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# ESR dating of teeth from Brazilian megafauna

**L C Oliveira[1], A Kinoshita[1,2], A M F Barreto[3], A M Figueiredo[4], J L L Silva[5] and O Baffa[1]**

[1]Departamento de Física e Matemática, FFCLRP, USP Ribeirão Preto, SP, Brazil.
[2]Universidade do Sagrado Coração, Bauru, SP, Brazil.
[3]Universidade Federal de Pernambuco, Recife, PE, Brazil
[4]Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, SP, Brazil
[5]Universidade Federal de Alagoas, Al, Brazil

E-mail: lcoliveira@biomag.usp.br

**Abstract**. The study of radiation defects created in biomaterials, such as bone and teeth, can be used in dating with importance to palaeontology and archaeology. Two Stegomastodon teeth (AL1 and AL2) from north-eastern Brazilian megafauna were studied by electron spin resonance (ESR) spectroscopy. The samples were collected in Fazenda Ovo da Ema, (913349 / 3714965) UTM, Alagoas state, Brazil. The dating of these samples can contribute to the better knowledge of megafauna presence in this region as well as to the events associated to the extinction of these species.

## 1. Introduction

Electron spin resonance (ESR) is a non-destructive method of measuring the concentration of paramagnetic centres and free radicals in solids and liquids. Its application to dating technique is based on the fact that fossil material received radiation from uranium, thorium, potassium and their decay products plus cosmic radiation during the period that it was buried. The absorbed dose can be converted in age through the annual dose rate of the place where the sample was collected and the internal dose rate given by the radioisotopes concentration. For teeth the ROSY ESR software has been successfully used to this calculation [1].

The ESR dating signal arises from carbonate impurities in the dahllite lattice [2]. It exhibits an axial powder pattern ESR spectrum with g-value near 2.0018 and 1.997 (at 337.6 mT and 338 mT respectively in figure 1). Dose response of the peak-to-peak intensity of the signal at g=2.0018 (signal A) is routinely used in ESR dating of tooth enamel to determine the equivalent or archaeological dose (AD).

The ESR measurement is relatively simple, requires a small quantity of material, and the ESR technique has a wide range of age applicability (from a few hundreds to million years). The amount of material to be dated can be an impediment for the use of others conventional techniques. Higher microwave frequency has been used as an alternative in these cases, allowing the use of ESR dating for small sample masses and also getting spectrum with higher resolution and sensitivity [3]. Kinoshita et al, 2005 [4] demonstrated that the K-Band (24GHz) ESR spectra of fossil teeth presents similar resolution obtained using Q-Band (35GHz) with advantage in the signal quantification that is more precise in comparison with 35GHz. The ESR dating has generated relevant data for archaeological studies, especially in cases where fossilization process does not allow the use of the conventional C-14. These results are in agreement with data from others techniques [5,6,7,8].

It is important to stress that this dosimetric/dating technique not destroy the paramagnetic centers during the measurement process and in situ measurements can also be performed with appropriate instrumentation [9].

In the north-eastern Brazil countryside a case of extinct wildlife Pleistocene of large mammals, known as megafauna, has been documented. This fauna, tiger-teeth-of sable, mastodontes, giant armadillos, giant Sloths, toxodon, paleolhama, among others, are found mainly in deposits of tanks, which are depressions in crystalline embasement of the Pre-Cambrian, which formed old lagoons. It is common assign to these animals an age which is linked to the end of the Pleistocene, or approximately 10 thousand years before the present. After the interstadial stage (+ / - 60,000 years), a warmer phase of the last glacial period in the Late Pleistocene. Possibly climate changes with a tendency for more dry and warm periods, leading to reduction in the supply of water in the region caused changes in vegetation composition that nowadays have the predominance of plants with leaf that has little mass and little nutritional value. The extinction of these mammals and fauna are associated mainly to these changes.

## 2. Materials and methods

### 2.1. Sample preparation and measurement set up

Two Stegomastodon teeth samples were obtained from Fazenda Ovo da Ema, (913349 / 3714965) UTM, Alagoas state, Brazil. The enamel was mechanically separated from dentin and chemically treated with a saturated solution of NaOH (30%) in an ultrasound bath, in order to remove the remaining dentin. The samples were etched in an HCl solution (1:10) and an external layer of ~ 500μm was eliminated. Later, the enamel was powdered in fine particles ($\phi < 0.5$mm), divided in 14 aliquots of about 100 mg and a set of additive dose, up to 2500 Gy was given. The enamel powders were irradiated by $^{60}$Co γ-rays at room temperature with a dose rate of 4.47 kGy/h with an appropriate build up layer. The doses were 0, 10, 20, 50, 100, 200, 300, 400, 600, 800, 1000, 1500, 2000 and 2500Gy respectively, for each aliquot.

ESR measurements were performed at room temperature, after two months, with a Varian E-4 X-band spectrometer. The magnetic field was modulated at 100 kHz with peak-to-peak amplitude of 0.2 mT. A 20 mW microwave power was used in order to avoid saturation of the ESR signals. A scan range of 10 mT with a scan time of one minute and time constant of 200 ms was taken, given 300 data points resolution.

### 2.2. g factor measurement

The absolute measurement of g factor requires knowledge of the microwave frequency and the resonant magnetic field. A number of systematic errors can enter [10] in this determination; hence absolute measurements are rarely attempted. Instead, it is usually employed standards for which the g factors are well known. In this work, the DPPH (α, α-diphenyl-β-picrylhydrazyl) powder with g factor of 2.00037±0.0002 was used as standard. The unknown g factor $g_X$ is then calculated from

$$g_X = \frac{g_S H_S}{H_X} = \frac{g_s H_S}{H_S - \Delta H} \cong g_s \left(1 + \frac{\Delta H}{H_S}\right) \tag{1}$$

here $g_S$ is the g factor of the standard and $H_S$ and $H_X$ are the resonant magnetic fields for standard and unknown, respectively, and $\Delta H = H_S - H_X$ .

### 2.3 Additive dose method and age

In this work the peak-to-peak method was used. This method consists on taking the amplitude between the top to the bottom of a chosen ESR line, as showed in Figure 1 represented by the letter A. A sample irradiated with known doses (Q) yields a growth curve. For each aliquot measurement the distance A is taken and plotted against the received dose. Later, the experimental data points are fitted to a mathematical expression. The model that best express the growth curve as function of received dose was discussed by Ikeya to be an exponential that is expressed in equation (2).The following equation was used to relate the natural dose or archaeological dose (AD) received by the sample up to the present:

$$I(Q) = I_s(1 - e^{-(Q+AD)/SD}) \tag{2}$$

where $I_S$ is the saturation intensity, $SD$ is the saturation dose in a laboratory irradiation. Thus, by fitting the experimental data (dose response) to equation 2, the equivalent/archaeological dose (AD) can be found out.

The age $t$ of a tooth is determined by the ratio of the equivalent dose to the effective annual dose rate $d$, which is composed of external ($d_{ext}$) and internal ($d_{int}$) components. This can be done under the hypothesis that the annual dose rate presently determined is the same as in previous time and that the fading of signal is negligible. Therefore, an integral expression is [11] is used to solve for $t$:

$$AD(t) = \int_0^t d\, dt \tag{3}$$

where, $AD$ is obtained through the additive dose method. The value for $d$ as well as for $t$ was found out by using the ROSY software through the radioisotope's concentration in the sediment and in the sample [3]. The concentration of $^{238}$U and $^{232}$Th present in the samples and from the soil where the samples were buried were obtained by neutron activation analysis (NAA) and the concentration of potassium in the samples was determined by atomic absorption spectroscopy.

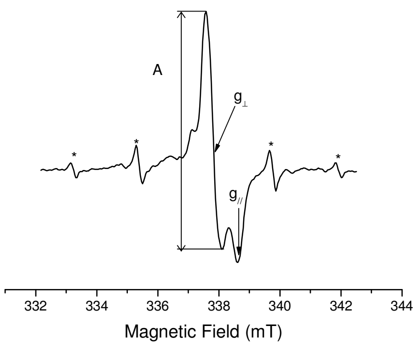


**Figure 1.** ESR spectrum of tooth enamel (AL2). Signal amplitude at g⊥ was used to determine the AD. * indicates the isopropyl $(CH_3)_2C$.-R) signal.

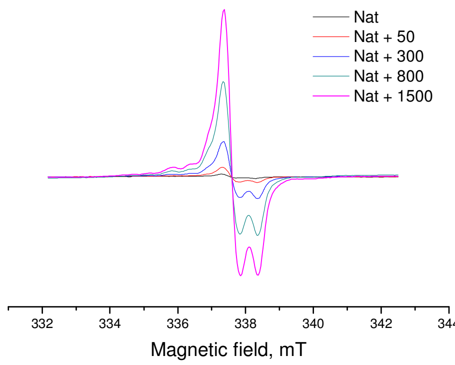


**Figure 2.** Enhancement of the ESR signal of the AL2 tooth sample obtained after 50, 300, 800 and 1500Gy, respectively of $^{60}$Co irradiation.

## 3. Results and discussions

The native ESR spectrum of these samples shows a strong signal with spectroscopic factors at $g_\perp$ = 2.0025 and $g_{//}$ = 1.9973 related to $CO_2^-$ radical in hydroxyapatite. Figure 1 shows the native spectrum of sample AL2. We can also verify the presence of the signal of isopropyl radical with hyperfine splitting of 2.17 mT. This septet signal was observed by others authors in middle Pleistocene tooth samples [11].

The additive dose method was used to plot the dose-response curve (figure 3) and an archaeological dose (AD) of 24.5 ± 0.5 Gy and 87.8 ± 0.5 Gy, for AL1 and AL2, respectively, were found out by using exponential fitting, through the equation (2). Carefully measurements made it possible to find a correlation level higher than 0.999. Through the figure it is possible see that the fitting is visually very good.

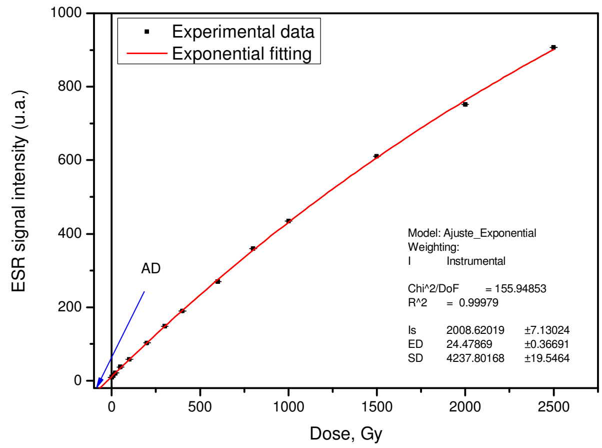


**Figure 3**. Dose–response curves of sample AL1 fitted by Equation (2).

The total annual dose rate and the sample age were found by using the ROSY software [1] where we introduced the concentration of uranium-238, thorium-232 and potassium-40 as well as the cosmic rays rate. The concentration of these radioactive elements was found by NAA technique. The results of this analysis are reported in Table 1. With these data on hand and the archaeological dose the age of the two samples were calculated. In Table 2 the age of the two teeth sample are presented as well as the environmental annual dose rate, where the samples were buried. The values, for the annual dose rate, are relatively high when they are compared with the earth's dose rate that is generally between 0.5 and 1.0 mGy/a. However, other author has found value of 1.7 mGy/a (for more details see reference [5]). Nevertheless, values lower than 0.5 mGy/a or higher than 5mGy/a are rarely to be found at an ordinary place. This fact, allow us to conclude that these values are acceptable.

Our results indicate dates that are coherent with other archaeological and paleontological findings by others authors in Brazil [12].

**Table 1**. Radioisotope concentrations in the tooth (enamel and dentine) samples and soil obtained by NAA (µg g-1).

| Sample | [$^{238}$U] (ppm) | [$^{232}$Th] (ppm) | [$^{40}$K] (ppm) |
|---|---|---|---|
| AL1- Enamel | < 0.05 | <0.01 | <750 |
| AL2- Enamel | < 0.05 | <0.01 | <750 |
| AL1- Dentine | 10.9 ± 0.5 | <0.01 | <750 |
| AL2- Dentine | 2.9 ± 0.5 | <0.01 | <750 |
| Soil | 4.1±0.8 | 22.7±0.2 | 17837±444 |

**Table 2.** Ages and total dose rate ($D_t$) of the tooth samples. The cosmic rays dose of 250 µGy/a was considered.

| Sample | AD | EU age | EU $D_t$ | LU age | LU $D_t$ |
|---|---|---|---|---|---|

| | (Gy) | (ka) | (mGy/a) | (ka) | (mGy/a) |
|---|---|---|---|---|---|
| AL1 | 24.5±0.5 | 10±0.5 | 2.355 | 10±0.5 | 2.340 |
| AL2 | 87.8±0.5 | 39.5±1 | 2.220 | 39.8±1 | 2.202 |

**Conclusions**

Based on knowledge of the physics of stable radiation defects created in hydroxyapatite, present in enamel, it has been possible to determine the accumulated dose in the material and by modeling the dose deposition the age can be calculated. Our results indicate dates that are coherent with other archaeological and paleontological findings in Brazil.

The ESR dating of Stegomastodon waringi tooth are the first ones that were done on mammals fossils on Alagoas state. The ages obtained by ESR suggest that this animal had lived on this region between the interstadial and on the end of the Pleistocene period. This warmer period was indicated by the appearing and predominance of plants with little leaf mass on the semi-arid region of the Brazilian northeast.

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