

OPTICALLY STIMULATED LUMINESCENCE DATING OF ARCHAEOLOGICAL CERAMICS FROM OSVALDO AND LAGO GRANDE SITES IN CENTRAL AMAZON

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ABSTRACT

Thermoluminescence (TL) and optically stimulated luminescence (OSL) dating are two important techniques for dating archaeological and geological material, especially suitable for archaeological ceramics, where samples for ¹⁴C dating are not available. In this work, five pottery shards from Osvaldo and Lago Grande archaeological sites were dated by OSL. For measurements, it was used the SAR protocol. The annual dose rates were estimated by the contents of U, Th and K, determined by instrumental neutron activation analysis (INAA) of the pottery shards and clay samples near both sites. Lago Grande and Osvaldo represent a microcosm of the region, and their proximity and high density of archaeological record turn them interesting to study possible relations of cultural and/or commercial exchange. Calculations showed that the water content is an important variable that cannot be neglected in OSL dating of pottery shards from central Amazon, due to the high humidity in regional soils. The results between 867 ± 101 and 1154 ± 62 years AD agreed with the average time span for the archaeological sites occupation found in the literature.

1. INTRODUCTION

1.1. Principles of Luminescence Dating

Thermoluminescence (TL) and optically stimulated luminescence (OSL) dating are two important techniques for dating archaeological and geological material, especially suitable for archaeological ceramics, where samples for ¹⁴C dating are not available. In TL, the luminescence signal for dating, emitted by the constituent mineral grains, is released by heating the material, whereas for OSL the signal is emitted by directing a light beam onto the sample [2]. One of the important advantages of OSL over TL is that the any residual signal after the deposition of the archaeological artifact is lower.

The basic principle of the technique is that the TL or OSL signal intensity emitted by the material will be proportional to the accumulated ionizing radiation dose, or palaeodose (P, in Gy). The ionization creates metastable centers constituted by trapped electrons and holes in the crystal lattice. When the crystal is heated or stimulated with light, the electrons can be

released from the traps and recombine with holes, emitting luminescence. Therefore, luminescence intensity is proportional to the metastable centers concentration, which is proportional to the time elapsed since the last luminescence “zeroing event”, where the luminescence signal is assumed to be near zero. This event can be the last pottery firing or exposition to daylight, and is regarded as the sample age determined by luminescence dating techniques. The ionizing radiation in that context is mainly due to natural radioactivity from the emission of ^{40}K , ^{238}U and ^{232}Th (inside the sample and in the surrounding sediment), cosmic radiation and ^{187}Rb (in a minor extent), which provide an annual dose rate flux in the sample (\dot{D} in Gy/years). The age (A) can be evaluated by the equation [2]:

$$A = P/\dot{D} \quad (1)$$

In the TL and OSL measurement procedures, the “as-found” luminescence signal is compared to some artificial signals obtained by irradiation with a beta source, for example.

1.2. The Archaeological Context

In the confluence region of Negro and Solimões rivers, in central Amazon, Brazil, there are more than 100 registered archaeological sites. Lago Grande and Osvaldo are related to that group of sites, for which archaeological analyzes of excavated material suggested the existence of human occupation associated to the ceramic phases Açutuba, Manacapuru and Paredão [4,12].

One of the main discussions in the Amazonian archaeology is the interpretation of the archaeological record in terms of whether there were interconnections among groups that lived in central Amazon prior to the European contact in the 16th century. It would be an additional evidence of the existence of large tribes interconnected in the past, the *cacicados*, contrasting with the ethnographic picture observed actually for that region, where sparse and small groups are the most frequent pattern [9].

Osvaldo and Lago Grande sites represent a microcosm of the region. Their proximity and high density of archaeological record turn them interesting to study possible relations of cultural and/or commercial exchange. There are evidences of ceramic types characteristic of one site in the archaeological record of the other site. For more details, refer to [4, 7, 8, 12].

The OSL dates obtained in this work would be used for comparison with ^{14}C datings published in the literature [7] and to assess the contemporaneity of the pottery shards used for a project for comparing the archaeological record of both sites [5].

2. MATERIALS AND METHODS

2.1. Sample Preparation

The samples used for dating and some important parameters are related in Table 1. The pottery shards were provided by the Museum of Archaeology and Ethnology of the University of São Paulo.

Table 1: Samples for OSL dating

| Sample | Arch. Code* | Site | Ceramic phase | Depth (cm) |
|--------|-------------|-------------|---------------|------------|
| R1 | 12-511-14 | Lago Grande | Paredão | 30-40 |
| R2 | 9-320-2 | Osvaldo | Manacapuru | 0-10 |
| R3 | 12-558-1 | Lago Grande | Paredão | 60-70 |
| R4 | 9-223-16 | Osvaldo | Manacapuru | 30-40 |
| R5 | 9-223-3 | Osvaldo | Manacapuru | 30-40 |

*Archaeological code used at the Museum of Archaeology and Ethnology of the University of São Paulo.

For dating, it is necessary to obtain powder from the pottery shards. Firstly, it was used a sandpaper type 80 to remove all the external sample surfaces up to a depth of 1 or 2 mm. Then, the fragments were ground in an alumina mortar, avoiding strong strokes that could generate triboluminescence. Then, the magnetic particles were removed with a magnet. Finally, the powder was sieved to obtain a granulometry between 149 μm (100 mesh) and 250 μm (60 mesh).

The chemical treatment before the luminescence measurements has the objectives of isolating the mineral of interest (quartz, in this work), and removing the alpha particle contribution to the total dose [10]. The chemical cleaning steps for OSL dating are discriminated as follows. The samples were washed four times with deionized between each step.

- Addition of H_2O_2 (34-37% in volume) enough to cover the sample inside a beaker during 24 hours to remove organic matter.
- Addition of HF, a silicate solving acid (around 0,09% in volume) for the corrosion of quartz crystals surfaces, in order to discount the effects of natural alpha irradiation in the calculations, and to dissolve feldspars. It was left working for 2 hours.
- If the sample still presented a dark color, the last step was repeated with HF acid 28% in volume.
- Addition of HCl (around 14% in volume) to remove carbonates that emit spurious signal for OSL.

2.2. OSL Measurements

The samples were heated to 180 °C prior to each measurement, during 10 s. This preheating procedure is used for emptying unstable traps. It was used 8 aliquots for sample R1 (due to its lower luminescence signal in a preliminary test) and 5 aliquots for the others. The irradiation doses were 2, 3 and 4 Gy for samples R1, and 2 and 4 Gy for samples R2, R3, R4 and R5,

due to their relative high luminescence. The measurements were carried out at 120 °C and followed the SAR protocol.

The OSL measurements were performed using a RisØ TL/OSL reader with a $^{90}\text{Sr}/^{90}\text{Y}$ β -particle source and a 9635QA photomultiplier tube. The optical stimulation was with blue light, with wavelength equal to 470 nm and the detection optics used was an optical filter of 7.5 mm Hoya U-340.

2.3. Determination of the Annual Dose Rate

The local radioactivity was not measured with dosimeters in the region of the Negro and Solimões rivers, in central Amazon. Hence, the annual dose rate was estimated by the concentrations of U, K and Th, determined by instrumental neutron activation analysis of the pottery shards and clays near both sites [1].

The annual dose rate can be attenuated due to absorption by water [6, 14]. Considering the effect of moisture and disregarding the alpha irradiation, the dose rate can be expressed as [6]

$$\dot{D} = \frac{\dot{D}_\beta}{1 + 1.25 \frac{W_p}{100 - W_p}} + \frac{\dot{D}_\gamma}{1 + 1.14 \frac{W_s}{100 - W_s}} + \dot{D}_{cosmic} \quad (2)$$

Where W_p is the water content in the pottery shard for beta irradiation, and W_s is the water content in the surrounding soil for the gamma irradiation during the burial period.

The cosmic component of annual dose was determined according to the procedure suggested in Prescott & Hutton [13], as a function of the geographic coordinates, depth and altitude of the samples. For \dot{D}_0 it was used the full expression proposed by Barbouti and Rastin, cited in [13], for depths x below the ground level, written as

$$\dot{D}_0 = \frac{C}{[(x + d)^\alpha + a](x + H)} e^{-Bx} \quad (3)$$

Where $[\dot{D}_0] = \text{Gy.k.a}^{-1}$; $[x] = \text{hg.cm}^{-2}$; $C = 6072$; $B = 5.50 \cdot 10^{-4}$; $d = 11.6$; $\alpha = 1.68$; $a = 75$; $H = 212$. The expression 3 is valid from surface down to 10^4 hg.cm^{-2} of standard rock. The geomagnetic latitude was calculated by the expression

$$\sin \lambda = 0.203 \cos \theta \cos(\varnothing - 291) + 0.979 \sin \theta \quad (4)$$

Where λ is the geomagnetic latitude, θ is the geographic latitude and \varnothing is the geographic longitude. Finally, the dose rate at geomagnetic latitude λ and altitude h from D_0 was calculated by the following expression

$$\dot{D} = \dot{D}_0 [F + J e^{h/H}] \quad (5)$$

Where $[D] = \text{Gy.k.a}^{-1}$, $[h] = \text{km}$ and the parameters F , J and H were obtained from Fig. 2 in [13].

3. RESULTS AND DISCUSSION

An initial attempt was made in order to date the samples by thermoluminescence, but it was not successful. The explanation for the low signal to noise ratio of the thermoluminescence measurements was found to be the residual TL dominance in the natural glow curve that had been acquired prior to the deposition, associated to traps that are hard to bleach. In quartz grains, the trap associated to the TL peak at 325 °C is the only easily bleachable. Once OSL is presumed to be associated mainly to that trap, it was the most appropriate technique for the samples in this work [2]. Figure 1 shows decay curves for natural and beta irradiated samples related in Table 2, used for palaeodose determinations.

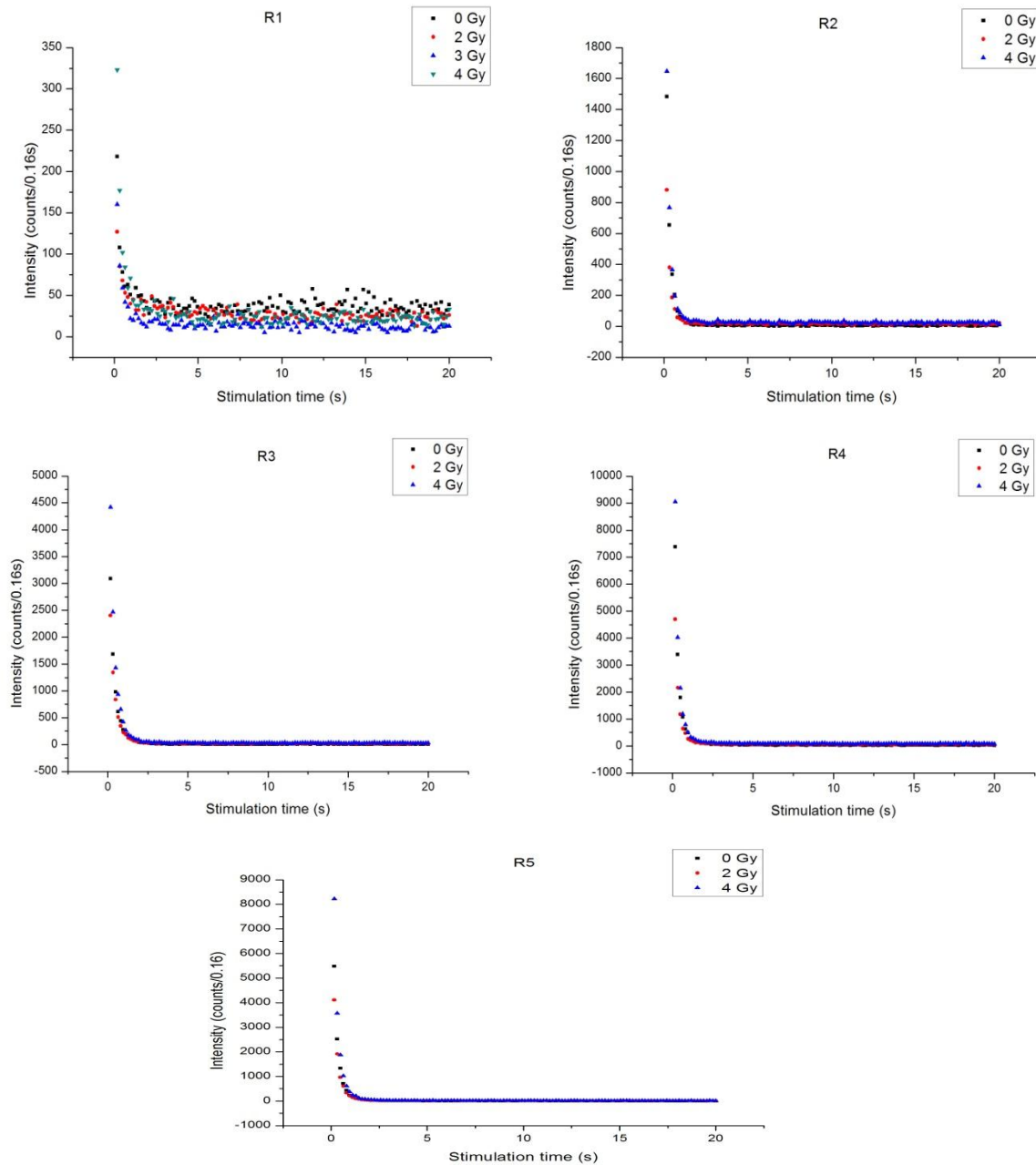


Figure 1: Decay curves for natural and beta irradiated samples from Osvaldo and Lago Grande archaeological sites

The accumulated dose, or palaeodose for the non-irradiated samples, was obtained by fitting a straight line to the dose response measurements, comprising the initial part of the OSL signal (3 first measurements) for all the aliquots. The background was subtracted by averaging over the last 20 measurements, representing the tail of the decay curves in Figure 1 [11]. The results are presented in Table 5.

The results for the concentrations of U, Th and K in the pottery shards, determined by INAA, are presented in Table 2. The element Rb was ignored in the calculation due to its reduced contribution to annual dose rate, when compared to other elements [6].

Table 2: Concentrations of elements in pottery shards for annual dose rate calculations. Units are $\mu\text{g.g}^{-1}$

| Sample | U | ^{232}Th | K |
|--------|-------------------|--------------------|--------------------|
| R1 | 4.392 ± 0.598 | 16.127 ± 0.901 | 12581 ± 1265 |
| R2 | 4.747 ± 0.733 | 10.928 ± 0.612 | 10128 (estimated*) |
| R3 | 4.149 ± 0.351 | 15.725 ± 0.880 | 9800 ± 1199 |
| R4 | 3.046 ± 0.698 | 17.082 ± 0.980 | 14267 ± 2678 |
| R5 | 3.133 ± 0.461 | 13.424 ± 0.752 | 7856 ± 752 |

*Average for 36 samples from Osvaldo

The equations 3-5 were used to calculate the cosmic component of annual dose. Table 3 summarizes the results.

Table 3: Calculation of cosmic radiation dose rate in Osvaldo and Lago Grande

| Sample | Site | Geographic coord. | h (m) | Depth(cm) | \dot{D}_0 | λ | F | J | H (km) | \dot{D} (Gy.k^{-1}) |
|--------|------|----------------------------|-------|-----------|-------------|-----------|-----|------|--------|----------------------------------|
| R1 | LG | 3° 14' S 50° 24' W | 92 | 35 | 0.20 | -0.25 | 0.4 | 0.52 | 4.38 | 0.19 |
| R2 | O | 3° 11' 15" S 60° 20' 41" W | 60 | 5 | 0.21 | -0.26 | 0.4 | 0.52 | 4.38 | 0.19 |
| R3 | LG | 3° 14' S 50° 24' W | 92 | 65 | 0.20 | -0.25 | 0.4 | 0.52 | 4.38 | 0.18 |
| R4 | O | 3° 11' 15" S 60° 20' 41" W | 60 | 35 | 0.20 | -0.26 | 0.4 | 0.52 | 4.38 | 0.19 |
| R5 | O | 3° 11' 15" S 60° 20' 41" W | 60 | 35 | 0.20 | -0.26 | 0.4 | 0.52 | 4.38 | 0.19 |

*LG = Lago Grande; O = Osvaldo

Considering the quartz grains in the pottery shards to have a finite size, the gamma dose for the sediments was used, instead of the internal gamma dose rate of the material [6]. For such an approach, the concentrations of ^{238}U , ^{232}Th and ^{40}K for the sediments were approximated by the concentrations of such elements in clay samples near both sites (results in Table 4). For beta internal dose rate, the concentrations in Table 2 were used.

The effect of moisture at the excavation sites must be taken into account, as it can have strong influence in age determination. Amazonian tropical forests soils can have soil moisture in the range of $0.38\text{-}0.53 \text{ m}^3.\text{m}^{-3}$ considering dry and wet seasons, up to a 10 m depth [3]. These values were used to estimate Ws in equation 2. For the estimation of the content of water in

the samples, W_p (related to porosity), the weights of 15 pottery shards were measured in three conditions [15]: i) before drying ii) after drying at 110 °C for 24h and iii) after soaking pottery shards in water, to measure saturation. Table 4 summarizes the results for the beta and gamma components of annual dose rate, as expressed by equation 2.

Table 4: Annual dose rates for pottery shards from Lago Grande and Osvaldo

| Sample | Site | U ($\mu\text{g.g}^{-1}$) | Th ($\mu\text{g.g}^{-1}$) | K ₂ O (%) | W _p (%) | W _s (%) | D _{β} (mGy/a) | D _{γ} (mGy/a) |
|--------|------|----------------------------|-----------------------------|----------------------|--------------------|--------------------|---|--|
| R1 | LG | 4.167 \pm 0.208 | 19.467 \pm 0.723 | 2.433 \pm 1.155 | 13.9 | 28.4 | 1.5 | 1.3 |
| R2 | O | 4.400 \pm 0.424 | 16.300 \pm 0.707 | 1.755 \pm 1.485 | 13.9 | 28.4 | 1.3 | 1.1 |
| R3 | LG | 4.167 \pm 0.208 | 19.467 \pm 0.723 | 2.433 \pm 1.155 | 13.9 | 28.4 | 1.3 | 1.3 |
| R4 | O | 4.400 \pm 0.424 | 16.300 \pm 0.707 | 1.755 \pm 1.485 | 13.9 | 28.4 | 1.5 | 1.1 |
| R5 | O | 4.400 \pm 0.424 | 16.300 \pm 0.707 | 1.755 \pm 1.485 | 13.9 | 28.4 | 1.1 | 1.1 |

Table 5 presents the results of OSL dating. The average palaeodose and annual dose rates by summing the cosmic, beta and gamma components from Tables 3 and 4, as expressed in equation 2, are showed. Equation 1 was used for age calculations. For the uncertainties, it was considered the highest value between one standard deviation for the sample aliquots, and the variation in the ages supposing 0 and 100% of water saturation in the pottery shards and minimum and maximum humidity in soil.

Table 5: OSL dates for Lago Grande and Osvaldo pottery shards. ¹⁴C dates for comparison were listed in Lima [7]

| Sample | Site | Depth (cm) | ¹⁴ C age (years A.D.) | P (Gy) | \dot{D} (mGy/a) | Age (years A.D.) |
|--------|-------------|------------|----------------------------------|--------|-------------------|------------------|
| R1 | Lago Grande | 30-40 | 1040-1170 | 3.13 | 3.0 | 967 \pm 477 |
| R2 | Osvaldo | 0-10 | >770 | 2.96 | 2.6 | 867 \pm 101 |
| R3 | Lago Grande | 60-70 | >1110 | 2.40 | 2.8 | 1154 \pm 62 |
| R4 | Osvaldo | 30-40 | \approx 620-770 | 3.08 | 2.8 | 906 \pm 81 |
| R5 | Osvaldo | 30-40 | \approx 620-770 | 2.52 | 2.4 | 938 \pm 77 |

Some observations can be made from the results of Table 5. The average dates of the samples vary between 867 and 1154 A.D., a time interval of 287 years. The uncertainties in the ages vary between 5% (for R3) and 49% (for R1). The higher value for the error of sample R1 when compared to other samples is due to its lower luminescence signal. In a preliminary test prior to beta irradiation, sample R1 had 150 counts, when compared to R3, with 8000 counts, which had the lowest age error. Besides the extreme value for R1 error, all the other four samples had uncertainties lower than 12%.

According to calculations of the variation in the ages using the minimum values of water content in pottery and sediments (lowest values for W_p and W_s), and supposing water saturation (highest values for W_p and W_s), the effect of moisture variation can affect the error up to 10%. Considering the environmental conditions of Amazon related to high humidity in air and soil, the effect of water content in the OSL dating cannot be neglected. Calculations showed that ignoring water content in the samples would add between 202 and 262 years to

the determined ages, yielding newer ceramic artifacts that are not in agreement with literature expected values.

The Lago Grande dates agree with the time interval assumed for this site in the literature, from 8th to 12th centuries. In Osvaldo archaeological sites, two human occupations were identified in the archaeological record. The last one, denser, is associated to anthropogenic soils and it is assumed to cover the periods between the 7th and 8th century [7]. The OSL dates in Table 5 suggest that the occupation of the site would extend until the 10th century. However, more samples should be analyzed to check the time span for both sites, for more conclusive considerations.

The test for averages with 95% of confidence level showed, as predicted, that it is not possible to reject the null hypothesis for equality of the two Lago Grande ages. It was expected since the error for sample R1 is higher than the time interval for all the ages determined by OSL. So, it is not possible to reject the contemporaneity of both samples, besides differences in the stratigraphic levels. Comparing R3, from Lago Grande, with R2, R4 and R5 samples from Osvaldo, the hypothesis test of equality for the averages indicated that it is possible to reject the null hypothesis. i.e. the three samples from Osvaldo are older than sample R3 from Lago Grande. Considering that the human occupation in Lago Grande lasted longer (until 12th century) when compared to Osvaldo, (until 8th-9th century), these results could be expected.

By comparison of ¹⁴C and OSL dates in Table 5, R4 and R5 are the samples with the highest deviations from the expected results by ¹⁴C. However, the expected dates must be considered carefully, once they were estimated from literature by comparison of stratigraphies, and the phenomenon of bioturbation is widely identified for the region [4, 7]. In general terms, the results corroborate the average time span for the human occupations in Osvaldo and Lago Grande considered in the literature [4, 7, 12].

4. CONCLUSIONS

The ages of the five pottery shards from Osvaldo and Lago Grande sites obtained by OSL varied between 867 ± 101 and 1154 ± 62 A.D., a time interval of 287 years. The results agree with the average time span for both sites occupations found in the literature. Calculations showed that ignoring water content in the samples would add between 202 and 262 years to the determined ages, yielding results that are not in agreement with literature expected values.

Although the results for both sites cover close periods of time, the contemporaneity of the samples could not be established by the results of this work. However, a period of contemporaneity for the occupation of both sites is referred to in literature [7]. The newer dates obtained for Lago Grande could be expected since the human occupation in that site lasted longer (until 12th century) when compared to Osvaldo (until 8th-9th century).

The number of samples analyzed in this work was limited by availability of the pottery shards provided by the museum (many of them did not have a convenient size for OSL dating, or could not be destroyed). For future works, one should analyze more samples from both sites, trying to cover different stratigraphies and excavation units. It would yield more conclusive considerations about the chronology of Osvaldo and Lago Grande occupations. Furthermore,

it would be convenient to analyze more soil samples near both archaeological sites for a better U, Th and K estimation in gamma annual dose calculations. Finally, the installation of dosimeters in the region could yield estimations of annual dose rate for comparison with the values found in this work, using radioisotopes concentrations.

ACKNOWLEDGMENTS

The present work was realized with the support from “Sao Paulo Research Foundation” – FAPESP – Brazil. Process Number: 2010/07659-0. The authors also thank Eduardo Góes Neves, Brazilian archaeologist of the Museum of Archaeology and Ethnology of the University of São Paulo, for the samples.

REFERENCES

1. G. Adamiec, M. J. Aitken, “Dose-rate conversion factors: update”, *Ancient TL*, **16**, pp. 37-50 (1998).
2. M. J. Aitken, *An Introduction to Optical Dating*, Oxford University Press, New York, USA (1998).
3. R. D. Bruno, H. R. Rocha, H. C. Freitas, M. L. Goulden, S. D. Miller, “Soil moisture dynamics in an eastern Amazonian tropical forest”, *Hydrological Processes*, **20**, pp. 2477-2489 (2006).
4. P. B. Donatti, *A ocupação pré-colonial da área do Lago Grande, Iranduba, AM*. Master’s Dissertation. Universidade de São Paulo, São Paulo (2003).
5. R. Hazenfratz, G. Mongeló, C. S. Munita, E. G. Neves, “Comparison of INAA elemental composition data between Lago Grande and Osvaldo archaeological sites in the central Amazon: a first perspective”, *Journal of Radioanalytical and Nuclear Chemistry* (2011).
6. M. Ikeya, T. Miki., *ESR Dating and Dosimetry*. Ionics Publishing Company (1985).
7. H. P. Lima, *História das Caretas: A Tradição Borda Incisa na Amazônia Central*, PhD Thesis, Museu de Arqueologia e Etnologia, Universidade de São Paulo (2008).
8. H. P. Lima, E. G. Neves. “Cerâmicas da Tradição Borda Incisa/Barrancóide na Amazônia Central”, *R. Museu Arq. Etn.*, **21**, pp. 205-230, 2011.
9. J. S. Machado, “Dos artefatos às aldeias: os vestígios arqueológicos no entendimento das formas de organização social da Amazônia”, *Revista de Antropologia*, **49** (2006).
10. D. F. Mosquera, J S. Sánchez. “A Simple Method to Separate Quartz and Feldspar and its Application to TL/OSL Methods”. *Geochronometria*, **30**, pp. 41-47 (2008).
11. A. S. Murray, A. G. Wintle, “Luminescence Dating of Quartz using an Improved Single-aliquot Regenerative-dose Protocol”, *Radiation Measurements*, **32**, pp. 57-73 (2000).

12. R. C. Portocarrero, *A variabilidade espacial no sítio Osvaldo: Estudo de um assentamento da tradição barrancóide na Amazônia central*, Master's Dissertation, Museu de Arqueologia e Etnologia, Universidade de São Paulo (2006).
13. J. R. Prescott, J. T. Hutton, "Cosmic ray contributions to dose rates for luminescence and ESR dating: Large depths and long-term time variations", *Radiation Measurements*, **23**, pp. 497-500 (1994).
14. N. Zacharias, J. Buxeda i Garrigós, H. Mommsen, A. Schwedt, V. Kilikoglou. "The effect of post burial alterations of ceramics on the TL/Osl dating", *Proceedings of the 6th European Meeting on Ancient Ceramics*, Fribourg, Switzerland, 3-6 October 2001, pp. 335-343 (2001).
15. A. J. C.Zink, G. J. Susino, E. Porto, T. N. Huffman, "Direct OSL dating of Iron Age pottery from South Africa – Preliminary dosimetry investigations", *Quaternary Geochronology*, **8**, pp. 1-9 (2012).