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OSL and FTIR -VIS Spectroscopy Analysis of Mammal-Bearing Pleistocene Deposits

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Abstract— In the present work, Pleistocene records of fluvial deposition, with megafauna bones fossils, are dated with optically stimulated luminescence (OSL) method using single aliquots of quartz and SAR protocol. The basal fluvial samples supplied a precise OSL ages in an interval of 15.7 ka to 19.6 ka, which can be related to Last Glacial Maximum. FTIR-VIS spectroscopy experiments were made to determine the rates between hematite (Hm) and goethite (Gt), (Hm/(Hm+Gt). The obtained rates ranging from 0.06 to 0.24 were indicating wetter and cooler climatic conditions, in agreement with OSL ages and with megafauna extinction time.

Keywords—OSL dating, hematite and goethite rate, carbonate, Quaternary.

1. INTRODUCTION

The most commonly used methods in dating of continental carbonates are radiocarbon, ESR and the decay curve of the ²³⁰Th/²³⁴U. The use of radiocarbon dating can generate some errors due to the effect of water or residual carbon from source area, which can makes older age than expected. ESR method can be used in the dating of speleothems and is usually combined with results from the uranium series dating. The method of $^{230}\text{Th}/^{234}\text{U}$ has been used successfully in dating speleothems, the achievement of this approach will depend on if the detrital matter did not contaminate the sample with external isotopes, which can be added to the analysis, therefore, the method is used in pure calcite cements, most samples dated by this method are tufa, travertine and calcretes (Takamassa et al. 2013; Hameau et al., 2007 and Michel et al. 2013). In the present study, quartz crystals from calcretes were used, pioneering in Brazil, for OSL dating. Calcrete is formed on calcareous materials as a result of climatic fluctuations in arid and semiarid regions; therefore, it is used in climatic changes studies.

Recently, Kock, et al. (2009) showed dating results of pedogenic carbonate crust from fluvial gravel using OSL and Uranium-series dating, they obtained OSL ages of 30 ± 15 ka and 13 ± 11 ka, correlated with the cold periods of the Last Glacial Maximum and the Younger Dryas. However they found discrepancy comparing to U-series ages, due to external isotopes incorporation. They concluded that the age uncertainty increases with sample age, so that, for U/Th dating is expected to be more reliable in older sample (>100 ka) age.

Corresponding Author Phone: +55 13 3523 5065; Email: Sonia.tatumi@gmail.com We also utilized FTIR-VIS technique to determine iron oxide contents in paleosol, specially hematite (α Fe2O3) and goethite (α FeOOH) rates, whichcan be used in paleoclimatic analysis. It is known from the literature, that warner dried climatic environments favorhematite growth; however, goethiteformation is favored by cooler, wetterand less seasonal climatic conditions.



Fig. 1: Map showing the South America, Brazil and State of Pernambuco. Below is the São bento da Una municipality (8°31'20''S; 36°26'37''W) the location of study area. The strata are situated in São Bento do Una municipality, Tamanduá de Cima fossil locality, State of Pernambuco, situated at northeast region of Brazil (Fig. 1). The upper deposit is carbonate cemented or calciferous sandstone, sorted and poorly coarse grained, containing predominantly granules of quartz and display a small scale (up to 12 cm thick) trough crossbedding sets. arranged in up to 20 cm thick, in tabular packages. The facies and textural analyses suggest that the sandstones are predominantly fluvial in origin. From this level seven samples were collected in two different sectors I and II at depths of 80, 90 and 100 cm, see Table 1.

The lower deposit is composed by an unconsolided massive argillite and it was noted the occurrence of isolated bones of typical late Pleistocene large mammals (megafauna).

2. SAMPLES AND EXPERIMENTS

OSL curves were measured using an automated TL/OSL reader, model Risø-DA20. The luminescence wasdetected in UV region using a U-340 filter. The single-aliquot regenerative dose (SAR) protocol on coarse grain quartz was employed for D_e evaluation, according to Murray and Wintle (2000). For natural radioisotopes determination gamma spectroscopy experiments were made with highpurity Germanium (HPGe) detector, Canberra 373 model and standard soils samples JR-1, JG-1a, JB-3 and JG-3. The measurements were performed with about 100 g of the sediment, which were previously stored and sealed in a plastic container during two weeks to assure the secular equilibrium. Water content was also measured for the annual dose rate correction and the cosmic rays contribution was evaluated theoretically using Prescott and Hutton (1994) equation.

Before OSL measurements, the mineral was separated following standard laboratory procedures. The grains size fraction between 60 and 100 μ m were selected by sieving and organic matter was eliminated using 30% hydrogen peroxide solution during 12 h, after the samples were etching with 40% HF during 45 minfor eliminated carbonates and alpha ionization contribution, and treated with 10% HCl during 2 hours to removed some fluorite formed by HF etching. Sodium polytungstatewith density of 2.62 gcm⁻¹was used to separate heavy mineral and feldspar, all the process was carried out in the laboratory, under subdued red safe light environment.

FTIR analysis was carried out with ThermoNicolet spectrometer, model 5Siand for UV-VIS regions was Femto 600 plus model. For determinations ofhematite and goethite concentrations, initially, a mass of 2 g of the samplewas inserted into 10 ml of NaOH. Then, the solution was stirred in a centrifugeat 3800 rpm for 15 min, according toResende et al. (1987) and after thesolution was sieved. Subsequently, the sample was separated in two portions: first portion for iron oxide

(hematite) analysis and the second for ironhydroxide (goethite). In the firstportion, silicates and gibbsite wereeliminated by addition of NaOH andwash with 0.5 M HCl (Norrish andTaylor, 1961). After this process thesample was dried at 70 °C. The second portion was washed withethanol and acetone in order to remove the organic matter and free iron oxide.

Then, calcium was added, according to Jackson (1956), to obtain a concentrated solution of iron hydroxide (goethite).

UV-VIS spectra were obtained andbands at of 450 and 850 nm were used to evaluate hematite and goethiteconcentrations, respectively.

The quantities of hematite and goethite were determined from the followingequations (Resende et al 1987):

$$H_m(\%) = \frac{R}{\left[\frac{Agt}{AHM}0.9845 + 0.9675\right]}$$
(1)

$$G_t(\%) = \frac{R}{\left[\frac{AHM}{Agt}0.6850 + 0.6970\right]}$$
(2)

where:

 H_m (%) = percentage of Hematite

 G_t (%) percentage of goethite

$$R = \text{content of } Fe_2O_3$$

Agt = goethite peak area

AHM = Hematite peak area

3. RESULTS AND DISCUSSION

3.1 OSL Analysis

Table 1 shows homogenies values forradioisotopes contents determined in thesamples, and the water contents foundare low, because, nowadays, this site isin semi-arid region, with rainfallsaverage of 187 mm/a. Cosmic rayscontribution values are also shown in the Table 1.

Based on preheat plateau, thermal transfer and dose recovery tests apllied between 190 to 280 °C, a preheat at 260 °C for 10 s was determined and used for all the samples. An example of OSL shinedown curve supplied by SBU I4 and SBU II3are shown in Fig. 2, for natural and irradiated aliquots, the mass of each aliquot used is about 3 mg and a fast decay behavior can be observed in OSL signal, suggesting that these quartz grains are easily to bleach.

OSL shinedown curves can be theoretically fitted by an exponential decay function, depend on the optically active traps envolved in the emission, if we have two active traps, the OSL intensity can be describe by:

$$I_{OSL} = I_1 exp\left(-\frac{t}{\tau_1}\right) + I_2 exp\left(-\frac{t}{\tau_2}\right)$$
(3)

S	d cm	SN.	U ppm	Th ppm	K-40 %	W %	CR Gy/ka
Ι	80	SBU I1	2.26±0.42	12.50 ± 0.08	1.79±0.07	3.2	0.184
	90	SBU I2	2.27±0.08	10.68±0.18	1.68±0.03	2.6	0.181
	90	SBU I3	2.99±0.10	12.15±0.017	1.69±0.02	2.8	0.181
	100	SBU I4	2.11±0.54	11.24±1.17	1.89±0.07	2.8	0.178
Ι	80	SBU II1	4.92±0.12	11.80±0.16	1.70±0.02	2.7	0.184
	90	SBU II2	2.77±0.08	11.35±0.16	1.70±0.02	2.9	0.181
	100	SBU II3	2.59±0.08	10.79±0.16	1.55±0.0	2.8	0.178

Table 1: Sampling description, S=section where the samples was collected, d= depth of the samples, SN=sample name, radioisotopes concentrations, W=watercontents and CR=cosmic rays contribution.

Where I₁ and I₂ are the initial luminescence intensities of the exponential curves, which corresponding to the faster and slower components of the total IOSL, t is the time and decay constants τ_1 and τ_2 (McKeever and Chen, 1997). In the case of natural sample SBU I4 $\tau_1 = (3.009 \pm 0.006)s$ and $\tau_2 = (0.58 \pm 0.08)s$ were evaluated, and for SBU II3 were $\tau_1 = (1.45 \pm 0.04)s$ and $\tau_2 = (0.255 \pm 0.004)s$.



Fig. 2: Typical OSL shinedown curves obtained with quartz single aliquots with about 3mg of mass, (a) SBU I4 and (b) SBU II3.

Initially, about 42 aliquots of each sample were measured and only the aliquots, which were approved in recycling test, which values between 0.9 to 1.1 and recuperation test < 5%, were used in the final De calculation.

Fig.3 shows some typical distribution found in the radial plot result of SBU I4, SBU II1, SBU II2 and SBU II3.

Although the samples have basal fluvial origin, they present a precisely OSL age, with recycling test values are close to unity, from 0.96 to 1.02, and recuperation test lower than 2.9%, which indicates an insignificant charge transfer process during the measurements. These satisfactory luminescence characteristics of these quartz crystals indicate that reliable ages for fluvial sediment can be determined by the SAR protocol.



Fig. 3: Examples of radial plot results obtained for thesamples (a) SBU I4, (b) SBU II1, (c) SBUII2 and (d) SBU II3.

Therefore, the obtained ages show, precisely, the beginning and end of this fluvial carbonate. It was found ages from 15.4 to 19.6 ka, which can be referred to Last Glacial Maximum (LGM) related to a cold phase in the global climate, when the ice sheets were most extended than the contemporary ones, at 19 ka. Theseglacial advance impacted deeply the climate, causing, desertification, and a dramatic decline in sea levels around the north hemisphere. In the studied site, many megamammal fossil remains were buried under the lower levels of the deposit dated at 19.6 ka, suggesting that the species which did not adapted to the colder environments

SN	<i>T1</i>	T2 %	n	AD Gy/ka	De Gy	Age ka
SBU I1	1.01±0.02	2.9	20	3.52±0.10	55.0± 1.4	15.6±0.6
SBU I2	0.97±0.01	2.6	18	3.27±0.03	52.9±1.7	16.2±0.5
SBU I3	1.01±0.02	2.1	26	3.58±0.03	58.0±2.9	16.2±0.8
SBU I4	0.96±0.01	2.6	18	3.48±0.13	60.8±1.5	17.5±0.8
SBU II1	1.00±0.03	2.2	30	4.33±0.03	62.4±2.3	15.4±0.6
SBU II2	1.02±0.03	2.0	35	3.83±0.03	67.9±3.1	196. ±0.9
SBU II3	1.00±0.02	2.4	28	3.22±0.02	61.4±5.3	19.3±1.8

Table 2: Samples names and results related to D_e determination using SAR protocol. SN = sample name, T₁ = recycling test, T2= recuperation Test, n= number of aliquots and AD= annual dose rate.

in LGM and exemplifying an ecosystem which no longer exists.

Other data for this same time span was found in a very long cave named Toca da Boa Vista, situated at State of Bahia, Brazil (10008'26''S; 40051'08''W) far about 570 km away from the present site; in the Toca da Boa Vista were found secondary carbonates depositions with ages between 17.3 ka to 20.1 ka, demonstrating that the water table level was 13 ± 1 m higher than the current one and therefore, suggesting a wetter climate (Auler and Smart, 2002; Auler, 1999).

Another site named cave Toca do Serrote das Moendas (8040'0'S, 42033'0''W), State of Piauí, Brazil, can be correlated to the current results too. The cave locates at about 810 km away from the present studied site, and containing fossil remains; recently two teeth of cervid (*Blastocerusdichotomus*) were dated by electron spin resonance (ESR) by two independent laboratories (Kinoshita et al, 2014), resulting in ages of 29 ± 3 ka and 24 ± 1 ka. The carbonate layer capping this fossils stratum was dated by OSL of the quartz grains in 21 ± 3 ka.

Therefore, these sites presented ages that corroborate each other and can be characterized Pleistocene mammalbearing correlated with the last glacial period.

3.2 FITIR-VIS Analysis

The rate of hematite and goethite was evaluated with FITR-VIS results and using the equations (1) and (2). The rate are listed in Table 3 and varied from 0.08 to 0.24, therefore, there is a predominance of goethite phase, which can be also related to a wetter and cooler climatic conditions, in agreement with above cited Auler and Smart, 2002 work.

Recently, similar results were found by Lyons et al. (2014), they studied climatic changes records in a site locate at central South Africa along the Modder River, using OSL dating and complementary techniques as mineral magnetic and diffuse reflectance spectroscopy, for analyze the concentrations of magnetite/maghemite and ratio of hematite and goethite in paleosoils. They

obtained ratios of hematite and goethite of about 0.15 and concluded that between 18 to 15.5 ka the climate become progressively cooler and drier and the rainfall was lower than 100-200 mm/a.

 Table 3: Quantitative characterization of iron oxide phase in calcrete samples.

Sample name	Goethite (µg/l) (490nnm)	Hematite (µg/l) (850nm)	$\frac{H_m}{H_m + G_t}$
SBU I1	0.593	0.045	0.07
SBU I2	0.440	0.141	0.24
SBU I3	0.541	0.09	0.14
SBU I4	0.562	0.083	0.13
SBU II1	0.616	0.039	0.06
SBU II2	0.650	0.051	0.07
SBU II3	0.471	0.14	0.23

4. CONCLUSION

Quartz crystal selected from calcretesamples collected from paleontologicalsite located at northeast of Brazil weresuccessfully dated by OSL with singlealiquot SAR protocol, and indicated thatcalcrete formation occurred at 19.6 up to 15.6 ka,taking in account the studied remainterrace.

The use of FITR technique, prior tospecifically chemical treatment used inthis work, to obtain hematite andgoethite concentration, was useful and supplied consistent results, based on thelow hematite and goethite ratios theclimate conditions was wetter and cooler during the LMG in the investigated area.

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