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Research paper

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

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ABSTRACT

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 ^{234}U/^{238}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.

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 μg 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.

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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}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}U over ^{238}U (e.g. chapter V in Cherdyntsev, 1971), caused by alpha recoil of the decaying ^{238}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}U. Alternatively, the recoiled atom can be directly ejected from the mineral surface into the solution. In the terrestrial environment the ^{234}U/^{238}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}U/^{238}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}Th/^{234}U and ^{234}U/^{238}U ratios and the simultaneous solution for age and initial ^{234}U/^{238}U ratio. For bones, however, the age calculation has to take into account that the ^{234}U/^{238}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

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

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}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':

$$t' = \frac{Dt}{Rl^2}, \tag{2}$$

where l 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.

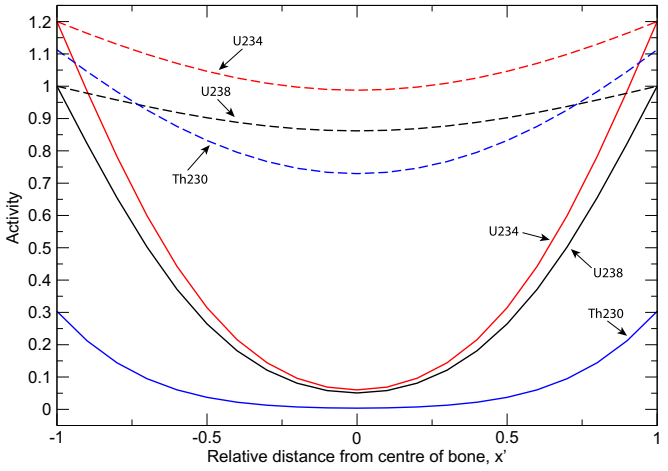

Fig. 1. Activity profiles as a function of relative position across a bone predicted by the new theory. Solid lines are plotted at dimensionless time of $t' = 0.1$ and dashed lines are for $t' = 0.9$. Black lines show activity profiles of ^{238}U (calculated using eqn. (6)), red lines are for ^{234}U (calculated using eqn. (11)–(18)), and blue lines for ^{230}Th (calculated using eqn. (26)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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}U and ^{234}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}U, ^{234}U and ^{230}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^{VI+} state and is taken up in bone by a process of diffusion and adsorption. Henceforth we represent the number of atoms of ^{238}U as N_1 and its activity as $A_1 = \lambda_1 N_1$, where λ_1 is the decay constant for ^{238}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}U at point x in the bone is governed by the partial differential equation,

$$\frac{\partial N_1}{\partial t} = -\lambda_1 N_1 + \kappa \frac{\partial^2 N_1}{\partial x^2}, \tag{3}$$

where κ is the rate of diffusion and equal to $D/(R+1)$. Laboratory experiments of Millard (1993) showed that typically the volumetric