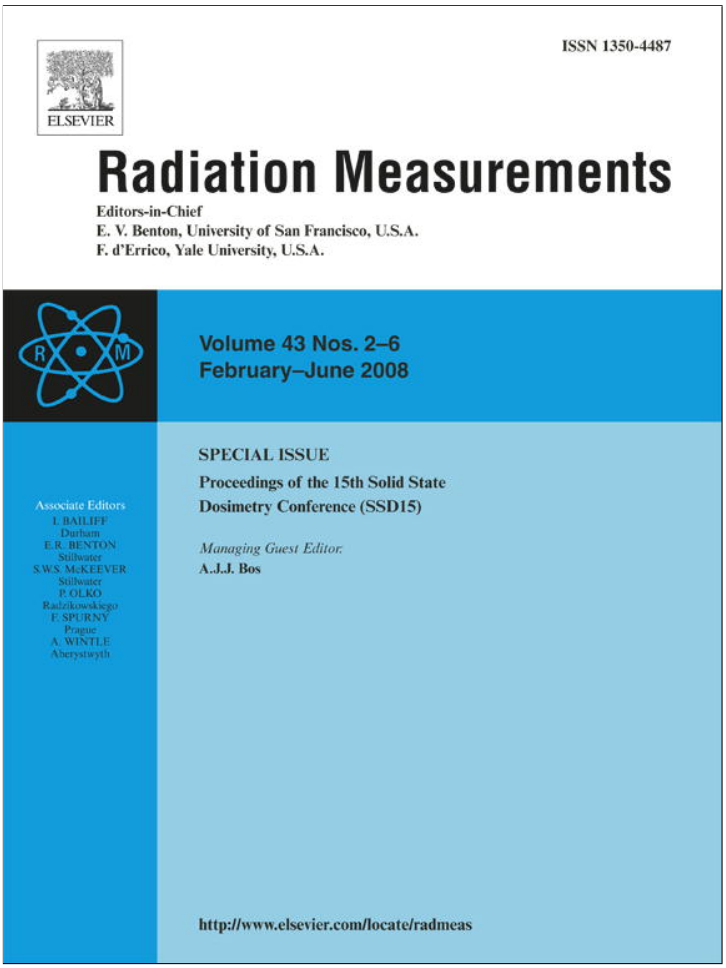

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ESR dating of teeth from northeastern Brazilian megafauna

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Abstract

Two *Stegomastodon waringi* teeth from Brazilian northeastern megafauna were dated by electron spin resonance (ESR) spectroscopy. The samples were collected in Pernambuco state, Brazil. The dating of these samples will contribute to the better knowledge of megafauna presence in this region as well as to the events associated to the extinction of these species. Additive dose method was used to evaluate the archeological dose (AD) and a non-linear relation between ESR signal amplitude and dose was obtained. The AD obtained by the exponential fitting was 120 ± 1 and 112 ± 1 Gy, leading to an estimation of an age of 63 ± 8 and 60 ± 9 ky for radioisotope early uptake model, 64 ± 8 and 60 ± 9 ky for linear uptake and 60 ± 9 ky for a combination of uptake processes.

Keywords: ESR dating; X-band; Fóssil tooth enamel; Brazilian megafauna

1. Introduction

Two *Stegomastodon waringi* teeth from Brazilian northeastern pleistocenics mammals (megafauna) were studied by electron spin resonance (ESR) spectroscopy. The samples were collected in Fazenda Logradouro (9094505/0812382) UTM, Pernambuco state, Brazil. This deposit is 3.2 m deep and presents three different stratigrafic levels formed by gravitational debri flows. Teeth, bones and dermic plates from pleistocenic mammals were found in the intermediate level, 80 cm thick (bone bed) at 1.8–2.0 m from surface. The layer presents bioclasts entire and fragmented. The arrangement is chaotically and densely packed, forming a monotypical concentration (only mammals), poliespecific (*Eremotherium laurillardi*, *Toxodon platensis*, *Gliptodon owen*, *S. waringi*). The layer has calcite cement (calcrete) representing an event of massive death of these animals.

The dating of these samples will contribute to the better knowledge of megafauna presence in this region as well as to the paleoclimatic events associated to the extinction of these species, mainly herbivorous (Figs. 1 and 2).

The ESR dating is based on the fact that ionizing radiation can create stable free radicals in insulating materials, like tooth enamel and bones (Grün, 2006). The concentration of these radicals—determined by ESR—is a function of the dose deposited in the sample along the years. In fossil samples, the dose was deposited by the cosmic rays and radioactive materials present in the soil like uranium, thorium, potassium that decay and irradiate the sample during the time that it was buried. Assuming that the "artificial radiation"—made in laboratory—produces the same defects of the natural radiation we can determine a relationship between the ESR signal amplitude and the artificial dose leading to the assessment of the archeological dose (AD). Using this piece of information and the concentration of U, Th and K (in the fossil samples and in the soil) the age of the samples was calculated using the software "ROSY ESR dating program" (Brennan et al., 1997, 1999). ESR has been successively used in several cases with tooth enamel (Baffa et al., 2000; Kinoshita et al., 2002, 2005). It is possible to ascertain that having precise information about the radioactive content of the soil surrounding the sample it is

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doi:10.1016/j.radmeas.2007.11.075

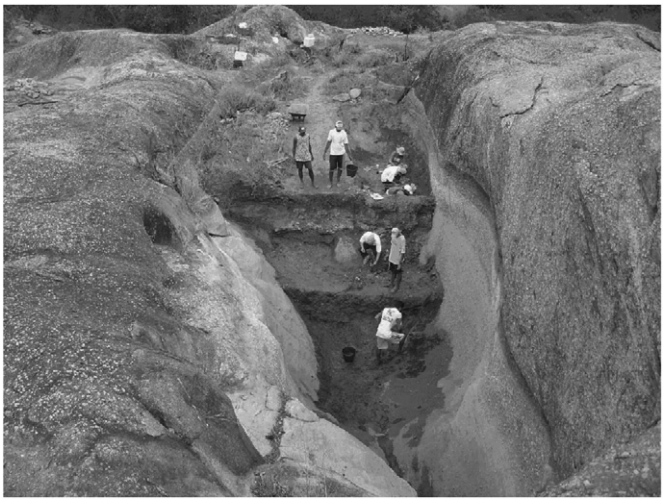

Fig. 1. View of the sample's collection site at Fazenda Logradouro, Inço, Fazenda Nova, Pernambuco. The pothole in the rock acts like a reservoir to collect and store the samples.

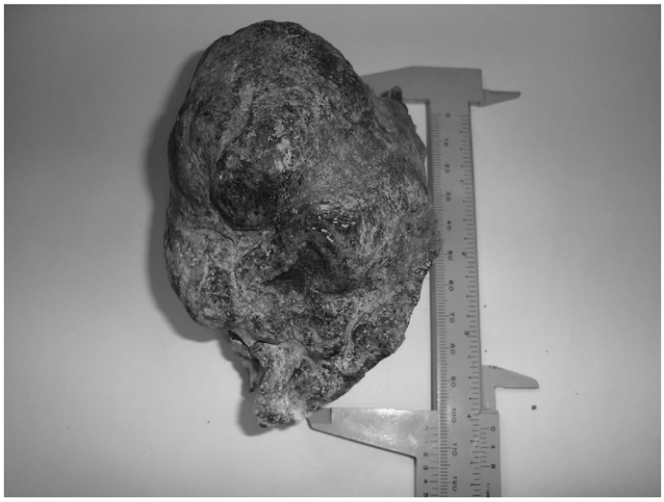

Fig. 2. One of the *Stegomastodon* teeth used in this study, the dimensions of the tooth is shown by a caliper with an opening of approximately 100 mm.

feasible to date tooth enamel with good precision. Since ESR dating can cover a range from thousands to one million years old period this technique is useful to cover an important gap separating the end of C-14 method to the beginning of other radioisotope methods as U/Th (Ikeya, 1993; Rink, 1997).

2. Methods

The enamel was mechanically separated from dentin using a scalpel and chemically treated with a 30% NaOH solution in an ultrasound bath to clean of remaining dentin. After, samples were etched in an HCl solution (1:10) and an external layer of $\sim 500\,\mu m$ was eliminated. The enamel was powdered in fine particles ($\phi < 0.5$ mm), divided in aliquots (~ 100 mg) and a set of additive dose was given. These samples were irradiated with γ rays, using a Gammacell source in air, at room temperature using $0.4\,g/mm^2$ thick Lucite build-up cap over the samples.

ESR spectra of samples were recorded in a Varian E-4 X Band ($\nu \sim 9$ GHz) spectrometer, equipped with a digital lock-in amplifier and magnetic field controller, allowing computer controlled signal acquisition. Typical measuring conditions were modulation amplitude 0.2 mT, scan range 10 mT, scan time 1 min, nominal microwave power 20 mW, below signal saturation.

3. Results and discussion

The native ESR spectrum of these samples shows a strong signal with axial symmetry having spectroscopic g factors $g_\perp = 2.0025$ and $g_\parallel = 1.9973$ related to the CO_2^- radical in hydroxyapatite (Schramm and Rossi, 2000; Callens et al., 1989). Fig. 3 shows the spectrum of sample 2. After irradiation with cobalt-60 the effect on the signal amplitude was evaluated. Fig. 3 shows how the signal changes for increasing doses. It can be

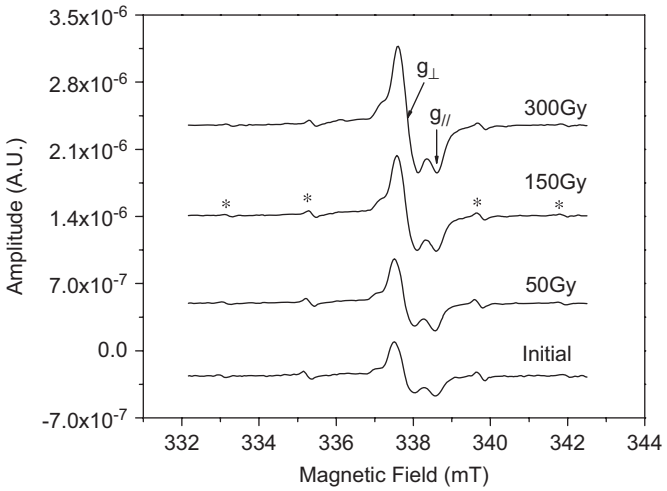

Fig. 3. ESR spectrum of tooth enamel (Sample 1) for different post irradiation doses. Signal amplitude at $g_\perp$ was used to determine the AD. The isopropyl $(CH_3)_2C$–R signal is indicated by and asterix mark (*).

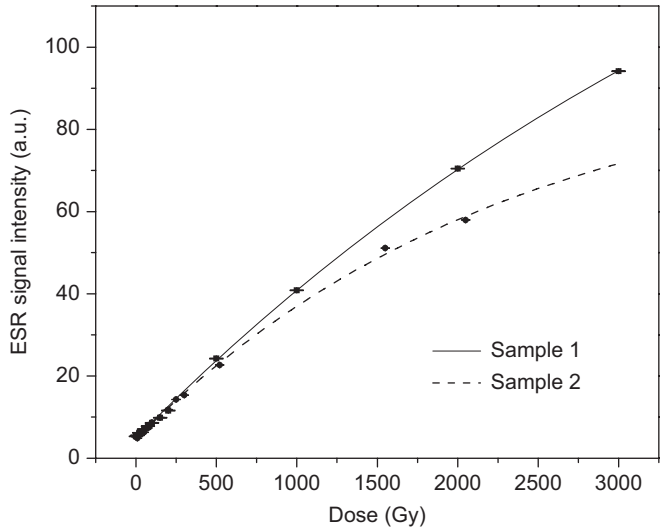

Fig. 4. Dose–response curves of samples 1 (A) and 2 (B) fitted by Eq. (1).

noticed that the central region corresponding to the CO_2^- radical increased with the dose while the other regions of the spectrum remained unchanged. We can also note the presence of the signal of isopropyl radical with hyperfine splittings of 2.17 mT. This septet signal was also observed by other authors in middle Pleistocene tooth samples (Ikeya, 1993). The amplitude of the spectral feature at $g_\perp = 2.0025$ was used to construct the additive signal curve. Additive dose method was used to plot the dose–response curve (Fig. 4) and an AD of 120 ± 1 and 112 ± 1 Gy, respectively, was found using exponential fitting:

$$I = I_0[1 - e^{-(D+\mathrm{AD})/D_0}], \quad (1)$$

where I is the signal intensity, I_0 is the signal intensity at saturation, D is an additional dose and AD the archeological dose. The fitting was done using the software Microcal Origin 6.0 (Microcal Software Inc, Northampton, MA, USA) and the data points were weighed by using the instrumental weight option. In summary this option weighs the results by $w_{ji} = 1/(s_{ji})^2$, where s_{ji} is the error bar associated with the signal amplitude uncertainty; thus the lower points get higher weights. This procedure is reasonable, since the lower points are more influenced by the original sample and has been used by other authors (Skinner et al., 2000). The others fitting parameters founded were $I_0 = 201 \pm 16$; $D_0 = 4950 \pm 50$ and $I_0 = 97 \pm 1$; $D_0 = 2315 \pm 30$ for samples 1 and 2, respectively. These results seem to be in agreement with other findings indicating the possible age of this archeological site. It is interesting to note that although the AD was about the same for both samples the aspect of the dose additive plot is different. As can be seem from Fig. 4, the exponential fitting was the best choice for both teeth; however, there was a small difference in the fitting parameters, showing the importance of obtaining the signal versus dose for each sample. As it is known the ESR signal detected depends on the presence of carbonate ions, that as a dopant substance, can vary from sample to sample.

Table 1
Ages of the tooth samples considering early uptake (E.U.), linear uptake (L.U.) and combination uptake (C.U.) models for uranium accumulation

	AD (Gy)	E.U. (ky)	L.U. (ky)	C.U. (ky)
Sample 1	120 ± 1	63 ± 8	64 ± 8	63 ± 8
Sample 2	112 ± 1	60 ± 9	60 ± 9	60 ± 9

The Cosmic rays dose of 250 μGy/yr was considered.

Table 2
Radioisotope concentration obtained by neutron activation analysis (NAA) and coupled plasma mass spectrometry (ICP-MS)

	^{238}U (ppm)	^{232}Th (ppm)	K (%)
Enamel 1	0.24 ± 0.02	0.127 ± 0.009	0.0407 ± 0.002
Dentine 1	0.31 ± 0.02	0.089 ± 0.006	0.0482 ± 0.002
Soil 1	1.95 ± 0.24	13.28 ± 3.50	2.65 ± 0.63
Enamel 2	0.008 ± 0.001	0.075 ± 0.005	0.032 ± 0.002
Dentine 2	0.015 ± 0.001	0.075 ± 0.005	0.0465 ± 0.002
Soil 2	2.22 ± 1.20	15.06 ± 3.70	2.30 ± 0.60

The ages of the samples were calculated by the ROSY ESR Dating program and the results are reported in Table 1. The early uptake (E.U.), linear uptake (L.U.) and combination uptake (C.U.) models for uranium accumulation were considered in age calculation. In the E.U. model, the uranium uptake occurs at the initial stage in a short time relative to the age and remains constant. In the L.U. model, the uptake of uranium occurs at a constant rate (Ikeya, 1993). The concentration of ^{238}U, ^{232}Th and potassium present in the samples and from the soil where the samples were buried were obtained by neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS). Because the inhomogeneity of the soil, six aliquots collected at the level of the sample were analyzed. The average and standard deviation of radioisotopes concentration (Table 2) was considered in the age calculation. Table 3 lists the dose rates from enamel, dentine and sediment to enamel for each uranium uptake model. The value of 0.15 was used for k-value, that is, the ratio of defects creation efficiency for α particles to internal dose rate calculation (DeCanniere et al., 1986). The energy released by α particles by the soil was not considered because the maximum penetration depths of these particles are 40–60 μm, shorter than the layer extracted in the sample preparation. The cosmic and γ rays dose in the site where the samples were collected is 250 μGy/yr and initial ^{234}U/^{238}U ratio of 1.4 was assumed for age calculations.

The ages found in this work are compatible with the historical period (Pleistocene last glaciation) of the existence of these species. The age of the samples are also compatible with the age found in others fossils samples in Brazil, dated by ESR (Baffa et al., 2000; Kinoshita et al., 2005) and U/Th (Auler et al., 2006).

Table 3
α, β, γ dose rates (μGy/yr) from enamel, dentine and sediment to enamel calculated by ROSY ESR dating software

	Early uptake			Linear uptake			Combination uptake		
	$\dot{D}_\alpha$ (μGy/a)	$\dot{D}_\beta$ (μGy/a)	$\dot{D}_\gamma$ (μGy/a)	$\dot{D}_\alpha$ (μGy/a)	$\dot{D}_\beta$ (μGy/a)	$\dot{D}_\gamma$ (μGy/a)	$\dot{D}_\alpha$ (μGy/a)	$\dot{D}_\beta$ (μGy/a)	$\dot{D}_\gamma$ (μGy/a)
Dentine 1	0.00	1.24	0.00	0.00	0.87	0.00	0.00	0.87	0.00
Enamel 1	65.42	53.22	0.00	36.49	42.45	0.00	65.43	53.22	0.00
Sediment 1	0.00	42.79	1496.43	0.00	42.79	1496.43	0.00	42.79	1496.43
Dentine 2	0.00	0.56	0.00	0.00	0.55	0.00	0.00	0.55	0.00
Enamel 2	10.85	25.37	0.00	9.89	25.02	0.00	10.85	25.37	0.00
Sediment 2	0.00	40.65	1526.62	0.00	40.65	1526.62	0.00	40.65	1526.62

Acknowledgments

To Brazilian agencies Fundação de Amparo a Pesquisa do Estado de Sao Paulo (FAPESP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação Aperfeiçoamento do Pessoal de Ensino Superior (CAPES) for partial financial support. IPEN for the irradiation of samples and C.A. Brunello and Lourenço Rocha for technical support.

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