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Research paper

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)

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ABSTRACT

The present work reports the first numerical ages obtained for two highest fluvial terraces (Qt1 and Qt2) of the Alcanadre River system (Northeastern Spain) representing the earliest remnants of Quaternary morphosedimentary fluvial activity in the Ebro basin. ESR dating method was applied to optically bleached quartz grains and both the Al and Ti centers were measured, in accordance with the Multiple Center approach. The results are overall in good agreement with the existing preliminary chronostratigraphic framework and our interpretation indicate that terraces Qt1 and Qt2 have an ESR age of 1276 ± 104 ka and 817 ± 68 ka, respectively. These data provide some chronological insights on the beginning of the fluvial sedimentary processes in a scenario of incision maintained over Quaternary in the Ebro Basin. These are among the first numerical ages obtained for such high terraces in the Iberian Peninsula.

Our results demonstrate the interest of using the Multiple Center approach in ESR dating of quartz, since the two centers provide complementary information, i.e. an independent dose control. The overall apparent consistency between the ESR age estimates and the existing preliminary chronostratigraphic framework may be considered as an empirical evidence that the Ti–Li center may actually work for Early Pleistocene deposits, whereas the Ti–H center shows some clear limitations instead. Finally, these results demonstrate the interest of using ESR method to date Early Pleistocene fluvial terraces that are usually beyond the time range covered by the OSL dating method.

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1. Introduction

Fluvial terrace sequences are known to be valuable Quaternary continental archives that can record regional paleoclimatic, palaeoenvironmental or paleogeographic fluctuations (e.g. Bridgland et al., 2004; Bridgland and Westaway, 2008), markers of long-term landscape development (e.g. Wegmann and Pazzaglia, 2009; Westaway et al., 2009) and evidence of prehistoric hominid occupations (see a review in Mishra et al., 2007). This is why

establishing accurate chronologies of these deposits has always been of crucial importance (e.g. Hosfield and Chambers, 2005; Bidgland et al., 2004). Many tools are available for this purpose. For example, if paleontological remains have been preserved in the sediment and may be identified, biostratigraphy may rapidly give a first overview of the chronological framework. Then, provided that the sedimentary context is suitable for palaeomagnetic studies, which is not systematic in presence of coarse deposits (Tauxe, 2010), further age constraint may be obtained in case some geomagnetic polarity reversals may be identified. However, as soon as higher chronological resolution is required, these data must be complemented with numerical ages. A wide range of dating methods is potentially available in that regard, but their use actually depends on several factors, such as the nature of the

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sedimentary environment, the material that may be found within the deposits, as well as the age of these deposits. This is why some reference radiometric methods like radiocarbon, U-series or Argon–Argon may be punctually very useful to provide high-precision ages (e.g. Bridgland et al., 2004; Sharp et al., 2003; Schulte et al., 2008; Pan et al., 2003), but their application to fluvial terraces remains nevertheless overall somewhat limited. In contrast, other numerical methods like Terrestrial Cosmogenic Nuclides (TCN), Optically Stimulated Luminescence (OSL) or Electron Spin Resonance (ESR) that are based on minerals that are commonly found in fluvial environment, such as silicates and particularly quartz, offer perhaps a greater potential in this specific context.

Actually, Electron Spin Resonance (ESR) and Optically Stimulated Luminescence (OSL) dating methods can be both applied to optically bleached quartz grains to date the same event, i.e. when the sediment has been last exposed to sunlight. These two palaeodosimetric or trapped charge dating methods are based on the same principles, i.e. the study of the effect of the natural radioactivity on materials, which is quantified in terms of radiation absorbed dose values. To do so, they focus on radiation-induced signals by looking at either paramagnetic (ESR) or luminescent (OSL) properties of materials (see basic principles in Aitken, 1998; Ikeya, 1993). Actually, OSL is widely used to date Late Pleistocene to Holocene fluvial deposits, but the rapid saturation of the signal make that the standard dating approach can generally not go beyond ~200 ka, depending mainly on the magnitude of the dose rate, which means that most of the Early to Middle Pleistocene terraces can simply not be dated with this technique (e.g. Schulte et al., 2008; Lewis et al., 2009; Martins et al., 2009). It is nevertheless worth mentioning that some new approaches have been recently developed to go further back in time (see a review in Arnold et al., 2014), but their use remains for the moment quite limited given the time required for data acquisition and reduction. In comparison with OSL signals, paramagnetic centers measured by ESR in quartz for geochronological purpose such as Aluminum (Al) or Titanium (Ti) centers have greater saturation levels with the dose (Duval, 2012; Duval and Guilarte, 2015), and have shown an interesting potential in fluvial context to date complete River terrace systems covering the whole Pleistocene time range (e.g. Voinchet et al., 2010). As shown by Cordier et al. (2012), it can actually offer a valuable alternative to the OSL method to refine the chronology of the oldest terraces of fluvial terraces systems that are frequently lacking of numerical ages. The Iberian Peninsula is an excellent example in that regard (see Santisteban and Schulte, 2007). However, perhaps the major challenge in ESR dating lies in evaluating whether the signal has been fully reset prior to sediment deposition, given that the Al center is known to have not only a somewhat slow bleaching kinetics but also an unbleachable (=residual) component of its ESR signal (e.g. Toyoda et al., 2000; Tissoux et al., 2007; Voinchet et al., 2003), in contrast with the Ti-center that is, however, more complicated to measure (e.g. Duval and Guilarte, 2015 and references therein). To address this issue, some authors proposed the combined analysis of both Al and Ti centers in quartz samples, the so-called multiple center approach (Toyoda et al., 2000), but its potential remains nevertheless to be better defined.

Actually, the Ebro Basin drainage (Northeastern Spain) is a typical example where the ESR dating method can be especially useful for constraining the chronology of the staircase fluvial terraces. Specifically, the Alcanadre River developed an extensive terrace sequence made of nine strath levels (Fig. 1) very suitable for numerical dating. OSL dating method was applied to the lowest terraces providing preliminary Late Pleistocene ages (for further details, see Calle, 2012; Calle et al., 2013). For the older

terrace deposits, ongoing magnetostratigraphic studies indicate some inverse polarity intervals that may be correlated to the Matuyama chron (>0.78 Ma), suggesting thus an Early Pleistocene chronology. In particular, the oldest terrace of the Alcanadre River sequence (South Pyrenean piedmont) exhibits large preserved outcrops and includes interesting paleogeographical information, at regional scale, because representing the earliest morphosedimentary pulse under exoreic conditions (Alberto et al., 1983) after the opening of the Tertiary Ebro Basin toward the Mediterranean Sea between 13 and 8.5 Ma ago (García-Castellanos et al., 2003).

In order to improve and refine the current chronostratigraphic framework, we collected four sediment samples from the two highest terraces of the Alcanadre River for ESR dating purpose, which was also an excellent opportunity to evaluate the potential of multiple center method for this specific time range.

1.1. The multiple center (MC) approach: basic principles

First suggested by Toyoda et al. (2000) after observing the large variability of the bleaching kinetics of various paramagnetic centers measured in quartz grains, this approach consists in measuring the ESR signals of both the Aluminum (Al) and Titanium (Ti) centers in a given sample in order to evaluate whether full bleaching of the Al center has been achieved prior to sediment deposition.

Actually, the signal of the Al center has been so far the most widely used for geochronological purpose since the pioneering work by Yokoyama et al. (1985). It has the main advantage to be observed in almost any quartz samples, and usually has an intensity that is high enough to ensure repeatable measurements (e.g. Duval and Guilarte Moreno, 2012), given that Aluminum (Al^{3+}), as a precursor of the Al paramagnetic center, is usually the most abundant impurity present in alpha quartz (Preusser et al., 2009). The ESR signal associated with the Al center is known to have a high thermal stability and radiation saturation level (e.g. Toyoda and Ikeya, 1991; Duval, 2012) so that it could be used to date Early Pleistocene materials (e.g. Rink et al., 2007; Duval et al., 2015), or even older (Laurent et al., 1998). However, its bleaching kinetics is quite slow and there is a residual component that can simply not be optically bleached (e.g. Voinchet et al., 2003; Tissoux et al., 2012). Since the level of this residual ESR intensity is sample dependent, it must be thus systematically evaluated for every sample analyzed in order to avoid D_E overestimations. Laboratory experiments suggest that several tens of days would be required in the nature to reset the signal to its residual level (durations of bleaching may vary quite a lot depending on both the samples and experimental conditions, e.g. Rink et al., 2007; Toyoda et al., 2000; Tissoux et al., 2007; Voinchet et al., 2003), even though a field study by Voinchet et al. (2007) showed instead that a complete bleaching of the signal might nevertheless be obtained quite fast, i.e. within the first 1 km of transportation. Consequently, given these long durations, when using the Al center alone for dating purpose there is some uncertainty on whether complete bleaching has been achieved (i.e., whether the ESR signal has been reset to its residual component) prior to sediment deposition. If not, then calculated ESR-Al ages would overestimate the true age. This is why ESR age estimates derived from the Al center and based on the assumption of a complete bleaching should be considered in first instance as maximum possible ages (unless evidence of sediment reworking leading to partial resetting of the signal): this calculated age may be either consistent with the true age of the deposits, or older, but in any case not younger. To avoid misunderstandings, such consideration does not mean that ESR-Al ages are systematically overestimated, as several dating

Fig. 1. General context of the study area: geographical location (NE Spain) (a), geomorphological mapping of the Alcanadre River terraces system (b) and location of the ESR samples collected in Qt1 and Qt2 terraces (c).

studies have already previously shown ESR dating results being consistent with independent age control (e.g. Duval et al., 2015; Rink et al., 2007), thus indirectly confirming that the initial assumption of a complete resetting of the bleachable component of the ESR-Al signal was correct in these cases.

Perhaps the main challenge in ESR dating of optically bleached quartz grains based the Al center consists in minimizing this uncertainty, and several strategies may be employed for this purpose. One of them is to get a good independent age control, as previously mentioned (e.g. Duval et al., 2015; Rink et al., 2007). Another option would be to collect modern analog sediment samples from a similar environment to that of the sediment dated, in order to use it as a proxy of the bleaching conditions in the past. However, the reliability of this approach is limited by many factors (e.g. Jain et al., 2004), and the basic assumption that actual and past bleaching conditions were similar can hardly be verified, so that it might actually bring more uncertainty on the age result. But the best option is probably to take advantage of the presence of other light-sensitive ESR signals in quartz. In that regard, the Ti-centers, namely the Ti–Na, Ti–H and Ti–Li centers depending on the compensating cation, have a signal that may be zeroed by sunlight exposure. The intensity of the Ti–H center can apparently be zeroed within a day, while it might take less than 20 days for the Ti–Li center (e.g. Toyoda et al., 2000; Rink et al., 2007; Tissoux et al., 2007). Even though these durations are quite variable from one study to another and are clearly sample dependant, the bleaching kinetics of the Ti centers is nevertheless undoubtedly much faster than that of the Al center.

Assuming that all the centers from a given quartz sample should actually provide the same estimation of the dose effectively absorbed by this sample during its burial, any difference in the D_E values derived from the Al and Ti centers would simply be due to incomplete bleaching of the former prior to sediment deposition. This is the basic principle of the MC approach proposed by Toyoda et al. (2000), but from a practical perspective its verification is actually limited by the difficulty to measure the Ti center in routine. The ESR intensity of this signal is usually quite low, significantly lower than that of the Al center. Achieving repeatable measurements is quite a challenge given the low signal to noise (S/N) ratios

(Duval and Guilarte, 2015) that require to keep the experimental conditions at low temperature stable for much longer times than with the Al center. For example, based on our experience, and with our analytical procedure, the ESR measurement of all the aliquots of a given sample may take around 1 h for the Al center and between 3 and 5 h for the Ti center. This is probably the main reason why the MC approach has been finally very little tested for dating purpose (e.g. Rink et al., 2007; Tissoux et al., 2007, 2008; Burdette et al., 2013), most of the studies being rather focused on a single center (e.g. Voinchet et al., 2010; Moreno et al., 2012; Liu et al., 2010, etc.). In addition, if there has been for many years an uncertainty about the stability of the signal associated to the Ti centers over a long time range, the consistent results obtained by Rink et al. (2007) suggest the Ti–Li center may actually be useful up to the Early Pleistocene time range. In contrast, the interest of the Ti–H center is very likely limited to Middle to Late Pleistocene deposits, since it is known to saturate much earlier with the dose (Tissoux et al., 2007; Duval and Guilarte, 2015).

More recently, Rink et al. (2007) pushed a bit further the basic principle of this MC approach by proposing a new criterion as a quality control on the calculated ESR age results: “both the Al signal and Ti signal ages must agree to insure accurate burial ages” (p. 1618). The relevancy of this criterion will be discussed in the present paper in the light of the results obtained from the Alcanadre terraces.

1.2. The Alcanadre River system: chronostratigraphic context

The Alcanadre River is a tributary of the Cinca River which in turn flows into the Ebro River (Northeastern Spain) (Fig. 1). Its headwaters are located in the External Pyrenees and it flows with a meridian trend across the Ebro southern foreland basin. The Alcanadre River developed an extensive Quaternary staircase terrace system made of nine strath or cut-in-bedrock terraces (Calle et al., 2013). These are named as follows, from the highest to the lowest: Qt1 (between +200 m above the active channel in the northern part and +160 m at the South of the valley), Qt2 (+190 – 100 m), Qt3 (+130 – 55 m), Qt4 (+65 – 30 m), Qt5 (+55 – 20 m), Qt6 (+40 – 25 m), Qt7 (+35 – 10 m), Qt8 (+15 – 3 m), Qt9 (floodplain)

Fig. 2. Chronostratigraphic framework available for the Alcanadre River system based on a combination of morphostratigraphic, palaeomagnetic and numerical dating studies (modified from Calle et al., 2013). From these analysis, the Brunhes–Matuyama (B–M) boundary have been positioned within Qt3. ESR age results obtained in the present study have been included: for Qt1, this is a weighted mean ESR age based on the Ti–Li D option age results obtained for the two samples, while for Qt2 a weighted mean age from the ESR–Al and –Ti–Li age results obtained for sample AL1203 only has been considered as the most reasonable age estimate (see manuscript for further details). Key: (*) age estimation from Calle et al. (2013).

(Calle et al., 2013) (Fig. 2). Longitudinal profiles slightly diverge towards the headwaters located in South Pyrenees (Calle, 2012).

A combination of ongoing magnetostratigraphic and OSL dating studies has yielded a first insight of the chronostratigraphic framework of this terrace system. Preliminary numerical ages were obtained following a standard multiple quartz grains SAR procedure (180–250 μm size fraction). OSL dating performed on terraces Qt7 and Qt6 provided weighted mean ages of 9.9 ± 0.4 ka ($n = 2$) and 18.6 ± 0.7 ka ($n = 3$), respectively (Calle et al., 2013). Qt5 yielded a single OSL age estimate of 44 ± 2 ka, while the samples were collected from Qt4 yielded only provided minimum ages given the saturation of the OSL signal. To complement these first results, sediment samples were collected for palaeomagnetic analysis from terrace Qt6 to Qt1. Current available data (Calle et al., 2013) require additional work to be validate and results should thus be taken as indicative. Normal polarities were identified for the terraces Qt6, Qt5 and Qt4, indicating thus that the deposits may be correlated to the Brunhes chron, which is consistent with the OSL dating results. In contrast, paleomagnetic data from the oldest terraces are somewhat more complex to interpret, since they showed reverse and normal polarities. According to its morphostratigraphic position, the age of Qt3 could be around the Brunhes–Matuyama (B/M) boundary dated to ~ 0.77 Ma (Singer, 2014), while Qt2 did not yield any conclusive palaeomagnetic data. In a consistent morphostratigraphic framework, the reverse polarity identified within Qt1 should be attributed to the Matuyama chron, while the normal polarity interval could be tentatively correlated to a normal subchron (Jaramillo [~ 1.01 – 1.08 Ma] or Cobb Mountain [~ 1.19 – 1.22 Ma]; Singer, 2014). Although these preliminary data need to be refined in the future with additional sampling and analysis, they are nevertheless overall in fair agreement with the terrace sequence of the Cinca River valley (base level of the Alcanadre River) based on a combination of palaeomagnetic analysis, OSL dating and soil stratigraphy (Sancho et al., 2007; Lewis et al., 2009).

2. Material and methods

2.1. Sediment samples

Four sediment samples were collected in June 2012 (Fig. 3): two from the Qt1 terrace (ALC1201 and ALC1202) and other two from the Qt2 (ALC1203 and ALC1204). Altitude separation between both terraces exceeds 50 m. Terrace treads are underlain by 11 m (Qt1)

and 5 m (Qt2) of cobble-sized gravels in a sandy matrix with sparse sand lenses. Sand lenses were specifically selected for ESR sampling. Within Qt1, ALC1201 was coming from the upper part of the stratigraphic sequence, while ALC1202 was located about 10 m below, in the lower part of the section. In comparison, ALC1203 and ALC1204 were laterally distant by a few tens of meters from a given outcrop belonging to Qt2.

Sampling was performed by inserting opaque PVC tubes into the section. Additional sediment samples were collected at the same sampling spots for water content evaluation and further laboratory measurements. *In situ* measurements of the natural radioactivity were carried out with a 1.5*1.5 inch NaI(Tl) probe coupled with an Canberra Inspector1000 multichannel analyzer (see details of the device in Arnold et al., 2012) at the exact location of the ESR samples.

2.2. Analytical procedure

2.2.1. Sample preparation

Sample preparation and ESR measurements were carried out at CENIEH (Burgos, Spain). Sediment samples were prepared in the laboratory under conditions of limited illumination. The 100–200 μm size fraction was collected after wet sieving. HCl (36%) was used to dissolve carbonates and H_2O_2 (30%) to eliminate organic matter. Heavy minerals and feldspars were removed with Sodium Polytungstate (SPT) solutions at $d = 2.72$ and $d = 2.62$ g/ml, respectively. The resulting samples were treated with HF (40%) for 40 min to eliminate the remaining feldspars and to etch quartz grains. Then, HCl (18%) was added in order to remove any soluble fluoride. Finally, magnetic minerals were eliminated using a strong neodymium magnet.

Quartz grains were dated by ESR using the Multiple Aliquots Additive (MAA) dose approach. Each natural sample was divided into 13 multiple grains aliquots. Eleven of these aliquots were irradiated using a ^{137}Cs Gammacell gamma source at the following doses: 197, 393, 590, 982, 1474, 2456, 4912, 7860, 11,789, 19,649, 29,473 and 49,121 Gy. The non-bleachable residual ESR signals of the Aluminum center were obtained after exposing one aliquot of each natural sample in a SOL2 (Dr Hönle) solar light simulator for about 1460 h.

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2.2.2. ESR measurements

ESR measurements were carried out with an EMXmicro 6/1 Bruker X-band ESR spectrometer coupled to a standard

Fig. 3. Pictures of the four spots where sediment samples have been collected. (A) and (B): samples ALC1201 and ALC1202 from terrace Qt1 around Lagunarrota. (C), (D) and (E): samples ALC1203 and ALC1204 from terrace Qt2 near Berbegal.

rectangular ER 4102ST cavity. To ensure constant experimental conditions over time, the temperature of the water circulating in the magnet is controlled and stabilized at 18 °C by a water-cooled Thermo Scientific NESLAB ThermoFlex 3500 chiller, and the temperature of the room is kept constant at 20 °C by an air conditioning unit. ESR measurements were performed at low temperature (–90 K) using a ER4141VT Digital Temperature control system based on liquid nitrogen cooling. Further details about the setup and about its stability over time can be found in [Duval and Guilarte Moreno \(2012\)](#).

Following the MC method suggested by [Toyoda et al. \(2000\)](#), both ESR signals of the Aluminum (Al) and Titanium (Ti) centers were studied. For the ESR signal associated to the Al center, the following acquisition parameters were used: 10 mW microwave power, 1024 points resolution, 20 mT sweep width, 100 kHz modulation frequency, 0.1 mT modulation amplitude, 40 ms conversion time, 20 ms time constant and 1 scan. In contrast, the ESR signal associated to the Ti centers was measured as follows: 5 mW microwave power, 1024 points resolution, 20 mT sweep width, 100 kHz modulation frequency, 0.1 mT modulation amplitude, 60 ms conversion time, 40 ms time constant and between 2 and 4 scans to ensure a reasonable S/N ratio. Each of the thirteen aliquots (one natural, one optically bleached and eleven gamma irradiated aliquots) of a given sample were measured 3 times after a ~120° rotation in the cavity in order to consider angular dependence of the signal due to sample heterogeneity. Then, measurements were repeated three times over distinct days in order to check the reproducibility of the D_E values. This procedure was carried out for both the Al and Ti signals. Examples of ESR spectra are shown in [Fig. 4](#).

2.2.3. D_E determination

The ESR intensity of the Al signal was extracted from peak-to-peak amplitude measurements between the top of the first peak ($g = 2.0185$) and the bottom of the 16th peak ($g = 1.9928$) ([Toyoda and Falguères, 2003](#)). Following the conclusions from [Duval and Guilarte \(2015\)](#), the ESR intensity of the Ti centers was measured in three different ways ([Fig. 4](#)):

- Peak-to-peak amplitude measurement between $g = 1.979$ and the bottom of the peak at $g = 1.913$ (option A).
- Peak-to-baseline amplitude measurement around $g = 1.913$ – 1.915 (option D).
- Peak-to-baseline amplitude measurement around $g = 1.915$ (Ti–H center).

Actually, options A and D are most likely made by a mixture of Ti–Li and Ti–H centers since they have both a line around $g = 1.913$, but results from [Duval and Guilarte \(2015\)](#) suggested that the contribution from the Ti–H line was in most cases not significant. In contrast, the left peak at $g = 1.915$ is only made by the contribution of the Ti–H center.

For each aliquot, final ESR intensities of Al and Ti centers corresponded to the mean values derived from the repeated measurements, previously corrected by the corresponding receiver gain value, number of scans, aliquot mass and a temperature correction factor ([Duval and Guilarte Moreno, 2012](#)). The fitting procedures were carried out with the Microcal OriginPro 9.1. software using a Levenberg–Marquardt algorithm by chi-square minimization. For the Al center, an exponential + linear function (EXP + LIN) was fitted through the experimental points, and data were weighted by the inverse of the squared ESR intensity ($1/I^2$). D_E values were obtained by extrapolating the EXP + LIN function to the residual ESR intensity (so-called total bleach method, [Forman et al., 2000](#)). For the Ti-centers, two fitting functions were tested for D_E calculation as described in [Duval and Guilarte \(2015\)](#): the single saturating exponential function (SSE) and the so-called Ti-2 function, which was initially proposed by Woda et Wagner (2007). Equations of the fitting functions are provided in supplementary information. With the SSE, data were weighted by the inverse of the squared ESR intensity ($1/I^2$), whereas equal weights were used with the function Ti-2. The goodness-of-fit was 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 (see the Origin 8 User Guide for further details). Two examples of dose response curves (DRCs) are given in [Fig. 5](#).

Fig. 4. Examples of ESR spectra of the Al and Ti centers obtained from the measurement of sample ALC1202 (natural aliquot and gamma irradiated one at $D = 1792$ Gy). The ways ESR intensities are extracted are also indicated. Left: ESR signal of the Ti-centers; Right: ESR signal of the Al center.

2.2.4. Dose rate evaluation and ESR age calculation

The total dose rate value was derived from a combination of *in situ* and laboratory measurements. External gamma dose rate were derived from *in situ* measurements by using the “threshold technique” (Duval and Arnold, 2013). For each dated samples, the corresponding radioelement (U, Th, K) concentrations in the sediment were determined by ICP-MS analysis of about 5 g of dry raw sediment. In addition, ~150 g of this same raw sediment, previously dried and powdered, were analysed by High Resolution Gamma spectrometry (HRGS) using a Canberra Extended Range (XtRa) HpGe detector in order to identify possible disequilibrium in the U-238 decay chain. Concentration values were used to derive external alpha and beta dose rate components using the dose rate conversion factors from Guérin et al. (2011). Dose rate values were calculated assuming a mean grain size of 150 μm , and an assumed thickness removed by HF etching of 20 μm . Values were corrected with beta and alpha attenuation values for spherical grains (Brennan et al., 1991; Brennan, 2003) and water attenuation formulae from Grün (1994). Actual and saturated water contents were evaluated in the laboratory by drying the sediment at 50 °C in an oven during three weeks. Internal dose rate was assumed to be 50 ± 30 uGy/a, based on the work from Vandenberghe et al. (2008) and assuming an alpha efficiency k of 0.15 ± 0.10 (Yokoyama et al., 1985). The cosmic dose rate was calculated using formulae from Prescott and Hutton (1994), with depth, altitude and latitude corrections (Prescott and Hutton, 1988).

ESR age calculation were performed using a non commercial SCILAB based software, with error calculations based on Monte Carlo simulations, considering the following sources of

uncertainties: concentrations, depth, water content, *in situ* gamma dose rate, beta dose rate attenuations, D_E values. ESR ages are given at 1σ .

3. Results and discussion

3.1. ESR data

All the DRCs derived from the evaluation of the Al, Ti–Li A option, Ti–Li D option, and Ti–H centers for the four quartz samples are shown in supplementary information (Fig. S1 to S4). All experimental ESR intensities are given in Table S2 to S7.

3.1.1. Al center

Regarding the Al center, repeated ESR measurements carried out for each sample showed a very good reproducibility of the D_E values, with a variation between 3 and 5% for three samples and around 7% for sample ALC1203. In other words, all D_E values derived from measurements performed on three different days were within error at 1 sigma for a given sample. Consequently, for a given sample, a final D_E value was calculated by considering for each aliquot the average ESR intensities from the three repeated measurements.

The relative bleached component values calculated for the 4 samples are all very close (~59–60%), indicating similar bleaching conditions. A slight difference may be observed between samples from Qt1 and Qt2, but it does not seem to be significant (Table 1). From a methodological point of view, following some of the criteria defined for fossil tooth enamel (Duval et al., 2013), fitting results

Fig. 5. Examples of two DRCs obtained in the present work. Left: Sample ALC1201, Al center. Right: sample ALC1203, Ti–Li D option.

may be considered as reliable: Adjusted r^2 values are systematically >0.99 , indicating an excellent goodness-of-fit, and relative errors on each fitted parameter are $<25\%$. Relative age errors (1σ) are ranging between 8% (ALC1202) and 13% (ALC1201) and are on average around 10.4%. D_E values obtained for samples from Qt1 are higher and somewhat more scattered than those obtained for Qt2, but all D_E values are nevertheless consistent within error for a given terrace.

3.1.2. Ti–Li center

For the evaluation of the Ti–Li center, we followed the quality control procedures recommended by Duval and Guilarte (2015): ESR intensities were measured following options A and D (Fig. 4) and D_E values were calculated using both the SSE (with $D_{\max} = 12$ kGy, i.e. the dose corresponding to the maximum ESR intensity) and Ti-2 functions (on full dose range). Results were overall consistent at 1σ (see summary Table S8), whatever the function or option considered, indicating thus the reliability of the dataset. In addition, repeated ESR measurements carried out for each sample on different days showed a very good reproducibility of the D_E results: a relative variation between 1 and 9% was observed, depending on the samples, and all D_E values derived from repeated measurements were within 1σ error for a given sample. Consequently, in agreement with the recommendations by Duval and Guilarte (2015), a final D_E value was calculated for a given sample by using a Ti-2 function (with equal weights, EW) and considering for each aliquot the average ESR intensities (taken from option D) from the three repeated measurements.

Fitting results fulfill the criteria defined in Duval and Guilarte (2015) to ensure a reliable fitting. Adjusted r^2 values are systematically >0.99 , showing a high goodness-of-fit. For three of the four samples, D_E values are somewhat lower than those derived from the Al center, the exception being ALC1204. It seems nevertheless that each terrace shows a different pattern: for samples from Qt1, the deviation between $D_E(\text{Al})$ and $D_E(\text{Ti})$ is quite important, between 14% and 20%, whereas for the other samples from Qt2 deposits, the two data sets are much closer, with a relative difference of 6% max. This might indicate that the ESR signal of the Al center has been fully, or almost, bleached for the samples from Qt2, while it does not seem the case for the samples from Qt1. These data suggest different transportation and bleaching conditions between the deposits of each terrace.

Finally, it should be mentioned that Ti–Li E option has also been tentatively measured as defined by Duval and Guilarte (2015), since it is virtually the only way to measure the contribution of the Ti–Li center alone. However, the fitting carried out with the Ti-2 function on the four samples did not provide reliable results, as the adj. r^2 values were between 0.80 and 0.85 (indicating thus a poor goodness-of-fit), and the relative D_E errors were ranging from 55% to 65%. Consequently, no conclusive results could be obtained with option E for these four samples.

3.1.3. Ti–H center

For information, the fitting results derived from the

measurement of the Ti–H center (option C in Duval and Guilarte, 2015) are also provided (Table 1). DRCs are shown in supplementary information. This center potentially offers many interests for dating purpose, and especially to detect small dose values given its higher radiation sensitivity in comparison with the other Al and Ti-centers (e.g. Duval and Guilarte, 2015). In addition, it also shows a faster bleaching kinetics (e.g. Tissoux et al., 2007), minimizing thus the uncertainty associated to potential incomplete bleaching prior to sediment deposition. However, the low ESR intensity of the signal makes it in general quite difficult to measure, resulting in scattered DRC and unsatisfactory goodness-of-fit (e.g. Duval and Guilarte, 2015). In addition, the ability of this center to accurately register dose values higher than a few hundreds of Gy has been questioned (e.g. Asagoe and Toyoda, submitted), leaving quite a large uncertainty about its interest for dating Early Pleistocene samples.

Repeated measurements performed on the four samples show good reproducibility in the D_E values, which are varying within a narrow range (between 0.4 and 6.7%). Consequently, final D_E values were calculated by considering the average ESR intensity over the three repeated measurement for each aliquot of a given sample.

Final D_E values derived from the Ti-2 function are ranging from 886 ± 273 and 1395 ± 379 Gy (Table 1). However, these data should be considered with much caution, since they actually do not fulfil the standards defined by Duval and Guilarte (2015) to ensure a reliable fitting. The very low r^2 values (<0.95) indicate a very poor goodness-of-fit. This may be clearly observed on the DRCs shown in supplementary information. If D_E values consistent at 1 sigma with those derived from the Ti–Li signal, this is only the result of very large D_E errors. Actually, D_E values are systematically lower than those from the Ti–Li signal, which is most likely because the Ti–H signal saturates much earlier with the dose (around 2000 Gy for the four samples). This is in agreement with previous observations (e.g. Tissoux et al., 2007; Duval and Guilarte, 2015). The use of an SSE until apparent saturation ($D_{\max} = 5$ kGy) instead of the Ti-2 function may seem more appropriate in this case since adj. r^2 result in similar or higher values, but they nevertheless remain overall below the standards to ensure reliable fitting (between 0.9812 and 0.9113). With this function, calculated D_E values are even smaller in comparison with those derived from the Ti-2 function (see summary Table S8). If these data are definitely not reliable enough to draw any definitive conclusion, they nevertheless seem to confirm the limited interest of this signal for samples with doses >1 kGy.

3.2. Dose rate evaluation

Radioelement contents were determined by ICP-OES/MS and HRGS and Table 2 shows that these two techniques provide very consistent results. Except for two values, the relative deviation for a given element is not exceeding 3%. Actually, all but two activity values are in agreement at 1σ , and all of them are in agreement at 2σ . HRGS values indicate that no significant disequilibrium is observed in the U-238 series of the four sediment samples, activity values for Rn-222 and U-238 being all consistent within error.

Table 1
ESR data and fitting results obtained for Al and Ti centers.

Sample	Al			Ti–Li D option		Ti–H	
	Bleach. coef. (%)	Adj. r^2	D_E (Gy)	Adj. r^2	Ti-2 D_E (Gy)	Adj. r^2	Ti-2 D_E (Gy)
ALC1201 (Qt1)	60.6 ± 1.3	0.99185	1827 ± 237	0.99460	1566 ± 115	0.94228	1395 ± 379
ALC1202 (Qt1)	60.1 ± 1.4	0.99652	1535 ± 128	0.99238	1221 ± 115	0.92931	886 ± 273
ALC1203 (Qt2)	59.3 ± 1.2	0.99484	1443 ± 157	0.99377	1381 ± 113	0.85365	931 ± 436
ALC1204 (Qt2)	59.2 ± 1.3	0.99577	1389 ± 130	0.99359	1478 ± 119	0.92009	1092 ± 352

Table 2
Comparison of the radioelement concentration values obtained by ICP and HRGS. for the values derived from ICP, an error of 2% was assumed and concentrations in ppm were converted into activity values for facilitating the comparison.

Sample	ICP measurements			High resolution Gamma spectrometry			
	U-238 (Bq/kg)	Th-232 (Bq/kg)	K-40 (Bq/kg)	U-238 (Bq/kg)	Rn-222 (Bq/kg)	Th-232 (Bq/kg)	K-40 (Bq/kg)
ALC1201 (Qt1)	11.563 ± 0.231	15.228 ± 0.305	0.912 ± 0.018	13.177 ± 1.262	12.609 ± 0.881	14.914 ± 0.925	0.882 ± 0.029
ALC1202 (Qt1)	12.558 ± 0.247	12.541 ± 0.251	0.796 ± 0.016	12.876 ± 1.230	13.020 ± 0.846	12.191 ± 0.750	0.722 ± 0.024
ALC1203 (Qt2)	14.671 ± 0.289	20.603 ± 0.412	1.329 ± 0.027	14.794 ± 1.406	13.622 ± 0.885	20.865 ± 1.249	1.296 ± 0.043
ALC1204 (Qt2)	10.765 ± 0.215	11.849 ± 0.237	0.706 ± 0.014	10.967 ± 1.063	10.419 ± 0.682	11.815 ± 0.742	0.699 ± 0.023

Table 3 shows a comparison of gamma dose rate values derived from *in situ* and laboratory (ICP and HRGS) measurements. As expected, the gamma dose rates derived from laboratory measurements and assuming either equilibrium or disequilibrium in the U-238 series are all consistent at 1 sigma. However, when comparing these values with those derived from *in situ* measurements, significant deviations may be observed: the values measured *in situ* are systematically lower by between 3% (ALC1204) and 39% (ALC1202). Actually, such a difference is not really a surprise, given the heterogeneity of the sedimentary context: as one may observe on Fig. 3, samples were systematically collected within lenses of fine sands surrounded by coarser deposits. This actually demonstrates the importance to carry out *in situ* measurements when collecting samples for ESR dating purpose in particular in a non-homogeneous sedimentary context, as frequently observed in fluvial environment. It is easier, faster and undoubtedly more accurate than collecting several sediment samples in the surroundings of the sample dated by ESR for reconstructing the radioactive environment from laboratory measurements, which are based on only a limited amount of material (between a few grams and <200 g of sediment). Actually, laboratory analysis should be preferentially used to derive alpha and beta dose rates, while the values measured *in situ*, at the exact location of the sample, should be intended for the evaluation of the gamma dose rate (see also Duval, *in press*).

3.3. ESR age estimates

ESR age estimates were calculated using the D_E values derived from both the Al and Ti–Li D option centers, alpha and beta dose rates based on ICP-OES/MS measurements and *in situ* gamma dose rates values. Results are shown in Table 4. The actual water content was found to be below 5% for all the samples, but the final water content used for the dose rate evaluation was assumed to be around 60% of the saturated water content measured in the laboratory. The resulting values are ranging from 16 to 20%. A quite large error of 5%

(1σ) was assumed in order to encompass any possible long and short term variations of the water content over time.

ESR age estimates based on the Al center are consistent at 1 sigma for the two samples from Qt1 terrace, whereas they are more scattered for Qt2. The same pattern is observed for the Ti-based age results. All ages are nevertheless consistent in indicating an Early Pleistocene chronology for both terraces. Age errors (1σ) are between 11.6% and 15.2% and between 10.8% and 12.4% for the Al and Ti–Li D option centers, respectively. For Qt1, ESR-Al ages are around 1.50–1.60 Ma, while ESR-Ti ages are in agreement at 1σ, but nevertheless younger, around 1.25–1.30 Ma. Weighted mean age values of 1566 ± 145 ka and 1276 ± 104 ka may be calculated for Qt1 terrace formation based on Al and Ti-centers from the two samples, respectively. Following the principle of the MC approach, such a difference in the ages may be interpreted as an evidence of an incomplete bleaching of the Al center prior to sediment deposition, given its slower bleaching kinetics in comparison with the Ti center (Toyoda et al., 2000). ESR-Al age estimates should be thus considered as maximum possible ages, whereas the ESR-Ti age results are most likely a better estimation of the true age of the deposits (Fig. 2). In that regard, the weighted mean age of 1276 ± 104 ka based on Ti–Li centers is in good agreement with the preliminary existing chronostratigraphic framework suggesting an Early Pleistocene chronology for Qt1. The normal polarity interval identified by Calle et al. (2013) lead the authors to suggest a correlation with a normal subchron such as Jaramillo (~1.01–1.08 Ma) or Cobb Mountain (~1.19–1.22 Ma) (Singer, 2014), which is consistent with the ESR chronology available for this terrace.

Regarding Qt2 samples, age estimates are very scattered, with 842 ± 109 and 1317 ± 159 ka (Al center) for samples ALC1203 and ALC1204, respectively. The ESR age estimates based on the Al center differ by a factor >50%, but are nevertheless consistent at 2 sigma, while there is a factor of ~75% of difference for the Ti–Li age estimates. However, in contrast with Qt1 terrace, the chronologies provided by each center are actually highly consistent for a given sample (Table 4), suggesting thus a complete, or almost, bleaching

Table 3
Comparison of gamma dose rates derived from *in situ* and laboratory measurements.

Sample	Method	Gamma dose rate (μGy/a)				Ratios			
		Measured water content (%)							
		1	2	3	4	2/1	4/1	4/2	4/3
		<i>In situ</i>	Laboratory	Laboratory	Laboratory				
		Threshold	ICP full series ^a	HRGS Pre-Rn ^b	HRGS full series ^a				
ALC1201 (Qt1)	1.1	451 ± 27	500 ± 17	499 ± 67	503 ± 60	1.11	1.12	1.01	1.01
ALC1202 (Qt1)	4.1	313 ± 19	434 ± 15	416 ± 54	415 ± 49	1.39	1.33	0.96	1.00
ALC1203 (Qt2)	4.4	574 ± 34	666 ± 23	653 ± 83	662 ± 78	1.16	1.15	0.99	1.01
ALC1204 (Qt2)	3.1	382 ± 23	394 ± 14	390 ± 51	394 ± 47	1.03	1.03	1.00	1.01

^a Gamma dose rate calculated using the full series dose rate conversion factors from Guérin et al. (2011) (i.e. assuming equilibrium in the U-238 decay chain) and attenuated by the measured water content for a given sample.

^b Calculation performed assuming that a constant disequilibrium has prevailed over time within the U-238 series (pre-Rn dose rate conversion factors from Guérin et al., 2011) and attenuated by the measured water content for a given sample.

Table 4

ESR age estimates calculated for the four Alcanadre samples. The assumed water content used for the age calculation correspond to 60% of the saturated water content that has been determined the laboratory, with an associated uncertainty of 5%.

Sample	ALC1201	ALC1202	ALC1203	ALC1204
Terrace	Qt1	Qt1	Qt2	Qt2
Depth (m)	4 ± 2	14 ± 2	3 ± 2	2.5 ± 1
Assumed water content (%)	20 ± 5	18 ± 5	16 ± 5	20 ± 5
Internal dose rate (μGy/a)	50 ± 30	50 ± 30	50 ± 30	50 ± 30
Alpha dose rate (μGy/a)	18 ± 15	17 ± 14	26 ± 22	15 ± 13
Beta dose rate (μGy/a)	672 ± 54	601 ± 53	1012 ± 79	534 ± 42
Gamma dose rate (μGy/a)	356 ± 33	256 ± 24	495 ± 44	309 ± 28
Cosmic dose rate (μGy/a)	126 ± 44	37 ± 8	141 ± 25	152 ± 28
Total dose rate (μGy/a)	1222 ± 97	961 ± 79	1724 ± 124	1060 ± 79
D _E (Gy) Al	1827 ± 237	1535 ± 128	1443 ± 157	1389 ± 130
D _E (Gy) Ti–Li D option	1566 ± 115	1221 ± 115	1381 ± 113	1478 ± 119
Age (ka) Al	1504 ± 229	1606 ± 187	842 ± 109	1317 ± 159
Age (ka) Ti–Li D option	1282 ± 139	1269 ± 157	801 ± 87	1394 ± 152

of the Al-ESR signal prior to deposition. This large difference in age (whatever the center considered) raises some interrogations about the true age of Qt2, since no meaningful mean value can be extracted from the two samples. Given these results, two main hypotheses may reasonably be envisaged: (i) either one of the two samples strongly underestimates or overestimates the true age of the deposits, (ii) or both ages accurately reflect the age of the deposits.

Actually, since the D_E values are very similar, the difference between the two samples is most likely coming from the evaluation of the total dose rate: the value calculated for sample ALC1204 is significantly lower (–40%) than that obtained for ALC1203. It is worth mentioning that sediment samples for laboratory analyses were systematically taken from the same exact spot where ESR samples were collected. Consequently, the possibility of an inaccurate external alpha and beta dose rate evaluation due to lateral variations of dosimetry in the sedimentary context may reasonably be excluded here. In addition, the overall excellent agreement between the ICP and HRGS results based on two subsamples of a few g and ~110 g, respectively, show the homogeneity of the sediment at the ESR sampling points. Although concentrations of Th-232 and K-40 measured for ALC1204 are actually almost half of the values of ALC1203 (Table 2), we do not observe any significant disequilibrium in the U-238 that could suggest a recent change in the geochemical conditions and significantly impact the dose rate in one direction or another. Another possibility would be that the estimation of the water content used in the age calculation might be inaccurate for one of the two samples. To test the impact of the water content on the calculated ages, simulations performed using a water content of 15 ± 5 and 10 ± 5% for sample ALC1204 indicate that the ESR ages would be younger by about 6% and 11%, respectively, i.e. still within error. Consequently, from a methodological perspective, we do not have any objective reason to discard the age obtained for one sample or the other.

However, it is also possible that both samples accurately reflect the true age of the deposits. Nevertheless, in the light of the ESR dating results obtained on Qt1 and the existing chronostratigraphic framework, terrace Qt2 should be younger than Qt1. This would suggest that among the two samples from Qt2, ALC1203 is most likely the one providing the best estimation of the age of Terrace Qt2, with an age result of 842 ± 149 ka based on the Al center. The older age obtained for sample ALC1204 might indicate that the sediment have been reworked from older deposits, may be from a remnant from terrace Qt1. However, given the agreement between ESR Al and Ti–Li age estimates for this sample, this reworking must have occurred without exposing the sediment to sunlight, or for

such a short time that it has not been recorded by the Ti–Li signal. Actually, the incorporation of sediment coming from remnants of older terraces into younger terraces also has been previously argued by Lewis et al. (2009) to establish the OSL dating chronology of the Upper Pleistocene terraces of the Cinca River sequence.

Consequently, we would consider a weighted mean age of 817 ± 68 ka derived from the ESR-Al and –Ti–Li age results obtained for ALC1203 as the most reasonable age estimate for the Terrace Qt2 (Fig. 2).

Finally, although Rink et al. (2007) suggested that age consistency between Al and Ti centers for a given sample is an evidence for age accuracy, our results obtained from terraces Qt1 and Qt2 do not support this hypothesis. Actually, ESR ages derived from Al and Ti–Li centers for a given sample are not independent ages. They only differ on the D_E determination and share many sources of uncertainty. Any bias in the stratigraphical positioning of the sample, the sample preparation or dose rate evaluation would actually make both Al and Ti-ESR ages inaccurate.

3.4. Geomorphological interpretation of the ESR age results

The interpretation of our ESR age results indicates that an age of 1276 ± 104 ka and 817 ± 68 ka may be considered for terraces Qt1 and Qt2, respectively (Fig. 2). These are the first numerical ages obtained for these two highest terraces of the Alcanadre River system. These morphosedimentary archives have been mapped and described for a long time (Bomer, 1979; Alberto et al., 1983; Rodríguez-Vidal, 1986; Sancho, 1991). In particular, the complex multi-storey calcrete profiles identified on Qt1 terrace (Sancho and Meléndez, 1992; Meléndez et al., 2011) indicate a high degree of soil development that is in good agreement with the numerical age reported here.

The provided ages record the earliest fluvial sedimentary activity in the Tertiary Ebro basin under exoreic conditions and therefore represent a paleogeographic and geomorphological landmark of high interest in the long-term landscape evolution in the northeastern Iberian Peninsula. Indeed, fluvial downcutting and erosion related processes lasted several million years in the Tertiary Ebro Basin between its opening toward the Mediterranean Sea (13–8.5 Ma ago) (García-Castellanos et al., 2003; Ache et al., 2010; Vázquez-Urbez et al., 2013) and the Alcanadre Qt1 terrace dated here to ~1.3 Ma. It is remarkable that these fluvial culminant levels are also recognized in most valleys of the Southern Pyrenean sector of the Ebro Basin (e.g. Noguera Ribagorçana, Cinca and Gállego Rivers). The implications of these first numerical ages obtained in the area on the landscape evolution and other associated

processes will be further explored in detail in a forthcoming paper by Sancho et al.

At the moment, only some paleomagnetic data have been produced for Early Pleistocene terraces in the Ebro Basin. Besides, these chronological inputs come from fluvial units affected by synsedimentary karstic subsidence in the Gállego River valley (Benito et al., 1998) and the Ebro River valley (Gil et al., 2013). At a larger scale, some palaeomagnetic data from Early Pleistocene terraces have been recently reported in the Iberian Peninsula, for example by Pérez-González et al. (2013) in the Tagus River valley, Benito-Calvo et al. (2008) in the Arlanzón River valley (Duero Basin) and Baena and Díaz del Olmo (1994) in the Guadalquivir River valley. There is, however, a clear lack of numerical ages for these old terraces as highlighted by Silva et al. (2013) and Santisteban and Schulte (2007), which makes virtually impossible any attempt of high resolution correlations between the various basins of the Iberian Peninsula. To our knowledge, only two Early Pleistocene terraces of the Arlanzón River in the Duero Basin provided numerical ages (Moreno et al., 2012): 1.14 ± 0.13 Ma for the so-called T3 terrace (+70–78 m), 0.93 ± 0.10 Ma and 0.78 ± 0.12 Ma for T4 (60–67 m). However, these ESR age results based on optically bleached quartz grains are derived from the measurement of the Al center only, and should therefore be considered as maximum possible ages. In addition, the Vera Basin (SE Spain) has also yielded several ESR age estimates of >1.5 Ma (Wenzens, 1992) from travertines. However, as mentioned by Santisteban and Schulte (2007), these results represent “only crude age estimates” (p. 2747), and in absence of a detailed description of the methodology, it is actually impossible to further evaluate the reliability of these ages.

4. Concluding remarks

This study presents several ESR ages for the two highest terraces (Qt1 and Qt2) of the Alcanadre River system, providing some insights on the beginning of the Quaternary fluvial morphosedimentary activity in the Ebro Basin in a context of continuous entrenchment of the network. These results are in good agreement with the available loose yet chronostratigraphic framework based on palaeomagnetic data. In the light of these encouraging data, additional ESR samples should be specifically collected in younger terraces as well as in other Quaternary fluvial sequences outcropping in adjacent River valleys, in order to improve the regional chronostratigraphic scenario.

From a methodological point of view, our results show the importance to measure both Al and Ti centers for dating purpose, which is so far the best way to have an idea about whether the Al center has been fully bleached or not prior to sediment deposition. Without the measurement of the Ti-center, ESR age estimates based on the Al center alone may by default be considered as maximum possible ages, given the significant uncertainty arising from the slow bleaching kinetics of the signal. First suggested by Toyoda et al. (2000), the use of the MC approach in ESR dating of optically bleached quartz grain appears to be a major improvement for the reliability of the dating method, since both the Al and Ti centers show complementary strengths and weaknesses. At some point, one may reasonably wonder whether the systematic measurement of these two centers in a given sample should not become a standard requirement for the analytical dating procedure in the future. The overall apparent consistency between the ESR age estimates and the existing preliminary chronostratigraphic framework may be considered as an empirical evidence that the Ti–Li center may actually work for Early Pleistocene deposits (in agreement with previous observations by Rink et al., 2007), whereas the Ti–H center shows some clear limitations instead. Additionally, the age scattering observed in Qt2 illustrates the necessity to rely on

more than one sample to get a reliable estimate of the chronology of a given terrace.

Finally, the present work contributes to fill a gap in the chronological framework of the Early Pleistocene terraces of the Ebro basin and to improve the Quaternary stratigraphy of the Iberian Peninsula. The results obtained demonstrate the interest of using ESR dating of optically bleached quartz grains in fluvial context in order to get some numerical ages for the oldest Quaternary fluvial terraces that can usually not be dated by other means.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.quageo.2015.06.006>.

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