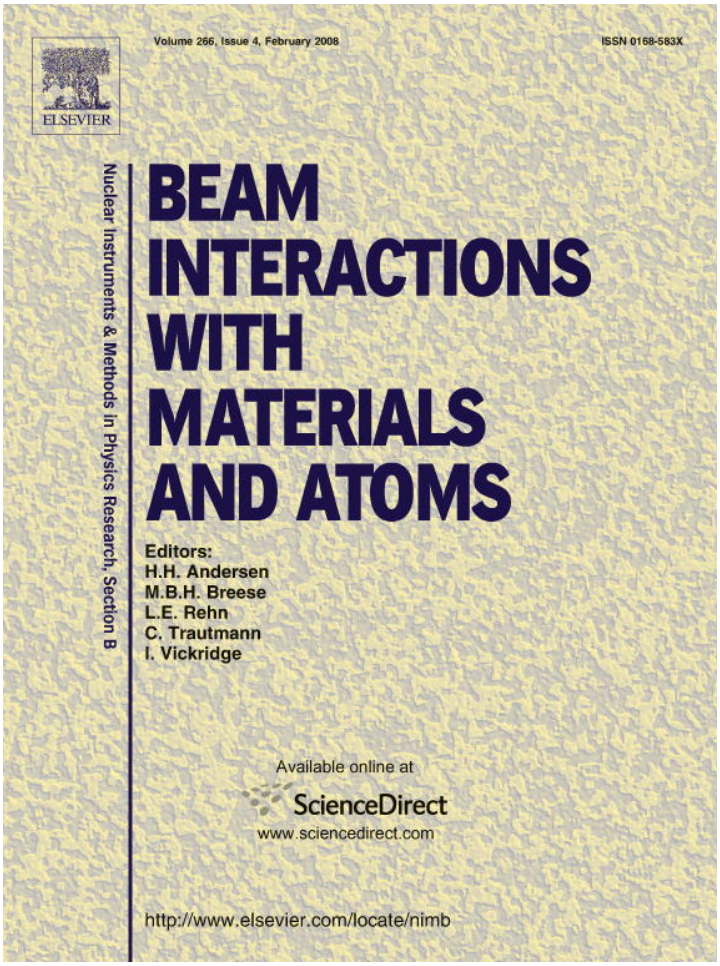

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Electron spin resonance dating of human teeth from Toca da Santa shelter of São Raimundo Nonato, Piauí, Brazil

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Abstract

Results of the dating of fossil human teeth excavated from a shelter in the surroundings areas of the Serra da Capivara National Park, São Raimundo Nonato, Piauí, Brazil are presented. This shelter was partially excavated to search for more data that could improve the archaeological context of the Garrincho's limestone hill sites, where the Toca do Gordo do Garrincho shelter provided two human teeth dated by conventional C-14 in (12,170 ± 40) yBP (years before present) and calibrated age (2 Sigma, 95% probability) 15,245–14,690 yBP (Beta 136204) [E. Peyre, C. Guérin, N. Guidon, I. Coppens, CR Acad. Sci. Paris, Sciences de la terre et des planètes/ Earth & Planetary Sciences 327 (1998) 335, [1]].

This region is challenging the classical theories about the peopling of America. In agreement with such theories the first human groups would have arrived in America, through Behring, only about 20,000 years ago. The site Toca do Boqueirão da Pedra Furada is a rock-shelter situated at the cliff that is the frontier between the Pré-Cambrian São Francisco plain and the Devonian-Permian highlands of the Maranhão-Piauí basin. It was excavated from 1978 till 1988 and presented a very consistent stratigraphy, with thousand of lithic implements and hearths [F. Parenti, Le gisement quaternaire de la Pedra Furada (Piaui, Brésil), Stratigraphie, chronologie, évolution culturelle, Editions Recherches sur les civilisations, Paris, 2002, [2]; F. Parenti, Le Gisement Quaternaire de la Toca do Boqueirão da Pedra Furada (Piauí, Brésil) dans le Contexte de la Préhistoire Américaine Fouilles, Stratigraphie, Chronologie, Évolution Culturelle, Ph.D. diss, École des Hautes Ètudes en Sciences Sociales, Paris, 1993, 411p, [3]; F. Parenti, M. Fontugne, N. Guidon, C. Guérin, M. Faure, Chronostratigraphie des gisements archéologiques et paléontologiques de Sao Raimundo Nonato (Piaui, Brésil): contribution à la connaissance du peuplement pléistocène de l'Amérique, Supplément de la Revue d'Archéométrie, 1999, p. 327, [4]].

Seventy C-14 dates were obtained going from 59,000 yBP to 5000 yBP at the actual soil [G.M. Santos, M.I., Bird, F. Parenti, L.K. Fifield, N. Guidon, P.A. Hausladen, Quaternary Sci. Rev. 22 (2003) 2303, [5]]. Beneath the date of 59,000 yBP it was found 1.5 m of archaeological layers, till the rock base. The cobbles that composed the structure of the hearths placed on top of the rock base were dated by thermoluminescence and the date of them is 100,000 yBP [H. Valladas, N. Mercier, M. Michab, J.L. Joron, J.L. Reiss, N. Guidon, N., Quaternary Sci. Rev. 22 (2003) 1257, [6]; H. Valladas, N. Mercier, M. Michab, J.L. Joron, J.L. Reyss, N. Guidon, Datações por Termoluminescência de Seixos de Quartzo Queimados da Toca do Boqueirão da Pedra Furada (Piauí, Nordeste do Brasil), Fumdhamentos III, 1 (2003) 35 (in Portuguese), [7]]. Thus chronological information is of paramount importance to contextualize and to understand the many questions regarding the human occupation of these sites [N. Guidon, A.M. Pessis, G. Martin, O Povoamento Pré-Histórico do Nordeste do Brasil, Proposta da: Fundação Museu do Homem Americano, e do Núcleo de Estudos Arqueológicos, da UFPE, CLIO ARQ, Recife 1 (6) (1990) 123, [8]]. To obtain more information Toca da Santa shelter, the nearest site to Toca do Gordo do Garrincho shelter, was also excavated and three incomplete skeletons with teeth were found at 80 cm depth. The teeth were cleaned and acid etched and enamel completely removed from dentine and crushed in particles smaller than 0.5 mm. Enamel was irradiated with a Co-60 source

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and measured with an ESR spectrometer (X-band) to obtain the signal versus dose curve. The archeological doses obtained by the fitting were (5.94 ± 0.07) Gy and (5.97 ± 0.08) Gy. Using the ROSY program an age of 5,700 ± 200 yBP was found for both teeth.

PACS: 76.30.−v; 93.85.+q; 87.53.Bn; Dq

Keywords: ESR dating; Human teeth dating; Peopling of America

1. Introduction

In the limestone hills, in the region of the Serra da Capivara National Park, paleontological and archeological remains are found in the interior of caves as well as in the rock-shelters at the external walls of the cliffs. The soil of these rock-shelters contain an archaeological diversity of remains with different chronologies ranging from recent ceramists groups dating 300 yBP to human fossil skeletons with ages older than 9000 yBP. Hearths and bones from the fossil animals such as *Catonix cuvieri*, *Scelidodon* sp., *Eremoterium lundi*, *Pampaterium humboldti*, *Gliptodon*, *Arctodus cf. bonaerense*, *Felis yagouaroundi*, *Macrauchenia*, *Toxodon* and others [9,10]. On the overall the region, that was declared a Human Heritage site by UNESCO, has up to the present 940 archeological sites registered by the National Institute for the Historical and Artistic Heritage (Instituto do Patrimônio Histórico e Artístico Nacional-IPHAN). Among those sites, 45 were already excavated and the data collected show a continuous human occupation since at least 100,000 yBP.

This occupation has been confirmed through the studies of lithic remains, done by Prof. Robson Bonnichsen from Texas University, that prove a human work elaboration and use of tools stones that are associated with a layer 100,000 years old.

In this article we discuss the dating of two human teeth from skeletons 2 and 3 excavated at Toca da Santa shelter of São Raimundo Nonato, Piauí, Brazil using Electron Spin Resonance (ESR). The results show good agreement with a shallow stratigraphy (the burials were only at 80 cm deep) with homogeneous sediments (clay/sand) and the lithic artifacts associated with the burials.

Fig. 1. (a) General view of Toca da Santa shelter and (b) close up of the human jaw with the teeth used in the dating.

2. Methods and materials

This site was explored before by the actual inhabitants looking for the limestone rock that they use to produce lime. So, the actual soil was covered by a 20 cm layer of limestone debris that protected the archaeological layers. Fig. 1 shows a general view of the site at the beginning of the excavations in 2003. The Toca da Santa rock-shelter is located by geographical coordinates UTML 763324 e UTMN 9012144. We found three burials, with incomplete skeletons, in a layer 80 cm deep. Two skeletons (burial 1 and burial 3) lay over the left side of the body and in fetal position. In the third (burial 2) all the bones were together and it seems to be a secondary burial. Lithic artifacts were found associated with the burials, but no residues of bonfire were found so far.

Two teeth from different skeletons were separated from the remaining jaw and soil sediments were collected for analysis of the U, Th and K content. Initially the enamel was separated from the teeth by thermal shock by freezing teeth in liquid nitrogen and thawing it at ambient temperature. The difference in dilation coefficients of dentine and enamel produces a detachment of the parts. Sample of dentine from each tooth was saved for NAA analysis. To remove the remains of dentine it was placed in a saturated solution of NaOH (30%) for several hours with ultrasound vibration. This solution dissolves the organic components of teeth. Enamel was acid etched in 10% HCl to remove

the outer layer and gently ground in an agate mortar and pestle into fine particles ($\phi \leqslant 0.5$ mm). The reduction of the sample into small particles was performed to eliminate the sensitivity of the measurements due to sample orientation and the optimum particle size was adopted [11,12]. The acid attack also removes the outer layer of enamel assuring that there is no contribution from alpha irradiation to the sample.

The material obtained was then divided into three aliquots of about 50 mg each and placed inside small plastic tubes for irradiation in the laboratory with a Gammacell 220 irradiator with a Co-60 gamma source a dose rate of 1 Gy/min in air, at room temperature, using 0.4 g/cm^2 thick Lucite build-up cap (build-up filter) over the samples. An accuracy of ±5% was achieved in the determination of the dose delivered to the sample.

After irradiation and weighing, the samples were transferred to quartz tubes and the ESR signal measured with a modernized VARIAN E-4 spectrometer operating at X-band ($v \approx 9$ GHz) and equipped with a rectangular cavity (TE-102, model E-231). More details on the improvements made in the spectrometer can be found in [13,14]. The spectrometer parameters used were Central field 338 mT; Scan Range 10 mT; Modulation 0.2 mT; Modulation frequency 100 kHz; Time constant 0.250 s and Microwave Power 20 mW. After ESR measurements, the aliquots were irradiated with additional doses and the same process was repeated until getting 10 data points of ESR signal amplitude as a function of dose. The given doses ranged from 0 to 70 Gy.

For neutron activation analysis (NAA) samples and standards were irradiated for 8 h at a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} at the IEA-R1m nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in a GX20190 hyperpure Ge detector (Canberra). The multi-channel analyzer was an 8192 plug-in-card in a PC computer. The resolution (full width at half maximum-FWHM) of the system was 1.90 keV for the 1.332 keV gamma-rays of ^{60}Co. Counting of radioactivity was performed about 10 days after irradiation with 10 cm distance between sample and detector. Counting times varied from 1 to 10 h. The gamma-ray spectra were processed by the VISPECT software, which locates peak positions and calculates the energies and net areas [15].

The ESR peak to peak intensities of the $g_\perp$ signal were normalized by the sample weights. The choice of the fitting model has long been a source of discussion. For example in Mascarenhas et al. [16], Kinoshita et al. [14] and Baffa et al. [13] a linear fitting of ESR signal intensity versus dose were used and the data appear to be in very good agreement with the linear fit. Thus in the present work a linear fitting was also used with good agreement.

3. Results and discussion

The ESR spectra corresponding to the sample without any laboratory radiation is shown in Fig. 2. The signal

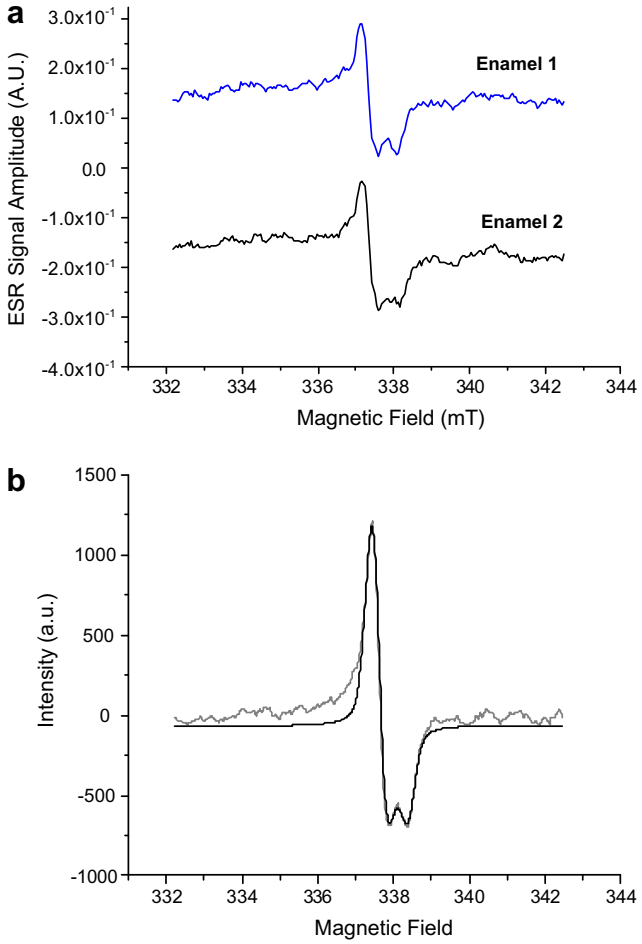

Fig. 2. (a) ESR spectra of the teeth enamel before irradiation with cobalt-60, normalized by aliquot mass. The signal is characteristic of CO_2^- with Landé factor at $g_\perp = 2.0025$ and $g_\parallel = 1.9973$. The spectrum has a signal to noise ratio of about 20. (b) Experimental and simulated spectrum of irradiated tooth enamel with an additional dose of 50 Gy.

has a signal to noise ratio of about 20. The spectrum was analyzed with simulation software SimFonia-Bruker and it was possible to identify the paramagnetic species as the axial CO_2^- with Landé factor at $g_\perp = 2.0025$ and $g_\parallel = 1.9973$ in agreement with other reports [17,18]. The signal amplitude due to the paramagnetic centers increases with dose as shown in Fig. 3 for the enamel extracted from the two teeth. The archeological dose (A_D) obtained by linear fitting are a-AD = (5.94 ± 0.07) Gy and b-AD= (5.97 ± 0.08) Gy. After finding AD a crucial step is to find the dose rate to convert AD into an age. The software ROSY [19] allows the calculation of the age of an enamel sample by taking into account the dose contribution due to radioisotopes from the adjacent layers. The software computes the age based on three models from uranium absorption: linear, early uptake and a combination of both processes. NAA analysis gave the same concentration of the Uranium and Thorium for both teeth and the results shown in Table 1.

For age calculation we used the typical values for the density of soil, enamel and dentine: 2.00, 3.00 and 2.82 g/cm^3,

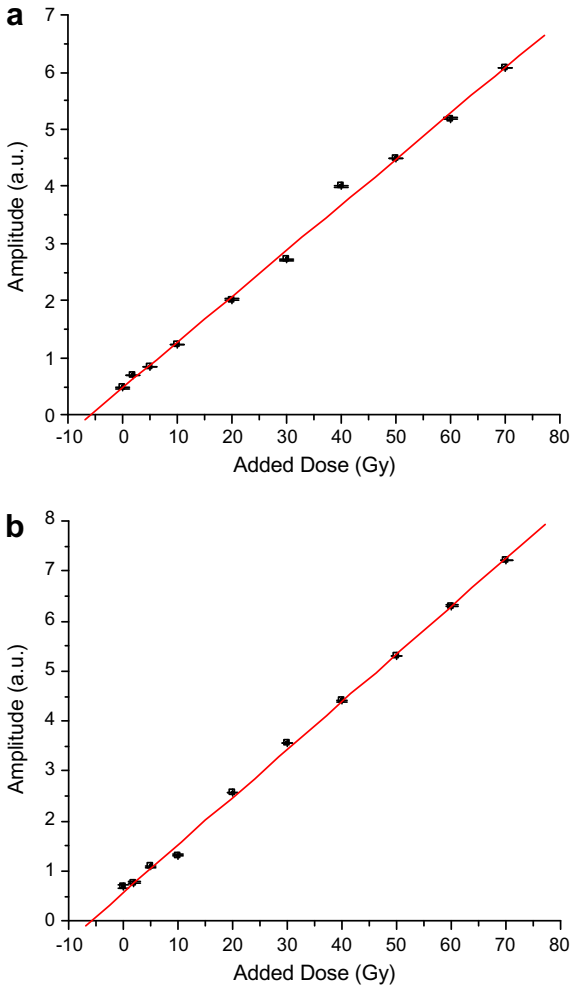

Fig. 3. Signal versus dose growth showing the linear fitting used. (a) archeological dose AD = (5.94 ± 0.07) Gy and (b) AD = (5.97 ± 0.08) Gy, correlation coefficients were 0.998 and 0.999, respectively.

Table 1
Concentration of Uranium and Thorium determined by neutron activation analysis, concentration was the same for both teeth

Sample	Uranium (ppm)	Thorium (ppm)	Potassium (ppm)
Soil	2.4 ± 0.2	9.3 ± 0.1	3.9 ± 0.4
Dentine	<0.05	<0.01	<0.06
Enamel	<0.05	<0.01	<0.06

respectively. The thickness of enamel and dentine are 1 mm and 5 mm. The layer of enamel stripped off from each side by acid etching is approximately 50 μm what prevents the possible contribution to the dose deposited in the sample by alpha particles.

Using these values and the radioisotopes concentration listed in Table 1, the contribution to dose rates of alpha, beta and gamma radiation for each radioisotope in enamel, dentine and sediment were obtained using Rosy software and the results are listed in Table 2. These results are the same for any model of uranium absorption. We considered the dose rate of 250 μGy/year for the cosmic radiation, a

Table 2
Dose rate obtained from radioisotopes concentration, local cosmic radiation and total dose rate

	Alpha (μGy/year)	Beta (μGy/year)	Gamma (μGy/year)	Cosmic (μGy/year)	Total (μGy/year)
Uranium	0	49.09	271.20		
Thorium	0	33.15	442.68		
Potassium	0	0	0		
Dentine	0	0	0		
Enamel	0	0	0		
Sediment	0	82.24	713.88	250	1046.12

figure that is used by many authors [20] so an age of 5700 ± 200 yBP was found for both samples.

The age found in this work is in agreement with the findings in the region, were charcoal found in the same depth, 80 cm from the actual soil, gave similar dates. This dating work was obtained in a relatively straightforward way, requiring only a few grams, showing some of the advantages and characteristics of the ESR dating method. This fact encourage the use of this technique to other samples of teeth and bones found in the Serra da Capivara National Park, in especial those teeth and bones that the fossilization process do not allow the use the traditional C14 dating method.

Acknowledgments

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