

Na, K, Ca, Mg, and U-series in fossil bone and the proposal of a radial diffusion–adsorption model of uranium uptake



A.S. Cid^a, R.M. Anjos^{a,*}, C.B. Zamboni^b, R. Cardoso^a, M. Muniz^a, A. Corona^c,
D.L. Valladares^d, L. Kovacs^b, K. Macario^a, D. Perea^c, C. Goso^c, H. Velasco^d

^a LARA – Laboratório de Radioecologia e Alterações Ambientais, Instituto de Física, Universidade Federal Fluminense, Av. Gal Milton Tavares de Souza, S/N, Gragoatá, 24210-346, Niterói, RJ, Brazil

^b Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN), Centro do Reator de Pesquisa (CRPq), Av. Lineu Prestes 2242 – Cidade Universitária, 05508-000, São Paulo, SP, Brazil

^c Departamento de Evolución de Cuencas, Facultad de Ciencias, UDELAR, Iguá 4225, Montevideo 11400, Uruguay

^d GEA – Instituto de Matemática Aplicada San Luis (IMASL), Universidad Nacional de San Luis, CCT-San Luis CONICET, Ej. de los Andes 950, D5700HHW, San Luis, Argentina

ARTICLE INFO

Article history:

Received 30 March 2014

Received in revised form

20 May 2014

Accepted 23 May 2014

Available online

Keywords:

Fossil bone

Gamma-ray spectrometric U-series dating

Neutron activation analysis

Uranium uptake

Radial diffusion–adsorption model

ABSTRACT

Fossil bones are often the only materials available for chronological reconstruction of important archaeological sites. However, since bone is an open system for uranium, it cannot be dated directly and therefore it is necessary to develop models for the U uptake. Hence, a radial diffusion–adsorption (RDA) model is described. Unlike the classic diffusion–adsorption (D–A) model, RDA uses a cylindrical geometry to describe the U uptake in fossil bones. The model was applied across a transverse section of a tibia of an extinct megamammal *Macrauchenia patachonica* from the La Paz Local Fauna, Montevideo State, Uruguay. Measurements of spatial distribution of Na, K, Ca, and Mg were also performed by neutron activation analysis (NAA). Gamma-ray spectrometric U-series dating was applied to determine the age of the bone sample. From U concentration profile, it was possible to observe the occurrence of a relatively slow and continuous uranium uptake under constant conditions that had not yet reached equilibrium, since the uranium distribution is a U-shaped closed-system. Predictions of the RDA model were obtained for a specific geochemical scenario, indicating that the effective diffusion coefficient D/R in this fossil bone is $(2.4 \pm 0.6)10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Mean values of Na, K, Ca, and Mg contents along the radial line of the fossil tibia are consistent with the expected behavior for spatial distributions of these mineral elements across a modern bone section. This result indicates that the fossil tibia may have its mineral structure preserved.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Bones and teeth constitute an important component of Pleistocene geological deposits. They are primary archaeological materials, providing a chronology for our understanding of archaeology, paleontology, paleoclimatic changes, and later human evolution (Pike et al., 2002). Fossil bones are the often the only available material for chronological reconstruction of important sites. Several dating methods have been applied to archaeological materials: radiocarbon, amino acid racemization (AAR), electron spin resonance (ESR), optically stimulated luminescence (OSL), and U-series dating. There are problems specific to each of these methods

and it is desirable that important archaeological or paleontological sites are dated by as many methods as possible to provide independent checks on the results (Pike and Pettitt, 2003). For instance, AAR requires detailed knowledge of the environmental chemical conditions at the bone deposition site, not to mention calibration problems with the method. For both the ESR and OSL methods, the radiation dose rate to which the bone has been exposed must be estimated. It depends on environmental factors (such as humidity of deposits) and lithology. Knowledge about layer/site geometry is necessary as well (Van Der Plicht et al., 1989). OSL is widely used in Quaternary units. Luminescence age is a time measurement since the last exposure of sediments to heat or sunlight. Fossil bone comes, in general, from subaerial mudflow deposits, which are amongst the worst kind of sediments to OSL dating because of the lack of uniform exposure to sunlight. This can result in wrong ages (Corona et al., 2012).

* Corresponding author. Tel.: +55 21 26295843; fax: +55 21 26295887.

E-mail address: meigikos@mail.if.uff.br (R.M. Anjos).

By far, the most widely applied method of bone dating is radiocarbon analysis, especially by Accelerator Mass Spectrometry (AMS), based on bone or teeth collagen and context mollusk shells carbonate (Cione et al., 2001; Tonni et al., 2003; Gutiérrez et al., 2005; Corona et al., 2012). However, ^{14}C -AMS dating on bone collagen can be unreliable when preservation of bony material is poor, allowing a possible introduction of “young” contaminants, which cannot be completely eliminated during the sample pretreatment (Cione et al., 2001). If the radiocarbon sample preparation based on bone collagen does not follow strict criteria, ^{14}C ages obtained may be significantly younger than dates from other material in same context (Cione et al., 2001). According to Hedges and van Klinken (1992), the samples must fulfill the following conditions: no exogenous organic matter present, enough sample material, and well-preserved bone with more than 4% collagen. These restrictions prevent a number of bone samples from the Pleistocene megafauna to be dated by ^{14}C -AMS, since it is very difficult to find fossil bone with well-preserved collagen (Corona et al., 2012). Furthermore, the measurable age is limited to about 50 kyr.

For bones that are older than this limit or for which collagen is not well-preserved to be dated by ^{14}C -AMS, the ages can be obtained from the uptake of trace elements from the environment. Fossilization of bones and teeth occurs with profound changes in chemistry and structure, including orders of magnitude increases in trace elements, and massive recrystallization of original biogenic Ca-phosphate crystallites (Kohn, 2008). Living bone, for example, contains a few parts per billion ($\mu\text{g}/\text{kg}$) of U, but archaeological bone may contain 1–100 parts per million (mg/kg), taken up from the burial environment. The use of uranium as a tracer of fossil material has the potential to provide chronologies of up to 500 kyr, covering a section of the Pleistocene (Pike et al., 2002). Many attempts have been made, therefore, to date bones and teeth using the U-series methods. However, since bone is an open system for U, it cannot be dated directly (Millard and Hedges, 1996; Pike et al., 2002, 2005; Kohn, 2008). Implicit in the calculation of a date from U-series method is a model that can describe U uptake, and the reliability of a U-series date is dependent on the validity of this uptake model. Hence, several models for U uptake description have been developed (Pike and Pettitt, 2003). The most commonly employed model is the Early Uptake model, where U is deemed to have been taken up sufficiently shortly after burial for the bone to be approximate to a closed system. According to Ivanovich and Harmon (1992), U is fixed in the bone in the U^{IV} oxidation state, facilitated by the reduction of U^{VI} by decay products of the organic phase of bone, collagen. Since the bulk of collagen is lost rapidly from the bone (on the U-series time-scale at least), it is assumed that U will be taken up rapidly, and then uptake will cease. As an alternative to the early uptake assumption, the linear uptake, assumes that bones and teeth continue to take up U at a constant rate. While there have been some successful applications of these models, none have been found to be universally applicable, and in order to find a reliable method of U-series dating of bones and teeth new approaches to the modeling of U uptake in bones and in teeth were developed (Pike and Pettitt, 2003).

Millard and Hedges (1996) considered the chemistry of bone-uranium interactions and developed a diffusion–adsorption (D–A) model that 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. With the D–A model, they proposed that U was diffusing into bone as uranyl complexes, and adsorbing to the large surface area presented by the bone mineral hydroxyapatite. In other words, this model assumes diffusion followed by adsorption of U (an open system process from the geochemical point of view) and assumes no later migration of U-series isotopes (close system behavior). The D–A model predicts not only the rate of U uptake by bone but also

the spatial distribution of both U (concentration profiles) and U-series isotopes (apparent closed-system date profiles) across a bone section. Under constant conditions, U is diffusing from the inner and outer surfaces of the bone, giving a U-shaped U concentration profile that gradually flattens with time to a uniform U distribution when the bone reaches equilibrium with the U in the groundwater. Because the U is equilibrating with the outer portions of the bone section first, closed system U-series dates approach the true age of the bone toward the surfaces, but are underestimated toward the centre (Pike and Pettitt, 2003).

Pike et al. (2002) extended the D–A model by looking at how U uptake changes with changes in the burial environment. For example, a decrease in the uranium concentration in the groundwater will lead to desorption and diffusion of uranium out of the bone. U can be leached out of a bone in this way, but the insoluble Th would remain, giving a falsely high U-series date calculated using the closed system assumption. Because the U is leached from the outer and inner surfaces of the bone first, the U concentration profile becomes a characteristic M-shape at first, becoming U-shaped as leaching progresses, and will eventually become uniform at the new equilibrium concentration. In this scenario, an overestimation of the age of a bone can occur when calculated by U-series dating. Similarly, an increase in U concentration in the groundwater causes increased uptake of U by the bone, thereby giving underestimated closed system ages (Pike and Pettitt, 2003). Hence, Pike et al. (2002) proposed to use the shape of measured U concentration and U-series isotope profiles to identify and reject leached and recent uptake bones. This procedure also allows us to identify the mechanisms by which bones can undergo early uptake. Then, bones that show evidence of leaching or that show irregular profiles, are rejected as unsuitable for U-series dating.

Bones that fit the D–A model under constant conditions, show U-shaped date profiles, and the D–A model can be used to calculate an open system date. Results of its application have shown a good agreement between the calculated U-series dates and control dates (Pike et al., 2002; Pike and Pettitt, 2003). However, for any modeling work, it is important to build models as close to nature as possible, being essential to use all available information to describe the studied system. For U-series bone dating using U uptake models, an important factor to be considered is geometry. The D–A model is based in the solution of the diffusion adsorption equation (Fick's Second Law), approaching a fossil bone as an infinite plane slab. This procedure can be consistent with a tooth; however, it is not always the best geometry for a long bone, such as a tibia. Crank (1975) shows that there are a few differences in total uptake between a hollow cylinder, a solid cylinder, and a plane slab.

The primary objective of this paper is to provide a radial D–A model for U uptake, modifying the one dimensional D–A model proposed by Millard and Hedges (1996) and Pike et al. (2002). This approach that uses a cylindrical geometry to uptake of U across a transverse section of a long bone was applied in a tibia of an extinct megamammal *Macrauchenia patachonica* from Uruguay to estimate the effective diffusion coefficient D/R in this fossil bone. The behavior of other trace elements in fossil skeletal material, including its elementary constituents, such as Ca, K, Mg, and Na, are also shown to provide additional information about the conservation of this tibial bone tissue.

2. Materials and methods

2.1. Experimental procedure

2.1.1. Sample: origin and description

The Litopterna were native ungulates that inhabited South American terrestrial environments. They became extinct at the end

of the Pleistocene and beginning of the Holocene (Scherer et al., 2009). *M. patachonica* was an herbivore mammal representative of this order, with long and slender legs, long neck, small head and teeth well adapted to eating tough grass. With about 2.5 m in body length, and about 1.8 m high at the shoulder, it had a massive skeleton (weight ~1 tonne). The original specimen was discovered by Charles Darwin during the voyage of the Beagle (Owen, 1838; Keynes, 2001). Since then, more *Macrauchenia* fossils have been found, mainly in Patagonia, Argentina, but also in Bolivia, Paraguay, Chile, Brazil, and Uruguay.

Fig. 1 illustrates the geographic distribution of the *M. patachonica* during the Pleistocene in South America (Scherer et al., 2009). This figure also shows the locality where the material described in this study was collected. The fossil remains come from a fossiliferous assemblage next to La Paz city (34° 45' 24" S, 56° 15' 53" W), Montevideo State, Uruguay. This fossiliferous assemblage, known as La Paz Local Fauna, includes skeletal remains of characteristic Pleistocene taxa: *Glyptodon* sp., *Doedicurus* sp., *Panochthus* sp., *Lestodon* sp., *M. patachonica*, *Stegomastodon waringi*, *Toxodon platensis*, *Arctotherium bonniense*, among others (Corona et al., 2012).

Previous studies (Sambridge et al., 2012) showed that solid thick bones, such as long bones, provide the best chance for obtaining U-profiles data sets that can be modeled. Bones with obvious porosities often show highly variable U concentration profiles close to the pores as well as the presence of detrital ^{238}U or ^{232}Th . Thus, the material studied was a tibial bone of *M. patachonica* collected by researchers of the Departamento de Evolución de Cuencas, Facultad de Ciencias, UdelaR, Uruguay. Since the application of the D–A model requires the measurement of spatial distributions of trace elements across a bone section, small transverse cross-sections of bone were removed from the mid-shaft of a long bone using a circular diamond saw. Fig. 2 shows this bone sample and its preparation procedure. Although it is a fossil bone, its macroscopic structure was not changed with respect to a modern bone. Externally, it is possible to observe a layer of a few millimeters thick of compact bone tissue and, internally, a spongy bone tissue. The space corresponding to the medullary cavity appears completely filled by a carbonate precipitate that is very common to be found at the sampling site. The most of the fossil bones from the La Paz Local Fauna have carbonate in the form of clast or as a cement. The crusts and carbonate nodules can be formed during the burial, mainly during the early diagenetic time (Corona et al., 2012).

The disk that was removed from the tibia (see Fig. 2) had an average diameter of 8 cm and 1 cm thick. Two sets (A_i and B_i , where

$i = 1–10$) were collected along its radial line to measure the Ca, K, Mg, Na, and U contents by neutron activation analysis. The transverse surface was roughly polished to remove major surface topography and then it was ultrasonicated in distilled water to remove as much sediment as possible. After, each one of 20 samples were ground to powder, dried, packed in polyethylene bags, and sealed. A second disk was removed to determine the disequilibrium between ^{230}Th and its parent ^{234}U by gamma-ray spectrometry.

2.1.2. Neutron activation analysis

Contents of Ca, K, Mg, Na, and U in fossil bone samples were measured by Neutron Activation Analysis (NAA), performed at the IEA-R1 research reactor, Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), Brazil. In this technique, fossil samples and certified standard reference material (NIST – 1486 Bone Meals, 1400 Bone Ash, and Standard solutions obtained from high purity metals) were irradiated together, with thermal neutrons, allowing the simultaneous activation of these materials under the exact same irradiation conditions. Gamma rays emitted by the radioactive isotopes were then analyzed by gamma spectrometry. Standard reference materials were analyzed for quality control.

Several aliquots of each one of 20 samples and the standard were accurately weighed, sealed into individual pre-cleaned polyethylene bag and irradiated in the IEA-R1 nuclear reactor (3–4.5 MW, pool type). Samples of 80–100 mg were irradiated for a short time (30–60 s) using the pneumatic station for Ca, K, Mg and Na determination. Samples of 200–250 mg were irradiated for a long time (4–8 h) in the core of the reactor for U determination. The determination of P, using ^{31}P (n, α) ^{28}Al reaction, was not possible due the interferences reactions ^{28}Si (n, p) ^{28}Al and ^{27}Al (n, γ) ^{28}Al . Gamma spectrometry was performed using a 60% efficiency high-purity Germanium detector (an extended range coaxial HPGe detector, model GX6020) coupled to a low-background shield (model 747), both manufactured by CANBERRA. Activity concentrations were obtained using an in-house software. The uncertainty associated ranged from 3 to 9% for Ca, K, Mg, Na, and U contents. Finally, spatial distributions of Na, K, Ca, Mg, and U across a transverse section of the fossil material were constructed. Mean values were obtained for each pair of samples A_i and B_i (A_i and B_i , where $i = 1–10$).

2.1.3. Gamma-ray spectrometry measurements

U-series dating relies on the fact that during fossilization bones may incorporate U but not Th or Pa. An age can be calculated from the activity of Th and Pa that has been produced by the decay of U in

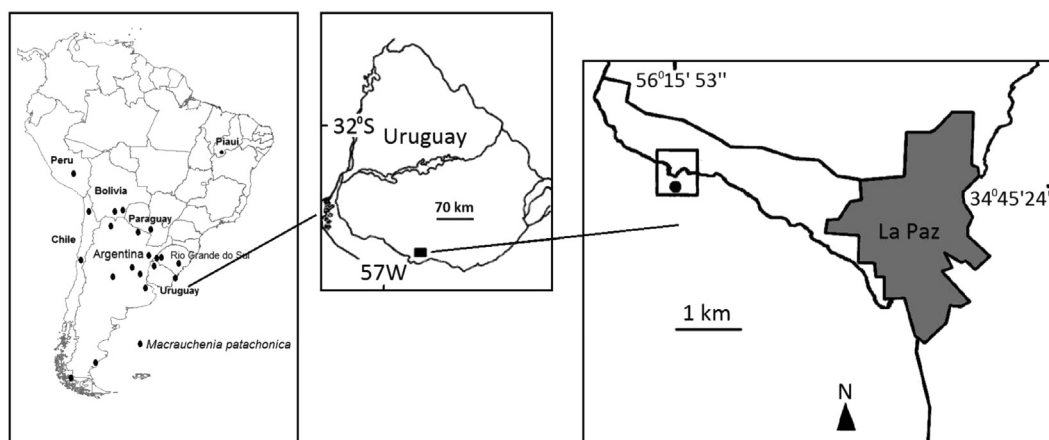


Fig. 1. Geographic distribution of the *Macrauchenia patachonica* during the Pleistocene in South America and the locality where the material described in this study was collected: The La Paz Local Fauna. Modified from Scherer et al. (2009) and Alvarenga et al. (2010).

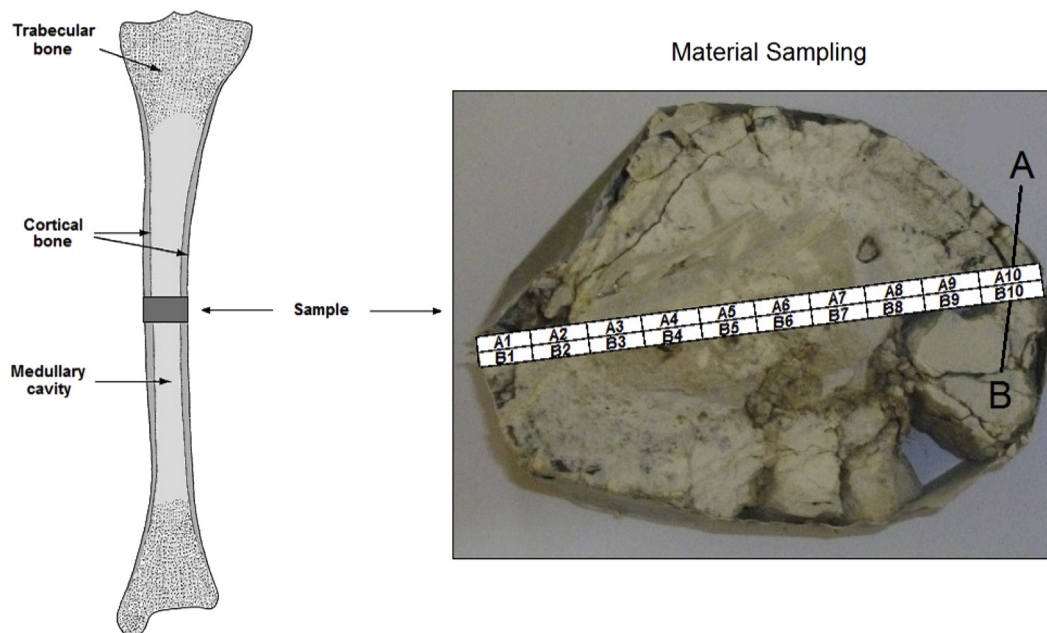


Fig. 2. Schematic section of the major components of a long bone, indicating the position where the fossil material sample was collected. Two sets (A_i and B_i , where $i = 1-10$) were collected along its radial line.

the fossil. The relevant age determining ratios of the ^{238}U and ^{235}U decay chains are those of $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$, respectively (Simpson and Grun, 1998).

Amounts of ^{234}U , ^{235}U , ^{238}U , ^{231}Pa , and ^{230}Th were obtained using the conventional technique of gamma ray spectrometry (Anjos et al., 2005, 2006, 2010). Samples were prepared and analyzed at the Laboratory of Radioecology of the Physics Institute of the Federal Fluminense University. In order to obtain $^{230}\text{Th}/^{234}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{231}\text{Pa}/^{235}\text{U}$ ratios it was used a 55% efficiency high-purity germanium detector (an extended range HPGe detector, model GX5522, with U-style cryostat) coupled to an ultra-low-background lead shield (model 777), both manufactured by CANBERRA. The energy resolution at the ^{60}Co gamma-ray line (1332 keV) was 2.0 keV.

The second disk removed from the mid-shaft of the tibia, with an average diameter of 8 cm and 1 cm thick, was also ground to powder, dried, carefully homogenate, packed in a cylindrical container, and sealed. The efficiency calibration was performed using International Atomic Energy Agency reference material for U activity determination: RGU-1 (IAEA, 1987). This reference material was also carefully homogenate and packed in an identical cylindrical container to avoid geometry corrections. Since this material has a density value next to bone sample, attenuation corrections due to the effects of self-absorption from low-energy gamma rays were also avoided. Before the measurements, the containers were kept sealed during 4 weeks, in order to reach the equilibrium of the ^{238}U and ^{232}Th series and their respective progeny. It was assumed that ^{220}Rn and ^{222}Rn could not escape from the sealed containers after closure. Energy spectra from each sample were accumulated during 24 h. The standard IAEA sample was measured at the same conditions and geometry to obtain the experimental efficiency–energy curve. After each measurement, one water-filled plastic cylindrical container was placed in the detection system during the same counting period, in order to collect the background count rates. A water-filled container gives a background radiation spectrum under the same conditions of the samples measured. In general, distilled water can be used as matrix, since it has similar

density of fossil bone samples and it is free of uranium-series isotopes.

The ^{234}U and ^{230}Th activities were determined directly from the gamma rays emitted from these nuclides at energies of 53.2 keV and 120.9 keV for ^{234}U and 67.7 keV for ^{230}Th . The ^{238}U activity was determined from its short-lived daughters, ^{234}Th and $^{234\text{m}}\text{Pa}$, at 63.3 keV, 92.6 keV, and 1001.2 keV. Since these gamma rays are situated near the extreme low or high energy ends of the spectrum, the gamma-rays emitted from ^{235}U at 143.8 keV, 163.4 keV, and 205.3 keV were used to check the ^{238}U activity in the intermediate energy part of the spectrum, using the established $^{235}\text{U}/^{238}\text{U}$ activity ratio of 0.046. The ^{231}Pa activity was measured from its short-lived daughters, ^{227}Th , ^{223}Ra , and ^{219}Rn at 50.2 keV, 154.3 keV, 236.0 keV, 269.4 keV, and 271.0 keV. Technical details of measurements and analysis can be obtained in Berzero and Caramella-Crespi (1997) and Yokoyama et al. (2008).

2.2. Radial diffusion–adsorption (RDA) model

The interpretation of U concentration profiles in fossil bones can be performed applying the Diffusion–Adsorption model (D–A model), proposed by Millard and Hedges (1995, 1996) and modified by Pike et al. (2002). It is based on the mathematical solution of a diffusion–adsorption equation, based in Fick's Second Law, where the rate of uranium diffusion is controlled by the diffusion coefficient, D ($\text{cm}^2 \text{s}^{-1}$), which is reduced for diffusion in a porous material such as bone (Crank, 1975; Pike et al., 2002):

$$\frac{\partial C}{\partial t} = \frac{D}{R+1} \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (2.1)$$

where C ($\mu\text{g g}^{-1}$) is the uranium concentration, R is the volumetric equilibrium constant: 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.

Solutions of Eq. (2.1) can be obtained for a number of initial and boundary conditions covering simple concentration distributions

and diffusion geometries. These solutions have two distinct types: either an infinite trigonometric series or solutions involving the error function (Crank, 1975). The most widely used geometry considers diffusion in a plane sheet, which considers a one-dimensional diffusion in a medium bounded by two parallel planes, e.g., the planes at $x = -l, x = l$. These will apply in practice to diffusion into a plane sheet of material so thin that effectively all the diffusing substance enters through the plane faces and a negligible amount through the edges. According to this approach, the uptake of uranium can be determined by four factors: the groundwater U concentration (C), the diffusion coefficient for uranyl in the pores of bone (D), the thickness of the bone ($2l$), and the volumetric equilibrium coefficient (R). The diffusion equation can be expressed in terms of the dimensionless variables reduced time (t') and reduced distance squared (X'^2), where $t' = tD/Rl^2$ and $X' = x/l$, t is time, l is the half-width of the tissue considered, and x is distance from the center of tissue.

According to the D–A model, a bone that has taken up U under constant conditions, but has not yet reached equilibrium, shows that U and closed-system date profiles are both U-shaped and so 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 (Pike et al., 2002). Many burial bones present a characteristic U-shaped diffusion profile as the concentration is measured from the surface to the interior of bone. Despite of the simplicity of the D–A model, it predicts this characteristic diffusion profile of uranium concentration which gradually levels out with time (see Fig. 3a). Given these parameters it is possible to calculate the uranium concentration at any time for any depth into the bone (Millard and Hedges, 1995; Pike et al., 2002).

The classical D–A model with plane sheet geometry has been successful in describing diffusion profiles of tooth enamel and cortical bone from the mid-shaft of long bones of larger mammals, with a thickness ranging from 1 to 6 mm (Millard and Hedges, 1995, 1996; Eggins et al., 2005; Kohn, 2008). However, taking into account the features of large bones (see Fig. 2) it is noted that this geometry of linear flux in a solid bounded by two parallel planes is not suitable for its study. However, we can build a new model with radial geometry (RDA model), as close to nature as possible, since for U-series bone dating using U uptake models geometry is an important factor. In this case, one might think about a long bone as a solid cylinder, with only one boundary condition (on the outside), so that diffusion occurs only from the outer surface toward the center. The way of viewing this problem involves a new line of symmetry, which defines the length scale. For the solid cylinder, that line is the center of the solid cylinder. For the plane sheet geometry, it occurs at the halfway point between the external surface of the bone and the inner boundary between the bone and the marrow cavity. The big difference between classical D–A and RDA models is the distance: for the solid cylinder, that distance is of several centimeters. For the plane sheet, it is the thickness of the bone wall divided by two. That might be on the order of a half cm or less.

Using coordinate transformations, Eq. (2.1) can be modified to describe radial flux in an infinite circular cylinder, in which the solution is of the form of Bessel's equation (Crank, 1975). If in a cylinder of radius a , the boundary conditions are:

$$\begin{aligned} C(r, t) &= C_0, & r &= a, & t > 0 \\ C(r, t) &= 0, & 0 < r < a & & t = 0 \end{aligned} \tag{2.2}$$

where C_0 is the U concentration in the sample surface.

The solution of Eq. (2.1) is (Crank, 1975):

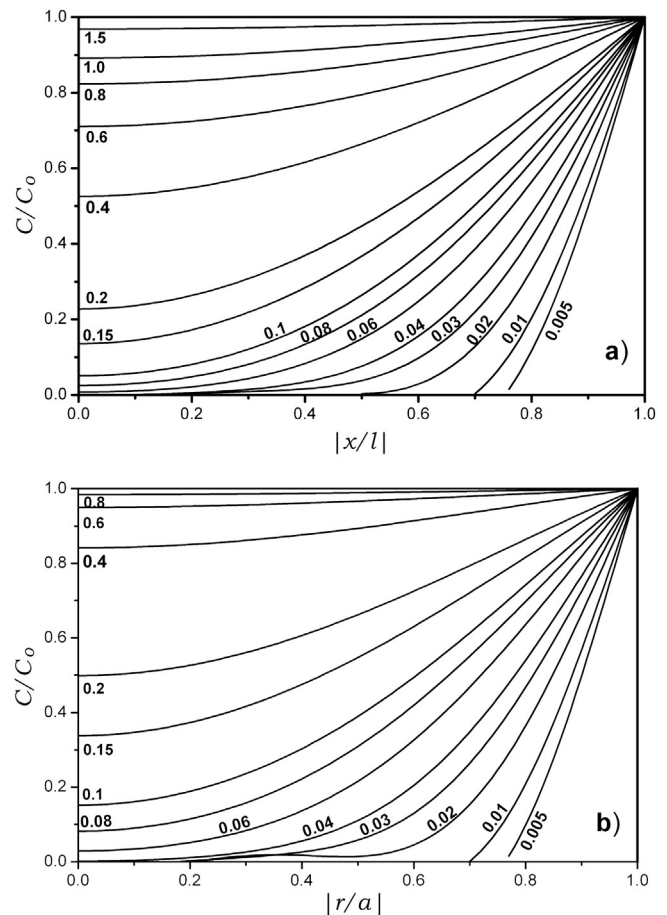


Fig. 3. Concentration distributions at various times in a) the sheet $-l < x < l$ (numbers on curves are values of $t' = tD/Rl^2$); and b) the solid cylinder of radius a (numbers on curves are values of $t' = tD/Ra^2$). Modified from Crank (1975).

$$C(r, t) = C_0 \left\{ 1 - 2 \sum_{n=1}^{\infty} \frac{1}{\alpha_n} \frac{J_0(r\alpha_n)}{J_1(a\alpha_n)} \exp\left(-\frac{D}{R} \alpha_n^2 t\right) \right\} \tag{2.3}$$

where $J_0(x)$ and $J_1(x)$ are the Bessel functions of the first kind of zero and first order, respectively; D is the diffusion coefficient for uranyl in the pores of bone; R is the volumetric equilibrium coefficient; and α_n are the positive roots of $J_0(a\alpha_n) = 0$.

The solutions of Eq. (2.3) can be written in terms of two dimensionless parameters $t' = tD/Ra^2$ and r/a . Curves showing C/C_0 as function of r/a for different values of t' are reproduced in Fig. 3b.

2.3. U-series disequilibrium dating

U-series disequilibrium dating method is based on the decay of ^{238}U and its radioactive daughter nuclei, provided the system is chemically closed. One of the decay products of ^{238}U is ^{234}U , which in turn decays with a half-life of $245,620 \pm 260$ yr into ^{230}Th . The ^{230}Th itself decays with a half-life of $75,584 \pm 110$ yr (Cheng et al., 2013). This decay is the only source for ^{230}Th available in nature (Van Der Plicht et al., 1989). Taking into account the decay of these nuclides, the age can be determined by the graphical solution of the relationship given by the $^{230}\text{Th}/^{234}\text{U}$ ratio, which is the extent of the growth of the daughter ^{230}Th toward secular radioactive equilibrium with its parent (Schwarcz, 1980; Ivanovich and Harmon, 1992):

$$\frac{{}^{230}\text{Th}}{{}^{234}\text{U}}(t) = \left[\frac{1 - e^{-\lambda_{230}t}}{\frac{{}^{234}\text{U}}{{}^{238}\text{U}}(t)} \right] + \left[\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right] \cdot \left[1 - \frac{1}{{}^{234}\text{U}/{}^{238}\text{U}}(t) \right] \cdot \left[1 - e^{-(\lambda_{230} - \lambda_{234})t} \right] \quad (2.4)$$

where ${}^{230}\text{Th}$, ${}^{234}\text{U}$ and ${}^{238}\text{U}$ represent activity of each of these three radionuclides in the bone sample and λ_{230} and λ_{234} are the decay constant of ${}^{230}\text{Th}$ and ${}^{234}\text{U}$, respectively. The solution of Eq. (2.4) represents the U–Th method.

In the case of ${}^{235}\text{U}$ decay series, the first decay product ${}^{231}\text{Th}$ has a half-life of only 25.6 h and decays promptly into ${}^{231}\text{Pa}$; the accumulation of ${}^{231}\text{Pa}$ is controlled by its own half-life of $32,760 \pm 220$ yr (Robert et al., 1969). When viewed on a time-scale measured in years, the half-life of intermediate product ${}^{231}\text{Th}$ is so short that its activity can be taken as always equal to that of ${}^{235}\text{U}$. The half-lives of all the decay products of ${}^{231}\text{Pa}$ are relatively short, so that they are essentially in equilibrium with ${}^{231}\text{Pa}$. The age of a fossil bone can be easily determined from the following equation (Berzero and Caramella-Crespi, 1997):

$${}^{231}\text{Pa} = {}^{235}\text{U} \left(1 - e^{-\lambda_{231}t} \right) \quad (2.5)$$

where ${}^{235}\text{U}$ and ${}^{231}\text{Pa}$ are the activities of each of these two radionuclides in the bone sample, respectively, and λ_{231} is the decay constant of ${}^{231}\text{Pa}$. The solution of Eq (2.5) represents the U–Pa method.

3. Results

3.1. Distributions of Ca, Mg, K, and Na

Contents of Ca, Mg, K, and Na in fossil bone material of the extinct *M. patachonica* were evaluated as well as the capability of such long bone to store these mineral elements. Analyses of these values reveal that the distributions of the elements in the sets A and B are similar. Therefore, Fig. 4 shows the mean values from sets A and B of Ca, Mg, K, and Na contents along the bone radial line. Given the heterogeneity of distribution of these elements, two main accumulation clusters of mineral elements were identified. The first relates to the outermost layer of the bone (cortical or compact tissue). The other relates to the interior cavity of the bone (marrow or medullary cavity). Observations show that the Ca distribution along the bone radial line is higher in the cortical bone. On the other hand, the distributions of Na, K, and Mg show an opposite behavior, being higher in the soft fatty tissue in the interior cavity of the long bone. These findings are consistent with that expected behavior for spatial distributions of mineral elements across a modern bone section (Maynard et al., 1979; Brickley and Ives, 2008). Table 1 shows the distribution of Ca, Mg, K, and Na in fossil bone matrix from our Pleistocene specimen, which is known to be highly susceptible to diagenesis (Brickley and Ives, 2008). Data were obtained from average values presented in Fig. 4. The values are expressed in units of equivalent ground concentrations: weight % of whole tissue with respect to the total inorganic plus organic phases. However, diagenesis would make the organic phase disappear from the examined fossil bone system. From this table, one can verify that Ca forms the main component of the fossil skeletal system ($35 \pm 5\%$). Proportions of other mineral elements were stored in small amounts (the total amount of Mg, K, and Na is around 1%). Composition of modern adult bones can be obtained from Maynard et al. (1979) and Elliott (2006), although the mineral composition of bones is somewhat variable according to age, state of nutrition, and species. Maynard et al. (1979) related that the

mean values of inorganic phase elements (obtained from ash, i.e., on moisture and fat free basis) is about 36% of Ca, 17% of P, and 0.8% of Mg. Bones also contain minor amounts of Na, K, Cl, F, and traces of others. As shown in Table 1, similar findings have also been reported by Elliott (2006): 36% of Ca, 0.7% of Mg, 0.3% of K, and 0.9% of Na. This information discloses that the examined fossil bone system has similar features to modern bones. Taking into account that the bones are subjected to several changes, depending on the burial environment and the that the organic phase could be absent due to diagenesis, then our results also suggest that the studied bone was not subjected to microbial or biotic erosion or the processes that are affected by drastic physical or chemical changes. Thus, the fossil bone sample analyzed in this work is well preserved in what concerns its mineral structure.

3.2. U distribution

Table 2 shows the amount of U present in the fossil bone sample from tibial tissue of *M. patachonica*. The high value of U content observed (50 ± 4 mg/kg) indicates the occurrence of a high U uptake. This finding suggests a fast and short U accumulation, which may be described by Early Uptake model.

The application of the D–A models requires the measurement of spatial distributions of U across a fossil bone section. Fig. 5 shows the mean values from sets A and B (see Fig. 2) of U contents along the radial line of the tibial bone tissue of *M. patachonica*. From this figure, it can be observed that the uranium uptake from the burial bone presents a characteristic U-shaped diffusion profile as the concentration is measured from the surface to the interior of bone. This shape of uranium concentration profile agrees with the assumptions made by the D–A models and can give us additional information on the uptake history of this bone.

Since U uptake, according to the D–A model, represents an equilibrium between the U adsorbed on the mineral surface of the bone and U in the groundwater, a drop in groundwater U concentration would cause desorption of U and diffusion in the reverse direction, leaching uranium from the bone and usually leading to characteristic M or n-shaped profiles (Millard and Pike, 1999; Pike and Hedges, 2001). So, one might use measured U profiles of bones to reject leached bones, bones that show inhomogeneity such as cracks or patchy diagenetic alteration or where a complex geochemistry renders simple monotonic diffusion invalid (Pike and Hedges, 2001). Taking into account these arguments, Fig. 5 (and Table 2) suggests that the fossil bone studied can be considered as a closed-system, which has taken up uranium under constant conditions, but has not yet reached equilibrium. In this condition, the D–A model gives the same data at all positions of the bone. Therefore, we can calculate an overall date as the mean of the D–A dates in the profile and use the standard error of this mean as a measure of reliability (Pike et al., 2002).

Like the classical one-dimensional D–A model (for plain geometry) of Millard and Hedges (1996), our RDA model cannot be directly solved for time t , but given the parameters a , D , and R , a date t' with uptake according to the RDA model can be calculated using Eq. (2.3). The parameter t' and associated confidence limits can be estimated from a measured U concentration profile by fitting of the RDA model to U profile (Pike et al., 2002). Fig. 5 shows the least squared fit of U profile from tibial bone tissue of the *M. patachonica*, using the RDA model with cylindrical geometry (Eq. (2.3)), resulting in the value of $t' = 0.10 \pm 0.03$ (Fig. 3b).

In Fig. 6 we aim to compare this finding with those predicted by classical D–A model to verify the magnitude of error that would be introduced if the two models were used inappropriately. It shows a fit of the diffusion equation for an infinite plane slab (see Fig. 3a). In this situation, a good fit can also be achieved, but with different

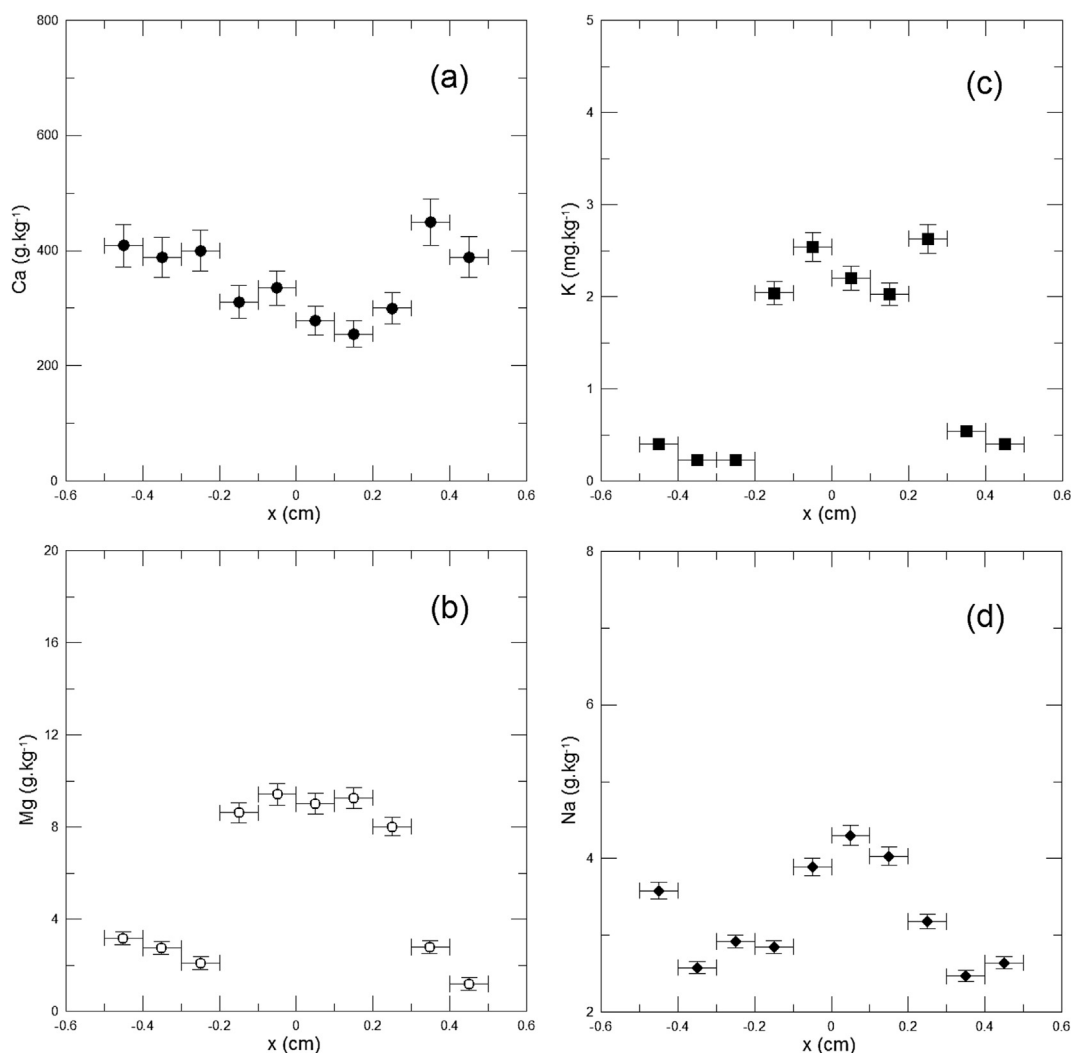


Fig. 4. Mean values from sets A and B (Fig. 2) of concentrations of (a) Ca; (b) Mg; (c) K; and (d) Na across a radial line of the tibial bone tissue from an extinct *Macrauchenia patachonica*.

value of $t' = 0.15 \pm 0.03$. The findings of $t' = 0.10 \pm 0.03$ (RDA model) and $t' = 0.15 \pm 0.03$ (classical D–A model) are not different from the statistical point of view. However, they suggest a discrepancy between our RDA model and the one-dimensional D–A model of Millard and Hedges (1996), stating the importance of choosing the best geometry for the U uptake. Undoubtedly, it is necessary to take more measurements of bone samples in order to obtain more results about the advantages of using RDA model. Unfortunately, a bone section is required if profiles are to be measured for the application of the RDA model. Understandably, museum curators are reluctant to allow the most valuable specimens to be cut or drilled.

Table 1

Composition of Na, K, Mg, and Ca along the bone radial line, a tibia (fossil remain) of extinct *Macrauchenia patachonica*. Data were obtained from average values presented in Fig. 4. Values of moderns adult bone composition is from Elliott (2006).

Element	Fossil bone (%)	Modern bone (%)
Ca	35 ± 5	36
Mg	0.6 ± 0.3	0.7
K	0.10 ± 0.08	0.3
Na	0.30 ± 0.06	0.9

The parameter t' is linearly correlated with D/R , since $t' = tD/Ra^2$. 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. According to Pike et al. (2002), D/R may be reduced by a factor of 100 in very dry conditions compared with those that are water saturated. Additionally, the main difference between cortical and trabecular (or medullary cavity) tissues is the lower porosity. This has the effect of reducing the diffusion coefficient (D), and the partition coefficient (k_d) of U and hydroxyapatite. According to Pike and Hedges (2001), bone, in typical burial environments, has D/R ranging from 10^{-14} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Taking into account that we are studying a cross section of a tibia and analyzing the variation in the U contents in its radial line, it is expected that the value of D/R is higher than in the cortical tissue. Thus, the value of D/R should be on the order of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$.

In order to test the RDA model for U uptake it is necessary to have data about the U distribution within bones of known age and environment. The age was obtained from gamma-ray spectrometry measurements and applying the U–Th and U–Pa methods. The findings are presented in Table 2. From this table, it is possible to

Table 2
Activity ratios and U-series ages (gamma spectrometry) for the fossil bone sample from an extinct *Macrauchenia patachonica*. ^{14}C -AMS age of enamel samples of a proboscidean molar, from the same stratigraphic level, is also reported. Values are in the 2σ range.

U (mg/kg)	$^{230}\text{Th}/^{232}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{231}\text{Pa}/^{235}\text{U}$	U–Th age (kyr)	U–Pa age (kyr)	^{14}C -AMS age (kyr cal BP)
50 ± 4	30 ± 5	1.00 ± 0.04	0.190 ± 0.008	0.35 ± 0.05	23.0 ± 1.1	20.4 ± 3.5	$20.9\text{--}21.6$

observe that the bone sample show high $^{230}\text{Th}/^{232}\text{Th}$ activity ratio, indicating that there has been little or no contamination with environmental Th. The accuracy evaluation of the U–Th and U–Pa methods can be obtained by comparing the results with those obtained by the radiocarbon method. Table 2 also shows results of enamel samples of a proboscidean molar from the same stratigraphic level, which was previously dated to $17,620 \pm 100$ yr BP by ^{14}C -AMS (Gutiérrez et al., 2005). Since this value represents a conventional radiocarbon age, the calibration was performed using the OxCal v4.2.3 software (Bronk Ramsey, 2009) with atmospheric data for Southern Hemisphere from Hogg et al. (2013) in the 2σ range. Therefore, the probability interval lies between 21580 and 20914 cal BP with 95.4% confidence. Table 2 shows the very good agreement found in the age determination between T–Th, U–Pa,

and ^{14}C -AMS methods, since it is possible to observe the values of 21.5–24.5 kyr, 16.9–23.9 kyr, and 20.9–21.6 kyr cal BP for U–Th, U–Pa and ^{14}C -AMS methods, respectively. Additionally, this probability interval is in agreement to radiocarbon dating performed on materials from the Guerrero Member of the Luján Formation, Argentine; which suggest that fossil deposition began about the Last Glacial Maximum (about 21 kyr BP) and continued until at least 10 kyr BP (Tonni et al., 2003). The agreement between such different methods again suggests that closed-system behavior can be assumed for this fossil bone. Applying the value of $t' = 0.10 \pm 0.03$ and the mean value of three ages (21.6 ± 1.0) kyr in $t' = tD/Ra^2$, we obtain the value of $D/R = (2.4 \pm 0.6)10^{-12} \text{ cm}^2\text{s}^{-1}$. On the other hand, if we had used the geometry of an infinite plane slab for the diffusion equation, the value obtained would be $(3.7 \pm 0.9)10^{-12} \text{ cm}^2\text{s}^{-1}$.

It is well known that modern bones contain only very small amounts of $U < 1\text{--}50 \mu\text{g kg}^{-1}$ and, as seen above, archaeological specimens may contain a few mg kg^{-1} . If U-uptake is the dominating geochemical process (as observed by the simple fact that fossil bones have higher U-concentrations than modern bones), a D/R ratio and hence the U profile age determination (based on a closed system assumption) would underestimate the correct age of the bone.

Sambridge et al. (2012) have proposed a new model, which is described for the uptake of U in an open system applied to the dating of fossil 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 . It constitutes a forward model for predicting ^{238}U , ^{234}U and ^{230}Th activity profiles across a bone given an age and diffusion coefficient. This model is based on the assumption of constant $^{234}\text{U}/^{238}\text{U}$ ratio at the surface making the age estimate critically dependent on the $^{230}\text{Th}/^{234}\text{U}$ ratios, while the measured $^{234}\text{U}/^{238}\text{U}$ ratios have only a small effect on the apparent ages inside the bone. This does not apply to closed system age calculations, which are also strongly dependent on measured $^{234}\text{U}/^{238}\text{U}$ ratios.

If we consider this model and suppose $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios are 1.0 and 0.19, respectively, lead to a closed system D/R of $2.4 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$, whereas the new model results is D/R of $2.6 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$. This indicates that corrections due to the U-dating bone in open systems should be important for older bones, and we can use a simple RDA model in order to estimate buried bone ages of the order of tens of kyr.

Thus, the value obtained is very important to support further dating studies, showing the feasibility of the application of new dating techniques on buried fossil samples, for which it is not possible to apply the ^{14}C -AMS technique, due to the difficulty of obtaining well-preserved bone with more than 4% collagen or the need to provide chronologies of more than 50 kyr.

4. Conclusions

In order to deepen the state of knowledge about the behavior on U profiles in fossil bones, we modified the one-dimensional D–A model of Millard & Hedges to account for radial diffusion of uranium. This procedure was adopted since the features of long bones,

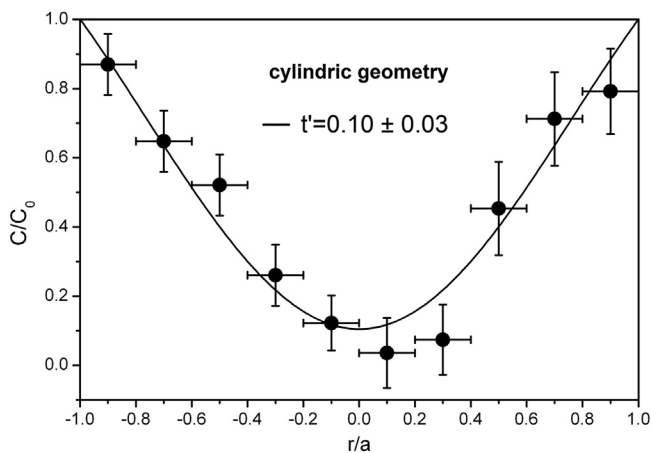


Fig. 5. Mean values from sets A and B (Fig. 2) of U contents across a radial line of the tibial bone tissue from an extinct *Macrauchenia patachonica*. The solid curve represents a fit of the diffusion equation for an infinite circular cylinder geometry, and obtaining $t' = 0.10 \pm 0.03$ (see Fig. 3b).

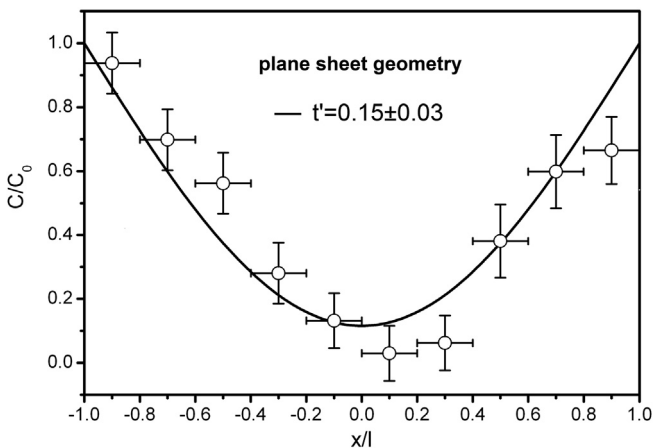


Fig. 6. Mean values from sets A and B (Fig. 2) of U contents across a radial line of the tibial bone tissue from an extinct *Macrauchenia patachonica*. The solid curve represents a fit of the diffusion equation for an infinite plane sheet geometry, obtaining $t' = 0.15 \pm 0.03$ (see Fig. 3a).

such as tibia, are not suitable for geometry of linear flux in a solid bounded by two parallel planes. In this way, it was developed the Radial Diffusion–Adsorption (RDA) model of U uptake using a cylindrical geometry for fossil bones. For any modeling work, it is important to build models as close to nature as possible. This model was applied in a transverse section of a fossil bone from an extinct megamammal *M. patachonica*. Bone samples were collected in the La Paz Local Fauna, Montevideo State, Uruguay, which is a fossiliferous assemblage with abundant remains of typical southern South American Pleistocene mammals. The results show an excellent fit to spatial distributions of U across a transverse section of its tibia, allowing the estimation of the diffusion adsorption (D/R) parameter to be $(2.4 \pm 0.6)10^{-12} \text{ cm}^2\text{s}^{-1}$, which is within the range of previously published values. If the classical D–A model predicted by Millard & Hedges was applied, it was also observed a good fit, but the value obtained would be $(3.7 \pm 0.9)10^{-12} \text{ cm}^2\text{s}^{-1}$. Unfortunately, we were only able to measure one fossil bone sample to test the RDA model. Well preserved samples of extinct megamammal specimens are hard to find. Understandably, museum curators are reluctant to allow the most valuable specimens to be cut or drilled. However, our findings state the importance of choosing the best geometry for the U uptake. From U–Th and U–Pa measurements and radiocarbon dating, it was possible to determine the age of this bone sample, being 21.6 ± 1.0 kyr. Additionally, results from Ca, K, Mg, and Na profiles suggest that the fossil bone sample is well preserved in what concerns its mineral structure and the specimen used to be healthy. However, having in mind that the content of ions not only depends on the life cycle of animal, but are also affected by the nearby burying environment condition, this study deserves further extension to more samples and sites.

Acknowledgments

The authors would like to thank the following funding agencies for their financial support: CNPq (Grant numbers 402309/2013–8, 472155/2013–0, and 301805/2011–3), CAPES/Udelar (grant number 1576/2010), and CAPES/MINCYT (grant number 1129/2014), and CSIC (Udelar). They also wish to thank Matthew J. Kohn and Valeria Mesa for his enlightening discussions of parts of this research.

References

- Alvarenga, H., Jones, W., Rinderknecht, A., 2010. The youngest record of phorusrhacid birds (Aves, Phorusrhacidae) from the late Pleistocene of Uruguay. *Neues Jahrbuch Geol. Paläont. Abh.* 256, 229–234.
- Anjos, R.M., Veiga, R., Soares, T., Santos, A.M.A., Aguiar, J.G., Frasca, M.H.B.O., 2005. Natural radionuclide distribution in Brazilian commercial granites. *Radiat. Meas.* 39, 245–253.
- Anjos, R.M., Veiga, R., Macario, K., Carvalho, C., Sanches, N., Bastos, J., 2006. Radiometric analysis of quaternary deposits from the southeastern Brazilian coast. *Mar. Geol.* 229, 29–43.
- Anjos, R.M., Macario, K.D., Lima, T.A., Veiga, R., Carvalho, C., Fernandes, P.J.F., 2010. Correlations between radiometric analysis of quaternary deposits and the chronology of prehistoric settlements from the southeastern Brazilian coast. *J. Environ. Radioact.* 101, 75–81.
- Berzero, A., Caramella-Crespi, V., 1997. Direct gamma-ray spectrometric dating of fossil bones: preliminary results. *Archaeometry* 39, 189–203.
- Brickley, M., Ives, R., 2008. *The Bioarchaeology of Metabolic Bone Disease*. Elsevier, Amsterdam.
- Bronk Ramsey, C., 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51, 337–360.
- Cheng, H., Edwards, R.L., Shen, C.-C., Polyak, V.J., Asmerom, Y., Woodhead, J., Hellstrom, J., Wang, Y., Kong, X., Spötl, C., Wang, X., Alexander Jr., E.C., 2013. Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth Planet. Sci. Lett.* 371, 82–91.
- Cione, A.L., Figini, A.J., Tonni, E.P., 2001. Did the megafauna range to 4300 Bp in South America? *Radiocarbon* 43, 69–75.
- Corona, A., Perea, D., Toriño, P., Goso, C., 2012. Taphonomy, sedimentology and chronology of a fossiliferous outcrop from the continental Pleistocene of Uruguay. *Rev. Mex. Cienc. Geol.* 29, 514–525.
- Crank, J., 1975. *The Mathematic of Diffusion*. Oxford University Press, Oxford, UK.
- Eggins, S.M., Grun, R., McCulloch, M.T., Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer, G., Shelley, M., Murray-Wallace, C.V., Spotl, C., Taylor, L., 2005. In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology. *Quat. Sci. Rev.* 24, 2523–2538.
- Elliott, 2006. *Bone Mineral Chemistry and Structure*. Department of Anatomy and Developmental Biology University College London (UCL). <http://www.homepages.ucl.ac.uk/~ucgatma/Anat3048/LECTURES/Elliott%20Mineral%202006.pdf>.
- Gutiérrez, M., Alberdi, M.T., Prado, J.L., Perea, D., 2005. Late Pleistocene Stegomastodon (Mammalia, Proboscidea) from Uruguay. *Neues Jahrb. Geol. Paläontol. Monatsheft.* 11, 641–662.
- Hedges, R.E., van Klinken, G.J., 1992. A review of current approaches in the pre-treatment of bone for radiocarbon dating by AMS. *Radiocarbon* 34, 279–291.
- Hogg, A.G., Hua, Q., Blackwell, P.G., Niu, M., Buck, C.E., Guilderson, T.P., Heaton, T.J., Palmer, J.G., Reimer, P.J., Reimer, R.W., Turney, C.S.M., Zimmerman, S.R.H., 2013. SHCal13 Southern Hemisphere Calibration, 0–50,000 Years cal BP. *Radiocarbon* 55 (4), 1889–1903.
- IAEA, 1987. Preparation and Certification of IAEA Gamma Spectrometry Reference Materials, RCU-1, RGTh-1 and RKG-1. International Atomic Energy Agency. Report-IAEA/RL/148.
- Ivanovich, M., Harmon, R.S., 1992. *Uranium Series Disequilibrium*. Clarendon Press, Oxford, pp. 302–325.
- Keynes, R.D., 2001. *Charles Darwin's Beagle Diary*. Cambridge University Press, Cambridge.
- Kohn, M.J., 2008. Models of diffusion-limited uptake of trace elements in fossils and rates of fossilization. *Geochim. Cosmochim. Acta* 72, 3758–3770.
- Maynard, L.A., Loosli, J.K., Hintz, H.F., Warner, R.G., 1979. *Animal Nutrition*, seventh ed. McGraw-Hill Book Co., New York.
- Millard, A.R., Hedges, R.E.M., 1995. The role of the environment in uranium uptake by buried bone. *J. Archaeol. Sci.* 22, 239–250.
- Millard, A.R., Hedges, R.E.M., 1996. A diffusion-adsorption model of uranium uptake by archaeological bone. *Geochim. Cosmochim. Acta* 60, 2139–2152.
- Millard, A.R., Pike, A.W.G., 1999. Uranium-series dating of the Tabun Neanderthal: a cautionary note. *J. Hum. Evol.* 36, 581–585.
- Owen, R., 1838. Fossil Mammalia. In: Darwin, C.R. (Ed.), *Zoology of the Voyage of H.M.S. Beagle, under the Command of Captain Fitz-roy, during the Years 1832 to 1836*. Smith Elder and Co, London.
- Pike, A.W.G., Hedges, R.E.M., 2001. Sample geometry and U uptake in archaeological teeth: implications for U-series and ESR dating. *Quat. Sci. Rev.* 20, 1021–1025.
- Pike, A.W.G., Pettitt, P.B., 2003. U-series dating and human evolution. *Rev. Mineral. Geochem.* 52, 607–630.
- Pike, A.W.G., Hedges, R.E.M., Van Calsteren, P., 2002. U-series dating of bone using the diffusion-adsorption model. *Geochim. Cosmochim. Acta* 66, 4273–4286.
- Pike, A.W.G., Eggins, S.M., Grun, R., Hedges, R.E.M., Jacobi, R.M., 2005. U-series dating of the late pleistocene mammalian fauna from Wood Quarry (Steetley), Nottinghamshire, UK. *J. Quat. Sci.* 20, 59–65.
- Van Der Plicht, J., Van Der Wijk, A., Bartstra, G.J., 1989. Uranium and thorium in fossil bones: activity ratios and dating. *Appl. Geochem.* 4, 339–342.
- Robert, J., Miranda, C.F., Muxart, R., 1969. Mesure de la période du protactinium-231 par microcalorimétrie. *Radiochim. Acta* 11, 104–108.
- Sambridge, M., Grün, R., Eggins, S., 2012. U-series dating of bone in an open system: the diffusion-adsorption-decay model. *Quat. Geochronol.* 9, 42–53.
- Scherer, C.S., Pitana, V.G., Ribeiro, A.M., 2009. Protheroheriidae and Macraucheniiidae (Litopterna, Mammalia) from the Pleistocene of Rio Grande do Sul State, Brazil. *Rev. Bras. Paleontol.* 12, 231–246.
- Schwarcz, H.P., 1980. Absolute age determination of archaeological sites by uranium-series dating of travertines. *Archaeometry* 22, 3–24.
- Simpson, J.J., Grun, R., 1998. Non-destructive gamma spectrometric U-series dating. *Quat. Geochronol.* 17, 1009–1022.
- Tonni, E.P., Huarte, R.A., Carbonari, J.E., Figini, A.J., 2003. New radiocarbon chronology for the Guerrero Member of the Luján Formation (Buenos Aires, Argentina): palaeoclimatic significance. *Quat. Int.* 109–110, 45–48.
- Yokoyama, Y., Falguères, C., Sémah, F., Jacob, T., Grun, R., 2008. Gamma ray spectrometric dating of late Homo erectus skulls from Ngandong and Sambungmacan, Central Java, Indonesia. *J. Hum. Evol.* 55, 274–277.