VARIATION OF U-MICRODISTRIBUTION IN FOSSIL HIPPARION TEETH AS A COMPLICATING FACTOR IN DATING STUDIES

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Five Upper Miocene fossil Hipparion molars were studied for U-distribution by Fission Track. U-uptake has reached the whole mass of the teeth and no saturation fronts seem to occur in the interior layers. Mean U-concentration in dentine, cement and enamel was 157, 139 and 78 ppm, respectively. $U_{enamel}/U_{dentine} \approx 0.5$ is considerably higher than 0.1 reported in the past for Upper-Quaternary mammoth teeth. These features are disadvantageous for ESR-dating in Hipparion enamel, although a long-lived signal (g=2.0018) is apparent. Leaching phenomena occur in the outer regions of these teeth. Inner enamel folding seems to have hindered a more uniform U- distribution in the teeth.

Introduction

The uranium concentration and microdistribution in fossil bones and teeth plays critical role when one deals with chronological studies. It has been shown that uranium content in those materials is about 3-4 orders of magnitude higher than in recent bones (AITKEN).[1] This is a complicating factor for most dating techniques applied to them (ESR, U-series, TL), as the rate of uranium uptake during the geological time is not known. So far, several models concerning the above rate have been proposed.[2-4]

Furthermore, the uranium concentration and microdistribution is not always uniform in different areas of the same skeletal part.[5,8] For ESR-dating purposes, where enamel is the most favorable dental tissue, WIESER et al.[6] recommend selection of enamel from areas of low uranium concentration, e.g., from areas inside the tooth that have the lightest coloration. Sampling of the white central part of enamel is also recommended by CHONG et al.[7] These authors, however, do not take into account the fluctuation of uranium concentration inside the enamel. Such fluctuations were observed so far by GRÜN and INVERNATI.[5] THEODOROU et al.[8] describe similar fluctuation in a series of teeth from Suidae, Felidae, Hippopotamidae and Equidae. It is not clear whether the central or the lighter colored part of the dental tissue contains less uranium. Numerous factors affect

the uranium uptake and distribution in fossil teeth and bones in ways not well known. Some of these are: the age of the buried skeletal part, the degree of the uraniferous solutions' offer from the environment, the oxidizing/reducing conditions dominating near the buried skeletal part, the percentage of hydroxyapatite existing in each tooth or dental tissue, the thickness of each dental tissue, the orientation of the teeth, the existence of microcracks in enamel, the degree of wear on the chewing surface, the complexity and folding of enamel etc. Meanwhile, the uranium accumulation procedure can be momentarily or permanently inverted due to leaching effects at any time after saturation.[9]

The fission track micromapping of uranium seems to be the most versatile technique for studies of uranium concentration and distribution in fossil Vertebrate skeletal parts. In this paper a collection of fossil Hipparion molars has been studied for uranium concentration and microdistribution using the above technique. The main goal of the work is to examine the influence of the complicated geometry of enamel on the uranium distribution of fossil Hipparion teeth, while other factors remain steady. Given that the data published concerning the matter deal mainly with fossil bones and teeth of Quaternary age, an extension of the study on materials of pre-Quaternary age seems to be worthwhile. The Hipparion molars were chosen because their enamel shape is very complicated. Additionally, the fact that in one maxilla there exist molars of the same morphology but of different degrees of wear, makes them ideal for comparative studies. By using more than one teeth from one maxilla, we can compare teeth that had exactly the same orientation during burial. The ESR-dating suitability of enamel is also discussed.

Experimental

For the purposes of this study we used suitable material from the collections of the Museum of Geology and Paleontology of Athens University. The material comes from Pikermi locality (Attica, Greece) and it was dug up in 1860.[10,19,20] Its geological age is Upper Miocene (about 9-5.5 Ma BP).

Totally, five fossil Hipparion molars along with parts of maxillary bone were analyzed for uranium concentration and distribution. Three of them (m^1, m^2, m^3) belong together in one upper maxilla (A), while two other molars (m^2, m^3) belong to another upper maxilla (B) (Figs 1 and 2). The material selected for this study had the same age, being derived from the same locality. So the same environmental conditions were ensured during the burial of these skeletal parts. The conditions of uranium deposition might be slightly different for each maxilla, although the same orientation is ensured for the molars of each group.

We chose two parts of Hipparion superior maxilla, according to the following criteria:

It was considered necessary to have at least one unworn molar on each maxilla so that we could compare the uranium microdistribution in molars having different enamel geometry. At unworn molars the protocone is closed with enamel on its chewing surface. So, if enamel, due to its high density, hinders uranium penetration, the uraniferous solutions can enter the protocone cavity only from its bottom side, at the base of the tooth. On the contrary, at worn molars the protocone is opened at both of its ends.

The enamel should have as less as possible cracks, as they could affect the inner uranium microdistribution, allowing uraniferous solutions to enter through them.

A total of fourteen sections have been done in these teeth (see Figs 1 and 2). Six of them are vertical sections, while the other are horizontal sections. The vertical sections
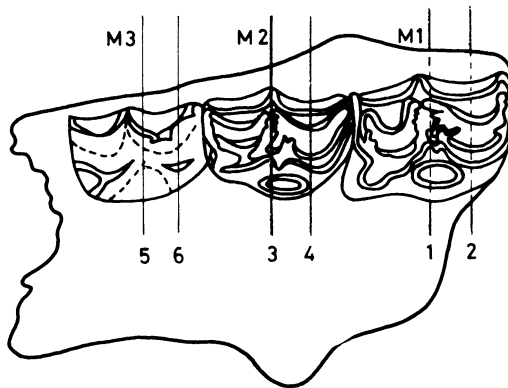

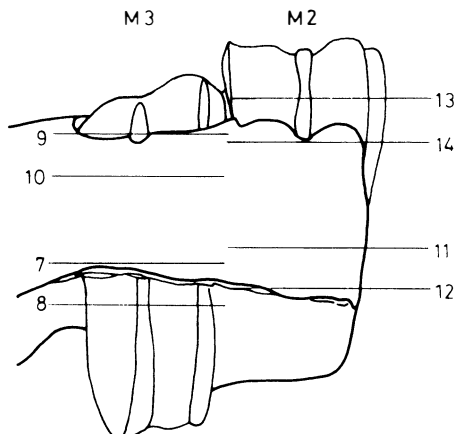Fig. 1. Maxilla A. The lines and numbers correspond to the vertical sections

Fig. 2. Maxilla B. The lines and numbers correspond to the horizontal sections

were made in three molars (m^1, m^2 and m^3) belonging to maxilla A. The horizontal sections were made in the two molars (m^2 and m^3) of maxilla B with a vertical succession.

External plastic detectors and standards were used as follows. A sheet of Makrofol detector (200 μm thick) was firmly attached on each section in order to detect the ^{235}U fission on the surfaces of the sections due to neutron bombardment. The material was irradiated by thermal neutrons in the research reactor facility of the N. R. C. S. "Demokritos". Along with the teeth, two pieces of Standard Corning Glass #1 (40 ppm U) were at the same time irradiated. The two standard glasses (also covered with Makrofol sheets) were placed at the two edges of the irradiated package. This treatment ensured that any possible inhomogeneity of the neutron flux in the thermal column can be easily checked. The neutron flux was $2 \cdot 10^{10}$ n $\cdot$ cm^{-2} $\cdot$ s^{-1} and the samples were irradiated for 45 hours. After the irradiation the detectors were etched in 7N NaOH for 9.5 minutes, at 70 °C. Process and measurements were carried out as described by WAGNER[11] and BASSIAKOS.[12]

The uniformity of the fission tracks registered by the standard detectors showed that the neutron flux was homogeneous. Measurements on these detectors were carried out by 30% overlapping fields. More than 100 measurements on each standard detector were performed by two persons. Thus, the systematic errors, resulting from rapid measurements based on computerized facilities, were eliminated. Nevertheless, the accuracy of the measurements on the standard detectors depends on the counting statistics and the total error of the uranium analyses is about 5%.

A total of fourteen uranium micromaps (one of each section) have been composed. The dimensions of each Hipparion tooth were about 40–50 mm in height and 15–25 mm in length or width. The thickness of the dental tissues varied as follows: enamel 0.8–1.8 mm, dentine 2.0–3.5 mm, cement 1.8–3.0 mm.

Results and discussion

Uranium concentration was measured in the following dental tissues existing in Hipparion molars: enamel, dentine and cement. Totally, more than 500 uranium analyses were obtained from the sections studied. Particular attention was given to studying the uranium distribution along worn and unworn protocones. Besides, pieces of fossil maxillary bone that surround the roots of the teeth were also studied. The same was done for the sedimentary fillings (calcite and clay) that often occur in the pulp cavity and in the cancellous part of the bone. It was observed that cancellous parts of maxillary bone are filled mainly with clay, while calcitic fillings occur less often. The opposite happens in the pulp cavities of the molars, were calcitic fillings predominate.

In Table 1 a set of analytical results is presented in a comprehensive form along with data from statistical processing. From these data it can be deduced that enamel contains

U-distribution in Hipparion molars, maxilla bone and associated sediments (in ppm)

Tooth section	Vertical sections (Maxilla A)							Horizontal sections (Maxilla B)						
	Molar M1		Molar M2		Molar M3			Molar M3'			Molar M2			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Tooth component: Enamel														
Population of														
U-analyses (n)	8	12	31	21	13	12	8	4	6	8	9	9	9	9
Mean value (x)	77	66	94	93	72	67	67	83	72	64	85	88	74	98
St. Dev. (Sx)	11.1	12.2	25.2	17.9	16.9	12.0	5.3	n. e.	n. e.	8.6	17.2	14.7	15.1	20.3
Tooth component: Dentine														
Population of														
U-analyses (n)	4	10	15	15	14	26	9	5	5	9	11	7	9	8
Mean value (x)	103	91	176	199	150	163	123	101	150	129	195	207	204	211
St. Dev. (Sx)	n. e.	42.0	20.9	26.5	39.9	26.1	11.1	n. e.	n. e.	16.3	28.2	11.0	22.3	28.0
Tooth component: Cement														
Population of														
U-analyses (n)		n. o.	18	10	5	6	5	2	2	4	7	7	7	7
Mean value (x)		n. o.	156	169	113	118	123	121	133	115	158	158	160	145
St. Dev. (Sx)		n. o.	23.0	17.2	n. e.	n. e.	n. e.	n. e.	n. e.	n. e.	33.1	26.7	23.4	26.5
Calcitic fillings of pulp cavities														
Population of														
U-analyses (n)		n. o.	n. o.	2	1	5	5	4	2	5	1	3	2	4
Mean value (x)		n. o.	–	4	1	6	15	3	6	15	14	5	8	18
St. Dev. (Sx)		n. o.	–	n. e.	–	n. e.	n. e.	n. e.	n. e.	n. e.	–	n. e.	n. e.	n. e.
Maxilla bone														
Population of														
U-analyses (n)	3	3	1	2	4	n. o.	3	n. o.	2	3	1	1	1	3
Mean value (x)	106	110	124	139	92	–	88	–	103	94	182	137	158	92
St. Dev. (Sx)	n. e.	n. e.	–	n. e.	n. e	–	–n. e.	–	n. e.	n. e.	–	–	–	n. e.
Clay fillings of porous maxilla bone														
Population of														
U-analyses (n)	12	10	2	5	n. o.	5	6	3	2	3	5	4	2	1
Mean value (x)	5	12	6	9	–	6	12	14	10	9	22	8	5	9
St. Dev. (Sx)	3.5	7.4	n. e.	n. e.	–	n. e.	n. e.	n. e.	n. e.	n. e.	n. e.	n. e.	n. e.	–

n. o. – not observed.

n. e. – not estimated.

Total analytical error: ±5%

always less uranium than the other dental tissues and even than the surrounding bone. This observation is in agreement with previous studies.[5, 8, 13] However, the mean uranium content in enamel appears to be 45% to 55% of the mean uranium content existing in the adjacent layers of dentine or cement. This value is considerably higher than 10%, which is given by the above authors. Additionaly, when making such comparisons we have in mind that the uranium microdistribution is not uniform in thick enamel of some animals.[8] Moreover, the mean uranium concentration in cement appears to be systematically lower than in dentine.

It has been supported that the outer layers of a large size tooth act as a buffer for the interior part.[13] This aspect has been based on the observation that in the outer layers the measured uranium content is much higher than in the interior ones. That was deduced from a detailed study of a fossil mammoth molar of Upper Quaternary age.[5]
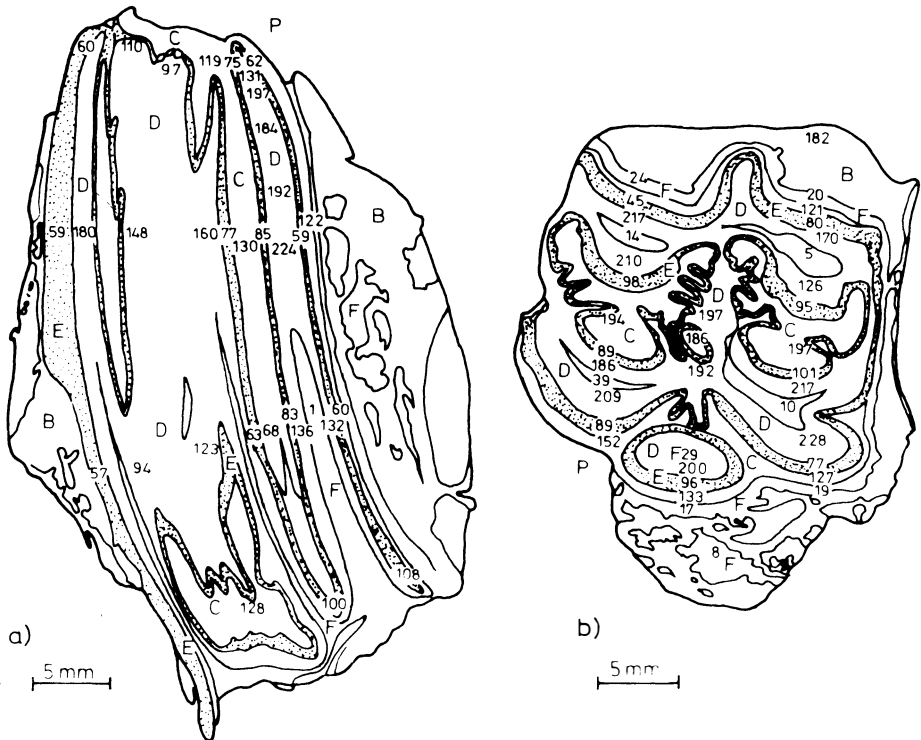

Fig. 3. Sections of fossil Hipparion teeth and respective uranium distribution (in ppm); a – vertical section No. 5; b – horizontal section No. 11 (see Figs 1 and 2 and Table 1). Different dental tissues, as well as associated sediments, are indicated by letters: E–enamel, D–dentine, C–cement, B–bone, F–sedimentary filling. P indicates the protocone. Enamel is also spotted. Note that no considerable variation in uranium concentration exists between external and internal layers of the same dental tissue.
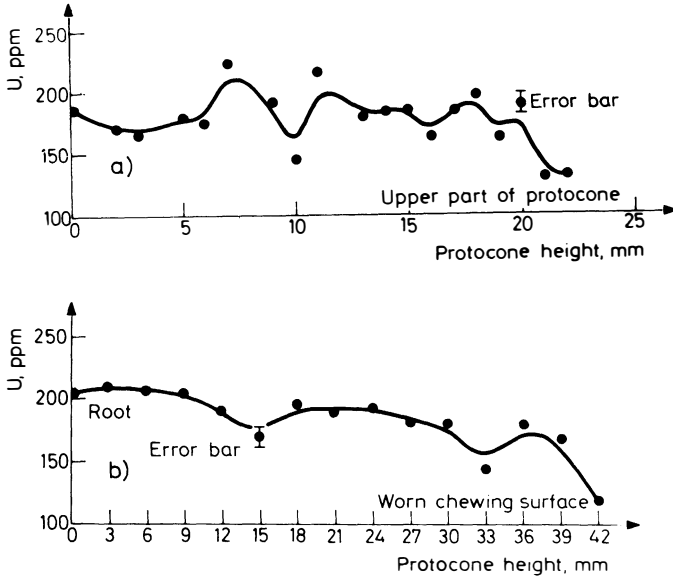
Fig. 4. a– Uranium distribution in dentine along the upper half of the „closed" protocone P (see Fig. 3a). Note that no considerable variation in uranium concentration exists between the central region and the closed edge of the protocone; b – Uranium distribution in dentine along an „open" protocone (section No 3; see Figs 1 and 2 and Table 1). The essential inclination of the „smooth" curve towards the „open" edge of the protocone is very probably attributed to leaching effects

However, since "it does not seem to be possible to establish a general model of uranium accumulation" as the above authors state, it is important to examine how uranium is accumulated in fossil teeth of older geological ages.

The uranium microdistribution is displayed in a vertical and a horizontal section of two separate Hipparion molars (Figs 3a and b, respectively). The vertical section 5 corresponds to molar m^3 of maxilla A and the horizontal section 11 corresponds to the molar m^2 of maxilla B. The following observations can be deduced from these sections:

(a) The interior structure of Hipparion molars is complicated, with many thin folded layers (or regions) consisting of enamel, dentine and cement. Associated sediments and surrounding bone are also apparent. Uranium analyses have been performed in all materials examined.

(b) We did not observe considerable differences between outer and inner parts consisting of the same dental tissue (e. g., enamel) as has been the case in the past with molars of animals with thick enamel.

(c) The area indicated by "P" in Fig. 3a corresponds to a protocone, i.e., a cylinder of dentine surrounded by enamel except in its bottom side (at the area of the root of the tooth). The upper half of this protocone has been more systematically examined. The

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distribution of uranium seems to be almost uniform along this area, with the exception of the tip near the closed unworn protocone. In Fig. 4a the measured values are plotted vs. the height of the protocone. However, it seems to be necessary to repeat similar studies many times on material deriving from different localities and/or having different age, in order to have results based on many observations. It is clear that such studies demand the destruction of many valuable fossils which are not easily available.

(d) Although these molars come from two different maxillea, the uranium content in the respective dental tissues appears to be comparable.

(e) The sediments associated with the tooth or the bone contain considerably less uranium than the fossil skeletal parts.

Similar observations can be deduced from all the uranium micromaps composed (fourteen; one for each section), which are not presented due to lack of space.

Attempting to examine the existence of a saturation uranium front into these pre-Quaternary teeth, we systematically studied the uranium distribution along the protocone of the molar m^2 of maxilla A, which was worn by chewing. The results of these measurements are displayed in Fig. 4b. It is shown in this figure that the uranium distribution along this open protocone seems to be uniform, expect for the upper part of the tooth (in the area of the chewing surface). Thus, in Figs 3a, 4a and 4b it can be shown that the saturation uranium front, proposed by GRÜN and INVERNATI,[5] does not seem to be confirmed in the pre-Quaternary material examined. In the case studied the uranium saturation seems to have reached the whole mass of the teeth at a certain time, during the very long period that they were buried (more than 5.5Ma). Phenomena of lower uranium concentration near the external surface of the teeth are observed not only in Fig. 4b. They also occur in Fig. 3a and even in all the other vertical sections studied (No. 1, 2, 3, 4 and 6; Fig. 1) and they concern all the dental tissues occurring in the outer parts of the teeth. Thus, unlike the observations made by GRÜN and INVERNATI,[5] in this case the external parts of the teeth contain systematically less uranium. This indicates that leaching procedures, reported also by BADONE and FARQUHAR,[9] may have affected these fossil teeth after saturation.

Enamel has been described as a dense, well crystallized dental tissue. It contains a high percentage of hydroxyapatite, even from the living period of the animal.[1,18] Post-mortem enamel preserves its crystalline structure (there is only a change from hydroxyapatite to fluoroapatite), while gradual crystallization and uranium accumulation happen in dentine and cement burial. Enamel behaves during fossilization as a less reactive substance, due to its density and its crystalline structure. Thus uranium may penetrate more easily the interior parts of the tooth through dentine and cement than through enamel. From this point of view, enamel can be considered as a barrier to uranium in the interior of the tooth. So different parts of a tooth are more or less exposed to the uraniferous solutions penetrating from the root area, the worn chewing surfaces and the

craks that often exist in fossil teeth. The complicated inner structure of enamel seems to be the main reason of the slight inhomogeneity of uranium content between similar dental tissues, also noted in the data given in Table 1. Fluctuations in uranium content between similar tissues are, however, limited, if comparisons are made among sections of the same tooth rather than of different teeth. Anyway, fluctuations in uranium concentration in Hipparion teeth are better expressed than in teeth with simple internal structure.

As a consequence of the well crystallized phase of enamel, the range of variation of uranium content in enamel is smaller than in dentine, cement or bone.

As mentioned above, three of the molars studied belonged to maxilla A, while the other two belonged to maxilla B. Hence, the orientation of the two groups of molars was not the same during burial. Analytical data cited in Table 1 show that the different relative orientation of the maxillae was not critical for uranium accumulation.

Concerning the uranium content of the associated sediments (clay and calcite), the following observations can be made. The uranium concentration in clay is within the regular ranges given elsewhere (1 – 13 ppm; IAEA),[14] moreover, fission track uranium analysis carried out on three other clay samples derived from the same area where the fossil Hipparion remains have been found, gave the following uranium contents: 2.9, 4.3 and 4.7 ppm. These values are comparable with the respective values given in Table 1. Unlike clay, the uranium content of the calcitic sediments that fill the pulp cavities is higher than usual in terrestrial calcite[17] and reaches a mean value of 8.6 ppm of uranium (Table 1). These relatively high values can be explained only if one takes into account that calcite, as a crystalline substance, is very tightly embedded into the pulp cavities, thus uranium can migrate to calcite from an adjacent dental tissue. On the contrary, clay seems to be less tightly embedded in the dental tissues or bone, as it can fill or be washed away from the cavities several times during the burial.

It was previously mentioned that the thickness of enamel varies in the material studied from 0.8 to 1.8 mm. Uranium analyses performed on vertical and horizontal sections showed that there is no considerable difference in uranium distribution between internal and external sites of the enamel. This observation is in agreement with data reported in the past,[8] where variations in enamel uranium content have been found only in thicker enamel layers (teeth of Suidae, Felidae and Hippopotamidae). Based on the available analytical data, we can assume that the enamel layers of Hipparion teeth have absorbed uranium from both of their sides and due to their thinness, the distribution of uranium appears to be uniform throughout them. The absence of a uranium saturation front in the interior parts of these long-buried teeth is an indicator that uranium saturation has reached the whole mass of the tooth during the first phases of fossilization. GRÜN and INTERNATI[5] mentioned that in one case the velocity of this uranium front was 1-3 cm/150.000 year.

Dating suitability of enamel

HENNIG and GRÜN[15] had first reported an ESR signal at g ~ 2.0020 in the spectra of a fossil tooth. Later, SCHWARCZ[16] and GRÜN[13] showed that the precise position of this signal is at g = 2.0018 and that it is long-lived (over 10^7a). The same signal is also apparent in the ESR spectra of all fossil Hipparion enamels studied in this work (see Fig. 5). The existence of such a long-lived ESR signal seems to be promising for dating
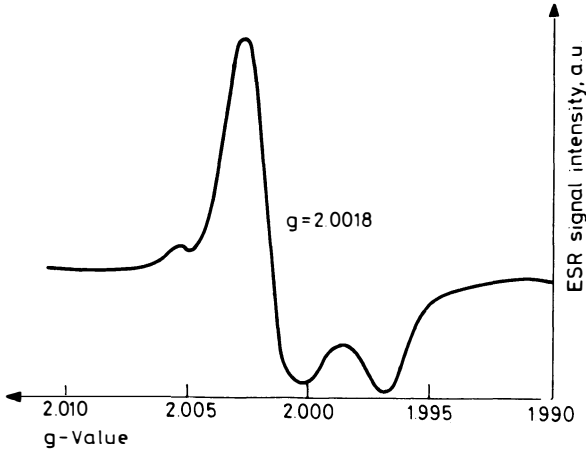

Fig. 5. ESR spectrum of fossil Hipparion tooth enamel from Pikermi, Attica, Greece. Microwave power = 7.9 mW, frequency = 9.429 GHz, gain = $4 \cdot 10^4$, modulation = 1.0 Gpp. Weight of sample = 100 mg. Taken on an ESR spectometer BRUKER ER 200 D–SRC at room temperature

of teeth beyond the limit of 1 Ma. Here the problems of uncertainties in dose rate, resulting from uranium uptake and radioactive disequilibrium are less critical. The main disadvantage in case of Hipparion teeth is that their very thin layers of enamel contain several tens of ppm uranium. Unfortunately, the inner parts of the teeth do not contain less uranium. However, fossil teeth with thick enamel which belong to animals of pre-Quaternary ages seem to be suitable material for ESR dating studies, if the internal parts of the enamel have not been affected by uranium diffusion.

In any case, fission track uranium mapping in proper sections of teeth, appears to be necessary if uranium diffusion and the dating suitability (by ESR or other techniques) are questionable for those materials.

Conclusions

Fission track studies for uranium distribution and concentration in Hipparion molars of Upper Miocene age showed that uranium was taken up throughout the mass of each tooth. Saturation fronts were not observed in the interior parts of these long-buried teeth. Uranium content is higher in dentine (up to 211 ppm), and lower in enamel (up to 98 ppm). The mean values for dentine, cement and enamel are 157, 139 and 78 ppm, respectively. The ratio of enamel to dentine mean uranium contents is 0.5. This value is considerably higher than the 0.1 reported for Quaternary fossil mammoth teeth. Values of uranium distribution in vertical and horizontal sections of the molars studied are comparable. However, deviations in uranium content along a dental tissue are higher, if comparison is made among different teeth rather than among sections belonging to a single tooth. Since the molars have the same age and uranium supply, the variations of uranium among them can be attributed to their complicated inner structure, which is not exactly the same in every molar. Lower uranium concentrations observed in the outer regions of the teeth, as well as in the root and on the chewing surfaces, can probably be attributed to leaching procedures that took place after saturation.

The uranium concentration and distribution in the associated sediments (clay and calcite) are regular for clay (mean value 9.7 ppm), but higher than normal in calcite that fills the pulp cavities (mean value 9.8 ppm). The tight accretion of calcite in the dental material seems to facilitate migration of uranium from the dental tissues to calcite.

The high concentration of uranium in enamel is disadvantageous for ESR-dating studies, although a long-lived ESR signal at $g = 2.0018$ is apparent in all the samples studied. However, searching and sampling of enamel regions that do not contain considerable amounts of uranium is advisable in other cases. This approach enables ESR-dating studies on dental materials of pre-Quaternary ages.

By all means, fission track micromapping on fossil teeth appears to be a very useful approach, contributing to the understanding of the uranium uptake mechanisms. It is also the only available technique that helps to recognize the ESR-dating suitability of fossil enamel. Moreover, in cases when the ESR-dating technique appears to be applicable, it contributes to a more precise estimation of the internal dose rate, often introducing errors in most ESR-dating studies. It is clear that in every analytical study or dating technique we should examine first the microdistribution of the elements involved.

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