PERGAMON

Quaternary Science Reviews 20 (2001) 1021–1025

QG QSR

Sample geometry and U uptake in archaeological teeth: implications for U-series and ESR dating☆

Alistair W.G. Pike*, Robert E.M. Hedges

Research Laboratory for Archaeology and the History of Art, University of Oxford, Oxford, UK

Abstract

Post-deposition U uptake by bones and teeth is the most significant source of inaccuracy in both U-series and ESR dating. In most cases assumptions about the form of U uptake are required to calculate a date. We have been using the diffusion–adsorption (D–A) model of U uptake to predict the rate of uptake and spatial distribution of U and U-series isotopes in bones, and calculate open-system ages. Here we develop a similar model to predict U uptake in enamel and enamel-dentine systems. We find that the traditional models of U uptake, namely linear and early uptake providing maximum and minimum ages, are not universally applicable. Geochemical changes in the burial environment can lead to leaching or recent accumulation of U. In addition, the geometry of the tooth affects the pattern of U accumulation, with some areas of the enamel showing uptake between early and linear, while other areas of the same tooth may exhibit sublinear (recent) uptake. We show, however, how the measurement of the U and U-series isotope distributions (profiles) for a tooth can be combined to model uptake, and provide more reliable U-series dates or ESR dosimetry. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The most significant source of inaccuracy in U-series dating of archaeological bones and teeth is the assumption of the form of post-depositional U uptake. Similarly, because U and its daughters contribute to the internal-radiation dose of a tooth, uncertainty in U uptake can affect ESR age calculations in teeth with higher U concentrations. A number of models of U uptake have been proposed, the simplest being the early uptake (EU) model where U is taken up relatively rapidly after burial and the system becomes closed to further migrations of U. Others include the Szabo–Rosholt model (Szabo and Rosholt, 1969), that of Hille (1979), the Chen–Yuan model (Chen and Yuan, 1988), the linear uptake (LU) model (Ikeya, 1982; Bischoff et al., 1995) and the coupled uranium-series electron–spin-resonance (US-ESR) model for teeth (Grün et al., 1988). While there are examples of their successful application, none has proved universally applicable and all are based primarily on mathematical descriptions of an assumed uptake.

The diffusion–adsorption (D–A) model, on the other hand, uses a physico-chemical description of U uptake (Millard, 1993; Millard and Hedges, 1996). It not only predicts the rate of uranium uptake, but also the spatial distribution of U within a bone. Following the successful application of this model to U-series dating of bone (Pike, forthcoming), we present here a similar application of the model to tooth enamel–dentine systems.

2. The diffusion–adsorption model and U-series dating of bone

Millard and Hedges (1996) propose that under hydrologically quiescent conditions U migrates into the bone as complexes of the uranyl ion (UO^{2+}) by a process of diffusion and subsequent adsorption onto the large surface area presented by the mineral fraction (hydroxyapatite). The D–A model predicts not only the rate of U uptake, but also the spatial distribution of U across a bone section.

Fig. 1 shows the predicted spatial distributions of U (U-profiles) across a section of bone according to the D–A model. Because U is diffusing from the peri- and endosteal surfaces the profile is initially ∪-shaped, gradually flattening over time until a uniform profile represents an equilibrium between the U in the bone and the groundwater. Fig. 2 shows the apparent EU ages predicted across a 10 ky bone for different values of the diffusion–adsorption parameter, D/R. Since the edges are

☆Paper published in December 2000.

* Corresponding author.
E-mail address: alistair.pike@rlaha.ox.ac.uk (A.W.G. Pike).

0277-3791/01/$ - see front matter
PII: S0277-3791(00)00063-9

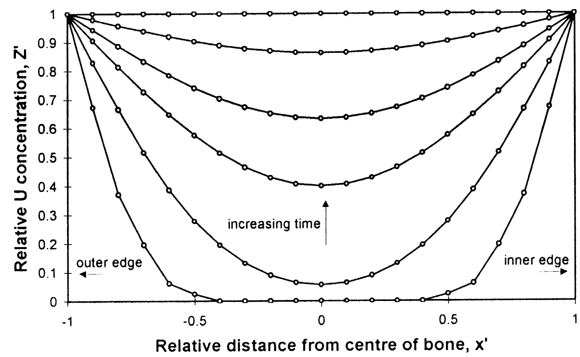

Fig. 1. Development of U profiles according to the D–A model. The U-concentration (y-axis) has been normalized to the equilibrium concentration for a given groundwater.

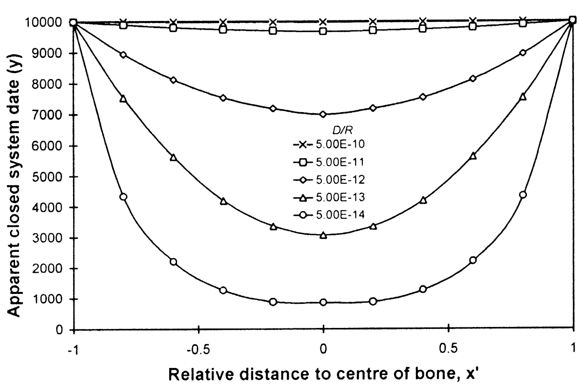

Fig. 2. Modelled closed system (EU) date profiles across a 10 ky bone ($^{234}U/^{238}U = 1$) for different values of the diffusion–adsorption parameter D/R.

equilibrating faster than the centre, the date is more severely underestimated towards the centre. The degree of underestimation depends on D/R which is related to the diagenetic state of the bone (increased porosity and loss of internal surface area) and the degree of water saturation of the burial environment (Millard and Hedges, 1996).

Since U uptake according to the D–A model represents an equilibration of the U adsorbed on the mineral surface of the bone and U in the groundwater, a drop in groundwater U concentration will cause desorption of U and diffusion in the reverse direction, leaching U from the bone and usually leading to characteristic M or ∩-shaped profiles (e.g. Millard and Pike, 1999)

Because leaching is essentially due to geochemical changes in the burial environment, teeth in the same environment as leached bone will also exhibit leaching. It is often suggested that tooth enamel is less affected by geochemical changes than bone, and although it is true that less U will be leached from enamel for a given drop in groundwater U concentration, it is also true that less U is taken up by enamel in the first place. Therefore the magnitude of the effect of leaching on a U-series date, being simply the reverse of U uptake, is approximately the same for bone and for tooth enamel under the same geochemical changes.

We use measured U profiles of bones to reject leached bones, bones that show inhomogenaities such as cracks or patchy diagenetic alteration or where a complex geochemistry renders simple monotonic diffusion invalid. By selecting bones that appear to have undergone simple diffusive uptake we can estimate the parameters of the D–A model. These can then be used in conjunction with date profiles measured using TIMS to calculate an open system date for the bone, and we find good agreement between our open system dates and control dates (Pike, forthcoming).

3. Application of the D–A model to teeth

The D–A model can also be applied to teeth. Although dentine is broadly similar to bone, enamel has a much lower organic component. Millard's (1993) laboratory experiments, however, show the limited role of organic matter in the uptake of U by bone, at least when compared to the large partition coefficient for uranyl and organic-free hydroxyapatite.

The major difference between enamel and bone is the lower porosity. This has the effect of reducing the diffusion coefficient, and the partition coefficient of U and hydroxyapatite — hence enamel has a U content much lower than bone or dentine. This is accounted for in the model by a reduction in the diffusion–adsorption parameter D/R. In practice, we would estimate this parameter from measured profiles, but in the presentation of these illustrative examples we have chosen typical values. Bone, in typical burial environments has D/R ranging from 10^{-14} to 10^{-12} cm^2s^{-1}, so assuming dentine will also fall in this range, we have used a value of 10^{-13}. Measurements of U profiles (McKinney, 1991) and calculations by Millard (1993) give a range of D/R between 10^{-17} to 10^{-14} for enamel. For these models we are assuming a value of 10^{-16}, towards the lower end of the range, but in keeping with the dating example presented below.

3.1. Geometry

Teeth have a more complex geometry than the infinite plane we are assuming for bone and we have defined enamel–dentine configurations that approximate to many of the samples removed routinely for ESR or U-series dating (Fig. 3).

3.2. Planar enamel system — effect of removing the enamel surface

While not a common sample geometry encountered in ESR dating, this example is included to illustrate the

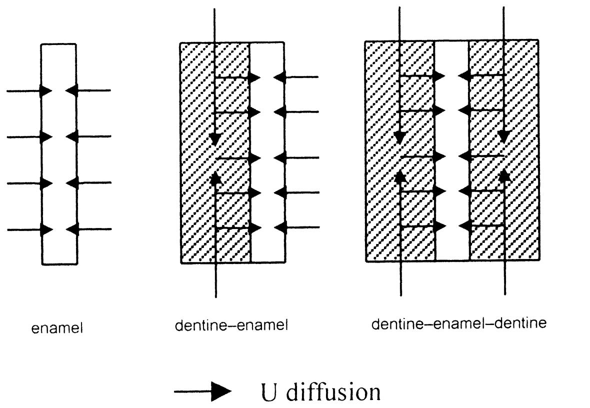

Fig. 3. The three dentine–enamel schemes used for modelling uptake in teeth.

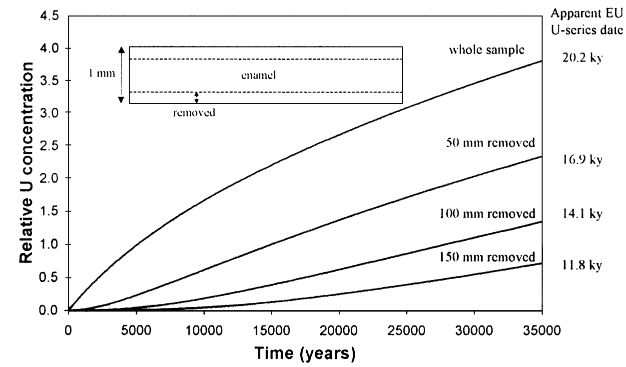

Fig. 4. Uptake in the planar enamel system with different thicknesses removed from the surfaces.

effect of removing a portion of the enamel surface. Fig. 4 shows modelled uptake over 35 ky for the planar enamel system for the whole enamel plate, and with different portions of the surface removed. The uptake for the whole plate lies somewhere between linear and early uptake giving an EU U-series date about 60% of the real age. However, as successive portions of the surface are removed the uptake pattern becomes more and more sublinear, showing more recent uptake. This is reflected in the modelled EU U series ages which are younger towards the central portion of the plate. In addition, the model predicts in this case a $\cup$-shaped distribution of U, that will only become uniform after 2.4 My, although if $D/R = 10^{-14}$ this may occur after 24 ky, but such a high value is exceptional. A higher concentration of U at the edges of the enamel, that is removed before ESR measurement, will have contributed to the internal dose of the enamel but will not be accounted for by the U concentration measured in the remaining portion, giving an underestimation of the internal dose rate.

3.3. Dentine–enamel system

In this system, the diffusion of U into one side of the enamel is limited by the diffusion of the U through the dentine. Although uptake is close to linear (Fig. 5) in all samples, removing more of the surface of the enamel would have the same effect as in Fig. 4. A $\cup$-shaped U profile exists both down the dentine and across the enamel, although the dentine will equilibrate substantially faster than the enamel (9.5–950 ky).

3.4. Dentine–enamel–dentine system

Samples deeper into the dentine–enamel sandwich show more marked sublinear uptake as the U diffusing into the enamel is limited entirely by diffusion into dentine (Fig. 6). The central sample shows such recent uptake that its U series date is just 6 ky for this 35 ky tooth.

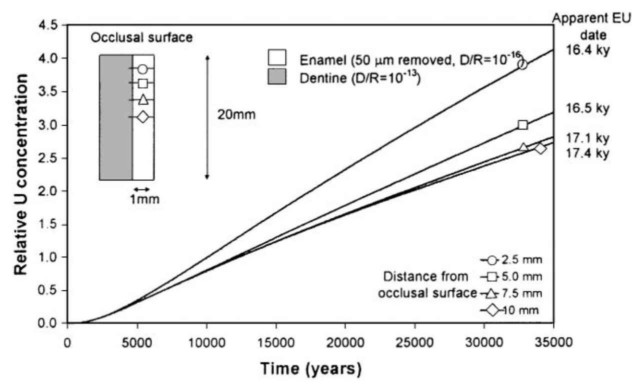

Fig. 5. Uptake in the dentine–enamel system for enamel samples taken various distances from the occlusal surface. 50 μm has been removed from the surface of the enamel.

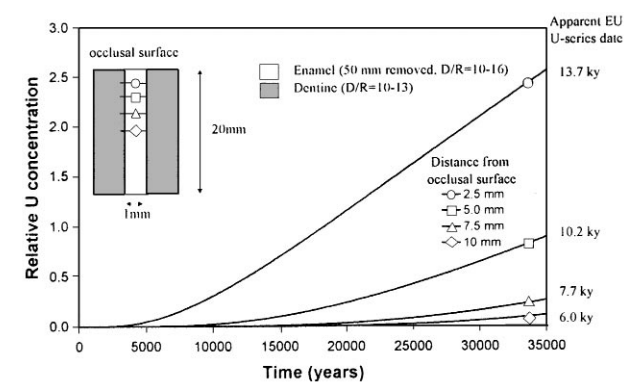

Fig. 6. Uptake in the dentine–enamel–dentine system. 50 μm has been removed from the surface of the enamel.

4. U-series dating of teeth using the D–A model

Although we prefer bone to tooth for U-series dating because of its simpler geometry and the problems encountered measuring profiles in thin enamel layers, it is possible to use these models to calculate an open system U-series date for a tooth.

A U profile and at least one date (a date profile is preferred) is required for both the enamel and the dentine to estimate the parameters of the model. Grün et al. (1999) measured U-series dates down dentine and enamel plates for two teeth from the Palaeolithic site of Pech de L'Aze II, France. Using a dentine–enamel system similar to Fig. 5, we have been able to fit diffusion profiles to the dentine and the enamel and estimate the parameters of the model (e.g. Fig. 7). The U profiles do not fit the data exactly but there is uncertainty in exactly how much enamel was removed (50–100 μm), and we cannot control for cracks and other deviations from ideal geometry such as the presence of cement. The present model is also restricted to two-dimensional diffusion, and in future it may be necessary to include diffusion in three dimensions to provide a realistic model. This probably accounts for the large range in D/R_{dentine} (1×10^{-13}–1.9×10^{-12}) for 626 necessary to fit both the U and date profiles of this sample. However, the enamel U (Fig. 7) and date profiles (Fig. 8) are relatively insensitive to D/R_{dentine} and the predicted date profile, shows a good agreement with the measurements, and shows the ages of the teeth to be close to 130 and 180 ky as suggested by Grün et al. (1999) even though the measured EU ages are less than 60 and 120 ky respectively. Full details of these calculations are given in Pike (forthcoming).

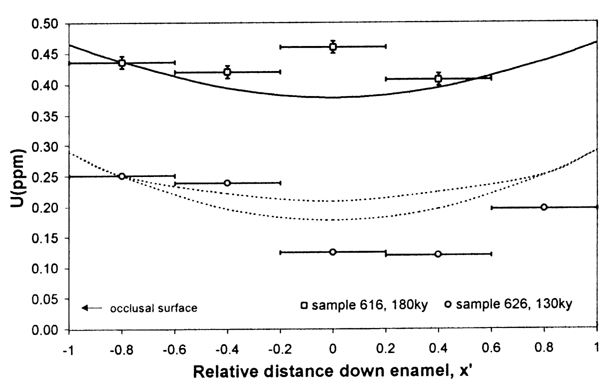

Fig. 7. Modelled (lines) and measured (points) U profiles for enamel from teeth 616 ($D/R_{\text{dentine}} = 1.3\times10^{-12}$; $D/R_{\text{enamel}} = 5\times10^{-16}$) and 626 ($D/R_{\text{dentine}} = 1\times10^{-13}$–$1.9\times10^{-12}$; $D/R_{\text{enamel}} = 1\times10^{-16}$). U data taken from Grün et al. (1999). The broken lines on 626 represent uncertainty due to the large range of D/R_{dentine}.

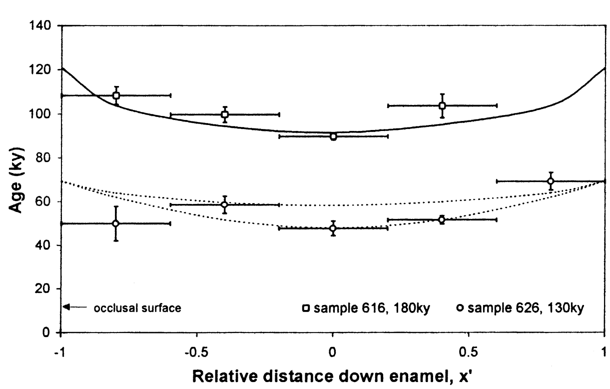

Fig. 8. Modelled (lines) and measured (points) date profiles for enamel from teeth 616 and 626. The model gives the expected profiles after 130 and 180 ky. TIMS dates taken from Grün et al. (1999). The broken lines on 626 represent uncertainty due to the large range of D/R_{dentine}.

5. Conclusions

We have briefly outlined our approach to U-series dating of bone, using the D–A model to predict U uptake. For U-series dating, we prefer bone to teeth, because of its simpler geometry and greater thickness. Our purpose in applying the D–A model to teeth is more to illustrate the expected pattern of U uptake rather than use the method routinely to calculate U-series dates. However, we have shown in the example above that by careful selection of teeth it is possible to use the D–A model to calculate U-series dates.

This work reveals some significant points of relevance to U uptake and ESR dating:

- Our work on bone has shown that in as many as a third of cases leaching has occurred. Because leaching is essentially a geochemical phenomenon, teeth from these environments will also be leached to the same relative degree. Thus, even a simple linear uptake model will be invalid unless additional evidence in the form of U profiles is provided.
- Although in geochemically stable environments the integrated U uptake of a whole enamel plate lies somewhere between linear and early uptake, the central portion of the enamel shows sublinear (more recent) uptake. Thus, removing the outer layer of enamel causes ESR dates that are calculated using the EU or LU assumption to be increasingly underestimated.
- The relationship between U concentration and pattern of uptake in a given tooth has implications for isochron methods that rely on differential internal doses due to differing U concentrations in subsamples of enamel. Samples that have lower U are likely to have undergone more recent uptake than the higher U samples.
- Except in very old teeth (several My) the enamel is highly unlikely to have reached equilibrium, and therefore an inhomgenous U distribution will exist. Discarding the outer layers, where the highest concentration of U is, will give inaccuracies in the calculation of the internal dose for ESR dating.
- In teeth where a significant dose is received by the enamel from U in the dentine, both the U uptake and the inhomgenous distribution of U in the dentine need to be considered. Equilibration may occur in dentine giving a homogenous U distribution, but this may take several 100 ky.

In the complex hydrological and geochemical environment that is the burial context, it is not possible to generalize U uptake universally in either bones or teeth. By modelling U uptake under different geochemical regimes, however, we can select bones or teeth on the basis of measured profiles that have undergone U uptake by mechanisms that we are confident to model. These models can then be used to predict U uptake for a given geometry, either for U-series dating or for ESR dosimetry calculations. The blind application of simple uptake models (e.g. EU or LU) can lead to gross under- or over-estimation of U-series and ESR ages.

Acknowledgements

The authors would like to thank Rainer Grün and colleagues for making their TIMS data available in advance of publication, Eddie Rhodes for valuable discussion, Peter vanCalsteren, Mabs Gilmour and colleagues at the NERC U-series Dating Facility, Department of Earth Science, Open University for their collaboration. AWGP is funded by a NERC studentship.

References

Bischoff, J.L., Rosenbauer, R.J., Moench, A.F., Ku, T.-L., 1995. Uranium series age equations for uranium assimilation by fossil bone. Radiochimica Acta 69, 127–135.

Chen, T., Yuan, S., 1988. Uranium-series dating of bones and teeth from Chinese Palaeolithic sites. Archaeometry 30, 59–76.

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

Grün, R., Yan, G., McCulloch, T., Mortimer, G., 1999. Detailed mass spectrometric U-series analyses of two teeth from the archaeological site of Pech de l'Aze II: implications for uranium migration and dating. Journal of Archaeological Science 26, 1301–1310.

Hille, P., 1979. An open system model for uranium series dating. Earth and Planetary Science Letters 42, 138–142.

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.

Millard, A.R., 1993. Diagenesis of archaeological bone: the case of uranium uptake. Unpublished D.Phil. Thesis. University of Oxford, UK.

Millard, A.R., Hedges, R.E.M., 1996. A diffusion–adsorption model of uranium uptake by archaeological bone. Geochimica et Cosmochimica Acta 60 (12), 2139–2152.

Millard, A.R., Pike, A.W.G., 1999. Uranium-series dating of the Tabun Neanderthal: a cautionary note. Journal of Human Evolution 36, 581–585.

McKinney, C.R., 1991. The determination of the reliability of uranium series dating of enamel, dentine and bone. Unpublished Ph.D Thesis, Southern Methodist University, USA.

Pike, A.W.G., Uranium series dating of archaeological bone by thermal ionization mass-spectrometry. D.Phil Thesis. University of Oxford, Oxford, UK. forthcoming.

Szabo, B.J., Rosholt, J.N., 1969. Uranium series dating of Pleistocene molluscan shells from southern California: an open system model. Journal of Geophysical Research 74, 3253–3260.