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## U-series dating of bone using the diffusion-adsorption model

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**Abstract**—U-series dating of bone has suffered problems of reliability since its inception because bone remains an open system with respect to uranium. Commonly applied a priori assumptions of U uptake, such as early uptake or linear uptake, are inadequate because they have no physical or chemical bases, no means of demonstrating which model is suitable for a particular bone, and no intrinsic tests of reliability. Despite this and numerous examples of anomalous U-series dates, such assumptions are still routinely applied. We address this problem using the diffusion-adsorption (D-A) model of U uptake (Millard and Hedges, 1996), which incorporates a physicochemical description of U uptake. Using this model, we show how the U uptake of a bone responds to geochemical changes in the burial environment, which can lead to phenomena such as the removal of U from bones (“leaching”) or U uptake late in their burial history (“recent uptake”), and we show how the overall uptake history is reflected in distributions (profiles) of U and U-series isotopes across a bone section.

We present measurements of U concentration profiles, and <sup>230</sup>Th/<sup>234</sup>U profiles on archeological bone from a number of different sites and burial environments and compare the results to profiles predicted by the D-A model. Bones that have undergone complex uptake histories (which include U leaching or recent uptake) are identified on the basis of these profiles and rejected as unsuitable for dating. For bones that appear to have undergone uptake under constant geochemical conditions, the D-A model is applied to calculate U-series dates, with much improved reliability. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

Uranium-thorium dating has the potential to provide chronologies of up to 500 ka, covering a section of the Pleistocene that is extremely important to our understanding of archeology, paleontology, paleoclimate change, and later human evolution. While the U-series dating of primary precipitates (e.g., speleothem) has gone some way in providing reliable age estimates for this period (e.g., Schwarcz, 1980; Edwards et al., 1997), it is limited to sites where such material is present and by interpretation of stratigraphic association. Directly dating bone would vastly expand the number and range of sites that can be dated and provide a much clearer picture of the past half million years.

There are several problems with U-series dating of bone (and teeth), the most fundamental being that bone does not conform to the standard “closed-system” assumptions that U is present initially in the system and is neither lost nor gained except through radioactive decay. Living bone contains a few parts per billion U (Iyengar et al., 1978), whereas archeological bone can contain hundreds of parts per million U. The U present is gained after burial (bone is an open system), and our ability to date bone depends on our understanding of this uptake.

The problem of U uptake by bone has been recognized from the outset. The earliest studies by Cherdyntsev et al. (1963) accounted for the disagreement between U-series dates and expected ages by suggesting that U had been leached out of a number of bones and taken up late in the burial history of others. Since then, a number of different approaches to the

problem of U uptake have been taken, but none has been found to yield a satisfactory solution. The most common approach is simply to assume the form of U uptake, usually either one of early uptake, an approximation to a closed system whereby the U is assumed to have entered the bone shortly after burial, at which point further migration ceases, or linear uptake, whereby U is taken up at a constant rate (e.g., Ikeya, 1982). However, disagreement between calculated U-series dates and the known ages of bones (e.g., Rae et al., 1989; Schwarcz and Grün, 1993) has led many to postulate that in some cases, U may be taken up late in the burial history of a bone, termed delayed or recent uptake, giving underestimated closed-system U-series dates, or that U, but not Th, can be leached out of a bone, leaving a Th excess and leading to overestimated U-series dates calculated using the closed-system assumption. While these phenomena have been identified in the past, no geochemical or diagenetic mechanism has been proposed to account for them.

More mathematically sophisticated models for uptake have been proposed, often using the two independent <sup>238</sup>U and <sup>235</sup>U decay series or additional electron spin resonance measurements to estimate the parameters of the model (e.g., Grün et al., 1988; Cheng et al., 1998), but they still rely on assuming an arbitrary form of U uptake. These assumptions generally have no reference to the physical or chemical processes involved in the interaction of U and bone but are usually built on simple and mathematically convenient descriptions of U uptake. Furthermore, there is rarely an independent check on the reliability of a U-series date on bone. Given, for example, that dates calculated using an early uptake assumption will be at least half those calculated using linear uptake, and models that assume that a fraction of U is leached (e.g., Szabo and Rosholt, 1969; Hille, 1979; Chen and Yuan, 1988) will give young dates

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compared with models that assume recent accumulation of U (e.g., Zhou et al., 1997), U-series dating of bone (and teeth) is rendered unreliable and virtually unusable unless justification can be given for the application of a particular uptake model to a particular bone.

The work presented here addresses these problems with reference to the diffusion-adsorption (D-A) model of Millard and Hedges (1996). Unlike the other uptake models, the D-A model has at its core a physicochemical description of U uptake and allows uptake by bone to be viewed within the geochemical context of bone–U–burial environment interactions. It predicts not only the rate of U uptake by bone but also the spatial distribution of both U (“U concentration profiles”) and U-series isotopes (“apparent closed-system date profiles”) across a bone section.

We present U and U-series isotope profiles measured using inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS) and compare them to predictions of the D-A model. We model the effects of changes in the geochemistry of the burial environment that lead to leaching and recent uptake and show how both phenomena can be identified by their U concentration profiles and apparent closed-system U-series date profiles and rejected as unsuitable for dating. By selecting bones on the basis of their profiles that show simple U uptake histories (e.g., under constant geochemical conditions or uptake rapid enough to approximate to a closed system), we can use the D-A model to calculate U-series dates with much improved reliability.

## 2. THE D-A MODEL

Millard and Hedges (1996) proposed that U is taken up by bone as complexes of the uranyl ion ( $\text{UO}_2^{2+}$ ) by a process of diffusion and subsequent adsorption onto the large internal surface area of the mineral fraction (nonstoichiometric carbonate hydroxyapatite). The assumption here is that uranium remains in the mobile  $\text{U}^{\text{VI}}$  state. This differs from earlier assertions, summarized by Rae and Ivanovich (1986), that suggest that  $\text{U}^{\text{VI}}$  is reduced to  $\text{U}^{\text{IV}}$  by collagen degradation products and then exchanges with  $\text{Ca}^{2+}$  in the bone, but it is supported by Millard and Hedges’s (1996) laboratory experiments, which show significant U uptake in protein-free hydroxyapatite under oxidic conditions.

The rate of diffusion is controlled by the diffusion coefficient,  $D$ , which is reduced for diffusion in a porous material such as bone. As uranium is diffusing into the bone, there is simultaneous adsorption onto the surface of the mineral crystals. Drawing on Crank (1975), they gave the equation for simultaneous diffusion and adsorption as follows:

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

This is a form of Fick’s second law (the diffusion equation), with  $D$  replaced by  $D/(R+1)$ .  $R$  is the “volumetric equilibrium constant” (Neretnieks 1980): the amount adsorbed per unit amount of solution. It is related to the partition coefficient ( $K_d$ ) by  $R = K_d/p$ , where  $p$  is the specific porosity of the bone. Millard’s laboratory experiments gave  $R$  from  $10^5$  to  $10^6$  so that  $D/(R+1) \approx D/R$ .

Using a modification of Crank’s (1975) equation for diffusion in an infinite planar slab, they derived the concentration,  $Z$  (ppm) at a point  $x$ :

$$Z_{(x)} = pRC_1 \cdot \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{\left[ \frac{-D(2n+1)^2\pi^2 t}{(R+1)4l^2} \right]} \cos \left[ \frac{(2n+1)\pi x}{2l} \right] \right), \quad (2)$$

where  $x$  is the distance from the center of the slab (cm),  $t$  is the time of burial (s),  $C_1$  is the environmental concentration of uranyl (ppm), and  $l$  is half the thickness of the bone (cm). To generalize, Millard and Hedges (1996) used three reduced dimensionless parameters:

$$Z' = Z/pRC_1, \quad (3a)$$

$$x' = (x-l)/l, \quad (3b)$$

$$t' = tD/(Rl^2). \quad (3c)$$

Under this scheme,  $Z'$  represents the fraction of the equilibrium concentration of uranium in the bone, because at equilibrium, the concentration of uranium,  $Z$ , is  $pRC_1$ . The parameter  $x'$  represents the fractional distance from the center of the bone section and takes values between  $-1$  and  $1$ . The parameter  $t'$  is a function of both time and  $D/R$  and is related to the “steepness” of the profile (see below). Young bones or bones with lower  $D/R$  values give smaller values of  $t'$  and steeper U profiles.

Making the implicit assumption that radiogenic  $^{230}\text{Th}$  remains in the bone, Millard and Hedges (1996) also provided a finite difference equation for calculating the apparent closed-system date at a point in the bone after a given period of uptake according to the D-A model:

$$\frac{\delta(^{230}\text{Th}/^{234}\text{U})}{\delta t} \approx \lambda_{230} \left( 1 - \frac{^{230}\text{Th}}{^{234}\text{U}} \right) - \frac{^{230}\text{Th}}{^{234}\text{U}} \left[ \frac{1}{Z} \frac{\partial Z}{\partial t} - \lambda_{234} \left( 1 - \frac{^{238}\text{U}}{^{234}\text{U}} \right) \right]. \quad (4)$$

Note that in Eqn. 4 and throughout this paper, ratios of radionuclides are expressed as activity ratios unless otherwise stated.

Figure 1 gives generalized profiles for different values of these reduced variables, assuming constancy of the model parameters over time. The figure shows an evolution of the U profile through time until equilibrium is reached (when  $t' \sim 3$ ) and a uniform profile is achieved. The actual time taken to reach equilibrium depends on the value of  $D/R$ , but Millard and Hedges’s (1996) measurements on archeological bone, and the results presented below, suggest that equilibrium would be reached between 6 ka ( $D/R \sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) and 600 ka ( $D/R \sim 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ) for a 0.5-cm thick bone.

Figure 2 shows the distribution of apparent closed-system dates across a bone section for a 10-ka bone for different values of the parameter  $D/R$ . Because the D-A model predicts in many

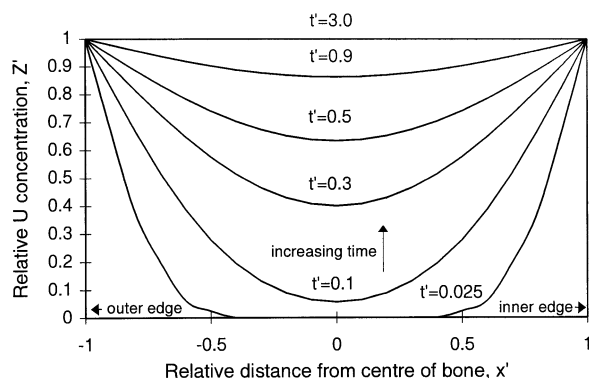


Fig. 1. U profiles generated using the diffusion-adsorption model under constant conditions.

cases that uptake occurs over a considerable time, apparent closed-system dates across a bone give younger values toward the center. The degree of underestimation depends on the parameter  $D/R$ , with lower values representing a slower equilibration of the bone with resulting younger dates toward the center. This has implications for the geometry of samples removed from a bone because the apparent closed-system date depends on the position of the sample. A similar but more pronounced relationship between sample geometry and the apparent closed-system U-series date has also been predicted for teeth (Pike and Hedges, 2001).

### 2.1. Factors Influencing $D/R$

The value of  $D/R$  is influenced by a number of characteristics of the burial environment and the state of preservation of a bone. In drier burial environments, the diffusive coupling between the soil pores and the pore space in the bones is reduced, along with the volume of groundwater and hence available U within the bone (Millard and Hedges, 1995; Hedges and Millard, 1995). Thus,  $D/R$  may be reduced by a factor of 100 in very dry conditions compared with those that are water saturated. Millard and Hedges (1996) showed in laboratory experiments that the complexing of uranyl in groundwater with

different species can also affect  $D/R$ , perhaps 10-fold, with carbonate species increasing  $D/R$  and cysteine reducing it. Similarly, changes in pH should affect the partition of U between the groundwater and bone mineral as the hydroxyapatite surface becomes increasingly negatively charged in more alkaline conditions. This effect is likely to be limited, however, because it is suggested that the bone pore water will be saturated with respect to the decay products of bone and buffered to a pH of  $\sim 7$  (Millard, 1993). The diagenesis of bone will also increase  $D/R$ . Measurements of diagenetic parameters (e.g., Hedges et al., 1995; Nielsen-Marsh et al., 2000; Nielsen-Marsh and Hedges, 2000; Pike, 2000) typically show an increase in the number and size of the larger pores and a decrease in the number of micropores ( $<40 \text{ \AA}$ ) as diagenesis progresses. An increase in the mean diameter of pores decreases the steric and Faxen drag effects of diffusion in a porous medium, thus increasing the diffusion coefficient. At the same time, the loss of the smallest pores, which represent the larger part of the internal surface area of the bone, decreases the surface available for adsorption, hence decreasing  $R$ . If burial conditions remain relatively water saturated, severe and rapid diagenetic alteration of a bone may increase  $D/R$  up to 70-fold, to the point at which the time taken to reach equilibrium with the U in the groundwater is short compared to the U-series timescale, providing the possibility for early uptake (see below), although we acknowledge that there may be cases in which diagenesis progresses at a slower rate.

### 2.2. D-A Dates

The D-A model cannot be directly solved for  $t$ , but given the parameters  $t'$ ,  $x$ , and a measured closed-system date for a sample, a date with uptake according to the D-A model (termed a D-A date) can be calculated by forward modeling using a procedure incorporating Eqn. 1 and 4. The parameter  $t'$  and associated confidence limits can be estimated from a measured U concentration profile using a "least squares maximum likelihood estimation" (e.g., Press et al., 1996, p. 548) by generating a U profile using the D-A model and comparing it to a measured profile. Calculating a D-A date for each isotopic measurement across a bone gives a D-A date profile. The shape of this profile gives us additional information on the uptake history of a bone (see below).

## 3. PREDICTIONS OF THE MODEL

For a number of different geochemical scenarios, we have used the D-A model to predict the U concentration and closed-system date profiles and where relevant calculated the D-A date profile. These are shown in Figure 3 and described below.

### 3.1. Relatively Slow Continuous Uptake, Constant Conditions

Figure 3A shows the U concentration, apparent closed-system, and D-A date profiles for a bone that has taken up U according to the D-A model under constant conditions but has not yet reached equilibrium. The U and closed-system date profiles are both U shaped, but the D-A date profile is uniform;

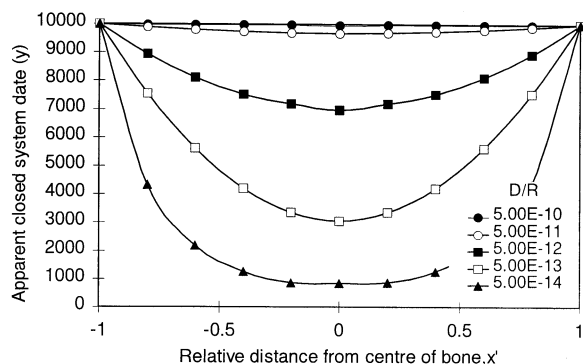


Fig. 2. Modeled U-series date profiles across a 10-ka bone according to the diffusion-adsorption model under constant conditions. The dates are calculated using the closed-system assumption.

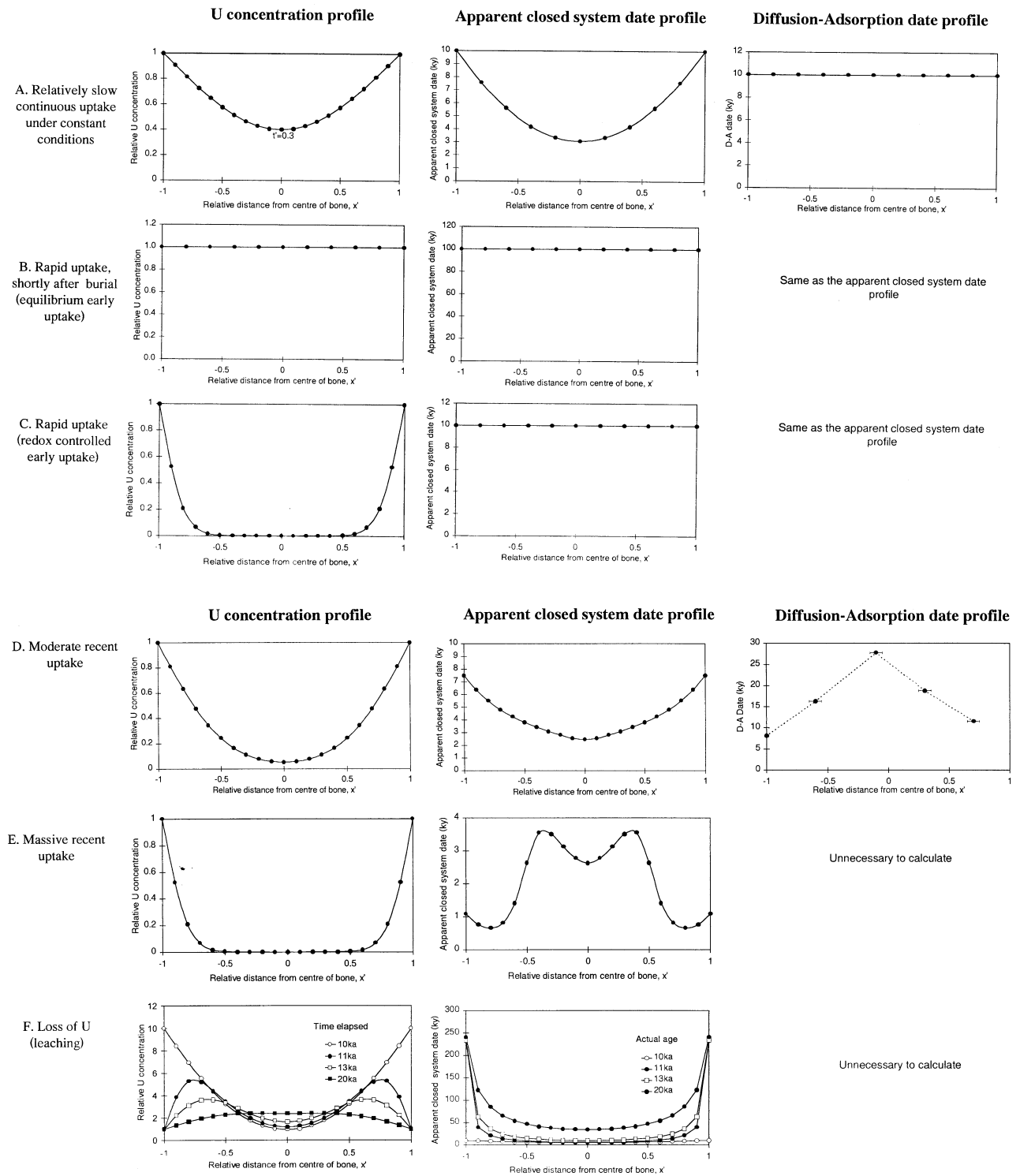


Fig 3. Predictions of the diffusion-adsorption (D-A) model for different geochemical scenarios.

Table 1. Time to reach equilibrium for a 0.5-cm thick bone and apparent closed-system dates calculated using the diffusion-adsorption model. Note that even bones that take as long as 60 ka to reach equilibrium show less than a 10% underestimation in their closed-system date after 100 ka.

D/R (cm <sup>2</sup> s <sup>-1</sup> )	Time to reach equilibrium (ka) <sup>a</sup>	Closed system date of 100-ka 0.5-cm bone (ka)
1 × 10 <sup>-14</sup>	600	66
1 × 10 <sup>-13</sup>	60	92
5 × 10 <sup>-13</sup>	12	98
1 × 10 <sup>-12</sup>	6	99

<sup>a</sup> Equilibrium is taken as when  $t' = 3$ , which strictly speaking is when the uranium in the whole sample reaches 99.95% of its equilibrium value.

that is, the D-A model gives the same date at all positions of the bone. We can calculate an overall date for such examples as the mean of the D-A dates in the profile and use the standard error of this mean as a measure of reliability.

### 3.2. Rapid Uptake Shortly After Burial

The D-A model predicts that under certain circumstances, uptake rapid enough to be considered “early” may occur. Early uptake requires that U is taken up for a short period (relative to the age of the bone), after which migration ceases, “closing” the system. We propose two mechanisms that could facilitate closure: the equilibration of the bone with U in the groundwater and the immobilization of U in the groundwater through redox changes in the burial environment.

The time taken to reach equilibrium depends on the parameter  $D/R$ , which increases as the bone undergoes diagenetic alteration. At equilibrium, under constant conditions, no further U will be taken up, effectively closing the system. If the bone is sufficiently old compared to the time taken to reach equilibrium, which would depend on the rate and magnitude of diagenetic change, the uptake can be considered early and the bone approximates to a closed system. Because the rate of U uptake is asymptotic, slowing as equilibrium is approached, even bones that take a considerable time to reach equilibrium can give closed-system dates close to the true age. Table 1 shows the modeled whole-bone, closed-system U-series ages for a 100-ka bone, revealing that bones of this age with  $D/R > 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup> should give closed-system dates <10% younger than the true age, even though they take up to 60 ka to reach equilibrium. Bones with a value of  $D/R$  of this order have been identified (see section 5). For early uptake bones of this kind, we expect both the U concentration and date profiles to be uniform (Fig. 3B), and an overall date can be calculated for the bone using the closed-system assumption.

Redox change in the burial environment may also prevent further uptake of U. Uranium in the environment exists in both the (IV) and (VI) oxidation states. U<sup>IV</sup> is relatively insoluble, whereas U<sup>VI</sup> forms many soluble complex ions. Both the valency and the complexation of U are determined by the Eh-pH conditions (e.g., Brookins, 1988). In oxidizing conditions, uranium is mobile as U<sup>VI</sup> (e.g., as the uranyl ion UO<sub>2</sub><sup>2+</sup> or

complexes of uranyl such as UO<sub>2</sub>[CO<sub>3</sub>]<sub>2</sub><sup>2-</sup>). In reducing conditions, U is immobile as U<sup>IV</sup> and is precipitated, although advective transport may occur in the presence of certain adsorptive colloidal particles. Early uptake may occur if, shortly after burial, although long enough for sufficient U to have been taken up, Eh-pH changes occur to prevent further uptake through the immobilization of U in the form of U<sup>IV</sup>.

There are several scenarios where this is possible. Baas Becking et al. (1960) noticed a relationship between water content of soils and their measured oxidation potential, with waterlogged and very wet conditions showing Eh sufficient to reduce U. Microbial decomposition of organic material can also reduce Eh. Figure 3C shows the profiles predicted for redox-controlled early uptake bones. Importantly here, the apparent closed-system date profile is uniform, although we predict relatively steep U concentration profiles. A similar effect may occur through extreme dehydration of the burial environment or when the bone becomes encrusted with calcite, preventing U migration.

### 3.3. Recent Uptake

The adsorption of U in bone (as uranyl species), according to the D-A model, represents an equilibration between the U in the bone pore water and U adsorbed on the surface of the bone mineral. Changes in the bone pore water U concentration will disrupt this equilibrium, causing further adsorption or desorption of uranyl. An increase in groundwater U later in the burial history of a bone will increase the rate of uptake and equilibrium concentration of U in the bone, leading to a decrease in <sup>230</sup>Th/<sup>234</sup>U and an underestimation of the date. Figure 3D shows the results of a recent uptake scenario according to the D-A model. In this scenario, the bone undergoes U uptake with a notional groundwater U concentration of 0.5 for 5 ka. After 5 ka, the groundwater U concentration is increased to 1, and uptake proceeds for a further 5 ka. Because of the additional uptake, the surface of this 10-ka bone gives a date of 7.5 ka, while the whole bone would give a date in the region of 6 ka. The resulting U and date profiles are not dissimilar to uptake under constant conditions (e.g., Fig. 3A), but the D-A date profile is a characteristic ∩ shape. In cases of massive and very recent uptake, the resulting closed system date profile is M shaped (Fig. 3E). This shows modeled profiles for a bone that has taken up U for 9 ka at a groundwater U concentration of 0.01 followed by uptake for 1 ka at a U concentration of 1.

### 3.4. Loss of Uranium From the Bone (Leaching)

The leaching of U from a bone is a phenomenon that has been frequently identified but not explained before the D-A model. Uptake of U followed by a loss of some of that U will leave an excess of the <sup>230</sup>Th and <sup>231</sup>Pa daughters, giving falsely high closed-system dates or leading to a <sup>230</sup>Th/<sup>234</sup>U greater than the theoretical equilibrium value (e.g., Szabo and Collins, 1975; Rae et al., 1989).

Figure 3F shows the development of U concentration and closed-system date profiles during a leaching scenario. Here, diffusive uptake occurs for 10 ka at a notional groundwater

concentration of 10, after which the concentration is dropped to 1. The resulting U profiles show an M shape initially as U is lost from the edges of the bone, becoming  $\cap$  shaped and gradually flattening at the new equilibrium concentration. The immobile radiogenic Th remains in the bone, so the loss of U increases  $^{230}\text{Th}/^{234}\text{U}$ . The effect on the apparent closed-system U-series date is marked, with the edges of the bone giving dates of  $\sim 240$  ka after just 1 ka of leaching. As leaching progresses, the center of the bone is more affected, giving an apparent date of  $\sim 50$  ka after 10 ka of leaching. Note that similar relative results would be obtained from the D-A model if the uptake and leaching periods were longer.

#### 4. MEASUREMENT OF U CONCENTRATION AND DATE PROFILES

##### 4.1. Dating Strategy

Given these predictions of the D-A model, our dating strategy is to select and date bones identified on the basis of their measured profiles that have undergone either early uptake or uptake according to the D-A model under constant conditions (e.g., Figs. 3A to 3C). The variations in the geochemistry that lead to leaching or recent uptake are considered too complex to model accurately, but we can identify such cases by their U and U-series date profiles and reject these samples as unsuitable for dating. The criteria by which bones are deemed datable are summarized in Figure 4.

##### 4.2. Measurement of U Concentration Profiles

As a preliminary measurement, U concentration profiles were measured using ICP-MS in advance of TIMS U-series measurements on selected bones. The examples illustrated in this paper come from the sites of Combe Sauniere (Sarlatiac-sur Isle, France), a rock shelter encompassing the entire French Upper Palaeolithic sequence (Genest in Rigaud, 1986); Boxgrove (West Sussex, UK), a Middle Pleistocene open site (Roberts and Parfit, 2000); Stanton Harcourt (Oxfordshire, UK), a paleochannel of the Thames believed to correlate with oxygen isotope stage 7 (Buckingham et al., 1996); Bercy (Paris, France), a Neolithic settlement on the banks of a paleochannel of the Seine (Bocherens et al., 1997); Abri Pataud (Dordogne, France), a large rock shelter with a virtually complete Upper Palaeolithic sequence extending from the earlier Aurignacian ( $\sim 34$  ka BP) to the early Solutrean ( $\sim 20$  ka BP; Movius, 1975); and Jinniushan (Liaoning Province, China), a cave site yielding hominid remains dating in excess of 220 ka (Chen and Yuan, 1988).

Transverse sections of cortical bone were obtained using a handsaw and cleaned in an ultrasonic bath in distilled water with repeated change of water until no visible sediment was ejected. After drying at  $105^\circ\text{C}$ , samples (2 to 15 mg) were removed at intervals across the bone section using a hand drill with a steel drill bit ( $\phi = 0.6$  to  $1.0$  mm, depending on the size of the bone). The drillings were ashed at  $550^\circ\text{C}$  for 24 h to remove any protein fraction in the bone and then dissolved in 30%  $\text{HNO}_3$ . Immediately before analysis, the sample solution was further diluted to give a total dilution of  $5000\times$  (w/v) and

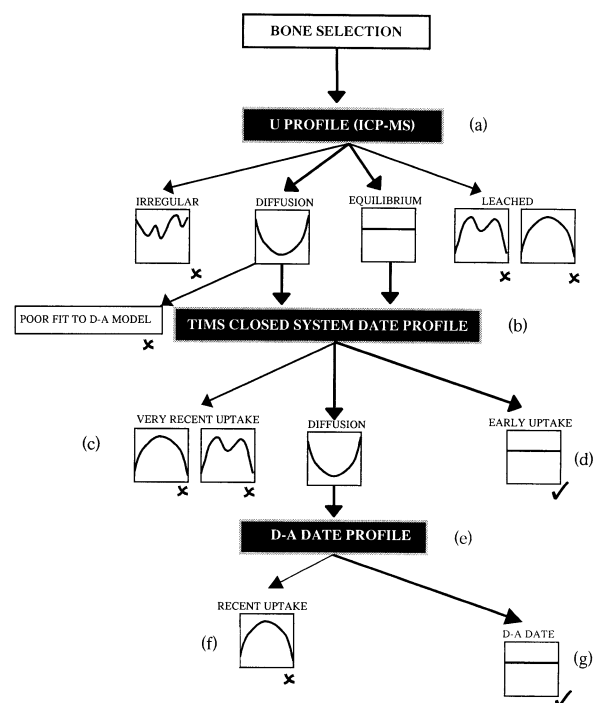


Fig. 4. Schematic of the dating process showing typical profiles for bones that are rejected (X marks) and those that give acceptable dates (check marks). (a) Preliminary measurement of U profiles by inductively coupled plasma mass spectrometry is used to reject irregular or leached profiles. (b) Thermal ionization mass spectrometry date profiles are measured on bones that show uniform profiles or those that fit the diffusion-adsorption (D-A) model under constant conditions. (c) Some bones are rejected as extreme cases of early uptake on the basis of their date profiles. (d) At this stage, early uptake bones are identified, and a date is calculated using the closed-system assumption. (e) The D-A model is then applied to produce a D-A date profile. (f) Further cases of recent uptake give a  $\cap$ -shaped D-A date profile and are rejected. (g) Bones that have undergone U uptake according to the D-A model under constant conditions give a uniform D-A date profile, and an open-system date is calculated.

a nitric acid strength of 3%. ICP-MS was undertaken at the Natural Environment Research Council (NERC) ICP-MS facility at Imperial College, Silwood Park, UK, using a Plasma-Quad PQ2 in peak-jumping mode and internally standardizing to  $^{42}\text{Ca}$ . The quantitative detection limits for the batches ( $10\sigma$  above background) fall between 0.002 and 0.071 ppm in the solid.

##### 4.3. Measurement of U-Series Date Profiles

U-series isotopes were measured using TIMS. Samples of bone (0.1 to 0.01 g) were removed from a transverse section as above, except ashing to remove protein was not undertaken because of likely contamination in the furnace. The sample was dissolved in Teflon-distilled (TD) 7-mol/L  $\text{HNO}_3$ . TD HF was used on any insoluble fraction, which was separated by centrifuging.

There is a well-documented problem with Th yields in the anionic exchange separation of U and Th in the presence of the

Table 2. Characterization of U concentration profile shape. We have reclassified Millard's (1993) profiles according to this scheme, which differentiates leached profiles ( $\cap$ ) from irregular profiles ( $\sim$ ).

Profile shape	Number of bones in this study	Number of bones in Millard (1993)	Total	%
–	9	10	19	24
U	27	9	36	44
$\cap$	11	6	17	21
$\sim$	7	2	9	11
Total	54	27	81	100

high concentrations of phosphate ions from dissolved bone. Using a method based on that of Chow and Carswell (1963), we have found that by ensuring a phosphate concentration in solution of  $<0.2$  mol/L before column separation, Th yields of  $>80\%$  can be achieved. U yields can be as low as 50%, but it is the abundance of  $^{230}\text{Th}$  in the sample that limits the TIMS analyses.

U and Th were separated by standard liquid chromatography methods, using  $4\text{ cm}^3$  of 1-X8 200-400 Biorad anionic resin and eluting Th in 7-mol/L HCl and U in 1-mol/L HBr (e.g., see McDermott et al., 1999). For the TIMS analysis, the samples were loaded on single Re filaments on graphite. Typical total procedural blank values for this sample preparation scheme were 10 to 40 pg for  $^{238}\text{U}$  and 5 to 20 pg for  $^{232}\text{Th}$ , low relative to the bone samples, so no blank correction was applied.

The mass spectrometry analyses were carried out using a high-abundance sensitivity thermal ionization mass spectrometer (Finnigan MAT 262-RPQ) in peak-switching mode using a low dark noise secondary electron multiplier/ion counting system (e.g., see van Calsteren and Schwieters, 1995). Repeat measurements of laboratory standards gave a  $2\sigma$  between run precision of 1.47% in  $^{230}\text{Th}/^{234}\text{U}$ , and 1.13% in  $^{234}\text{U}/^{238}\text{U}$ . A correction for detrital thorium was applied using an assumed  $^{230}\text{Th}/^{232}\text{Th}$  of the detritus as  $1.7 \pm 0.7$  (Kaufman, 1993).

In some cases, a large source of error in the calculated date comes from the application of the correction for detrital Th and U. The assumption of a detrital  $^{230}\text{Th}/^{232}\text{Th}$  is not ideal, although we see no systematic over- or underestimation of D-A dates calculated for the surface compared to the less detritally contaminated central samples, suggesting that the true value of the sediment  $^{230}\text{Th}/^{232}\text{Th}$  does not lie significantly outside this assumed range. In future, however, it may be necessary to measure  $^{230}\text{Th}/^{232}\text{Th}$  on sediment samples.

## 5. RESULTS

It is not possible to present all the measured profiles here (they are given in Pike, 2000). Example results are shown in the Appendix, but it is useful to present a qualitative overview of the full data set by characterizing the shapes of the U concentration profiles into U shaped, uniform (–), leached ( $\cap$ ), or irregular ( $\sim$ ) (Table 2). We see that about two thirds of the bones show uniform profiles or U profiles: both profile shapes that are predicted by the D-A model. In fact, because the D-A model also predicts  $\cap$  profiles in leached bones, it is only the

irregular profiles that are not qualitatively consistent with diffusive uptake.

Examples of the measured profiles are given in Figure 5 and summarized in Table 3. Four of the bones have profiles that we consider to give acceptable dates. Figures 5A and 5B show examples of profiles from bones that appear to have taken up U according to the D-A model under constant conditions. Both these bones give mean D-A dates in reasonable agreement with their uncalibrated  $^{14}\text{C}$  control dates. Some scatter in the individual D-A dates within a profile is inevitable and probably reflects deviation of the bone from ideal geometry, uncertainty in the position of the subsamples ( $x'$ ), and in some cases, the large error contribution from the application of a detrital correction.

The sample from Jinushian (B52, Fig. 5C) shows a uniform U concentration and closed-system date profile and is a case of equilibrium uptake (compare with Fig. 3B). The lower U concentration at the surface of the bone is probably due to dilution of the sample with contaminating sediment, which is reflected in the high  $^{232}\text{Th}$  concentration (6 ppm) and low  $^{230}\text{Th}/^{232}\text{Th}$  of these samples.

Although we predict equilibrium early uptake in bones that are severely diagenetically altered, the diagenetic alteration of the Jinnuishan bones can be described only as average (Pike, 2000). The Jinnuishan bones, however, are among the oldest dated in this study, and the time taken to reach equilibrium must be viewed relative to the age of a bone. Thus, even if these bones took 40 ka to equilibrate ( $D/R = 6.5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ), the D-A model predicts that the center of the bone would still give a date only 7 ka younger than the edge of the bone, a negligible underestimation on a 240-ka bone (see also Table 1).

We also see a case of redox-controlled early uptake from the site of Bercy (not shown in Fig. 5 but presented in Table 4). This site is interesting because it contains burial environments with different characteristic hydrologies and resultant contrasting states of bone preservation (Nielsen-Marsh, 1997; Nielsen-Marsh and Hedges, 2000). The deep channel deposits (a paleochannel of the Seine) are waterlogged and produce bone in a good state of preservation. Bone from the dry banks of the channel shows poor preservation characteristic of hydraulically active environments. These two burial environments produce very different patterns of U uptake. Both bones are of a similar age,  $\sim 6$  ka BP, yet their U concentration differs by a factor of 100. This could be accounted for by different U concentrations in their burial environments, but the U profiles (not shown) reveal that the bone from the dry bank is much closer to equilibrium than the deep channel bone. This suggests that the dry bank bone has continued to take up U, while the deep channel bone has not. Further evidence for this comes from the U-series dates. If both bones had continued to take up U, the dry bank bone, closer to equilibrium, would show a better estimate of the age. In fact, we see the reverse, with the closed-system dates from the deep channel bone (B5600) at  $\sim 5$  ka giving a better estimate of the age for the site ( $\sim 6$ ka BP), while the dry bank bone (B8400) gives a more underestimated closed-system date of 3.4 ka. The whole-bone U-series date for B8400 of 3.4 ka is consistent with continuous diffusive uptake, giving a D-A date of 5.3 ka.

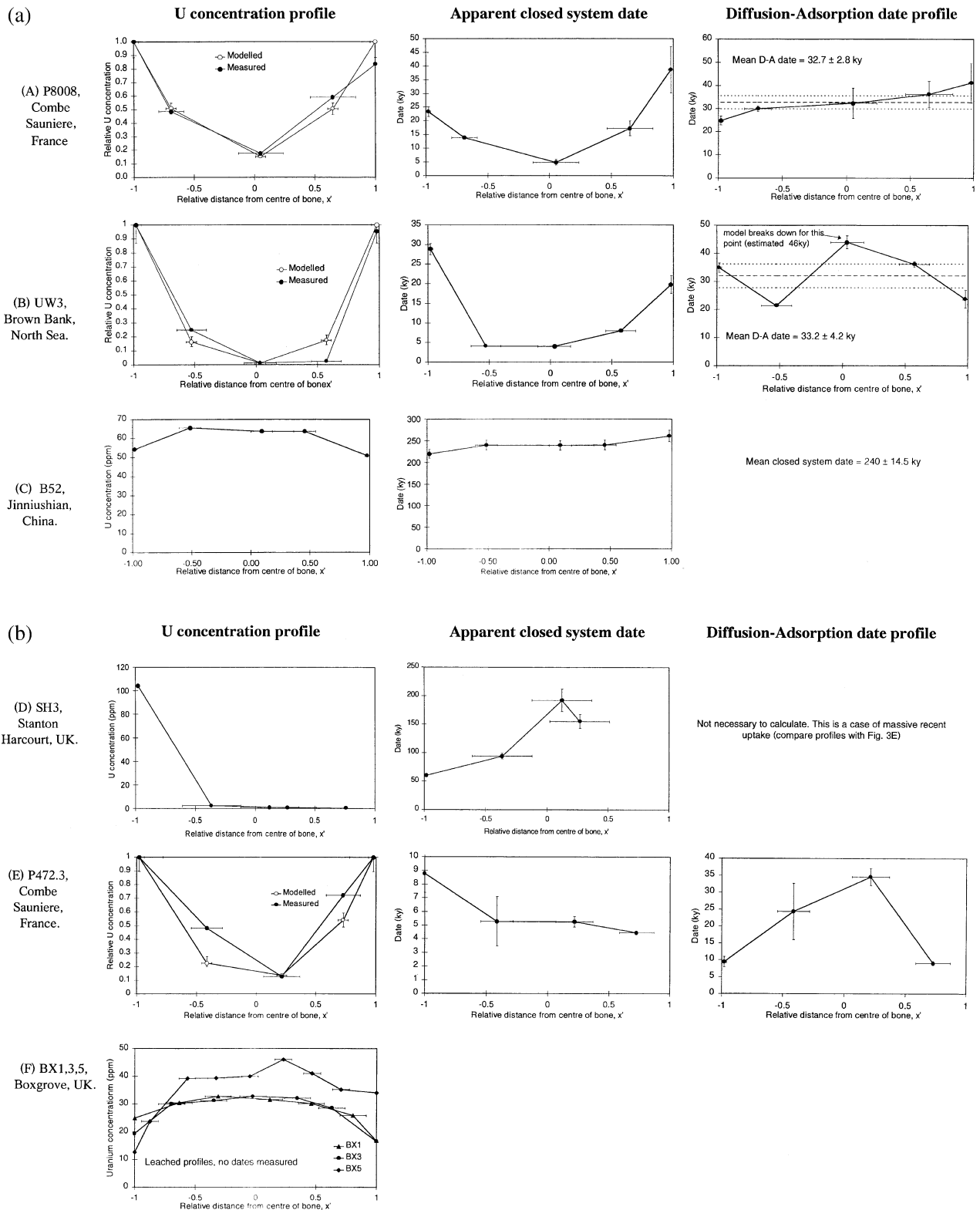


Fig. 5. U concentration, closed-system, and diffusion-adsorption (D-A) date profiles for selected bones. By comparison with the predictions of the D-A model (Fig. 3), these bones can be categorized into (A and B) those that appear to fit the D-A model under constant conditions, (C) equilibrium early uptake, (D) massive recent uptake, (E) moderate recent uptake, and (F) leached bones.



Table 3. U-series dates and control dates on bone samples.

Sample	Site	Est. whole early uptake bone date (ka) <sup>a</sup>	Mean diffusion-adsorption date (ka)	Std. error	Control date	Control date type/reference	Reliability criteria
P8008 (Fig. 5A)	Combe Sauniere, France	19.6	32.7	2.8	27690 ± 440 <sup>b</sup> yr BP	<sup>14</sup> C, OxA 6514 (unpublished date)	Acceptable
UW3 (Fig. 5B)	Brown Bank, North Sea	15.0	33.2	4.2	36600 ± 1200 <sup>b</sup> yr BP	<sup>14</sup> C, OxA 6307 (unpublished date)	Acceptable
B52 (Fig. 5C)	Jinnuishan, China	240	240	14.5	230–300 ky	Stratigraphy >213 ka (U-series on flowstone) and <300 <sup>231</sup> Pa- <sup>230</sup> Th concordance on bone (Chen and Yuan, 1988)	Acceptable (equilibrium early uptake)
B5600 (not shown)	Bercy, France (deep channel)	4.9 <sup>c</sup>	5.25 <sup>d</sup>	n/a	~6 ka	Middle Neolithic Chassean culture (Bocherens et al. 1997)	Acceptable (redox-controlled early uptake)
B8400 (not shown)	Bercy, France (dry bank)	3.4 <sup>c</sup>	5.3 <sup>e</sup>	n/a	~6 ka	Middle Neolithic Chassean culture (Bocherens et al. 1997)	Tentatively acceptable, but based on whole-bone U-series date
SH1 (not shown)	Stanton Harcourt, UK	5.2	17.3	4.8	190–250 ka	Oxygen isotope stage 7 (Buckingham et al. 1996)	Rejected as recent uptake on diffusion-adsorption date profile
SH3 (Fig. 5D)	Stanton Harcourt, UK	62	—	—	190–250 ka	Oxygen isotope stage 7 (Buckingham et al. 1996)	Rejected as recent uptake on closed-system date profile
P472.3 (Fig. 5E)	Abri Pataud, France	6.7	20.9	6.6	~28 ka	<sup>14</sup> C on associated material (Mellars, pers. comm.)	Rejected as recent uptake on diffusion-adsorption date profile; poor U profile fit
P8003 (not shown)	Combe Sauniere, France	— <sup>f</sup>	28.5	4.6	23850 ± 260 <sup>d</sup> yr BP	<sup>14</sup> C, OxA 6509 (unpublished date)	Possible leaching, not enough subsamples to be conclusive
BX 1,3,5 (Fig. 3F)	Boxgrove, UK	—	—	—			Clear leaching

<sup>a</sup> Estimated early uptake date if whole bone section was dated.

<sup>b</sup> Uncalibrated <sup>14</sup>C dates corrected for half-life of 5730 yr.

<sup>c</sup> Measured whole bone early uptake date.

<sup>d</sup> It was not possible to measure the date profile for this sample, so the diffusion-adsorption date is given as the mean of the dates from the two edges of the bone and a whole-bone date (see Table 4).

<sup>e</sup> Based on the measured whole bone date.

<sup>f</sup> Insufficient data.

Massive recent uptake is evident for the sample from Stanton Harcourt (Fig. 5D). The closed-system date profile is a characteristic  $\cap$  or M shape, and the U concentration profile is steep (compare with Fig. 3E). Closed-system dates on bones and teeth from Stanton Harcourt are consistently much younger than the proposed age of the site (>190 ka). For example, we obtain dates of 2.7 to 8.8 ka for bone SH1 (see Table A5), a massive underestimation. Typically, bones from Stanton Harcourt show steep U concentration profiles and unusually high U concentrations at the surface (66 to 664 ppm). For SH1, we see a difference in <sup>234</sup>U/<sup>238</sup>U at the surface of the bone (<sup>234</sup>U/<sup>238</sup>U=1.25) compared to the central samples (where <sup>234</sup>U/<sup>238</sup>U values are consistently around 1.13; see Table A5), which may be indicative of secondary uptake of uranium with a different <sup>234</sup>U/<sup>238</sup>U.

This site has remained waterlogged for most of its history, as witnessed by the preservation of organic material (e.g., wood and seeds; Buckingham et al., 1996), which may provide an explanation for the recent uptake. A bone sufficiently below the

water table would be isolated from mobile U, but higher in the sediment column, mobile U<sup>VI</sup> would be precipitated as U<sup>IV</sup> at the oxic-anoxic boundary, locally enriching the sediment with U (e.g., Thomson et al., 1993). An increase in oxidation potential, perhaps accompanying a fall in the water table, would lead to the remobilization of the U, giving an unusually high U concentration in the groundwater and leading to what we have termed massive recent uptake.

The sample from Combe Sauniere (P472.3, Fig. 5E) shows more moderate recent uptake. The closed-system dates fall in the range of 4.5 to 8.8 ka for this ~28-ka bone, and the bone is identifiable as a recent uptake bone by its  $\cap$ -shaped D-A date profile.

Of the 54 bones looked at in this study, ~20% showed evidence of leaching. We show example U concentration profiles for bones from Boxgrove (Fig. 5F), which have characteristic  $\cap$ -shaped leached U concentration profiles. Our interpretation of leaching is consistent with the dating evidence from other bones from the site, which give <sup>230</sup>Th/<sup>234</sup>U >

Table 4. Comparison of U-series and diagenetic measurement on bones from Bercy.

Sample	B8400	B5600
Burial environment	Dry bank	Deep channel
U (ppm)	39.7	0.298
Macro porosity ( $\text{cm}^3 \text{g}^{-1}$ )	0.287	0.073
Micro porosity ( $\text{cm}^3 \text{g}^{-1}$ )	0.032	0.077
$t'$	0.5	0.01
U-series date (ka)	$3.40 \pm 0.04$	$4.93 \pm .12^a$
Closed system		$5.31 \pm .57^b$
		$5.51 \pm .09^b$

<sup>a</sup> On whole bone.

<sup>b</sup> From outer edges of profile — the samples from the center of the bone failed. The value of  $t'$  gives an indication of the steepness of the U concentration profile (see Fig. 1); B8400 is much closer to equilibrium than B5600.

equilibrium (Rae, 1999). Because leaching is essentially a geochemical phenomenon, there is scope for a whole site to be affected. The three bones from Boxgrove, which appear to be leached to a similar degree, were from two different stratigraphic units separated horizontally by  $\sim 700$  m and vertically by  $\sim 1$  m (Pike and Hedges, in press). If leaching (or recent uptake; see below) can affect a whole site, U-series ages can be systematically overestimated, preserving stratigraphic relationships but still providing unreliable dates. On the other hand, it is possible that it is the response of the local soil matrix to changes in redox, hydrology, and U flux that controls the local U concentration in the groundwater through sorption or release of mobile U, so in some cases, leaching may be confined to a particular area of a site.

## 6. SUMMARY OF RESULTS

The dating technique we have developed requires the selection of either early uptake bones or those that have taken up U under constant geochemical conditions according to the D-A model and the rejection of bones that have undergone complex U uptake (e.g., leaching or recent uptake); see Figure 4. We

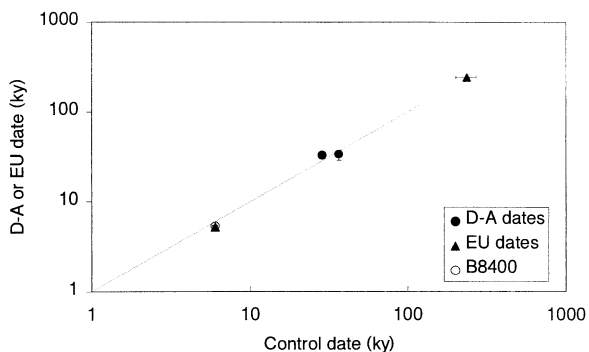


Fig. 6. Diffusion-adsorption (D-A) and early uptake (EU) dates on known-age bones (see also Table 3). The D-A dates and EU dates are accepted according to the criteria laid out in Figure 4. The result for B5600 (open circle) is speculative because it is based on a whole-bone U-series date rather than a date profile.

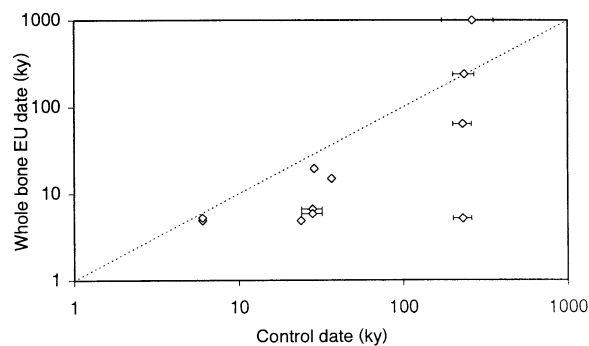


Fig. 7. Whole-bone closed-system dates on known-age bones. The closed-system ages have been estimated from the measured date profiles or measured on whole-bone samples. Note that U-series dates were not measured on obviously leached bones. Less than 30% of the early uptake (EU) dates agree with the control dates, demonstrating the unreliability of an a priori EU assumption.

give nine examples of bones we have attempted to date. Of these nine bones, four were found to pass the selection criteria, and the dates were calculated, two using the D-A model with constant conditions and two as cases of early uptake. All four agreed within error with the control dates (see Fig. 6). The remainder were rejected as recent uptake on the basis of their D-A or closed-system profiles, or they did not give sufficient data to be deemed acceptable.

As a complementary study, we have also measured closed-system whole-bone dates on samples that would normally be rejected on the basis of the U profiles alone. Combining these results with estimated closed-system dates on those for which profiles have been measured gives a picture of the overall reliability of U-series dating of bone using an a priori early uptake assumption (which approximates to the closed-system assumption). The comparison of early uptake dates with control dates is shown in Figure 7. Less than a third agree within error of their control dates, which clearly demonstrates the unreliability of the early uptake assumption. The picture is likely to be worse, because we did not date any bones that were clearly leached (and would give overestimated early uptake dates).

Although with our approach, we are forced to reject the majority of samples as unreliable, we believe that a single reliable U-series date is worth hundreds of dates for which the reliability is not known.

## 7. CONCLUSIONS

To understand U uptake in bone, it is necessary to view bone within the context of the burial environment, U-bone interactions, and bone diagenesis. Using Millard and Hedges's (1996) D-A model, we have illustrated how U uptake varies in response to geochemical changes in the burial environment.

Rather than assuming uptake as simply "early, linear," or somewhere in between, we predict complex patterns of uptake where the burial geochemistry is changing. The D-A model predicts the leaching of U from a bone in response to a drop in the U concentration of the groundwater or the increased uptake (termed "recent") whereby there is an increase in groundwater U. Furthermore, the D-A model predicts characteristic U and

U-series isotope profiles under these complex uptake schemes that allow the identification and rejection of these bones that would give grossly over- or underestimated U-series dates using the standard closed system assumption. By selecting bones on the basis of their measured profiles that appear to have undergone uptake under constant conditions, we can calculate a date using the D-A model with greatly improved reliability. In addition, we have identified and dated examples in which the U has entered the bone sufficiently rapidly to be considered early uptake, either because the bone has reached an equilibrium with the U in the groundwater or because redox changes shortly after burial have immobilized the U available for diffusion into the bone.

Despite the fact that datable samples are the minority, we believe that because the mode of U uptake is predicted from the profiles rather than being an a priori assumption, and the D-A model has a sound physical and chemical basis, this method of U-series dating of bone is more reliable than those currently employed.

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## REFERENCES

- Baas Becking L. G. M., Kaplan I. R., and Moore D. (1960) Limits of the natural environment in terms of pH and oxidation-reduction potentials. *J. Geol.* **68**, 243–284.
- Bocherens H., Tresset A., Wiedemann F., Giligny F., Lafage F., Lanchon Y., and Mariotti A. (1997) Diagenetic evolution of mammal bones in two French Neolithic sites. *Bull. Soc. Geol. Fr.* **168**(4), 555–564.
- Brookins D. G. (1988) *Eh-pH Diagrams for Geochemistry*. Springer-Verlag, Berlin, Germany.
- Buckingham C. M., Roe D. A., and Scott K. (1996) A preliminary report on the Stanton Harcourt channel deposits (Oxfordshire, England): Geological context, vertebrate remains and palaeolithic stone artefacts. *J. Quat. Sci.* **11**(5), 397–415.
- Chen T. and Yuan S. (1988) Uranium-series dating of bones and teeth from Chinese Paleolithic sites. *Archaeometry* **30**(1), 59–76.
- Cheng H., Lawrence Edwards R., Murrell M. T., and Benjamin T. M. (1998) Uranium-thorium-protactinium dating systematics. *Geochim. Cosmochim. Acta* **62**, 3437–3452.
- Cherdynstev V. V., Kazachevskii I. V., and Kuz'mina E. A. (1963) Isotopic composition of uranium and thorium in the supergene zone. *Geochemistry* **3**, 217–283.
- Chow S. N. and Carswell D. J. (1963) The effect of phosphate ion on the ion-exchange and solvent-extraction properties of thorium. *Aust. J. Appl. Sci.* **14**, 193–197.
- Crank J. (1975) *The Mathematics of Diffusion*. Oxford University Press, Oxford, UK.
- Edwards R. L., Cheng J. H., Murrell M. T., and Goldstein S. J. (1997) Protactinium-231 dating of carbonates by thermal ionization mass spectrometry: Implications for quaternary climate change. *Science* **276**, 782–786.
- Grün R., Schwarcz H. P., and Chadham J. (1988) ESR dating of tooth enamel: Coupled correction for U-uptake and U-series disequilibrium. *Nucl. Tracks Radiat. Meas.* **14**(1/2), 237–241.
- Hedges R. E. M. and Millard A. R. (1995) Bones and groundwater, towards the modelling of diagenetic processes. *J. Arch. Sci.* **22**(2), 155–165.
- Hedges R. E. M., Millard A. R., and Pike A. W. G. (1995) Measurements and relationships of diagenetic alteration of bone from three archaeological sites. *J. Arch. Sci.* **22**(2), 201–211.
- Hille P. (1979) An open system model for uranium series dating. *Earth Planet. Sci. Lett.* **42**, 138–142.
- Ikeya M. (1982) A model of linear uranium accumulation for ESR age of Heidelberg (Mauer) and Tautavel bones. *Jpn. J. Appl. Phys.* **21**(11), 690–692.
- Iyengar G. V., Kollmer W. E., and Bowen H. J. M. (1978) *The Elemental Composition of Human Tissue and Body Fluids*. Springer-Verlag, New York.
- Kaufman A. (1993) An evaluation of several methods for determining <sup>230</sup>Th/U ages in impure carbonates. *Geochim. Cosmochim. Acta* **57**, 2303–2317.
- McDermott F., Frisia S., Huang Y., Longinelli A., Spiro B., Heaton T. H. E., Hawkesworth C. J., Borsato A., Keppens E., Fairchild I. J., van der Borg K., Verheyden S., and Selmo E. (1999) Holocene climate variability in Europe: Evidence from δ18O, textural and extension-rate variations in three speleothems. *Quat. Sci. Rev.* **18**, 1021–1038.
- Millard A. R. (1993) *Diagenesis of Archaeological Bone: The Case for Uranium Uptake*. Ph.D. thesis, University of Oxford, Oxford, UK.
- Millard A. R. and Hedges R. E. M. (1995) The role of the environment in uranium uptake by buried bone. *J. Arch. Sci.* **22**, 239–250.
- Millard A. R. and Hedges R. E. M. (1996) A diffusion-adsorption model of uranium uptake by archaeological bone. *Geochim. Cosmochim. Acta* **60**, 2139–2152.
- Movius HL, ed. (1975) *Excavation of the Abri Pataud, Les Eyzies (Dordogne)*. American School of Prehistoric Research Bulletin No. 30. Peabody Museum of Archeology and Ethnology, Cambridge, MA.
- Neretnieks I. (1980) Diffusion in the rock matrix: An important factor in radionuclide retardation? *J. Geophys. Res.* **85**(B8), 4379–4397.
- Nielsen-Marsh C. M. (1997) *Studies in Archaeological Bone Diagenesis*. Ph.D. thesis University of Oxford, Research Laboratory for Archaeology, Oxford, UK.
- Nielsen-Marsh C. M. and Hedges R. E. M. (2000) Patterns of diagenesis in bone I: The effects of site environments. *J. Arch. Sci.* **27**(12), 1139–1150.
- Nielsen-Marsh C., Gernaey A., Turner-Walker G., Hedges R., Pike A., and Collins M. (2000) The chemical degradation of bone. In: *Human Osteology in Archaeology and Forensic Science* (eds. M. Cox and S. Mays), pp. 439–454. Greenwich Medical Media, London.
- Pike A. W. G. (2000) *U-Series Dating of Archaeological Bone Using TIMS*. Ph.D. thesis, University of Oxford, Oxford, UK.
- Pike A. W. G. and Hedges R. E. M. (2001) Sample geometry and U-uptake in archaeological teeth: Implications for U-series and ESR dating. *Quat. Sci. Rev.* **20**(5–9), 1031–1039.
- Pike A. W. G. and Hedges R. E. M. (in press) U uptake in Boxgrove bones: Implications for U-series and ESR dating. In *The Middle Pleistocene Site at Boxgrove, West Sussex, UK, Vol. II*. (eds. M. B. Roberts and S. A. Parfitt). English Heritage, London.
- Press W. H., Flannery B. P., Teukolsky S. A., and Vetterling W. T. (1996) *Numerical Recipes in Pascal*. Cambridge University Press, Cambridge, UK.
- Rae A. M. (1999) Uranium series dating. In: *Boxgrove: A Middle Pleistocene Hominid Site at Eartham Quarry, Boxgrove, West Sussex* (eds. M. B. Roberts and S. A. Parfitt), pp. 291–292. English Heritage, London.
- Rae A. M. and Ivanovich M. (1986) Successful application of uranium series dating of fossil bone. *Appl. Geochem.* **1**, 419–426.
- Rae A., Hedges R. E. M., and Ivanovich M. (1989) Further studies for uranium-series dating of fossil bones. *Appl. Geochem.* **4**, 331–337.
- Rigaud J.-P. (1986) Circonscription d'Aquitaine. *Gallia Préhistoire* **25**, 407–436.
- Roberts M. B. and Parfitt S. A. (2000) *The Middle Pleistocene Site at Boxgrove, West Sussex, UK*. English Heritage, London.

- Szwarcz H. P. (1980) Absolute age determination of archaeological sites by uranium series dating of travertines. *Archaeometry* **22**(1), 3–24.
- Szwarcz H. P. and Grün R. (1993) Electron spin resonance (ESR) dating of the lower industry. In: *The Lower Palaeolithic Site at Hoxne, England* (eds. R. Singer, B. G. Gladfelter, and J. J. Wymer), pp. 210–211. University of Chicago, Chicago.
- Szabo B. J. and Collins D. (1975) Ages of fossil bones from Br. interglacial sites. *Nature* **254**, 680–682.
- Szabo B. J. and Rosholt J. N. (1969) Uranium-series dating of pleistocene molluscan shells from southern California—An open system model. *J. Geophys. Res.* **74**(12), 3253–3260.
- Thomson J., Higgs N. C., Croudace I. W., Colley S., and Hydes D. J. (1993) Redox zonation of elements at an oxic/post-oxic boundary in deep sea sediments. *Geochim. Cosmochim. Acta* **57**, 579–595.
- van Calsteren P. and Schwieters J. B. (1995) Performance of a thermal ionisation mass spectrometer with a deceleration lense and post-deceleration detector selection. *Int. J. Mass Spectrom. Ion Processes* **146/147**, 119–129.
- Zhou L. P., McDermott F., Rhodes E. J., Marseglia E. A., and Mellars P. A. (1997) ESR and mass-spectrometric uranium-series dating studies of a mammoth tooth from Stanton Harcourt, Oxfordshire, England. *Quat. Sci. Rev. (Quat. Geochronol.)* **16**, 445–454.

**APPENDIX: INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) AND THERMAL IONIZATION MASS SPECTROMETRY (TIMS) RESULTS**

Table A1. ICP-MS U concentration profile measurements for Combe Sauniere bones. Samples are labelled a,b,c,... from the periosteal surface inward. All results are drift corrected. Sample width and distance into the bone (from the periosteal surface) were measured using vernier callipers. The parameter  $x'$  is the normalized position of the sample:  $x' = (x-l)/l$ , where  $x$  is the distance from the periosteal surface, and  $l$  is the distance to the center of the bone section (i.e., half the width). The error is calculated as the standard deviation of five replicate measurements on each sample. Site details given in Genest (in Rigaud, 1986).

Sample	Distance into bone (mm)	Sample width (mm)	$x'$	$dx'$	U (ppm)	Error ( $1\sigma$ )
P8003a	0.00	0.00	-1.00	0.00	0.708	0.022
P8003b	1.50	0.30	-0.68	0.06	0.312	0.023
P8003c	3.40	0.60	-0.27	0.13	0.083	0.015
P8003d	5.00	0.30	0.08	0.06	0.113	0.003
P8003e	7.90	0.30	0.70	0.06	0.287	0.014
P8003f	8.30	0.30	0.78	0.06	0.464	0.009
P8003g	9.30	0.00	1.00	0.00	0.387	0.018
P8004a	0.00	0.00	-1.00	0.00	0.272	0.002
P8004b	1.80	0.50	-0.63	0.10	0.306	0.023
P8004c	3.30	0.50	-0.31	0.10	0.226	0.016
P8004d	4.20	0.50	-0.13	0.10	0.255	0.009
P8004e	6.15	0.85	0.28	0.18	0.234	0.007
P8004f	9.60	0.00	1.00	0.00	0.258	0.011
P8008a	0.00	0.00	-1.00	0.00	1.953	0.021
P8008b	1.20	0.40	-0.76	0.08	1.347	0.032
P8008c	2.70	0.40	-0.46	0.08	0.698	0.032
P8008d	3.90	0.40	-0.22	0.08	0.400	0.003
P8008e	5.10	0.40	0.02	0.08	0.806	0.045
P8008f	6.40	0.40	0.28	0.08	1.050	0.040
P8008g	7.40	0.40	0.48	0.08	1.587	0.015
P8008h	10.02	0.00	1.00	0.00	2.090	0.036

Table A2. ICP-MS U concentration profile measurements for Bercy. Site details given in Bocherens et al. (1997).

Sample	Distance into bone (mm)	Sample width (mm)	$x'$	$dx'$	U (ppm)	Error ( $1\sigma$ )
B8400a	0.00	0.00	-1.00	0.00	54.00	0.27
B8400b	2.20	0.50	-0.41	0.13	49.18	0.22
B8400c	3.90	0.50	0.04	0.13	46.33	0.25
B8400d	6.00	0.60	0.60	0.16	33.89	0.32

Table A3. U concentration profile measurements for Boxgrove bones. Site details given in Roberts and Parfitt (2000).

Sample	Distance into bone (mm)	Sample width (mm)	$x'$	$dx'$	U (ppm)	Error ( $1\sigma$ )
BX1a	0.00	0.00	-1.00	0.00	24.94	0.13
BX1b	1.70	0.50	-0.63	0.11	30.51	0.18
BX1c	3.20	0.50	-0.31	0.11	32.77	0.22
BX1d	5.20	0.50	0.12	0.11	31.66	0.17
BX1e	6.80	0.50	0.46	0.11	30.18	0.15
BX1f	8.40	0.50	0.81	0.11	25.86	0.16
BX1g	9.30	0.00	1.00	0.00	16.776	0.093
BX3a	0.00	0.00	-1.00	0.00	19.48	0.13
BX3b	1.40	0.50	-0.70	0.11	30.07	0.23
BX3c	3.00	0.50	-0.35	0.11	31.20	0.18
BX3d	4.50	0.50	-0.02	0.11	32.85	0.23
BX3e	6.20	0.50	0.35	0.11	32.20	0.18
BX3f	7.50	0.50	0.63	0.11	28.54	0.15
BX3g	9.20	0.00	1.00	0.00	16.54	0.12
BX5a	0.00	0.00	-1.00	0.00	12.680	0.082
BX5b	0.90	0.50	-0.87	0.07	23.80	0.19
BX5c	3.10	0.50	-0.57	0.07	39.23	0.31
BX5d	4.80	0.50	-0.33	0.07	39.35	0.20
BX5e	6.80	0.50	-0.05	0.07	40.07	0.33
BX5f	8.80	0.50	0.23	0.07	46.11	0.21
BX5g	10.50	0.50	0.47	0.07	41.05	0.19
BX5h	12.20	0.50	0.71	0.07	35.22	0.33
BX5i	14.30	0.00	1.00	0.00	34.06	0.25

Table A4. TIMS U-series date on "whole"-bone sample B5600. Note: isotopic ratios given are activity ratios.

Sample	U (ppm)	$^{230}\text{Th}/^{232}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	Early uptake date
B5600	$0.29760 \pm 0.00202$	22.9	$1.1881 \pm 0.0150$	$0.04441 \pm 0.00102$	$4.93 \pm 0.12$

Table A5. U-series date profiles measured by TIMS.

Sample	$x$ (mm) <sup>a</sup>	$dx$ (mm) <sup>b</sup>	$x'$	$dx'^b$	U (ppm)	$^{230}\text{Th}/^{232}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	Early uptake date <sup>d</sup>
SH1a	0.10	0.10	-1.00	0.00	$644.12 \pm 9.49$	2324.6	$1.2515 \pm 0.0270$	$0.350 \pm 0.237$	Failed
SH1b	1.60	1.60	-0.67	0.33	$74.030 \pm 0.624$	811.8	$1.1427 \pm 0.0108$	$0.04371 \pm 0.00638$	$4.86 \pm 0.72$
SH1c	4.35	1.15	-0.11	0.23	$66.815 \pm 0.458$	401.7	$1.1259 \pm 0.0106$	$0.024320 \pm 0.000295$	$2.67 \pm 0.04$
SH1d	6.40	0.90	0.31	0.18	$134.838 \pm 0.805$	1605.5	$1.13267 \pm 0.00518$	$0.051323 \pm 0.000304$	$5.72 \pm 0.09$
SH1e	8.55	1.25	0.74	0.26	$163.37 \pm 1.06$	2704.6	$1.13469 \pm 0.00584$	$0.077967 \pm 0.000557$	$8.82 \pm 0.14$
SH3a	0.00	0.00	-1.00	0.00	$104.42 \pm 2.00$	369.3	$1.4063 \pm 0.0247$	$0.43561 \pm 0.00695$	$60.12 \pm 1.4$
SH3b	1.30	0.50	-0.37	0.24	$2.315 \pm 0.116$	124.0	$1.4670 \pm 0.0408$	$0.6018 \pm 0.0188$	$94.08 \pm 4.8$
SH3c	2.30	0.50	0.12	0.24	$0.90191 \pm 0.00786$	82.0	$1.4709 \pm 0.0348$	$0.8907 \pm 0.0354$	$192.4 \pm 19.9$
SH3d	2.60	0.50	0.27	0.24	$0.60396 \pm 0.00480$	109.2	$1.5077 \pm 0.0274$	$0.8113 \pm 0.0314$	$155.9 \pm 12.0$
SH3e	3.60	0.50	0.76	0.24	$0.56402 \pm 0.00407$	Failed	$1.3266 \pm 0.0354$	Failed	Failed
B5600 a	1.65	1.65	-0.70	0.30	$0.76073 \pm 0.00109$	50.4	$1.1428 \pm 0.0145$	$0.04770 \pm 0.00498$	$5.31 \pm 0.57$
B5600 b	4.45	1.15	-0.18	0.21	$0.001511 \pm 0.000123$	Failed	Failed	Failed	Failed
B5600 c	6.70	1.10	0.23	0.20	$0.001311 \pm 0.000104$	Failed	Failed	Failed	Failed
B5600 d	9.35	1.55	0.72	0.28	$0.25155 \pm 0.00272$	31.1	$1.1541 \pm 0.0171$	$0.049503 \pm 0.000628$	$5.51 \pm 0.09$
B52a	0.00	0.00	-1.00	0.00	$54.364 \pm 0.336$	41.4	$1.56095 \pm 0.0916$	$0.9473 \pm 0.0152$	$220.1 \pm 10.0$
B52b	0.80	0.30	-0.52	0.18	$65.511 \pm 0.242$	41039.5	$1.55811 \pm 0.00663$	$0.97618 \pm 0.00577$	$239.8 \pm 11.0$
B52c	1.80	0.30	0.09	0.18	$63.733 \pm 0.137$	7354.1	$1.56209 \pm 0.00345$	$0.97472 \pm 0.00410$	$238.5 \pm 11.0$
B52d	2.40	0.30	0.45	0.18	$63.772 \pm 0.105$	21167.0	$1.56550 \pm 0.00357$	$0.97722 \pm 0.00498$	$240.0 \pm 11.0$
B52e	3.30	0.00	1.00	0.00	$50.937 \pm 0.182$	63.8	$1.59860 \pm 0.00504$	$1.0078 \pm 0.00950$	$261.5 \pm 13.0$
UW3a	0.00	0.00	-1.00	0.00	$37.759 \pm 0.200$	19.3	$1.19318 \pm 0.00649$	$0.25160 \pm 0.00243$	$28.86 \pm 1.40^c$
UW3b	2.15	0.55	-0.53	0.12	$9.3754 \pm 0.0511$	325.5	$1.15373 \pm 0.00674$	$0.037263 \pm 0.000427$	$4.13 \pm 0.06$
UW3c	4.70	0.60	0.03	0.13	$0.42239 \pm 0.00123$	24.0	$1.16380 \pm 0.00782$	$0.03609 \pm 0.00182$	$4.00 \pm 0.20$
UW3d	7.15	0.55	0.57	0.12	$0.91872 \pm 0.00299$	112.4	$1.18485 \pm 0.00846$	$0.07085 \pm 0.00178$	$7.98 \pm 0.21$
UW3e	9.10	0.00	1.00	0.00	$35.9417 \pm 0.0893$	8.2	$1.18346 \pm 0.00254$	$0.20238 \pm 0.00255$	$19.82 \pm 2.30^c$
P8003a	0.10	0.10	-0.98	0.03	$0.51585 \pm 0.00570$	5.5	$1.1672 \pm 0.0321$	$0.26034 \pm 0.00829$	$23.48 \pm 5.1^c$
P8003b	1.55	0.65	-0.61	0.16	$0.9270 \pm 0.0109$	2.4	$1.1343 \pm 0.0334$	$0.1627 \pm 0.0100$	$5.9 \pm 7.3^c$
P8003c	3.60	0.60	-0.10	0.15	$0.03766 \pm 0.00114$	Failed	$1.6367 \pm 0.0812$	Failed	Failed
P8003d	5.40	0.60	0.35	0.15	$0.070186 \pm 0.000654$	Failed	$1.2471 \pm 3.6191$	Failed	Failed
P8003e	7.90	0.10	0.98	0.03	$0.40084 \pm 0.00226$	5.8	$1.0859 \pm 0.0171$	$0.33913 \pm 0.00872$	$33.43 \pm 6.5^c$
P8008a	0.00	0.00	-1.00	0.00	$1.34500 \pm 0.00323$	13.3	$1.06397 \pm 0.00606$	$0.21600 \pm 0.00211$	$23.38 \pm 1.6^c$
P8008b	1.50	0.50	-0.69	0.10	$0.65329 \pm 0.00144$	58.9	$1.05234 \pm 0.00635$	$0.12288 \pm 0.00277$	$13.87 \pm 0.5^c$
P8008c	5.10	0.90	0.05	0.19	$0.23698 \pm 0.00172$	7.9	$1.0514 \pm 0.0220$	$0.05444 \pm 0.00385$	$4.83 \pm 1.0^c$
P8008d	8.00	0.90	0.65	0.19	$0.79448 \pm 0.00218$	7.7	$1.05266 \pm 0.00716$	$0.18051 \pm 0.00368$	$17.21 \pm 2.4^c$
P8008e	9.70	0.00	1.00	0.00	$1.12098 \pm 0.00571$	6.3	$1.0855 \pm 0.0117$	$0.37079 \pm 0.00555$	$38.72 \pm 6.0^c$
P472.3a	0.00	0.00	-1.00	0.00	$4.17887 \pm 0.00997$	7.0	$1.07710 \pm 0.00475$	$0.1004 \pm 0.00119$	$8.80 \pm 1.40^c$
P472.3b	2.70	0.60	-0.41	0.13	$2.01119 \pm 0.00455$	81.6	$1.07350 \pm 0.00369$	$0.0475 \pm 0.01584$	$5.29 \pm 1.80$
P472.3c	5.60	0.70	0.22	0.15	$0.53365 \pm 0.00200$	16.6	$1.08445 \pm 0.00724$	$0.0522 \pm 0.00128$	$5.25 \pm 0.39^c$
P472.3d	7.95	0.65	0.73	0.14	$3.01866 \pm 0.00861$	477.5	$1.08140 \pm 0.00541$	$0.0403 \pm 0.00067$	$4.47 \pm 0.08$
P472.3e	9.20	0.00	1.00	0.00	Failed	Failed	Failed	Failed	Failed

All errors quoted at  $2\sigma$ . All isotopic ratios quoted as activity ratios.

<sup>a</sup> To center of sample.

<sup>b</sup> Radius of sample.

<sup>c</sup> Corrected for detrital thorium.

<sup>d</sup> Date calculated using measured machine precision or counting statistic errors if they are greater. Additional site details given in Buckingham et al. (1996), Chen and Yuan (1988), and Movius (1975).