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Case study

Dating and determination of firing temperature of ancient potteries from São Paulo II archaeological site, Brazil by TL and EPR techniques

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ABSTRACT

Pottery fragments from São Paulo II (SPII) archaeological site were dated by means of thermoluminescence (TL) and electron paramagnetic resonance (EPR). EPR was used to study the firing temperature using the iron signal (Fe^{3+}) as a firing temperature reference. The ages of the samples were found to be between 793 ± 102 and 1184 ± 142 a.C. The firing temperature of ceramics was found to be around 600–650 °C. Our study, based on the combination of EPR and TL techniques to study SPII archaeological site pottery, will be helpful for archaeologists in Brazil. With the results of this research, we can understand the chronology and determine areas of dispersion and density of archaeological occupation.

1. Introduction

TL and EPR are widely used methods for dating pottery [1–5]. Dating by TL and EPR techniques is a particular application of dosimetry in which there is a source of constant irradiation (the natural radioactivity from radionuclides in the soil where the ceramics is buried).

In the case of ceramics, the ionic crystals are the quartz grains contained in the clay from which the ceramics are made. The zeroing of the archaeological clock is defined by the moment the clay mould is heated to high temperature to produce ceramics.

The accumulated dose (D_{ac}) is determined from the ratio TL_{ac}/TL_0 where TL_{ac} is the TL value obtained from a given mass of quartz grains and TL_0 is the TL emitted by annealed quartz grains of same mass. Finally, annual dose rate (D_{an}) is calculated from measurements of the radioactive elements within the material and its surroundings where the pottery was collected and from the radiation dose rate from cosmic rays. The age of the pottery can be calculated by the D_{ac} divided by the D_{an}.

EPR spectroscopy, based on the absorption of microwave radiation by paramagnetic centres in the ionic crystal, has two roles in the study of pottery fragments. Firstly, it is used in dating to cross check TL results. Secondly, it can be used to find the firing temperature of ceramics [6–8].

Ceramics are among the oldest and most important technological innovations in human history and were one of the first truly synthetic materials. The investigation of ceramics under different aspects can provide us with the methodology used in manufacturing ceramics, dynamics of economical nature and cultural and social development of ancient societies. Such investigation has contributed in understanding not only geographical occupation, but also the cultural heritage of ancient people that reflect the particular style and traditions that can today be tracked through time and space. The dating of ceramics provides an important parameter of the history.

The SPII archaeological site is located on the left margin of the Solimões River, and also in the middle and down river regions in the municipality of Coari and 380 km away from and to the west of the city of Manaus, Amazon State, Brazil. This region occupies an area of ~ 5 ha. The people who inhabited this region had a vast territory, made war, trade with each other and spoke different languages [9].

There are indications of existence of pre-ceramists in the Amazons during the 7510–2550 b.C period. After a relatively long time gap of about 300 years, there was emergence of four occupations

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of ceramicists associated with the Amazonian Polychrome tradition. The Açutuba phase during the period 450 b.C to 360 a.C, the Manacapuru incised edge tradition phase dated around 425 a.C and 650 a.C and Paredão phase associated with the construction of artificial structures dated to be in the 750 a.C and 1250 a.C period. The most recent and superficial occupation is related to the Guarita phase, which has been dated to be in the 800 a.C and 1500 a.C period [10,11].

The Polychrome Tradition is associated with the people of Tupi language and is dispersed in the Amazon region. Several hypotheses have been made concerning the mobility and expansion of these people based on ethnographic, linguistic and archaeological data [9].

The São Paulo archaeological site is uni-componential with Guarita phase ceramics and represents a break in the form of occupation and in the form of ceramic production. The ground is relatively plane formed by organic, black-anthropogenic soil and is characterized by high values of pH, calcium, magnesium, zinc, manganese and phosphorus all indicators of intense human occupation. This aspect is interpreted as a cultural and social chronological marker. It also indicates a demographic density increase and an establishment of sedentary settlements [9].

2. Research aims

The number of archaeological research in the Brazilian Amazon has been increased in recent years due to the implementation of projects related to preventive archaeology in the region, which includes rescue and salvage of materials and archaeological sites. One of the sites studied is the São Pablo II (SPII) archaeological site.

The present work aims at elucidating the chronology of this archaeological site and technology applied in the fabrication of ceramics by ancient people who lived in this region of the central Amazon using the techniques of TL and EPR.

3. Experimental

The ceramics collected from SPII archaeological site were sandpapered to a depth of about 2 mm throughout the ceramic surface to remove any external unknown effect. The samples were later crushed and subjected to chemical washing with H_2O_2, HF and HCl to eliminate organic and some inorganic particles and separate the quartz as best as possible [4,12].

The quartz grains obtained after chemical treatments and magnetic separation were sieved and grains of size between 0.180 and 0.080 mm in diameter were selected for OM, TL and EPR measurements, while grains smaller than 0.080 mm were used for X-ray diffraction analysis.

To analyze the presence of any amorphous materials like spicules, an optical microscope (Bioval make, Model U000T), which has the magnification between 40× and 1600× was used.

XRD measurements were performed using a Rigaku X-ray diffractometer which utilizes a source of Cu K_α with wavelength of 1.5418 Å.

The accumulated dose (D_{ac}) was determined using the additive dose procedure assuming that the sensitivity to the laboratory radiation was the same as it has been for radiation during burial [13]. In this method, quartz grains extracted from the pottery are irradiated with laboratory dose in the range from a few to 5 Gy. The measured thermoluminesce is plotted as a function of dose. The accumulated dose D_{ac} is derived by extrapolating the plotted line to the negative dose axis. Initially, the sample of quartz grain was divided in 6 aliquots of approximately 30 mg each. One aliquot was used to obtain the TL curve of the natural sample and the others five were irradiated respectively with doses of 0.5, 1.0, 1.5, 2.5 and 5.0 Gy. Irradiation of samples has been carried out with gamma radiation from ^{60}Co source. An amount of 4 mg of the sample was used for each TL measurement. TL measurements were carried out in an automatic TL reader (Daybreak model 1100) keeping a heating rate of 4 °C/s in the interval of 0 to 450 °C. Each point in the TL glow curve represents an average of five readings.

The D_{an} is estimated by measuring the concentration of ^{238}U, ^{232}Th and ^{40}K in the sample determined by instrumental neutron activation analysis (INAA) and using for example, the Table 4.5 by Ikeya [2]. Cosmic rays contribution of about 0.25 mGy/year was added in D_{an}.

For determination of concentration of U, Th and K in the pottery by means of INAA, the ceramic fragments were washed with water using a brush of fine bristles. Then, the external surface of the ceramics was cleaned with tungsten carbide drill bits, with the prevention of any contamination in the analysis, since the fragment collected was dirty. Then, with the objective of assuring the chemical homogeneity, about five holes in different internal parts of each of the fragments were made. A mass of 500 mg was obtained in the form of powder from each fragment and this amount of sample was dried in 104 °C for 24 h [14]. For the total powder mass of 500 mg, 120 mg was separated for INAA analysis. This material was weighed in polyethylene packaging and sealed with iron, with the same amount of Standard Reference Material NIST-SRM 1633b, used as standard. After this procedure, the samples and standard were irradiated for 1 h at the IEA-R1 reactor of IPEN-CNEN/SP, under a thermal neutrons flux of 8.92×10^{12} n·cm^{-2}·s^{-2}. Two countings were carried out: K and U were determined after seven days of decay. After 25 days of decay, Th was determined.

EPR measurements were performed at room temperature utilizing a Bruker EMX spectrometer with a rectangular cavity (ST ER4102) and at a microwave frequency of 9.75 GHz (X-band) and with 20 mW microwave power and a modulation field at 100 kHz.

4. Results and discussions

Fig. 1 shows XRD pattern of the sample of this work and that of pure standard quartz. The result of XRD was analyzed using computer software and compared with the standard spectrum of quartz cataloged by JCPDS (Joint Committee Powder Diffraction Standards). Inset of the Fig. 1 shows the microphotograph of the quartz grains obtained with optical microscope.

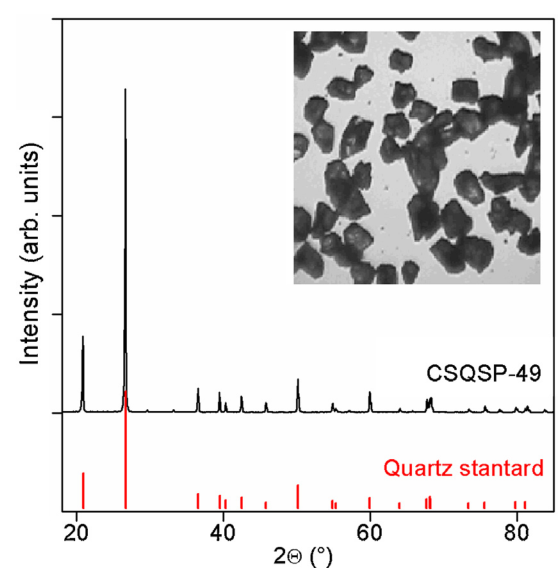

Fig. 1. XRD of quartz for the analyzed sample and standard quartz (red). Inset of the figure shows the photograph of quartz grains found in the sample labeled as SP49.

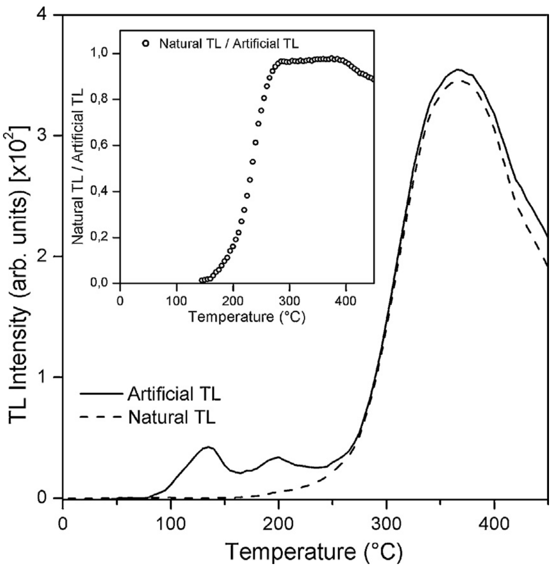

Fig. 2. TL glow curves of natural sample and sample after gamma-ray irradiation. In inset the Plateau Test, ratio of the natural TL intensity and artificial TL.

Fig. 2 shows the glow curves corresponding to the natural TL and to the artificial TL following 1.4 Gy of gamma irradiation. The peak in the region of 320 and 370 °C of the natural sample is evidently composed of a number of overlapping peaks and it is to be inferred that there are several types of trap present. The presence of several types of trap permits the "plateau test" to be used to check as to whether the traps associated with a given temperature range are deep enough for stable retention of electrons during antiquity. The ratio between natural TL and artificial TL as function of temperature is shown in inset of the Fig. 2. The onset of the plateau is indicative that a sufficiently high glow curve temperature has been reached for the TL to be associated with traps that are deep enough to retain their electrons with negligible leakage during archaeological times. The onset of the plateau is around 300 °C.

Fig. 3 shows the TL glow curves of the quartz grains with peaks at 120, 200 and 320–370 °C. The high temperature peak was used and doses of 0.5, 1.0, 1.5, 2.5 and 5 Gy were given for determination of D_{ac} by additive method. In inset of Fig. 3, the increase in the intensity of the 345 °C TL peak with γ dose is shown for the pottery sample SP49.

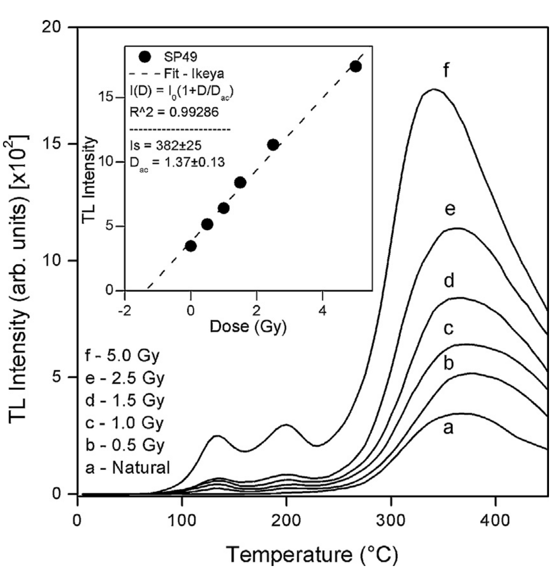

Fig. 3. TL glow curves of quartz grains obtained from the sample SP49 plus additional gamma-doses up to 20 Gy. Inset of the figure shows the TL intensity of the 345 °C peak as a function of the dose given to quartz grains extracted from sample SP49 for the determination to D_{ac}.

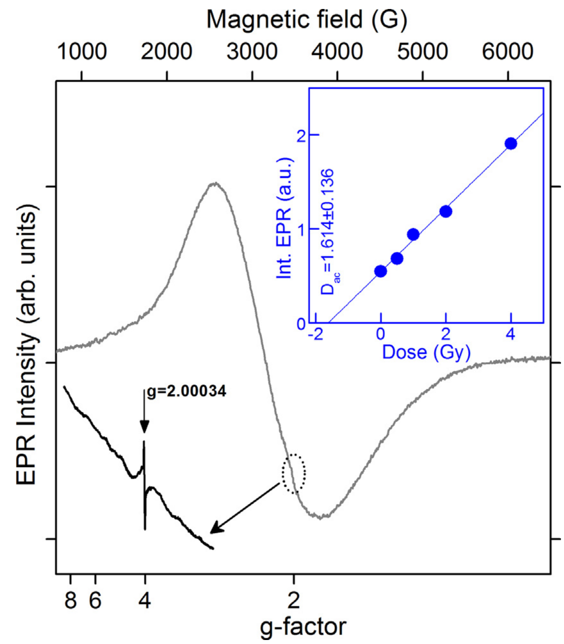

Fig. 4. EPR spectrum of quartz grains extracted from sample SP05. Inset of the figure shows peak-to-peak EPR intensity versus gamma dose of the EPR signal at g = 2.00034 due to E'_1-center.

The EPR spectrum of the quartz grains is shown in Fig. 4. In all the ceramic samples investigated here, an intense and asymmetric line at the g = 2 region was observed. This line is characteristic of Fe^{3+} ion in an octahedral site [7,8,15,16]. Another EPR line of low intensity was detected in the region 3458–3478 G. This line is shown in an expanded scale (black line) and is characterized by a g-value of 2.00034. This signal is due to the well-known E'_1-center in quartz and represents an electron bound to an oxygen vacancy [2,17]. According to Chen et al. [18], this center is thermally stable at temperatures below 500 °C regardless of heating time. In inset of Fig. 4, EPR intensities of E'_1-centers with increasing dose in samples irradiated with radiation dose up to 4 Gy are shown. The additive method was applied to calculate the D_{ac} using the g = 2.00034 EPR signal due to E'_1-centers.

From the concentration of ^{238}U, ^{232}Th and ^{40}K estimated by neutron activation analysis, D_{an} values were calculated using Tables 4.3 and 4.4 in Ikeya [2]. These calculated D_{an} values are listed in Tables 1 and 2.

Tables 1 and 2 shows the D_{ac}, the D_{an} and the age of ceramics using TL and EPR techniques, respectively. The age of the samples obtained by EPR method are comparable to the value obtained by TL measurements. These results confirm the archaeological interpretation of the phases of occupation of the ancient people who lived in this region of Amazon.

The firing temperature of the ceramics artefacts was determined by successive thermal treatment at high temperature where the

Table 1
Annual dose (D_{an}), accumulated dose (D_{ac}) and age of the fragments of ceramic samples obtained by TL technique.

Sample	D_{an} (mGy/year)	D_{ac} (Gy)	Age by TL (year a.C)
SP06	2.58 ± 0.12	2.61 ± 0.26	1000 ± 112
SP11	2.06 ± 0.08	2.51 ± 0.19	793 ± 102
SP28	3.35 ± 0.17	2.77 ± 0.46	1184 ± 142
SP49	1.29 ± 0.13	1.37 ± 0.13	947 ± 140

Table 2
Annual dose (D_{an}), accumulated dose (D_{ac}) and age of the fragments of ceramic samples obtained by EPR technique.

Sample	D_{an} (mGy/year)	D_{ac} (Gy)	Age by EPR (years a.C)
SP05	1.66 ± 0.17	1.61 ± 0.14	1039 ± 132
SP30	2.83 ± 0.18	2.76 ± 0.23	1037 ± 103
SP56	2.15 ± 0.20	2.14 ± 0.11	1017 ± 106

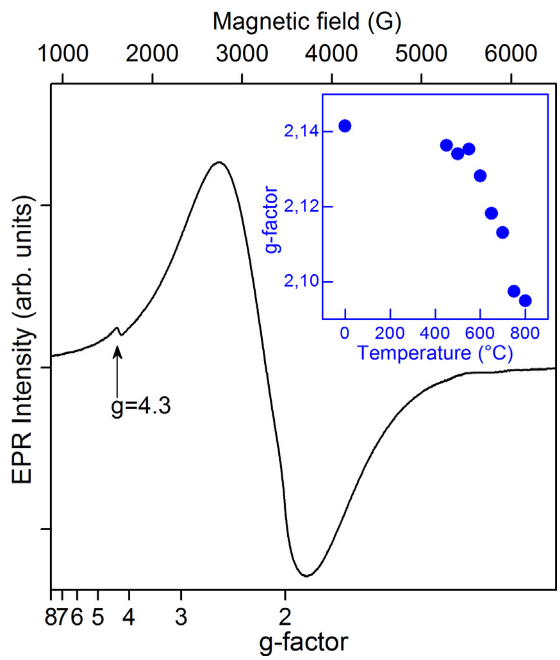

Fig. 5. EPR spectrum of the sample SP49 without chemical treatment. The variation of g-factor of Fe^{3+} with heating temperature of the experimental sample is shown in inset of figure.

Table 3
Results firing temperature for analyzed samples.

Samples	Firing temperature (°C)
SP02	650 ± 50
SP06	650 ± 50
SP11	600 ± 50
SP28	600 ± 50
SP47	650 ± 50
SP49	600 ± 50

g-value of Fe^{3+} changes [6]. Thermal treatment was performed in preheated oven in the temperature range 450 up to 800 °C. Every sample was thermally treated for 30 min.

Fig. 5 shows the EPR spectrum of the raw sample (ceramics powder), resulting from breaking and sieving of the pottery. We observed a broad absorption around $g = 2$; this line is characteristic of Fe^{3+} ion in an octahedral site. Furthermore, these ions are associated with hydrated species of Fe^{3+} ions, which can be oxidized to Fe_xO_y or FeOOH [17]. The EPR spectrum also shows another line in the region of $g = 4.3$, typical of Fe^{3+} in an orthorhombic site [7,16,19]. The intensity of this line is about 40 times lower than the EPR line at $g = 2.0$. The behaviour of the g-factor as a function of the temperature of the pottery sample SP49 is shown in the inset of Fig. 5. In all cases, g-value changed above 500–600 °C, indicating that the firing temperature for production of ceramics reached 600 to 650 °C.

Table 3 shows the values of the firing temperatures for six samples. This table shows that the firing temperatures of ceramic fragments are very close.

5. Conclusions

Seven ceramics sample from SPII archaeological site investigated here do not contain spicules, in contrast to many ceramics from other sites in the same region, which have been found to contain spicules. For Brazilian potteries, relatively old ages ranging between 895 and 1142 years have been obtained. Therefore, the results confirm the archaeological interpretation on the chronology of the occupation by Indian communities that occurred in the central Amazon of Brazil. EPR signal intensity of Fe^{3+} indicates that a heat treatment with temperatures around 600 to 650 °C was used to burn clay to produce ceramics. Therefore, this technique is useful to find temperatures, which were used to produce ceramics.

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