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Keywords

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High resolution analysis of uranium and thorium concentration as well as U-series isotope distributions in a Neanderthal tooth from Payre (Ardèche, France) using laser ablation ICP-MS

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Abstract

We have mapped U (^{238}U) and Th (^{232}Th) elemental concentrations as well as U-series isotope distributions in a Neanderthal tooth from the Middle Palaeolithic site of Payre using laser ablation ICP-MS. The U-concentrations in an enamel section varied between 1 and 1500 ppb. The U-concentration maps show that U-migration through the external enamel surface is minute, the bulk of the uranium having migrated internally via the dentine into the enamel. The uranium migration and uptake is critically dependent on the mineralogical structure of the enamel. Increased U-concentrations are observed along lineaments, some of which are associated with cracks, and others may be related to intra-prismatic zones or structural weaknesses reaching from the dentine into the enamel. The uranium concentrations in the dentine vary between about 25,000 and 45,000 ppb. Our systematic mapping of U-concentration and U-series isotopes provides insight into the time domain of U-accumulation. Most of the uranium was accumulated in an early stage of burial, with some much later overprints. None of the uranium concentration and U-series profiles across the root of the tooth complied with a single stage diffusion–adsorption (D–A) model that is used for quality control in U-series dating of bones and teeth. Nevertheless, in the domains that yielded the oldest apparent U-series age estimates, U-leaching could be excluded. This means that the oldest apparent U-series ages of around 200 ka represent a minimum age for this Neanderthal specimen. This is in good agreement with independent age assessments (200–230 ka) for the archaeological layer, in which it was found.

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1. INTRODUCTION

In recent years, micro-analytical techniques have greatly advanced through the development of *in situ* laser ablation sampling combined with inductively coupled plasma mass spectrometry analysis (LA-ICP-MS; Eggins et al., 1998a,b). This technique is highly sensitive to uranium, allowing the analysis of sub-ppb concentrations with a spatial resolution of in the range of 100 by 10 μm .

The direct dating of human remains, that are older than 50 to 60 ka (the present uppermost limit for radiocarbon dating of bones: Higham et al., 2006; Jacobi et al., 2006), is confined to U-series and ESR (Grün, 2006). Both methods are seriously compromised by the fact that bones and teeth accumulate large amounts of uranium following their deposition in sediments. Over the past 30 years, a range of models have been developed to account for this uranium uptake and provide a basis for open system dating. The diffusion–adsorption (D–A) model, developed by Millard (1993) and Millard and Hedges (1996), refined by Pike (2000) and Pike et al. (2002) is the most sophisticated of these. It is based on a continuous diffusion of uranium from

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the outside of a bone or tooth towards the interior, and on the assumptions that the partitioning between the bone and solution (groundwater) and the U-concentration in the solution are constant. The bone or tooth is treated as a homogeneous medium. Under constant conditions, the cross-sections of bones that conform with the D–A diffusion model are expected to have both U-shaped U-concentration and apparent U-series age profiles, with the apparent ages at the surface being closest to the correct age of the sample. Deviations from the ideal profiles can be explained either by leaching or changes in the U-concentration in the solution. In the first applications of the D–A model, U-concentration profiles and U-series measurements were based on a few mechanically drilled samples, chemical separation of U and Th isotopes and their measurement either with an ICP or thermal ionisation mass spectrometer (e.g. Pike, 2000). Laser ablation ICP-MS provided a breakthrough in micro-scale U and U-series analyses and has subsequently been used to measure these isotopes continuously along profiles (Eggins et al., 2003, 2005). Grün et al. (1988) suggested combining U-series and ESR to simultaneously estimate the uranium diffusion process and age of a sample. The sensitivity of this combined approach could be checked by comparing ages based on continuous diffusion (Grün et al., 1988) and a single stage U-uptake (Grün, 2000). Laser ablation D–A U-series dating was recently applied to the human material from Tuinplaas (Pike et al., 2004), and combined U-series/ESR dating, based on laser ablation measurements, to Banyoles (Grün et al., 2006a) and Irhoud (Smith et al., 2007). The laser ablation scans on a dentine sample from Banyoles revealed that large contrasts in apparent U-series ages (57 and <2 ka) may occur within only a few hundred micrometer, a micro-distribution previously not thought possible.

Numerous faunal teeth from the Middle Palaeolithic site of Payre have been analysed for a range of isotopic techniques. We selected a Neanderthal tooth to evaluate and advance *in situ* analyses, including U-series, Sr, Ca and O isotopes. Preliminary results on oxygen isotope analysis using SHRIMP (with spot sizes of 35 µm diameter, about 2 µm deep, allowing a potential weekly to bi-weekly resolution for human molars) and Sr elemental distributions on this tooth using laser ablation were further reported by Grün et al. (2006b), maps of Sr isotopes by Aubert et al. (2007). In this paper, we present the first high resolution U (^{238}U) and Th (^{232}Th) elemental concentration and U-series isotope maps on a human fossil and discuss their implications for future dating studies.

The site of Payre is located 60 m above the Payre river, a small tributary of the Rhône river, on a cliff opening towards the southeast. Regular excavations have taken place since 1990 (Combiér, 1967; Moncel, 2003). The site belongs to the Jurassic and Cretaceous complexes, which cover a large part of the right edge of the middle Rhône Valley (Debard, 1988). It yielded a sequence with different archaeological layers, numerous artifacts, and fauna remains (Debard, 1988; Moncel et al., 2002; Moncel, 2004). The human remains, consisting of 14 teeth and a fragment of a parietal, were discovered in the different archaeological levels (Moncel and Condemi, 1996, 1997).

The sedimentary sequence was about 5 m thick and composed of five main levels (from top to bottom: A–B, C–D, E, F, and G) each of them including sub-layers. Twenty-five to 60 m² have been excavated down to the substratum. Layers A and B were formed of karstic sediments and did not contain any archaeological remains. Layers C and D consisted of brown clay and stony sediments, and Layer E of large blocks of limestone indicating the collapse of the cave's roof. Layer F contained seven cyclic deposits of grey sediments and beds of rubble and clay. This layer contained four separate human occupation layers, which alternated with those indicating cave bear occupation. Layer G consisted of orange clays containing pebbles and blocks. It yielded two distinguishable phases of human occupation. This clastic sequence was underlain by a stalagmitic floor, which was subdivided into six separate units (H2 to H7). An additional stalagmitic unit (H1) was difficult to associate with the other sedimentary layers.

Most of the human remains were found in the oldest level G, which yielded nine teeth and one fragment of a parietal. These human remains were found close to each other. Four teeth belong to the oldest human settlement (sub-level G_b) and the others, including the fragment of a parietal, to sub-level G_a. Level F yielded three teeth, the Level E one, and the upper level D one (Moncel and Condemi, 1996, 1997; Moncel et al., 2002).

The human behaviour was the same in all archaeological levels. Seasonal occupations (evidence of hunting of cervids, associated to equids and bovinds) were observed associated with a discoid debitage on flint, which came from local and semi-local outcrops. Other stones were also used, such as quartz, quartzite, basalt and limestone for a secondary flaking, hammers and pebble tools. The lithic assemblage belongs to Early Middle Palaeolithic, typical of Middle Rhône Valley and South France (Moncel, 2003). It is different from Orgnac 3, dated of MIS 9 and 8, where Levallois flaking was observed (Moncel et al., 2005).

The dating studies involving a range of methods has recently been summarised by Valladas et al. (2008). Layers D and E yielded ESR/U-series age estimates on faunal materials as well as thermoluminescence results on burnt flint in the vicinity of 150,000 years, while those on Layers F and G were in the range of 200,000–300,000 years without being distinguishable between these two layers. The underlying stalagmitic floor yielded a TIMS U-series ages in the range of 230–290 ka.

The Neanderthal tooth (# 1) was found in Level G, Layer D, Square N8, at a depth of 400 cm below datum. Considering the recent dating results, its age can be expected to fall within a range of 200,000–230,000 years (the older age bracket provided by the more reliable TIMS dating results on the underlying speleothems).

2. EXPERIMENTAL

The tooth was cut into halves with a thin (100 µm) diamond saw (Fig. 1) along the buccal–lingual (cheek to tongue) axis. The enamel section analysed covers the lingual half (facing the mouth) of the tooth (for details on tooth histology see Hillson, 1986). One-half was imbedded in a

Fig. 1. Photos of the Neanderthal tooth from Payre. Area 1 was scanned for U (^{238}U) and Th (^{232}Th) elemental concentrations, Area 2 for U and Th elemental concentrations and U-series isotopes. The arrows indicate the directions of the laser tracks.

removable resin, which is required for SHRIMP oxygen isotope analysis. The imbedded sample was then mounted in a sample holder so that the sectioned surface lies in the focal plane of the laser. After analysis, the two halves can be glued back together with little visible damage. The greatest material loss derives from the cutting width.

The analyses were carried out using a custom-built laser sampling system interfaced between an ArF Excimer laser (193 nm; Lambda Physik LPX120i) and an ICP mass spectrometer. Elemental U and Th distributions were measured on a Quadrupole Varian-820, U and Th isotopic distributions on a multi-collector Finnegan Neptune. Details of this system and its capabilities have been described previously (Eggins et al., 1998a,b). In brief, it employs a single long-working distance lens to project and demagnifying (by a factor of 20) the image of a laser-illuminated aperture onto the sample surface, which enables a range of geometries to be ablated within bounding dimensions of between 1 and 400 μm . In this study, laser pulse rates of 10 Hz were employed with a fluence of 10 J/cm² (power density 0.3 GW/cm²), the latter resulting in removal of a uniformly thick layer ($\sim 200 \mu\text{m}$) from the targeted sample site with each laser pulse. The in-house developed laser ablation cell produces very fast response times, which permits high spatial resolution analysis.

Data reduction followed established laser ablation ICP-MS protocols (after Longerich et al., 1996), using the international glass reference materials NIST SRM610 glass and a rhinoceros tooth (where the U-series ratios were established by repeated TIMS analysis) for external calibration, tailing correction and elemental fractionation. Mean background count rates measured with the 'laser off' were subtracted from all measured isotope intensities. All measured atomic ratios were converted into activity ratios, unless indicated otherwise.

3. RESULTS AND DISCUSSION

Prior to interpreting the results it should first be noted that the scans showed in various places small spots of anomalously high Th and/or U-concentrations (some are

clearly visible in the resin, see e.g. Fig. 3: lower left area). These may either be due to small sample fragments dislocated by the laser pulsing, air bubbles in the resin and other voids that have been filled with some sample material during polishing.

In a first exploration of the U-distribution, 21 parallel scans were measured, covering a cross-section of occlusal and lingual enamel and the adjacent dentine (for the approximate position of Area 1 see Fig. 1). The laser tracks had a width of 85 μm , with a spacing of 100 μm (centre to centre). The measurements covered an area with a width of about 2085 μm and a length of about 5500 μm . Each scan consisted of 1100 individual measurements. These were smoothed using a sliding 20-point average. The data were then interpolated for a three-dimensional presentation using the commercial SigmaPlot (Ver. 10) software. There is a very large contrast between the U-concentrations in the dentine and enamel, uranium concentrations vary overall between about 1 and 40,000 ppb. A linear scale enhances the details in the U-distribution of the dentine while the U-concentrations in the enamel are indistinguishable from background (Fig. 2A). In contrast, a logarithmic scale enhances the details in the enamel (Fig. 2B). The U-concentration contrast between enamel and dentine is sharp, dropping from about 25,000 ppb in dentine to a few 100 ppb in enamel, by a factor of around 100. Much of the apparent width of this concentration slope is due to the spot size of the laser. A sharp concentration contrast (e.g. a step function in U-concentration) is widened (i) over the laser spot size of 85 μm , which corresponds to approximately 17 measurement cycles and (ii) by the averaging process, which widens the U-concentration transition by another 20 cycles. The observed U-decrease at the dentine–enamel junction (DEJ) takes place within 25 and 40 cycles, which is an indication that the U-concentrations drop instantly at the DEJ and demonstrates the extremely fast response of the RSES laser ablation system. Similar large concentration contrasts (~ 100) in the U-concentrations between dentine and enamel have previously been observed in a range of faunal teeth (Eggins et al., 2003).

Fig. 2. Uranium concentration distributions in Area 1. (A) Linear scale; (B) logarithmic scale.

Fig. 3 shows maps of the U and Th elemental distributions in the enamel. Th is predominantly enriched right at the surface of the enamel (Fig. 3C) and is there associated with detrital coatings (see Fig. 1). In the three-dimensional presentation, this thin veneer occurs as separate isolated cones, which is the result of rastering caused by the track width and interpolation strategies of the software. The Th concentrations on the occlusal surface are lower than on the lingual surface. This is partly due to the angle between the surface and the laser track. The ablation tracks passed the occlusal surface at approximately right angles, so that less volume of the thin surface layer was measured here than at the lingual surface, where the tracks passed the surface at shallow angles and partly ran along the surface (see Track 21 between Cycles 400 and 600 in Fig. 3C).

There is an approximately 1 mm wide rim on the outside of the tooth (between the surface and the dotted line in Fig. 3C) with enriched Th concentrations in the range of 10–20 ppb, irrespective of the nature of the dental tissue. Only near the occlusal surface of the tooth, is a minor contrast observable between the Th concentrations in the dentine (around 1–6 ppb) and enamel (around 0.3–1 ppb; see DEJ below Cycle 600). Relatively high Th concentration in enamel occur above Cycle 800, a region which also contains elevated U (Fig. 6) and Sr concentrations (Grün et al., 2006b; Aubert et al., 2007). Nevertheless, there does not seem to be any evidence for Th diffusion paths into the tooth, although it is clear that this tooth contains significantly higher Th concentrations than observed on modern humans, which average Th concentrations in bones in the sub-ppb range, as we have measured on modern teeth.

Uranium diffusion into the enamel did not follow a simple D–A model with constant conditions, which would have produced U-shaped U-distributions. In general it is expected that uranium migrates from the dentine side into

the enamel, the surface being more or less impenetrable to U-diffusion as long as the outer non-prismatic layer is intact (e.g. Eggins et al., 2003). Starting from the DEJ, we have observed in many samples a more or less steady U-concentration decrease across the enamel layer, with increased U-concentrations right at the outer surface. The enamel of the Payre Neanderthal has on its outside a thin veneer of high U-concentrations, particularly at the base where up to 25,000 ppb is observed. Similar to the Th distribution, near the occlusal surface the U veneer is less pronounced with U-concentrations in the range of only 500 ppb. This may simply indicate variable amounts of detrital residue on the surface (see Fig. 1).

Within the enamel, the U-distribution varies by several orders of magnitude. The lowest concentrations are found near the occlusal surface where U-concentrations drop to less than 10 ppb, indicating little or no U-uptake. Elsewhere uranium has migrated into the enamel in a variety of modes. Firstly, U is concentrated along visible cracks. There is a clearly visible crack starting from the cusp of the dentine reaching to the surface (just above “I” in Fig. 3A and B). Uranium is also enriched along other linear features, as shown in Fig. 4. At least three different lineaments with enriched U-concentration are visible, all running at shallow angles to the surface and the DEJ. It becomes obvious that U-mapping is essential to understanding the mode of U-migration. If Track 4 was taken in isolation, significant U-diffusion normal to the surface could be postulated (Fig. 4C). Instead, U migrated within the enamel along a lineament, which forms a shallow angle to the surface. Given the observed concentration gradient, it seems that U migrated from the outer surface into the enamel. Whether this particular feature or the other lineaments are associated with cracks or inter-prismatic zones has yet to be confirmed. There is also a lineament of in-

Fig. 3. (A) SEM image of Area 1. (B) U-distribution. The solid lines indicate the enamel boundaries and lineaments of increased U-concentration. The squares indicate enhancements in Figs. 4 and 5. (C) Th distribution. The dotted line limits an area of higher Th concentration, which is unrelated to the dentine–enamel junction (DEJ).

creased U-concentration in the lingual enamel, perpendicular to the DEJ (Tracks 11–15, around Cycle 725, see Figs. 3B and 5B).

The most obvious feature in the enamel is a relatively large domain of greatly increased U-concentrations of up to 1500 ppb (around Cycle 500 in Tracks 9–14, Fig. 3B, enhanced in Fig. 5A). Uranium migrated from the dentine into the enamel along two pathways leading to a more or less constant enrichment in an area which reaches about 600 μm into the enamel and has a width of about 800 μm . From this area there is a series of smaller linear diffusion paths further into the enamel. This domain of high U can obviously not be explained by monotonic diffusion into a homogeneous layer, but more likely is due to a mineralogical change in this area or its subsurface. The SEM (Fig. 3A) indicates that this area is dominated by relatively large prismatic bundles, which perhaps allow preferential U-migration along wider intra-prismatic zones. Unfortunately, we cannot further investigate the mineralogical

structure in this area, because the sample has been polished several times for subsequent analyses and due to the complexity of the three-dimensional structure of enamel (e.g. Macho et al., 2003). It is interesting to note that the enamel has also experienced a significant uptake of Sr. However, we do not find a similar distinct accumulation of Sr in this particular area (Aubert et al., 2007).

Near the base of the lingual enamel, U-concentrations drop from about 300 ppb close to the dentine to about 100 ppb close to the surface, implying that U-diffusion had penetrated the enamel over its whole thickness (Fig. 5B).

One can use the position of the Th peak to fix the boundary between detrital surface contamination and the enamel, on the assumption that there is no Th diffusion into the enamel. The comparison of the Th with the associated U-peak allows the assessment of any U-diffusion from the surface into the enamel. Fig. 6 shows one of the largest effects of U migrating perpendicular from the surface into the

Fig. 4. Details of increased U-concentrations along lineaments. (A) Enhancement of Fig. 3A. (B) Individual tracks (reversed to (A)). (C) U and Th concentrations along Track 4. As a stand alone measurement the wide U-peak between Cycles 150 and 200 would indicate a significant U-migration perpendicular from the surface of the tooth.

enamel (Track 16). At the occlusal side of the enamel, the potential U-diffusion may be on a length scale of up to 30 μm and perhaps 60 μm at the lingual side. Correcting for the incident angle between laser track and enamel surface, and excluding the effect of lineaments reaching the surface (see Fig. 4C), we observe an average diffusion of uranium of about 5 μm (1 cycle) into the enamel at the occlusal surface (Tracks 1–15; between Cycles 130 and 190), and about 20 μm at the upper part of the lingual enamel (Tracks 16–20, Cycles 170–350) and 15 μm at the lower end (Tracks 9–20, Cycles 680–1100).

The uranium concentrations in dentine ranged from about 25,000 to 45,000 ppb (Fig. 7A). The higher concentrations are observed in the region that is not covered by enamel (see Track 1, Cycles 1050–1100 in Figs. 2A and 7). There is a general gradient from the centre of the dentine (Cycles 500–800, Tracks 1–5) towards the enamel. It is unclear whether this is the result of diffusion, or whether this is due to different adsorption capacity in different domains in the dentine. The increased U-concentration at the lower end of the dentine (Track 1, between Cycles 1050 and 1100) is

due to diffusion into the dentine not covered with enamel (see Fig. 9, below). As mentioned above, the Th distribution in the dentine was not associated with the U-distribution, nor with the DEJ. The elemental U/Th ratio was in most areas well above 10,000, the lowest values in the range of 2600. This implies that any U-series age calculations on dentine are not affected by detrital Th contamination.

The U-concentrations in the enamel were too low to obtain meaningful U-series data using laser ablation. For the scanning of U-series isotopes, we therefore decided to investigate a cross-section of the root, most closely assembling a bone cross-section (see Fig. 1 for the approximate position of Area 2). Area 2 includes the part of the dentine where the uranium increased significantly in Area 1.

^{238}U , ^{234}U and ^{230}Th were measured on the Neptune sector ICP-MS. The laser track width was 178 μm and track spacing 150 μm , during each measurement cycle the track advanced by 10 μm . The total area analysed was about 900 μm wide and 3000 μm long. Fig. 8 shows the effect of data reduction, after applying a 20 cycle sliding average, and calculating the mean value and error of the mean.

Fig. 5. (A) Details of increased U-concentration in the central part of the lingual enamel. (B) Details of increased U-concentration at the base of the lingual enamel.

Fig. 6. U and Th measurements along Track 16.

Fig. 7. Details of U (A) and Th (B) distributions in dentine. The outer enamel boundary is indicated by the dotted lines.

Fig. 9A shows an SEM photograph of the approximate dentine region of Area 2. This SEM was recorded some time after the U-series isotopes and subsequent analyses were carried out and shows an area that lies about 50 μm below the original tracks. Fig. 9B shows the ^{232}Th distribution in Area 2. Th was adsorbed at the outside of the dentine and shows no sign of diffusion into the dental tissue. Inside the dentine, the elemental U/Th ratios were well above 10,000. U-series ratios and age estimates were calculated from the U maxima at the surfaces of the dentine (Fig. 9C–E). At the outside surface, elemental U/Th concentrations ratios were as low as 350, at the inside surface well in excess of 1000. This again implies that none of the U-series age calculations were affected by the presence of detrital ^{230}Th , particularly those of Track 6 (see below).

The uranium concentrations in Area 2 ranged from about 27,000 to 39,000 ppb, similar to the concentrations in Area 1. It can also be seen that the higher U-concentrations in the dentine of Area 1 (Track 1, Cycles 1050–1100 in Figs. 2A and 7A) seems to have originated from a volume in the dentine that was not covered by enamel (see Tracks 3–6, Cycles 60–85 in Fig. 9C). The structure of U-distribution, however, is much more complex than in Area 1.

The U-concentrations show distinct peaks at the outside surface of the dentine, where it was not covered by enamel (Tracks 5 and 6, cycle 60–75, Fig. 9C). Tracks 1 and 2 show the gradual increase of the U-concentration from the DEJ, as observed for most of the dentine in Area 1. In Tracks 3

and 4, the U-maximum was located somewhat further to the inside, about 400 μm from the dentine outer surface. At the inside surface of the dentine, all tracks had their U-maximum at or near the surface. Tracks 1–5 had a second maximum further to the inside. U-series isotope ratios and ages were only calculated in the region between the U-concentration maxima on the outside and inside surfaces. This avoided any potential problems with detrital Th contamination.

The $^{234}\text{U}/^{238}\text{U}$ ratios (Fig. 9D) varied within a small band width, the average value being 1.202 ± 0.023 ($1 - \sigma$ standard deviation of all calculated values). The $^{230}\text{Th}/^{234}\text{U}$ ratios (Fig. 9E), on the other hand, varied greatly along and between the tracks. The same applies, of course, to the calculated apparent U-series age estimates (Fig. 9F). It can be seen, however, that there are some systematic patterns in the apparent U-series age estimates. Depending on the relationships between U-concentration and apparent U-series ages, we can distinguish four regions (I–IV, marked in Fig. 9C). In Region I, at and near the inner surface of the dentine, the highest U-concentrations are associated with the higher apparent U-series ages. This is generally expected from the predictions of the D–A model. The oldest ages occur at the inner surface (Cycles 240–260) and are steadily increasing from Track 1 to Track 6. Region II shows some distinct U maxima and minima, and these are inversely associated with U-series ages, i.e. in areas of relative high U-concentration, the ages are lower than in

Fig. 8. Effect of data reduction for the measurements in Area 2. Errors of the means are indicated by the error bars. (A) U-concentration. (B) $^{234}\text{U}/^{238}\text{U}$ activity ratio. (C) $^{230}\text{Th}/^{234}\text{U}$ activity ratio. (D) U-series age.

areas with relatively low U-concentration. In the central Region III, the U-concentrations are lowest, but the apparent U-series ages are significantly higher than in the surrounding Regions II and IV. Region IV shows a similar pattern as Region II. The apparent U-series ages near the

outer surface (Cycles 40–80, Region IV) are significantly lower than on the opposite side (Region I). When transferring these regions of distinctive U-concentration and U-series patterns onto the SEM image (Fig. 9A), it can be seen that Region I closely correlates to the darker rim around the pulp cavity (see Fig. 1), which consists of secondary dentine and/or weathered primary dentine. Region II seems to be dominated by tubules, while Regions III and IV are undistinguishable in the SEM characteristics with a non-directional patterns, perhaps caused by an overprint of secondary dentine or other secondary minerals.

To investigate whether there is a systematic relationship between U-concentration and apparent U-series age estimate, these two parameters were plotted on top of each other in Fig. 10A–F. In Region I, high U-concentrations are associated with high U-series ages (see Tracks 3–6). This is expected from the D–A model for the volumes at and near the surface. In most of the other areas, relatively high U-concentrations are associated with relatively low U-series ages and vice versa. Closer to the outer surface, U-series ages generally increase and are not immediately affected by the high concentrations at the outside (see Tracks 5 and 6, Cycles 60–70). However, the U-concentration peaks slightly further to the inside in Tracks 3 and 4, around Cycles 80–90, are clearly associated with significantly younger U-series ages, indicating that these peaks are the result of a relatively recent accumulation of U. The older apparent ages in the central part of the dentine (Region III in Fig. 9, Tracks 2–6, between Cycles 100 and 160) are clearly not associated with distinct minima in U-concentration.

None of the profiles show distributions in U-concentration and/or apparent U-series age estimates predicted from a single stage D–A model. The distributions of U-concentration and U-series ages in Regions II and IV point to at least two distinct phases of U-uptake. Nonetheless, if the age of the specimen is indeed somewhere in the 200–230 ka region, the age estimates near the inside surface and in some central parts come close to this expected age range, implying some early U-accumulation in these domains.

In order to gain some insight about the U-uptake history, it was assumed that the age of the tooth was 200 ka. This corresponds to a $^{230}\text{Th}/^{234}\text{U}$ ratio of about 0.875 for a $^{234}\text{U}/^{238}\text{U}$ ratio of 1.2. Using a simple two stage model of U-uptake, namely that the first stage of U-uptake was rapid around 200 ka ago and a second stage followed in recent times, the U-concentration distribution of the first stage of U-uptake can be calculated from the measured $^{230}\text{Th}/^{234}\text{U}$ ratios. For example, a data point with a $^{230}\text{Th}/^{234}\text{U}$ ratio of 0.5 would have acquired about 57% of its present day U-concentration 200 ka ago (this fraction has a $^{230}\text{Th}/^{234}\text{U}$ ratio of 0.875) and 43% most recently (with $^{230}\text{Th}/^{234}\text{U} = 0$; Fig. 10G–L). All profiles of these calculated initial U-concentrations show a more or less monotonic decrease from the inner to the outer surface, from about 30 to 20 ppm, respectively. This continuous concentration drop may well be associated with changes in the mineralogical composition of the dentine or size of its internal surface for U-adsorption. Only Tracks 5 and 6 have a distinct U-concentration peak at the outer surface, most

Fig. 9. Elemental, isotopic and age distributions in Area 2. (A) SEM of the dentine in Area 1, but about 50 μm below in depth. The large red square is for orientation subdivided into 50 cycle sections. Black lines indicate the boundaries of Regions I–IV (see C)). (B) Th elemental distribution. (C) U elemental distribution, Regions I–IV indicate areas of different relationships between U-concentrations and U-series age calculations. (D) $^{234}\text{U}/^{238}\text{U}$ ratios. (E) $^{230}\text{Th}/^{234}\text{U}$ ratios. (F) U-series age estimates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this paper.)

Fig. 10. (A–F) Age and U-concentration along the individual Tracks 1–6. (G–L) Calculation of a two phase model of U-uptake. The early one at 200 ka ago, the latter recently. The modelled U-concentrations are derived from the difference of the measured $^{230}\text{Th}/^{234}\text{U}$ ratio and that of 200 ka. The amount of late U-accumulation is the difference between the modelled and measured concentrations.

probably in the cement layer. On the whole, these calculated U-concentration profiles are closer to those expected

from a single stage D–A model, than the measured ones. The second phase of U-accumulation is particularly strong

in the outer volume (about Cycles 60–100) and around Cycles 180–220. It cannot entirely be excluded that the high ages of Region III and the low ages in the surrounding regions are the result of relatively recent U-leaching from Region III and re-deposition in Regions II and IV. However, this would require U-migration against the U-concentration gradient. One has to remember that U-redistribution must not necessarily only take place in the measured plane. U-injection may have originated in a volume above or below.

4. IMPLICATIONS FOR DATING

The U-concentration and U-series profiles measured in Area 2 of the dentine do not concur with a single stage D–A model. As such, this sample should be disregarded for dating (Pike, 2000; Pike et al., 2002). Nevertheless, some domains in the dentine yielded U-series results that are close to the expected age of the sample. In view that laser ablation provides insight into detailed U-migration, it is possible to investigate U-leaching and Th contamination. U-leaching would be expressed by a drop of U-concentration near the outside with an associated increase in the U-series age. This would generally look similar to the pattern shown in Track 3 between Cycles 40 and 80 (Fig. 10C), except that here the mapping indicates a secondary overprint. Near the inner surface, there is no sign of U-leaching, so that the apparent U-series ages in Region I, around 200 ka, can be regarded as minimum age estimates for the tooth. The same restrictions (i.e. that the U-series results are only minimum age estimates) also apply to bones that concur the D–A model under constant conditions (see Grün, 2006).

Data from laser ablation tracks have also been used for assessing U-concentrations and U-series isotope ratios on dentine and enamel for ESR dating analysis (e.g. Grün, 2006; Grün et al., 2006a; Smith et al., 2007). For any open system modelling, bulk data are required, because ESR measurements do not allow for spatial resolution (at least for the spin concentrations usually found in fossil human teeth, see Oka et al., 1997). It is clear from the U-distribution in the enamel that for this sample, any single laser ablation track would yield U-concentrations that may be completely unrelated to the bulk U-concentration that is required for ESR dating. Similarly, the U-concentration distribution in the dentine is not homogeneous, and the critical $^{230}\text{Th}/^{234}\text{U}$ ratios vary greatly. When laser tracks show such inhomogeneities, it seems necessary to carry out bulk analyses on the dental tissues that were used for ESR dating.

5. CONCLUSIONS

The detailed mapping of U-concentration data in dentine and enamel give insight into the U-migration patterns in these tissues. However, it is necessary to measure U-series isotope ratios to understand aspects of the time domain of these U-migration patterns. The U-uptake into the enamel does not follow any model that has been proposed so far. While some regions in the dentine may concur with a single stage D–A model, most regions do not. Laser abla-

tion mapping allows the investigation of U-leaching and if this process can be excluded, the derived apparent U-series data provide a minimum age estimate for the specimen. Single tracks are critically dependent on the mineralogical structure of the measured tissue. The U-series results and their interpretation may vary greatly, depending on where the track was measured.

The areas measured here are still too small to obtain a clear picture how uranium behaved in this particular tooth. We shall attempt to provide a complete map of the whole cross-section. Even here, U-concentrations and isotopes will still be affected from the volumes below and above the measured cross-section. Although it is desirable to obtain three-dimensional distributions, this is clearly not feasible in view of the exceptional value of human fossils. Furthermore, it is also a question whether the detailed insights obtained from one tooth are applicable to any other teeth from the same site. Nevertheless, a complete map will only require about two to three days of measuring time, which is very short when comparing this to mechanical drilling, isotope separation and subsequent TIMS measurements that used to be carried out for obtaining D–A data. The latter could only provide a few coarsely spaced measurements. It also seems necessary to find out where the uranium is located, i.e. whether it all accumulated on crystal surfaces or whether some of it was incorporated into the hydroxyapatite structure, for example replacing Ca ions.

U-concentration and U-series data derived from single laser ablation tracks may be a poor proxy for bulk data. When solution analysis is not an option, for example when analysing human fossils (Grün, 2006), laser ablation mapping should be carried out.

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