Quaternary Geochronology 29 (2015) 58–69

Contents lists available at ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

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)

Mathieu Duval [a, b, *], Carlos Sancho [c], Mikel Calle [d], Verónica Guilarte [a], José Luis Peña-Monné [e]

[a] Program of Geochronology, Centro nacional de investigación sobre la evolución humana (CENIEH), Burgos, Spain
[b] Research School of Earth Sciences, The Australian National University, Canberra, Australia
[c] Ciencias de la Tierra, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain
[d] National Museum of Natural Sciences (MNCN), CSIC, Madrid, Spain
[e] Geografía y Ordenación del Territorio, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

A R T I C L E I N F O

Article history:
Received 9 January 2015
Received in revised form
1 June 2015
Accepted 3 June 2015
Available online 5 June 2015

Keywords:
Quaternary geochronology
Electron spin resonance dating
Optically bleached quartz grains
Fluvial deposits
Terraces
Alcanadre river
Ebro basin

A B S T R A C T

The present work reports the first numerical ages obtained for the 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.

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, biostratigraphy may rapidly provide a first approximate chronological estimation. 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 sedimentary environment, the

* Corresponding author. Program of Geochronology, Centro nacional de investigación sobre la evolución humana (CENIEH), Burgos, Spain.
E-mail address: mathieu.duval@cenieh.es (M. Duval).

http://dx.doi.org/10.1016/j.quageo.2015.06.006
1871-1014/

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) 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 makes that the standard dating approach can generally not go beyond ~200 ka, depending mainly on the magnitude of the dose rate. This 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 the 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 (Notheastern 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 mophosedimentary 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., in press), 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. Walther and Zilles, 1994; 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). 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 previous dating studies have already shown ESR results being consistent with independent age control (e.g. Duval et al., in press; Rink et al., 2007), thus indirectly confirming that the initial assumption of a complete resetting of the