Age of the oldest hominin settlements in Spain: contribution of the combined U-series/ESR dating method applied to fossil teeth

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Abstract

This paper presents a synthesis of the combined Uranium-Series/ESR age results obtained on fossil teeth from several Early Pleistocene archaeological and/or palaeontological Spanish localities: Atapuerca Gran Dolina TD-6, Fuente Nueva-3, Barranco León, Venta Micena and Vallparadís. While the age results show some scattering, they are nevertheless encouraging and provide a significant contribution to the understanding of the first hominin settlements in Western Europe.

These “old” samples are mainly characterized by high $^{230}\text{Th}/^{234}\text{U}$ activity ratios that may sometimes exceed secular equilibrium, and by high Uranium concentrations (several tens of ppm or more). Consequently, the modeling of U uptake is really crucial for the age calculation process. In the case of the combined US-ESR approach, this uptake is derived from the U-series data measured in dental tissues, which seem to be strongly dependant on the hydrogeological context. Consequently, when dating “old” samples, a special attention has to be paid to the accuracy and the meaning of the U-series data collected from the dental tissues, which may be influenced by several factors such as spatial heterogeneity and recent U uptake overprint. Some rapid scanning procedures should be developed in order to pre-identify the samples that are the most suitable for ESR dating.

Keywords: combined Uranium-series/Electron Spin Resonance dating, fossil teeth, Early Pleistocene, Iberian Peninsula.

1. Introduction

Since the beginning of the 1990s, increasing evidence of hominin presence during Early Pleistocene times have been discovered throughout the entire continent (e.g. [Arzarello et al. 2007](#); [Despriée et al., 2006](#); [Gabunia and Vekua, 1995](#); [Parfitt et al., 2010](#)). In this context, the Iberian Peninsula is of major interest, not only because it documents an significant contribution to the ancient European archaeological record ([Carbonell et al., 1995, 2008](#); [Oms et al., 2011](#); [Martínez et al., 2010](#)), but also because of its strategic geographical location for the study of animal and hominid migration between Africa and Europe, as it could have acted either as a migration route between both continents or as a “cul-de-sac” during this period (e.g. [O’Reagan, 2008](#); [Straus, 2001](#)).

For about 20 years, part of our research has focused on dating fossil teeth from Early Pleistocene Spanish sites by means of the combined Uranium-series/Electron Spin Resonance dating method. From this work, we now present a synthesis of age results obtained at several localities distributed across the Iberian Peninsula ([Fig. 1](#)): in the Northern part at Atapuerca Gran Dolina (AGD), in Southern Spain at Fuente Nueva-3 (FN-3), Barranco León (BL) and Venta Micena (VM) and also in the Eastern part at Vallparadís (EVT). The relatively large data set enables us to obtain an overview of the real potential of the combined U-series/ESR dating method for the time range of >0.78 Ma.

2. Combined Uranium-Series/ESR dating method using the US model

Dating fossil teeth by ESR is especially complex because of the sample geometry and the number of components (several dental tissues and sediment) that have to be considered. In addition, dental tissues behave as open systems for uranium, i.e. the modelling of uranium uptake into dental tissues with time is highly crucial for the dose

rate assessment, especially for samples showing high concentrations (Grün and McDermott, 1994). Grün et al. (1988) proposed for such description to combine U-series and ESR data, using the following function (US model): $U(t) = U_m (t/T)^{p+1}$, where $U(t)$ is the uranium concentration at the time t , U_m is the measured, present-day Uranium (U) concentration, T is the age of the sample and p is the uptake parameter. Frequently used parametric U uptake models are special cases of the US model: a p -value of -1 corresponds to the Early Uptake (EU) model (closed system assumption), $p=0$ to the Linear Uptake (LU) model and $p \gg 1$ approximates the Recent Uptake (RU) model (for basic concepts of the respective models, see Bischoff and Rosenbauer, 1981; Ikeya, 1982; Blackwell et al., 1992). The systematics of dating old fossil teeth by using the US model through the combined U-series/ESR method (US-ESR approach) has been recently discussed by Grün et al. (2010) and Duval et al. (2011a, b, 2012). All U-series and ESR numerical data obtained for the samples set are shown in Table S1.

3. Results

3.1. Atapuerca Gran Dolina TD-6 (Burgos, Castile and León)

Three teeth were analyzed from layer TD-6 (Falguères et al., 1999), at the bottom of the Aurora stratum where several hominid remains attributed to *Homo antecessor* were found in association with Mode 1 lithic artifacts (Carbonell et al., 1995). By combining these US-ESR results with those from the palaeomagnetism, the chronology of TD-6 was suggested to be most likely between 0.78 and 0.86 Ma. This estimation was recently reinforced by luminescence ages (TL and IRSL) obtained on the upper part of the sequence (Berger et al., 2008). Such results showed that the US-ESR approach could be routinely applied up to, at least, ~0.8 Ma.

The mean US-ESR age of 0.73 ± 0.06 Ma (Falguères et al, 1999) is often used as a reference for TD-6 (e.g. Berger et al., 2008; Rodriguez et al., 2011). However, considering more recent dating experience with old samples from various sites (see following sub-sections), this should be now considered with caution. Indeed, two of the samples (AT9602 and AT9603) give similar age estimates (0.76 ± 0.11 Ma and 0.77 ± 0.12 Ma, respectively) while the third one (AT9601) provides a younger result (0.68 ± 0.10 Ma). Because D_E values are all very close, such age difference seems mainly related to the apparent U-series ages (>350 ka) of both dentine and cement tissues of AT9601 sample that are much older than those from the two other samples (Table S1), perhaps indicating a more recent U-leaching overprint process. In particular, the $^{230}\text{Th}/^{234}\text{U}$ activity ratio value of 1.07 ± 0.02 measured in the cement is located at the limits of the US model (Grün et al., 1988) (see also Fig. 2). Such a high activity ratio causes p to approach -1 for the age calculation, thus overestimating the dose rate for that tissue and subsequently underestimating the age, as previously shown by Duval (2008). Consequently, age results obtained for AT9602 and AT9603 are more reliable and should be used as references. A mean combined US-ESR age of 0.77 ± 0.12 Ma extracted from these two samples is therefore a more accurate age estimate of TD-6 level. This result agrees well with palaeomagnetic data that puts the Brunhes-Matuyama (B-M) boundary ~ 1.5 m above the teeth (Parés and Pérez-Gonzalez, 1999), and with the late Early Pleistocene biostratigraphic estimate (Cuenca-Bescos et al., 2011). This proposed ESR chronology will be completed in the future by new ESR ages obtained on optically bleached quartz grains extracted from sediments that were recently collected all along the sequence (Moreno, 2011).

3.2. Venta Micena (Orce, Andalusia)

Five equid fossil teeth were selected from two outcrops (Sites A and B) of the Early Pleistocene palaeontological level of VM. Stratigraphical correlations and faunal evidence indicated that both outcrops are coeval (see details in [Duval et al., 2011b](#)). Results derived from palaeomagnetism and biostratigraphy data suggest that the palaeontological level is most likely chronologically located between Olduvai and Jaramillo subchrons, i.e. in the 1.78-1.07 Ma interval ([Oms et al., 2000](#); [Duval et al., 2011b](#) and references therein).

However, samples from each site show quite distinct patterns of ESR and U-series data ([Fig. 2](#)). Indeed, samples from site A (VM0401, VM0402 and VM0403) have similar D_E values, 1658 ± 64 Gy in average (coefficient of variation: CV=4%), homogeneous $^{234}\text{U}/^{238}\text{U}$ activity ratios of 1.268 ± 0.040 (CV=3%) and relatively young apparent U-series ages of 178 ± 32 ka (CV=18%), while site B samples (VM0501 and VM0502) show more heterogeneous data: lower D_E values, 1237 ± 69 Gy (CV=6%), higher $^{234}\text{U}/^{238}\text{U}$ activity ratios, 1.368 ± 0.078 (CV=6%), recent apparent U-series ages in enamel (150 ± 57 ka, CV=38%) but older ones in dentine and cement tissues (282 ± 147 ka). In addition, U-concentrations measured in dentine as well as in cement from site A samples are higher than those from site B (86.4 ± 11.7 vs 64.3 ± 6.3 ppm and 75.7 ± 7.9 vs 51.8 ± 0.5 ppm, respectively). All these disparities indicate that both loci underwent distinct geochemical histories.

These differences are also reflected in the calculated US-ESR ages. Teeth from site B give a mean ESR age of 0.62 ± 0.03 Ma that seems very young compared to the Early Pleistocene ages suggested by palaeomagnetic and biostratigraphic data (see [Fig. 3](#)). Such an underestimate may arise from a relatively recent U leaching from the teeth ([Duval et al., 2011b](#)). In comparison, the US-ESR age results obtained for site-A show a

large scatter (from $0.96 \pm 0.18/-0.17$ to $1.79 \pm 0.30/-0.23$ Ma). Because the exact location of the samples from site A is not known (the 3 teeth were taken from early 1980s excavation collections), age calculations were performed using an average gamma dose rate value calculated from several *in situ* measurements and sediments samples collected in the site. These data show the heterogeneity of the radioactive environment, most likely related to lateral variations of bone density (up to 80-90 elements/m² in some areas, [Arribas and Palmqvist, 1998](#)), which may explain some of this US-ESR age scattering ([Duval et al., 2011b](#)). Nonetheless, despite this scatter, the ESR age results are in general agreement with the palaeomagnetic analysis. Together, they clearly indicate an Early Pleistocene chronology for VM. This site usually considered as biochronologically contemporaneous with the archaeological locality of Pirro Nord, Italy ([Arzarello et al., 2007](#); [Oms et al., 2000](#)), and to be older than the other Orce sites of Barranco León (BL) and Fuente Nueva-3 (FN-3).
Venta Micena-A definitely shows a good potential for the US-ESR dating approach, and future excavations at this site would be a perfect opportunity to collect suitable samples within a well-controlled radioactive environment.

3.3. Barranco León (Orce, Andalusia)

We applied the US-ESR method to 3 teeth originating from the archaeological level D of BL locality. The sediments correspond to fining upwards sandy fluvial deposits containing faunal remains and lithic artifacts attributed to the Mode 1 technocomplex (e.g. [Oms et al., 2011](#); [Toro-Moyano et al., 2011](#)). For this site, both the palaeomagnetic and biostratigraphic data suggest an age between Olduvai and Jaramillo Subchrons, at 1.78-1.07 Ma ([Oms et al., 2011](#)).

Unlike the VM teeth, BL samples show characteristics that are probably the less suitable for US-ESR dating: scattered D_E values (from 1285 to 2021 Gy), quite heterogeneous $^{234}\text{U}/^{238}\text{U}$ activity ratios in all dental tissues with 12% variation (1.492 ± 0.187), and $^{230}\text{Th}/^{234}\text{U}$ activity ratios systematically greater than equilibrium in the cement and dentine, up to 1.782 (mean value of 1.493 ± 0.152), but the enamel ratios give finite apparent U-series ages, from 302 to 427 ka. The high $^{230}\text{Th}/^{234}\text{U}$ activity ratios in the dentine and cement tissues indicate that U had leached from these tissues (Figure 2). Such characteristics prevent the use of the US model (Grün et al., 1988) and therefore no US-ESR age can be calculated for these samples.

Additional fossil teeth were collected in 2010 and future investigations will be focused on the U-series spatial distribution and homogeneity within the dental tissues by using Laser Ablation ICP-MS, following the protocol proposed by Duval et al. (2011a), in order to try to understand the U mobility underlying such problematic U-series data.

3.4. Fuente Nueva-3 (Orce, Andalusia)

We collected six fossil teeth at FN-3, three from the upper archaeological level, which yielded faunal remains in association with an Mode 1 technology lithic industry (e.g. Oms et al., 2011; Toro-Moyano et al., 2011), and three from the lower levels of the sequence (details in Duval et al., 2012). Similarly to BL, combination of paleomagnetism and biostratigraphy suggest an age ranging between Olduvai and Jaramillo subchrons, 1.78-1.07 Ma (Oms et al., 2011), for FN-3.

Four out of six samples show U-leaching for at least one tissue (Fig 2 and Table S1), thus preventing any combined US-ESR age calculation. One of the 2 remaining

samples, FN0308, gives a surprisingly recent age result of $0.52 \pm 0.09/-0.08$ Ma. This underestimation could be related to the high U concentration in the enamel (~ 9 ppm), which may have lead ESR signal to locally saturate (Chen, 1997) or to a change in the alpha efficiency (Bahain et al., 1992). Lastly, FN0304 gave an age of 1.19 ± 0.21 Ma, which agrees well with the previously established chronological framework. This age may be also used as an indirect reference for the nearby BL site, which cannot be chronologically distinguished from FN-3 with palaeomagnetism and biostratigraphy. Additional fossil teeth were collected in 2010 in order to consolidate this initial promising chronology.

3.5. Vallparadís (Terrassa, Catalonia)

Combined US-ESR dating method was applied on 2 teeth from the archaeological level 10 at Vallparadís (EVT), where a huge number of faunal remains was found in association with Mode 1 lithic artifacts (Martinez et al., 2010). The combination of palaeomagnetism and biostratigraphy suggest a Matuyama age for the level 10, between Brunhes and Jaramillo normal events, i.e. 0.99-0.78 Ma (Martinez et al., 2010).

These 2 samples show distinct U-series data. EVT0601 gave relatively young, consistent apparent U-series ages, from 226 to 293 ka, whereas EVT0602 had more scattered values (from 288 ka to 477 ka) and very high $^{230}\text{Th}/^{234}\text{U}$ activity ratios > 1.051 in all tissues. It clearly exceeds the limits of the DATA program (Grün, 2009b) used for age calculations, although its high $^{234}\text{U}/^{238}\text{U}$ ratios, 1.752-2.100, hint that U leaching has not occurred. Such high $^{234}\text{U}/^{238}\text{U}$ values may indicate very particular geochemical conditions in the surrounding environment (Osmond and Ivanovitch, 1992 and references therein). EVT0601 sample provides a US-ESR age of 0.83 ± 0.07 Ma, in

agreement with the chronological framework based on palaeomagnetism and biostratigraphy. This chronology is also reinforced by consistent additional ESR dates obtained on optically bleached quartz grains (Duval et al., 2011c), yielding a mean age of 0.83 ± 0.07 Ma for the level 10 of Vallparadís. These results do not differentiate chronologically EVT and Gran Dolina sites, although the rodents may suggest that Gran Dolina would be somewhat younger (Martinez et al., 2010).

4. Discussion

For the discussion, the U-series data set is completed by one supplementary tooth from Atapuerca Sima del Elefante TE-9 (ASE) (unpublished data), whose chronology was also attributed to Early Pleistocene (see Carbonell et al., 2008 and Rodriguez et al., 2011 and references therein).

88% of the teeth with a cement tissue show higher U concentrations in the dentine than in the cement, respectively averaging 58.5 ± 25.5 ppm and 41.5 ± 21.7 ppm. Values measured in enamel are about 20 to 30 times lower (2.3 ± 1.8 ppm). The high coefficients of variation for each dental tissue ($43.6\% < CV < 77.2\%$) show the heterogeneity of the whole data set. No significant direct correlation is observed between the age of the site and the U-concentrations. For example, dentine tissues from Atapuerca Gran Dolina (AGD) have the lowest U concentrations values, whereas those from EVT have some of the highest, yet both sites are coeval. D_E values range from 813 ± 58 Gy to 3151 ± 69 Gy and are quite scattered (mean value of 1720 ± 696 Gy, $CV=40\%$). Even for a given site, the samples may sometimes show very different U-series and ESR data, as it is also quite frequent to have samples that can be dated and others not (e.g. FN-3, EVT). Nevertheless, despite the apparent heterogeneity of the data set, some general trends can be identified.

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236 All dental tissues from a given site apparently have relatively consistent U-series data
237 (Fig. 2). In other words, it seems that each site shows a specific isotopic signature and
238 could be potentially differentiated by the ($^{230}\text{Th}/^{234}\text{U}$; $^{234}\text{U}/^{238}\text{U}$) data pair measured in
239 dental tissues (see ellipses in Fig. 2). It is even more obvious for the $^{234}\text{U}/^{238}\text{U}$ activity
240 ratio values, which generally vary within a narrow range for a given site. The best
241 examples are probably FN-3 and EVT sites, whose samples show very distinct features
242 from the other remaining teeth (see corresponding data points in Fig. 2). Samples
243 coming from two distinct localities of the same site have relatively close values, such as
244 Atapuerca (ASE and AGD). A similar trend is observed at Venta Micena, with close
245 values for the enamels from VM-A and VM-B, even if the other tissues show more
246 distant data probably due to recent U mobilization at VM-B (Duval et al., 2011b). This
247 suggests that the U-series data measured in dental tissues are highly influenced by the
248 hydrogeological context, in a broad sense (i.e. including nature and composition of the
249 sediments, geochemistry of the surrounding water), rather than by the real age of the
250 samples, for which no obvious specific pattern is observed in Fig. 2. Detailed
251 information about the geological context of the sites may be found in Table S2. In that
252 regard, by extension, one might consider that if a tissue has U-series data showing a
253 major deviation from the general trend drawn by the samples from a given site, then the
254 meaning and the correctness of the U-series data collected for this tissue may be
255 reasonably questioned. Part of the scattering observed inside the U-series data set from a
256 given site may be potentially explained by two main factors: (i) the origin of the
257 samples (i.e., the animal species) and (ii) the spatial distribution of the U-series data
258 throughout the teeth. Water circulation and radioelement migration into the tissues
259 depend on the nature and geometry of the teeth (e.g. Duval et al., 2011a). However,

since all but two samples (TE0601 and AT9603) are equid fossil teeth, the uncertainty associated to the animal origin of the tooth can reasonably be considered as minimum. In contrast, the U-series maps performed on several cross-sections of one tooth from FN-3 (FN0306) showed the spatial heterogeneity, both horizontally and vertically, of the U-series data within the tissues (Duval et al., 2011a). This is most likely the main factor responsible of the variations within the U-series pattern observed for a given site in Fig. 2.

These fossil teeth are mainly characterized by high U-concentrations values measured in dentine and cement (up to ~106 ppm), which give to the dental tissues a major weight in the total dose rate. Consequently, the age result is highly sensitive to the U-uptake history considered. As an example, basic U-uptake assumptions such as Early uptake (EU) and Linear uptake (LU), have an important impact on the final age result, since the age can be multiplied by a factor of up to 1.85 (LU/EU ratio), with an average value of 1.69 ± 0.21 for our data set (Figure S1). For the combined US-ESR approach, this U-uptake history is mainly modelled from the U-series data measured in dental tissues ($^{230}\text{Th}/^{234}\text{U}$; $^{234}\text{U}/^{238}\text{U}$). Consequently, the reliability of the calculated age is highly dependent on the accuracy of these U-series data, which may be influenced by many factors such as, for example, spatial homogeneity and preservation of the sample (Duval et al., 2011a) or recent U mobilizations that may overprint past U uptake history (Duval et al., 2011a,b). Figure 3 illustrates how the U-series data influence the US-ESR ages. While US-ESR age results are highly contrasted between VM-A and VM-B, the EU-ESR and LU-ESR ages for both sites agree well, indicating that the U-series data more likely have caused the disagreement in the combined ages. The same observation is done, in a lesser extent, for AGD site, between AT9601 and the two other samples.

However, even if our results show some limits of the US-ESR approach, the parametric models that pre-assume uptake are not good alternatives, because they are based on incorrect statements (i.e. the closed system assumption for the EU uptake; Duval et al., 2011a) and they oversimplify the complexity of U uptake into, and potential loss from, the different tissues in some teeth (Grün et al., 2009b). For example, all calculated EU-ESR ages show a Middle Pleistocene chronology (0.49 ± 0.13 Ma on average), in clear contradiction with independent age control (Fig. 3). In addition, the usual affirmation that the real age lies somewhere between EU-LU age range is not verified by our data set. Moreover, the solutions of either calculating an EU-ESR age for teeth showing U leaching, or just fixing to -1 the p-parameter (i.e. assuming EU) of a problematic tissue, have to be considered with caution. Such attempts do not have major consequences in case of Late Pleistocene samples, for which the dose rate associated to dental tissues is usually a minor component (e.g. Bahain et al., 2010). However, for older samples the EU assumption may lead to severe overestimation of the dose rate associated to dental tissues and therefore, to age underestimations (e.g. Falguères et al., 1999; Martínez et al., 2010). For Early Pleistocene samples, an inverse relation has hence been already observed between the number of fixed p-parameters ($p = -1$) in a tooth and the combined US-ESR age value (Duval, 2008), i.e. the age gets younger when the number of dental tissue with $p = -1$ increases.

Finally, no significant correlation was observed between the age of the samples and the accuracy of the US-ESR ages obtained (Fig. 3). U leaching occurred frequently in some sites (FN-3, BL), but rarely in others, and showed no relationship with the site's age (Fig. 2). In addition, despite their age (>0.78 Ma), some tissues show very recent U

uptake (< 150 ka). In that regard, the neighbouring open air sites of VM and BL probably show the most striking contrast. Even biochronologically older, VM gives more consistent age results than BL. The homogeneous micritic limestone including the palaeontological level of VM has probably limited and slowed any recent U-mobilization, unlike the highly detritic sediment at BL, through which water, and hence, soluble radioisotopes have likely moved (Duval et al., 2012). In addition, this specific context at VM also favoured the preservation of the palaeontological remains, by comparison with other sites from the same area (Arribas and Palmqvist, 1998).

5. Conclusions

The combined US-ESR approach was applied to several fossil teeth from Spanish archaeological and/or palaeontological sites whose chronologies range from mid to late Early Pleistocene. The large size of the dataset (20 teeth and 57 dental tissues in total) for such ancient time range (>0.78 Ma) and the diversity of sedimentary contexts (cave, fluvio-lacustrine...) provides a reliable base to critically ascertain the method's real potential.

At some sites, no sample could be dated (BL). Meanwhile, at AGD, VM-A and EVT, the combined US-ESR ages agreed with other independent age estimates, but at VM-B, the age results are strongly underestimated. Interestingly, no age overestimates were observed. Such trend may be partially explained by recent works focused on ESR measurements of enamel fragments in order to identify the various contributions to the overall radiation-induced ESR signal of enamel (see Joannes-Boyau and Grün, 2011 and references therein). These authors suggest that the preferential creation of unstable non-oriented CO_2^- radicals after laboratory gamma irradiation may be a major source of error in the D_E assessment, and would potentially generate systematic age

underestimations. This would partially explain why some of the ESR ages are too young and none of them are too old. However, a similar study should be performed on such old samples before drawing any definitive conclusion, in order to assess the real impact of this parameter on the calculated D_E .

Due to the high U-concentration values of these dental tissues, the U uptake becomes the most crucial parameter in the age calculation process. In the US-ESR approach, this parameter is mainly modelled from the U-series data ($^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$) collected for each tissue. Our results show that these data are strongly influenced by the hydro-geological context of each site, which does not only print a specific isotopic signature to the samples, but has also a major influence on their suitability for the ESR dating method. As an example, at two localities (FN-3 and BL), the large majority of the tissues show apparent U-leaching, preventing then the use of the US model. Other additional limiting factors are also the spatial heterogeneity of the U-series data within the tissues or the potential recent U-uptake process overprints. Consequently, when dating old sites, a special attention has therefore to be paid on the meaning and the interpretation of the U-series data collected from the dental tissues, since the reliability of the US-ESR ages mainly lies on the accuracy of these data. In addition, the development of new U-uptake models that could accurately consider U-leaching process (e.g. [Shao et al., 2012](#)) is also clearly an avenue worth exploring in the future.

Finally, despite these limitations, the ESR dating is still the only absolute method that has been systematically applied to all these sites, and the chronology detailed in our work contributes to understanding the first hominin settlements in Western Europe. In addition, our results also suggest that the basic assumption that every tooth analysed should yield a reasonable age result is simply wrong when dating such old site. To quickly ensure that one sample may be suitable or not for US-ESR dating, some rapid

scanning procedures should be developed in order to: (i) assess the amount of unstable radicals generating the ESR signals, through the ESR measurement of enamel fragments, (ii) obtain U concentration and U-series data by laser ablation ICP-MS analysis. Then, samples showing either a large proportion of unstable ESR signals, a high U concentration in enamel, or a $^{230}\text{Th}/^{234}\text{U}$ activity ratio above equilibrium, should be rejected before any further analysis.

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References

- Arribas A, Palmqvist P., 1998. Taphonomy and palaeoecology of an assemblage of large mammals: hyaenid activity in the Lower Pleistocene Site at Venta Micena (Orce, Guadix-Baza basin, Granada, Spain). *Geobios* 31, 3-47.
- Arzarello, M., Marcolini, F., Pavia, G., Pavia, M., Petronio, C., Petrucci, M., Rook, L., Sardella, R., 2007. Evidence of earliest human occurrence in Europe: the site of Pirro Nord (Southern Italy). *Naturwissenschaften* 94, 107-112.
- Bahain, J.-J., Yokoyama, Y., Falguères, C., Sarcia, M.N., 1992. ESR dating of tooth enamel: a comparison with K-Ar dating. *Quaternary Science Reviews* 11, 245-250.
- Bahain, J.-J., Falguères, C., Dolo, J.-M., Antoine, P., Auguste, P., Limondin-Lozouet, N., Loch, J.-L., Tuffreau, J.-L., Tissoux, H., Farkh, S., 2010. ESR/U-series dating of teeth recovered from well-stratigraphically age-controlled sequences from Northern France. *Quaternary Geochronology* 5, 371-375.
- Berger, G.W., Pérez-Gonzalez, A., Carbonell, E., Arsuaga, J.L., Bermúdez de Castro, J.-M., Ku, T.L., 2008. Luminescence chronology of cave sediments at the Atapuerca paleoanthropological site, Spain. *Journal of Human Evolution* 55, 300-311.
- Bischoff, J.L., Rosenbauer, R.J., 1981. Uranium-series dating of human skeletal remains from the Del Mar and Sunnyvale sites, California. *Science* 213, 1003-1005.

392 Blackwell, B., Porat, N., Schwarcz, H., Debenath, A., 1992. ESR dating of tooth enamel
393 - comparison with Th-230/U-234 speleothem dates at La-Chaise-de-Vouthon
394 (Charente), France. *Quaternary Science Reviews* 11, 231-244.

395 Carbonell, E., Bermudez de Castro, J.M., Arsuaga, J.L., Diez, J.C., Rosas, A., Cuenca-
396 Bescos, G., Sala, R., Mosquera, M., Rodriguez, X., 1995. Lower Pleistocene
397 hominids and artifacts from Atapuerca-TD6 (Spain). *Science* 269, 826-830.

398 Carbonell, E., Bermudez de Castro, J.M., Parés, J.M., Pérez-Gonzalez, A., Cuenca-
399 Bescos, G., Olle, A., Mosquera, M., Huguet, R., van der Made, J., Rosas, A., Sala, R.,
400 Vallverdu, J., Garcia, N., Granger, D., Martínón-Torres, M., Rodriguez, X.P., Stock,
401 G., Verges, J., Allue, E., Burjachs, F., Caceres, I., Canals, A., Benito, A., Diez, C.,
402 Lozano, M., Mateos, A., Navazo, M., Rodriguez, J., Rosell, J., Arsuaga, J.L., 2008.
403 The first hominin of Europe. *Nature* 452, 465-470.

404 Chen, T.-M., Yang, Q., Hu, Y.-Q., Bao, W.-B., Li, T.-Y., 1997. ESR dating of tooth
405 enamel from Yunxian *Homo erectus* site, China. *Quaternary Science Reviews*
406 (*Quaternary Geochronology*) 16, 455-458.

407 Cuenca-Bescos, G., Rofes, J., López-García, J., Blain, H.-A., De Marfá, R., Galindo-
408 Pellicena, M., Bennásar-Serra, M., Melero-Rubio, M., Arsuaga, J., Bermúdez de
409 Castro, J., Carbonell, E., 2010. Biochronology of Spanish Quaternary small
410 vertebrate faunas. *Quaternary International* 212, 109–119.

411 Despriée, J., Gageonnet, R., Voinchet, P., Bahain, J.-J., Falguères, C., Varache, F.,
412 Courcimault, G., Dolo, J.-M., 2006. Une occupation humaine au Pléistocène
413 inférieur sur la bordure nord du Massif central. *Comptes Rendus Palevol* 5, 821-828.

414 Duval, M., 2008. Évaluation du potentiel de la méthode de datation par Résonance de
415 Spin Electronique (ESR) appliquée aux gisements du Pléistocène inférieur: étude des
416 gisements d'Orce (bassin de Guadix-Baza, Espagne) et contribution à la
417 connaissance des premiers peuplements de l'Europe. Ph.D. thesis, Muséum National
418 d'Histoire Naturelle, Paris, France.

419 Duval, M., Aubert, M., Hellstrom, J., Grün, R., 2011a. High resolution LA-ICP-MS
420 mapping of U and Th isotopes in an Early Pleistocene equid tooth from Fuente
421 Nueva-3 (Orce, Andalusia, Spain). *Quaternary Geochronology* 6, 458-467.

422 Duval, M., Falguères, C., Bahain, J.-J., Grün, R., Shao, Q., Aubert, M., Hellstrom, J.,
423 Dolo, J.M., Agustí, J., Martínez-Navarro, B., Toro-Moyano, I., 2011b. The challenge
424 of dating Early Pleistocene fossil teeth by the combined uranium series–electron spin
425 resonance method: the Venta Micena palaeontological site (Orce, Spain). *Journal of*
426 *Quaternary Science* 26, 603-615.

427 Duval, M., Moreno, D., Shao, Q., Voinchet, P., Falguères, C., Bahain, J.-J., Garcia, T.,
428 García, J., Martínez, K., 2011c. Datación por ESR del yacimiento arqueológico del
429 Pleistoceno inferior de Vallparadís (Terrassa, Cataluña, España). *Trabajos de*
430 *Prehistoria* 68, 7-24.

431 Duval, M., Falguères, C., Bahain, J.-J., Grün, R., Shao, Q., Aubert, M., Hellstrom, J.,
432 Dolo, J., Agustí, J., Martínez-Navarro, B., Toro-Moyano, I., submitted. Combined
433 US-ESR dating of fossil teeth from two Early Pleistocene archaeological sites of the
434 Orce area (Guadix-Baza basin, Spain): beyond the limits of the method?. *Quaternary*
435 *Research*.

436 Falguères, C., Bahain, J.-J., Yokoyama, Y., Arsuaga, J.L., Bermudez de Castro, J.M.,

437 Carbonell, E., Bischoff J.L., Dolo, J.M., 1999. Earliest humans in Europe: the age of
 438 TD6 Gran Dolina, Atapuerca, Spain. *Journal of Human Evolution* 37, 343-352.

439 Gabunia, L., Vekua, A., 1995. A Plio-Pleistocene hominid from Dmanisi, East Georgia,
 440 Caucasus. *Nature* 373, 509-512.

441 Grün, R., 2009a. The DATA program for the calculation of ESR age estimates on tooth
 442 enamel. *Quaternary Geochronology* 4, 231-231.

443 Grün, R., 2009b. The relevance of parametric U-uptake models in ESR age calculations.
 444 *Radiation Measurements* 44, 472-476.

445 Grün, R., McDermott, F., 1994. Open system modelling for U-series and ESR dating of
 446 teeth. *Quaternary Science Reviews (Quaternary Geochronology)* 13, 121-125.

447 Grün, R., Schwarcz, H.P., and Chadam, J., 1988. ESR dating of tooth enamel : coupled
 448 correction for U-uptake and U-series disequilibrium. *Nuclear Tracks Radiation*
 449 *Measurements* 14, 237-244.

450 Grün, R., Aubert, M., Hellstrom, J., Duval, M., 2010. The challenge of direct dating old
 451 human fossils. *Quaternary International* 223-224, 87-93.

452 Ikeya, M., 1982. A model of linear uranium accumulation for ESR age of Heidelberg
 453 (Mauer) and Tautavel bones. *Japanese Journal of Applied Physics* 21, 690-692.

454 Joannes-Boyau, R., Grün, R., 2011. A comprehensive model for CO₂- radicals in fossil
 455 tooth enamel: Implications for ESR dating. *Quaternary Geochronology* 6(1), 82-
 456 97.

457 Ludwig, K.R., 2003. User's Manual for Isoplot 3.00. Manual, Berkeley Geochronology
 458 Center: Berkeley, CA.

459 Martínez, K., Garcia, J., Carbonell, E., Agustí, J., Bahain, J.-J., Blain, H.-A., Burjachs,
 460 F., Cáceres, I., Duval, M., Falguères, C., Garcés, M., Gómez, M., Huguet, R., 2010.
 461 A new Lower Pleistocene archaeological site in Europe: Vallparadís (Barcelona,
 462 Spain). *Proceedings of the National Academy of Sciences* 107, 5762-5767.

463 Moreno, D., 2011. Datation par ESR de quartz optiquement blanchis (ESR-OB) de la
 464 région de Atapuerca (Burgos, Espagne). Application au site préhistorique de Gran
 465 Dolina (contexte karstique) et aux systèmes fluviaux quaternaires de l'Arlanzón et
 466 l'Arlanza. Ph.D. thesis, Rovira i Virgili Univ., Tarragona, Spain and Muséum
 467 National d'Histoire Naturel, Paris, France.

468 Oms, O., Agustí, J., Gabas, M., Anadon, P., 2000. Lithostratigraphical correlation of
 469 micromammal sites and biostratigraphy of the Upper Pliocene to Lower Pleistocene
 470 in the Northeast Guadix-Baza Basin (southern Spain). *Journal of Quaternary Science*
 471 15, 43-50.

472 Oms, O., Anadón, P., Agustí, J., Julià, R., 2011. Geology and chronology of the
 473 continental Pleistocene archeological and paleontological sites of the Orce area
 474 (Baza basin, Spain). *Quaternary International*. Doi:10.1016/j.quaint.2011.03.048.

475 O'Reagan, H., 2008. The Iberian Peninsula – Corridor or cul-de-sac? Mammalian faunal
 476 change and possible routes of dispersal in the last 2 million years. *Quaternary*
 477 *Science Reviews* 27, 2136-2144.

478 Osmond, J.K., Ivanovich, M., 1992. U-series mobilization and surface hydrology.
 479 *Uranium-Series Disequilibrium: Application to Earth, Marine, and Environmental*
 480 *Sciences*. M. Ivanovich and R. S. Harmon. Oxford, UK, Clarendon: 259–289.

- Palmqvist, P., Martínez-Navarro, B., Toro, I., Espigares, M.P., Ros-Montoya, S., Torregrosa, V., Pérez-Claros, J.A., 2005. Réévaluation de la présence humaine au Pléistocène inférieur dans le Sud de l'Espagne. *L'Anthropologie* 109, 411-450.
- Parés, J., Pérez-Gonzalez, A., 1999. Magnetochronology and stratigraphy at Gran Dolina section, Atapuerca (Burgos, Spain). *Journal of Human Evolution* 37, 325-342.
- Parfitt, S., Ashton, N., Lewis, S., Abel, R., Russell Coope, G., Field, M., Gale, R., Hoare, P., Larkin, N., Lewis, M., Karloukovski, V., Maher, B., Peglar, S., Preece, R., Whittaker, J., Stringer, C., 2010. Early Pleistocene human occupation at the edge of the boreal zone in northwest Europe. *Nature* 466, 229-233.
- Rodríguez, J., Burjachs, F., Cuenca-Bescós, G., García, N., Van der Made, J., Pérez González, A., Blain, H.-A., Expósito, I., López-García, J., García Antón, M., Allué, E., Cáceres, I., Huguet, R., Mosquera, M., Ollé, A., Rosell, J., Parés, J., Rodríguez, X., Díez, C., Rofes, J., Sala, R., Saladié, P., Vallverdú, J., Bennisar, M., Blasco, R., Bermúdez de Castro, J., Carbonell, E., 2011. One million years of cultural evolution in a stable environment at Atapuerca (Burgos, Spain). *Quaternary Science Reviews* 30, 1396-1412.
- Shao, Q., Bahain, J.-J., Falguères, C., Dolo, J.-M., Garcia, T., submitted. A new U-uptake model for combined ESR/U-series dating of tooth enamel. *Quaternary Geochronology*.
- Straus, L.G., 2001. Africa and Iberia in the Pleistocene. *Quaternary International* 75, 91-102.
- Toro-Moyano, I., Barsky, D., Cauche, D., Celiberti, V., Grégoire, S., Lebègue, F., Moncel, M.H., Lumley, H. de, 2011. The archaic stone tool industry from Barranco León and Fuente Nueva 3, (Orce, Spain): Evidence of the earliest hominin presence in southern Europe. *Quaternary International* 234, 80-91.

Figure captions

Figure 1: Site locations.

Figure 2: U-series data ($^{230}\text{Th}/^{238}\text{U}$ vs $^{234}\text{U}/^{238}\text{U}$) measured in dental tissues. (A): Dentine and cement, (B): Enamel. The graphs were done using Isoplot software (Ludwig, 2003). The ellipses suggest the specific trend drawn by each site. Data point that fall outside the isochrons (i.e. located on the right of the last isochron labeled 600 ka) indicates apparent U-leaching. Data points that fall between the red dashed $^{230}\text{Th}/^{234}\text{U}=1.05$ line and the 600 ka isochron are located within the problematic area of the US model, where the age calculation process is often not possible (see Grün, 2009a).

Fig. 3: EU-ESR, LU-ESR and US-ESR ages calculated from all samples. The grey areas are the expected ages of the sites, based on the combination of palaeomagnetism and biochronology, i.e. pre-Jaramillo age (>1.07 Ma) for VM, BL and FN-3 sites, and post-Jaramillo age (<0.99 Ma) for AGD and EVT sites.