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Research paper

U-series dating of bone in an open system: The diffusion-adsorption-decay model

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A B S T R A C T
A new theory is described for the uptake of U in an open system applied to the dating of archaeological bones. Analytical solutions are obtained for the rate of radioactive decay of $^{238}$U, $^{234}$U and $^{230}$Th as a function of position for the case where both $^{238}$U and $^{234}$U diffuse across a bone, and where external supply of $^{234}$U is not in equilibrium with $^{238}$U. The new theory constitutes a forward model for predicting $^{238}$U, $^{234}$U and $^{230}$Th activity profiles across a bone given an age and diffusion coefficient. The forward model can be used in an inversion process whereby observations of activity profiles of $^{238}$U, $^{234}$U and $^{230}$Th as a function of position are used to infer the bone age of a sample together with robust measures of uncertainty. Differences from previous studies are that no closed system assumptions are required and no apparent age calculations necessary, while diffusion of $^{234}$U across the bone is accounted for in the inversion process. The procedure also does not require U-concentration profiles for the calculation of model parameters. The measurement of U-concentration profiles are, however, useful for the assessment of the reliability of the calculated results. Because of the assumption of constant $^{238}$U/$^{234}$U ratios at the boundaries of the bone, DAD age results are generally older than closed system U-series results derived from the same isotopic data. Allowance is made for both correlated and uncorrelated errors in activity measurements as well as theoretical error caused by inhomogeneities in the sample. The implementation of the new approach (which we term the DAD model for Diffusion–Adsorption–Decay) is straightforward and efficient enough to allow estimation of age and its uncertainty on a desktop computer. Software for performing age estimation with the new model is available from the corresponding author.

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1. Introduction

It is well known that bones and teeth are open systems to uranium (U). Under normal circumstances, samples that show open system behaviour are discarded for dating purposes. Nevertheless, there have been numerous attempts to apply U-series dating to bones and teeth, because of the lack of other suitable material for dating and the age restrictions of radiocarbon dating at archaeological sites (Rae et al., 1987; McDermott et al., 1993; Grün and McDermott, 1994). Modern bones and teeth contain only very small amounts of U ($<1–50$ ng g$^{-1}$, Tandon et al., 1998), whereas archaeological specimens may contain several hundreds of mg g$^{-1}$ U. For dating, the temporal uptake of U has to be reconstructed. If U-uptake is the dominating geochemical process (as observed by the simple fact that archaeological bones have higher U-concentrations than modern bones), a U-series age determination (based on a closed system assumption) would underestimate the correct age of the bone.

The mechanism of U-uptake in bones and teeth is governed by diffusion of uranyl ($UO_2^{2+}$), followed by adsorption of the uranyl ion onto the large surface area of the bone mineral hydroxyapatite (Millard, 1993; Millard and Hedges, 1996; Pike, 2000; Pike et al., 2002). Th is not soluble in water and assumed not to diffuse into, or within, a bone. The diffusion–adsorption ($D$–$A$) model of these authors predicts the spatial distribution of U and U-series isotopes across a bone or tooth enamel section. The constant diffusion of U from the outer to the inner surfaces leads to the development of concave U-concentration profiles. Over time, these profiles will gradually reach an equilibrium, uniform profile as the bone equilibrates throughout with the U in solution. The distribution of apparent U-series ages follows a similar pattern, with apparent ages decreasing towards the centre of the bone. If the adsorption of the U is a continuing process without changes in the adsorption rate, the modelled $D$–$A$ ages will be consistent throughout the bone. The $D$–$A$ model has the great advantage, in that it allows the identification of bones with different U-uptake histories.
The problems in the application of the previous $D$–$A$ model are as follows: (i) none of the papers relating to the $D$–$A$ model provides the complete set of formulae that are required for age calculation and error estimation, (ii) an open source program for $D$–$A$ age and error calculation is presently not available and (iii) we are not able to assess whether $^{234}\text{U}$ excess is correctly applied in the $D$–$A$ model.

The latter refers to the fact that most natural waters have an excess of $^{234}\text{U}$ over $^{238}\text{U}$ (e.g. chapter V in Cherdyntsev, 1971), caused by alpha recoil of the decaying $^{238}\text{U}$ atoms: when an alpha particle is emitted, the decaying atom recoils, which in turn leads to a damaged lattice position. Atoms resident in damaged lattice positions are preferentially leached during weathering processes, as a consequence, natural aqueous solutions are enriched with $^{234}\text{U}$. Alternatively, the recoiled atom can be directly ejected from the mineral surface into the solution. In the terrestrial environment the $^{234}\text{U}/^{238}\text{U}$ ratio is geographically highly variable and may be as high as 10 (Cherdyntsev, 1971). This process is ongoing, and lacking evidence to contrary, it is reasonable to assume that the natural waters in the vicinity of a bone have constant $^{234}\text{U}/^{238}\text{U}$ activity ratios over time (isotopic ratios will refer to activity ratios, unless specified otherwise). In closed systems, $U$-series ages are calculated from the measured $^{230}\text{Th}$/$^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios and the simultaneous solution for age and initial $^{234}\text{U}/^{238}\text{U}$ ratio. For bones, however, the age calculation has to take into account that the $^{234}\text{U}/^{238}\text{U}$ ratio of the atoms entering the bone is constant over time. Therefore, conventional closed system age calculations cannot be applied. From our understanding of published $D$–$A$ age calculations, however, it seems that these involve at least partially closed system age calculations.

2. A Diffusion–Adsorption–Decay model

2.1. Age estimation with the diffusion–adsorption model

The $D$–$A$ model was developed by Millard (1993); Millard and Hedges (1996) to describe the diffusion of $U$ across a bone. It is based on the mathematical solution of the 1-D diffusion problem by Crank (1975) describing the simultaneous adsorption and diffusion of uranyl with concentration $C$ as a function of position $x$. The governing equation is given by

$$\frac{\partial C}{\partial t} = \frac{D}{R^2} \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where $D$ is the diffusion coefficient within the bone, $t$ is time, and $R$ is the volumetric equilibrium constant. The latter term is equal to the ratio of the partition coefficient and the specific porosity for details (Millard, 1993, Millard and Hedges, 1996). If $U$ enters the bone at some initial time, it diffuses across the bone according to Eq. (1) while simultaneously undergoing radioactive decay. The diffusion equation above simply states that the rate of change with time of uranyl concentration, $C$, due to diffusion is proportional to the second spatial derivative of $C$. With suitable boundary conditions (e.g. a constant $^{238}\text{U}$-concentration at the boundary), an analytical solution can be derived and concentration profiles, $C(x)$, may be conveniently calculated and plotted as a function of time. For example, see Eq. (3) and Fig. 1 of Millard and Hedges (1996). As shown by Millard and Hedges (1996), the solution to Eq. (1) results in a $U$-concentration profile controlled by the dimensionless time parameter $t'$:

$$t' = \frac{Dt}{R^2} \quad (2)$$

where $t$ is the (half) thickness of the bone. This expression connects the bone age, $t$, with the ratio $D/R$, both of which are unknowns to be determined. Millard (1993) proposed a method for estimating bone age from relative $U$-series concentrations across a bone, which was used and extended by Pike et al. (2002, 2005). In these papers the dimensionless time parameter, $t'$, is estimated directly from the $U$-concentration profile, which provides a relationship between the two unknowns in Eq. (2). At each point, $x$, across the bone a conventional bone age is determined using the assumption that, locally, the system is closed. This is then designated as an ‘apparent’ closed system age and combined with the $t'$ estimate to find an overall best fit bone age using a least squares procedure.

A limitation of this approach is the need for a closed system assumption at each point across the bone. This is clearly not valid since both $^{238}\text{U}$ and $^{234}\text{U}$ diffuse and decay over time as a function of position. In the treatment that follows, we re-examine this problem from first principles and derive a set of partial differential equations for $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$, which describe how all three activities vary with position when diffusion and decay processes are coupled. We derive analytical solutions to these equations, which are an extension of those in the original $D$–$A$ model of Millard (1993); Millard and Hedges (1996). The new solutions constitute a ‘forward theory’ as they allow prediction of activity profiles of $U$-series isotopes when bone age and $D/R$ ratio are known. We then address the inverse problem of estimating bone age and its uncertainty from observations of activity profiles.

2.2. Diffusion–Adsorption–Decay model

Following Millard and Hedges (1996), we assume that $U$ remains in the mobile $U^{4+}$ state and is taken up in bone by a process of diffusion and adsorption. Henceforth we represent the number of $^{238}\text{U}$ as $N_1$ and its activity as $A_1 = \lambda_1 N_1$, where $\lambda_1$ is the decay constant for $^{238}\text{U}$ ($\lambda_1 = 1.55125 \times 10^{-10}$ a$^{-1}$). Jaffey et al. (1971). Assuming a 1-D infinite planar slab geometry (Millard, 1993), the amount of $^{238}\text{U}$ at point $x$ in the bone is governed by the partial differential equation,

$$\frac{\partial N_1}{\partial t} = -\lambda_1 N_1 + \frac{\partial^2 N_1}{\partial x^2} \quad (3)$$

where $x$ is the rate of diffusion and equal to $D/(R + 1)$. Laboratory experiments of Millard (1993) showed that typically the volumetric
equilibrium constant, \( R \), ranges from 10^5 to 10^6 and so to a good approximation \( \kappa = D/R \) (Pike et al., 2002). Expressed in words, Eq. (3) states that the rate of change of the number of 238U atoms at point \( x \) is given by the change due to diffusion minus the loss due to radioactive decay. Typical values of \( D/R \) are 10^{-12} to 10^{-14} (Pike et al., 2002) thus \( \lambda_1 < \kappa \) and hence we may write
\[
\frac{\partial N_1}{\partial t} = \kappa \frac{\partial^2 N_1}{\partial x^2},
\]
(4)

which is in effect Eq. (1). Multiplying through by \( \lambda_1 \) gives
\[
\frac{\partial A_1}{\partial t} = \kappa \frac{\partial^2 A_1}{\partial x^2},
\]
(5)

which shows, unsurprisingly, that the 238U activity profile is dominated by diffusion. The solution to (5) corresponds to the D–A model of Millard (1993), which we write as
\[
A_1(x, t) = A_{1,0} \left( 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \left( \frac{n}{2n+1} \right)^r e^{-l^2 \pi^2 (2n+1)^2 t} \cos \left( \frac{2n+1}{2} \pi x \right) / l \right),
\]
which is in effect Eq. (1). Multiplying through by \( \lambda_1 \) gives
\[
\frac{\partial A_1}{\partial t} = \kappa \frac{\partial^2 A_1}{\partial x^2},
\]
(5)

where \( A_{1,0} \) is the activity of 238U on the surface of the bone \((x = \pm l)\). This solution satisfies the boundary conditions that the activity on the surface is constant over time and initially zero within the bone
\[
A_1(x, 0) = 0, \quad (-l < x < l)
\]
(7)

The closed form solution (6) allows evaluation of the 238U activity profile for any time, \( t \). The shape depends only on the surface value \( A_{1,0} \), a dimensionless time, \( \tau = kt/l^2 \), and position, \( x = kl/l \).

The decay of 238U leads to production of 234U at each point across the bone. Simultaneously, 238U also decays to 234Th and diffuses. If we let \( N_2 \) be the number of 238U atoms at any point then combining these effects we have
\[
\frac{\partial N_2}{\partial t} = -\lambda_2 N_2 + \lambda_1 N_1 + \kappa \frac{\partial^2 N_2}{\partial x^2},
\]
(9)

where \( \lambda_2 = 2.8263 \times 10^{-6} \text{ a}^{-1} \), Cheng et al. (2000) is the decay constant for 238U, and we have assumed that the rate of diffusion is unchanged. Multiplying through by \( \lambda_2 \) gives
\[
\frac{\partial A_2}{\partial t} = -\lambda_2 A_2 + \lambda_2 A_1 + \kappa \frac{\partial^2 A_2}{\partial x^2},
\]
(10)

where \( A_2 = \lambda_2 N_2 \) is the activity of 234U. This is a partial differential equation for \( A_2 \), which is coupled to the solution for \( A_1(x, t) \). It is convenient to rewrite the \( A_2 \) activity profile in the following way
\[
A_2(x, t) = A_1(x, t) + \Delta A_2(x, t).
\]
(11)

The term \( \Delta A_2(x, t) \) represents that part of the 234U activity which is not in equilibrium with 238U. Substituting (11) into (10) gives
\[
\frac{\partial A_1}{\partial t} + \frac{\partial \Delta A_2}{\partial t} = -\lambda_2 \Delta A_2 + \kappa \frac{\partial^2 A_1}{\partial x^2} + \kappa \frac{\partial^2 \Delta A_2}{\partial x^2}.
\]
(12)

Since \( A_1(x, t) \) satisfies Eq. (5) this simplifies to
\[
\frac{\partial \Delta A_2}{\partial t} = -\lambda_2 \Delta A_2 + \kappa \frac{\partial^2 \Delta A_2}{\partial x^2}.
\]
(13)

We see that then the disequilibrium component, \( \Delta A_2 \), follows a similar partial differential equation to \( A_1 \), only now the decay term cannot be neglected. The boundary conditions for \( A_2(x, t) \) are similar to that for \( A_1 \), i.e., \( A_2 \) is a constant on the boundary for all time, \( A_{2,0} \), and its activity is initially zero in the bone
\[
A_2(x, 0) = 0, \quad (-l < x < l)
\]
(14)

\[
A_2(I, t) = A_2(-l, t) = A_{2,0}.
\]
(15)

In terms of \( \Delta A_2 \), these become
\[
\Delta A_2(x, 0) = 0, \quad (-l < x < l)
\]
(16)

\[
\Delta A_2(I, t) = \Delta A_2(-l, t) = A_{2,0} - A_{1,0} = \Delta A_0.
\]
(17)

To find the activity profile \( A_2(x, t) \), we must solve Eq. (13) with boundary conditions given by (16)–(17). A closed form solution to this problem was given by Carslaw and Jaeger (1959) (p. 135) in the context of linear flow of heat in a rod. Their solution, slightly modified to fit our problem, is
\[
\Delta A_2(x, t) = \Delta A_0 \left( \frac{\cos(\lambda_2/k)\tau}{\cos(\lambda_2/k)\tau} \right) - \frac{4}{\pi} \sum_{n=1}^{\infty} \left( \frac{n}{2n+1} \right)^r e^{-l^2 \pi^2 (2n+1)^2 t} \cos \left( \frac{2n+1}{2} \pi x \right) / l \right),
\]
(18)

where \( \beta_2 = 1 + (\lambda_2^2 / (2n+1)^2 \pi^2 k) \). This expression is a generalization of the D–A model solution (6). As before, it is straightforward to evaluate \( \Delta A_2(x, t) \) given \( A_{2,0}, \lambda_2, \) and \( t \). By adding \( \Delta A_2(x, t) \) to \( A_1(x, t) \), we obtain the activity profile \( A_2(x, t) \) for any time.

The final step in the decay chain is the production of 230Th from decay of 234U. In this case we assume no diffusion is present and we have
\[
\frac{\partial N_3}{\partial t} = -\lambda_3 N_3 + \lambda_2 N_2,
\]
(19)

where \( N_3 \) is the number of atoms of 230Th and \( \lambda_3 = 9.1577 \times 10^{-4} \text{ a}^{-1} \), Cheng et al. (2000) is the corresponding decay constant. Multiplying through by \( \lambda_3 \) and using \( A_3 = \lambda_3 N_3 \), we have
\[
\frac{\partial A_3}{\partial t} = -\lambda_3 A_3 + \lambda_3 A_2.
\]
(20)

This is the governing differential equation for the activity of 230Th with boundary conditions
\[
A_3(x, 0) = 0, \quad (-l < x < l)
\]
(21)

\[
A_3(I, 0) = A_3(-l, 0) = 0.
\]
(22)

which indicate that initially the activity of 230Th is everywhere zero. To solve this system, we use standard methods to get
\[
\frac{\partial (A_3 e^{\lambda_3 t})}{\partial t} = \lambda_3 A_2 e^{\lambda_3 t}.
\]
(23)

Rearrangement gives
\[
A_3(x, t) = \lambda_3 e^{-\lambda_3 t} \int A_2(x, t) e^{\lambda_3 t} dt + f(x) e^{\lambda_3 t},
\]
(24)

where the term \( f(x) \) is required to satisfy the boundary conditions (21)–(22). Using (11), this expression may be rewritten
\[
A_3(x, t) = \lambda_3 e^{-\lambda_3 t} \int (A_1(x, t) + \Delta A_2(x, t)) e^{\lambda_3 t} dt + f(x) e^{\lambda_3 t}.
\]
(25)
Substituting for $A_1(x, t)$ from (6) and $\Delta A_2(x, t)$ from (18), and after some algebra, we arrive at a solution for $A_3(x, t)$

$$A_3(x, t) = f(x) + A_{1,0} \left[ 1 + \frac{(A_{2,0} - 1)}{(A_{1,0})} \right] \left( \frac{\cosh(k_{0,1}x)}{\cosh(1/k_{0,1})} \right)$$

$$- \frac{4}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \gamma_n e^{-x^2(2n+1)^2\pi^2t/4\ell^2} \cos \left( \frac{(2n+1)\pi x}{\ell} \right).$$

where the parameter $\gamma_n$ is given by

$$\gamma_n = \frac{1}{\beta_3 + \frac{1}{x}} + \frac{(A_{2,0}')}{(A_{1,0})} \frac{e^{-x^2(2n+1)^2\pi^2t/4\ell^2}}{\beta_2 \beta_3}$$

and

$$\beta_3 = \beta_1 - \frac{A_{2,0}'}{2\ell^2} x^2.$$

To complete the solution, we need to find the function $f(x)$ using the boundary conditions (21)–(22). Rewriting the solution for $A_3$ as

$$A_3(x, t) = f(x) + Z_3(x, t),$$

where $Z_3(x, t)$ represents the second term in (26), then $f(x)$ may be simply evaluated

$$f(x) = -Z_3(x', 0), \quad (-l < x < l).$$

We now have closed form solutions for the activity profiles of $^{238}\text{U}$, $^{234}\text{U}$, and $^{230}\text{Th}$, and can easily compute them given surface values, diffusion coefficient, $x$ and bone age, $t$. Fig. 1 shows examples of the three profiles for the two cases $t' = 0.1$ and $0.9$, corresponding to values of $D/R = 1.0 \times 10^{-11}$ and bone ages, $t = 31.7$ ka, 285 ka. For this demonstration we choose values of the surface activity of $^{238}\text{U}$ and $^{234}\text{U}$ of 1.0 and 1.2 respectively, while that of $^{230}\text{Th}$ is initially zero and builds up over time. As shown below, when it comes to using the activity data to solve for the burial age the ratio of the surface values is treated as an unknown to be solved for. The $^{238}\text{U}$ activities predicted by the DAD model are the same as those predicted by the $D$–$A$ model (e.g. Fig. 2 of Pike et al. (2005)), while the other solutions are from the theory described here. In this example, at $t' = 0.1$, the excess component of $^{234}\text{U}$ slowly decays away as one moves into the bone, for $t' = 0.9$ the same is true although by this time the diffusion of both $^{238}\text{U}$ and $^{234}\text{U}$ add significantly to both profiles.

### 2.3. Age estimation with the Diffusion–Adsorption–Decay model

The new DAD model constitutes the solution of a “forward problem”, i.e., given values of the surface activity ($A_{1,0}$ and $A_{2,0}$), the diffusion constant, $\ell$, and the bone age, $t$, the corresponding normalized position $x'$ across the bone, and a (possibly) different number of observational errors of $^{234}\text{U}/^{238}\text{U}$ ratios as a function of normalized position $x'$ across the bone, and a (possibly) different number of observational errors of $^{230}\text{Th}/^{238}\text{U}$ ratios as a function of $x'$. Estimates of observational errors are required for each observation, $\sigma_i(i = 1, ..., N)$. Each observed activity ratio, $A_{\text{obs}}^{(i)}(x', t)$, will have an associated normalized position $x'$, which we assume is accurately measured. For an initial guessed set of the unknowns $(x, t)$, Eqs. (6), (18) and (26) are used to calculate the corresponding predicted values $A_{\text{pred}}^{(i)}(x', t)$, and hence evaluate the data misfit function, $\phi(x, t)$. By finding the values of $(x', t)$, which minimize $\phi$, we obtain a least squares estimate of the unknowns. Since the predicted activity profiles in the DAD model all depend on the initial $^{234}\text{U}/^{238}\text{U}$ ratio, i.e., at $x = \pm 1$, and this quantity, when measured, will contain observational error, then it must also be treated as unknown in the inversion. For convenience, we denote this variable as $r_{\text{obs}}$, and so the optimization problem becomes over three unknowns, $(x, t, r_{\text{obs}})$. Here $^{230}\text{Th}/^{238}\text{U}$ ratio has been added to the synthetic observations. b) Same as a) for $^{234}\text{U}/^{238}\text{U}$ ratio profile. Here 2.5% random noise has been added. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\phi(x, t) = \sum_{i=1}^{N} \frac{(A_{\text{obs}}^{(i)} - A_{\text{pred}}^{(i)}(x', t))^2}{\sigma_i^2}.$$

Here, $A_{\text{obs}}^{(i)}$ is the $i$th activity ratio observation and $A_{\text{pred}}^{(i)}(x', t)$ the corresponding prediction, $N$ is the number of data and $\sigma_i$ is the standard error of the $i$th observation. There is some flexibility in what we take as the data. Here, we assume to have one or more observations of the $^{234}\text{U}/^{238}\text{U}$ ratio as a function of normalized position $x'$ across the bone, and a (possibly) different number of observations of $^{230}\text{Th}/^{238}\text{U}$ ratios as a function of $x'$. Estimates of observational errors are required for each observation, $\sigma_i(i = 1, ..., N)$.

Here, $A_{\text{obs}}^{(i)}(x', t)$ will have an associated normalized position $x'$, which we assume is accurately measured. For an initial guessed set of the unknowns $(x, t)$, Eqs. (6), (18) and (26) are used to calculate the corresponding predicted values $A_{\text{pred}}^{(i)}(x', t)$, and hence evaluate the data misfit function, $\phi(x, t)$. By finding the values of $(x, t)$, which minimize $\phi$, we obtain a least squares estimate of the unknowns. Since the predicted activity profiles in the DAD model all depend on the initial $^{234}\text{U}/^{238}\text{U}$ ratio, i.e., at $x = \pm 1$, and this quantity, when measured, will contain observational error, then it must also be treated as unknown in the inversion. For convenience, we denote this variable as $r_{\text{obs}}$, and so the optimization problem becomes over three unknowns, $(x, t, r_{\text{obs}})$.
Many numerical optimization methods are available for the task. We choose a simple and reliable technique known as the downhill Simplex search algorithm (Nelder and Mead, 1965; Press et al., 1992). The Simplex algorithm is a derivative free search algorithm, which means that we only need to be able to evaluate \( f \) for given values of the unknowns. The Simplex algorithm works by iteratively refining a set of initial guesses for \( (x, t, r_{\text{age}}) \) until the function \( f(x, t, r_{\text{age}}) \) is minimized. To start four sets of \( (x, t, r_{\text{age}}) \) values are required and at each iteration a new set of values are obtained, the corresponding activity ratios predicted, and the misfit function \( f(x, t, r_{\text{age}}) \) evaluated and fed back to the algorithm. Convergence is achieved when the changes to the unknowns are deemed insignificant, i.e., typically changes less than 0.01%.

An example of the results of the Simplex algorithm on a synthetic data set are shown in Fig. 2. Using a bone age of \( t = 70 \) ka, \( k = 1.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \) and initial \( 235\text{U}/238\text{U} \) ratio of 1.2, we generated 21 pairs of synthetic \( 235\text{U}/238\text{U} \) and \( 239\text{Th}/238\text{U} \) ratios at evenly spaced points across a bone using the DAD model (Eqs. (6), (18) and (26)). Gaussian random errors were added to the activity ratios with a 2σ value equal to 10% for the \( 235\text{U}/238\text{U} \) data and 2.5% for the \( 239\text{Th}/238\text{U} \) values. The noisy synthetic data (shown as black dots in Fig. 2) were then inverted by minimizing \( f(x, t) \) with the Simplex algorithm. Best fit values of \( t = 68.5 \) ka, \( k = 1.03 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \) and \( r_{\text{age}} = 1.203 \) were obtained after 78 iterations of the algorithm. The red curve in Fig. 2 shows the predicted activity ratios for the best fit solution. Clearly, the recovered values of diffusion coefficient, bone age and initial activity ratio are all close to the true values. As one may expect, the noise added to the observations moves the least squares solution away from the true solution. This was verified by performing the same experiment without adding noise to the observations. In that case near perfect values of the unknowns were recovered \( (t = 70 \) ka, \( k = 9.99 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \) and \( r_{\text{age}} = 1.20) \).

Reassuringly, these results suggest that the problem is well posed and a least squares estimation of the unknowns is sufficient for accurate recovery of bone age. Further experiments (not shown) indicate that convergence of the Simplex algorithm does not depend significantly on the choice of initial guesses for the unknowns. Our implementation is also computationally efficient. A single run of the Simplex algorithm takes a few seconds on a standard desktop computer. In practice, this figure is largely controlled by the computing time required to evaluate the predicted activity ratios, which itself directly depends on the number of terms used in the summations of (6), (18) and (26). Here, we use 100 terms of the series, which is more than adequate in most cases.

### 2.4. Uncertainty estimation

Having obtained a best fit solution, the remaining question is what are the formal errors in the solution? A Bayesian approach provides a convenient way of answering this question (Box and Tiao, 1973; Smith, 1991; Mosegaard and Sambridge, 2002). In this framework, the constraints on the two primary unknowns, \( (x, t) \) provided by the data are represented by a probability density function (PDF), \( p(x, t|a^{\text{obs}},j) \), where we use the vector \( a^{\text{obs}} \) to represent the combined set of observed activity ratios. Here, the vertical bar notation indicates that terms to the right are fixed while those to the left are variable. Hence \( p(x, t|a^{\text{obs}}) \) can be interpreted as the probability density on the unknowns \( (x, t) \) given the observations, \( a^{\text{obs}} \). For simplicity, we ignore errors propagated into the estimated \( r_{\text{age}} \) ratio from hereon. Bayes’ theorem shows how observational errors may be combined with prior information and propagated into the unknowns. We have

\[
p(x, t|a^{\text{obs}}) = p(a^{\text{obs}}|x, t) \cdot p(x, t).
\]

The first term, \( p(a^{\text{obs}}|x, t) \), is the Likelihood function, which measures how well any particular pair of values \( (x, t) \) fit the data, while the second term, \( p(x, t) \), is the prior PDF, which represents what we know about the unknowns before we collect the data. Here, all three terms in (33) are PDFs with quantities to the left of the vertical bar indicating variables and those to the right indicating fixed values. The role of the constant of proportionality, missing from (33), ensures that the PDF integrates to unity over the parameter space of unknowns, but as we shall see can be neglected.

Bayes’ theorem is a way of combining ‘what we know’ before collecting the data with what the data tell us, all expressed in terms of PDFs. Assuming the noise on the observed activity ratios follow a Gaussian distribution (as in our example), then the likelihood function is simply related to the least squares data misfit measure (32), i.e., we have

\[
p(a^{\text{obs}}|x, t) = \text{ke}^{-\frac{\phi(x, t)}{2}},
\]

where \( k \) is a constant. If we assume that we have some upper and lower bounds on the unknowns, e.g., \( (k_1, k_2) \) and for bone age \( (t_1, t_2) \), then it is convenient to assume that the prior PDF \( p(x, t) \) is uniform within these bounds, and hence, the prior probability density becomes

\[
p(x, t) = \frac{1}{(k_2 - k_1)(t_2 - t_1)}
\]

The prior is therefore a constant, which integrates to unity over the parameter space, as all PDFs must. Substituting (35) and (34) into (33) gives

\[
p(x, t|a^{\text{obs}}) \propto \exp(-\frac{\phi(x, t)}{2})(t_1 \leq t \leq t_2; k_1 \leq k \leq k_2).
\]

This is now the final ‘posterior’ PDF describing the information on the unknowns, which becomes proportionate to the Likelihood function because the prior is a constant. It follows that the pair of values \( (x, t) \), which minimize \( \phi \) (found by the Simplex algorithm), will also maximize \( p(x, t|a^{\text{obs}}) \). As we may expect, the solution which fits the data, also has highest probability density. More generally, this expression is useful because it enables us to determine the uncertainty in the solution. Since we are largely interested in uncertainty in bone age only, then probability theory says that we must integrate \( p(x, t|a^{\text{obs}}) \) over the unwanted variable, i.e., \( k \). Doing so gives a probability density function for bone age alone

\[
p(t|a^{\text{obs}}) \propto \int_{k_1}^{k_2} \exp(-\frac{\phi(x, t)}{2}) \, dk.
\]

In the nomenclature of probability theory, the function \( p(t|a^{\text{obs}}) \) is called a marginal PDF, and represents the constraint on the bone age alone, given the observations. Using standard numerical integration techniques it is possible to evaluate this integral (up to a multiplicative constant) for any value of \( t \). Here, we implement this with a regular grid of \( t \) values between the limits \( (k_1, k_2) \). For any chosen \( t \), the quantity \( e^{-(\phi(x, t)/2)} \) is summed over \( k \) to give \( p(t|a^{\text{obs}}) \). In this way we are able to plot the PDF for bone age as a function of \( t \). The constant of proportionality is not needed since the curve is easily normalized to unit area.

2.4.1. An example with synthetic data

Fig. 3 shows the result of calculating the posterior PDF on bone age, \( p(t|a^{\text{obs}}) \), for the numerical example of the previous section both without noise added to the data (Fig. 3a), and with noise
added (Fig. 3b). From a Bayesian perspective, the PDFs in Fig. 3 represent all information we have on the bone given the data and the physics of the measurement process (assumed equivalent to the DAD model). These curves are interpreted just like any other PDFs of random variables, with area under the curve representing the probability of the variable (which integrates to unity). The width of the curve reflects the uncertainty in the constraint placed on the bone age by the data. In the noise free case, Fig. 3a, the peak of the PDF is close to the correct bone age, $t = 70$ ka (green line), and the best fit solution (dashed line) is co-incident with the true value. For the synthetic activity profiles with added noise (shown in Fig. 2), the best fit solution ($t = 68.5$ ka) is slightly younger than the true value and the PDF width is broader indicating increased uncertainty. In both cases the PDF is near Gaussian, but there is no requirement that this be the case.

A standard way of representing uncertainty for general 1-D PDFs is to calculate the 95% credible interval, which corresponds to the interval on the $t$-axis enclosing 95% of the area under the curve. If the PDF were a Gaussian, the 95% credible interval would correspond to the ±2σ from the mean. These are calculated for the two cases and plotted as red bars in Fig. 3a, b. For the noise free case we get 95% credible intervals of (68.27, 71.90) ka with a rather small half width of $\Delta t = 1.82$ ka, which is extremely precise. When noise is added to the data, the credible intervals become larger (65.21, 72.10) ka and the half width almost doubles to a value of $\Delta t = 3.45$ ka. As expected, the noise in the data have resulted in larger uncertainty in the estimated bone age. Nevertheless, the uncertainty estimation is consistent with the true solution in both cases and behaves as expected for this synthetic example.

### 2.5. Correlated errors

The use of a standard in the isotope measurements implies that each data point has a certain correlated error. This may be small in
solution analyses but is significantly larger in laser ablation analyses. This means that the treatment of data fit in Section 2.3 needs modification. Specifically, the least squares expression in (32) must be generalized to

$$\phi(k, t, r, e) = r^T C^{-1} r,$$

(38)

where $r$ is the vector of residuals ($r_i = A_{obs}^{i} - A_{pred}^{i}$) and $C$ is the covariance matrix of the errors. The particular expression in (32) corresponds to the case of uncorrelated (independent) random errors and results in a diagonal covariance matrix with the $i$th element given by $C_{ii} = \sigma_i^2$. If a second correlated error with variance $\sigma_{cj}^2$ is added to the uncorrelated error, then the usual method of quadrature would suggest one simply adds the additional variances along the diagonal of $C$, and the new correlation matrix becomes

$$C_{ii} = \sigma_i^2 + \sigma_{cj}^2.$$

(39)

While this approach increases the overall size of errors, it does not introduce correlation in the error measurements because the covariance matrix remains diagonal. A non-diagonal covariance matrix is required for correlated errors. It can be shown that the appropriate covariance matrix for correlated errors is given by

$$C_{ij} = \delta_{ij} \sigma_i^2 + \frac{1}{N} \sigma_{ci} \sigma_{cj},$$

(40)

where $\delta_{ij}$ is Kronecker delta ($\delta_{ij} = 1$, for $i = j$, and 0 otherwise). This matrix has terms smaller than in the independent case (39) along the diagonal, because the number of data scales the correlated error variance. Off diagonal elements, however, are all increased from zero to $1/N \sigma_{ci} \sigma_{cj}$. The effect of the new covariance matrix given by (40) is to introduce appropriate correlation between data errors and ensure that the average residual is the same as in the uncorrelated case (39). This matrix must then be inverted and used in the general expression (38) to determine the correct misfit measure for correlated errors.

In our analysis, the correlated error of a data set is a constant percentage of the observed activity ratio, and so we write

$$\sigma_{cj} = \sigma_{48c} A_{obs}^{j},$$

(41)

where $\sigma_{48c}$ is the standard deviation of the fractional error in $^{234}$U/$^{238}$U observations induced by the standard and similarly $\sigma_{48c}$ for the $^{230}$Th/$^{238}$U. Hence, with two values of correlated error variance, $\sigma_{48c}$ and $\sigma_{48c}$, we may calculate covariance matrices for each data set and evaluate the misfit in (38) by summation.

2.6. Theoretical errors

A third type of error contaminating the real data case, which was also absent in the synthetic case, is the ‘theoretical error’. This describes the situation when the observed activity ratios across the sample have significant variation, which is incompatible with the known observational errors. This may be due to a number of unquantifiable effects, such as some heterogeneity in the sample.

An example is shown in Fig. 5b where the variation in the observed

![Fig. 5](image-url)

*a) Marginal probability density function of bone age for sample 2319 taking into account all three error types, random, correlated and theoretical. The best fit age found by maximizing the likelihood with respect to all three unknowns is given by 134 ka and represented by the green bar. Dashed line shows the peak of the marginal PDF. Red bars show the 95% credible interval which has a half width of 13.9 ka; b) shows the data fit of the Maximum Likelihood solution for the $^{230}$Th/$^{238}$U activity ratio. Observations are given by solid black line, predictions by the red line; c) Same as b) but for the $^{234}$U/$^{238}$U activity ratio. This example shows a successful fit to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)*
$^{230} \text{Th}^{238} \text{U}$ activity ratio is much larger than the observational errors (represented by vertical bars) would suggest. Compare this to the synthetic example in Fig. 2 where no theoretical error is present and therefore noise and data variations are consistent. Theoretical errors are common in many real data fitting problems and they usually have no effect on the optimization stage of the fitting process. Hence, they do not influence the calculation of the maximum likelihood (best fit) solution. However, it can significantly influence the uncertainty estimation. This is because theoretical error can be larger than observational errors, as in Fig. 5a, and ignoring them can severely underestimate how errors propagate into the results. Fortunately, there is a simple solution to the problem, which is to calculate a theoretical error factor and use this to rescale the data errors used in the uncertainty estimation procedure. The method is standard and described in Press et al. (1992). In short, we calculate a $\chi^2$ measure of data fit, which is simply a rescale version of the data misfit

$$
\chi^2 = \frac{1}{N} \sum_{i} \phi(k_i, t, r_g),
$$

where $N$ is the total number of observations being fit, i.e., number of $^{234} \text{U}^{238} \text{U}$ plus $^{230} \text{Th}^{238} \text{U}$ activity ratios. The theoretical error factor $F$ determined from the best fit solution and given by

$$
F = \frac{1}{\sqrt{\phi(k, t, r_g)}},
$$

When all standard deviations of errors are multiplied by this value, the $\chi^2$ of the best fit solution becomes unity. Hence using this procedure to properly account for theoretical errors means we forsake any ability to quantify goodness of fit of each predicted activity ratio profile to the observations (since they are guaranteed to fit well now that the data errors have been appropriately increased in size). With the rescaled errors uncertainty estimation may then be performed to obtain more realistic errors in the bone age using the procedure described in Section 2.4.

2.6.1. Implementation issues

A practical issue with the uncertainty estimation is the need to provide upper and lower bounds on both bone age and diffusion coefficient ($t_1$, $t_2$) and $(k_1, k_2)$. The user must supply values, which bound the true solution for the uncertainty estimation to be representative. A second use of the bounds is to generate the three bound the true solution for the uncertainty estimation to be repeated for 100 values of bone age, $t$, and ignoring them can severely underestimate how errors propagate into the results. Fortunately, there is a simple solution to the problem, which is to calculate a theoretical error factor and use this to rescale the data errors used in the uncertainty estimation procedure. The method is standard and described in Press et al. (1992). In short, we calculate a $\chi^2$ measure of data fit, which is simply a rescale version of the data misfit

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The samples were analysed with laser ablation, multi-collector ICPMS using the system at RSES, ANU. For the experimental set-up see Eggins et al. (2003, 2005), and for applications on human fossils Grün et al. (2005, 2006, 2008). U and Th concentrations were derived from repeated measurements of the NBS-610 standard, U-isotope ratios from the dentine of a rhinoceros tooth from Hexian (sample 1118, see Grün et al., 1998. Measurements used spot analysis where the laser was kept in a fixed position for 60 s, creating a small pit (130 μm in diameter, approximately 50 μm deep) in the bone by ablation. The ANU Neptune MC-ICPMS has one central ion counter, which needs to be used for both 230Th and 234U measurements. In practice, the 234U/238U ratios in bones change significantly less than the 230Th/238U ratios. Each line of spot analyses consists of twice as many 230Th/238U than 234U/238U analyses, the latter being offset by a few 100 μm (see Fig. 4). The errors in the measured U-series isotope ratios are derived from the counting statistics of the isotope and background measurements. These are assumed independent of each other. Correlated errors arise from repeated laser ablation measurements of the standard and the earlier repeated TIMS analyses of the standards, that are used for the calculation of the isotope ratios.

It is difficult to derive accurate U-concentrations from laser ablation MC-ICPMS data, which are unable to be normalized for ablation yield. For two of the bones (2319, 2404), the U-concentrations were measured along continuous tracks parallel to the spot sequences by LA-ICPMS, using a Varian 820 quadrupole ICPMS. In this case, 40Ca is used as an internal standard to correct for ablation yield. The positions of the spots on each bone were rescaled to a cross section starting at −1 and finishing at +1. Note that the x-positions for the 230Th/238U spots are different from those of the 234U/238U spots.

3.1. Results

Activity ratio data from the three samples (2319, 2284, 2404) were run through the inversion procedure based on the DAD theory. All three sources of error were allowed for, uncorrelated measurement error, correlated (fractional) error induced by the standard, as well as theoretical error as described above. Table 1 shows all ratio data as well as correlated and uncorrelated errors used for the three samples.

Fig. 5 shows the results for sample 2319. The marginal PDF of the bone age, found using the procedure described in Section 2.4, is shown in Fig. 5a. It is a simple single peaked PDF with some slight asymmetry (and hence not Gaussian). The maximum likelihood (ML) bone age obtained was 134 ka, represented as a green bar, and a 95% credible interval half width of 14.0 ka, shown as red bars. The dashed line is the peak of the marginal PDF, which differs from the maximum likelihood solution because the latter is the best fit overall three parameters (κ, t, r48). The ML solution for κ was 6.285 × 10−13 cm2 s−1 and r48 was 1.17. Fig. 5b and c show the fit of the ML solution to the 230Th/238U and 234U/238U ratios respectively. Both profiles are fit well in this case. For this sample, all indications are that the inversion procedure has performed well and the results are satisfactory.

Fig. 6 shows the results for sample 2284. The marginal bone age PDF is shown in Fig. 6a. In this case the ML solution for age is 139 ka with 95% credible interval half width of 16.6 ka. Other values are
\( \kappa = 6.503 \times 10^{-13} \text{ cm}^2 \text{s}^{-1} \) and \( r_{58} = 1.16 \). Bone ages for run 2319 and 2284 are in good agreement. Fig. 6b shows the fit of the ML solution to 230Th/238U ratios, which is reasonable given the variability of the observations. Fig. 6c is the fit for the 234U/238U ratios. Here, a slight offset can be seen between model predictions of the ML solution and the observations. All data values lie above the predicted curve (in red). This can be explained by the inclusion of correlated errors in the model fitting formulation, as represented by the modified data covariance matrix in Eq. (40). By definition correlated errors will tend to move the entire set of observations up or down, and hence if they are taken into account properly then the optimization for the bone age will be tolerant of similar discrepancies between data and predictions. Technically, correlated offsets between data and predictions are allowed by the likelihood term in Eq. (38) when the covariance matrix takes the form of Eq. (40). For all three samples the 230Th/238U data are more numerous and hence dominate the likelihood value. In the case of 2284, the optimal bone age is achieved by preferentially fitting these data and inducing a correlated shift in the 234U/238U residuals. Fig. 6d shows the same data set for a separate run with all correlated errors set to zero. In this case, the 234U/238U predictions pass through the centre of the observations in keeping with the presence of only uncorrelated errors.

Fig. 7 shows the results for sample 2404. The marginal bone age PDF is shown in Fig. 7a. In this case the ML solution for age is 268 ka with 95% credible interval half width of 78 ka. Other values are \( k = 6.922 \times 10^{-14} \text{ cm}^2 \text{s}^{-1} \) and \( r_{58} = 1.16 \). This solution is clearly inconsistent with the previous two samples. Fig. 7b shows the fit of the ML solution to 230Th/238U ratios, and Fig. 7c is the fit for the 234U/238U ratios. Here the observation at position \( x = 0.854 \) (see Table 1) appears to be an outlier and is omitted from the inversion. The 230Th/238U ratios show considerable variation as well as asymmetry across the sample. The ML solution provides only a poor fit to the data. The 234U/238U ratios show less variation. The offset between ML predictions and observations, due to correlated errors, is again visible in Fig. 7c. Overall the inconsistencies in this data set mean that the maximum likelihood solution gives a poor fit, which suggests that the information content of the data is questionable. A separate test was performed with the 230Th/238U observations with \( x > 0.5 \) removed. The corresponding predicted activity profiles is shown as a dashed red line on Fig. 7, and gives a more symmetrical set of observations, although centred on \( x' = -0.15 \). For this subset of 230Th/238U ratios the best fit age decreased to 202 ka with 95% credible interval half width of 47 ka which becomes more consistent with the previous samples. In contrast to the D–A model, the DAD model does not require U-concentration profiles for age calculations. This is advantageous when using isotope ratio analyses determined on spots by laser ablation MC-ICPMS as quantitative U-concentration profiles are difficult to establish using this technique (see above). Nevertheless, U-concentration profiles can be used as a diagnostic tool. Fig. 8 shows the profiles for samples 2319 and 2404. 2319 has an inverted U-concentration profile, which, according to the D–A model, may imply U-leaching from outer parts of the bone section.

**Fig. 7.** a) Marginal probability density function of bone age for sample 2404; b) data fit for 230Th/238U activity ratios. The final measurement at \( x' = 0.85 \) (see Table 1) falls below the range of the figure and was not used in the analysis; c) data fit for 234U/238U activity ratio. In b) and c) the red line is the predicted activity ratio when all 19 230Th/238U activity ratios are used in the inversion, and the dashed red line when the three values with \( x > 0.5 \) are removed. The best fit age found by the algorithm is given by 268 ka with a 95% credible interval half width of 77 ka, but falls to 202 ka for the reduced data subset (dashed). All other details are the same as in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
However, no corresponding increase of $^{230}$Th/$^{238}$U are detected in the $x'$-ranges of $-1$ to $-0.75$ or around $+1$. Note the large positive $^{230}$Th/$^{238}$U excursions near $x' = -0.31$ and 0.28 correspond to large fluctuations in the U-concentrations, probably caused by pores. In contrast, sample 2404 shows very large, fluctuating increases in U-concentration toward the bone margin in the domain $x' > 0.8$. In this region, the $^{230}$Th/$^{238}$U ratio drops from around 1.17 to 0.46 (see Table 1), consistent with a much later phase of increased U-uptake. The bulk of the 2404 profile is also inverted, but here the decreasing U-concentrations are correlated with increasing $^{230}$Th/$^{238}$U ratios. In the $x'$-range of $-0.5$ to nearly $-1.0$, U-concentrations drop by around 40%, while the corresponding $^{230}$Th/$^{238}$U ratios increase by a similar amount. Between $x'$ of 0.4–0.8, U-concentrations drop by around 20% while the $^{230}$Th/$^{238}$U ratios increase by around 40%.

The inverted U-concentration profile of 2319 points may be explained by microstructural differences, perhaps to a reduction in the internal surface area in the domains that are close to bone exterior. The U-concentration profile of 2404 reveals complex history of U-migration within the bone that cannot be solved by the fitting of a simple diffusion model. It is not possible to extract a meaningful age estimate from this sample. Considering the value of the U-concentration profiles for interpretation of the DAD results, we strongly recommend that these are routinely measured.

A remaining question relates to potential for differences between D-A and DAD age results. Unfortunately, we have been unable to compare these models due to our inability to access the existing D–A program. Nevertheless, our assumption of constant $^{234}$U/$^{238}$U ratio at the surface makes DAD age estimations critically dependent on the $^{230}$Th/$^{238}$U ratios, while the measured $^{234}$U/$^{238}$U ratios have only a small effect on the apparent ages inside the bone. This does not apply to closed system age calculations, which are, particularly for older bones, also strongly dependent on measured $^{234}$U/$^{238}$U ratios. For example, $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U ratios of 1.4 and 0.7, respectively, lead to a closed system age of 72.8 ka, whereas the assumption of a constant $^{234}$U/$^{238}$U ratio results in an age of 75.7 ka. For older samples, for example, with $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U ratios of 1.4 and 1.3, respectively, closed system calculations yield an age of 219 ka whereas the DAD model results in 288 ka. Similar differences could occur between D–A and DAD results.

We found that solid thick bones, e.g. long bones, provide the best chance for obtaining U-series data sets that can be modelled. Bones with obvious porosities often show highly variable $^{230}$Th/$^{238}$U ratios close to the pores as well as the presence of detrital Th. So far we have analysed very few samples that showed any indication that our base assumption of a constant $^{234}$U/$^{238}$U ratio over time did not apply. Furthermore, we have occasionally observed some evidence for Th diffusion (e.g. Grün et al., 2010; their Fig. 2). In such cases, the elemental U/Th ratios are usually well above 100. This means that even for those samples any $^{230}$Th diffusion would be negligible. Nevertheless, any samples where the presence of $^{232}$Th indicates detrital contamination, or perhaps Th diffusion, should be avoided for U-series age assessment altogether. Inhomogeneities in diffusivity within the bone will likely induce irregularities in activity ratios measured within the sample. Presumably this is a contributing factor to the variability in $^{230}$Th/$^{238}$U profiles seen in all three samples, which cannot be accounted for by observation errors alone. Our method for correcting for such effects is to propagate a theoretical error through to the age estimates, as described in Section 2.6.

4. Summary

We have presented a new theory for uptake of U in an open system applied to the dating of archaeological bones. A mathematical model is presented which predicts the activity profile of $^{234}$U, $^{238}$U, and $^{230}$Th as a function of position across the bone. The model includes the coupled effects of both radioactive decay and diffusion of each isotope as well as realistic boundary conditions. Analytical solutions are obtained which allow for each activity profile to be evaluated given the bone age, diffusion coefficient and initial $^{234}$U/$^{238}$U ratio. The new model may be combined with a robust inversion procedure which allows direct estimation of burial age from $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U ratios, without the need to calculate apparent ages based on closed system assumptions. Uncertainty in bone age is estimated using a rigorous approach which incorporates effects of both correlated and uncorrelated random errors as well as unmodelled theoretical error.

The inversion is illustrated on synthetically generated data, which shows it is able to satisfactorily recover known ages and their uncertainty from imprecise measurements. Application to real measurements shows that the two bones, 2319 and 2284, are well suited for the inversion procedure and have 95% credible age ranges of 127–147 ka (2319) and 123–156 ka (2284). This result confirms with the assumption that both bones should have a closely similar
age. The third bone, 2404 is ill-suited due to inconsistency of the measurements and shows that a careful selection of samples is required. The U-concentration profiles indicate domains that have potentially experienced recent U-uptake or U-leaching. Such bones, e.g. sample 2404, will not provide any meaningful age results. The U-concentration profiles may also be used to reject certain data points (e.g. close to pores or where concentrations fluctuate widely), due to possible micro-scale U-migrations.

5. Conclusions

Our algorithm provides an easily accessible, robust platform for the calculation of open system ages and associated uncertainties on bones. Recent advances in laser ablation mass spectrometric analysis have opened the possibility of rapidly analysing many U-series data points across a bone. From our experience so far, we prefer spot analysis over continuous tracks. While the DAD model does not require U-concentration profiles, these have an important role in the recognition of U-micro-migration of U-leaching processes, which have the potential for rendering DAD results meaningless. For optimal fitting results, we recommend use of as many $^{234}$U/$^{238}$U as $^{230}$Th/$^{238}$U analyses as possible. While we expect increasing interest from the archaeological and Quaternary science communities in the routine U-series analysis of bones, we advise some caution in the interpretation of the result, because the age estimates give insights when U-migration has taken place, but this may have commenced a significant time after the bone’s original burial.

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