standard dating procedure (Duval...
and Guilarte, 2015; Duval et al., 2017). Despite this accepted approach, substantial residuals, particularly in the case of [AlO₄/h]⁰ signals, are expected in ESR measurements, even following prolonged light exposure. As yet, the true magnitude of ESR signal residuals remains poorly quantified.

Most authors report residual values as a proportion of natural signal intensity; for example, Walther and Zilles (1994) report a residual level at 44% of the natural, and Voinchet et al. (2003) report a maximum bleached value of 50% of the natural. Following light exposure for 80 h under a SOL2 solar simulator (equivalent to 53 days of 12 h exposure to sunlight), Rink et al. (2007) observed that the remaining signal was 56% of the natural ESR intensity measured prior to light exposure. Voinchet et al. (2015) examined modern samples from various sedimentary environments (fluvial, marine and aeolian) and reported bleaching rates (% of the total signal that can be bleached) of up to 22%. Tsukamoto et al. (2017), also working with modern aeolian samples, quantified the [AlO₄/h]⁰ ESR equivalent doses and reported values of >1700, >1200 Gy, 463, 238 and 134 Gy.

The first ESR natural dose-response curve for Chinese loess (aeolian sedimentary quartz) was recently derived and indicated an intercept at about 500 Gy for [AlO₄/h]⁰ (Tsukamoto et al., 2018). Natural dose response curves can be constructed only in the presence of independent age control for a suite of samples of different ages. For extended loess-palaeosol sequences this age control is available through the correspondence of the ages of loess/palaeosol boundaries to the ages from marine isotope data as time marker horizons. In ESR dating natural dose response curves are constructed by plotting the natural signal intensity of the paramagnetic centres against the expected natural dose. As such, the intercept of the natural dose response curve can be regarded as a best estimate of the residual signal. The investigation of natural dose response curves is an excellent test for the accuracy of dating. However, besides the ESR study of Tsukamoto et al. (2018), to our knowledge, this approach was so far applied only in two other studies on optically stimulated luminescence dating of loess (Chapat et al., 2012; Timar-Gabor and Wintle, 2013) and has yet to be applied systematically for different signals as well as different types of samples.

Here we investigate the magnitude of residual dose by applying a multiple–aliquot, additive-dose approach to quantify the residual doses of modern and young sedimentary quartz samples of different origins. This investigation has the advantage that the true equivalent dose is known, since all samples have been securely dated using optically stimulated luminescence (OSL).

The second central challenge for ESR dating concerns our limited understanding of the physical bleaching mechanism of [AlO₄/h]⁰ centres. The uncertainty surrounding this mechanism has broader implications for fundamental assumptions regarding the recombination process and utility of quartz for dating. Al³⁺ is one of the most common substitutional cations replacing Si⁴⁺ within the quartz crystal lattice; charge is compensated by a mono-valent cation (generally Li⁺, Na⁺ or H⁺). It is widely accepted that upon irradiation at room temperature, the defect traps an electronic hole created by ionising irradiation. By this and the diffusion of the cation, the [AlO₄/h]⁰ paramagnetic centre is formed. In luminescence dating terminology, this Al defect represents a possible recombination centre.

A terminology of deep (unbleachable) aluminium traps and shallow (bleachable) aluminium traps has been used in ESR dating literature to explain the observations on the unbleachable component of the ESR signal (Voineas et al., 2012; Voinchet et al., 2015). Based on isothermal annealing experiments thermal activation energies between 1.3 and 2.4 eV were obtained for [AlO₄/h]⁰ (summarised by Richter et al. (2019)), while density functional theory calculations yield a defect state of 2.2 eV above the valence band edge (Gudmundsdottir et al., 2015). It is hard to reconcile these with the proposed model of two components, one that is bleachable and one which is not. The importance of this [AlO₄/h]⁰ defect as an electron-hole recombination centre has been previously proposed and widely discussed (Martini et al., 1995, 1999; Itoh et al., 2002; Williams and Spooner, 2018). If one considers the bleaching mechanism to be due to electrons released from unknown trapping center recombining at the [AlO₄/h]⁰ centres, which act as recombination centres, we can expect residuals to be preserved in our signal, as explained below.

Al is by far the most significant impurity in quartz, its concentration surpassing the concentration of Ti, Ge or other impurity atoms in most natural quartz minerals (see Preusser et al., 2009 and references). When [AlO₄/h]⁰ is formed during irradiation, for each hole trapped at Al-sites, charge neutrality principle dictates that there must be a corresponding electron trapped as well. Our ongoing studies show that [AlO₄/h]⁰ ESR signal is not fully saturated at doses as high as 100 kGy (Benzid and Timar-Gabor, in press), high above the saturation limit of other dose dependent ESR or luminescence signals. Based on all these, it is reasonable to assume that in irradiated quartz the [AlO₄/h]⁰ defect is significantly more abundant than other individual impurity-related electron traps. The bleaching of different thermoluminescence signals in quartz is highly complex (e.g. Chruścińska, and Przęszęka, 2005). It is well known that not all electron traps are light sensitive, and there is charge trapped in deep, thermally disconnected traps as well, facts long taken into account in previous models for optical bleaching of luminescence signals (McKeever, 1994; Chruścińska, 2006; Bailey, 2001). If the bleaching mechanism of [AlO₄/h]⁰ signal is electron-hole recombination, then it follows that residual values will likely be dependent on preceding accrued doses as there will be more holes trapped at Al sites than electrons that can be released during bleaching from light sensitive electron traps. It is reasonable to expect that the difference between the hole population trapped at Al sites and electron population trapped in bleachable electron traps will increase with dose, up to a certain saturation level.

This possibility of having dose-dependent [AlO₄/h]⁰ signal residuals has not been systematically investigated experimentally, even though it poses major problems for dating protocols that apply residual dose corrections. The few investigations which have so far been undertaken give substantial cause for concern. In one example, samples irradiated with a dose of 6000 Gy on top of the natural and then exposed to the equivalent of 119 days of sunlight yielded signal intensities 12% of the initial value, but still had not reached the same residual level observed in the non-irradiated natural sample (Rink et al., 2007). In another study, dose dependence was observed in quartz from Quaternary volcanic tephra but not in alluvial quartz (Tissoux et al., 2012). Given the implications for reliable dating of dose-dependent residuals in Al paramagnetic signal, clearly a more systematic study of this phenomenon is required.

Here, we investigate the dependence of the [AlO₄/h]⁰ signal residuals as a function of given dose for sedimentary quartz samples. We compare our results with the outcomes of computer simulations of the charge carrier transport processes during the irradiation and the optical bleaching.

2. Materials and methods

2.1. Samples

We chose to work with sedimentary quartz samples of different grain sizes from different locations (sand from Australia and loess from Ukraine) that had previously been securely dated by OSL. We selected our samples based on depositional age, since we aimed to investigate modern analogues/young samples, in other words samples that have been bleached as recently as possible, as well as based on the availability of sufficient material for ESR measurements, and the high purity of the quartz extracts. Quartz was extracted according to standard OSL preparation techniques, under subdued red light. More detailed information on sample preparation is provided in the respective OSL dating articles (EVA samples: Fitzsimmons et al., 2014; Rox MIX: An Cheitri-Deacu et al., 2019).
Investigations were carried out on different grain-size fractions of coarse (>90 μm) grains. Coarser grains were selected for measurement since we have previously shown that when performing standard measurements of the Al signal, the spectrum is interfered with by a variety of peroxo signals whose intensities are much more significant in smaller grain sizes (Timar-Gabor, 2018). For coarse grains, based on Easy Spin spectra simulations (data not shown here) we are confident that the signal is dominated by [AlO₂/h]³⁺. Also, it was inferred that coarser grain sizes are better bleached and more appropriate for ESR analysis (Voinchetch et al., 2015). Table 1 summarises the relevant sample information. The sample mass was 200 mg with a relative variation of maximum 5%. Mass normalisation was performed for measured signals where relevant.

2.2. Instrumentation and measurement protocols

ESR analyses were carried out using an X band Bruker EMX plus spectrometer equipped with a variable temperature unit. The samples had not been exposed to direct sunlight prior to ESR measurement and their exposure to weak natural light during measurements was kept to a minimum, unless stated otherwise. Parameters employed for recording Al paramagnetic signals included measurement temperature of 90 K; modulation frequency 100 kHz; modulation amplitude 0.1 mT; 330 mT centrefield; 30 ms sweep width; 120 s sweep time; 40 ms conversion time; 40.96 ms time constant; microwave power was 2 mW. A single scan was carried out and the average of two to five measurements was computed. For Ti centres the measurement temperature was kept at 90 K; modulation frequency 100 kHz; modulation amplitude 0.1 mT; 349 mT centrefield with a 22 ms sweep width; 22 s sweep time; 10 ms conversion time; 20.48 ms time constant. Microwave power was 10 mW and 20 scans were performed. As in the case of [AlO₂/h]³⁺ signals, the average of two to five measurements was computed. Signals for [AlO₂/h]³⁺ and [TiO₃/Li]²⁺ respectively were quantified using peak to peak height from g = 2.018 to g = 1.993 (Toyoda and Falguères, 2003) and g = 1.978 to g = 1.913 (Duval and Guilarte, 2015) (Fig. 1). Unless otherwise stated, three measurements were carried out over different days on a single aliquot for each dose point. Samples have not been preheated prior to ESR measurements.

Theloluminescence measurements were carried out using a Risø TL/OSL DA-20 reader with automated Detection and Stimulation Head (DASH) (Lapp et al., 2015). For these measurements, 9 mm aliquots were prepared by depositing a monolayer of grains on stainless steel discs. Each measurement was carried out on a minimum of five different aliquots. No preheat was applied.

Irradiation was undertaken at the Centre for Nuclear Technologies, Technical University of Denmark (DTU NUTECH) using a calibrated ⁶⁰Co-60 gamma cell, with a dose rate of about 2 Gy/s (dose rate to water) at the time of irradiation. Dose rate to quartz was estimated to be 0.941 (with a relative error of 2.2%) of dose rate to water based on Monte Carlo simulation considering the irradiation geometry used.

Light exposure under controlled laboratory conditions was carried out using an array of TL29D16/09N lamps (spectral characteristics are similar to natural sunlight and can be found in Petrušić et al., 2011), delivering a power of approximately 1000 W/m². We have estimated that 1 h of exposure to this lamp corresponds to 1 h of daylight exposure during summertime.

2.3. Modelling

A kinetic model used in the simulations of electron and hole transport during trap filling (irradiation) and bleaching, together with the values of kinetic parameters, is presented in Section 3.3. All calculations were performed using the differential equation solver – ode15s, which is specially designed in the MATLAB environment for stiff equation sets such as the kinetic equations used here.

3. Results and discussion

3.1. ESR equivalent doses obtained using modern analogues (young sedimentary samples)

For quantifying the values of the residual dose, we measured young aeolian samples that had previously been dated using OSL (equivalent doses of 8, 15 and 37 Gy, respectively (Fitzsimmons et al., 2014, Anechitei-Deacu et al., 2019). Such equivalent doses are effectively negligible for ESR dating given the dose range usually employed in this method. A standard additive dose procedure was applied, the equivalent dose being determined by extrapolation.

![Fig. 1. Comparison of ESR spectra line shape for [AlO₂/h]³⁺ and Ti signals, dominated by [TiO₃/Li]²⁺ from the Rox MIX 125–180 μm quartz sample, prior and subsequent to 1788 h of light exposure.](image-url)
The results obtained using both [TiO$_4$/Li]$^0$ and [AlO$_4$/h]$^0$ signals for 125–180 μm quartz from Ukrainian loess, and three different grain sizes of quartz (90–125 μm, 125–180 μm and 180–212 μm) from Australian sand, are presented in Table 1. The corresponding dose response curves are depicted in Figure S1 (supplementary material). Despite relative large uncertainties, it is evident that Al signals preserve substantial residual dose values of around 500 Gy. Quantifying the intensities of the [AlO$_4$/h]$^0$ ESR signal using peak-to-peak intensities of the first peak (visible hyperfine transition) as described by Tsukamoto et al. (2018), resulted in values of the residuals of a similar magnitude.

By comparison, the Ti signals are more easily bleached and yield lower residuals corresponding in general to doses on the order of 100 Gy, although the large error due to limited number of data points prevents more precise estimation. The values obtained are similar to the values obtained by Tsukamoto et al. (2017) on modern aeolian sediments and it is interesting to note that they are not consistent with zero.

Fig. 1 shows that prolonged exposure of samples to light reduces the Ti ESR signal to zero; this is however not the case for [AlO$_4$/h]$^0$ ESR signal. The shape of the [AlO$_4$/h]$^0$ ESR signal does not change after exposure to light. Even after 1788 h of light exposure, the hyperfine transitions of the [AlO$_4$/h]$^0$ ESR signal (Yokoyama et al., 1985) remains clearly visible (upper panel of Fig. 1).

3.2. Bleaching kinetics of [AlO$_4$/h]$^0$ signals and dependence of [AlO$_4$/h]$^0$ residual signal as function of previous dose

We investigated the effect of bleaching as a function of previous given doses for the Rox MIX sample. Subsamples were given different doses, exposed to light for variable lengths of time (360 h, 485 h, 585 h, 685 h, 802 h, 1129 h, 1629 h, and 1788 h), with the dose-response curve measured after each exposure. The first exposure (360 h) was performed under natural daylight conditions during summertime (equivalent to 30 days of sunlight). All subsequent exposures were carried out under the lamps (Section 2.2). The results are shown in Fig. 2. Despite the long exposure times, no signals reach zero. In order to confirm that these non-zero signals indeed represent residual values for the [AlO$_4$/h]$^0$ signal following light exposure, we additionally exposed two of the subsamples bleached for 1788 h (both aliquots of the natural sample and of material irradiated with approximately 10000 Gy) to a high flux of violet photons. After further exposing these subsamples for 10 min to the 405 nm (violet) 100 mW power laser in a Riso TL/OSL reader (Jain, 2009), the residual [AlO$_4$/h]$^0$ signal did not change.

Our experimental results show moreover that larger applied doses result in larger residual values. Prolonged light exposure reduces the natural signal to ~70% of its initial value. In the case of subsamples irradiated with about 1000 Gy in addition to the natural dose, the reduction in natural signal is up to 40%. Furthermore, in the case of an added applied dose of about 40000 Gy, despite the signal being reduced to about 30% of its initial value, the peak-to-peak intensity (expressed as arbitrary units of this residual) is 1.7 times higher than the residual obtained following the bleaching of the natural, and 1.25 times the value of the natural unbleached signal.

For the natural sample as well as for the samples for which laboratory doses were given on top of the natural accrued dose, the magnitude of the remaining [AlO$_4$/h]$^0$ signal as function of bleaching time can be fitted by a single exponential decay function of the form:

$$ S = S_0 \exp \left( -\frac{t}{\tau} \right) + S_{res} $$

(1)

Where $S$ is the value of the signal measured following an exposure time, $S_0$ is the amplitude, $t$ is the exposure time, $\tau$ is a decay constant characteristic of the bleaching process, and $S_{res}$ is the residual value.

The results for all investigated doses are presented in Table S1. It is important to note that the use of a hyperbolic function (Walther and Zilles, 1994) or a sum of more than one exponential function neither represents the dataset well nor improves the fit.

Fig. 3 presents the dependence of the normalised ESR signal as a function of the bleaching time recorded for both the natural and four irradiated subsamples of sample Rox MIX.

We found that the decay rate did not depend significantly on the preceding dose (column 6 in Table S1, supplementary material). This result suggests that the same physical process is taking place irrespective of the magnitude of the given dose, at least in the investigated dose range. However, the value of the residual increases with the previous dose.

The residual signal values (denoted by $S_{res}$ in function (1)) are plotted as a function of previous given dose (Fig. 4). A single saturating exponential model was observed to represent the trend reasonably well:

$$ S_{res} = S_{res} \max \left( 1 - \exp \left( -\frac{(D - D_0)}{D_{\text{th}}} \right) \right) $$

(2)

![Fig. 2. Magnitude of the [AlO$_4$/h]$^0$ ESR signals (Rox MIX 125–180 μm quartz) as function of given dose before and after bleaching for different time durations. Black squares correspond to the dose response curve used for equivalent dose estimation (Figure S1). Each data point represents the average of two measurements. The lowest dose data point represents the natural. Note the logarithmic scale. For clarity reasons, the dose scale of the natural samples is shifted to 50 Gy.](image1)

![Fig. 3. [AlO$_4$/h]$^0$ ESR signals as function of bleaching time for Rox MIX sample. All values are normalised to the value of the unbleached signal. Data are shown for subsamples of the natural and of subsamples receiving four different given doses. Each data point represents the average of 2 measurements. The data was fitted using a single exponential decay function.](image2)
where $S_{\text{res}}$ is the value of the residual, $S_{\text{res max}}$ is the amplitude, $D$ represents the value of the previous given dose, $D_c$ is the intercept, and $D_0$ is the dose saturation characteristic.

For the Rox MIX dataset presented in Fig. 4, values of $S_{\text{res max}} = (1.3 \pm 0.6)$ a.u., $D_c = (16 \pm 18) \times 10^3$ Gy, and $D_0 = (22 \pm 12) \times 10^3$ Gy were obtained. The large errors are to be expected due to the scatter of the data points, as the residual signals were determined by exponential extrapolation of the signal decay with light exposure time. $D_c$ is consistent to zero within error. $D_0$ is a parameter that characterises the onset of saturation of the exponential dependence. For doses larger than $2D_0$ one expects that the residuals do not longer significantly increase with dose.

The dependence of the residual signal with dose, as observed above, can be expected due to charge neutrality, if: the $[\text{AlO}_4^-/\text{h}^-]$ defects acting as a recombination centre; the bleaching mechanism is electron-hole recombination; electron traps are emptied selectively by exposure to light; and if there is charge trapped in deep thermally disconnected traps. These are all reasonable assumption give the knowledge available so far on luminescence processes in quartz. Although further work is needed to prove beyond doubt that this mechanism is at play, results of the modelling for simple luminescence models, presented in the next subsection, show a very similar behaviour of the concentration of holes in recombination centres.

Partial supporting information is obtained by thermoluminescence (TL) measurements. It is still debatable whether one can see the emission of $[\text{AlO}_4^-/\text{h}^-]$ defects in TL, however this defect has been proposed as a possible recombination centre. For example, in a recent study, Williams and Spooner proposed a model that predicts $[\text{AlO}_4^-/\text{h}^-]$ emissions at $380$ nm, $394$ nm and $408$ nm (Williams and Spooner, 2018).

We recorded glow curves on quartz from the Rox MIX bleached sample (exposed to the lamp for 1788 h). Measurements have been carried out on the same material that was previously gamma irradiated and measured by ESR. Thermoluminescence signals were recorded up to $500$ °C without any preheat. Emissions in the high temperature ($300$–$500$ °C) range under both UV (Hoya U 340; 260–400 nm with maximum transmittance at $340$ nm) and blue detection windows (Schott BG-39 and BG-3: 330–480 nm, with maximum transmittance at about $400$ nm) were observed (Fig. 5a and b). The signal detected through the blue filter is significantly more intense than the one detected through the UV window. At this point it remains to be investigated through more precise spectroscopic techniques whether these signals represent two separate emissions, or we are partially detecting a strong blue emission through the Hoya filter, especially as the spectral regions of the filters partially overlap.

Fig. 4. Values for absolute $[\text{AlO}_4^-/\text{h}^-]$ ESR residual signals (a.u.) (sample Rox MIX) represented as a function of previous given dose. The data is fitted using a single saturating exponential function. The plotted values of the residual were obtained based on exponential fitting of signal dependence as a function of bleaching time. Please note the logarithmic scale.

Fig. 5. Average (5–12 aliquots per dose) TL glow curves obtained on Rox MIX sample previously irradiated with 1882, 18820 and 37640 Gy, respectively, recorded under Hoya U340 filter (a) and a combination of Schott BG-39 and BG-3 filters (b). The heating rate was $5$ °C/s (c) TL integrals (300–500 °C) of the emission recorded under Hoya U 320, as function of the gamma dose given before the extended bleaching. Each data point presents the average of 5–17 measurements. (d) Same TL integrals for the blue filter pack. Please note the logarithmic scale. As in the case of data presented in Fig. 4, data presented in panels c) and d) was fitted using a saturating exponential function of the form $T_L = T_L_{\text{res max}} (1 - \exp (-D/D_c)/D_0)$. The parameters obtained from fitting are $T_L_{\text{res max}} = (1 \pm 400) \times 10^4$ cts, $D_c = (2 \pm 5) \times 10^5$ Gy, $D_0 = (700 \pm 2) \times 10^5$ Gy in the case of the emission recorded through Hoya U 340 and $L_{\text{res max}} = (1 \pm 2) \times 10^5$ cts, $D_c = (8 \pm 6) \times 10^5$ Gy, $D_0 = (2 \pm 1) \times 10^5$ Gy for the blue filter, respectively. A sigmoid function (depicted with a dotted line) seems to fit the data better, but the interpretation of such a model remains yet to be understood. Please note that the dependencies presented in Fig. 5a and d can only be compared to the one depicted in Fig. 4 qualitatively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
ESR investigations conducted in our laboratory on heated samples of calibration quartz and other sedimentary quartz samples show that $[\text{AlO}_4/\text{h}]^3$ signal is fully annealed only at temperatures about 500 °C (Figure S2). As such, $[\text{AlO}_4/\text{h}]^3$ centres could be a centre involved in the production of these thermoluminescence signals. We acknowledge the possibility that other possible recombination centres besides $[\text{AlO}_4/\text{h}]^3$ centres could also be at play and we are currently investigating this. Nevertheless, the integrals of both these recorded signals are dose dependent, showing a remarkable increase for previous given doses above 10000 Gy (Fig. 5c). This trend is very similar to the one observed for the residual $[\text{AlO}_4/\text{h}]^3$ ESR signal (Fig. 4).

3.3. Simulations of the charge carrier transport during optical bleaching

The mechanism of generation of the residuum of hole concentration in the hole centre after the optical bleaching and the dependence of the residuum on the dose previously absorbed in a sample may be explained using the simulations of the charge transfer in the crystal during the irradiation and the optical bleaching. Such simulations were performed for a kinetic model including four traps and two hole centres (recombination centres). Two of the traps are emptied during the bleaching (bleachable traps) and are thermally stable during irradiation and bleaching. Another trap is shallower than the bleachable traps, it is not thermally stable and is also slowly optically emptied. The fourth trap is deep and is not thermally or optically emptied in the simulated processes (Fig. 6).

During the simulations, the number of holes remaining in the recombination centres after the optical bleaching was monitored for various times of irradiation and bleaching. The model used in simulations is significantly simpler than the model of band structure of quartz, which usually contains more than two recombination centres and more than four kinds of traps. Our intention, however, was not to reconstruct in detail the processes in quartz, as in our opinion the current state of knowledge is not sufficient for the purpose of such reconstructions.

For the above described model, the following system of differential equations (so-called kinetics equations) has been solved to simulate in detail the processes in quartz, as in our opinion the current state of knowledge is not sufficient for the purpose of such reconstructions.

\[
\frac{dn_i}{dt} = -s \cdot \exp(-E_i/kT) - f \cdot \sigma \cdot n_i + A_i (N_i - n_i) \cdot n_c \quad ; \quad i = 1, ..., 4 \quad ;
\]

\[
\frac{dn_j}{dt} = A_{ij} (M_j - m_j) \cdot m_j - \beta_j m_j n_i \quad ; \quad j = 1, 2;
\]

Where $N_i$ (cm$^{-3}$) and $n_i$ (cm$^{-3}$), $i=1, ..., 4$, are the concentrations of trapping states and trapped electrons in the traps, respectively; $M_j$ (cm$^{-3}$) and $m_j$ (cm$^{-3}$), $j=1, 2$, are the concentrations of recombination centres and the concentrations of holes trapped in these centres; $n_c$ (cm$^{-3}$) and $m_c$ (cm$^{-3}$) are the free electrons and holes, respectively; $A_1$ (cm$^{-3}$ s$^{-1}$), $i=1, ..., 4$, are the probabilities of electron trapping in the traps, $A_{ij}$ (cm$^{-3}$ s$^{-1}$) are the probabilities of hole trapping in the recombination centres, $\beta_j$ (cm$^{-3}$ s$^{-1}$), $j=1, 2$, are the probabilities of a free electron recombination with a hole trapped in the recombination centres; $R$ is the intensity of the excitation irradiation producing pairs of free electrons and holes (it is taken as 10$^{16}$ cm$^{-3}$ s$^{-1}$ during the excitation process and 0 for other processes), $E_i$ (eV) and $s_i$ (s$^{-1}$), $i=1, ..., 4$, are the depths and the frequency factors of the traps, respectively; $\sigma_i$ (cm$^2$), $i=1, ..., 3$, are the optical cross-sections of the traps; $f$ is the photon flux density of the light used for the optical stimulation (here is taken as 10$^{15}$ cm$^{-2}$ s$^{-1}$ during the bleaching while $f = 0$ during the excitation and relaxation).

The values of model parameters that were constant during all simulations are: $A_1 = A_2 = A_3 = A_4 = 10^{-10}$ cm$^{-3}$ s$^{-1}$; $N_1 = N_2 = N_3 = 10^{12}$ cm$^{-3}$; $N_4 = 2 \cdot 10^{12}$ cm$^{-3}$; $\beta_1 = 5 \cdot 10^{-8}$ cm$^2$ s$^{-1}$; $\beta_2 = 10^{-8}$ cm$^2$ s$^{-1}$; $A_{11} = A_{21} = 10^{-11}$ cm$^{-3}$; $M_1 = M_2 = 10^{13}$ cm$^{-3}$; $E_1 = 0.97$ eV, $s_1 = 5 \cdot 10^{-12}$ s$^{-1}$; $E_2 = 1.6$ eV, $s_2 = 5 \cdot 10^{14}$ s$^{-1}$; $E_3 = 2$ eV, $s_3 = 5 \cdot 10^{-14}$ s$^{-1}$; $E_4 = 2$ eV, $s_4 = 10^{10}$ s$^{-1}$; $T = 293$ K; $\sigma_1 = 10^{-16}$ cm$^2$; $\sigma_2 = 2 \cdot 10^{-17}$ cm$^2$; $\sigma_3 = 5 \cdot 10^{-18}$ cm$^2$.

The simplest possible model was used to approximate the situation present in quartz, meaning the presence of more than one kind of recombination centre as well as more than one kind of trap active in the OSL process, at least one kind of shallow trap and one kind of deep thermally disconnected trap that are also resistant to optical bleaching. However, it should be mentioned that similar effects related to the residual level of hole concentration in recombination centres was also observed for a very simple model including only one recombination centre, one kind of the OSL trap and one kind of deep disconnected trap. The existence of the latter is responsible for the residual level of the hole concentration in recombination centres. Due to charge balance in the crystal, the number of holes in the recombination centres after the optical bleaching is equal to the number of electrons staying in traps. Both depend on the dose applied before optical bleaching.

Fig. 7 shows an example of simulation resulting for the equal concentrations of the recombination centres and the recombination coefficient of centre 1($\beta_1$) assumed to be five times higher than of centre 2 ($\beta_2$).

The changes in the hole concentrations in the both recombination centres ($m_1$ and $m_2$) with the irradiation dose are presented for various bleaching times. Both recombination centres are populated after bleaching but the residual level of hole concentration after bleaching is significantly lower for recombination centre 1 which has the larger recombination coefficient. The hole concentration in this centre, for a selected irradiation dose, is also more sensitive to bleaching duration. The inset of Fig. 6 presents the outcome of fitting of the residual hole concentration in centre 1 using a single saturating exponential function (as it has been performed for the $[\text{AlO}_4/\text{h}]^3$ signal residual values in section 3.2). The quality of fitting is similar to that presented for the experimental data in Fig. 4.
3.4. Implications for residual dose corrections in ESR dating

Residual dose corrections are trivial if the value of the residual dose is known and does not depend upon previous dose. Such a correction can be performed by subtracting the value of the residual signal (as measured following prolonged exposure to light) from the values of the signals used to construct the dose-response curve. The new, corrected dose-response curve is then fitted, and the corrected equivalent dose obtained by extrapolation (see Tissoux et al., 2012).

However, if residual signals are dose-dependent, as implied by our experimental results here, this has significant implications for ESR dating. One cannot know the magnitude of dose accrued in the crystal prior to the bleaching event. As yet there is not entirely satisfactory or universally applicable approach to estimate the value of residual doses preserved within sediment samples. One approach is by using a modern analogue, meaning a young sample from the same sedimentary context, that is assumed to have accumulated a negligible dose since deposition. However, correction by this method is accurate only if an important assumption is fulfilled, namely that the modern analogue sample has the same origin, composition and history as the sample to be dated. Another assumption is fulfilled, namely that the modern analogue sample has the same origin, composition and history as the sample to be dated. Another assumption is fulfilled, namely that the modern analogue sample has the same origin, composition and history as the sample to be dated.

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Fortunately, it is important to note that at least in the case of the sample investigated here, major uncertainties on the obtained residual are introduced only if the dose (i.e. the palaeodose) of the natural sample is higher than about 10000 Gy (note that the values of residuals plotted in Fig. 4 do not have a significant variations in the lower dose range). Samples with equivalent doses this high are not routinely dated using ESR [AlO<sub>4</sub>/h<sub>0</sub>].

Here we further test a residual dose correction procedure on sample Rox MIX. For this sample, application of the standard additive dose [AlO<sub>4</sub>/h<sub>0</sub>] ESR dating procedure without residual correction resulted in an equivalent dose of 543 ± 31 Gy (Table 1). This value substantially overestimates the expected equivalent dose of 15 Gy obtained by OSL dating. Fig. 8 presents the uncorrected and the corrected dose response curves. We performed our correction by subtracting the unbleached component from the natural ESR signal of the [AlO<sub>4</sub>/h<sub>0</sub>].

We chose to perform dose correction using the residual of the natural bleached sample because this procedure is that most commonly used in dating studies and is the reasonable assumption. Choosing a residual value obtained from bleaching experiments of samples irradiated with larger doses would potentially introduce additional uncertainty. There is furthermore no justification for corrections using the residual obtained following bleaching of subsamples irradiated with large doses; for example, the magnitude of the signal attributed to material irradiated with approximately 40000 Gy is 1.25 times that of the natural unbleached signal (section 3.2).

This correction approach substantially improves the accuracy of the equivalent dose obtained for samples of known age, yet the obtained value (164 ± 3 Gy) is still one order of magnitude higher than the expected equivalent dose (15 Gy). The possibility that other signals are interfering with the [AlO<sub>4</sub>/h<sub>0</sub>] measurement and are at least partially responsible for this inaccurate estimation (Timar-Gabor et al., 2018) remains of serious concern and must be addressed in future.

4. Conclusions

In this investigation, we measured equivalent doses in young sedimentary quartz samples of known OSL ages, using of [AlO<sub>4</sub>/h<sub>0</sub>] centres and ESR spectroscopy, and obtained residual values corresponding to doses on the order of 500 Gy. Such values undermine the accuracy and
applicability in using \([\text{AlO}_4]/\text{h}\)^0 signal for dating unless residual dose corrections are performed.

We investigated the dose dependence of residual signals of \([\text{AlO}_4]/\text{h}\)^0 in quartz extracted from a Holocene soil and observed an exponential increase of residual value with preceding given dose. This result is interpreted in the light of the assumption that the bleaching mechanism of \([\text{AlO}_4]/\text{h}\)^0 signal is electron-hole recombination with electrons released by light from optically sensitive traps. The modelling of such processes using a basic model including four electron traps and two recombination centres was performed and the results allow drawing preliminary conclusions. When the deep traps, which are not emptied during bleaching are present, the residual level of the hole concentration in the recombination centres has a magnitude that depends on the irradiation dose previously delivered and the relation of the efficiency of recombination in the centres participating in the process. Details of the residual level dependency on the mutual relations of the parameters of traps and recombination centres are worth further investigations.

As far as dating applications are concerned, this exponential dependence, if proven to be characteristic to various samples poses significant problems for performing residual dose corrections in ESR dating. We consequently reinforce the application of multiple centres ESR dating and recommend that: (i) the dose dependence of \([\text{AlO}_4]/\text{h}\)^0 signal residuals to be tested before applying bleaching corrections, and (ii) modern analogues, when available, should be used in parallel with natural bleached samples for quantifying the values of residuals for \([\text{AlO}_4]/\text{h}\)^0 signals.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A: Supplementary data

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References


