

Defining minimum reporting requirements for ESR dating of optically bleached quartz grains

Mathieu Duval,^{1*} Jean-Jacques Bahain,² Melanie Bartz,³ Christophe Falguères,²
Verónica Guilarte,⁴ Davinia Moreno,⁴ Hélène Tissoux,^{2,5} Miren del Val,⁶
Pierre Voinchet,² Lee J. Arnold⁷

¹Australian Research Centre for Human Evolution (ARCHE), Environmental Futures Research Institute, Griffith University, Nathan QLD 4111, Australia.

²Département de Préhistoire, Muséum National d'Histoire Naturelle, UMR 7194, Paris, France.

³Institute of Geography, University of Cologne, Albertus-Magnus-Platz, 50923 Cologne, Germany.

⁴Centro Nacional de Investigación Sobre Evolución Humana (CENIEH), Paseo de la Sierra de Atapuerca 3, 09002 Burgos, Spain.

⁵Service Géologique National - BRGM. 45060 Orléans Cedex 2, France.

⁶Department of Mineralogy and Petrology, UPV/EHU University of the Basque Country, B Sarriena, s/n, 48940 Leioa, Spain.

⁷School of Physical Sciences, Institute for Photonics and Advanced Sensing (IPAS) and Environment Institute, University of Adelaide, North Terrace Campus, Adelaide, SA 5005, Australia.

*Corresponding Author: m.duval@griffith.edu.au

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Abstract

More than 30 years after the first Electron Spin Resonance (ESR) dating application to optically bleached quartz grains by Yokoyama et al. (1985), the absence of standardization for reporting methodology and age results remains an obstacle for the development and recognition of the ESR dating method within the Quaternary scientific community. To overcome this issue, the present work proposes some basic guidelines which should hopefully be useful not only for the ESR dating community, but also for any potential reviewers who may not be familiar with the specificities of this field.

Keywords: Electron Spin Resonance (ESR) dating; Quartz grains; Aluminium centre; Titanium centre; Equivalent Dose; Dose rate

1. Introduction

In any scientific paper, regardless of the field considered, the section dedicated to the description of the method is by definition of crucial importance: it must contain the minimum information about experimental conditions to provide the reader a clear and precise understanding of the analytical procedure that has been followed. This is a necessary requisite for not only evaluating the reliability and validity of the methodology that has been employed, but also to open the possibility to replicate the experiment under similar conditions (e.g. Azevedo et al., 2011; Kallet, 2004).

In geochronology studies this section is especially important, and minimum information should be reported with enough details so that the reader can correctly assess the reliability and interpret the meaning of the age estimates that have been produced. The data set provided should also be detailed enough to permit independent age re-assessments, in light of methodological advances that will be progressively made in the future (Duller, 2008). The importance of

standardizing the reporting of methodology and age results has already been carefully considered for many Quaternary dating techniques, such as radiocarbon (e.g. Millard, 2014, and references therein), Ar-Ar (Renne et al., 2009), U-series (Dutton et al., 2017) and luminescence dating (Forman et al., 2000; Duller, 2008). This is, however, somewhat contrasting with the situation in ESR dating.

Four decades after the first use of ESR spectroscopy for dating purpose (Ikeya, 1975), and 30 years after the first applications to optically bleached quartz grains (Yokoyama et al., 1985), the absence of a minimum standardization for reporting research in this field is a concern. It remains an obstacle for the development and recognition of the ESR dating method within the Quaternary scientific community. So far, the only attempt in this direction was made by Grün (1992) who produced some general recommendations for most of the materials that were then usually dated by ESR (mainly tooth enamel and carbonates).

More than 20 years later, one may observe an increasing number of ESR dating studies based on optically bleached quartz grains, using aluminum (Al), titanium (Ti) or germanium (Ge) paramagnetic centres, but the information reported varies greatly among papers. As with luminescence dating, an ESR age estimate based on optically bleached quartz grains is basically derived from the determination of two main parameters: the equivalent dose (D_E), which is the laboratory estimate of the palaeodose, i.e. the total dose absorbed by the sample since the ESR signal has been last reset to zero by sunlight exposure, and the dose rate (\dot{D}), which is an estimation of the mean dose annually absorbed by the sample. However, there are several ways to evaluate these two parameters, and so far there is no standardization of analytical procedures within the ESR dating community to determine the D_E or \dot{D} term (notations from Grün (1992)). For this reason, providing only these two values in a scientific publication is not sufficient for the reader to gain a clear idea of the meaning and implications of the age results that have been obtained. It is frequently the case that the information presented in publications is not sufficient for external critical assessment. Given this situation, it now seems timely to define some minimum requirements for reporting methodology and ESR age estimates based on quartz grains.

2. Reporting ESR methodology

The standard ESR dating analytical procedure is usually made by five main steps: (i) sample collection, (ii) sample preparation, (iii) ESR dose response curve reconstruction and D_E determination, (iv) dose rate estimation and (v) age calculation. The following sub-sections 2.1 to 2.5 describe step by step the minimum information that should be reported, while an overview is given in Table 1.

2.1. Sample collection

The most crucial information to report here is any basic details regarding the position of the samples within the

stratigraphic sequence, their depth, as well as the geographic location of the sampling locality (including altitude). It may also be mentioned whether additional sediment samples were collected for water content or additional laboratory analyses. Lastly, in cases where *in situ* dosimetry measurements have been carried out on site, the following should be briefly specified: (i) the relative position of the *in situ* measurement with respect to the ESR samples, (ii) the technique that has been used (e.g., thermoluminescence (TL) or optically stimulated luminescence (OSL) dosimeter, gamma spectrometry), (iii) how the calibration, if applicable, was performed, (iv) and how the data were extracted and converted to dose rate values (e.g., “energy windows,” “threshold”). For points (iii) and (iv), referencing of previous work that already details the required information would be sufficient. Note that it may be more convenient to include points (ii) to (v) in the methods section dedicated to dose rate evaluation.

In particular, special emphasis should be given to the stratigraphic relationship between the dating event of interest and the sample being dated, i.e., whether the sample provides a direct, indirect, minimum, maximum or equivalent age estimate for the event/artefact/object/fossil under consideration. Additionally, the physical proximity (distance) of the sample to the event/artefact/object/fossil under consideration should be stated. Often this information is overlooked but it is critical to interpret the meaning of the final age estimate.

Additional information may be especially useful for the reader, like the sampling conditions (e.g., PVC tubes, blocks) and the precautions taken to minimize exposure to sunlight, if any (e.g., night sampling, day sampling under an opaque plastic cover), as bleaching rates of the ESR signals are known to be slower than that of the OSL signals (e.g., Duval et al., 2017). Brief description of the sedimentary context and geological characteristics of the deposits such as their origin (e.g., volcanic) or grain size could be provided as well, as they may give some insights about bleaching conditions during sediment transport (e.g., Voinchet et al., 2015). Pictures of the samples in their sedimentary context could also be used to provide complementary information for the reader.

2.2. Sample preparation

The main objective of sample preparation is the extraction of pure quartz grains from the raw sedimentary matrix. This is usually carried out by combining wet sieving and subsequent chemical treatment in order to remove carbonates, organics and other minerals (e.g., feldspars, magnetic minerals). In particular, hydrofluoric acid (HF) is not only used to remove all the minerals except quartz, but also to etch the external layer of the quartz grains for eliminating (or at least minimizing) the external alpha particles contributions. As a result of this operation, the external beta particle contribution to the dose rate may also be significantly impacted. Reporting full details of the analytical procedure should probably not be considered as mandatory, as this information is not directly useful to evaluate data reliability. However, it will indirectly affect the results as the preparation impacts the purity of the prepared samples. Consequently, we would suggest

Table 1: Summary checklist detailing the minimum information that should be provided when reporting ESR dating methodology based on optically bleached quartz grains.

Step	Minimum information that should be reported	Additional useful information that may be reported
1. Fieldwork	<ul style="list-style-type: none"> • Stratigraphic (unit/level) position of the samples • Stratigraphic relationship between the dating event of interest and the sample being dated, i.e., whether the sample provides a direct, indirect, minimum, maximum, or equivalent age estimate for the event/artefact/object/fossil under consideration • Geographic location and altitude of the sampled outcrop/site • If <i>in situ</i> measurements were carried out: (i) their position with respect to the ESR samples, (ii) the technique employed (e.g., TL dosimeter, gamma probe),¹ (iii) its calibration, and (iv) data reduction procedure to derive dose rate values (e.g., “energy windows,” “threshold”)¹ 	<ul style="list-style-type: none"> • Geological context and origin of the quartz grains • GPS coordinates of the site • Additional sediment samples collected for water content or future laboratory analysis?² • Pictures of the samples in their sedimentary context • Sampling conditions and precautions to minimize sunlight exposure
2. Sample preparation	<ul style="list-style-type: none"> • Initial grain size fraction selected • Conditions of HF etching (concentration and duration) 	<ul style="list-style-type: none"> • Conditions of laboratory illumination during the preparation • Each step of the procedure, preferentially in chronological order (e.g., wet sieving, chemical reaction, magnetic separation, density separation) • Chemical products used (type and concentration)
3. D_E reconstruction	<ul style="list-style-type: none"> • Experimental conditions of the ESR measurements (experimental setup, acquisition parameters, number of repeated measurements, number of rotations in the cavity, temperature of the ESR measurements)¹ • For the AI centre: bleaching conditions for the evaluation of the residual ESR intensity (UV simulator and lamp details, duration of the bleaching experiment)¹ • Evaluation of the ESR signal intensity (peak-to-peak measurement, peak-to-baseline, deconvolution)^{1,2} • Corrections of the ESR intensities (sample weight, temperature of the cavity, receiver gain value, number of scans, mean value derived from tube rotations, averaging of the repeated measurements) • Equation of the fitting function¹ • Data weighting used for the fitting • Fitting program and error evaluation • Error reporting nomenclature (whether errors are reported at 1 sigma or 2 sigma confidence levels) 	
4. Dose rate evaluation	<ul style="list-style-type: none"> • Technique(s) used to determine either the concentration of the radioelements in the sediment or the total alpha, beta, and gamma dose rate values¹ • Origin (reference) of the conversion and correction factors that have been used: dose rate conversion factors, alpha and beta attenuation factors for spherical grains, water attenuations, alpha efficiency^{1,3} • Thickness, measured or assumed, removed from the grains by HF etching¹ • Details about the cosmic dose rate calculation: depth (thickness of the sediment cover above the sample), altitude, GPS coordinates, water correction and reference(s) for the equation used. In case of caves/rock shelters, some detail should be provided about how additional partial/complete shielding of bedrock has been factored into the equations used.¹ • Water content (% dry or % wet weight) value used (measured or assumed)? if measured, specify how? If assumed, provide details about how a suitable value has been derived¹ • Whether equilibrium or disequilibrium in the U-238 and Th-232 series has been considered for dose rate calculation¹ • Error reporting nomenclature (whether errors are reported at 1 sigma or 2 sigma confidence levels) 	
5. ESR age calculation	<ul style="list-style-type: none"> • Details about the age calculation program used and error evaluation³ • Error reporting nomenclature (whether errors are reported at 1 sigma or 2 sigma confidence levels) 	

¹Some aspects of the analysis may be the same as previously published, so that referring to another study may be sufficient.

²This may be indicated in a figure showing the ESR signal that is analysed

³There is now an increasing number of software available to the community for dose rate and age calculations (e.g. AGE, DRAC, DRC). Consequently, it may be as simple as citing the corresponding publication for the software. In such cases, special care should be taken to ensure that the empirical water content term is expressed in the same terms used in the software (% dry or wet mass).

that each step of the procedure is briefly reported at least in supplementary material (e.g., conditions of laboratory illumination, information concerning the wet sieving, details of the chemical digestion, kind of magnetic and density separation, post-HF sieving), preferentially in chronological order. An example of a standard report for sample preparation may be found in Liu et al. (2010), Duval et al. (2015b), or Voinchet et al. (2007).

Instead, the basic minimum information that should be known here is the selected initial grain size fraction after sieving and the conditions of HF etching (concentration and the duration of the etching), as they have a direct impact on the final grain size of the grains (Bell & Zimmerman, 1978; Bell, 1979; Yokoyama et al., 1985; Porat et al., 2015; Duval et al., 2015a), and thus on the alpha and beta attenuation values (Bell, 1980; Mejdahl, 1979). Laboratory water content evaluation of the sediment (i.e., current water content and, if applicable, saturated water content) should also be described, either here or in the dose rate evaluation section.

It is worth emphasizing for non-ESR dating specialists that the relative slow, wavelength-dependent optical bleaching properties of quartz ESR signals essentially preclude the need for strict laboratory lighting protocols during sample preparation. Both the Al and Ti centre ESR signals are apparently mostly depleted by UV wavelengths, primarily UVA and UVB (Tissoux et al., 2007), although mechanical resetting processes might also play a role in sedimentary settings (Liu & Grün, 2011). Laboratory bleaching experiments undertaken using sunlight simulators have shown that the Al signal reaches a minimum intensity after several hundreds of hours of bleaching, while the Ti-Li signal is fully reset in <50 h. In comparison, <4 h are required to zero the ESR signal of the Ti-H centre (see Figure 1 in Duval et al., 2017). However, it should be noted that these bleaching rates may vary greatly (albeit within the same order of magnitude) depending on the sample analysed and the experimental setup. A complete discussion of ESR signal bleaching may be found in Duval et al. (2017) and references therein. It is clear from existing experimental datasets that quartz ESR bleaching rates are significantly slower than those of quartz OSL signals (see comparison in Duval et al., 2017), and that short exposure of a few minutes to natural light, or several hours to UV-depleted laboratory lights, will have no measurable impact on the ESR signals. For this reason, ESR lighting condition requirements are not as strict as those employed for luminescence dating, although some basic precautions should nevertheless be taken (see some recommendations for sampling in Moreno et al., Accepted). Until further evidence demonstrating the opposite emerges, it is not considered essential to detail sample preparation lighting conditions in ESR papers.

2.3. ESR dose reconstruction

Acronyms usually employed in luminescence dating may also be used for ESR, depending on whether Single or Multiple Aliquot(s) and Additive or Regenerative dose methods have been employed (e.g. MAA, MAR, SAR, SARA,

MARA, SAA). It could also be specified whether single grain or multiple grain analyses have been carried out, even if the former remains experimental in ESR dating (Beerten & Stesmans, 2005).

In most cases, ESR dose reconstructions of quartz grains are performed using a Multiple Aliquots Additive (MAA) dose approach, which means that the D_E value is obtained by back extrapolation of the fitting function to the abscissa axis. It is thus crucial to specify the number and the distribution of the irradiation dose steps (see discussions in Grün & Rhodes, 1991, 1992), as well as some basic information about the type and dose rate of the irradiation source (e.g., in Gy/h or Gy/s) that has been employed. Independently of whether ESR measurements have been performed at room temperature (for the Ge centre) or close to liquid nitrogen temperature (for Al and Ti centres), the following basic details about D_E measurement conditions should be specified:

- Experimental setup (type of spectrometer, ESR resonator, temperature control system).
- Acquisition parameters (microwave power, resolution, sweep width, modulation frequency, modulation amplitude, conversion time, time constant, number of scans, measurement temperature; see Grün (1992)).
- Number of rotations of the tube in the cavity for each aliquot and/or number of repeated measurements for each sample that have been carried out in order to evaluate the angular dependence of the signals due to grain heterogeneity and the repeatability/precision of the ESR data set.

Among the three main centres commonly used for dating purpose, the Al centre is unique in having an unbleachable component that gives rise to a residual ESR signal intensity. This residual signal must therefore be evaluated in order to avoid major D_E overestimation (Voinchet et al., 2003). Consequently, it is important to describe how this residual ESR intensity has been determined in the laboratory. For instance, quartz samples are sometimes simply directly exposed to natural sunlight to assess the unbleachable signal component. However, most of the time UV sunlight simulators are used to artificially bleach one aliquot: in this case, the type of simulator and lamps (electromagnetic spectrum covered), as well as the duration of the bleaching experiment should be specified.

The methods used to extract ESR intensities from the measured ESR spectra may vary from one centre to another. While there is apparent agreement in the scientific community regarding evaluation of the Al centre (Yokoyama et al., 1985; Toyoda & Falguères, 2003) or Ge centre (Falguères et al., 1991; Walther & Zilles, 1994), evaluation of the Ti centres remains somewhat debated (see Duval & Guilarte, 2015 and reference therein). Consequently, it is important to explain how the ESR intensities were evaluated (e.g. peak-to-peak measurement, peak-to-baseline, deconvolution) and which peaks were used for D_E determination. This may be simply shown in a figure (see examples in Liu et al., 2010; Tissoux et al., 2007).

Finally, the data reduction and analysis procedures used for D_E evaluation should be briefly described:

- Whether ESR intensities from repeated measurements were averaged out and corrected (e.g., according to weight, temperature variations, number of scans, receiver gain).
- Whether (and how) the residual ESR intensity has been taken in consideration in the evaluation of the D_E value (for the Al centre only). This is usually done following the total bleach approach, as described in (Forman, 1989). A figure may simply be provided (see Figure 4 from Voinchet et al., 2003)
- Basic details about the fitting procedure: the function that has been used (including preferably the equation or at least citing a previous paper where this is specified, as there may be slight variations of a given function, e.g. Duval, 2012), the data weighting, the fitting program, error evaluation and whether errors are reported at 1 sigma or 2 sigma confidence levels.

This last point is of crucial importance. Indeed, because of the use of the additive dose method for ESR dose evaluation, the D_E value is obtained by extrapolation of the fitted function (unlike the regenerative dose method where the D_E value is obtained by interpolation instead; see Forman, 1989). Consequently, the value of the D_E estimate is directly and significantly dependent on the fitting function and options employed (see Duval, 2012 and Duval & Guilarte, 2015 and references therein).

2.4. Dose rate evaluation

Unlike fossil teeth for which uranium uptake in dental tissue has to be modeled (e.g., Grün, 2009a), the internal and external dose rate associated to quartz grains is usually assumed to remain constant over time. Consequently, the basic dose rate equation may be expressed as follows:

$$\dot{D} = \dot{D}_{int} + \dot{D}_{ext} + \dot{D}_{cosmic} \quad (1)$$

where \dot{D} , \dot{D}_{int} , \dot{D}_{ext} , and \dot{D}_{cosmic} are the total, internal, external and cosmic dose rate components, respectively. ESR dating of quartz is mostly performed on grains whose diameter is between 60 and 300 μm , which means that the internal component, if existing, mainly comes from the alpha and beta particles contribution. Depending on the authors, the internal dose in quartz grains is usually either neglected, given the low concentrations of radioelements found in most quartz grains (e.g., Vandenberghe et al., 2008), or an assumed value is adopted (e.g., Duval et al., 2015a). Irrespective, the treatment of internal dose rate components should be clearly specified in the manuscript, particularly as it can constitute an important variable in environments with low external dose rates.

The external dose rate may be divided into several components as follows (detailed equations may be found in Grün, 1989):

$$\dot{D}_{ext} = [\dot{D}_{\alpha} + \dot{D}_{\beta} + \dot{D}_{\gamma}]_{ext} + \dot{D}_{cosmic} \quad (2)$$

where \dot{D}_{ext} , \dot{D}_{α} , \dot{D}_{β} , \dot{D}_{γ} , and \dot{D}_{cosmic} are the alpha, beta and gamma dose rates, respectively. These components are directly calculated from the activities or concentrations of radioelements (mainly U-238, Th-232 and K-40) present in the quartz grains and surrounding environment. The technique used to obtain these values (ICP-MS and/or ICP-OES, High Resolution Gamma Spectrometry, alpha counting) should be specified, as they utilise very different amounts of material, and results obtained may be of variable representativeness for different components of the external dose rate. The measured radionuclide activities / concentrations are transformed into dose rate values using conversion factors that are specific to each element and the particle or ray emitted. The most commonly used are those published by Adamiec & Aiken (1998), recently updated by Guérin et al. (2011). It should be specified whether dose rate calculation has been performed by considering either secular equilibrium or disequilibrium in the U-238 and Th-232 series. If apparent disequilibrium is detected, then some discussion should also be provided about the possible effects on the final ages of assuming different time-dependent dose rate scenarios. As previously mentioned, the gamma dose rate may also be derived from *in situ* measurements: in that case, the comments made in Section 2.1 should be taken into consideration.

These external dose rate values are then corrected according to different factors related to the site history or to the sample preparation, such as water content or grain size. Water content correction is crucial for the alpha, beta and gamma dose rate components: it should be specified if the value is expressed as a % of wet sediment weight or a % of dry sediment weight, whether this water content of the sediment has been measured or assumed, and how this has been taken into consideration in the dose rate calculation. Further details about this issue may be found in Grün (1994) and references therein. The reason/justification for using a particular assumed water content value should also be clearly stated in any study, i.e., the authors should specify what factors have been considered in deriving a representative assumed long term water content. The initial and final (after HF etching) grain size fraction will determine the value of the attenuation factors for the internal and external alpha and beta components. If the grains are sufficiently etched, the external alpha dose rate component may be simply eliminated from the external dose rate calculation. It is not mandatory to indicate the values of these attenuations factors, since these can be derived independently using initial and post-etching grain sizes. It is, however, important to specify the source of the attenuation factors used in the study. The values from Brennan et al. (1991) and Brennan (2003) for spherical grains have been widely used over the last decades. Updated values have recently been presented by Nathan (2010) and Guérin et al. (2012), taking into account grain size, shape, density, and the radioelements that are involved. Finally, the alpha efficiency value used for correction of the external and/or internal alpha dose rate (if not null) should be specified.

For the cosmic dose rate, it should be specified whether this component has been measured or estimated via exist-

	Minimum information that should be reported
Summary Table 1	<ul style="list-style-type: none"> Radioelement concentrations (ppm or %) or activities (Bq/kg) of the surrounding sediment used for the external dose rate calculation, depth below surface (in m), water content of the sediment (% dry or % wet weight)
Summary Table 2	<ul style="list-style-type: none"> Value and associated error for each component of the dose rate (internal, external alpha, beta and gamma, cosmic), the total dose rate (in $\mu\text{Gy/a}$ or Gy/ka), the D_E (in Gy) and the calculated ESR age estimates (in ka or Ma) When using the Al centre: the relative level of the residual ESR intensity in comparison with the natural ESR intensity (in %)
Figure 1	<ul style="list-style-type: none"> Examples of the ESR signal that has been measured
Figure 2	<ul style="list-style-type: none"> Some examples of dose response curves
	Additional information that may be reported
Table	<ul style="list-style-type: none"> Numerical estimators to evaluate goodness-of-fit for each sample (e.g., adjusted r^2 value, least-square values, chi-square values). This information can also be included in Figure 2 of the main manuscript and/or the figure with the DRCs in supplementary material
Figure	<ul style="list-style-type: none"> A stratigraphic column presenting the ESR age results in stratigraphic position
Supplementary material	<ul style="list-style-type: none"> Figures showing all the dose response curves (ESR intensities vs. Dose + the fitting function) Numerical data (ESR intensities vs. Dose) in a spreadsheet

Table 2: Summary checklist detailing: (i) the minimum information that should be provided when reporting ESR dating results based on optically bleached quartz grain; and (ii) additional useful information that may be reported.

ing tables. The latter is usually preferred, using the equation from Prescott & Hutton (1988). In addition, the correction factors considered for the calculation such as altitude, latitude, depth, as well as the estimated ground density (Prescott & Hutton, 1994), or the water content (Readhead, 1987) should be mentioned. In the case of samples from caves/rock shelters, it is also useful to detail how additional partial/complete shielding by bedrock has been factored into the cosmic dose rate calculation.

Finally, the evaluation of the error on the dose rate should be briefly described. Some guidelines on this issue may be found in Aitken (1985) and Grün (1992). Error reporting nomenclature should be specified, i.e. whether errors are reported at 1 sigma or 2 sigma confidence levels.

2.5. Age calculation

ESR age calculation is quite straightforward when the dose rate is assumed to be constant over time. In such cases, an age is simply derived from the division of the D_E value by the total dose rate. However, details should be given about how the errors have been calculated and propagated to the final age values. There is now a range of dose rate and age calculation software available to the community (among others, AGE, DRAC and DRC; see Grün, 2009b, Durcan et al., 2015, and Tsakalos et al., 2016, respectively). Although most of these have been designed for luminescence dating, they may easily be adapted to the specificities of ESR dat-

ing. Consequently, the age calculation process may simply require citing the corresponding publications where basic information (error calculations, dose rate conversion factors, correction factors) about the software is presented. Error reporting nomenclature should be specified, i.e., whether errors are reported at 1 sigma or 2 sigma confidence levels.

3. Reporting ESR results

ESR age estimates and associated results should be reported in several tables and figures (see a summary in Table 2). Usually, a series of summary tables including radioelement concentrations, and details of the dose rate and D_E components are sufficient.

In addition to these numerical data, several supporting figures should be provided. It is recommended to show at least one ESR spectrum for the signal that has been analysed, indicating how the signal intensity has been evaluated (e.g. see Toyoda & Falguères, 2003 for the Al centre, Walther & Zilles, 1994 for the Ge centre, and Beerten et al., 2008 for the Ti centres) as debate remains over this issue within the community for some paramagnetic centres. Alternatively, it may be possible to refer to a previous study where appropriate details have been provided elsewhere. The most important figure to provide is undoubtedly related to the Dose Response Curves (DRCs). Because the reliability of the D_E values is

highly dependent on whether the function is well fitted or not through the experimental data points, some graphical examples of ESR DRCs must be presented in the main text (e.g. Duval et al., 2017). Ideally, all DRCs should be included in supplementary information (e.g., Duval et al., 2017) as this is the best way for the reader to evaluate the quality of the ESR data set and, thus, the reliability of the fitting results. In addition, it may be particularly useful to provide some numerical estimators (e.g., adjusted r^2 value, least square values, chi-square values) for the goodness-of-fit achieved for each sample, since this may be quite variable from one sample to another, even within a given site or section (e.g., Duval et al., 2017). Following on from these guidelines it may be worth discussing within the ESR dating community the interest of systematically providing the complete ESR data sets (i.e., ESR intensities and corresponding irradiation doses) in numerical format (spreadsheet).

4. Conclusion

To avoid misunderstandings it is worth mentioning here that the purpose of the present paper is not to standardise analytical procedures in the ESR dating community, or to provide recommendations for the most reliable analytical practices in ESR dating of quartz (see for example Moreno et al., Accepted for some fieldwork recommendations). We have instead aimed to provide some guidelines for reporting ESR methodology and results, in order to make sure that the basic minimum information is available for external critical assessment. A series of summary checklists are provided here in Tables 1 and 2. These recommendations are open to revision and should be considered as a starting point for further discussion. It is worth emphasizing that these recommendations may also be used as guidelines when peer-reviewing papers dealing with ESR dating results. In particular, they may be useful for potential reviewers who are not familiar with the specificities of this field.

It is common for ESR dating applications published by a given laboratory to employ the same analytical procedure, with very little variation from one study to another. Consequently, for some aspects of the ESR dating procedure it may be possible to refer to previous publications where the corresponding information has been detailed. This may be particularly useful if manuscript length is an issue. However, most journals now offer the possibility to include online supplementary information, which means that the restricted length of the main manuscript should no longer be a limitation for providing all the required information. This approach would ensure easy and direct access to the complete analytical procedure, and avoid the need to search through previous publications that may not be readily accessible.

Adhering to the suggested reporting requirements should enable more straightforward age and data re-assessments in light of progressive improvements in understanding of the ESR dating method. This may occur, for example, via the update of published parameters (e.g., dose rate conversion factors, alpha and beta attenuations) or the identification of

more appropriate fitting functions, thereby enhancing the scientific vitality of the field.

Finally, it should also be emphasized that the recommendations discussed in the present work are only intended for ESR dating studies applied to optically bleached quartz grains. ESR dating applications involving other materials, such as fossil teeth, corals, carbonates, require the provision of different supporting information, as recommended by Grün (1992).

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References

- Adamiec, G. and Aiken, M. *Dose-rate conversion factors: update*. *Ancient TL*, 16(2): 37–50, 1998.
- Aitken, M.J. *Thermoluminescence Dating*. Academic Press, London, 1985.
- Azevedo, L.F., Canario-Almeida, F., Almeida Fonseca, J., Costa-Pereira, A., Winck, J.C., and Hespanhol, V. *How to write a scientific paper - Writing the methods section*. *Revista Portuguesa de Pneumologia*, 17(5): 232–238, 2011.
- Beerten, K. and Stesmans, A. *Single quartz grain electron spin resonance (ESR) dating of a contemporary desert surface deposit, Eastern Desert, Egypt*. *Quaternary Science Reviews*, 24(1–2): 223–231, 2005.
- Beerten, K., Rittner, S., Lomax, J., and Radtke, U. *Dose recovery tests using Ti-related ESR signals in quartz: First results*. *Quaternary Geochronology*, 3(1–2): 143–149, 2008.
- Bell, W.T. *Attenuation factors for the absorbed radiation dose in quartz inclusions for thermoluminescence dating*. *Ancient TL*, 8: 2–13, 1979.
- Bell, W.T. *Alpha dose attenuation in quartz grains for thermoluminescence dating*. *Ancient TL*, 12: 4–8, 1980.
- Bell, W.T. and Zimmerman, D.W. *The effect of HF acid etching on morphology of quartz inclusions for thermoluminescence dating*. *Archaeometry*, 20: 63–65, 1978.
- Brennan, B.J. *Beta doses to spherical grains*. *Radiation Measurements*, 37(4–5): 299–303, 2003.

- Brennan, B.J., Lyons, R.G., and Phillips, S.W. *Attenuation of alpha particle track dose for spherical grains*. *Nuclear Tracks and Radiation Measurements*, 18(1–2): 249–253, 1991.
- Duller, G.A.T. *Luminescence dating: Guidelines on using luminescence dating in archaeology*. English Heritage, Swindon, 2008.
- Durcan, J.A., King, G.E., and Duller, G.A.T. *DRAC: Dose Rate and Age Calculator for trapped charge dating*. *Quaternary Geochronology*, 28: 54–61, 2015.
- Dutton, A., Rubin, K., McLean, N., Bowring, J., Bard, E., Edwards, R.L., Henderson, G.M., Reid, M.R., Richards, D.A., Sims, K.W.W., Walker, J.D., and Yokoyama, Y. *Data reporting standards for publication of U-series data for geochronology and timescale assessment in the earth sciences*. *Quaternary Geochronology*, 39: 142–149, 2017.
- Duval, M. *Dose response curve of the ESR signal of the Aluminum center in quartz grains extracted from sediment*. *Ancient TL*, 30(2): 1–9, 2012.
- Duval, M. and Guilarte, V. *ESR dosimetry of optically bleached quartz grains extracted from Plio-Quaternary sediment: evaluating some key aspects of the ESR signal associated to the Ti-center*. *Radiation Measurements*, 78: 28–41, 2015.
- Duval, M., Campaña, I., Guilarte, V., Miguens, L., Iglesias, J., and González Sierra, S. *Assessing the uncertainty on particle size and shape: Implications for ESR and OSL dating of quartz and feldspar grains*. *Radiation Measurements*, 81: 116–122, 2015a.
- Duval, M., Sancho, C., Calle, M., Guilarte, V., and Peña-Monné, J.L. *On the interest of using the multiple center approach in ESR dating of optically bleached quartz grains: Some examples from the Early Pleistocene terraces of the Alcanadre River (Ebro basin, Spain)*. *Quaternary Geochronology*, 29: 58–69, 2015b.
- Duval, M., Arnold, L.J., Guilarte, V., Demuro, M., Santonja, M., and Pérez-González, A. *Electron spin resonance dating of optically bleached quartz grains from the Middle Paleolithic site of Cuesta de la Bajada (Spain) using the multiple centres approach*. *Quaternary Geochronology*, 37: 82–96, 2017.
- Falguères, C., Yokoyama, Y., and Miallier, D. *Stability of some centers in quartz*. *Nuclear Tracks and Radiation Measurements*, 18(1–2): 155–161, 1991.
- Forman, S.L. *Applications and limitations of thermoluminescence to date Quaternary sediments*. *Quaternary International*, 1: 47–59, 1989.
- Forman, S.L., Pierson, J., and Lepper, K. *Quaternary Geochronology: Methods and Applications*, chapter Luminescence Geochronology, pp. 157–176. American Geophysical Union, 2000.
- Grün, R. *Electron Spin Resonance (ESR) Dating*. *Quaternary International*, 1: 65–109, 1989.
- Grün, R. *Suggestions for minimum requirements for reporting ESR age estimates*. *Ancient TL*, 10(3): 37–41, 1992.
- Grün, R. *A cautionary note: use of ‘water content’ and ‘depth for cosmic ray dose rate’ in AGE and DATA programs*. *Ancient TL*, 12(2): 50–51, 1994.
- Grün, R. *The relevance of parametric U-uptake models in ESR age calculations*. *Radiation Measurements*, 44(5–6): 472–476, 2009a.
- Grün, R. *The “AGE” program for the calculation of luminescence age estimates*. *Ancient TL*, 27(2): 45–46, 2009b.
- Grün, R. and Rhodes, E.J. *On the selection of dose points for saturating exponential ESR/TL dose response curves*. *Ancient TL*, 9(3): 40–46, 1991.
- Grün, R. and Rhodes, E.J. *Simulations of saturating exponential ESR/TL dose response curves - weighting of intensity values by inverse variance*. *Ancient TL*, 10(3): 50–56, 1992.
- Guérin, G., Mercier, N., and Adamiec, G. *Dose-rate conversion factors: update*. *Ancient TL*, 29(1): 5–8, 2011.
- Guérin, G., Mercier, N., Nathan, R., Adamiec, G., and Lefrais, Y. *On the use of the infinite matrix assumption and associated concepts: A critical review*. *Radiation Measurements*, 47(9): 778–785, 2012.
- Ikeya, M. *Dating a stalactite by electron paramagnetic resonance*. *Nature*, 255(5503): 48–50, 1975.
- Kallet, R. *How to write the methods section of a research paper*. *Respiratory Care*, 49(10): 1229–1232, 2004.
- Liu, C.R. and Grün, R. *Fluvio-mechanical resetting of the Al and Ti centers in quartz*. *Radiation Measurements*, 46: 1038–1042, 2011.
- Liu, C.R., Yin, G.-M., Gao, L., Bahain, J.-J., Li, J.-P., Lin, M., and Chen, S.-M. *ESR dating of Pleistocene archaeological localities of the Nihewan Basin, North China - Preliminary results*. *Quaternary Geochronology*, 5(2–3): 385–390, 2010.
- Mejdahl, V. *Thermoluminescence dating: beta-dose attenuation in quartz grains*. *Archaeometry*, 21: 61–72, 1979.
- Millard, A.R. *Conventions for reporting radiocarbon determinations*. *Radiocarbon*, 56(2): 555–559, 2014.
- Moreno, D., Richard, M., Bahain, J.-J., Duval, M., Falguères, C., Tissoux, H., and Voinchet, P. *ESR dating of sedimentary quartz grains: some basic guidelines to ensure optimal sampling conditions*. *Quaternaire*, Accepted.
- Nathan, R.P. *Numerical modelling of environmental dose rate and its application to trapped-charge dating*. PhD thesis, University of Oxford, 2010.
- Porat, N., Faerstein, G., Medialdea, A., and Murray, A.S. *Re-examination of common extraction and purification methods of quartz and feldspar for luminescence dating*. *Ancient TL*, 33(1): 22–30, 2015.
- Prescott, J.R. and Hutton, J.T. *Cosmic ray and gamma ray dosimetry for TL and ESR*. *Nuclear Tracks and Radiation Measurements*, 23(2–3): 497–500, 1988.
- Prescott, J.R. and Hutton, J.T. *Cosmic ray contributions to dose rates for luminescence and ESR dating: Large depths and long-term time variations*. *Radiation Measurements*, 23: 497–500, 1994. ISSN 1350-4487.

- Readhead, M.L. *Thermoluminescence dose rate data and dating equations for the case of disequilibrium in the decay series*. Nuclear Tracks and Radiation Measurements, 13: 197–207, 1987.
- Renne, P.R., Deino, A.L., Hames, W.E., Heizler, M.T., Hemming, S.R., Hodges, K.V., Koppers, A.A.P., Mark, D.F., Morgan, L.E., Phillips, D., Singer, B.S., Turrin, B.D., Villa, I.M., Villeneuve, M., and Wijbrans, J.R. *Data reporting norms for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology*. Quaternary Geochronology, 4(5): 346–352, 2009.
- Tissoux, H., Falguères, C., Voinchet, P., Toyoda, S., Bahain, J.-J., and Despriée, J. *Potential use of Ti-center in ESR dating of fluvial sediment*. Quaternary Geochronology, 2(1–4): 367–372, 2007.
- Toyoda, S. and Falguères, C. *The method to represent the ESR signal intensity of the aluminum hole center in quartz for the purpose of dating*. Advances in ESR Applications, 20: 7–10, 2003.
- Tsakalos, E., Christodoulakis, J., and Charalambous, L. *The Dose Rate Calculator (DRC) for luminescence and ESR dating - A Java application for dose rate and age determination*. Archaeometry, 58(2): 347–352, 2016.
- Vandenbergh, D., De Corte, F., Buylaert, J.P., Kučera, J., and Van den haute, P. *On the internal radioactivity in quartz*. Radiation Measurements, 43(2–6): 771–775, 2008.
- Voinchet, P., Falguères, C., Laurent, M., Toyoda, S., Bahain, J.-J., and Dolo, J.M. *Artificial optical bleaching of the Aluminium center in quartz implications to ESR dating of sediments*. Quaternary Science Reviews, 22(10–13): 1335–1338, 2003.
- Voinchet, P., Falguères, C., Tissoux, H., Bahain, J.-J., Despriée, J., and Pirouelle, F. *ESR dating of fluvial quartz: Estimate of the minimal distance transport required for getting a maximum optical bleaching*. Quaternary Geochronology, 2(1–4): 363–368, 2007.
- Voinchet, P., Toyoda, S., Falguères, C., Hernandez, M., Tissoux, H., Moreno, D., and Bahain, J.-J. *Evaluation of ESR residual dose in quartz modern samples, an investigation on environmental dependence*. Quaternary Geochronology, 30: 506–512, 2015.
- Walther, R. and Zilles, D. *ESR studies on flint with a difference-spectrum method*. Quaternary Science Reviews, 13(5–7): 635–639, 1994.
- Yokoyama, Y., Falguères, C., and Quaegebeur, J.P. *ESR dating of quartz from quaternary sediments: First attempt*. Nuclear Tracks and Radiation Measurements, 10(4–6): 921–928, 1985.

Reviewer

Lee Arnold

Editor's Note

The manuscript was reviewed by Lee Arnold. The authors decided that his review made significant contributions to the manuscript, which warranted his inclusion as co-author of the study. The Editor agreed to this change after the manuscript had been accepted.