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Highlights

1) TL Dating of archaeological potteries from Amazon
2) Electron paramagnetic resonance (EPR) application for potteries firing temperature analysis.
3) U, Th and K concentrations obtained by instrumental neutron activation analysis (INAA)

A preliminary study of ceramics from São Paulo II archaeological site by means of TL, EPR, XRD, INAA and OM techniques

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Abstract

Ceramics from São Paulo II archaeological site were dated by means of thermoluminescence (TL) and the annual doses was determined by U, Th and K concentrations obtained by instrumental neutron activation analysis (INAA). The presence of crystalline and amorphous quartz were studied by X-ray diffraction (XRD) and optical microscopy (OM). Electron paramagnetic resonance (EPR) was used to study the firing temperature using the iron signal (Fe^{3+}) as a firing temperature reference. The age of the samples was found between 895±92 and 1142±100 years and no amorphous quartz was found. The firing temperature was 600-650 ^{o}C.

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1. Introduction

Dating by TL is a particular application of TL dosimetry in which there is a source of constant irradiation (the natural radioactivity of the ceramics), the activity of which can be independently determined.

The duration of irradiation is taken to be the same as the age of the ceramic, and this is proportional to the amount of the TL signal. The duration of underground should be the same as the age of the ceramics which is proportional to the amount of the TL signal (Aitken, 1985).

TL, OSL and EPR dating of ancient ceramics as based on quartz grain in it contained. The natural radiation that induces the luminescence in quartz grains comes from radioactive ^{40}K, cosmic rays and radionuclides from ^{238}U, ^{232}Th and ^{235}U radioactive series. Actually, ^{235}U series contributes little and not taking into account. These radiation sources determine also the annual dose rate, D_{an}

(Ikeya, 1993; Bartoll and Ikeya, 1997).

A pottery is produced heating the clay mold at temperature higher than 500 °C. Heating at such high temperature erase any previous radiation effect, hence if the pottery is buried underground, until it is collected for dating the effect of natural radiation will be accumulated. The accumulate dose (D_{ac}) is measured using additive or regenerate method in the TL technique. The age of the material can be calculated by the D_{ac} divided by the D_{an} (Aitken, 1995; Zimmerman, 1971).

The EPR spectroscopy, based on absorption of microwave by an ionic crystal placed in an external static magnetic field, has two roles as dating technique. One is the usual dating (Ikeya, 1993, Watanabe et al., 2008). The other is find the firing temperature to produce ceramics (Bensimon et al., 1998; Bensimon et al., 1999; Mangueira et al., 2011). The g-factor of EPR signal of some paramagnetic centers can vary with high temperature annealing. Such is the case of the signal associated with Fe^{3+} and can be used to find the firing temperature to produce ceramics.

The São Pablo II archaeological site is located on the left margin of the Solimões River, near the Coari city and 380 km away from the city of Manaus, Brazil (see Fig. 1). A previous study by Tamanaha (2012) has shown that ceramics belongs to a simple phase, Guarita.

By investigation of ceramics under different aspects we can find the methodology used in manufacturing ceramics, dynamics of economical nature, cultural and social development of ancient people. Such investigation has contributed to understand not only geographical occupation as well as cultural heritage of ancient people.

In many potteries from central Amazon investigated so far, spicules have been found. In the present case, optical microscopy (OM) and X-ray diffraction (XRD) were used to verify whether or not ceramics fragments here investigated contain spicules.

The TL was used to obtain information about the chronology of occupation of the site. The way it was produced and its ceramic firing temperature were determined by EPR.

2. **Experimental**

2.1*Sample preparation and chemical treatment*

The ceramics to be investigated were sandpapered to eliminate about 2 mm throughout the ceramic surface to remove any external effect. In the following, the samples were crushed and sieved to retain grain sizes between 0.08 and 0.180 mm. Thereafter, the powder was subjected to chemical cleaning with H_2O_2, HF and HCl procedure that helps to separate the quartz as well as possible (Watanabe et al. 2008). The quartz grains after dry have been subject to magnetic separation using a Nd magnet to remove magnetic material still present.

2.2*Analysis of quartz grains*

To analyze the presence or not of amorphous material, namely spicules, an optical microscope (OM) Bioval mark, model U-1000T in eyepiece version and capacity of increase between 40 and 1600x has been used.

The XRD measurement was performed using a X-ray diffractometer model Rigaku equipped with a source of Cu-k_α with wavelength λ of the monochromatic beam of 1.5418 Å. 100 mg of samples has been used for each measurement. The operating voltage was 40 kV and the operating current of 40 μA. The result of XRD was analyzed using computer programs and compared with the standard spectrum of quartz cataloged JCPDS

(Joint Committee Powder Diffraction Standards).

2.3*Electron paramagnetic resonance (EPR)*

The ceramics powder resulting from breaking and sieving was subjected to a heat treatment. Initially, 5 samples of ceramics fragments were chosen for heat treatment. Then nine samples were separated in powder form for each sample, these represent about 45 aliquots. Thermal treatment was performed in preheated oven and started with the temperature of 450 ºC up to 800 ºC. Every sample was thermally treated for 30 min.

Each measurement was made with 70 mg of the sample in powder form, placed inside quartz tube of 4 mm in diameter. The equipment used was the spectrometer Bruker EMX of the Institute of Physics of the University of São Paulo, Brazil. Its cavity with a ER 4102ST operate in X-band and possesses modulation of 100kHz at room temperature. 20 mW of microwave power and modulation of one G have been used.

2.4*Thermoluminescence (TL)*

The thermoluminescence measurements were carried out in an automatic TL reader Daybreak model 1100 TL, keeping a heating rate of 4 °C/s in the interval of 50 to 500 °C. For every reading of the sample was used an average of 4 mg. The irradiation of samples has been carried out with gamma radiation source of ^{60}Co at the Radiation Technology Center of IPEN/CNEN-SP, Brazil. The doses applied were 0.5; 1.0; 1.5; 2.5; 5.0; 10.0; 20.0 Gy and additive method was used to estimate accumulated dose (D_{ac}). Each glow curve represents an average of five measurements.

The annual dose rate (D_{an}) was calculated from the concentration of U, Th and K of ceramics determined by neutron activation analysis (NAA) at the IEA-R1 Reactor of IPEN/ CENEN-SP, Brazil. Cosmic rays contribution was added in D_{an}.

3. Results and Discussions

3.1*Optical microscopy and X-ray diffraction*

The Fig. 2 shows the microphotograph of the quartz grains obtained with optical microscope. Amorphous material (spicules) has not been observed. As already mentioned, spicules are frond in other ceramics material of the Amazon region.

Fig. 3 shows X-ray diffraction pattern of the sample of this work and that of pure standard quartz.

3.2*Electron paramagnetic resonance*

Fig. 4 shows the EPR spectrum of analyzed samples, an intense signal around g=2 region, which is characteristic of Fe^{3+} in an octahedral site (Warashina et al., 1981; Presciutti et al., 2005; Bensimon et al., 1999; Mangueira et al., 2011). The EPR spectrum too shows another signal at g=4.3, typical of Fe^{3+} in an orthorhombic site (Presciutti et al., 2005; Bensimon et al., 1999; Tani et al. 1997), also is observed.

The firing temperature of the ceramics was determined by successive thermal treatment at high temperature where the g-value of Fe^{3+} changes. The Fig 5 shows the behavior of the g factor as function of the temperature for the different potteries samples. All the samples present a variation of the g factor above 500-600 °C. It indicates that the firing temperature determined for the samples analyzed are within of an interval between 600 and 650 ºC.

Table 1 shows the values for the firing temperatures for six samples. As can be seen in Table, the values for firing temperatures of ceramic fragments are very close. So the result of the variation factor g indicates that the sample

burned ceramic in this temperature range.

3.3*Thermoluminescence*

Fig. 6 shows the TL glow curve of the quartz grains with peaks at 120, 200 and 320-370 ºC. The high temperature peak shifts from 370 ºC to 320 ºC with the dose. Anyway the high temperature peak was used for determination of accumulated dose, D_{ac} by additive method shown in Fig. 7.

An accumulated dose, D_{ac} of about 1,353 Gy was obtained. By neutron activation analysis, concentration of ^{238}U, ^{232}Th and ^{40}K were estimated and these values are listed in Table 2. From these values, D_{an}-values were calculated using Table 4.3 and 4.4 in Ikeya (1993), and ages by deviding D_{ac} by corresponding D_{an}-values, also listed in Table 2.

Using ^{14}C dating, Lima (2006, 2008) has shown that the chronology of the Guarita ceramic phase in Central Amazonian ranged from X to XVI centuries and conform approximately with the present result.

4. **Conclusions**

Four ceramics sample from São Pablo II archaeological site investigated here do not contain spicules, white many ceramics of from site in the same region have been found containing spicules. Relatively high annual dose rate values were obtained for all four samples. For Brazilian potteries relatively old ages ranging between 900 and 1200 years have been obtained. Therefore the results confirm the archaeological interpretation on the chronology of the occupation of the indian communities that occurred in this region of the central Amazon of Brazil. EPR signal intensity of Fe^{3+} indicates that a heat with a temperature around 600 to 650 °C was used to burn clay to produce ceramics.

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Figure Caption

Fig. 1 Map of São Paulo II archaeological site

Fig. 2 Photograph of quartz grains found in the sample

Fig. 3 X-ray diffractogram of quartz for the analyzed sample and the standard quartz

Fig. 4 EPR spectrum for sample CSQSP-49

Fig. 5 Variation of the value of g-factor to Fe^{3+} with temperature of heating the experimental sample

Fig. 6 TL glow curve of the sample to a dose of 0.5 to 20 Gy

Fig. 7 TL intensity in function of the dose added

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Figure

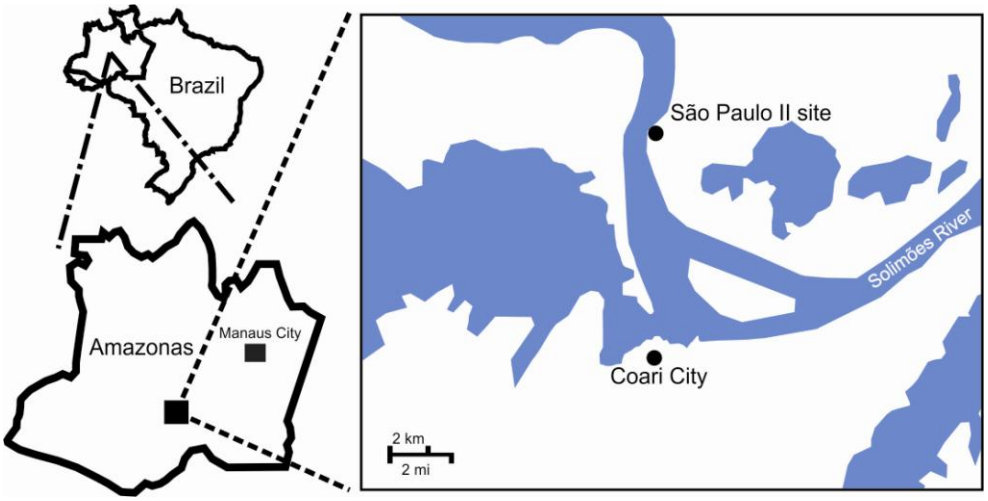

Fig. 1 Map of São Paulo II archaeological site.

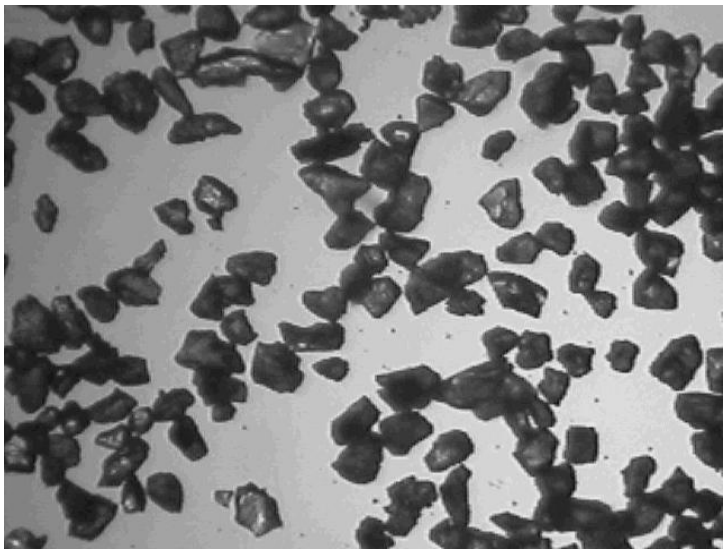

Fig. 2 Photograph of quartz grains found in the sample.

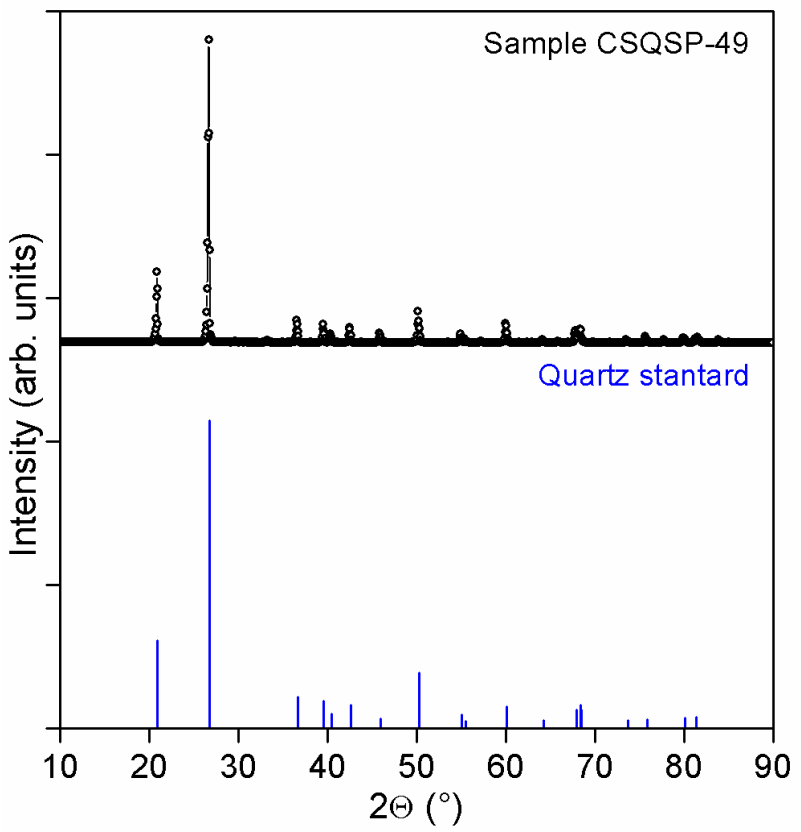

Fig. 3 X-ray diffractogram of quartz for the analyzed sample and the standard quartz.

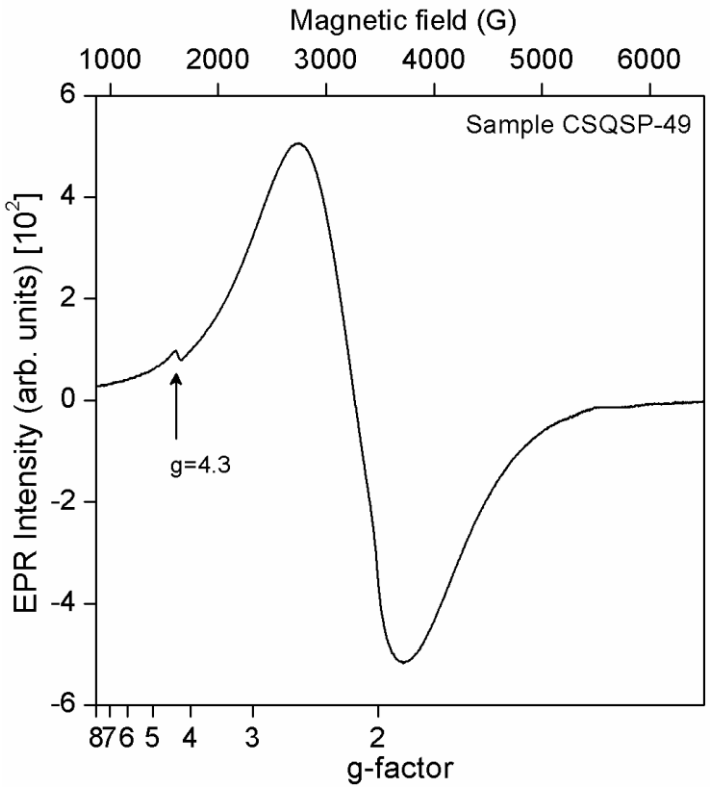

Fig. 4 EPR spectrum for sample CSQSP-49.

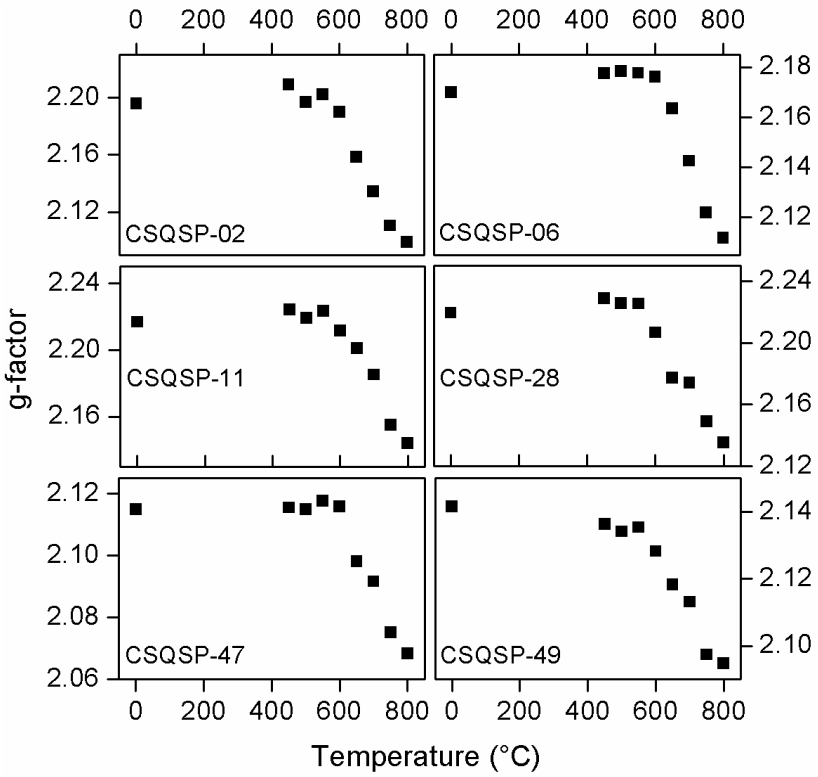

Fig. 5 Variation of the value of g-factor to Fe^{3+} with temperature of heating the experimental sample.

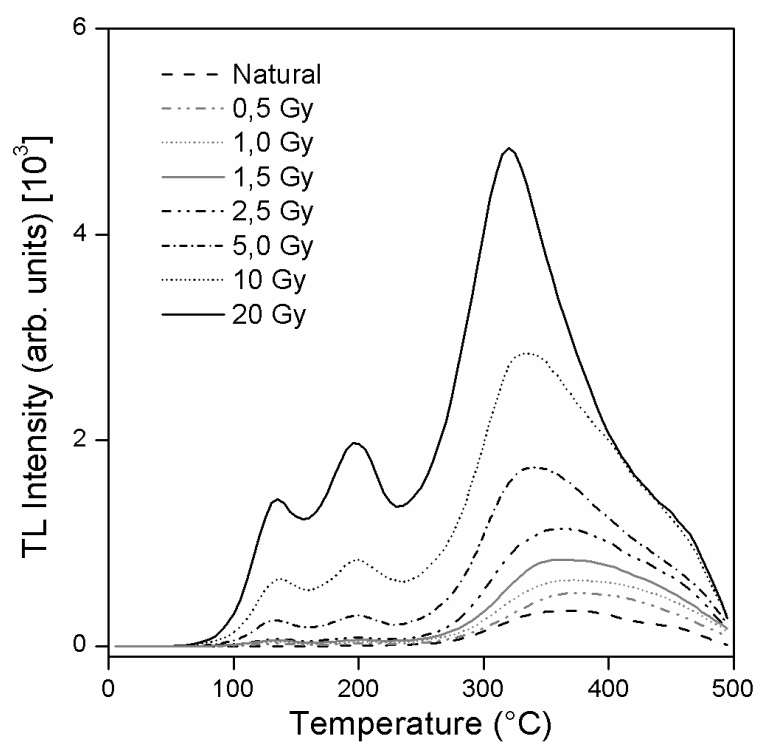

Fig. 6 TL glow curve of the sample to a dose of 0.5 to 20 Gy.

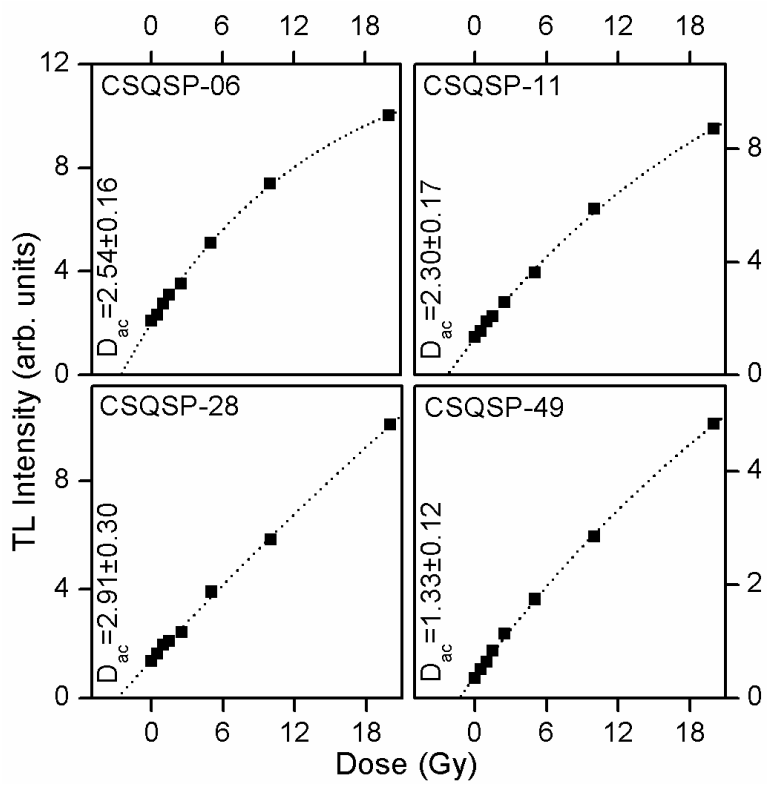

Fig. 7 TL intensity in function of the dose added.

Table 1 Results firing temperature for analyzed samples.

Samples	Firing temperature (°C)
CSQSP 02	650 ± 50
CSQSP 06	650 ± 50
CSQSP 11	600 ± 50
CSQSP 28	600 ± 50
CSQSP 47	650 ± 50
CSQSP 49	600 ± 50

Table 2 Accumulated dose, annual dose and age of the fragments of ceramic samples obtained by TL.

Sample	U (ppm)	Th (ppm)	K (%)	D_{an} (mGy/year)	D_{ac} (Gy)	Age (year)
CSQSP06	2.988±0,252	14.447±0.930	1.488±0.567	2.58±0.12	2.54±0.16	1027±78
CSQSP11	3.143±0,252	11.669±0.643	1.026±0.19	2.06±0.08	2.30±0.17	895±92
CSQSP28	4.429±0,276	8.114±0.520	2.501±1.309	3.35±0.17	2.91±0.30	1142±100
CSQSP49	2.653±0,484	9.967±0.725	0.299±0.040	1.286±0.126	1.33±0.12	978±141