

The effect of the spicules in the pottery dating by TL, OSL AND EPR

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Abstract

Pottery fragments from Hatahara archaeological site, Amazon Valley, have been dated by thermoluminescence (TL), optically stimulated luminescence (OSL) and electron paramagnetic resonance (EPR) techniques. X-ray diffraction measurements and optical microscopic observation revealed crystalline quartz grains and amorphous grains in the ceramics. These last grains in the form of needles are called spicules. The calculated ages are consistent with the periods of occupation of the Hatahara archaeological site as estimated by stratigraphy of the ceramics.

Keyword: Pottery, Spicules, Dating, TL, OSL, EPR

1. Introduction

Thermoluminescence (TL), optically stimulated luminescence (OSL) and electron paramagnetic resonance (EPR) are widely used methods for dating pottery. These techniques make use of the mineral grains as dosimetric material such as feldspar, quartz and other crystals present in the ceramics for dating (Aitken, 1985); mainly quartz grains.

In any of the above mentioned dating technique, two following basic quantities must be measured: one is the accumulated dose, D_{ac} and the other, annual dose rate, D_{an} . Since the moment a fragment of pottery becomes buried by some process, the natural radiation due to radioactive nuclides in the soil starts to irradiate that fragment and until the moment it is collected for dating accumulate radiation dose equal to D_{ac} . This natural radiation irradiate anything with a D_{an} per year.

In principle, if we measure TL-value induced per unit dose (Gy), TL_u , from TL-value of quartz grains in the pottery, TL_0 , the quotient of TL_0 by TL_u gives D_{ac} . However, in practice we used the so called additive method (alterative is regeneration method). In this method, to quartz grains in the pottery as received, we add laboratory radiation dose usually in the range of few to 30, up to 50 Gy. After measuring TL-values of these irradiated samples we plot TL-value as function of dose, usually resulting a straight line. Extrapolating the line to negative dose-axis, in the intersection with this axis we obtain a dose-value whose absolute value is D_{ac} . The annual dose rate D_{an} is estimated from measuring concentration of ^{238}U , ^{232}Th in ppm and ^{40}K in weight %, and using, for example, Table 4.5, Ikeya (1993). From the values of D_{ac} and D_{an} we obtain: $age = D_{ac}/D_{an}$

The Hatahara archaeological site is located in the district of Iranduba, 30 km southwest of Manaus, in the region located on the left margin of the Solimões River, next to the merging

of the Negro River (Rebellato, 2007). Machado (2005) describes history of four distinct phases of occupation: Paredão, Manacupuru and Guarita. These phases were established by archaeological criterion, namely the decoration, form of the vessel, and mostly by the kind of temper used in the paste. Such aspects characterize the site as complex in relation to its pre-colonial composition and age determination of the ceramics are important in understanding the development of these societies.

The pottery fabricated by these ancient populations presents different types of additives, such as freshwater sponge or other mineral grains. The skeleton of the freshwater sponge consists of spicules that are cemented through organic junctions (Keding et al., 2010). The spicules are composed of amorphous silicon oxide that are frequently used as seasoning in the manufacture of ceramics used by ancient populations, in the region of Amazon. Sponge spicules can also be found dispersed in the soil, therefore, it is possible that they are present in the clay used to produce ceramics (Felicissimo et al., 2010).

The present work aims at elucidating the effect of the spicules in the pottery dating by TL, OSL and EPR. This can be done by comparing the luminescence and EPR spectra of crystalline quartz mixed with spicules with these of spicules. Of course, we intend to confirm the chronology of the occupation of this site obtained by the stratigraphy of ceramics comparing with ages of ceramics.

2. Experimental

2.1 Samples

The archaeological samples used in this study are fragments of pottery collected in the excavations carried out by archaeologists from the MAE-USP, at the Hatahara archaeological site.

Seven ceramics have been selected, each one corresponding to seven different phases of occupation, following Nunes (2009) work. They were named CSNH-50, CSNH-67, CSNH-68, CSNH-69, CSNH-73, CSNH-78 and CSNH-93.

In order to observe the effect that produces the spicules in the TL, OSL and EPR spectra sponges with spicules have been collected from the margin of the Solimões River. These sponges were prepared and analyzed in the same way as the potteries.

2.2 Chemical treatment

Each fragment of pottery undergoes following process to be dated: (1) its surface must be rubbed with sandpaper to remove few mm of surface layer to eliminate unknown effects that can interfere with the main measurements; (2) it is crushed and sieved to retain grains size between 0.080 and 0.180 mm size; (3) submit to a chemical treatment in solutions of H_2O_2 , HCL and HF.

Grains with diameter smaller than 0.080 mm can be used to find uranium, thorium and potassium content for internal annual dose rate measurements. They also can be used for x-ray diffraction measurement. The chemical treatment has two purposes. One is to eliminate, although partially, organic and inorganic particles always present. Second purpose is to corrode partially surface of quartz grains such that the effect of α -particles can be neglected. Watanabe et al. (2008) have show that the optimum reaction time when using a solution of 40% HF and 37% HCl is 40 minutes. In this work we followed this procedure.

There are in the literature several papers dealing with chemical methods to reduce the intensity of EPR signal due to Fe^{3+} (Bensimon et al., 1998; Ferretti et al., 2002; Duttine et al., 2003). This signal is usually large enough to hide E'_1 -center signal used in EPR dating. In this work the method proposed by Watanabe et al. (2008) was used. With an additional chemical treatment with 40% NH_3 solution for 40 minutes, and then washing several times in Milli-Q water it is possible to remove iron agglomerates by dilution.

2.3 Instrumental apparatus

The pictures of ground samples were obtained using a digital camera attached to an optical microscope Bioval, model L-1000T. The XRD analysis was carried out in a Rigaku diffractometer with Cu-k_α radiation. The scan was conducted in the range 10 to 90° . The TL measurements were carried out in a Daybreak TL reader, model 1100, equipped with a photomultiplier (PMT) EMI 9235QA for light detection with Corning 7-59 and Schott BG-39 filters used in front of the PMT. The heating rate used in the TL measurements was 4°C/s in nitrogen atmosphere. Each point in the glow curve represents the average of five readings. The OSL measurements of the quartz samples were carried out using a Risø TL/OSL reader equipped with a $^{90}\text{Sr}/^{90}\text{Y}$ beta particle source (Botter-Jensen et al., 2000). The reader was equipped with a 9635QA photomultiplier tube. The stimulation wavelength is 470nm. The detection optics consisted of a 7.5 mm HoyaU-340 filter.

A Bruker EMX EPR spectrometer operating at X-band frequency with 100 kHz modulation frequency was utilized for the EPR measurements. For each measurement 100 mg of powdered sample were used.

3. Results and Discussions

3.1 Mineralogical analysis

The photographic and the XRD diffractogram of the samples, after soaking in acids, are shown in Fig 1 and 2, respectively. The Fig. 1 show characteristic features belonging to a mixture of quartz crystals and spicules. Fig. 2(a) shows x-ray diffraction pattern of spicules, in Fig. 2(b) that of quartz plus spicules from one the sample. To compare with we have in (c) diffraction pattern of pure α -quartz.

3.2 TL measurements

We used the additive method, mentioned in the Introduction, to evaluate accumulative dose, D_{ac} . About 3 mg each sample aliquot have been used. In Fig. 3 the glow curves of sample CSNH-68 irradiated to additional γ doses varying from 2 to 15 Gy are shown. This figure show two peaks TL, one around 160 °C and another broad peak centered at 400 °C.

As shown in the inset of Fig. 3, spicules produce large peak at 400 °C and the important 325 °C peak in quartz becomes hidden. If we subtract spicules glow curve from corresponding curve in Fig. 3, one should obtain 325 °C peak. Of course, we did not carrying out such procedure because it is too time consuming.

3.3 OSL Measurements

The accumulated dose was determined using a single aliquot regenerative-dose (SAR) procedure, named SAR-OSL protocol (Murray and Wintle, 2003; Murray and Wintle, 2003). In this protocol, the first cycle is intended to measure the OSL signal of the natural sample, eliminating the energy accumulated since the last time that was exposed to light. A second cycle was performed to regenerate the OSL signal of the natural sample previously

measured. In this cycle are given different doses of radiation using a $^{90}\text{Sr}/^{90}\text{Y}$ β source, then the OSL signal (Li) is measured. A pre-heat of 220 °C was used to eliminate 110 °C. Sensitivity changes that occur during the regeneration process of the OSL signal in laboratory are checked by the OSL response to a test dose (Ti), which is always constant. The accumulated dose is calculated by interpolation of the curve Li/Ti in function dose. Fig. 4 shows a typical SAR laboratory growth curve for one of the aliquots of the sample CSNH-86 and an OSL decay curve (Fig 4, inset) for the sample CSNH-68 and spicules. The growth curve is fitted acceptably to a linear equation. Fig. 4 is a representative example of the luminescence characteristics exhibited by our samples and illustrates their generally good behavior in the SAR protocol; recycling ratios are indistinguishable from unity and the growth curves pass very close to the origin. Furthermore, this figure shows a comparison of the OSL signal of quartz grains and spicules of the pottery and OSL signal of spicules pure obtained from freshwater sponge, both samples irradiated with gamma dose of 6 Gy. There is no interference on the OSL signal of quartz grains due to spicules, thus we affirmed that optical dating of fine-grained quartz using SAR-OSL can be used to establish chronology of the ceramics of the Hatahara archaeological site.

Histograms of accumulated dose distribution of sample CSNH-68 are shown in Fig. 5. All the samples show reasonably tight and symmetrical distributions, after rejecting only a few aliquots with high dose outliers which were considered as abnormal aliquots.

3.4 EPR Measurements

In the inset of Fig. 6 is shown the EPR spectrum before a treatment of the sample with a solution of HNO_3 and Fig. 6 itself shows the spectrum after such chemical treatment. A detail of the spectrum around $g=2.0092$ is shown detached. Although arbitrary unit used, a

same unit is used for EPR intensity, which means that it is far larger in the spectrum shown in inset than in the spectrum in main Fig. 6 have shown that HNO₃ is able to eliminate considerable concentrations of Fe³⁺. Since the spectrum shown in Fig. 6 is due to Fe³⁺, one can understand why the EPR intensity is much smaller in the sample submitted HNO₃ action. In all spectra of the ceramic analyzed samples, an intense and asymmetric line in the g=2 region was detected, which is characteristic of Fe³⁺ in an octahedral site (Warashina et al., 1981; Presciutti et al., 2005; Bensimon et al., 1999; Mangueira et al., 2011). Furthermore, this line at g=2 is associated to clusters of irons Fe³⁺ with hydrated species of Fe³⁺ that can be oxidized to Fe_xO_y or FeOOH (Bensimon et al., 2000). The EPR spectrum too shows another signal at g=4.3, typical of Fe³⁺ in an orthorhombic site (Presciutti et al., 2005; Bensimon et al., 1999; Tani et al. 1997). This line presents an EPR intensity that is, on average, 40 times lower than the line associated with the line at g=2.0. A line of low EPR intensity in the region between 3458-3478 G, was also detected. In the inset of Fig. 6 (blue line) shows amplified signal demonstrating g-values at 2.0092. This signal corresponds to the paramagnetic species E'₁, which represents an electron bound to an oxygen vacancy (Ikeya, 1993; Bensimon et al., 2000). According to Chen et al. (1997), this species is thermally stable at temperatures below 500 °C, regardless of heating time. The spicules obtained from freshwater sponges showed no EPR signal in the region of 500-6500 G.

The signal from the Fe³⁺ ions may overlap at the center signal E'₁. However, Watanabe et al. (2008) conducted a study on the signal of EPR samples of ancient potteries for dating noticing the same influence of the sign of the ions Fe³⁺ observed in this study, they

concluded that it is possible to perform the determination of the age of the sample by EPR for these types of samples with a broad iron sign.

The iron content ceramics in the samples proves that there is no doubt that iron produces an intense signal superposed to E'₁-signal, on the other hand, it is evident that the chemical treatment with HNO₃, allows the observation of E'₁-center signal, this center appears only when the samples are irradiated and used in EPR dating (Ikeya, 1993; Watanabe et al., 2008).

To determine the accumulated dose by the EPR method was used again the additive method. For this, we measured the intensity of the EPR signal of samples irradiated at room temperature with 3 to 30 Gy gamma rays. The center E'₁ appears with irradiation of samples and increases with the dose as shows in the Fig. 7a. In Fig. 7b the EPR intensity of the signal at g=2.0092 is shown as function of radiation dose. The intercept of the curve and dose axis gives the accumulated dose. This procedure was repeated for all samples in which it was possible observe the E'₁ center.

Table 1 shows the accumulated dose, the annual dose and the age of ceramics using the method of OSL and EPR dating. The annual dose determination was done by means of concentrations of ²³⁸U, ²³²Th and ⁴⁰K in the ceramic by using the method of analysis by instrumental neutron activation. The results shown in Table 1 confirm the archaeological interpretation of the phases of occupation of the ancient people that lived in this region of the Amazon.

4. Conclusions

The analysis of potteries of the archaeological site of Hatahara by OM and XRD diffraction, showed the presence of crystalline quartz and spicules. The spicules introduce large fluctuation in TL values and cannot be used the TL dating, however, in the dating by OSL and EPR produces no effect in determining the age of the samples. Through the techniques of dating by OSL and EPR was possible to confirm the archaeological interpretation on the chronology of the occupation of the indian communities that occurred in this region of the central Amazon in Brazil.

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Figure Caption

Fig. 1 (a) Optical microscopy image of quartz crystal mixed with spicules from pottery. (b) Optical microscopy image of spicules from freshwater sponge.

Fig. 2 Comparison of the powder X-ray diffraction of samples after chemical treatments: Quartz standard (blue), quartz and spicules from pottery (black), spicules from freshwater sponge (red).

Fig. 3 TL glow curves of the sample CSNH-68 and irradiated at several γ doses. In the inset of the figure, the TL glow curve of the spicules extracted from freshwater sponge irradiated to 10 Gy

Fig. 4 Representative SAR growth curve for a single aliquot of quartz grains extracted from sample CSNH-68 for determine to accumulated dose. The inset shows the OSL decay curves for a single aliquot of quartz grains mixed with spicules extracted from sample CSNH-68 and OSL decay curve for spicules extracted from freshwater sponge (blue).

Fig. 5 The histograms of D_{ac} distribution of sample CSNH-68 for thirteen aliquots ($n=13$).

Fig. 6 EPR spectrum for sample CSNH-68 before (in the inset of figure) and after chemical treatments with HNO_3 .

Fig. 7 (a) EPR spectrum of sample CSNH-68 after chemical treatments with HNO_3 and irradiated with 3, 6, 10, 15 and 30 Gy. (b) EPR intensity of peak-peak versus gamma dose of sample CSNH-68.

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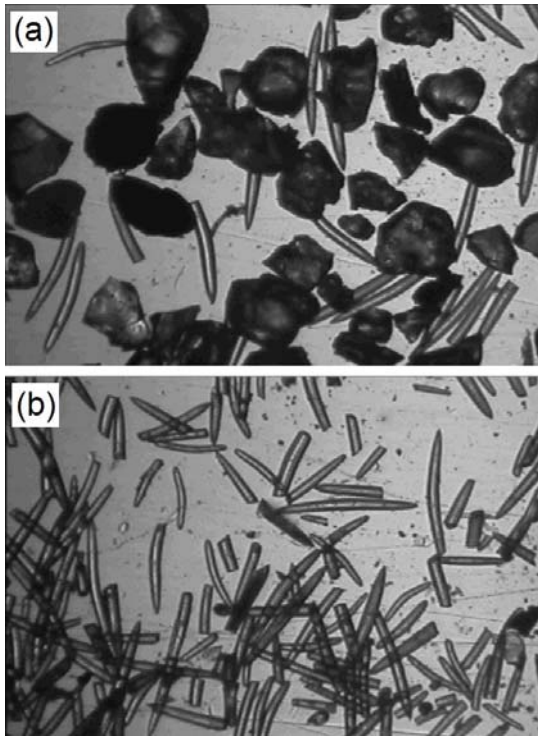


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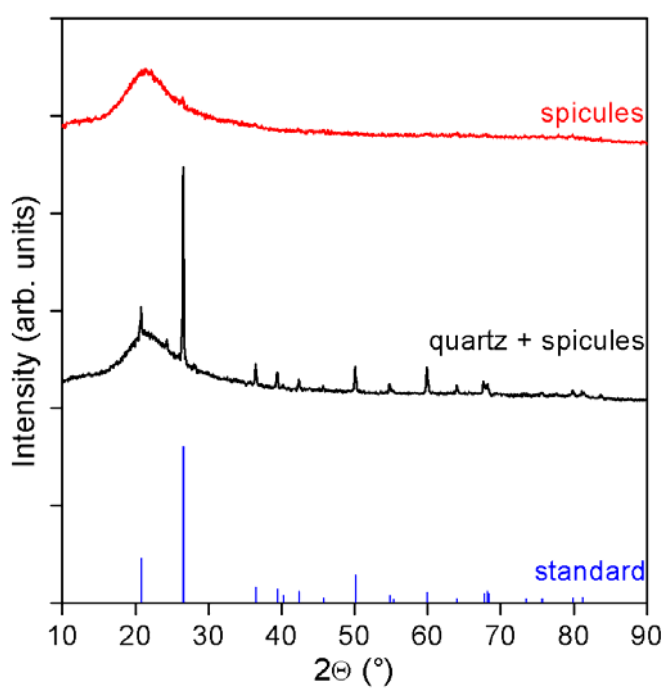


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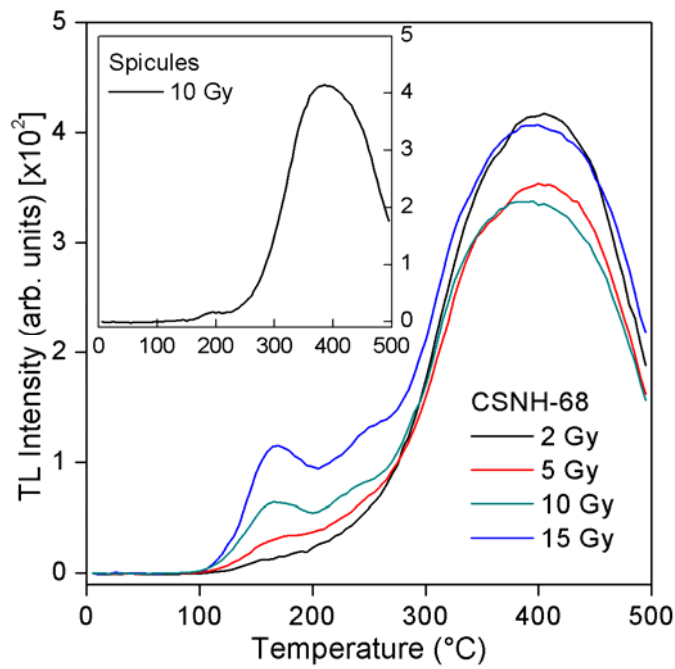


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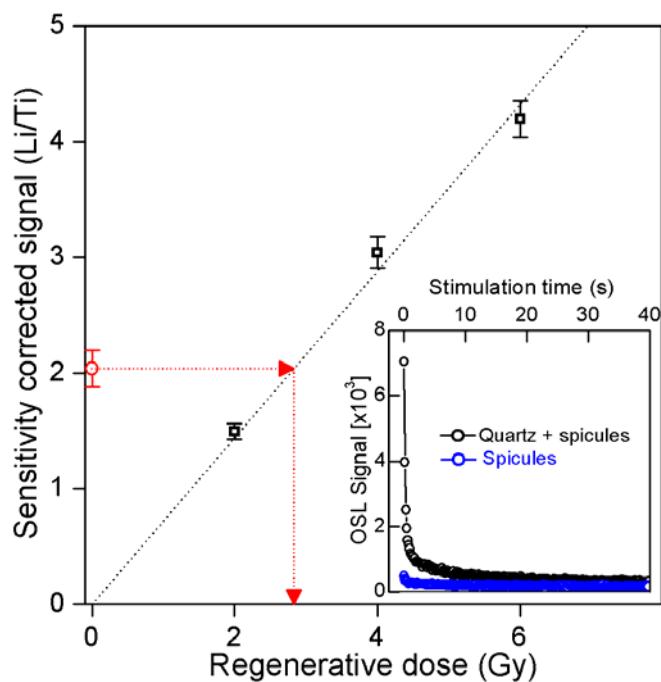


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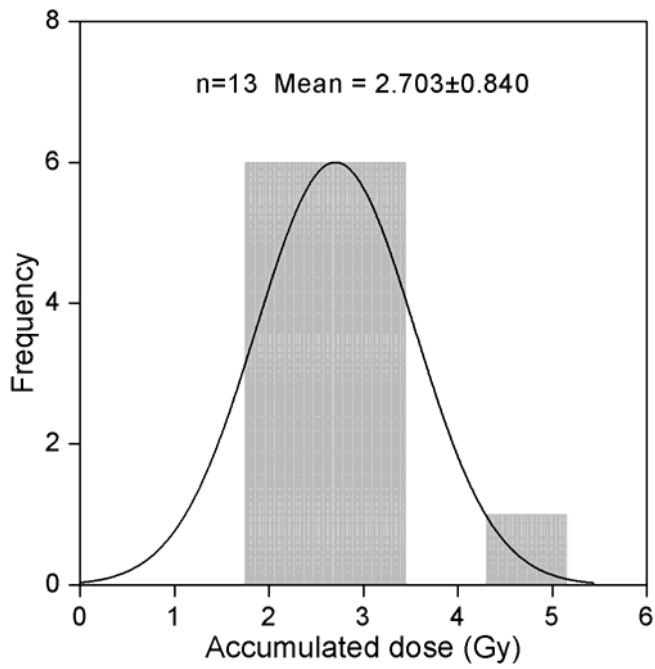


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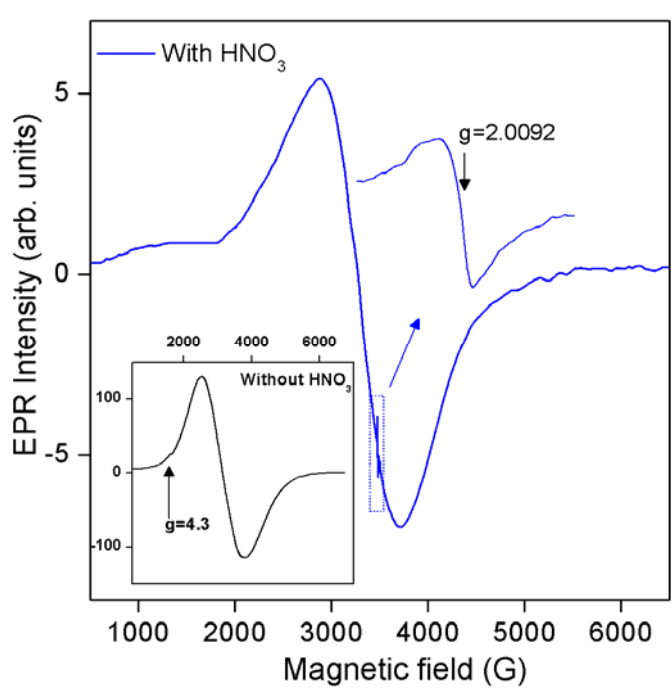


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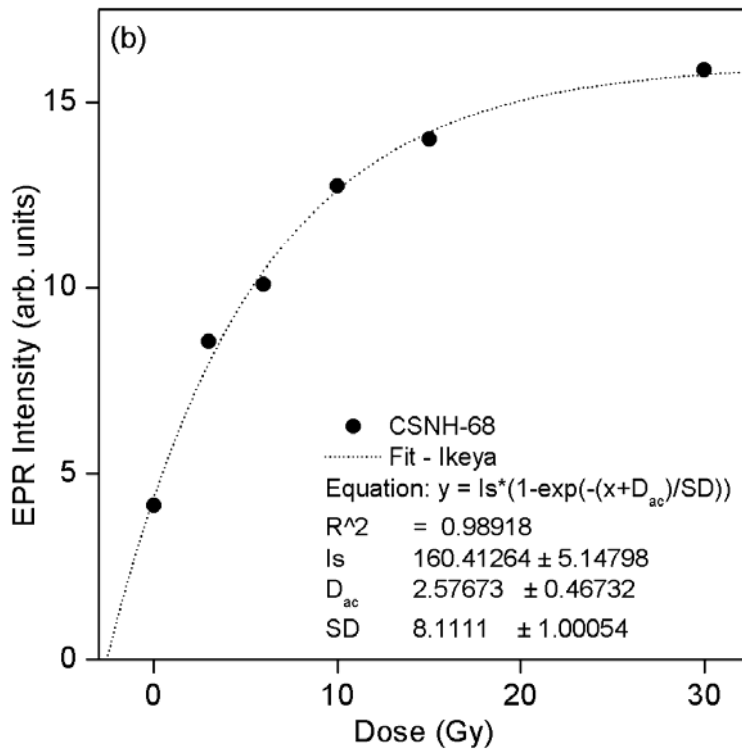
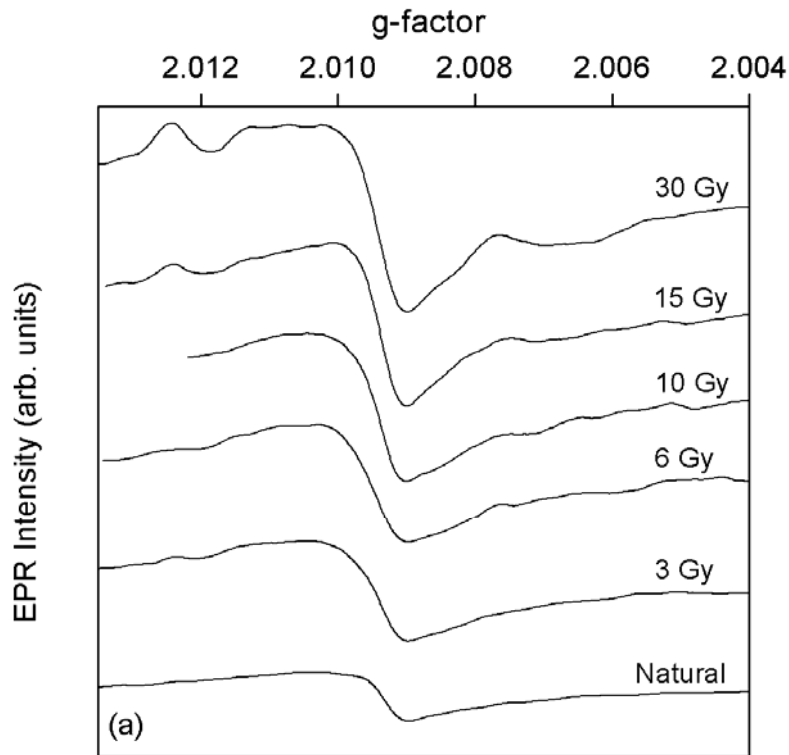


Fig. 7 (a) EPR spectrum of sample CSNH-68 after chemical treatments with HNO₃ and irradiated with 3, 6, 10, 15 and 30 Gy. (b) EPR intensity of peak-peak versus gamma dose of sample CSNH-68.

Table1 Accumulated dose, annual dose, age (by EPR and OSL dating) and phase cultural of the ceramics

Sample	Method				D_{an} (mGy/age)	Phase cultural
	D_{ac} (Gy)	EPR (a.C)	D_{ac} (Gy)	OSL (a.C)		
CSNH-50	3.928±0.240	718 ± 95	3.608 ± 0.840	604 ± 86	2.793	Manacapuru
CSNH-67	2.648±0.324	839 ± 86			2.261	Paredão
CSNH-68	2.577±0.468	866 ± 208	2.703 ± 0.840	810 ± 373	2.253	Paredão
CSNH-69			1.061 ± 0.167	1537 ± 75	2.242	Paredão, Manacapuru e Guarita
CSNH-73			2.595 ± 0.442	1023 ± 168	2.629	Paredão
CSNH-78	2.725±0.455	797 ± 273	2.617 ± 0.590	745 ± 211	2.158	Paredão, Manacapuru e Guarita
CSNH-93			3.133 ± 0.477	571 ± 218	2.178	Paredão, Manacapuru e Guarita