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Dating of fossil human teeth and shells from Toca do Enoque site at Serra das Confusões National Park, Brazil

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ABSTRACT

This work reports the dating of a fossil human tooth and shell found at the archaeological site Toca do Enoque located in Serra das Confusões National Park (Piauí, Brazil). Many prehistoric paintings have been found at this site. An archaeological excavation unearthed three sepulchers with human skeletons and some shells. Two Brazilian laboratories, in Ribeirão Preto (USP) and Recife (UFPE), independently performed Electron Spin Resonance (ESR) measurements to date the tooth and the shell and obtain the equivalent dose received by each sample. The laboratories determined similar ages for the tooth and the shell (~4.8 kyBP). The results agreed with C-14 dating of the shell and other samples (charcoal) collected in the same sepulcher. Therefore, this work provides a valid inter-comparison of results by two independent ESR-dating laboratories and between two dating methods; i.e., C-14 and ESR, showing the validity of ESR dating for this range of ages.

Key words: Dating, ESR, EPR, shell, tooth, enamel.

INTRODUCTION

The archaeological site Toca do Enoque is located in Serra das Confusões National Park (Brazil), 50 km away from Serra da Capivara National Park. The former Park has been a World Heritage Site since 1991 and contains many prehistoric paintings that have constantly been the object of studies (Guidon and Arnaud 1991, Guidon and Delibrias 1986, Kinoshita et al. 2014, Lahaye et al. 2013, Watanabe et al. 2003). The site consists of a shelter under rocks formed in a sandstone hillside molded by erosion. From 2008 to 2009, several archaeological

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excavations have uncovered cave paintings in Toca do Enoque. One of these excavations unearthed a collective sepulcher with 17 skeletons, as shown in Fig. 1. In addition, a very elaborate funerary trousseau was discovered (Guidon and Luz 2009). The bodies were covered with layers of sediment mixed with ashes, charcoal, and ocher; they had necklaces made of feline teeth and vegetable beads along with numerous pendants. Also, shells of *Megalobilumus* gastropods (Faure et al. 2011) were found with these decorations. One of these shells was removed for dating along with a tooth extracted from one of the skeletons, numbered as skeleton 5. This almost complete skeleton belonged to a young person measuring about 110 cm. It was lying in supine position with the head tilted to the side, oriented toward the south. Inside, the skull sediment was mixed with ocher. Around the skeleton, traces of braided cotton fibers, seeds, and beads made with cut and sanded animal bones were found as part of the funerary trousseau. There was an ornament consisting of the canines and incisor teeth of an ocelot and small vegetable beads. This site is part of an important complex, and dating it is essential to place it in a proper archeological context.

ESR spectroscopy detects free radicals and unpaired electrons. It may help to estimate the radiation dose accumulated in shells and teeth because the intensity of the ESR signal is proportional to the dose deposited by the natural background radiation. ESR dating has been well established for teeth, and some models of radioisotope uptake have been computationally implemented in programs such as ROSY (Brennan et al. 1999) and DATA (Grün 2009). ESR has also been used to date shells (Kinoshita et al. 2002, Lopes et al. 2014a, b, Mascarenhas et al. 1982, Blackwell et al. 2010)

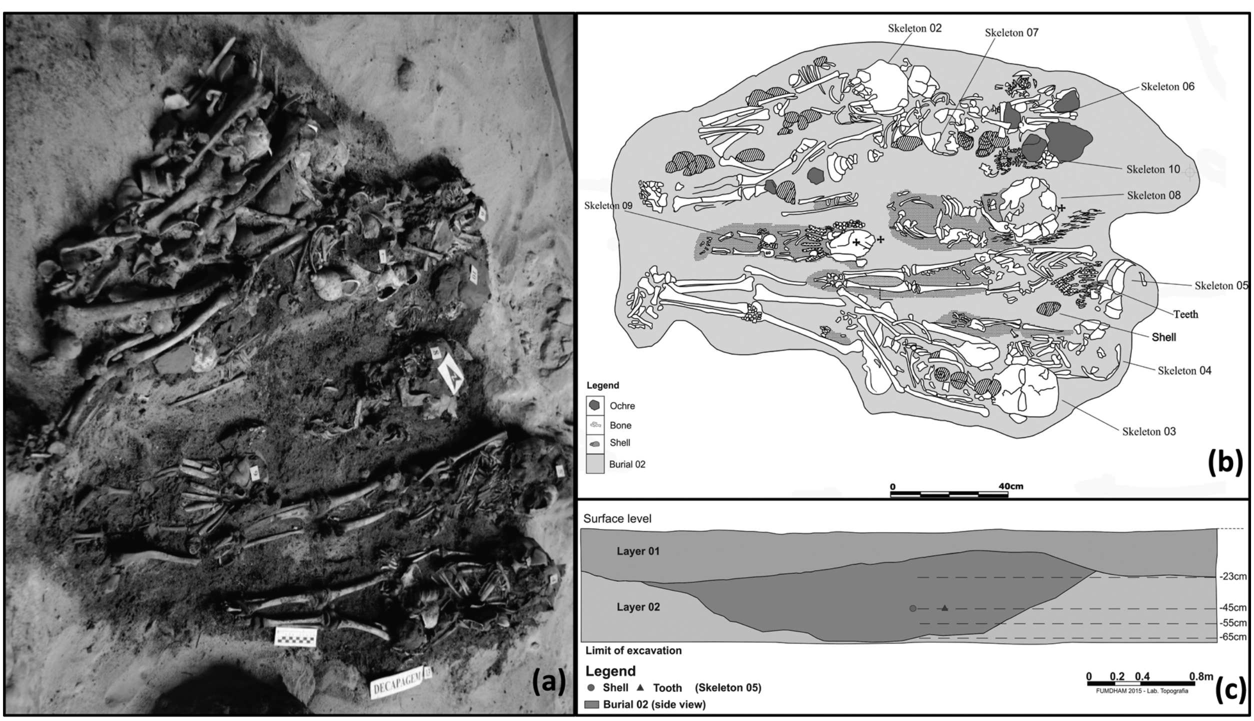

Figure 1 - (a) Photograph of the collective sepulcher (Burial 2) with many skeletons and shells found during excavation at Toca do Enoque, located in Serra das Confusões National Park (Brazil). North direction is indicated by an arrow, and a scale with 1 cm marks is shown. (b) Identification of skeletons and other adjacent materials studied herein. Skeleton 5, the tooth belonging to it, and the shell dated in this work are shown. (c) Side view of Burial 2 showing the relative position of the tooth from skeleton 5 and the shell dated in this work.

and other minerals (Kinoshita et al. 2005, Ikeya et al. 1982) especially when C-14 dating is not possible. In this work, ESR dating of a tooth and a shell were undertaken for appropriate placement of the archaeological findings in Toca do Enoque in time and for comparison between the ESR measurements conducted in two Brazilian Dating Laboratories.

MATERIALS AND METHODS

The tooth from skeleton 5 was cleaned with water, and the enamel was completely removed from dentine by freezing the tooth at 77 K in liquid nitrogen and letting it defrost to room temperature. The enamel was then easily detached from the dentine. One shell close to skeleton 5 was cleaned with water. After that, the tooth enamel and the shell were etched with acid in a 1:10 HCl solution, to remove an external layer of about 100 μm. They were then dried and crushed into particles smaller than 0.2 mm. The tooth and the shell samples were divided into aliquots and irradiated with doses ranging from 0 to 120 Gy by using a 5-mm Lucite build-up cap in a ^{60}Co Gammacell.

After irradiation and weighing, the ESR signal was independently measured in two laboratories by using X band spectrometers. A Jeol JES-FA200 spectrometer and a Bruker EMX10+ spectrometer were used at Universidade de São Paulo (USP) and Universidade Federal de Pernambuco (UFPE), respectively. Aliquots of approximately 50 mg of enamel or shell were placed in an ESR quartz tube with external diameter of 5 mm. The signal intensities in the ESR spectra were measured at least 24 h after irradiation of the samples. This ensured that transient signals had decayed by the time of ESR measurements. No preheat treatment was done. The ESR signals were normalized by the sample mass.

All the ESR spectra were recorded at room temperature. The microwave power was set below saturation, and all the other spectrometer parameters were optimized according to the experiment in each laboratory.

The conversion of D_e into age was performed with the DATA (Grün 2009) program, by using the concentration of radioisotopes present in the samples and sediment, which were used to calculate the internal and external dose rates, respectively. The contribution of cosmic radiation was accounted for in the external dose rate by considering the latitude, longitude, altitude, and depth of the place where the samples were collected.(Prescott and Hutton 1994)

Neutron Activation Analysis (NAA) and gamma spectrometry afforded the concentrations of radionuclides present in the samples and in the soil, respectively.

To determine the natural radionuclides in the sediments, sediment samples were collected near skeleton 5 and placed in plastic containers. For these measurements, the samples were crushed and mixed for homogenization, and a sample was placed in an acrylic cylindrical pot (diameter of 5 cm) and weighed. Then, the pot was sealed and stored at room temperature for 30 days, to obtain the secular equilibrium between ^{226}Ra and ^{222}Rn (and its daughter products) and allow estimation of U-238 and Th-232 concentration from the contents of daughter nuclides. The gamma spectrum was measured for five days, and the net gamma spectrum was obtained by subtraction of the background spectrum. The spectrometry system consisted of a high-purity germanium (HPGe) detector model GC1518 coupled with multichannel analyzers (Canberra, Model Eagle Plus). U-238 activity was evaluated by taking the areas of the photo peaks of its daughter nuclides Pb-214 (at 295.1 and 351.92 keV) and Bi-214 (at 295.1 and 351.92 keV) and correcting them by photo-peak efficiency detection, previously determined with the Eu-152 source, and by the relative abundances of each gamma energy photon. Th-232 activity was evaluated through the photo peaks of its daughter nuclides Pb-212 (238.63 kV) and Ac-228 (at 338, 911.2 and 966 keV). The gamma photo peak at 1460.8 keV aided determination of K-40 activity.

For comparison, one aliquot of the same shell dated by ESR was sent to Beta Analytic Laboratory for dating by radiocarbon using Accelerator Mass Spectrometry (AMS).

RESULTS AND DISCUSSION

To identify the radicals present in the shell, the spectrum of an aliquot irradiated with a dose of 700 Gy was recorded in the JEOL X-band spectrometer, with the secondary standard of Mn^{2+} present in the cavity shown in Figure 2a. In the figure, the third (g = 2.03284) and fourth (g = 1.98102) Mn^{2+} lines are indicated by * and were used to calibrate the magnetic field and g-factors. There is a signal with g factor at 2.0060 that corresponds to the SO_2^- radical. The other lines belong to the radical CO_2^- ($g_\perp$= 2.0025 and $g_{//}$=1.9973). Figure 2b shows the spectrum centered in the g~2 region for the samples irradiated with different doses. The CO_2^- intensity increases with the dose. Figure 2c contains the initial spectrum of sample (0 Gy) after 1000 scans (JEOL), which clearly shows the signals corresponding to CO_2^-. The signal-to-noise ratio is approximately 8 in this spectral region, ensuring distinction of the signal and its measurement. The stability of the spectrometer allows for the storage of many scans, enabling detection of low doses, near the detection limits. More specifically, in our previous work we demonstrated that detecting a dose of 100 mGy in 25 mg of enamel, a low dose in a very small mass (Gómez et al. 2011), is feasible. Here, we present the spectrum of a recent sample of *Megalobilumus* shell together with the spectrum of the fossil shell. Comparison of these spectra reveals perfect distinction between the archeological sample, irradiated for a long time, and the recent shell, which does not present any ESR signal. These findings strongly evidence that these shells can help to estimate low doses like the doses measured here because the intrinsic concentration of paramagnetic centers in this region of the spectrum is negligible, which apparently is a problem with other shells (Kinoshita et al. 2002, Blackwell et al. 2010, Molodkov 1988).

Because the CO_2^- radical in the shell displays composed structure, we applied spectral simulation (JEOL Simulation version 2.1.1) to extract the axial component of the signal, as demonstrated in Figure 2c. Figure 2d details the spectral components. The spectrum is composed mainly of two radicals attributed to CO_2^-; the first has axial symmetry ($g_\perp$ = 2.0025 and $g_{//}$ = 1.9973), whereas the second is isotropic (g = 2.0007) (Ikeya, 1993). The simulated signal is fitted to the experimental region, and the amplitude of the R_1 component at $g_\perp$ is used to obtain the calibration curve. Figure 3 illustrates the dose-response curve of the shell constructed by using the intensities of the CO_2^- axial component obtained by USP and UFPE. UFPE used the Simfonia Bruker software to fit the spectra.

In contrast to the shell, the spectrum of the fossil tooth enamel is dominated by CO_2^-, without interferences. Consequently, the peak-to-peak distance is usually measured to construct the dose response curve (Kinoshita et al. 2008, 2014, Avilla et al. 2013). Figure 4 contains the dose response curves for the tooth enamel obtained by both laboratories. Each point represents the results of three measurements, and error bars are the standard deviation.

The experimental data points were fitted by using the equation (Ikeya 1993):

$$I = I_0 \left\{ 1 - e^{-\left[\frac{(D+D_e)}{D_0} \right]} \right\}$$

where I is the signal intensity; I_0 and D_0 are the intensity and dose at saturation, respectively; D is the added dose; and D_e is the equivalent dose.

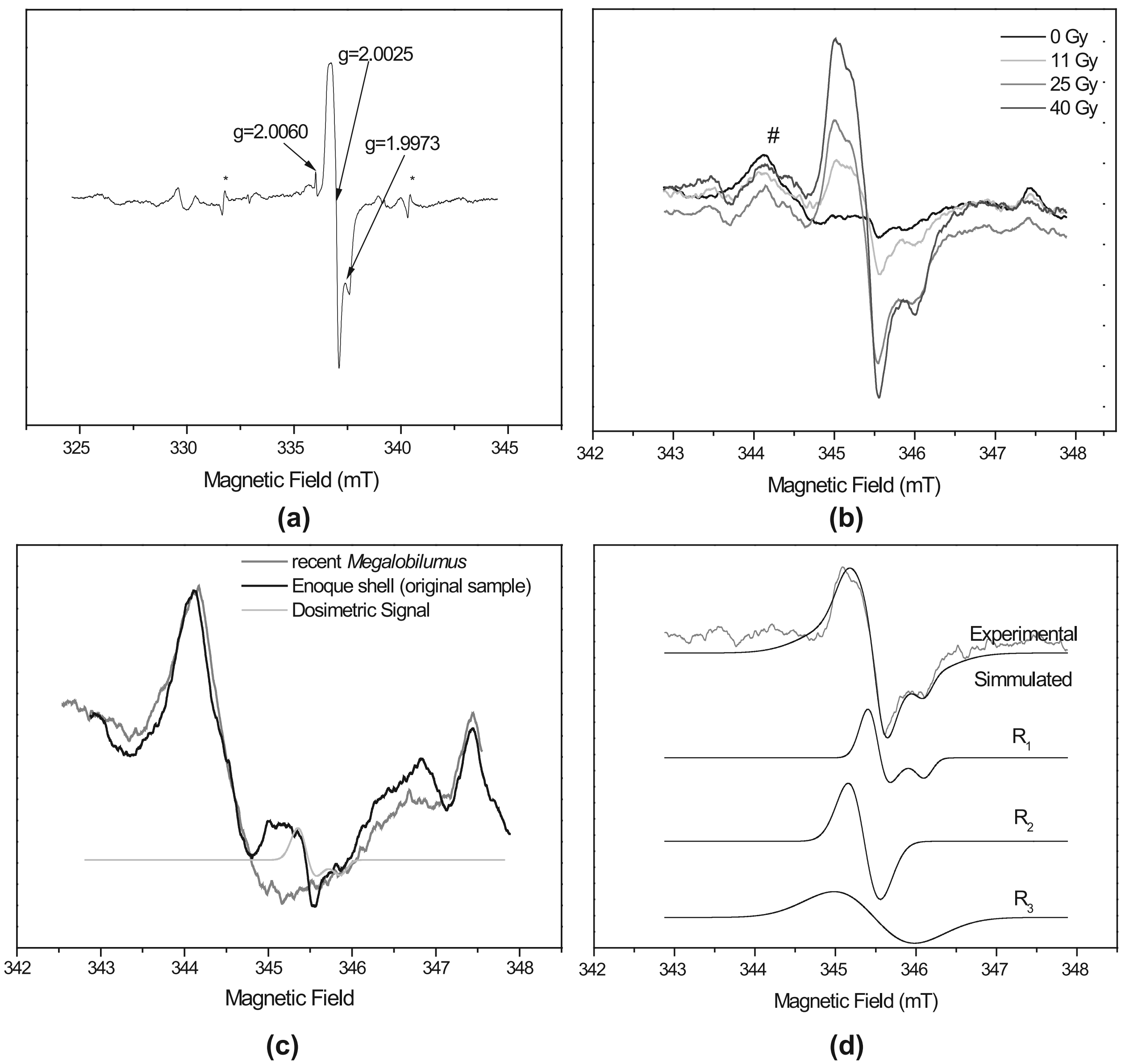

Figure 2 - ESR X-Band spectrum of the shell recorded in the Jeol spectrometer (USP). (a) Spectrum of the aliquot irradiated with a dose of 700 Gy recorded together with the secondary standard of Mn^{2+}, showing the main radicals present in the g~2 region. The * indicates the 3rd and 4th Mn^{2+} lines. Modulation amplitude = 0.05mT, microwave power = 1 mW, scan width = 20 mT, total of 10 scans. (b) Spectrum of irradiated aliquots centered in the g~2 region, showing intensification of the CO_2^- signal and the SO_2^- radical region (#) (c) Spectrum of the original sample (0 Gy) after storage of 1000 scans (black line), showing the dosimetric signal superposed by the spectrum simulation of the CO_2^- radical (light gray line) and the spectrum of recent Megalobilumus. (d) ESR spectrum deconvolution showing the main paramagnetic centers created by irradiation. R_1 is the axial CO_2^- radical with $g_\perp = 2.0025$ and $g_{//} = 1.9973$, and R_2 is the isotropic CO_2^- radical with g = 2.0007. R_3 is an unknown radical.

The equivalent dose (D_e) was obtained by fitting the data with the Origin 8.5 software and setting the *Instrumental weighing* (Skinner 2000) to calculate the uncertainty in De. Table I depicts the results for the dose-response curves of the shell and the human tooth evaluated at USP and UFPE. This dose results from exposure of the sample to the environmental radiation in the past and is related

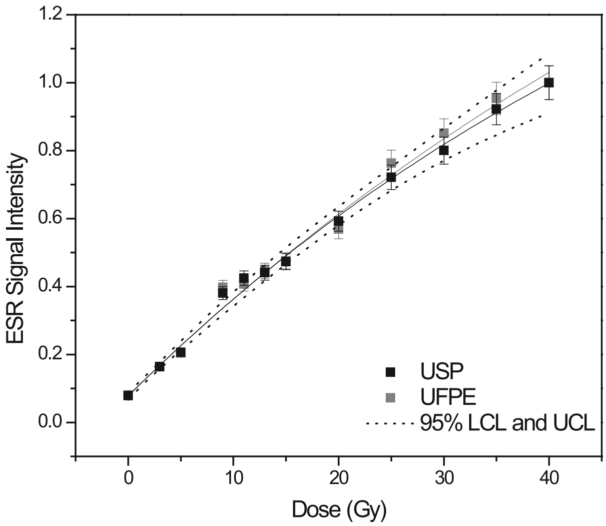

Figure 3 - Dose-response curve for the shell obtained using the axial CO_2^- radical signal intensity measured at USP (black) and UFPE (gray). Equivalent Doses found at USP: D_e=2.46±0.25 Gy and at UFPE: D_e=2.56±0.32 Gy.

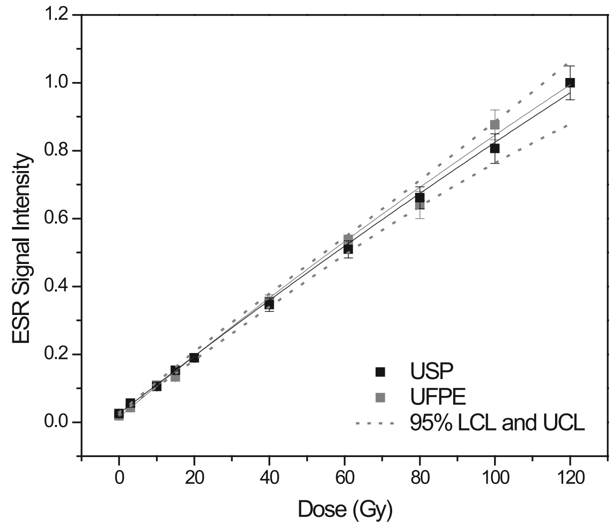

Figure 4 - Dose-response curve for the tooth enamel obtained using the axial CO_2^- radical signal intensity measured at a) USP, D_e = 2.9±0.3 Gy, and b) UFPE, D_e = 2.8±0.3 Gy.

to age. The data show that D_e values obtained for the enamel and the shell in both laboratories agree well, attesting to the precision of the methodology. Ikeya *et al*. reported a D_e value in shell buttons collected from A-Bomb victim. Their D_e was similar to the D_e found in this work (~2Gy) based on CO_2^- species for retrospective dosimetry (Ikeya 1993, Ikeya et al. 1984).

D_e was converted to age with the DATA (Grün 2009) software, by using the concentrations of radioisotopes present in the sediment, tooth, and shell given in Table II. The concentrations of radioisotopes in the shell, dentine, and enamel are below the detection limits of the Neutron Activation Analysis technique, which are 0.05, 0.01, and 750 ppm for U, Th and K, respectively.

TABLE I
Equivalent dose of the shell and human tooth of Toca do Enoque evaluated at USP and UFPE.

Sample	Equivalent Dose (Gy)
Shell (USP)	2.46 ± 0.25
Shell (UFPE)	2.56 ± 0.32
Human Tooth (USP)	2.9 ± 0.3
Human Tooth (UFPE)	2.8 ± 0.3

TABLE II
Concentration of the radioisotopes present in the samples.

Sample	^{238}U (ppm)	^{232}Th (ppm)	^{40}K (%)
Enamel	< 0.05	< 0.01	< 0.075
Dentine	< 0.05	< 0.01	< 0.075
Shell	< 0.05	< 0.01	< 0.075
Sediment	0.22 ± 0.07	2.13 ± 0.11	0.507 ± 0.015

The contribution of cosmic radiation is 253 μGy/a, obtained after corrections of latitude and longitude (09°14'653"S 43°55'625"W), altitude (~400 m a.s.l), and depth (~5 m) of the place from where the sample was collected (Prescott and Hutton 1994)

To calculate the age of the shells, the values for the efficiency of alpha radiation to produce radicals, α_{eff} = 0.10 ± 0.02, and density, d = 2.71 ± 0.02 g/cm^3, were adopted based on the literature (Blackwell et al., 2010). For the tooth, the α_{eff} = 0.13 ± 0.02, d = 3.0 ± 0.02 g/cm^3 (enamel), and d = 2.82 ± 0.02 g/cm^3 (dentine). Table III lists the results for the components of dose rates and ages. In both cases, the internal dose rate is negligible because the concentration of radioisotopes in the samples is low. However, when this is not the

TABLE III
Components of the Dose rate and result of ages for the shell and human tooth obtained by both laboratories. The contribution of cosmic radiation is 253 µGy/a.

	Shell		Tooth	
	USP	**UFPE**	**USP**	**UFPE**
D_e (Gy)	2.46 ± 0.25	2.56 ± 0.32	2.9 ± 0.3	2.8 ± 0.3
$\gamma_{external}$ (µGy/a)	489 ± 9	489 ± 9	489 ± 9	489 ± 9
$\beta_{sediment}$ (µGy/a)	23 ± 1	23 ± 1	21 ± 1	21 ± 1
$D_{internal}$ (µGy/a)	0	0	0	0
Total (µGy/a)	512 ± 9	512 ± 9	510 ± 9	510 ± 9
Age (k.a.)	4.8 ± 0.4	5.0 ± 0.6	5.6 ± 0.5	5.4 ± 0.5

case, the internal dose rate depends on the way in which the radioactive elements are incorporated by the sample. Some theoretical models for uranium uptake have been developed and implemented in a computational algorithm; for example, Early uptake, which provides the minimum age of the sample, and Linear Uptake (LU) (Ikeya 1993), which considers that uranium is absorbed at a constant rate. As already mentioned, these models were implemented in the ROSY (Brennan et al. 1999) and DATA (Grün 2009) software for tooth dating. The Recent Uptake (RU) model provides de maximum age and assumes that the uranium present in the tissues has been incorporated recently (Blackwell and Schwarcz 1993). However, when the U-series is coupled to ESR, the uptake history can be determined by solving the equation proposed by (Grün et al. 1988) with no need to assume a uranium uptake model. This is important in cases where high concentrations of radioisotopes exist in the tooth and has been applied in several problematic dating (Falguères et al. 2010, Duval et al. 2011, 2012). Fortunately, in the present case the age and isotope concentrations are such that these more sophisticated models are not necessary.

Radiocarbon ages obtained by the analyses conducted in the Beta Analytic Laboratory on the shell were (4360 ± 30) years BP-Measured Age and (4560 ± 30) years BP-Conventional Age.

Regarding the external dose rate, Figures 1b and 1c show that the tooth was not connected to the mandible but it was loose in sediment. The same was true for the shell, and there was a 45-cm layer of soil around them. According to Aitken (1985), the g contribution to the sample when 40 cm of sediment is homogeneously distributed around it is 100% of the total dose. Therefore, there is no need to correct the dose rates due to the sediment. Another point to discuss is that both materials are close to the bone that may accumulate uranium, leading to increased dose rate. Although we did not assess the contents of radioisotopes in bone, the good agreement between the ages obtained by C-14 and ESR for the shell leads to the conclusion that this variation in dose rate should lie within the precision of our measurements and go unnoticed. Furthermore, the concentration of radioisotopes in the shells, enamel, and dentin fall below the level of detection, so a similar pattern should emerge in bones.

The ages obtained by ESR agree with the values obtained by C-14, reinforcing the reliability of ESR dating. Radiocarbon analysis accomplished by Beta Analytic Laboratory on charcoal samples found in the sepulcher near Skeletons 1 and 2 indicate ages ranging from 5930 ± 50 BP for skeleton 1, 6220 ± 40 BP for the beginning of the burial of skeleton 2, and BP 6610 ± 40 for the level of skeletons (Guidon and Luz 2009). These variations suggest that the bodies were placed on the sandstone block engraved with unrecognizable artwork at different times. DNA analyses are currently being performed to establish a hypothetical membership of family groups. More recently, dating of feline coprolites near a skeleton from this site (Sianto et al. 2014) resulted in ages over 6000 years. The age found in this work agrees with findings in this region reported in other studies.

The acidity of the soil precluded several attempts at C-14 dating of the fossil bones found at this site and in the region around the site due to degradation of the organic part of the sample. Dating of the shell is a good indicator of the age of the skeleton because this shell was in the same stratum, and its position indicated that it was associated with the burial. Therefore, ESR dating of the human tooth and the shell proved to be a very convenient and useful method.

CONCLUSIONS

ESR dating is an environmental mediated dating technique and is prone to many interfering factors. However, in some cases it is the only possible way to date a fossil because there is not enough carbon available or the fossil is out of the range for C-14 dating. Hydroxyapatite (tooth) and Calcite (shell) differ in terms of the spectral characteristics and sensitivity to radiation. The D_e results found by both laboratories are similar, which adds reliability to the results. Therefore, this inter-comparison study is relevant and shows that the dating results obtained by the two laboratories and the radiocarbon technique are in good agreement.

The results of this study shall encourage the use of this technique to date other samples where the fossilization process does not allow the use of the C-14 dating method.

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RESUMO

Este trabalho relata a datação de um dente humano e concha fóssil encontrados no sítio arqueológico Toca do Enoque, localizado no Parque Nacional da Serra das Confusões (Piauí, Brasil), onde muitas pinturas pré-históricas foram encontradas. Durante uma escavação arqueológica, três enterramentos com esqueletos humanos e algumas conchas foram encontrados. Para a determinação da dose equivalente recebida por cada amostra, as medidas de Espectroscopia por Ressonância do Spin Eletrônico (ESR) para as datações do dente e da concha foram realizadas de forma independente por dois laboratórios brasileiros, em Ribeirão Preto (USP) e em Recife (UFPE). As idades obtidas para o dente e a concha por ambos os laboratórios são semelhantes (~ 4.8kyBP). Estes resultados estão de acordo com a datação por C-14 da concha e outras amostras (carvão) encontradas no mesmo sepultamento. Assim, este trabalho oferece uma comparação válida de resultados de datação por ESR de dois laboratórios independentes e entre dois métodos de datação, ou seja, C-14 e ESR com resultados que mostram a validade para a datação por ESR para essa faixa de idades.

Palavras chave: Datação, ESR, EPR, concha, dente, esmalte.

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