

## ESR dating at K and X band of northeastern Brazilian megafauna

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### Abstract

The archaeological dose (AD) was measured in three tooth samples of giant mammals that belonged to Brazilian megafauna using electron spin resonance (ESR) spectroscopy at X-band ( $\nu \sim 9.5$  GHz) and K-band ( $\nu \sim 24$  GHz). Samples were collected in Lagoa de Dentro, Puxinanã city in Paraíba, a northeast state in Brazil and were identified as *Haplomastodon waringi* (Holland) (two teeth) and one tooth sample of *Xenorhinotherium bahiense* (Cartele and Lessa). The average AD led to an age for the *Haplomastodon* samples of 11.6 ky bp. For one sample (*Haplomastodon*) K-band was also employed to evaluate the AD. The K-band spectrum had three components, determined using spectral simulation as follows: a wide isotropic line with  $g$  factor 2.0048, an orthorhombic line with  $g_x = 2.0034$ ,  $g_y = 2.0022$  and  $g_z = 1.9974$ , and another isotropic line with  $g$  factor 2.0008. The amplitude of these three signals increase with the added dose and the average dose found was  $26 \pm 5$  Gy. This result is compatible with the AD determined with X-band  $21 \pm 3$  Gy.

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### 1. Introduction

The Brazilian state of Paraíba is considered rich in sedimentary deposits which contain fossils of giant quaternary mammals that lived throughout Brazil's northeastern region and South America. These deposits have been studied, especially their taxonomic and

taphonomic aspects. Nevertheless, few research studies offer absolute dating of these mammals so far, though it has been estimated that their age must be, at most, the end of Pleistocene or the early years of Holocene, when drastic weather changes would have caused or accelerated the extinction of the giant mammals.

Lagoa de Dentro, Puxinanã, in Paraíba state, is a sedimentary deposit in a lake with fossiliferous materials, bones and teeth in whole and in pieces, which reveal an exceptional degree of preservation. Due to their better state of preservation, two tooth samples of

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*Haplomastodon waringi* (Holland) and one tooth sample of *Xenorhinotherium bahiense* (Cartele and Lessa) were selected for electron spin resonance (ESR) dating.

ESR dating is based on the fact that ionizing radiation can create stable free radicals in insulating materials, like tooth enamel and bones. 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, and potassium that decay during the time that the sample was buried. Assuming that “artificial radiation”- made in the laboratory—produces the same defects as natural radiation, we can determine a relationship between ESR signal amplitude and artificial dose, and from that the archaeological dose (AD) is found. Using this piece of information and the concentration of U, Th, and K, the ages of the samples were calculated using the software “ROSY ESR dating program” (Brennan et al., 1997, 1999).

The spectrum of the fossil tooth enamel in X-band shows a signal with axial symmetry. Usually the amplitude of this signal is used for AD determination. However, it is known that several paramagnetic centers contribute to this signal (Callens et al., 1989; Schramm and Rossi, 2000; Vanhaelewyn et al, 2000; Callens et al., 2002). A K-band (24 GHz, central field  $\sim 850$  mT for  $g \sim 2.00$ ) spectrometer was used in order to get better spectral resolution and to evaluate how the composition of lines can affect the estimate of the AD in X-band. Each line is characterized by its  $g$ -factor. Eq. (1) shows that when there are two lines with  $g_1$  and  $g_2$ , the separation ( $\Delta H$ ) in the recorded spectrum as a function of magnetic field is proportional to the microwave frequency  $\nu$ . Thus, the spectrum at 24 GHz (K-band) presents almost a three fold increase in spectral resolution in comparison with X-band.

$$\Delta H = h\nu \left( \frac{1}{g_1\beta} - \frac{1}{g_2\beta} \right). \quad (1)$$

The possibility of precise quantification of the signal in irradiated enamel at K-band frequency has been studied previously (Kinoshita et al., 2002).

## 2. Experimental

A fraction of each sample was washed with water and dried in vacuum. The external thin layer of about 1 mm was carefully removed with a scalpel before samples were crushed. The samples were crushed manually to grain sizes of about 0.75 mm for use in X-band and 0.2 mm for use in K-band. This grain size produced spectra with no angular variation in the magnetic field. The material obtained was divided in aliquots of about 200 mg and placed inside plastic tubes. All tubes, except

one, were irradiated with gamma rays, using a tele-radiotherapy source (Gammatron-S Siemens) in air, at room temperature with a dose rate of 1.2 Gy/min using 0.4 g/mm<sup>2</sup> thick Lucite build-up cap over the samples. The doses used were 30, 60, 120, 150, 180, 210, 240, 270 and 300 Gy. After irradiation, the samples were transferred to ESR quartz tubes with 5 mm diameter. The ESR signals were measured in a computer interfaced Varian E-4 X-band spectrometer, equipped with a rectangular cavity (TE-102, model E-231). The spectrometer parameters used were central field 328 mT, scanning field 10 mT, modulation amplitude 0.2 mT, modulation frequency 100 kHz, and microwave power 20 mW. This microwave power was chosen after a saturation plot of our sample was made for our spectrometer. The amplitude of the signal ( $g_{\perp}$ ), normalized with the sample mass, was related with the dose. A linear fitting was used for determination of the AD. An average sample mass of 100 mg was used in this experiment.

The K-band spectrometer was assembled in our laboratory with a 12' electromagnet (Varian), a magnetic field controller, a microwave bridge and cylindrical cavity (Bruker), a microwave digital frequency counter (HP), and a lock-in amplifier (EG&G). This equipment is controlled by a microcomputer via GPIB card. The data acquisition is made by software written in the HP-VEE platform. The spectrometer parameters used were central field 854 mT, scanning field 10 mT, modulation amplitude 0.2 mT, microwave power 0.63 mW, modulation frequency 50 kHz, and microwave frequency 23.9 GHz. The K-band quartz tube has a diameter of 3 mm and  $\sim 10$  mg of sample was used. The amplitude of each component of spectrum, normalized by mass, was measured as a function of the dose.

## 3. Results

The ESR spectra using X-band of natural and irradiated sample of *Haplomastodon* are presented in Fig. 1. In these spectra we can identify the signal with axial symmetry ( $g_{\parallel} = 2.0024$  and  $g_{\perp} = 1.9977$ ), usually used for AD determination. Measuring the intensity of this signal peak-to-peak for each additional dose, we get the dose–response curve. Fig. 2 shows the dose–response curve for the three samples. To fit the data, a linear and an exponential fitting were tried; the data were best fitted by a linear function. The ADs are  $21 \pm 3$  Gy,  $22 \pm 4$  Gy,  $26 \pm 6$  Gy, respectively, for *Haplomastodon* (samples 1 and 2) and *Xenorhinotherium*.

The ages of the samples were calculated by the ROSY ESR dating program and the results are reported in Table 1. The concentration of <sup>238</sup>U and <sup>232</sup>Th present in the samples and from the soil where the samples were buried were obtained by neutron activation analysis

(NAA). The concentration (%) of potassium in the samples was determined by atomic absorption spectroscopy. Table 2 shows these data. The value of 0.15 was used for *k*-value, that is, the ratio of defects creation efficiency for  $\alpha$  particles to internal dose rate calculation.

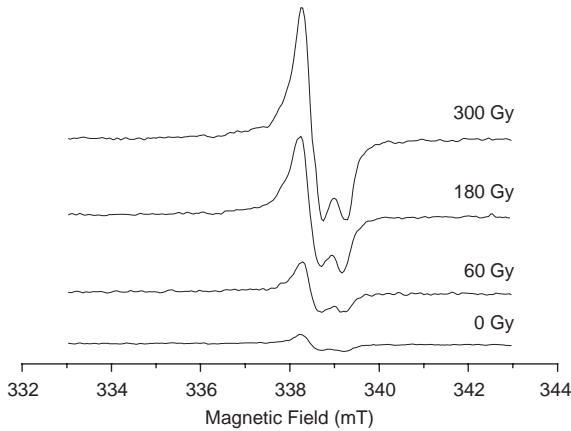


Fig. 1. Natural and post-irradiated ESR spectra using X-band of *Haplomastodon* tooth enamel

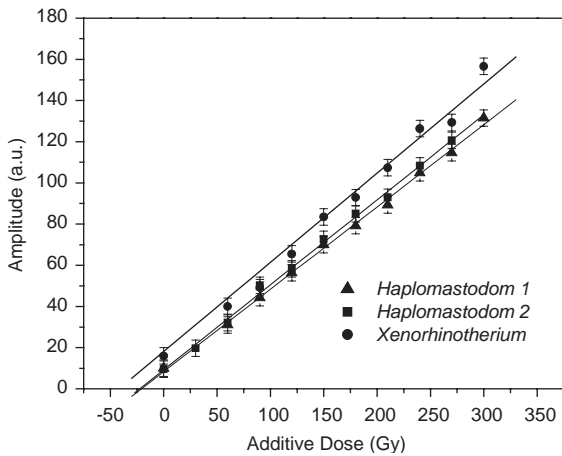


Fig. 2. Dose–response curve of the samples: *Haplomastodon* (two teeth) and *Xenorhinotherium* (one tooth).

The energy released by  $\alpha$  particles by the soil was not considered because the maximum penetration depths of these particles are 40–60  $\mu\text{m}$ , shorter than the layer removed in the sample preparation. The cosmic and gamma rays dose in the site where the samples were collected is 250  $\mu\text{Gy}/\text{y}$  and an initial  $^{234}\text{U}/^{238}\text{U}$  ratio of 1.4 was assumed for age calculations.

Fig. 3 relates the K-band ESR spectra for irradiated tooth enamel of *Haplomastodon* (sample 1) and a comparison between the X- and K- band, showing an improvement in spectral resolution. Fig. 4 shows the three components of this signal. Spectra simulations (SimFonia-Bruker software) were used to determine these components as well as their amplitudes, which are a wide and isotropic line at  $g = 2.0048$ , an orthorhombic line with  $g_x = 2.0034$ ,  $g_y = 2.0022$  and  $g_z = 1.9974$  ascribed to  $\text{CO}_2^-$  radical, and an isotropic line at  $g = 2.0008$  also attributed to  $\text{CO}_2^-$  radical (Callens et al., 1989; Schramm and Rossi, 2000). The summation of the three components obtained shows a good agreement with the experimental spectrum. Fig. 5 shows the dose–response curve for each component of K-band spectrum. The ADs extrapolated from this curve are  $26 \pm 5$  Gy for orthorhombic signal,  $28 \pm 3$  Gy for the wide and isotropic line, and  $25 \pm 7$  Gy for the isotropic line. The average AD is  $26 \pm 5$  Gy and was used for age determination.

#### 4. Discussion and conclusion

The work of Jonas and Grün (1997) already called our attention to the fact that the use of the directly observed signal of axial symmetry in X-band must be taken as an estimate of the AD. Studies in Q-band show the components of this axial signal and the possibility that the value of AD estimated in X-band is being affected by the presence of other superimposed signals. However, quantitative measurements in the Q-band are extremely difficult due to the diverse sources of imprecision, mainly related to the reduced amount of material and sample positioning in the resonant cavity. High doses of radiation are necessary to get a signal with reasonable signal/noise ratio (Skinner et al., 2000; Callens et al., 2002).

Table 1

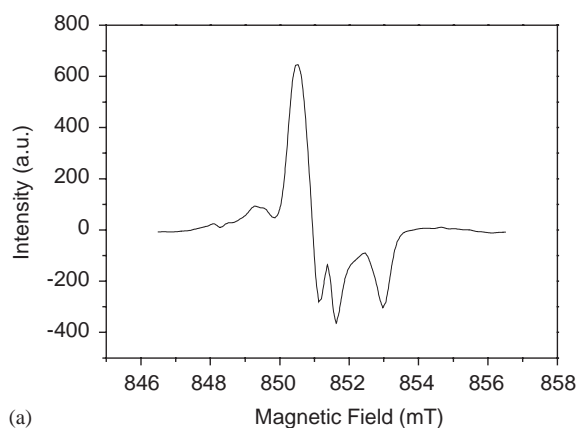
Ages and total dose rate ( $D_t$ ) of the tooth samples. The gamma + cosmic rays dose of 250  $\mu\text{Gy}/\text{y}$  was considered

Sample	AD (Gy)	EU age (ka)	EU $D_t$ (mGy/a)	LU age (ka)	LU $D_t$ (mGy/a)
<i>Haplomastodon 1</i> *	$21 \pm 3$	$30 \pm 5$	$704 \pm 10$	$40 \pm 6$	$518 \pm 4$
<i>Haplomastodon 1</i> **	$26 \pm 5$	$36 \pm 7$	$727 \pm 10$	$49 \pm 10$	$530 \pm 5$
<i>Haplomastodon 2</i>	$22 \pm 4$	$39 \pm 7$	$570 \pm 8$	$49 \pm 9$	$452 \pm 5$
<i>Xenorhinotherium</i>	$26 \pm 6$	$39 \pm 9$	$672 \pm 8$	$52 \pm 12$	$504 \pm 5$

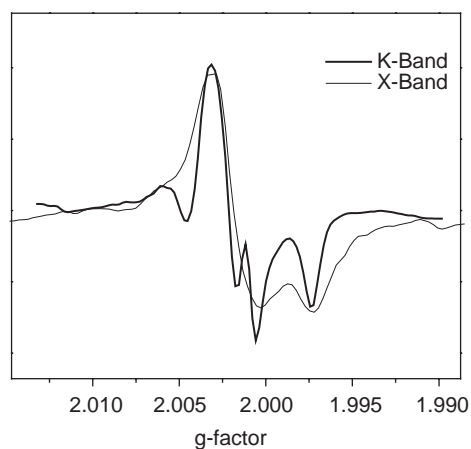
Ages calculated with the AD obtained with spectra recorded in X-band (\*) and K-band (\*\*).

Table 2  
Radioisotope concentrations in the tooth (enamel and dentine) samples

Sample	[ <sup>238</sup> U] (ppm)	[ <sup>232</sup> Th] (ppm)	[K] (%)
<i>Haplomastodon</i> 1 (en)	1.6 ± 0.2	0.5 ± 0.2	0.017 ± 0.005
<i>Haplomastodon</i> 1 (dent)	1.8 ± 0.2	4.8 ± 0.1	0.036 ± 0.005
<i>Haplomastodon</i> 2 (en)	0.9 ± 0.1	0.5 ± 0.2	0.021 ± 0.005
<i>Haplomastodon</i> 2 (dent)	1.7 ± 0.2	4.8 ± 0.1	0.030 ± 0.005
<i>Xenorhinotherium</i> (en)	1.3 ± 0.1	0.5 ± 0.2	0.018 ± 0.005
<i>Xenorhinotherium</i> (dent)	1.8 ± 0.2	4.7 ± 0.1	0.027 ± 0.005
Soil	2.2 ± 0.2	5.1 ± 0.1	0.063 ± 0.005



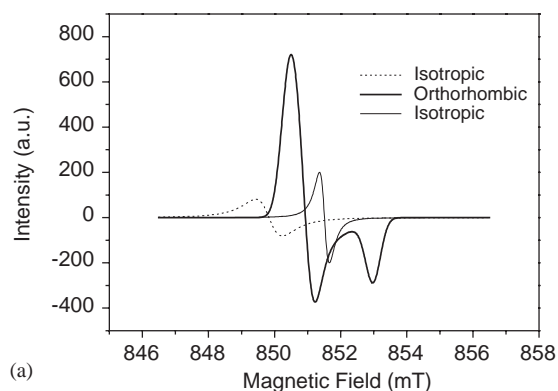
(a)



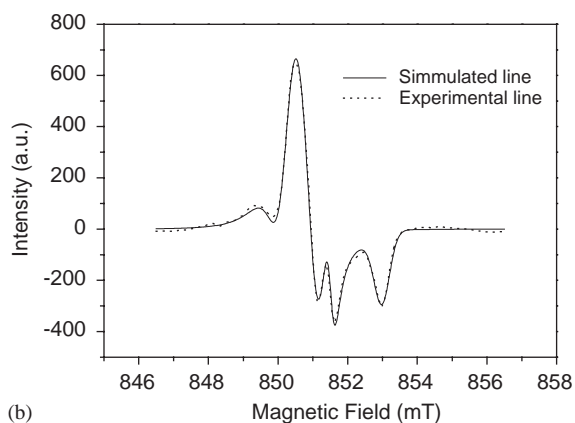
(b)

Fig. 3. K-band ESR spectrum of irradiated (300 Gy) fossil tooth enamel (*Haplomastodon* sample 1) (a) and comparison of X- and K- band spectra for the same sample. The better spectral resolution at K-band can be appreciated.

In this work it was shown that using K-band, signals with spectral resolution as good as that of Q-band are obtained with better precision in the quantification. The cavity has 2 cm height, allowing a larger amount of mass in comparison to Q-band cavities. Therefore, fewer additive doses can be used, allowing the construction of



(a)



(b)

Fig. 4. Deconvolution of the three components of the K-band spectrum (a) and (b) comparison of sum of components (simulated) and the experimental curve.

the dose–response curve with more compatible values with the AD deposited in the samples. On the other hand, comparing K-band with X-band, usually used for dosimetry and dating, we observe that the amount of sample used is about ten times smaller. In some situations, such as when human tooth enamel is extracted in vivo to be used, the reduced amount of

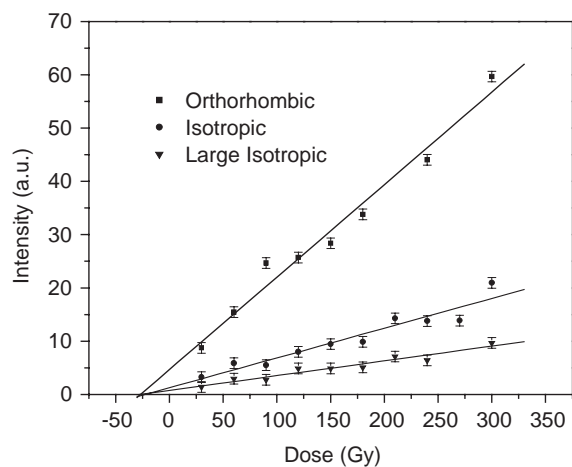


Fig. 5. Dose–response curve for each component present in the ESR K-band spectrum of the tooth *Haplomastodon* (sample 1).

sample is very important. Therefore, ESR at K-band, with its inherently better spectral resolution, appeared to be a good alternative for spectrum recording requiring quantitative measurements.

The results of AD of *Haplomastodon* (sample 1) are  $21 \pm 3$  Gy using X-band and  $26 \pm 5$  using K-band. The last result is obtained by averaging the ADs for each one of the spectrum components. The ages are compatible with the historical period (Pleistocene) of the existence of these species. The ages of the samples are compatible with the age found in other fossil samples in Brazil, dated by ESR (Baffa et al., 2000).

Finally, the precision in spin concentration quantification using K-band can be improved even more by using a secondary standard, in order to correct the variations that occur in the tuning of the cavity when the samples are exchanged.

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