Ancient TL

Uranium and thorium in the constituents of fossil teeth

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Abstract
In the course of ESR dating studies we have analysed the constituents of 67 teeth from 12 archaeological sites in Australia, China and South Africa for uranium and thorium by ICP-MS. We find that there is no relationship between the uranium and thorium concentrations in either dentine or enamel and that there is also no correlation between the thorium concentrations in adjacent dentine and enamel layers. There is some relationship between the uranium concentrations of adjacent enamel and dentine layers, the U concentration in dentine being about 20 times higher than in enamel. There is also hardly any connection between uranium and thorium concentrations and time which precludes any predictions of the mode of uranium and thorium accumulation.

Introduction
For recent ESR dating studies, we have switched from neutron activation analysis to inductively coupled plasma mass spectrometry, ICP-MS, for the analysis of elemental concentrations in teeth. Due to the small sample size, in the range of a few hundred mg, it is difficult to determine Th concentrations, therefore, it was usually assumed that the constituents of teeth are basically Th free and only uranium was determined. The application of ICP-MS allows the scanning of a variety of elements in one run with very high sensitivity (better than 1 ppb) on small samples (< 100 mg). In the context of ESR and U-series dating, it is not only important to know the concentrations of radioactive elements in the sample and its surroundings but also whether and how radioactive elements, particularly uranium, migrate into the samples (see Grün 1989, Millard 1993, McDermott et al. 1993). It is well known that fossil bones and teeth have significantly higher concentrations of uranium than recent specimens and this effect has been used for crude dating purposes (Oakley 1980).
The geochemistry of uranium and thorium has been described in detail in Ivanovich & Harmon (1992). Basically, U^{6+} is water soluble, thus mobile, whereas Th is water insoluble and is quantitatively absorbed by particles. Therefore, percolating water contains traces of uranium but is virtually free of thorium. When bones, teeth and other organic material are buried, the decomposition of the organic constituents produces a reducing environment in which U^{6+} is reduced to the insoluble form of U^{4+}. This leads to an enrichment of uranium in the initial stages of the fossilisation of bone material. Furthermore, U^{4+} and U^{6+} can be incorporated into apatite (replacing Ca^{2+}), which is the main mineral constituent of bones and teeth.
Both ESR and U-series dating results are strongly affected by mobilisation of uranium (McKinney 1991, Grün et al. 1987). In order to address the problem of uranium uptake for ESR dating, two models are used for calculating ESR age estimates (Ikeya 1982):

1) Early U-uptake: the measured uranium concentration was accumulated by the specimens shortly after burial;
2) Linear U-uptake: the uranium was continuously accumulated over time.

It is clear that both models can only approximate the real U-uptake, as this will strongly depend on the geochemistry of the sediments, water availability, temperature, bacterial activity etc. One would expect, however, if linear uptake is the closer approximation to a general U-uptake history, that older samples have generally higher U-concentrations than younger samples.

Grün et al. (1988) proposed to combine ESR and U-series analyses which then allows the simultaneous estimation of the mode of uranium uptake and the age of the sample. The model was successfully tested with a variety of samples from Israeli archaeological sites (McDermott et al. 1993). The open system modelling (Grün & McDermott 1994) revealed that most of these samples accumulated the uranium a short time after burial, however, some samples showed late uranium uptake. The main conclusion of this study was, that the uranium uptake was not predictable.

ICP-MS Analysis

The elemental analysis was performed on a Fisons VG PlasmaQuad. Homogenised enamel (50 mg) and dentine (30 mg) samples were dissolved in 4ml 6N nitric acid and 3 drops of concentrated perchloric acid and refluxed in capped teflon bottles on a hotplate at 150°C for at least 4 hours. The solutions/suspensions were then evaporated down to a residual pellet, resuspended and dissolved in 2% nitric acid and refluxed at 120°C for at least 24 hours. Whist the enamel samples are readily soluble using the above procedure, dentine samples vary in their ease of solubility due to the presence of metallic oxides, organics and other compounds. Partly insoluble dentine samples were treated with 1 to 2 ml 4N hydrochloric acid when approximately half of the 6N nitric acid had evaporated. In many samples this treatment results in complete dissolution, in others, the addition of several drops of perchloric acid and/or hydrogen peroxide, refluxing for several hours at 150°C alternating with 15-20 minute ultrasonic bath sessions, completes dissolution. The inclusion of hydrochloric acid requires evaporation to a pellet, resuspension/dissolution in 6N nitric acid, evaporation to a pellet and resuspension/dissolution in 2% nitric acid. Milli-Q water is used throughout and all reagents apart from hydrogen peroxide are the refined products of sub-boiling distillation. The 2% solution is transferred, along with several 2% nitric acid rinsings of the teflon bottle, to a 125 ml polypropylene bottle to which is also added a spike (internal standard) to give a final concentration in 50g (taken to final weight with 2% nitric acid) of approximately 1ppb ^{233}U and 7ppb ^{115}In. The sample is now ready for ICP-MS. Blank preparations, for each batch of samples put through the dissolution procedure are prepared in the same manner as for assay samples. Additional blanks are prepared to check polypropylene bottles, ICP-MS uptake tubes, teflon bottles and fresh reagents.

The judgement of whether a sample is in complete solution is based on visual appraisal; it is therefore important to consider that the sample may not be in complete dissolution. To address this issue repeats can be performed and UV-VIS spectrum analysis can be made. Only a few dentine samples have resisted the dissolution procedures as described above, in these cases the dissolution procedure has been repeated on a new sub-sample and if insolubility persists, the suspension is centrifuged and the supernatant removed for analysis along with the supernatant from several 2% nitric acid washings of the pellet. The latter analysis is unsatisfactory due to the unknown chemical composition of the pellet.
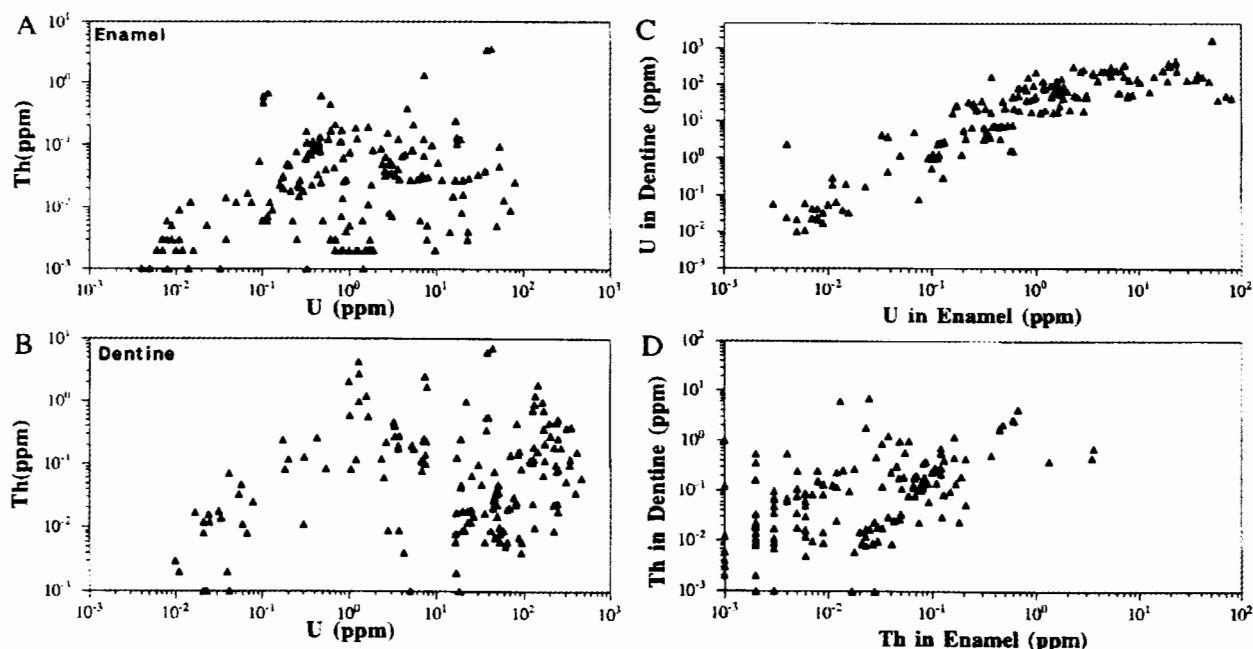

Figure 1

Plot of Th versus U concentrations in enamel (1A) and dentine (1B) and plot of U(1C) and Th (1D) concentrations in dentine versus the respective concentrations in enamel. Figures 1A, 1B and 1D show that the measured Th concentrations show hardly any relationship to the other parameters. The U concentration in dentine is approximately 20 times higher than the U concentration in an adjacent enamel layer (r = 0.89).

Dissolution using a high performance microwave digestion unit will be considered for future dentine samples as the higher temperatures attainable are suitable for dissolving refractory minerals.

The random errors for fully prepared solutions which have been analysed in different session are < 2% for Th concentrations of between 22 and 34,149 ppb and for U concentrations of between 256 and 7,325 ppb
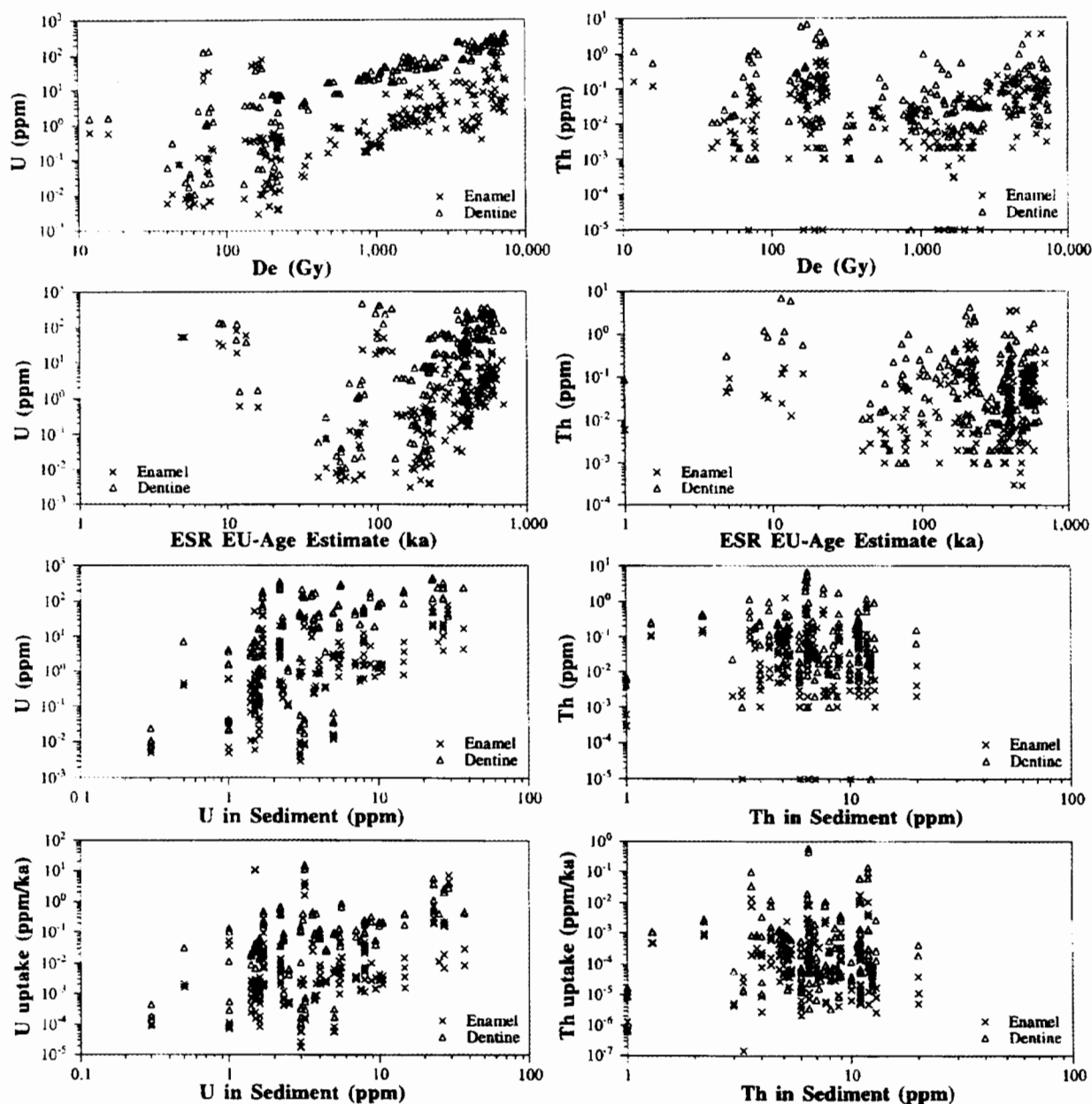

Figure 2

Relationship between U (left) and Th (right) and the measured dose value (top row); the ESR age estimate (second row), the respective element in the sediment (third row). The bottom row shows the relationship between U and Th uptake versus the concentration of the respective elements in the sediment. There is a reasonable correlation between the U-concentrations and the measured dose value (enamel: r = 0.66; dentine: r = 0.77). All other U relationships have r values between about 0.35 and 0.6 indicating some weak relationships. Th in teeth is basically not related to any of the shown parameters (r < 0.2).

Results and Discussion

The teeth analysed were collected from a variety of sites ranging in their estimated geological age between about 5,000 years to greater than one million years. Figure 1 shows the results of 197 adjacent enamel and dentine layers. The correlation coefficients are given for the logarithmic values as shown in the diagrams. Figures 1A and 1B show that there is no relationship between uranium and thorium either in enamel ($r = 0.29$) or in dentine ($r = 0.22$). Relative high Th concentrations (> 0.5 ppm) were measured in 8 enamel samples and 17 dentine samples. There is a clear relationship between the uranium concentrations in enamel and dentine ($r = 0.89$, Figure 1C). The average uranium concentration in dentine (92 ± 204 ppm) is about 20 times higher than the average U concentration in enamel (5.7 ± 2.6 ppm). It also seems that dentine reaches saturation in the range of about 100 to 1000 ppm. Figure 1D shows that there is a weak correlation ($r = 0.51$) between the Th concentrations in dentine (average: 0.32 ± 0.87 ppm) and the adjacent enamel layers (0.01 ± 0.38 ppm), the Th concentrations in dentine being about 30 times higher than in enamel.

Figure 2 shows the relationship between the U and Th concentrations with the past radiation dose, D_E, the approximate age of the samples and the concentrations of the respective elements in the sediment. The only clear relationship exists between the measured D_E and the uranium in enamel ($r = 0.66$) and dentine ($r = 0.77$). This is hardly surprising as the influence of the external gamma and beta dose rate from the sediment on the total dose rate diminishes with increasing U-concentration in the constituents of the teeth. Th, on the other hand, has only a minor influence on the total dose rate, and, hence, no relationship between Th concentrations and D_E value can be observed; the relationship between Th and the dose is for enamel: $r = 0.11$ and for dentine: $r = 0.037$.

One would generally expect that there is either a relationship between the uranium in teeth and age, the uranium in sediment or the combination of the two. As shown on the left had side of Figure 2, however, there is hardly any relationship between these parameters. The best relationship exists between the uranium concentration in dentine and age ($r = 0.61$), followed by correlation of the uranium in enamel and age ($r = 0.35$). The relationships between the U in dentine and enamel and U in sediment or uranium uptake vs U in sediment have all r-values in the range of 0.4 to 0.5 which indicate that there is only some weak influence between the chosen parameters. The diagrams of the Th concentrations in the constituents of teeth versus the other parameters clearly demonstrate that neither time nor the Th concentrations of the environment relate to the measured Th concentrations of the teeth. The highest correlation coefficients can be found between Th concentrations of the teeth and age (enamel: $r = 0.19$; dentine $r = 0.11$). The other relationships have r-values of less than 0.05.

Our results clearly imply that there is no relationship between the thorium concentration and any other parameter considered in this study. The thorium concentrations are usually very low (enamel: 0.01 ± 0.38ppm; dentine: 0.32 ± 0.87 ppm) even in those samples that show high U-concentrations. The question is whether Th can produce a significant contribution to the total dose rate. One has to keep in mind that the alpha and beta dose rates of 1 ppm Th is only about 28% and 20% of the corresponding U dose rates. By far the highest Th/U ratios were measured in sample 1030 from Florisbad, where the average Th/U ratios (of three subsamples) in enamel and dentine are 5.3 ± 0.6 and 2.5 ± 0.6, respectively. The measured Th concentrations increase the total dose rate by 7%. All other samples from Florisbad have much lower Th/U ratios (in the range of 0.01 to 0.2) so that no obvious explanation can be given for the unusual Th/U ratios of sample 1030. Considering that all other samples have significantly lower Th/U ratios, the effect of moderate Th concentrations, as found in this study, can generally be neglected.

The results also show almost no relationship between the uranium concentration and the age of the samples. This supports the findings of Grün & McDermott (1994) that it is not possible to postulate a particular mode of uranium uptake for age calculation without the combination of ESR and U-series analyses.

Conclusions

High thorium concentrations that may have an influence on the total dose rate seem to be exceptional. The results clearly imply that it is not possible to use a particular U-uptake model for calculating ESR age estimates of tooth enamel.

References

Grün, R. (1989) Electron spin resonance (ESR) dating. Quaternary International 1: 65-109.

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Grün, R. & McDermott, F. (1994) Open system modelling for U-series and ESR dating of teeth. Quaternary Geochronology (QSR) **13**: 121-125.

Grün, R., Schwarcz, H.P. and Chadam, J.M. (1988) ESR dating of tooth enamel, Coupled correction for U-uptake and U-series disequilibrium. Nuclear Tracks **14**: 237-241.

Grün, R., Schwarcz, H.P. & Zymela, S. (1987) ESR dating of tooth enamel. Canadian Journal of Earth Sciences **24**: 1022-1037.

Ikeya, M. (1982) A model of linear uranium accumulation for ESR age of Heidelberg, Mauer, and Tautavel bones. Japanese Journal of Applied Physics **21**: L690-L692.

Ivanovich, M. & Harmon, R.S. (1992) *Uranium series disequilibrium: Applications to Earth, Marine, and Environmental Sciences.* Clarendon Press, Oxford.

McDermott, F., Grün, R., Stringer, C.B. & Hawkesworth, C.J. (1993) Mass-spectrometric U-series dates for Israeli Neanderthal/early modern hominid sites. Nature **363**: 252-255.

McKinney, C.R. (1991) The determination of the reliability of uranium series dating of enamel, dentine and bone. Unpublished PhD thesis, Dallas, Southern Methodist University.

Millard, A.R. (1993) Diagenesis of archaeological bone: the case of uranium uptake. Unpublished DPhil. Thesis, University of Oxford.

Oakley, K.P. (1980) Relative dating of the fossil hominids of Europe. Bulletin of the British Museum of Natural History (Geology) **34**: 25-46.

Reviewer
H.P. Schwarcz

Comments

The U content of fossil teeth and bone has long been thought to give a crude age estimate. K.P. Oakley championed the FUN method of dating (Fluorine, Uranium, Nitrogen). Oakley determined U by beta counting. This gave surprisingly good estimates of the relative ages of bones. This was apparently a case of "the right answer for the wrong reason", since most of the increase in β-activity must be due to the growth of ^{230}Th and its daughters from the parent U isotopes, whose concentration hardly altered.

The present paper attempts to place this concept on a firmer footing, comparing the U and Th contents of tooth components with each other, and with age, dose, and environmental concentrations. The data are from a wide range of sites and faunal types; some of the variation may be depend on these variables. Surely, if the LU model (or any other continuous uptake model) is generally valid there must be some correlation between U content and age. The data shown on Fig. 2 suggest that any such correlation, if present, is overshadowed by intersite differences, and vagaries of the sample materials. It is encouraging, at least, that U shows a considerably stronger dependence on age and environment than does Th, confirming our general conception of Th as a geochemically immobile element.

The ICP method for U and Th determination are useful additions to our literature on analysis of these ever-interesting elements.