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Dose response curve of the ESR signal of the Aluminum center in quartz grains extracted from sediment

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Abstract

A single saturating exponential (SSE) function is classically used in ESR dating to fit the experimental ESR data points derived from the aluminum (Al) center in quartz. However, this function has some obvious limits as it does not accurately fit the data points of the dose response curve. This results in unreliable equivalent dose (D_E) values which are highly dependent on the maximum irradiation dose.

Dose response curves of Al center in quartz show that the dose response data contain at least two components: a first one dominating at low dose (usually < 5 kGy) and saturating quite quickly and a second one dominating at higher doses with an almost linear behavior. These data are more appropriately fitted with a function combining an exponential with a linear term (EXP+LIN). Two variations of the EXP+LIN function were studied, each one corresponding to distinct physical assumptions. Since it is still unclear which one should be preferred, the mean D_E value extracted from the fitting of the two equations may be reasonably considered as the most reliable estimate of the true D_E value. In addition, to ensure accurate fitting of the linear part, it is important to have at least three data points at high doses (>10 kGy). It is also suggested to pool all the ESR intensities derived from repeated ESR measurements of each aliquot in the fitting process, in order to reduce the error in the D_E value.

Introduction

In ESR as well as in luminescence dating, the selection of the mathematical function to fit the experimental data point has a direct impact on the calculated equivalent dose (D_E) value. This is even more crucial when working with the additive dose method, which requires back extrapolation of the data to the X-axis. In the field of ESR dating, this topic has been widely discussed for carbonates (e.g. Grün et al., 1990; Barabas et al., 1992; Walther et al., 1992; Hoffmann et al., 2003) and fossil tooth enamel (Lee et al., 1997; Rink and Schwarcz, 1994; Duval et al., 2009). In contrast, there is little information available about the mathematical description of the

dose response curves of the aluminum (Al) center in sedimentary quartz.

Since the first applications of ESR to date optically bleached quartz grains extracted from sediment (e.g. Yokoyama et al., 1985), a single saturating exponential (SSE) function has been systematically used to fit the experimental Al-ESR dose response data (e.g. Rink et al., 2007; Liu et al., 2010; Voinchet et al., 2010). However, this function does not accurately describe the behavior of the Al-ESR signal with the absorbed dose, since it shows systematic deviations from experimental data sets. In addition, studies on the optical bleaching kinetics of the Al signal show that at least two components are involved in the process (Voinchet et al., 2003). It is therefore reasonable to explore the potential of a similar approach including more than one component to describe the creation of Al centers with absorbed dose. In this paper, the limits of the SSE function are discussed and the appropriateness of an alternative fitting approach combining the SSE function with a linear term (EXP+LIN) is assessed.

Material and method

The dose response curves (DRCs) of the Al center from 15 quartz samples were selected. The sediment samples were collected in diverse Plio-Pleistocene geological contexts from various areas of the Iberian Peninsula. Quartz grains were extracted according to a protocol similar to that described in Voinchet et al. (2007). Depending on the sample, irradiation involved 11 to 14 dose steps with maximum irradiation doses (D_{max}) between 23,100 and 40,000 Gy (Table 1). The residual ESR intensity of the artificially bleached component was first subtracted from the DRC values and then each DRC was normalized to the ESR intensity of the corresponding natural aliquot, to obtain comparable data. All ESR data are available in supplementary information. Two fitting functions were tested:

Single saturating exponential (SSE) function

The SSE function was first proposed by Apers et al. (1981), to account for saturation effects of the ESR

Sample	Site/Outcrop, Location	Number of dose steps	D _{max} (Gy)
1	Huescár-1, Guadix-Baza basin (Southern Spain)	14	40000
2	Huescár-1, Guadix-Baza basin (Southern Spain)	13	40000
3	Fuente Nueva-3, Guadix-Baza basin (Southern Spain)	11	25000
4	Vallparadís, Terrassa (Eastern Spain)	11	25000
5	Vallparadís, Terrassa (Eastern Spain)	11	25000
6	Villarroya, Ebro basin (Northern Spain)	12	25000
7	Villarroya, Ebro basin (Northern Spain)	12	25000
8	Tejares, Duero basin (Northern Spain)	12	25000
9	Tejares, Duero basin (Northern Spain)	12	25000
10	Barranco León, Guadix-Baza basin (Southern Spain)	11	24000
11	Atapuerca Sima del Elefante, Duero basin (Northern Spain)	11	23300
12	Atapuerca Sima del Elefante, Duero basin (Northern Spain)	11	22100
13	Maresa, Tajo basin (Central Spain)	11	22900
14	Valdocarros, Tajo basin (Central Spain)	11	22700
15	Cúllar de Baza, Guadix-Baza basin (Southern Spain)	11	23100

Table 1: Details of the fifteen ESR samples.

signal at high irradiation dose. By using this function, it is usually assumed that the ESR signal is dominated by a single paramagnetic center. The SSE function may be written as follows:

$$I(D) = I_{sat} \left[1 - \exp \left(-\frac{(D+D_E)}{D_0} \right) \right] \quad (1)$$

where D is the absorbed dose (Gy), I is the ESR intensity (in a.u.). Three parameters are fitted: the equivalent dose (D_E), the saturation ESR intensity (I_{sat}) and the characteristic saturation dose (D_0). Sometimes $1/D_0$ is used to express the radiation sensitivity of the sample.

Exponential+linear (EXP+LIN) function

This function is made by the sum of a SSE function and a linear term. This function was first introduced by Goldberg et al. (1973) and then taken up by Levy (1985) in order to describe the formation of radiation induced species for a system where several components are involved. This function was previously used in luminescence dating (Berger, 1990; Fattahi et al., 2004), in ESR studies of corals

(Grün, 1990; Walther et al., 1992) and enamel (Duval et al., 2009), but not for quartz, until the work by Duval et al (2011). Basically, the use of this kind of function suggests that the ESR signal is the result of two main components, one dominating at low irradiation doses and saturating at relatively low doses while the other is dominating at high doses. The EXP+LIN is usually considered appropriate for systems where traps are generated during irradiation (Levy, 1985). However, it can be also interpreted as a sum of two different saturation functions, including one with such a high saturation level that it may be approximated by a straight line (Walter et al., 1992). Following the second hypothesis, the equation may be written as follows:

$$I(D) = I_{sat} \left[1 - \exp \left(-\frac{(D+D_E)}{D_0} \right) \right] + m(D + D_E) \quad (2)$$

There are four fitted parameters with this function: D_E , I_{sat} , D_0 and m. The latter may be considered as an estimation of the radiation sensitivity of the second component.

The fitting procedures were carried out with the Microcal OriginPro 8.5 software using a Levenberg-Marquardt algorithm by chi-square minimization. Further details can be found in the Origin 8 User Guide (2007). The data points were weighted by the inverse of the squared ESR intensity ($1/I^2$). For a discussion of the weighting of luminescence and ESR data points, see Grün and Brumby (1994) and references therein. The goodness of fit is assessed through the adjusted r-square (r^2) value, which accounts for the degrees of freedom of the system, contrary to the classical coefficient of determination r^2 (for further details see the Origin 8 User Guide).

Apparent limitations of the SSE function

Fig. 1 shows a couple of examples of DRCs (samples #1 and #6). It is already visually obvious that the SSE function does not correctly fit the ESR data points. For sample #1, the SSE function is not only inappropriate in the high dose region ($D > 25$ kGy), with modelled ESR intensities significantly lower than the experimental ones, but also in the intermediate dose region (~ 6 kGy $< D < \sim 25$ kGy), in the maximum curvature area of the SSE where experimental data are not fitted at all. Lastly, in the low dose region ($D < \sim 6$ kGy), the curve goes through almost none of the points, and the SSE passes above the natural point. A similar trend is observed for sample #6. Other examples may also be found in Duval et al. (2011).

Sometimes, the SSE function resulted in a good fit (adjusted $r^2 > 0.99$) of the experimental data, but this applied only to two samples of the present data set: samples #3 and #9 (Table 2). The corresponding

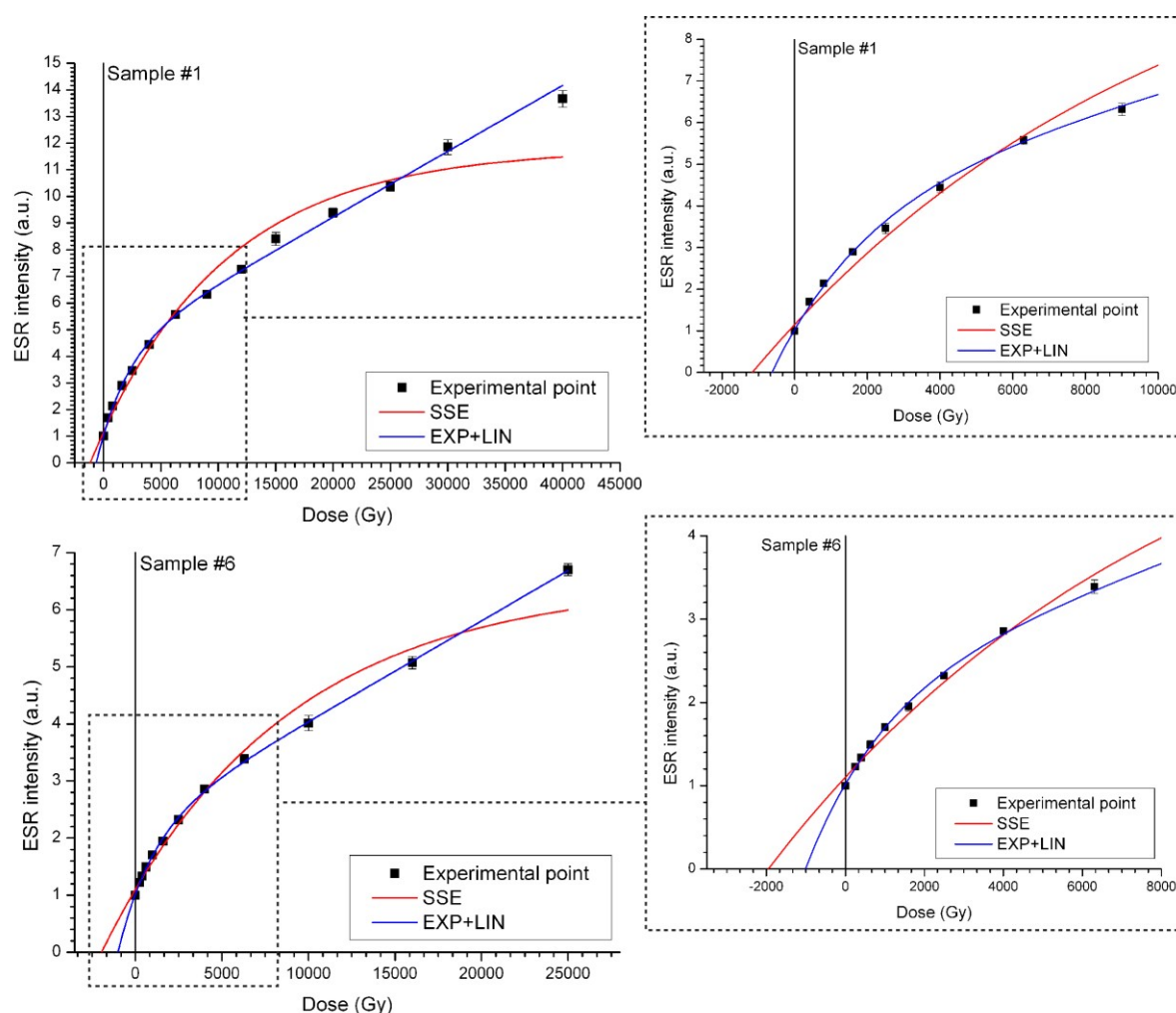


Figure 1: Examples of dose response curves (Samples #1 and #6). Mean ESR intensities were calculated from repeated ESR measurements of each sample. Errors on the ESR intensities correspond to 1 standard deviation.

Sample number	SSE - Equation (1)				EXP+LIN - Equation (2)							(EXP+LIN)/(SSE)	
	D_E	\pm	%	Adjusted r^2	D_E	\pm	%	I_{sat}	D_0	m	Adjusted r^2	D_E	Adjusted r^2
1	1166	180	15.4	0.97544	631	56	8.9	4.12	2639	0.000247	0.99708	0.54	1.022
2	742	131	17.7	0.97059	458	70	15.3	5.58	2707	0.000405	0.99060	0.62	1.021
3	1975	140	7.1	0.99446	1665	143	8.6	2.96	4541	0.000051	0.99773	0.84	1.003
4	2696	319	11.8	0.98489	1699	172	10.1	1.98	2982	0.000078	0.99781	0.63	1.013
5	4694	748	15.9	0.97292	1703	339	19.9	1.43	1862	0.000052	0.99137	0.36	1.019
6	1951	261	13.4	0.97736	1012	70	6.9	2.10	1986	0.000176	0.99903	0.52	1.022
7	1990	190	9.5	0.98841	1340	121	9.0	2.42	3114	0.000116	0.99783	0.67	1.010
8	3155	322	10.2	0.98691	1841	195	10.6	1.77	2820	0.000098	0.99792	0.58	1.011
9	2157	173	8.0	0.99172	1506	91	6.0	2.31	3492	0.000137	0.99915	0.70	1.007
10	1879	191	10.2	0.98874	1526	205	13.4	2.76	3719	0.000051	0.99432	0.81	1.006
11	1611	166	10.3	0.98918	1474	236	16.0	3.99	6093	0.000064	0.98876	0.91	1.000
12	2385	248	10.4	0.98783	2193	411	18.7	3.24	6463	0.000045	0.98674	0.92	0.999
13	2587	298	11.5	0.98502	1659	213	12.8	1.99	2745	0.000073	0.99637	0.64	1.012
14	1488	199	13.4	0.98083	933	70	7.5	2.61	2200	0.000129	0.99846	0.63	1.018
15	3228	364	11.3	0.98581	1937	141	7.3	1.73	2625	0.000056	0.99891	0.60	1.013
Mean	2247		11.7	0.98401	1438		11.4	2.73	3333	0.000118	0.99547	0.67	1.012
s.d.	960		2.9	0.00705	485		4.4	1.11	1375	0.000097	0.00410	0.15	0.008
c.v.	42.7%		25.0%	0.7%	33.7%		38.6%	40.8%	41.3%	82.1%	0.4%	22.9%	0.8%

Table 2: D_E values and other data associated to the fitting of both SSE and EXP+LIN functions. Keys: s.d.=standard deviation; c.v.=coefficient of variation.

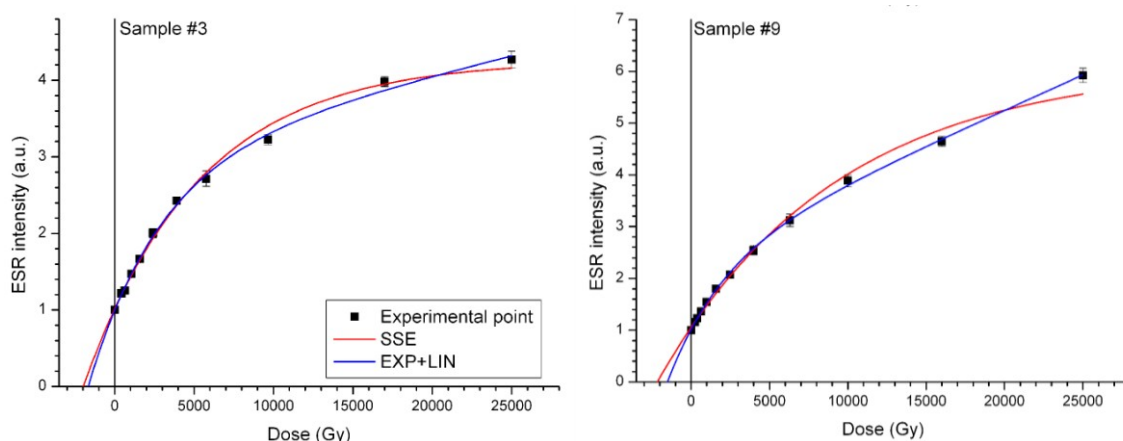


Figure 2: Dose response curves of samples #3 and #9, for which the SSE shows the best fitting of the data set ($\text{Adjusted } r^2 > 0.99$). Mean ESR intensities were calculated from repeated ESR measurements of each sample. Errors on the ESR intensities correspond to 1 standard deviation.

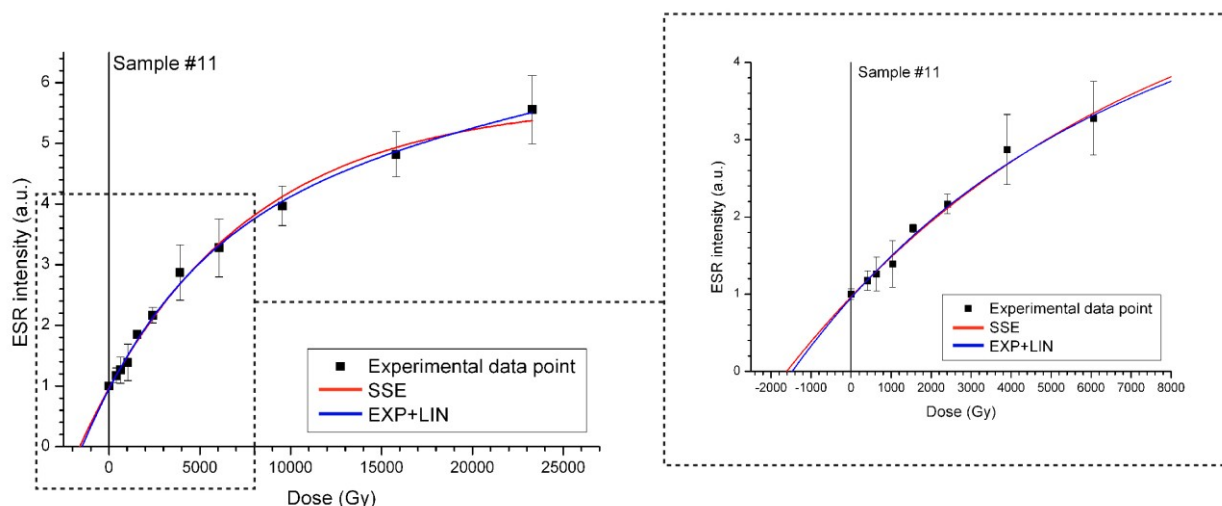


Figure 3: Example of a DRC with a high D_0 (6093 Gy): sample #11. Both SSE and EXP+LIN functions show close goodness of fit and D_E values. Mean ESR intensities were calculated from repeated ESR measurements of each sample. Errors on the ESR intensities correspond to 1 standard deviation.

DRCs are shown in Fig. 2. However, despite the apparent tight fit, one may observe that the experimental points are not particularly well fitted at doses higher than ~ 5 kGy. These observations suggest that the DRCs of the Al center in quartz cannot be correctly fitted with the SSE function.

Potential of the EXP+LIN function in comparison with the SSE

Two distinct domains can be identified in the DRCs shown in Fig. 1. First, the ESR signals increase quite rapidly with the dose in a few kGy, i.e. the natural ESR intensities are multiplied by a factor of ~ 3 -4 up from 0 to 4 kGy. Then the DRC grows more slowly at higher doses, with the ESR intensities multiplied by a factor of ~ 2 between 4 kGy and 25 kGy. Perhaps

the most striking observation is that there is almost no apparent saturation of the Al center at high doses (up to 40 kGy). This is in agreement with the data shown by Lin et al. (2006). The ESR signal grows almost linearly with the absorbed dose at irradiation doses in excess of ~ 4 -5 kGy (see also the DRCs shown in Duval et al. (2011) and Cordier et al. (2012)). Consequently, the hypothesis of a single component building the ESR signal, one of the basic assumption of the SSE function, is not valid. It seems that at least two components contribute to the ESR signal: the first saturates at low doses and the second shows no apparent saturation at high dose, with an almost linear behavior, justifying thus the use of an EXP+LIN function.

Like the SSE function, the EXP+LIN was fitted through the experimental data points of the 15 samples (see Table 2). Visually, the EXP+LIN function fits the data points much better than the SSE function (e.g. Fig. 1 and 2). This is confirmed by the adjusted r^2 values: the EXP+LIN function provides a better fit than the SSE for 13 of 15 samples, even for those that were already well fitted with the SSE (#3 and #9). The two remaining samples (#11 and #12) show very close adjusted r^2 values (Table 2). These were collected at the same cave site, Atapuerca Sima del Elefante, and show DRCs with the highest D_0 values of the data set (> 6 kGy). Consequently, it seems that a linear term could not be identified within the dose range used for the DRCs (Fig. 3). Here, at least a couple of additional irradiation steps at doses > 25 kGy would be useful to identify the linear term and to reduce the large D_E errors ($> 15\%$). In addition, the various ESR measurements of sample #11 show an especially quite poor precision, as indicated by the large errors in the ESR intensities (Fig. 3). This may explain why the adjusted r^2 values are < 0.99 for both functions, and suggest that the experimental data are not perfectly fitted for this specific sample. Basically, the best fits with the SSE are obtained for samples showing high D_0 values (e.g. samples #3, #9, #10, #11 and #12) but even there, the fitting with the EXP+LIN remains still very close or even better. In contrast, the DRCs from samples #5 and #6 have the lowest D_0 values of the data set, and the fitting of the SSE is totally inappropriate (adjusted $r^2 < 0.98$; e.g. Fig. 1).

Similarly to the previous results by Duval et al. (2009), D_E values calculated with the EXP+LIN function are systematically lower (on average by 37%) than those obtained with the SSE. The minimum deviations between the D_E derived from each function are around -8 % for the samples #11 and #12, i.e. those with the highest D_0 . The maximum deviation is obtained for samples with $D_0 < 2000$ Gy (samples #5 and #6), i.e. DRCs where the first exponential component saturates quite quickly and the second linear component takes over the former at relatively low dose values.

The impact of D_{max} on the fitting results for both functions is illustrated by Fig. 4 for samples #1 and #2 which had the largest number of data points (Table 1). Fig. 4A shows the evolution of the D_E values relative to the D_E values obtained at $D_{max}=40$ kGy. The application of the SSE function results in an almost linear increase of the D_E values: between $D_{max}=12$ kGy and $D_{max}=40$ kGy, the D_E value increases by a factor of ~ 1.4 - 1.6 for both samples. Such a strong correlation was one of the arguments against the use of the SSE function for tooth enamel

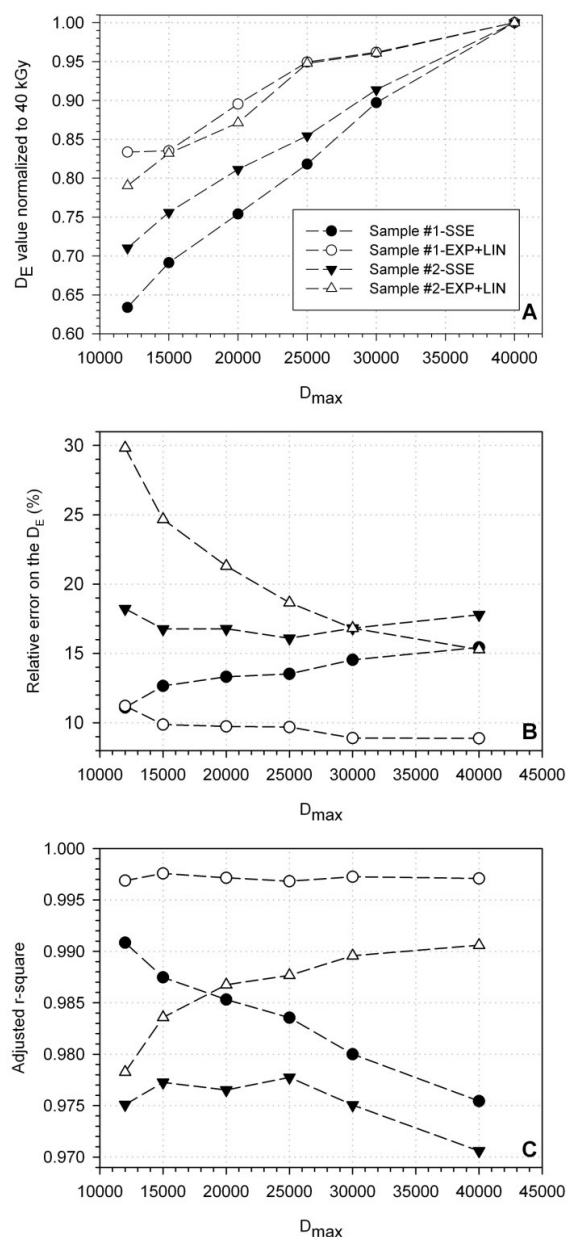


Figure 4: Influence of D_{max} on the fitting results: a couple of examples with samples #1 and #2. (A) Evolution of the D_E with D_{max} , from $D_{max}=12$ kGy to $D_{max}=40$ kGy. Current D_E values are normalized to the D_E obtained at $D_{max}=40$ kGy. (B) Evolution of the relative D_E error with D_{max} . (C) Evolution of the adjusted r^2 with D_{max} .

samples (Duval et al., 2009; Chen et al., 1997). With the EXP+LIN function, D_E values have a similar increase between $D_{max}=12$ kGy and $D_{max}=25$ kGy. However, from $D_{max}=25$ kGy to $D_{max}=40$ kGy, the D_E values remain almost constant with only a slight increase of $< 5\%$ over 15 kGy. Contrary to the SSE

function, the EXP+LIN function is much less dependent on the D_{\max} , but it is critically dependent on having sufficient data points to define correctly the linear term at high doses. Similar trends were observed with other samples of the data set: the EXP+LIN D_E values remain almost constant when progressively removing the last 3-4 points, while SSE D_E values significantly decrease. Fig. 4B shows the evolution of the relative D_E errors with D_{\max} . For the EXP+LIN, the errors are constantly decreasing when D_{\max} increases. In contrast, D_E errors from SSE remain either constant or increase when adding additional dose steps, as a result of the fitting becoming more and more problematic. This trend is also widely observed on the other DRCs of the data set. Fig. 4C shows that the goodness of fit of the EXP+LIN is systematically better than that of the SSE for a given sample and a given D_{\max} . In the case of the EXP+LIN function, the adjusted r^2 value increases or remains almost constant when the D_{\max} increases, contrary to the SSE.

Reducing the error in the D_E with the EXP+LIN function

The application of the EXP+LIN function results in larger errors than using the SSE because four instead of three independent parameters are optimized (see samples #10, #11 and #12 which have similar EXP+LIN and SSE D_E values, Table 2). This can be addressed by increasing the number of dose steps. Usually one considers that 3-4 points per fitted parameter are necessary (Lyons, 1992). Consequently, between 12 and 16 dose steps should be used to fit the EXP+LIN function, making sure that there are at least 3 to 4 points to describe the almost linear behavior of the ESR signal at high doses (> 10 kGy).

In addition to selecting an appropriate dose range for the DRCs, the precision of the measurements can be increased through repeated ESR measurements of the same aliquot. ESR measurements of quartz are complex since several parameters have an influence on the data reproducibility. They may be experimental, such as the temperature of the room, cooling water or the cavity (the ESR signal of Al center is only visible at liquid nitrogen temperature). Other error sources are intrinsic to the sample, like its homogeneity (the standard analytical procedure is usually based on multiple grains and multiple aliquot measurements) or the angular dependence of the ESR signal in the ESR resonator. To ensure precision of the data, it is necessary to carry out a series of repeated measurements of a given aliquot after various rotations in the cavity and over several days. For example, each aliquot from samples #1 and #2 were measured 3 times after a $\sim 120^\circ$ rotation in the resonator over 4 and 3 days, respectively. Then, the

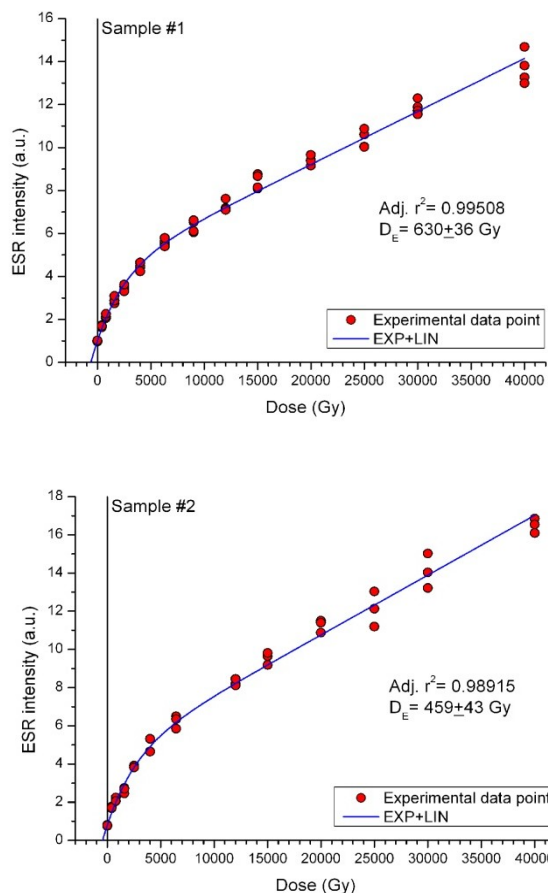


Figure 5: Influence of ESR data pooling on the D_E estimate (see comparison data from Table 2).

mean ESR intensities were extracted from each day of measurement and all these data may be plotted, making a data set of 51 and 39 data points for samples #1 and #2, respectively (Fig. 5). When comparing the results of the fitting with those derived from the initial fitting with one ESR data point for each aliquot, one may conclude that the impact on the D_E value is negligible ($\ll 1\%$, see Table 2), but the relative errors are much smaller by around 60% and 50%, respectively. These results are in agreement with the work by Grün and Brumby (1994) and Grün and Rhodes (1991, 1992) who showed that pooling of dose response points improve the random error in the D_E estimation.

Exploring a variation of the EXP+LIN function

As previously commented, the linear term may either correspond to the case where the second component saturates at such a high level that it may be approximated by a straight line (Walter et al., 1992), or where traps are generated during irradiation (Berger, 1990; Grün, 1990). With a linear term

Sample number	EXP+LIN - Equation (3)			Equations (3) / (2)
	D _E (Gy)	±	%	D _E ratio
1	729	70	9.6	1.16
2	545	91	16.6	1.19
3	1794	143	8.0	1.08
4	1891	201	10.6	1.11
5	1801	374	20.8	1.06
6	1173	89	7.6	1.16
7	1534	146	9.5	1.15
8	2116	248	11.7	1.15
9	1805	118	6.5	1.20
10	1631	211	12.9	1.07
11	1616	210	13.0	1.10
12	2385	330	13.8	1.09
13	1822	243	13.3	1.10
14	1032	81	7.8	1.11
15	2095	158	7.5	1.08
Mean				
		11.30	1.12	
s.d.		3.91	0.04	
c.v.		34.7%	4.0%	

Table 3: *D_E values obtained from the fitting of equation (3). Keys: s.d.=standard deviation; c.v.=coefficient of variation.*

expressed by $m \cdot (D + D_E)$, Equation (2) is basically supporting the first option. However, the impact of the second option on the D_E value may also be simply explored by slightly modifying the equation (2), as following:

$$I(D) = I_{sat} \left[1 - \exp \left(-\frac{(D + D_E)}{D_0} \right) \right] + mD \quad (3)$$

Table 3 shows the parameter values derived from the fitting of the equation (3). Basically, the equations (2) and (3) provide the same goodness of fit, similar relative errors ($11.4 \pm 4.4\%$ vs $11.3 \pm 3.9\%$ on average), D_0 and m values. The main differences lie in the modelled I_{sat} and the D_E values: using equation (3) systematically provides higher I_{sat} (+5% on average) and higher D_E values (+12% on average) than equation (2). However, it is worth noting that the D_E values obtained from each EXP+LIN function are consistent with unity at 1σ for 11 of 15 of the samples and at 2σ for all samples. D_E values derived from equation (3) are on average lower by about 26% than those obtained with the SSE.

The use of equation (3) would mean that the linear term is the specific result of high doses from laboratory irradiation, producing paramagnetic centers that would not be created in nature. However, because it is almost impossible to know whether the

first or the second option of the EXP+LIN should be preferred from a physical point of view, it seems reasonable for the time being to consider a mean D_E value extracted from the fitting of the two EXP+LIN functions (2) and (3) as the most reliable estimate of the true D_E value.

Conclusions

This work shows that the DRC of quartz is most appropriately fitted with an EXP+LIN function. This necessitates that the dose range for the DRC contains at least 2-3 data points at doses >10 kGy from which the linear section can be derived. Basically, if the linear part is not described, then the fitting procedure with the EXP+LIN becomes difficult, and sometimes impossible. This is the reason why it is recommended always to generate these high dose points, even when working with samples with D_E of a few hundreds of Grays, in order to minimize the impact of the D_{max} on the D_E value. The data set of this study (15 samples) shows the variety of DRC that may be encountered: the saturation dose D_0 varies by a factor of about 3.5 (from 1862 to 6493 Gy), indicating that some samples need to be more irradiated than others in order to get a good description of the linear term.

The preferential use of the EXP+LIN function to fit the experimental ESR data means that the ESR signal is driven by two main components, one dominating at low dose and the second dominating at high dose with an almost linear behaviour. This linear term may have two possible physical explanations, depending on the fitting equation selected. It could correspond to a component following a saturating exponential behaviour, but with such a large saturation dose that it can be approximated to a straight line. In that case, the paramagnetic center production is a continuing process. Such hypothesis is not so surprising, since the optical bleaching behaviour of the Al center also indicated the presence of two components (Voinchet et al., 2003), the first reducing the ESR intensity by about 50% within a few hours and the second further reducing the signal over several tens of days (Duval, 2008). Another hypothesis is that the linear term is only generated at high doses by laboratory irradiation, but not in nature. This would need to be further explored in the future. Given this uncertainty, the most reasonable option consists in considering a mean D_E value extracted from the fitting of both types of EXP+LIN functions, in order to encompass the two hypotheses.

On the other hand, the specificity of the D_E evaluation in ESR dating of quartz in comparison with other materials, or even with OSL dating, has to be considered. Since repeated ESR measurements of each aliquot are needed to ensure the data reproducibility, then all ESR intensities can be plotted and taken into account in the D_E assessment.

As soon as the data reproducibility is good, this would lead to a reduction of the error associated to the D_E value, in comparison with the plotting of a single set of mean ESR intensities. Such a procedure has been already suggested in the past by Grün et al (1992) and Grün and Brumby (1994), but the specificity of the ESR measurements of quartz makes now the pooling of ESR intensity necessary.

Finally, it is important to remind that even if the EXP+LIN function is more appropriate than the SSE to fit experimental data points of the Al center, this does not necessarily mean that the derived D_E values are accurate, i.e. the built-up of the natural ESR signal in the geological past may have been different to that reconstructed from additive dose points. It is obvious that additional experiments have to be carried out, such as comparing regeneration with additive DRCs on the same samples, and systematically comparing DRCs from geological successions, such as river terrace sequences where the quartz was most likely derived from the same source.

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Supplementary Information for this article is available at www.aber.ac.uk/ancient-tl

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