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On the limits of using combined U-series/ESR method to date fossil teeth from two Early Pleistocene archaeological sites of the Orce area (Guadix-Baza basin, Spain)

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A B S T R A C T

The combined U-series/electron spin resonance (ESR) dating method was applied to nine teeth from two Early Pleistocene archaeological sites located in the Orce area (Guadix-Baza Basin, Southern Spain): Fuente Nueva-3 (FN-3) and Barranco León (BL). The combination of biostratigraphy and magnetostratigraphy places both sites between the Olduvai and Jaramillo subchrons (1.78–1.07 Ma).
Our results highlight the difficulty of dating such old sites and point out the limits of the combined U-series/ESR dating method based on the US model. We identified several sources of uncertainties that may lead to inaccurate age estimates. Seven samples could not be dated because the dental tissues had (^{230}Th/^{234}U) activity ratios higher than equilibrium, indicating that uranium had probably leached from these tissues. It was however possible to calculate numerical estimates for two of the teeth, both from FN-3. One yielded a Middle Pleistocene age that seems to be strongly underestimated; the other provided an age of 1.19 ± 0.21 Ma, in agreement with data obtained from independent methods. The latter result gives encouragement that there are samples that can be used for routine dating of old sites.

Introduction

The Oldowan (i.e. Mode 1) lithic artefacts discovered in Fuente Nueva-3 and Barranco León sites (Orce, Guadix-Baza basin, Spain) are widely considered to be among the oldest evidence of hominid occupation in Western Europe (Oms et al., 2000b; Carbonell and Rodriguez, 2006). Based on a combination of paleomagnetism and biostatigraphy (Martínez-Navarro et al., 1997; Oms et al., 2000a, b; Agustí et al., 2007), the chronostratigraphical frameworks of both sites suggest an Early Pleistocene age (2.58–0.78 Ma; Cohen and Gibbard, 2011), most likely between Olduvai and Jaramillo subchrons, i.e. between 1.78 and 1.07 Ma (Gradstein et al., 2004). However, contrary to the Atapuerca sites located approximately 500 km northwards in Northern Spain (Falguères et al., 1999; Berger et al., 2008; Carbonell et al., 2008), the Orce sites have never been dated by numerical methods. In direct continuation of our recent efforts in providing numerical dating results for a number of sites in the Orce-Fuente Nueva-Venta Micena sector (Duval, 2008; Grün et al., 2010; Duval et al., 2011a, b), we display in the present paper the combined US-ESR analysis results of nine fossil teeth from Fuente Nueva-3 and Barranco León sites.

Orce sites

The Orce-Fuente Nueva-Venta Micena sector is located in Southern Spain, in the eastern part of the Guadix-Baza depression (Fig. 1), an intra-mountain Neogene–Quaternary basin of the central part of the Betic Cordillera (for further details see Sanz de Galdeano and Vera, 1992). This area is particularly known for its Pleistocene archeological and/or paleontological sites (see Oms et al., 2000a, 2011), like Venta Micena (VM), Fuente Nueva-3 (FN-3) and Barranco León (BL), among the most famous ones.

From a stratigraphical point of view, sedimentary outcrops at FN-3 and BL belong to the upper member of the Baza lacustrine formation (Oms et al., 2011). This Early Pleistocene unit was deposited during a phase of major expansion of a paleo-lake, which covered almost the

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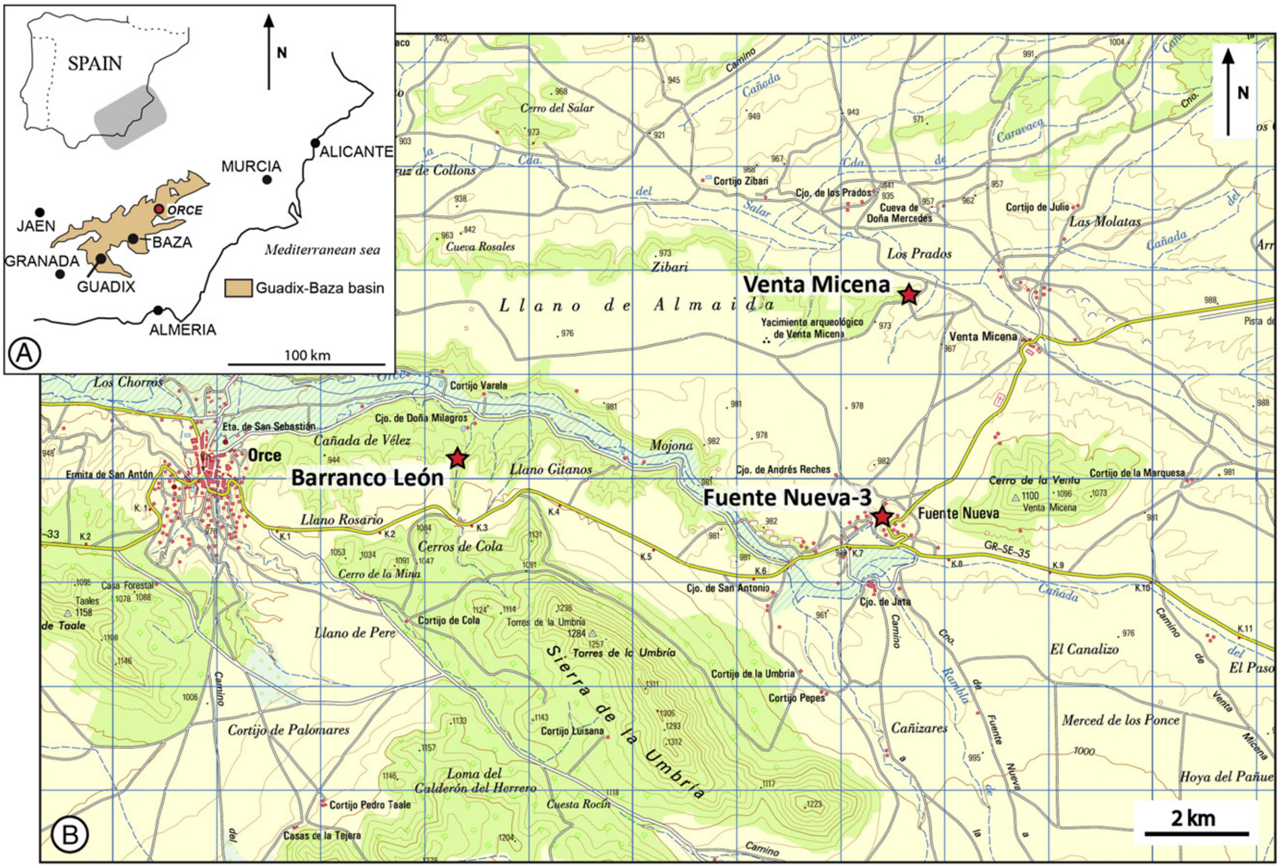

Figure 1. Geographical location of the sites. (A): within the Guadix-Baza basin; (B): within the Orce-Fuente Nueva-Venta Micena sector (*Instituto Geográfico Nacional* topographic map, ref. 951, scale 1:50.000).

whole eastern part of the Guadix-Baza basin at this period (Soria et al., 1987; García-Aguilar and Palmqvist, 2011). Both sites were located close to the lake margin (Oms et al., 2011).

FN-3 consists of an approximately 5-m-thick sedimentary sequence formed by a succession of carbonated deposits, mainly clays, sands and mudstones, starting and ending with a limestone unit (for further details, see Turq et al., 1996; Martínez-Navarro et al., 1997; Duval et al., 2010; Oms et al., 2011). An archaic lithic industry was found in association with faunal remains of large mammals in two levels within the sequence (Palmqvist et al., 2005; Toro-Moyano et al., 2010). These were associated with a shallow lacustrine environment with frequent immersions (Anadón et al., 2003; Oms et al., 2011). The lower archeological level yielded several hundreds of artefacts and is formed by an ~10-cm-thick layer of dark blue-green clayish and poorly carbonated deposits showing laterally some lenses of quartzitic sands. The upper archeological level is formed by blue-green sands showing lateral variations of granulometry, carbonatation, and induration. This level contains many faunal remains, especially dominated by megaherbivores, including a partial articulated skeleton of *Mammuthus meridionalis*, which is surrounded in part by hyena coprolites and lithic tools (Fajardo, 2008; Espigares Ortiz, 2010). The absence of any evidence for water transportation of the faunal material in the two archeological levels, combined with the fine granulometry of the sediments, suggests that the material experienced little—if any—transport by physical processes before burial in the sediment. In addition, there is no evidence of taphonomic reworking in the bone assemblage (Espigares Ortiz, 2010). This site has been interpreted as a waterhole where animals came to drink and were eventually hunted by hypercarnivores (e.g., saber-tooths and wild dogs) and subsequently scavenged by hyenas and hominids (Palmqvist et al., 2005; Toro-Moyano et al., 2010).

BL is a ravine with an almost S–N orientation, perpendicular to the Cañada de Velez canyon (Fig. 1), showing a spectacular 20-m-thick vertical outcrop into which several main lithostratigraphic units were identified and associated to lake-level oscillations (for further details, see Soria et al., 1987; Turq et al., 1996; Arribas and Palmqvist, 2002). Most sediments of the excavated section indicate a swampy environment (Turq et al., 1996), except Layer D, which shows fluvial features and encloses the archeological level. Layer D is about 70 cm thick and shows upward-fining sedimentation. Two sub-layers were separated (Anadón et al., 2003): an erosive base (D1) formed by coarse material such as pebbles and calcareous blocks coated in a matrix made by carbonated and quartzitic sands rich in gastropods shells, topped by quartzitic and bioclastic greyish sands showing some oxidation marks (D2). These sedimentary units represent a shallowing sequence filling a fluvial paleochannel, eroding the previously deposited swampy sediments (Arribas and Palmqvist, 2002). They are overlain by a white limestone rich in ostracods and molluscs (top part of D2 sub-layer), which indicates the normalization of the swampy sedimentary dynamics after the deposits that filled the paleochannel (Anadón et al., 2003; Palmqvist et al., 2005). Although a single archeological level is commonly documented, a few studies point out that the archeological and paleontological materials extracted from D1 appear more altered, fractured and rounded, which indicates that they experienced lateral transport by currents. In contrast, the few remains found in D2 do not show evidence of hydraulic transport or taphonomic reworking (Fajardo, 2008; Espigares Ortiz, 2010).

Further details about the faunal assemblages and the lithic artefacts excavated from both sites can be found in supplementary information. Complete faunal lists of both sites are detailed in Table S1.

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Previous chronostratigraphical framework

The large mammal assemblages of both sites are characteristic of Late Villafranchian period (Rook and Martinez-Navarro, 2010) and are quite similar to the nearby site of Venta Micena (VM), dated to about 1.4 Ma (Duval et al., 2011b), despite some minor differences (e.g., the presence of *Ammotragus europaeus* in FN-3 and of *Equus sussenbornensis* in BL, both species with very hypsodont teeth that indicate more arid conditions than in VM), suggesting slightly younger ages. Some species, like *Equus altidens* and *M. meridionalis*, are also found at the Early Pleistocene Georgian site of Dmanisi (Lordkipanidze et al., 2007), dated to about 1.8 Ma (Lordkipanidze et al., 2007; Garcia et al., 2010). Other taxa have been found in more recent sites, like *Canis mosbachensis* recorded at Atapuerca Sima del Elefante-TE9 (Spain) dated to about 1.2 Ma using ^{26}Al and ^{10}Be cosmogenic nuclides (Carbonell et al., 2008), or *A. europaeus* and *Stephanorhinus hundseimensis* in Le Vallonnet (France) (Moullé et al., 2006), dated around 1.0 Ma (de Lumley, 1988; Yokoyama et al., 1988). While the overall faunal assemblages of Le Vallonnet and the two Orce sites are similar, some taxonomic differences between the herbivore associations indicate a somewhat younger age for the French site (Moullé et al., 2006).

The microfauna assemblages at FN-3 and BL are characterized by an association of the rodents *Mimomys savini* (small) and *Allophaiomys* aff. *lavocati* (Agustí and Madurell, 2003) that places both sites into the same biozone of the recently updated biozonation scheme for the Guadix-Baza basin (Agustí et al., 2007). This biozone is located between the *A. ruffoi* biozone (Mm-Q2 of Agusti, 1986; equivalent to *A. pliocaenicus* biozone of Cuenca-Bescos et al., 2010), which includes the VM site, and the *Iberomys huescarensis*–*M. savini* biozone (Mm-Q3a of Agusti, 1986) with Huéscar-1 site (Agustí et al., 2010). Both FN-3 and BL sites may be slightly older than Sima del Elefante TE-9, where *I. huescarensis* and *A. lavocati* were identified (Carbonell et al., 2008), the latter showing some more advanced features (Agustí and Madurell, 2003). To conclude, biostratigraphy places the sites between about 1.8 Ma and slightly older than 1.0 Ma.

Paleomagnetic studies yielded a continuous reversed polarity in the two stratigraphic sequences, suggesting a correlation with the Matuyama chron which ranges between 2.58 and 0.78 Ma (Oms et al., 2000b). By combining paleomagnetic with biostratigraphical data it is possible to place the age of FN-3 and BL to between the Olduvai and Jaramillo subchrons, i.e. 1.78–1.07 Ma. Both sites are located within the upper member of the Baza formation and according to Oms et al. (2000a), BL is stratigraphically located slightly below FN-3. Consequently, while both sites cannot be distinguished by biostratigraphy and paleomagnetism, one may keep in mind that, stratigraphically, FN-3 may be slightly younger than BL.

The combined U-series/ESR dating method using US model

As dental tissues show open system behaviour for the U-series isotopes, the main complication of ESR dating of fossil teeth is the modelling of uranium uptake with time. In order to account for this process, Grün et al. (1988) proposed 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 U-concentration, T is the age of the sample and p is the uptake parameter which describes a continuous uptake with a constant rate or not. 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). If the US model is conveniently used through the combined U-series/ESR method to date Middle Pleistocene sites (e.g. Falguères et al., 2010), its application to Early Pleistocene samples is more problematic. The potential and limitations of fossil teeth dating by ESR using the US model were recently detailed by Grün et al. (2010) and Duval et al. (2011a, b). The main advantages of the US-ESR approach over the conventional EU-ESR, LU-ESR or RU-ESR approaches can be briefly summarized as follows:

- The U-uptake history is not *a priori* assumed, but mathematically assessed according to the present day U-series data, mainly (^{230}Th/^{234}U) and (^{234}U/^{238}U) activity ratios, measured in each tissue. As a consequence, only a single combined US-ESR age fits the available dataset. It should perhaps be noted that a compilation of published US-ESR data (Grün, 2009a) showed that there is virtually no reason to prefer one parametric U-uptake model over another, i.e. the preference of a particular U-uptake model for a given site is purely based on conjecture.
- Distinct U-uptake histories can be modelled for each dental tissue of a unique tooth. Again, Grün (2009a) recently showed that in most cases, the modelled U-uptake is significantly different in enamel, dentine and cement.

In contrast, the main limitations of the US model, may be resumed as follows:

- U-leaching from dental tissue cannot be modelled (Grün et al., 1988).

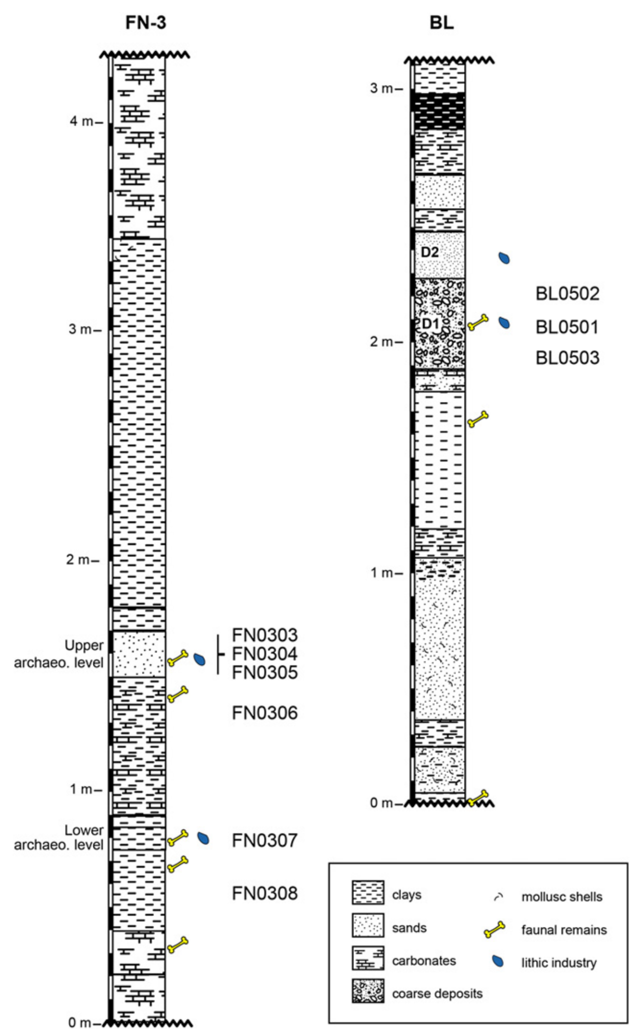

Figure 2. Stratigraphical position of the fossil teeth collected in FN-3 and BL sites. At BL, the sedimentary sequence is part of the stratigraphical unit E defined by Turq et al. (1996), which encloses several layers, including D1 and D2 (Anadón et al., 2003). Further details about the stratigraphy of both sites can be found in Duval et al. (2010), Oms et al. (2011) and Turq et al. (1996).

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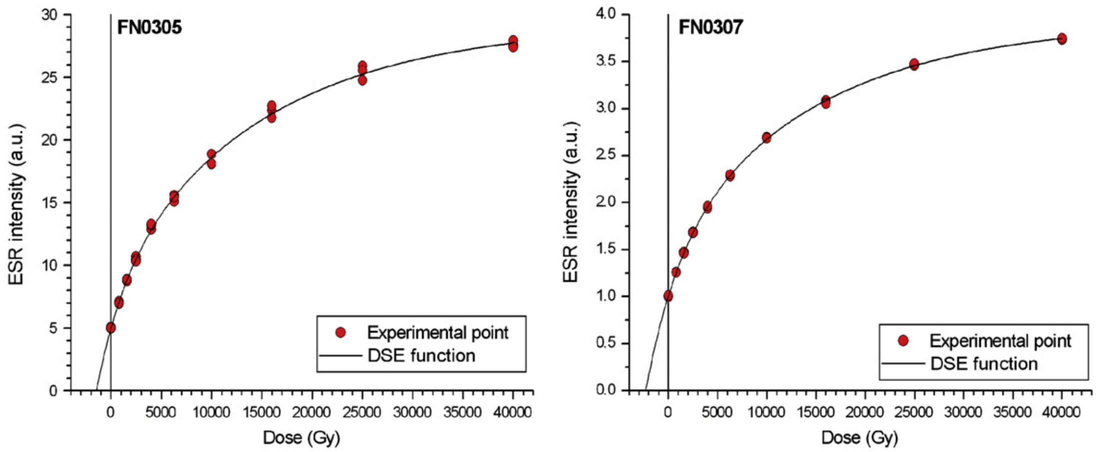

Figure 3. Two examples of dose response curves (samples FN0305 and FN0307). The experimental data points are fitted using a double saturating exponential (DSE) function.

– Combined US-ESR age calculations using DATA software (Grün, 2009b) are limited to samples showing (^{230}Th/^{234}U) activity ratios <1.04–1.05, even if these values are below secular equilibrium (see Duval et al., 2011a, 2011c).
– Spatial distribution of the U-series isotopes within the dental tissues is not considered, whereas fossil teeth may sometimes exhibit some spatial heterogeneity (e.g. Duval et al., 2011a).

These limitations may be especially problematic when dating old fossil teeth and will be further discussed later.

Sampling

The stratigraphic locations of the samples are shown in Figure 2. Six equid teeth (*E. altidens*) were collected *in situ* at FN-3 during field excavations in 2003. Three teeth (FN0303 to FN0305) came from the upper archeological level close to the previously mentioned *M. meridionalis* skeleton, while FN0306 to FN0308 were collected from the lower part of the FN-3 sedimentary sequence. Three equid teeth were collected *in situ* at BL in 2005 from layer D1.

Experimental methods

Sample preparation and ESR measurements were performed at the Department of Prehistory of the Muséum National d'Histoire Naturelle (MNHN, France) and followed the analytical procedures of Duval et al. (2011b). Gamma irradiations were carried out in the Laboratoire National Henri Becquerel (Commissariat à l'Énergie Atomique, France) using a ^{60}Co calibrated source. The ESR intensities were extracted from peak-to-peak amplitudes of the ESR signal of enamel (T1-B2; see Grün, 2000). The experimental data points were fitted with a double saturating exponential (DSE) function weighting the data by the inverse of the squared intensity (Duval et al., 2009). The dose-response curves obtained for samples FN0305 and FN0307 are shown as examples in Figure 3.

Table 1
U-series and ESR data obtained for all samples from FN-3 and BL sites. E = enamel, D = dentine, C = cement. Standard errors are 1 σ. (1): inner side of the enamel (i.e., dentine side); (2): outer part of enamel (i.e., cement side). Apparent U-series ages are calculated using Isoplot 3.00 macro (Ludwig, 2003).

Site	Sample	Tissue	U (ppm)	^{234}U/^{238}U	^{230}Th/^{234}U	^{222}Rn/^{230}Th	Apparent ^{230}Th/^{234}U age (ka)	T enam.[a] (μm)	T rem.[b] (μm)	Depth (m)	D_E (Gy)
Fuente Nueva-3	FN0303	C	33.40 ± 0.50	1.747 ± 0.003	1.281 ± 0.004	0.23 ± 0.01	n.c.		220 ± 22		
		D	50.00 ± 0.50	1.774 ± 0.003	1.001 ± 0.004	0.35 ± 0.02	244 +2/−2		80 ± 8		
		E	2.35 ± 0.08	1.656 ± 0.056	0.890 ± 0.050	0.64 ± 0.03	185 +23/−20	1400 ± 140		4 ± 1	2661 ± 178
	FN0304	C	29.80 ± 0.80	1.804 ± 0.003	0.951 ± 0.076	0.30 ± 0.02	211 +2/−2		110 ± 11		
		D	48.10 ± 0.90	1.840 ± 0.002	0.972 ± 0.106	0.37 ± 0.02	222 +2/−2		90 ± 9		
		E	2.57 ± 0.13	1.716 ± 0.085	0.748 ± 0.052	0.89 ± 0.04	131 +19/−17	1230 ± 123		4 ± 1	2150 ± 256
	FN0305	D	40.40 ± 0.60	1.848 ± 0.002	1.340 ± 0.006	0.27 ± 0.01	n.c.		110 ± 11		
		E	1.69 ± 0.05	1.791 ± 0.057	0.726 ± 0.069	0.78 ± 0.04	123 +15/−14	1220 ± 122	100 ± 10	4 ± 1	1456 ± 101
	FN0306	C	23.60 ± 0.50	1.899 ± 0.006	1.607 ± 0.009	0.24 ± 0.01	n.c.		170 ± 17		
		D	36.80 ± 0.70	1.898 ± 0.003	1.197 ± 0.005	0.39 ± 0.02	630 +37/−30		30 ± 3		
		E	1.020 ± 0.04	1.800 ± 0.081	1.054 ± 0.057	1.00 ± 0.05	286 +68/−45	1400 ± 140		5 ± 1	1623 ± 162
	FN0307	C	20.20 ± 0.80	2.005 ± 0.003	1.426 ± 0.006	0.30 ± 0.01	n.c.		80 ± 8		
		D	40.40 ± 0.60	2.075 ± 0.039	1.610 ± 0.007	0.24 ± 0.01	n.c.		90 ± 9		
		E	3.17 ± 0.10	1.582 ± 0.029	1.096 ± 0.029	0.64 ± 0.03	377 +67/−45	1430 ± 143		5 ± 1	2301 ± 69
	FN0308	C	33.47 ± 1.11	1.647 ± 0.005	0.944 ± 0.054	0.31 ± 0.02	214 +3/−3		110 ± 11		
		D	50.57 ± 0.87	1.718 ± 0.004	1.005 ± 0.123	0.55 ± 0.03	250 +5/−5		70 ± 7		
		E	8.87 ± 0.14	1.810 ± .0024	0.976 ± 0.020	0.72 ± 0.04	226 +11/−10	1030 ± 103		6 ± 1	2846 ± 284
Barranco León	BL0501	C	51.81 ± 0.85	1.531 ± 0.004	1.412 ± 0.005	0.36 ± 0.02	n.c.		70 ± 7		
		D	75.20 ± 0.57	1.536 ± 0.004	1.441 ± 0.009	0.39 ± 0.02	n.c.		40 ± 4		
		E	2.21 ± 0.04	1.311 ± 0.026	1.068 ± 0.029	0.73 ± 0.04	427 +213/−77	1390 ± 139		10 ± 2	1285 ± 96
	BL0502	C	53.85 ± 0.95	1.762 ± 0.004	1.531 ± 0.003	0.36 ± 0.02	n.c.		130 ± 13		
		D	61.29 ± 0.46	1.498 ± 0.002	1.367 ± 0.012	0.40 ± 0.02	n.c.		60 ± 6		
		E	1.95 ± 0.04	1.317 ± 0.029	1.009 ± 0.029	0.82 ± 0.04	302 +50/−35	1270 ± 127		10 ± 2	2021 ± 79
	BL0503	C	47.26 ± 1.22	1.742 ± 0.002	1.782 ± 0.016	0.27 ± 0.01	n.c.		130 ± 13		
		D	54.93 ± 0.75	1.562 ± 0.005	1.423 ± 0.005	0.36 ± 0.02	n.c.		230 ± 23		
		E	2.19 ± 0.08	1.221 ± 0.052	0.997 ± 0.056	0.68 ± 0.03	310 +177/−70	1640 ± 164		10 ± 2	1683 ± 35

[a] Initial enamel thickness.
[b] Removed enamel thicknesses used for US-ESR age calculation.

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Table 2
Combined US-ESR ages and associated data obtained for FN0304 and FN0308 tooth samples.

Site	Sample	Depth	$\alpha\pm\beta$ internal	β dentine	β cement	γ sediments + cosmic	Total dose-rate	p factor			US-ESR age
		(m)	(μGy/a)			(μGy/a)	(μGy/a)	Enamel	Dentine	Cement	(Ma)
Fuente Nueva − 3	FN0304	4 ± 1	274 ± 148	382 ± 67	171 ± 31	982 ± 95	1808 ± 191	2.66	− 0.27	− 0.09	1.19 + 0.21/− 0.21
	FN0308	6 ± 1	3803 ± 832	639 ± 92	250 ± 39	776 ± 150	5478 ± 851	− 0.62	− 0.72	− 0.55	0.52 + 0.09/− 0.08

The U-series isotopes in dental tissues were analysed with a combination of techniques. Laser ablation (LA) MC-ICP-MS analysis was performed on dentine and cement fragments at the Research School of Earth Sciences of the Australian National University (Australia), using a custom-built laser sampling system interfaced between an ArF Excimer laser and a MC-ICP-MS Finnigan Neptune (for details, see Eggins et al., 2003, 2005). Data reduction followed established laser ablation ICP-MS protocols (Longerich et al., 1996) using the dentine of a rhinoceros tooth from Hexian (sample 1118, see Grün et al., 1998) as a secondary matrix matched standard. Enamel was analysed by alpha-ray spectrometry using the standard procedures of Bischoff et al. (1988). U-concentrations of cement and dentine were assessed by gamma spectrometry (Yokoyama and Nguyen, 1980). The latter two analyses were carried out at the Department of Prehistory of the MNHN.

Combined US-ESR ages were calculated with the DATA programme (Grün, 2009b) using the following parameters: an alpha efficiency of 0.13 ± 0.02 (Grün and Katzenberger-Apel, 1994), Monte-Carlo beta attenuation factors from Brennan et al. (1997), dose-rate conversion factors from Adamiec and Aitken (1998), a water content of 5 ± 3 wt.% in dentine and cement and 10 ± 5 wt.% in sediments as evaluated by drying. Ra and Rn loss in each tissue was determined by gamma-ray spectrometry (Bahain et al., 1992). Depending on the samples, the gamma dose rate was derived by averaging *in situ* dose rates measured by either a portable gamma spectrometer (Inspector 1000 with a NaI(Tl) probe) or TL dosimeters (CaSO4:Dy), plus laboratory values obtained from the radioisotope analysis (U, Th and K) of the sediments surrounding the teeth (Yokoyama and Nguyen, 1980). The cosmic dose rate was calculated according to Prescott and Hutton (1988, 1994).

Results

All analytical results are shown in Table 1. Calculated D_E values for FN-3 and BL samples are somewhat scattered, ranging from 1285 ± 96 Gy to 2846 ± 284 Gy. U-concentrations in the enamel vary within 2.1 ± 0.6 ppm when excluding FN0308 that has a surprisingly high concentration of 8.9 ± 0.1 ppm. U-concentrations in the dentine and cement for a given site also vary in relatively small bands. The dentines of the FN-3 and BL samples contain 44.4 ± 5.9 ppm and 63.8 ± 10.4 ppm, respectively. The corresponding figures for cements are 28.1 ± 6.0 ppm and 51.0 ± 3.4 ppm. All samples show higher U-concentrations in the dentine than in the cement, 15.5 ± 5.7 ppm on average.

The most striking result is that seven of nine teeth contain dental tissues in which the ($^{230}Th/^{234}U$) activity ratio indicates U-leaching, i.e. values that are above secular equilibrium and lie outside the limits of the isotope-evolution diagram (see Grün et al., 2010; Duval et al., 2011a). In these cases it is not possible to calculate open-system US-ESR ages, because the model of Grün et al. (1988) explicitly excludes U-leaching. The US-ESR results of the remaining two teeth, both from FN-3, are listed in Table 2. The calculated age of 1.19 ± 0.21 Ma for FN0304 falls within the age range expected from biostratigraphy and magnetostratigraphy. In contrast, the age estimate of 0.52 + 0.09/− 0.08 Ma for FN0308 is clearly an underestimation.

Discussion

There is a factor of about 2 between the combined US-ESR ages of FN0304 and FN0308 (Table 2). As can be seen in Table 1, the only difference between the two samples is the high U-concentration in the enamel of FN0308, generating the calculation of a massive internal dose value that corresponds to more than 2/3 of the total dose rate. Using instead the average concentration of the enamels of the other samples from FN-3, 2.17 ± 0.37 ppm, an age of 1.11 ± 0.19 Ma is calculated, in agreement with the one obtained for FN0304. Repeated measurements performed on various enamel sub-samples from FN0308 confirmed such high U-concentration value. Previous works have identified the high U-concentration in enamel as a possible source of ESR age underestimation. According to Chen et al. (1997) this may lead to a phenomenon of local complete saturation of the ESR signal in the enamel. Bahain et al. (1992) suggested that high uranium concentration in enamel and the associated alpha-particles may locally destroy the crystalline structure of the dental tissue, rather than creating new paramagnetic radicals, and have hence a negative impact on the radiation-induced ESR signal. These authors proposed the USIC model, a variation of the US model, based on the assumption of an inverse correlation between the alpha efficiency (k-value) and the U-concentration, only valid for samples showing high concentration values in enamel ($\gg$5 ppm). Using the USIC model with a k = 0, an age estimate of 1.17 + 0.15/− 0.50 Ma is obtained for FN0308, i.e. a result consistent with that derived from FN0304. A similar age result of 1.14 + 0.13/−0.30 Ma can be calculated for FN0303 if the cement dose rate is calculated for an ($^{230}Th/^{234}U$) activity ratio that is in equilibrium, i.e. assuming an Early U uptake (p = − 1) for the corresponding tissue.

In order to understand U-migration in old teeth, we analysed by Laser Ablation ICP-MS the three dimensional distribution of U-series isotopes in FN0306, one of the best preserved samples from both sites. Three cross-sections were cut from the tooth sample and series of parallel laser ablation profiles were run on localized areas showing the three dental tissues (see details about methodology and results in Grün et al., 2010; Duval et al., 2011a). The distributions of $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ were used to identify domains that showed leaching and those that show U-uptake (see Fig. 4). The different sections showed complex U-mobilization processes over the last 100 ka, i.e. very recent processes in comparison with the geological age of the sample. Leaching from the tooth through the pulp cavity started by at least 93 ka with several later phases in various domains in the dentine and cement. This seemed to have been triggered by changes in the hydrological environment of the tooth which were caused by changes in the paleoclimate and associated increased erosion in the Guadix-Baza basin (for further details, see Duval et al., 2011b). In spite of its Early Pleistocene age, the tooth shows that secular equilibrium is almost absent in the dental tissues, and it only occurs in narrow and discontinuous bands between domains showing continuing U-uptake and U-leaching. U-uptake is particularly strong in the dentine from the upper section as well as in the thicker parts of the cement. U-leaching is observed throughout the cement layers and is increasing with depth in the dentine areas around the pulp cavity. The dentine close to the Dentine-Enamel junction (DEJ) seems much less affected by U-leaching. This area is associated with lower U-concentration values (see Fig. 3 of Duval et al., 2011a), i.e. shows the best potential for U-series bulk micro-sampling. U-concentration maps show a decreasing vertical gradient in dentine from the top section down to the base section, suggesting an U-uptake process through the occlusal surface (Duval et al., 2011a). U-concentration distribution in enamel follows the same vertical trend. This indicates that the adjacent tissues have a clear influence on U-migration into

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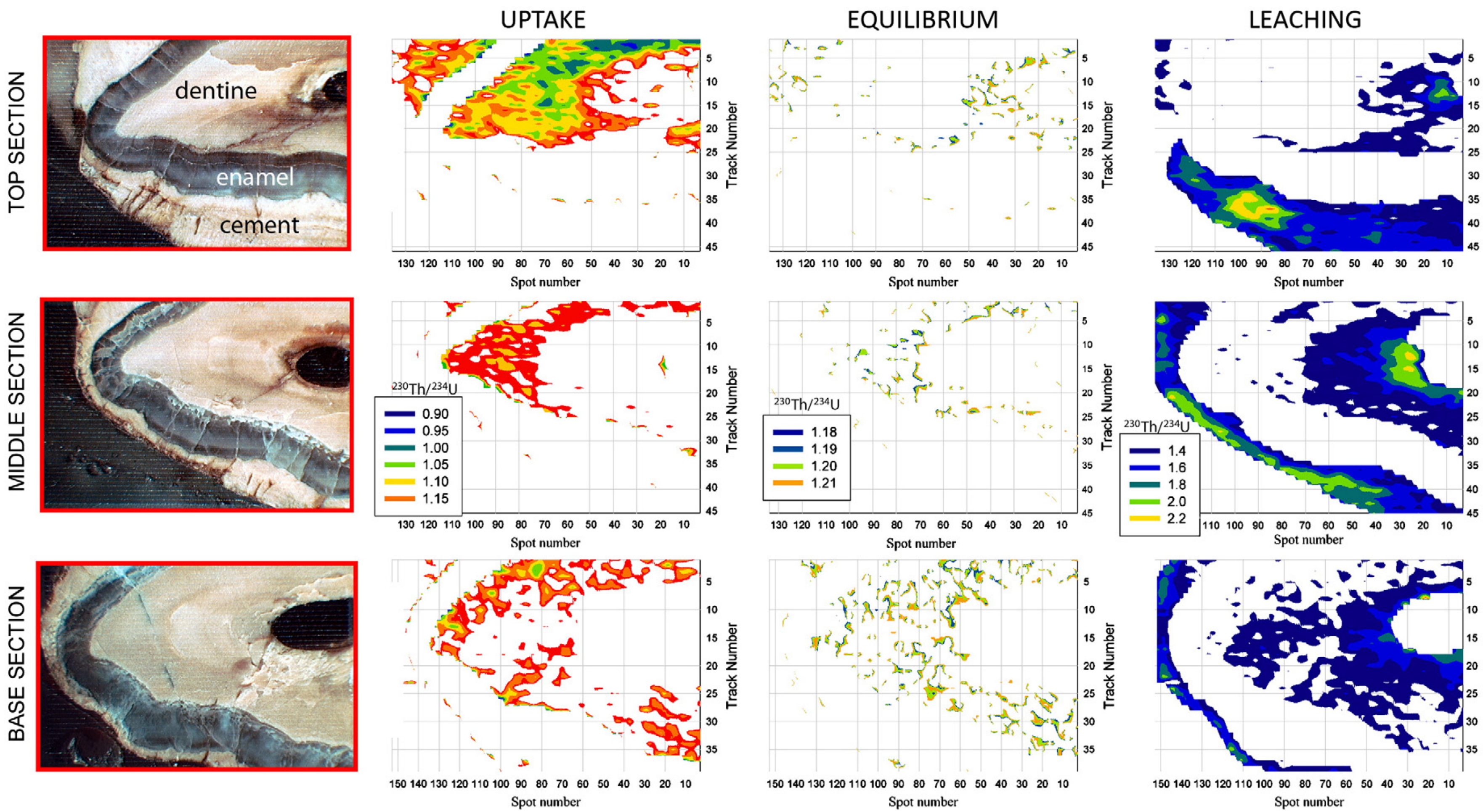

Figure 4. Detailed high-resolution isotopic mapping of $^{230}Th/^{234}U$ values showing various dominant geochemical processes within three transversal sections from FN0306 tooth sample (adapted from Duval et al., 2011a): U-uptake (second column), secular equilibrium (third column) and U-leaching (fourth column). ($^{230}Th/^{234}U$) activity ratio values at secular-equilibrium values were assessed from the average ($^{234}U/^{238}U$) activity ratio values measured in both dentine and cement for different cross sections, using the isotope evolution diagram of Kaufman and Broecker (1965). For all different tissues, these equilibrium values were within 1.17 ± 0.03. Domains that have smaller than equilibrium ($^{230}Th/^{234}U$) activity ratios experienced delayed U-uptake while domains with higher ratios indicated U-leaching. Values measured in the enamel have been deleted because of low U-concentration, which results in meaningless isotopic values.

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the enamel. Although the tooth has been deposited for more than 1 Ma, some domains within the enamel have experienced little to no uptake with U-concentrations of around 0.1 ppm. In contrast, other localized areas within the enamel show relatively high values (> 3 ppm) at the centre of the tissue (Fig. 5 of Duval et al., 2011a), suggesting that the elemental U-distribution does not only follow a simple diffusion path from the DEJ/CEJ into the interior of the enamel, but is more likely firstly driven by the mineralogical weaknesses of the tissue. Such processes may explain the heterogeneity of the U-concentrations measured in the enamel of BL and FN-3 samples (Table 1) and, especially, the high value obtained for FN0308.

With respect to this dating study, it becomes obvious that the average (^{230}Th/^{234}U) activity ratios that were obtained by bulk solution analysis of larger volumes may not be particularly relevant for the calculations of beta dose rates. For example, strong leaching near the pulp cavity will have little influence on the beta dose rate to the enamel, which will be dominated by the dentine volume close to the DEJ (see Fig. 4). For the upper two sections of sample FN0306, these volumes are dominated by U-uptake (i.e., (^{230}Th/^{234}U) activity ratios lower than equilibrium). Nevertheless, the U-series result of the dentine of the sample will be a straight average of the whole volume, indicating overall U-leaching. This bias in the (^{230}Th/^{234}U) activity ratio may well explain why sample FN0303 yields reasonable results when the (^{230}Th/^{234}U) activity ratio in the cement is slightly adjusted to equilibrium.

The same attempt performed with FN0305, i.e. assuming an Early uptake for the tissue showing U-leaching, led to an underestimated age result of 0.73 + 0.18/−0.09 Ma. This sample shows many similarities with FN0303 and FN0304, as it comes from the upper archeological level and has quite recent apparent U-series age in enamel (185 ka). However, the significantly lower D_E value obtained for FN0305 (−30% compared to FN0304, Table 1) is very likely the source of such a young age estimate. Indeed, an age of 1.17 + 0.33/−0.14 Ma is obtained when considering an average D_E value calculated from FN0304 and FN0303. The origin of the D_E value underestimation will be further discussed below.

The remaining samples, FN0306, FN0307, BL0501, BL0502 and BL0503 show similar geochemical behaviours, with apparent relatively early U-uptakes in the enamel (apparent U-series ages ranging from 286 to 427 ka) and (^{230}Th/^{234}U) activity ratio values above equilibrium in both dentine and cement tissues. Consequently, these samples are out of the limits of the US model. The detailed U-series maps of FN0306 show some domains within the tooth that are experiencing U-uptake, especially in the top section (Fig. 4). These domains are located close to the enamel layer and thus should be used to calculate more accurate beta dose rates (see mean U-series values in Table 3). However, even by considering these values, the combined US-ESR age is largely underestimated (~600 ka), similarly to what we observed on VM0502 sample from the nearby VM site (Duval et al., 2011b). In addition, the remaining samples from both sites show the same behaviour: calculations with (^{230}Th/^{234}U) activity ratios adjusted to equilibrium values for dentine and cement tissues yield systematic underestimated Middle Pleistocene ages (<600 ka).

We are now facing the actual limits of the combined U-series/ESR method applied to old fossil teeth: most of the samples are out of the US model application limits, and when data sets are slightly adjusted following simple assumptions (EU uptake for example), ages are still

Table 3
Mean U-series values obtained on the domains from the top section of FN0306 showing dominant U-uptake process (Fig. 3).

	Track number (Y-axis) / Spot number (X-axis)	U (ppm)	(^{234}U/^{238}U) activity ratio	(^{230}Th/^{234}U) activity ratio
Dentine	10–20/60–80	55.387 ± 4.567	1.816 ± 0.032	1.056 ± 0.036
Cement	3–8/110–122	42.958 ± 1.285	1.832 ± 0.042	1.127 ± 0.055

significantly underestimated. To explain such problematic results, we can reasonably envisage two main sources of errors, one associated to a dose-rate overestimation and another related to a systematic D_E underestimation. The first one is probably the easiest to identify, since some questions about U-series data collected from dental tissues have been previously raised in the present paper. However, it remains somewhat complex to evaluate the influence of a dose-rate overestimation, because several tissues have to be independently considered for a single tooth. Due to the high measured U-concentrations, the weight of the components associated to dental tissues in the total dose rate is dominant, making then the U-uptake history really crucial in the age calculation process (e.g., Grün and McDermott, 1994). This is the reason why the US-ESR ages of old samples are highly sensitive to (^{230}Th/^{234}U) activity ratio values, as also observed in Venta Micena (Duval et al., 2011b). For example, a 5% decrease in (^{230}Th/^{234}U) activity ratio values of all tissues from FN0304 results in a 16% older age estimate. Such sensitivity may cause problems, especially when the U-series data show spatial heterogeneity as observed in FN0306 (Fig. 4). To explain (^{230}Th/^{234}U) activity ratio values above equilibrium in dentine and cement tissues, the possibility of a single stage of recent U-leaching was suggested for the nearby VM site (Duval et al., 2011b). However, both processes most likely do not apply to the samples of this study. It shows that the actual U-series data measured in dental tissues reflects either more complex U-uptake histories that simply cannot be described by the US model, maybe made by successive U-uptake and U-leaching events for example, or massive recent U-mobilization processes that masked the original isotopic signature (Grün, 2009a; Duval et al., 2011a). As a consequence, the actual U-series data measured in most of the samples would simply be unusable for dating using the US model.

On the other hand, the possibility of systematic D_E underestimations has also to be explored. Such problem has been recently postulated by Joannes-Boyau and Grün (2011). Indeed, the major contribution to the radiation-induced ESR signal associated to fossil tooth enamel is due to several types of CO_2^- radicals (e.g. Callens et al., 1995; Brik et al., 2000). These radicals are usually classified in two main groups depending on their orientation dependence within the enamel layer (usually named oriented CO_2^- and non-oriented CO_2^- radicals) that show distinct thermal stabilities and radiation sensitivities (e.g. Scherbina and Brik, 2000; Vorona et al., 2006; Grün et al., 2008; Joannes-Boyau and Grün, 2009; Joannes-Boyau et al., 2010; Joannes-Boyau and Grün, 2011). According to Joannes-Boyau and Grün (2011), 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, which would generate systematic age underestimations. In the present study, the D_E values should be multiplied by a factor of 1.8 to 3, depending on the samples, to get an age similar to that obtained for FN0304. These values are far from the 30% age underestimation suggested by Joannes-Boyau and Grün (2011). However, these authors also admitted that such value should not be universally extrapolated to all sites and all samples, because it is based on studies performed on a very limited number of enamel samples and the influence of many factors should be first accurately assessed (e.g., age of the site, tooth type, species). Consequently, it seems that the D_E value underestimation might potentially explain part of the age underestimation. However, given the promising age estimate obtained for FN0304, and the massive D_E value underestimation that should be considered for the remaining samples, this seems very unlikely the major source of error.

In addition, the question of the U-mobility in sediment could be also reasonably raised as a supplementary source of uncertainty in the age calculation process. However, we have no clear data to support this hypothesis and any assumption would be then pure speculation. The US-ESR age calculations were performed assuming equilibrium in the ^{238}U-series of sediments (see details about the DATA programme in Grün, 2009b). It should be noticed that any U-mobilization in the sediments at FN-3 and BL would have its impact on the annual dose minored by three main factors. Firstly, all analyzed samples are equid fossil teeth, which are mainly characterized by the presence of cement (except FN0305) as an outer layer being directly in contact with the enamel layer. As a consequence, the sediment only contributes to the gamma dose rate, since the beta component of the external dose rate is due to cement and dentine. Then, high U-concentrations measured in dental tissues (several tens of ppm in dentines and cements) automatically limit the weight of the sediments in the total dose rate (from ~12% to ~47% for FN0304 and FN0308). Finally, the ^{238}U-series elements are only one of the three main contributors to the gamma dose rate, together with ^{232}Th series elements and ^{40}K. As an example, considering the samples that yielded US-ESR ages (i.e. FN0304 and FN0308), the contribution of the ^{238}U-series elements (assuming equilibrium) in the gamma dose rate is between ~36 and 42%, i.e. between ~6 and ~20% of the total dose rate. Now, assuming that this contribution has been overestimated of ~20% due to constant disequilibrium in the ^{238}U-series, their contribution decreases to 31 and 36% of the gamma dose, lowering the gamma dose value of about 7 and 8%, which has an impact of between 1 and 4% on the final US-ESR age of the two samples, i.e. within the total error on the age.

It is interesting to compare the results of the present work performed on FN-3 and BL sites with those of the nearby site of Venta Micena (VM), where it was at least possible to provide combined US-ESR age calculations for all the teeth analysed (Duval et al., 2011b). Indeed, samples from VM show some features that make them suitable for the combined US-ESR approach: very homogeneous (^{234}U/^{238}U) activity ratios in all tissues, in the vicinity of 1.2–1.3, i.e. lower than in the samples from FN-3 and BL (Table 1), and U-series ages indicating delayed U-uptake (Duval et al., 2011b). In contrast, BL samples show characteristics that are likely less suitable for dating (Table 1): very heterogeneous (^{234}U/^{238}U) activity ratios measured in the tissues of a single tooth, (^{230}Th/^{234}U) activity ratios that are systematically above the equilibrium in dentine and cement, as well as (^{230}Th/^{234}U) activity ratios in enamel that are systematically close to equilibrium (apparent U-series ages range from 302 to 427 ka). Interestingly, the biochronologically older site of Venta Micena contained more suitable samples for ESR dating, indicating that the geochemical context and diagenetic processes are probably of more importance for obtaining reasonable age results than the real age of the site. A similar result was found by Arribas and Palmqvist (1998) for the preservation of bone hydroxylapatite in the geochemical comparison by X-ray diffraction techniques of equid samples from Venta Micena with others from younger sites in the sedimentary basin. Formed by a homogeneous micritic limestone, the paleontological level of Venta Micena probably limited and slowed any recent U-mobilization, contrary to the highly detritic sedimentary context of BL, which may have contributed to water and, hence, radioelement circulations.

Conclusions

For both sites, our results highlight the actual limits of the combined U-series/ESR approach in dating old fossil teeth. The U-series data measured in dental tissues are probably the most crucial parameters in the age calculation for these kinds of samples. We identified several potential sources of error that may lead to inaccurate age results. High U-concentration measured in enamel is one of them, and may be reasonably considered for values $\gg 5$ ppm. Most samples show (^{230}Th/^{234}U) activity ratios above equilibrium, thus preventing the application of the US model. Such excess values may be simply due to the spatial heterogeneity within the dental tissues and/or to a recent single stage of U-leaching, as observed in Venta Micena (Duval et al., 2011b). Sometimes age underestimations can only be explained by a complex U-uptake history that simply cannot be described by the US model. Systematic underestimation of the D_E values due to unstable radicals, or U-mobility in sediments are also other potential sources of uncertainty. Nevertheless, considering the present data set, they do not seem to be the major factors behind inaccurate age results.

It is obvious that, even within a single locality, some samples are definitely more suitable than others for ESR dating of old sites. First of all, one has to be aware that many samples cannot be dated at all. In view of our results obtained for BL and FN-3 sites, criteria have to be defined to identify samples that can potentially yield reliable age results. For example, it is becoming necessary to perform a systematic U-series analysis prior to any other analyses or sample preparation. If domains with U-leaching are identified, samples should be discarded as any further analyses will not yield any reasonable age result with the US model. Laser ablation ICP-MS is the obvious choice for such initial analysis, because of minimal sample preparation, relatively fast acquisition and high spatial resolution. U-leaching would only have minor impact on the age calculations for samples with very low U-concentration in dental tissues (<10 ppm in dentine and cement), like those from Sterkfontein (Schwarcz et al., 1994). In addition, sampling strategies have to be modified, by significantly increasing the number of collected samples and by sampling from as many different sedimentary contexts as possible, in order to have a chance to obtain some samples that are potentially suited for U-series/ESR dating. However, it is also worth noting that systematic U-leaching in dental tissues from old fossil is not a fatality, since it may almost be absent in samples from Early Pleistocene sites, such as Venta Micena-A (Duval et al., 2011b) or Longgupo, China (Han, 2011). The U-series features of the samples seem strongly influenced by the hydrogeological context, as illustrated by the contrast between VM and BL.

Finally, one of the tooth samples studied (FN0304) gives an age of 1.19 ± 0.21 Ma, in agreement not only with results derived from paleomagnetism and biostratigraphy, but also with the US-ESR chronology obtained on the nearby site of Venta Micena (Duval et al., 2011b). Consequently, this age of about 1.2 Ma appears to be a reasonable estimate for the upper archaeological level of Fuente Nueva-3 site. It seems that dental tissues from this tooth preserved their original isotopic signature, contrary to the other samples from the same layer. However, more samples have to be collected in the future in order to support this first age estimate.

Our results show the complexity of dating Early Pleistocene fossil teeth by means of the combined U-series/ESR approach. From our experience with old samples, the improvement of the dating method reliability needs to go through the specific study of the following points:

- The understanding of the U-series element migration process into dental tissues. In that regard, it seems important to get spatially resolved U-series data for samples showing a good potential for dating (like those from VM), in order to get further information about U-series spatial distribution and homogeneity, and to compare with the results obtained from FN0306 (Duval et al., 2011a).
- The development of new models to describe U-uptake in dental tissues and overcome the limitations of the US model, especially for samples showing U-leaching. Some of them have been already proposed (Hoffmann and Mangini, 2003; Shao, 2011), but their potential has to be carefully assessed for such old samples.
- Understanding the specificity of samples showing high U-concentration in enamel ($\gg 5$ ppm). Their alpha efficiency should be assessed in order to confirm (or not) the hypothesis of an inverse correlation between this parameter and the high U-concentration (Bahain et al., 1992). In addition, it could be also interesting to try to correlate the domains of the samples showing high U-concentration values with their corresponding ESR intensities, by combining high-resolution analysis with LA-ICP-MS and

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ESR imaging, whose resolution has been recently significantly improved (e.g. Blank et al., 2009).
- A better understanding of the behaviour of the ESR signal in enamel in relation to the absorbed dose. If it has been demonstrated that the DSE function was more suited for old sample (Duval et al., 2009), further experiments need to be performed on these specific old samples to study the behaviour of the various radiation-induced radicals generating the overall ESR signal.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.yqres.2012.01.003.

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