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Dating human occupation at Toca do Serrote das Moendas, São Raimundo Nonato, Piauí-Brasil by electron spin resonance and optically stimulated luminescence

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ABSTRACT

Excavation of Toca do Serrote das Moendas, in Piauí state, Brazil revealed a great quantity of fossil wild fauna associated with human remains. In particular, fossils of a cervid (*Blastocerus dichotomus*) were found, an animal frequently pictured in ancient rock wall paintings. In a well-defined stratum, two loose teeth of this species were found in close proximity to human bones. The teeth were independently dated by electron spin resonance (ESR) in two laboratories. The ages obtained for the teeth were 29 ± 3 ka (thousands of years) and 24 ± 1 ka. The concretion layer capping this stratum was dated by optically stimulated luminescence (OSL) of the quartz grains to 21 ± 3 ka. As these values were derived independently in three different laboratories, using different methods and equipment, these results are compelling evidence of early habitation in this area.

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Introduction

Among the most controversial questions in the field of paleoanthropology is the spread of modern humans to the New World. The Clovis paradigm suggests that the first humans arrived in the New World via the Bering Land Bridge around 12,000 years ago. They developed the Clovis culture, exemplified by tool types found at Clovis, New Mexico (Hoffecker et al., 1993). This has been repeatedly challenged by the discovery of sites that suggest human occupation that predates any Clovis material (Waters and Stafford, 2007; Waters et al., 2011). Most of these sites rely on material evidence such as lithics and hearths, as actual human remains are scarce, and have been rejected by other paleoanthropologists on the grounds that the material evidence has no clear human link (e.g., Meltzer, 1995). The most compelling evidence of pre-Clovis human occupation currently comes from examination of coprolites containing human DNA at Paisley Cave, Oregon, dated to 14,600 years ago (Gilbert et al., 2008), although these have in turn been challenged (Sistiaga et al., 2014). Here we present evidence of pre-Clovis human occupation from human skeletal remains found at Toca do Serrote das Moendas in Serra da Capivara National Park, Piaui, Brazil (Fig. 1).

'Serrotes' are calcareous massifs, residual relief forms of meta-calcareous rock. They are seen in the landscape as a sequential set of small mountains, apparently isolated on the surface but linked in the subsoil, belonging to the same karstic system. As with any karstic system, complex hydrodynamics leading to dissolution of carbonate has resulted in the formation of rock shelters and

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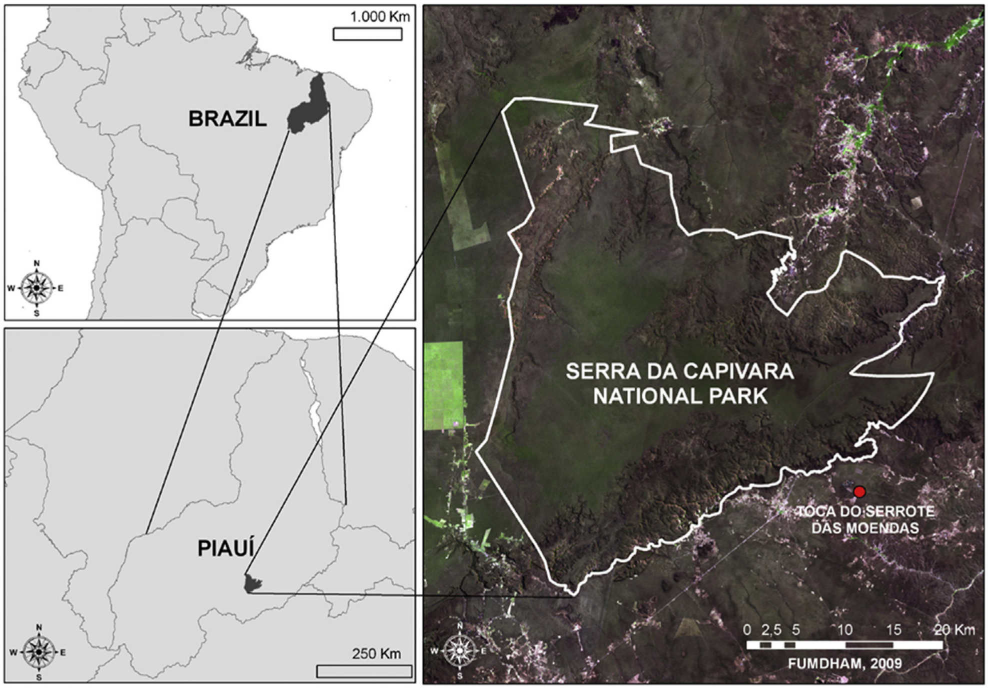

Figure 1. Map of the location of the archaeological site Toca das Moendas, São Raimundo Nonato, Piauí State, Brazil (UTM N 9025182 and UTM L 0785222).

caves, in which archaeological remains can be found. Excavations at the cave of Toca do Serrote das Moendas have yielded a wealth of megafaunal remains, lithic and other artifacts, as well as rock art and, most notably, three human skeletons. Dating this site is therefore of great importance in establishing the chronology of human occupation of this region, and by implication, other areas of the New World. Although repeated efforts to date human bones found at the site by ^{14}C were not successful, as it was not possible to recover enough ^{14}C to perform the analysis, other methods may yield reliable information. Thus electron spin resonance (ESR), with results obtained from two independent laboratories, was used to date two cervid teeth associated with the human remains, and optically stimulated luminescence (OSL) was used to date sediments from this site.

The excavations and archaeological finds

Toca das Moendas is a large cave, approximately 35 m in length and 23 m at its widest point (Fig. 2, which shows the position of the fossil paleofauna, stone tools, and three human skeletons when found). The cave floor slopes sharply downwards from NW to SE, falling some 9 m in all. In addition, roof fall has left large limestone blocks in many places. The site stratigraphy is diverse, depending on location within the cave. The components of the sediments include a silt matrix with small amounts of clay and sand, limestone fragments, and concretions. These concretions are a type of calcrete in which carbonate has been added to sediment post-depositionally as a result of water transport within the cave. The creation and extent of this formation depend on climate, with a period of calm environment being ideal for extensive calcrete formation. In addition to concretions, there are deposits of calcite over the surface in some areas. The inside of the cave was divided into five sectors (numbered 1–5) containing human bones and shells. Here we will be discussing in detail only Sector 2.

The first human skeleton found, below a concentration of blocks in sector 2, consisted of an incomplete set of the bones of a child, approximately two to four years of age. It was found in the same level as skeleton 3, approximately 2.5 m away. The recovered elements of skeleton 1 included several teeth. Electron spin resonance dating of immature teeth has been problematic in the past, and an attempt to date one of these teeth was not conclusive. The second skeleton of a child, also incomplete, was found in sector 3. The presence of sediment of different colors around and below the skeleton indicates that it was deposited in a pit. The third human skeleton, incomplete and very fragmented, was found in sector 2, in a friable layer of sediment (Layer B, Fig. 3) just below a concretion layer (Layer A, Fig. 3) consisting largely of calcite. Although only about two dozen bones or fragments could be assigned to skeletal parts, the bones of the hand were closely associated, as would be expected for elements in situ. Along with this skeleton, two teeth of a large deer, *Blastocerus dichotomus*, were found. Fig. 4 details the relative position of all of these elements. No artifacts were directly associated with the skeleton.

The stratigraphic sequence of sector 2 is shown in Fig. 4. The sequence is taken next to the cave wall and has six levels. The uppermost level (F) is a carbonate sediment followed by a concretion of calcite and sediment 30 cm thick (A). As shown in Fig. 3, the concretion extended over the area where the skeleton and teeth were found. The third layer (B) is characterized by 15 cm of a silt, sand and clay compacted sediment and a friable sediment of silt, sand and clay that is 40 cm thick, beginning at approximately at 45 cm depth. It is in this layer that skeleton 3 was found. Another concretion level (D), 10 cm thick, forms the fourth layer and this is followed by another friable layer 15 cm thick. The lowest layer found appears at a depth of 110 cm and is again characterized by compacted sediment. Bedrock was not reached during the excavation, so the total depth of the stratigraphic sequence is still unknown.

Dating considerations

Electron spin resonance is well established as a method to date dental material (Skinner, 2000) and is therefore appropriate for use with the cervid teeth found associated with the human material. While ^{14}C is the preferred method for determining ages in this time

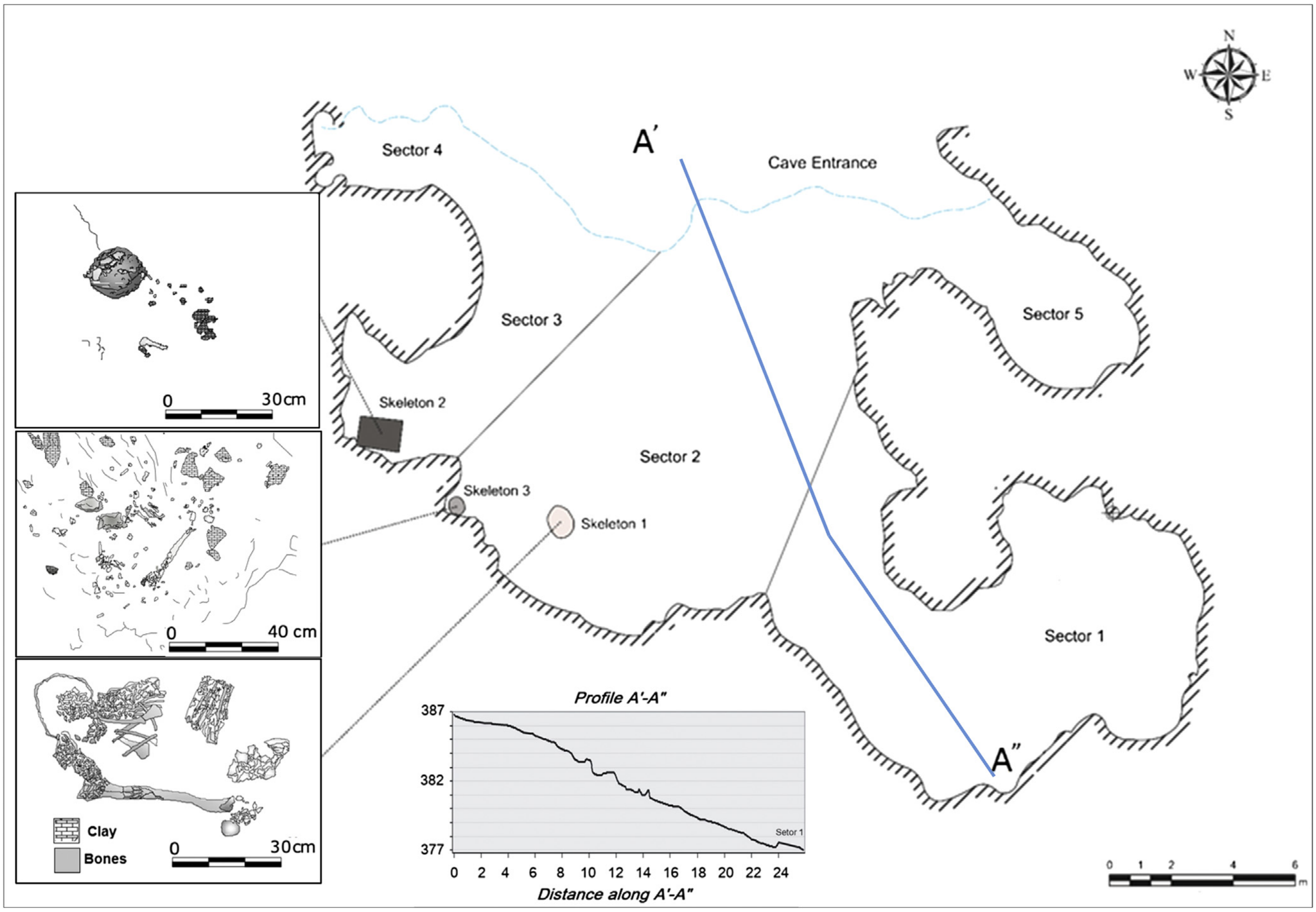

Figure 2. Layout of the Toca das Moendas indicating the sector division used to guide its exploration. The lower graph shows the level variation of about 9 m from the entrance to sector 1 following the line connecting these areas. Locations of the human skeletons found in different sectors of the cave are shown. The inset shows pictures of these remains as found.

range, trapped charge methods such as ESR and OSL provide reasonable alternatives. Most published work involving these two methods covers ages beyond the ^{14}C limit. However, specific comparisons between ESR and ^{14}C can be found in Rink et al. (1996) and Schellmann et al. (2008), as well as studies in the age range <40 ka (thousands of years) by Grün et al. (2010), Murray-Wallace and Goede (1995), Sastry et al. (2004), and Xu and Zhou (2008). For OSL, direct comparisons can be found in Richter et al. (2009) and Lee et al. (2011).

A significant problem for ESR dating of teeth is post-depositional uptake of uranium. A number of models can be considered. In recent years substantial progress has been made in distinguishing between these models by coupling ESR dating with U-series dating (Grün and McDermott, 1994). In the present case, the amount of material and the low uranium content did not warrant this additional step.

Materials and methods

The two cervid teeth associated with skeleton 3 were sent for ESR dating in two different laboratories, one of them to the Chemistry Department of Williams College (WC) and the other to Physics Department of FFLCRP, USP (Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo). Both groups worked independently to determine the age of the samples and results were compared only after all experimental work had been completed. Fig. 5 shows the two teeth (a) before cleaning and (b) after enamel extraction for one of them.

The two laboratories used different techniques for sample preparation. At USP, enamel was extracted from dentine by thermal expansion. The tooth was frozen by immersion in liquid nitrogen for a few minutes. The tooth was then removed and thawed at ambient temperature. Repeating this process a few times detached the enamel from the dentine. After mechanically removing the remaining dentine, enamel was immersed in an HCl solution diluted 1:10 for two minutes. Initially the enamel thickness was 500 μm and after the acid treatment a thickness of 300 μm was measured. Thus, this treatment removed about 100 μm from each side of the enamel fragments, ensuring that there would be no α-dose contribution from the dentine (Kinoshita et al., 2008).

The WC laboratory removed the dentine by mechanical drilling with a hand-held Dremel drill. Once all dentine had been cleaned off, the sample thickness was measured by a micrometer and an additional 20 μm of enamel was removed from each side, again in order to eliminate the effects of alpha radiation from the dentine. A minimum of 10 doses were used to determine the equivalent dose (D_e). Where the number of aliquots was less than this, ramping (re-irradiation) of aliquots occurred.

The added-irradiation procedure was also different between the two laboratories. The WC laboratory used a ^{137}Cs source at a rate of ~2.5 Gy/min. Samples were shielded by 5 mm of glass. The source has been calibrated at National Institute of Standards and Technology (NIST) with standard materials. The USP laboratory used a ^{60}Co source (1.25 MeV) at a dose rate of 1.2 Gy/min for ESR measurements. The samples were irradiated at ambient temperature

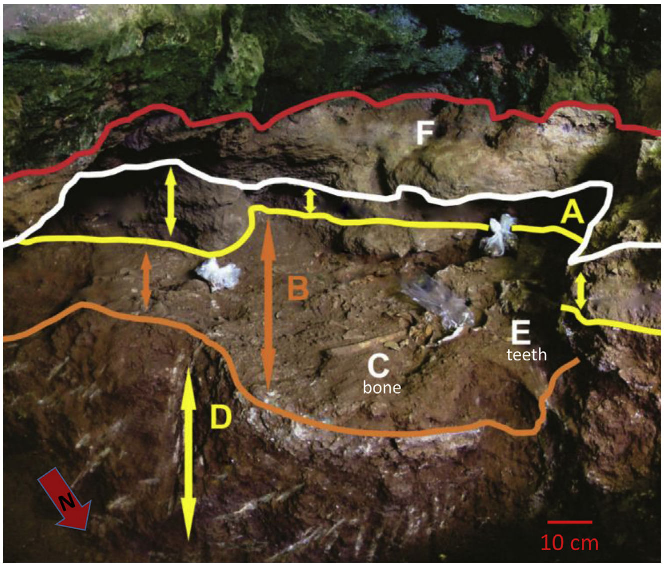

Figure 3. Relative positions of geological and archaeological elements. A. Concreted sediment dated by OSL. B. Loose sediment. C. Position of skeleton 3. D. Lower concretion. E. Teeth dated by ESR found 2 cm distant each other and 35 cm away from the human skeleton, in the same depth. F. Carbonate sediment.

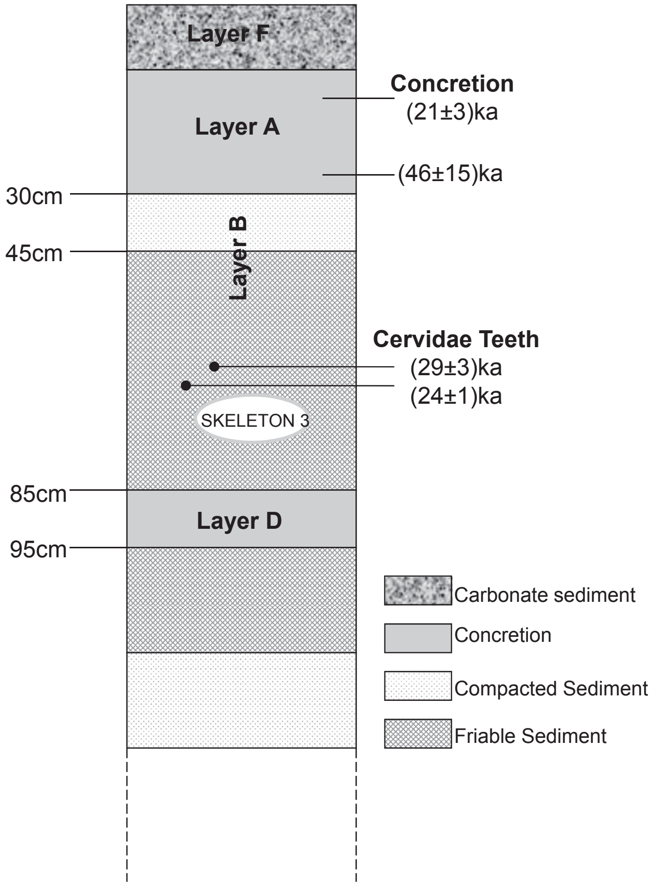

Figure 4. Stratigraphic representation of sector 2. Layer A is concretion dated by OSL (upper and lower region); layer B is friable sediment covered by compacted sediment where human bones and cervid teeth were found, layer D is concretion, layer F is carbonate sediment.

Figure 5. Pictures showing the two teeth (**A**) before cleaning and (**B**) after enamel extraction of the tooth studied at USP.

using a 5 mm plastic build up cover. This radiation source is used in radiotherapy and routinely checked for its dose rate according to the 398 IAEA (International Atomic Energy Agency) protocol, yielding an uncertainty smaller than 3%.

At USP, the ESR spectra of the enamel samples were obtained in a VARIAN E-4 and a JEOL FA200 spectrometer operating at X-band ($\nu \sim 9$ GHz). A rectangular cavity (TE-102 model E-231) for the VARIAN and cylindrical multipurpose cavity for the JEOL FA200 were used, and constantly purged with dry nitrogen. The signal was modulated at 100 kHz with modulation amplitude of 0.20 mT. The nominal microwave power was adjusted to 2 mW, below signal saturation. The central magnetic field, B_0, was 338 mT and the scanning field, ΔB, was 10 mT. Multiple one minute scans were averaged to obtain the final spectrum. A digital microwave frequency counter and manganese *g* marker allowed better precision in ensuring that the proper signal, at $g_\perp = 2.0025$ was being measured. The WC laboratory used a JEOL RE1X spectrometer, equipped with a multipurpose cylindrical cavity and operated at 2 mW power. Scan width was 10 mT at a scan speed of 1.25 mT/min. Modulation amplitude was 0.10 mT, time constant was 0.3 s, and gains for single spectra were adjusted to maximize signal-to-noise ratio.

Two samples extracted from the concretion that extended over the area where the skeleton and teeth were found were dated by OSL at UNIFESP (Universidade Federal de São Paulo). The OSL measurements were performed with a RISØ TL/OSL reader, model DA-20, blue light stimulation and for light detection an optical filter Hoya U-340 was used. For sample irradiations this apparatus is provided with ^{90}Sr/^{90}Y beta source with a rate of 0.089 Gy/s. The D_e was determined using the single aliquot-regenerative dose (SAR) method (Wintle and Murray, 2006), using single aliquots, as shown in Table 1.

The SAR protocol used pre-heating at 260 °C for 10 s to eliminate the unstable signal. The test dose used was 10% of the D_e. The D_e values were evaluated by the SAR protocol using 20 aliquots of ~3 mg each with 100 μm diameter, however, only the aliquots that passed the recycling test, which should be between 0.9 and 1.1, and a recuperation test, which should not exceed 5%, were used in the D_e determination. About 16–17 D_e values that passed all tests (recycling and recuperation) were used for final D_e calculation with a central model approximation (Galbraith et al., 1999).

Two different samples of a carbonate concretion, one near the lower edge and another one situated close to the upper edge were extracted. The samples were initially broken with a mortar and pestle and sieved to a size of 0.075–0.150 mm. They were subsequently treated with H_2O_2 to eliminate organic materials, HCl to eliminate carbonates, HF to eliminate feldspar and to remove a small surface layer of the grain, avoiding the alpha ionization contribution, HCl again to remove fluorides created by HF etching and finally SPT (Sodium Polytungstate) to separate the quartz grains from the heavy minerals. This chemical treatment yielded pure quartz grains from these samples.

Results

ESR dating

Fig. 6A shows ESR spectra of the original sample and the irradiated aliquots, recorded by the USP ESR spectrometer. The spectrum of the irradiated enamel is dominated by CO_2^- radical, with $g_\perp = 2.0025$ and $g_{//} = 1.9973$. Fig. 6B and C shows the dose-response curves of both teeth, constructed by measuring the peak to peak spectrum intensity at $g_\perp$. The experimental data points were fitted by a saturating exponential function (Ikeya, 1993):

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

where I is the ESR signal intensity, D the additive dose, D_e the archaeological dose, I_0 the intensity at saturation and D_0 the characteristic dose.

Table 1
Quartz single-aliquot regenerative-dose (SAR) protocol.

Step	Treatment	Observed
1	Give Dose	D_i
2	Pre heat (260 °C for 10 s)	
3	Stimulate for 40 s at 125 °C	L_i
4	Give test dose	D_t
5	Heat (260 °C)	
6	Stimulate for 40 s at 125 °C	T_i
7	Stimulate for 40 s at 280 °C	
8	Return to 1	

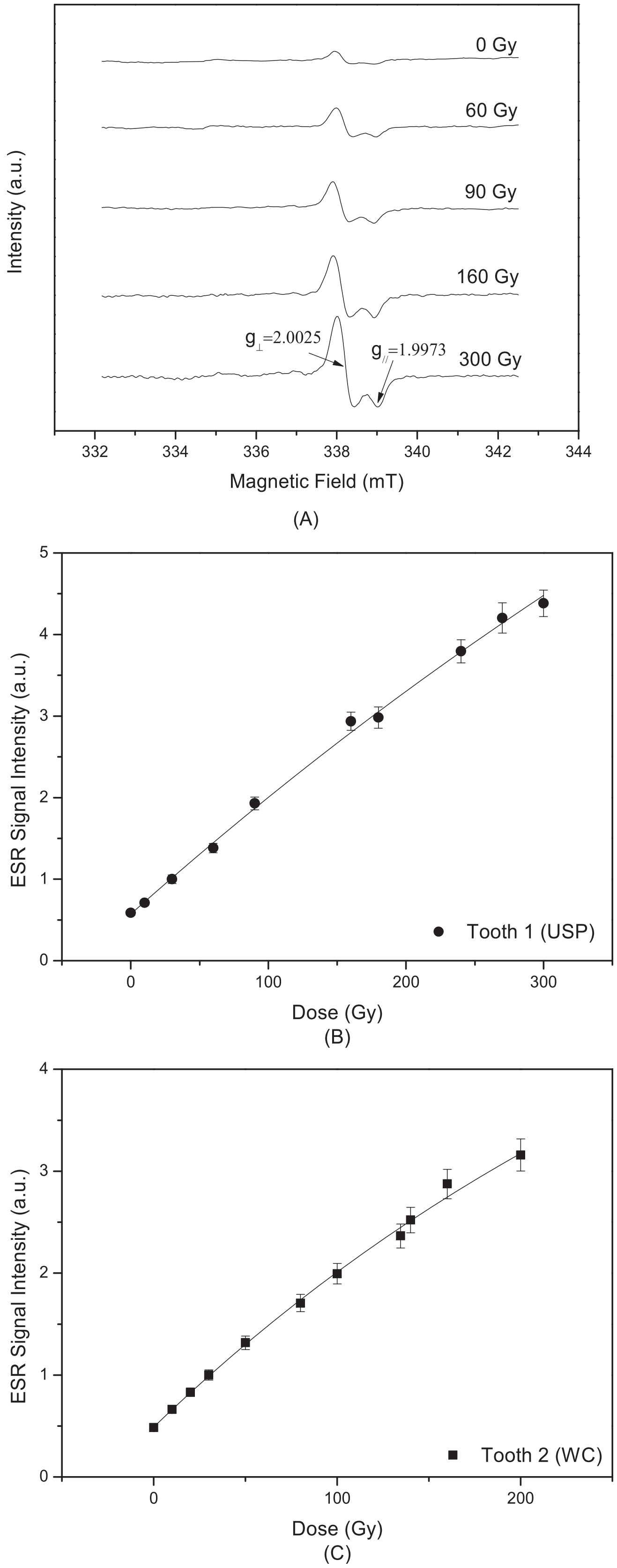

Figure 6. (**A**). ESR spectrum of original sample (0Gy) and irradiated aliquots of tooth 1, measured at USP. Dose response curves measured at USP (**B**) and WC (**C**).

The software Microcal Origin 8.5 (Microcal Software Inc, Northampton, MA, USA) was used at USP to determine D_e and associated uncertainties. The WC laboratory used the program VFIT. For both, the data points are weighted (w_{ij}) by the amplitude error bar (s_{ij}) through the relation $w_{ij} = 1/(s_{ij})^2$, which assures that the lower intensities related to the points at lower doses get higher weights (w_{ij}). This procedure has been used by the authors in other cases (Skinner et al., 2000) and is based on the fact that the lower dose points are more important in determining D_e because more of the intensity was produced by the natural radiation. The values of 37 ± 4 Gy and 32 ± 2 Gy were obtained for tooth 1 and tooth 2, respectively. A *t*-test was performed and no statistically significant difference ($p > 0.05$) was found.

The conversion of D_e to age was made using the ROSY ESR dating program (Brennan et al., 1999), with the annual dose rate determined from the main radioisotope concentrations (^{238}U, ^{232}Th and ^{40}K) present in the sediment and in the sample, and a cosmic dose rate at the site where the samples were collected of 0.934 μGy/a, calculated according to Prescott and Hutton (1994).

Table 2 shows the radioisotope concentration of the sediment, enamel and dentine, for both teeth. These measurements were performed in two laboratories (IPEN – Instituto de Pesquisas Energéticas e Nucleares, Brazil, and McMaster University, Canada). The uranium, thorium and potassium concentration were obtained by Neutron Activation Analysis (NAA) in both laboratories. The values in Table 2 show the average and standard deviation of the results. The ROSY ESR dating software was used to determine the internal (D_{int}) and external dose rates (D_{ext}) according to the radioisotope uptake model for age calculations. As radioisotope concentrations in the enamel are below detection limits, the D_{int} is negligible. The contribution of β and γ to D_{ext} are listed in Table 3; α irradiation has no contribution because samples are etched to remove the outer layer. According to Aitken (1985), the γ contribution to the sample when there are 20 cm of sediment homogeneously distributed around it is 97% of total dose. Thus, this factor was applied for age calculations. The values of 29 ± 3 ka and 24 ± 1 ka were found for the USP tooth and the WC tooth, respectively, considering the combination model for radioisotope uptake (Table 4). This model assumes that the absorption of radioisotopes into dentine is very quick, occupying only a small fraction of the burial time, as in an open system, and after this, further absorption can be neglected (early absorption), whereas in enamel the absorption process is slower and is best modeled as a linear function (linear uptake). However, within experimental error the ages are model-independent.

OSL dating

Fig. 7 shows the OSL shinedown decay curves, the typical single-aliquot regenerative dose growth curve, and radial plot results of D_e values obtained with the SAR protocol. As we can observe, the lower sample exhibited significant fluctuation in D_e values (Fig. 7c). Sixteen of a total of 20 aliquots of approximately 3 mg each were used, those that passed the recycling test (1.03) and recuperation test (1.12%), resulting in a $D_e = 141 \pm 45$ Gy. In the case of the upper sample we obtained a better result, where 93.8% of the aliquots are within ±2σ. Seventeen aliquots passed the recycling test (0.98) and recuperation test (1.19%) and the D_e was 50 ± 5 Gy. All of the results are summarized in Table 5. The D_e values differ significantly between lower and upper samples, indicating that they are two distinct samples. This is confirmed by dissimilarity in the natural radioisotope contents of the matrices surrounding the samples (Table 6).

Table 3
β and γ doses contribution to external (D_{ext}) dose rates according to the radioisotopes uptake models in the ESR dating of teeth.

	Early uptake		Linear uptake		Combination uptake	
	D_β (μGy/a)	D_γ (μGy/a)	D_β (μGy/a)	D_γ (μGy/a)	D_β (μGy/a)	D_γ (μGy/a)
Tooth 1 (USP)	305 ± 6	970 ± 60	214 ± 3	970 ± 60	305 ± 6	970 ± 60
Tooth 2 (WC)	352 ± 6	1010 ± 60	242 ± 3	1010 ± 60	352 ± 6	1010 ± 60

Table 4
Archaeological dose (De) and ESR Ages obtained on the teeth.

Sample	D_e (Gy)	E.U. (ka)	L.U. (ka)	C.U. (ka)
Tooth 1 (USP)	37 ± 4	29 ± 3	32 ± 4	29 ± 3
Tooth 2 (WC)	32 ± 2	24 ± 1	26 ± 1	24 ± 1

EU: Early Uptake; LU: Linear Uptake, CU: Combination Uptake.

The total annual dose rate was measured by the sum of measurements in situ for the external dose rate and in the laboratory for the internal dose rate. In situ measurement was performed with a NaI(Tl) gamma-spectrometer from Canberra. Radioisotope elements of the matrix were determined by gamma-spectroscopy with the same NaI(Tl) detector and Japanese standard soil samples JR-1, JG-1a, JB-3 and JG-3. About 100 g of the matrix were placed in a plastic box and sealed for at least one week, to ensure secular equilibrium was reached, after which the gamma spectra were measured. While this test could have been continued for an additional week, in our experience one week is sufficient within the precision of measurement. The water content in the matrix was negligible. As expected, the matrix is primarily carbonate, with quartz crystals and clay incorporated. Usually a pure carbonate found in caves such as a stalactite has few impurities, such as Sr, Pb, Ba and radioisotopes (Tatumi et al., 1993) due to the crystal structure, which rejects the incorporation of large ions (e.g., Th and U). The potassium content of the entire matrix was very low; below the detection limit in the upper part, and less than 1% in the lower part.

The internal dose rate D_i was calculated according to Bell's equation (Aitken, 1985):

$$D_i = D_\beta + D_\gamma^{in} \tag{2}$$

Beta (D_β) and gamma (D_γ^{in}) dose rates were calculated using natural radioisotope contents inside the concretion (Table 6). The

Table 2
Radioisotope concentrations measured in the tooth enamel and dentine and in the surrounding sediment for ESR dating.

Sample	^{238}U (ppm)		^{232}Th (ppm)		^{40}K (ppm)	
	IPEN	McMaster	IPEN	McMaster	IPEN	McMaster
Sediment	3.6 ± 0.4	3.29 ± 0.02	6.74 ± 0.03	8.45 ± 0.02	10000 ± 280	9800 ± 300
Enamel 1*	<0.05		<0.01		<750	
Enamel 2**		<0.01		<0.01		<30
Dentine 1*	7.5 ± 0.9		<0.01		<750	
Dentine 2**		8.77 ± 0.4				<30

Samples marked * sent to USP; ** sent to WC.

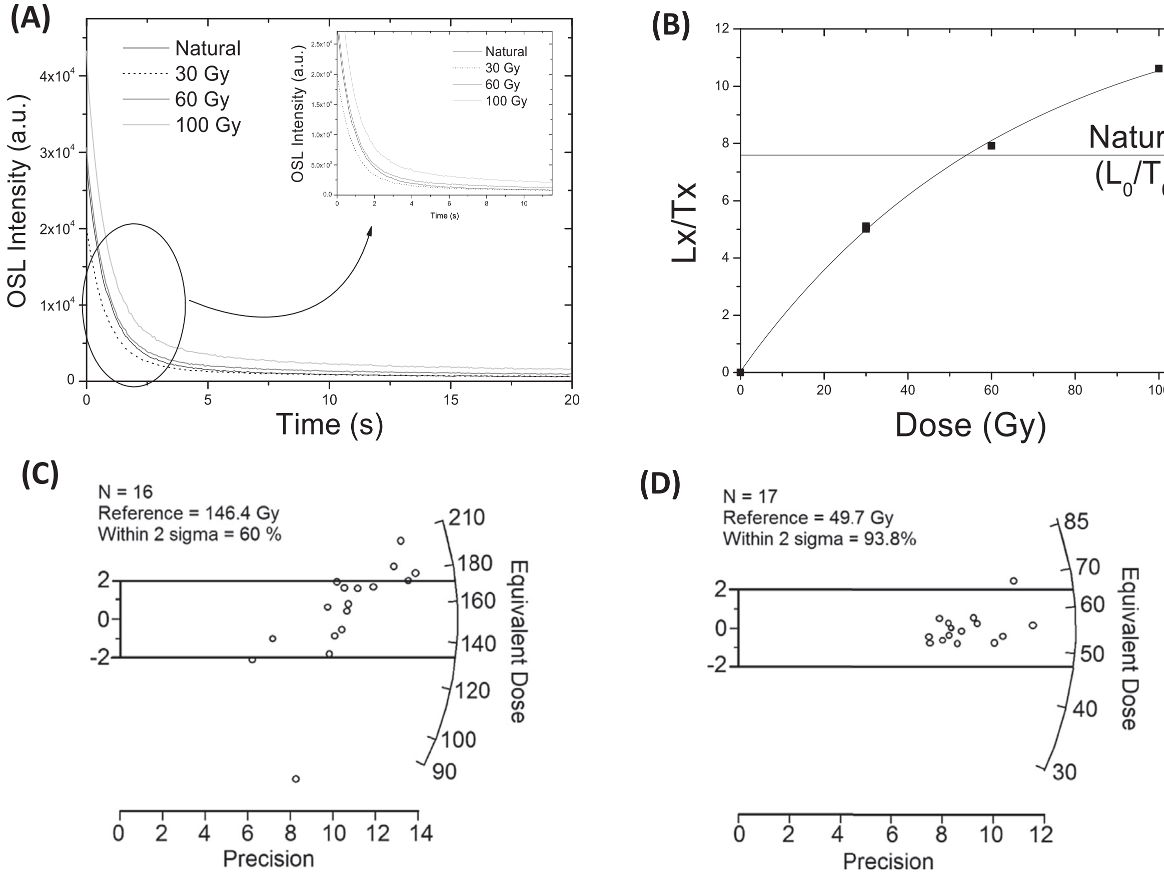

Figure 7. (**A**) OSL shinedown decay, (**B**) single-aliquot regenerative dose growth curve, Radial Plot results of D_e obtained by SAR/protocol with single aliquots of quartz grains, (**C**) lower sample, and (**D**) upper sample.

external gamma dose rate (D_γ^e), measured with a NaI(Tl) detector is (3080 ± 140) μGy/year and includes the cosmic ray contribution (D_C). The total gamma dose (D_γ) contribution in the sample was calculated using equation (3) (Aitken, 1985):

$$D_\gamma = D_\gamma^e + \frac{p}{100}\left(D_\gamma^i - D_\gamma^e\right) \quad (3)$$

where p is the self-dose percentage, obtained by multiplying the sample diameter (19 cm) with the stone density (2.5 g/cm^3). The annual dose rate D was determined by Aitken (1998):

$$D = 0.90D_\beta + D_\gamma \quad (4)$$

The results for both regions of concretion (lower and upper) and the calculated ages are given in Table 7.

These grains were presumably brought into the cave by the flow of water from outside. Grains near the bottom of the stream might well be at least partially shielded from light, while those near the surface would be completely bleached. In a calm environment within the cave, as the water evaporated and the grains were cemented into the concretion, the relative positions of the grains would have been maintained. This model could both explain the greater fluctuation in the lower sample and suggest that there was no mixing of sediment during deposition. Therefore, we have confidence that the age of 21 ± 3 ka for the capping layer is both accurate and precise.

Discussion

Three limitations must be considered when interpreting these results. Did the skeleton perhaps wash in from outside the cave, so that the dating, based on the environmental dose rate, is erroneous? Could the skeleton be an intrusive burial? Are the teeth truly associated with the skeleton? As noted earlier, taphonomic study of the skeleton shows association of critical skeletal elements such as the hand, consistent with their position in life and strongly indicating that the remains are in situ, not washed in either from outside the cave or from other areas of the cave. Determining a possible burial is more problematic. While sedimentology of the soil did not show disturbance, subtle signs could have been overlooked. However, both this possibility and the larger issue of association between teeth and skeleton are answered by the agreement of OSL and ESR. The capping layer eliminates the

Table 5
OSL/SAR-protocols test results, equivalent dose (D_e) calculated on the grains extracted from the capping layer (Fig. 3, layer A).

Sample Name	Total aliquot/Used	Recuperation test	Recycling test	D_e(Gy)
Lower	20/16	1.12%	1.03	141 ± 45
Upper	20/17	1.19%	0.98	50 ± 5

Table 6
Natural radioisotope contents in Lower and Upper samples from capping layer (Fig. 3, layer A).

Sample name	Th (ppm)	U (ppm)	K (%)
Lower	5.48 ± 0.20	1.72 ± 0.14	0.64 ± 0.09
Upper	3.87 ± 0.14	0.94 ± 0.13	b.d.l.

b.d.l. = below detection limit.

Table 7
Internal dose rate (D_i), in-situ external dose rate (D_γ^e), total gamma dose rate ($D\gamma$), annual dose rate (D) and age results calculated on for coarse grains from layer A (Fig. 3).

Sample name	D_i (μGy/a)	D_γ^e (μGy/a)	D_γ (μGy/a)	D (μGy/a)	Age (ka)
Lower	1570 ± 150	3080 ± 140	2220 ± 200	3068 ± 310	46 ± 15
Upper	560 ± 50	3080 ± 140	2110 ± 200	2330 ± 220	21 ± 3

b.d.l. = below detection limit.

possibility of burial or reworking outside the errors. At 2σ the minimum age of the cap would be ~15 ka, still considerably older than population diffusion based on the Clovis model. Additionally, the agreement of ESR results between two different labs using different protocols adds considerable confidence to the dates presented.

Notwithstanding the absence of direct dating of the human material, these results add significantly to the compelling evidence of pre-Clovis human occupation in the New World. Brazil has previously been suggested as an early occupation site (Guidon and Delibrias, 1986; Guidon and Arnaud, 1991; Roosevelt et al., 1996; Lahaye et al., 2013.). The contributions have, however, been challenged: in the case of Pedra Furada, cited by the two articles of Guidon and co-workers, by disagreements over the anthropogenic origin of lithics (Meltzer et al., 1994); in the case of Roosevelt's study of Monte Alegre by disputes over the ^{14}C dates (Tankersley, 1997). In Toca das Moendas, by contrast, we have a site with human remains and therefore definitive human occupation. The Clovis paradigm grew, in part, from the discovery of an ice-free corridor dating to ~14 ka. An earlier arrival would require new proposals for migration routes into the Americas. One possibility would be sea-based migration along the coast. Human use of boats perhaps as early as 40 ka has been documented elsewhere (Bulbeck, 2007). Any settlements along such a route would, unfortunately, now be below mean sea level. There is indirect evidence from the northwestern areas of North America that some areas now submerged were available for settlement during an earlier period (Wilson et al., 2009). Some such hypothesis gains new authority from the evidence presented here that people were present in northeast Brazil 24,000 years ago.

Author contributions

This work is the result of different contributions from the co-authors and it is important to acknowledge the participation of each one. O.B. and A.K. prepared samples, performed ESR measurements and analysis at USP and did part of the writing. A.S. prepared samples, performed the ESR measurements and analysis at WC and did most of the editing and final writing. N.G., E.I., G.D.F. and C.A.B. explored the archaeological site and described the stratigraphy and the samples. S.H.T. and M.Y. prepared samples, performed OSL measurements and analysis at UNIFESP, and A.M.G.F performed the NAA analysis.

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