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EPR dating of Sediments in the region of Iguape – Cananéia, Brazil.

Cortez[a] B., Chubaci[b] J.F.D., Gomes[a] M.B., Mendes[a] L., Rocca[c] R.R., Arizaca[b] E.C.E., Watanabe[b] S.

[a] *Instituto de Pesquisas Energéticas e Nucleares, Av. Professor Lineu Prestes 2242, 05508-000 São Paulo, SP, Brazil*
[b]*Instituto de Física - Universidade de São Paulo, Departamento de Física Nuclear, Rua do Matão, 137 , 05508-090 São Paulo, SP, Brazil*
[c]*Departamento de Ciências do Mar - Universidade Federal de São Paulo, Edifício Central - Rua Silva Jardim 136, 11015-020 Santos, SP, Brazil*

bcortez@outlook.com.br

ABSTRACT

Dating of sediments was performed by physics method in this work. Natural radioactivity is present in sediments, and this method is based on the measurement of energy of radiation stored in the solid. Gamma irradiation of sediments create deffects in quartz structure that stores energy by the absorption of radiation. In the present work, Icapara sediment dating was done by Electron Paramagnetic Resonance (EPR) spectroscopy method. The intensity of EPR signal corresponding to the number of lattice defects with an unpaired electron in sediment quartz could be measured to estimate the accumulated dose of natural radiation and to calculate the geologic age. Located in the region of Iguape at southeast coast of São Paulo State, Icapara is a large sand terrace that was formed due to sea level fluctation that occurred more than 130 thousand years ago. Samples were taken from a point about 9 - 10 meters above the current control of the sea. Ages of 38,000 ±12,000 and 46,000 ± 7,000 years were obtained in this study by EPR analysis that are correlated with the Quaternary Period.

Keywords: **EPR analyses, Sediments, Quartz, Cananéia**

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1. INTRODUCTION

According to geologist the sea level along Brazilian sea coast presented fluctuations in the past [1-4]. Obviously, such fluctuation had an important impact in the formation of the coastal plain, one of these refers to sand terraces that can be found be in several points of southeast sea coast.

Evidence along the coast of the state of Rio Grande do Sul, that allowed proposed age as 400,000 years before present (BP) can be divided into four periods of the formation of the state of Rio Grande do Sul. This is due to the fluctuation of sea level, Period I extends from about 325,000 years to more than 400,000 years (BP), Period II from 123,000 years (BP) to 325,000 years (BP), and Period IV from present to 5,000 years (B. P). It has been suggested the sea level rises 8 ± 2 m above the present one at 120,000 years B.P (or more) [4]. Martin et al. [5] during their studies of coastal plains along the coast of southeast Brazil proposed that they are from Period. All these terraces exception are found in the sea shore, except one is located in a place Known as Icapara. All the terraces are about 30 meters height. The coastal plain of Cananéia-Iguape has a length of about 40 km wide and 150 km long, bordering the Northeast Island of Iguape and Southeast Ilha do Cardoso.

The Terrace found contains high percentage of quartz, which will be used for dating by Electron Paramagnetic Resonance (EPR), by the feature of storing defects that facilitate the use of the technique. Natural quartz shows several EPR signals. Therefore, the vacancies become paramagnetic (with an electron), this characteristic, a procedure was done to stipulate the relative number of found vacancies of oxygen [6, 7].

The use of the E'_1 center in quartz depends on the treatment previously performed. It is observed that the EPR intensity of the center E'_1 of the thermal process used results in the number of oxygen vacancies found in quartz [7-10].

Using the suggested technique, it is possible to correlate the number of quartz oxygen vacancies and the sediment age found, in which the outer layer with the contribution of gamma and beta-rays to oxygen vacancies [9-14].

This paper focus on dating Icapara terrace sediments by Electron Paramagnetic Resonance (EPR) spectroscopy collected sediment to estimate its age and check if its origin is from Lagunasystem Pleistocene Barrier, of samples about 3 to 12 m from the vertical profile made on the terrace, in relation to the Relative Sea Level (RSL).

2. MATERIALS AND METHODS

2.1. Collection of Samples

Icapara sand terrace belongs to the company Pirâmide Extração, Ltda, located in the city of Registro, the company extracts sand. At the Icapara site, an excavation was opened previously by the company with the focus of study the sediment, and this site was used for excavation of sampling for this paper.

Samples were collected using a PVC tube 80 cm long and 3 cm in diameter, which was inserted horizontally into a vertical profile, the first collection was identified as IC1 (Figure 1a), the second collection was carried out horizontally in a vertical profile below the first collection with a distance 40 cm, this sample was identified as IC2 (Figure 1b).

Figure 1: *Collection of samples (a) IC1 and (b) IC2.*

(a) *(b)*

Tubes were placed in black plastic bags to protect from exposure to light and transported to the Laboratory. The geographical coordinates, RSL, and the direction of the tube are described in table 1.

Table 1: The geographical coordinates, RSL, and the direction of the tube.

Sample	Latitude	Longitude	RSL (m)	Tube
IC1	24º40’31"S	47º27’01"W	10	Horizontal
IC2	24º40’31"S	47º27’01”W	9	Horizontal

2.2. Experimental

Each tube was opened and a portion of the open tube, approximately 20 mg was removed and separated to determine the Th, U, and K contents, and previously it was also determined the amount of water. A sample was weighed on the analytical balance, then immediately placed overnight in the desiccator and weighed again to quantify the percentage of moisture contents. The detection of radioisotopes was performed by Gamma-spectroscopy with a Canberra hyper-pure Ge detector calibrated using standards of soil (JR-1, JG-1, JB-3 and JG-3). The sample was kept for a period of 30 days for counting the secular equilibrium of radionuclides. Afterwards, it was placed on GeHP chamber for 48 hours.

Another portion of the tube, with the aim of getting quartz grains from sediment samples, different chemical treatments were made in 14% $H_2O_{2\ (v/v)}$ to remove of organic material for 30 min, subsenquently they were treated with 48% $HF_{(v/v)}$ to remove oxides and other materials, and remove a layer of quartz, for 40 min. Finally, treatment with 37% $HCL_{(v/v)}$ to remove carbonate residue, fluorides were removed during chemical treatment with HF, for 1h. Between each chemical treatment samples were washed with distilled water [15,16].

The samples were dried, afterwards pulverized with a pistil, and sieved with granulometry between 75 µm and 180 µm, followed by better EPR emission, the particle sizes of the sample replicate the results of the experiment [17,18].

To determine accumulated dose (D_{ac}) using the EPR technique through the multiple-aliquot regenerative-dose (MAR) protocol was used for the calculation of D_{ac} using the EPR technique the samples were heat-treated at 450 ºC for 15 min. To determine the thermal treatment temperature at which the EPR intensity maximum, different temperatures of 0, 180, 230, 270, 290, 320, 350 ºC were carried out, 400 and 450 ºC for 15 min, but at 450 ºC, it was performed with 30 min to observe the zeroing of the natural sample. Before any event or period, since the formation of quartz there is constant natural irradiation by radionuclides, in the geological period. With the occurrence of an event (Erosion and transport), the optical bleaching zeroing occurs, being exposed to solar radiation. And the solar incidence causes excitation of electrons emitting light, resetting the quartz.

Portion of the chemically treated quartz sample was divided into 7 aliquot approximately 250 mg aliquots packed in small packs, already dry. Then irradiated at 10, 20, 40, 60, 80, 100 and 200 Gy, irradiations was carried out at CTR/ IPEN with a ^{60}CO Gamma-cell source.

The curves were calculated by extrapolating of accumulated dose-rate data with the equation Ikeya [19] :

$$I(Q) = I0(1 - e^{(-(D+De)/Ds)}) \quad (1)$$

where I(Q) is the signal intensity; I0 and Ds are the intensity and dose at saturation, respectively; D is the added dose; and De is the equivalent dose obtained.

EPR signals of the samples were measured with a MiniScope MS 5000 EPR spectrometer from Freiberg Instruments. The number of oxygen vacancies was measured as the intensity of the E'_1 center after gamma-ray irradiation and heating at 300 ºC for 15 min. [20,21].

The following measurement conditions of the EPR were used: the microwave power of 0.01 mW, the magnetic field modulation frequency of 100 kHz, its amplitude of 0.1 mT, the centre field of 336.0 to 337.0 mT and a sweep time of 80 s. The measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

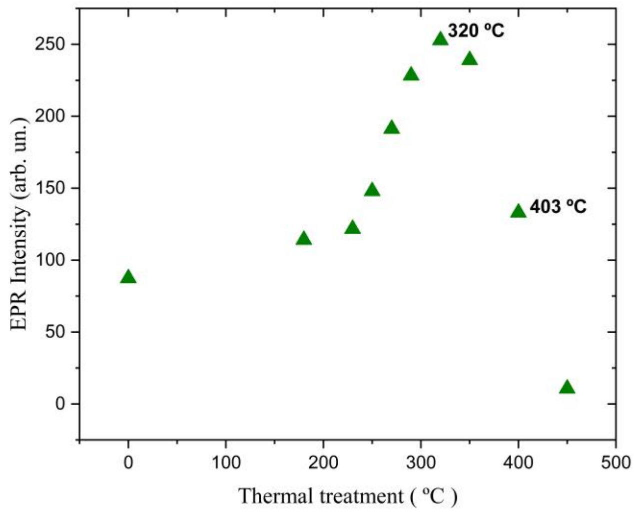
3.1. The E'_1 center and the oxygen vacancy in Quartz

The E center was used by Jani [11] with the EPR technique for dating. There are centers associated with oxygen vacancies that in their structure contain a proton and with different relaxations being E. Figure 5 shows the grown curves of the IC1 sample, and the aim was determine the highest signal of the E’1 center for the preheating of the samples regenerative doses. The preheating used for the E'_1 center is an indicator of the relative amount of oxygen vacancies, the typical change in heating the signal strength in quartz is observed from 230 °C to 320 °C, the increase of the E'_1 signal with heating for transferring holes to neutral oxygen vacancies [10-14].

The results preliminates shows of the heat treatment around 320 °C stabilized and reached the highest intensity, and in heat treatment at 450 °C, completely eliminated the E'_1 center. Thereby, the electron unpaired is located in the hybrid orbital, makes silicate adjacent to vacancy, and the number of oxygen vacancies increases with age.

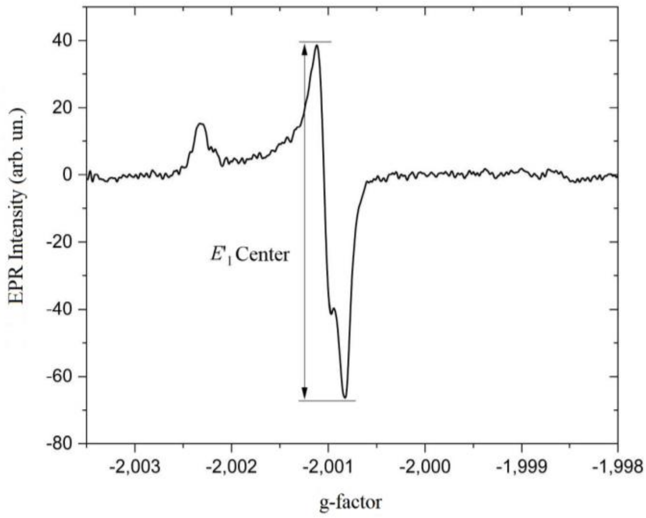
The use of the E'_1 center in quartz depends on the treatment previously done. The procedure used was performed by gamma irradiation at 200 Gy followed by heating at around 300 ºC for 15 minutes. It is observed that the EPR intensity of the center E'_1 of the thermal process used depends on the number of oxygen vacancies found in quartz [19, 20]. Using the suggested technique, it is possible to correlate the number of quartz oxygen vacancies, and the sediment age found.

Figure 5: *Thermal treatment test at different temperatures of 0, 180, 230, 270, 290, 320, 350, 400 and 450 ° C for 15 minutes.*



EPR spectrum of the E'_1 center has orthorhombic symmetry possible three g-factors being 2.00179, 2.00053, and 2.00030 [11], characteristic of E'_1 center in the quartz crystal is shown in Figure 6, which is dependent on previous thermal treatments in the sample, we observed a broad absorption around g= 2.00179. A variation of the g factor was identified in the temperature region 320 °C, this behavior of the g factor as a function of the firing temperature of the quartz sample.

Figure 6: *Study* E'$_1$ *Center of Quartz observed for sample IC1.*



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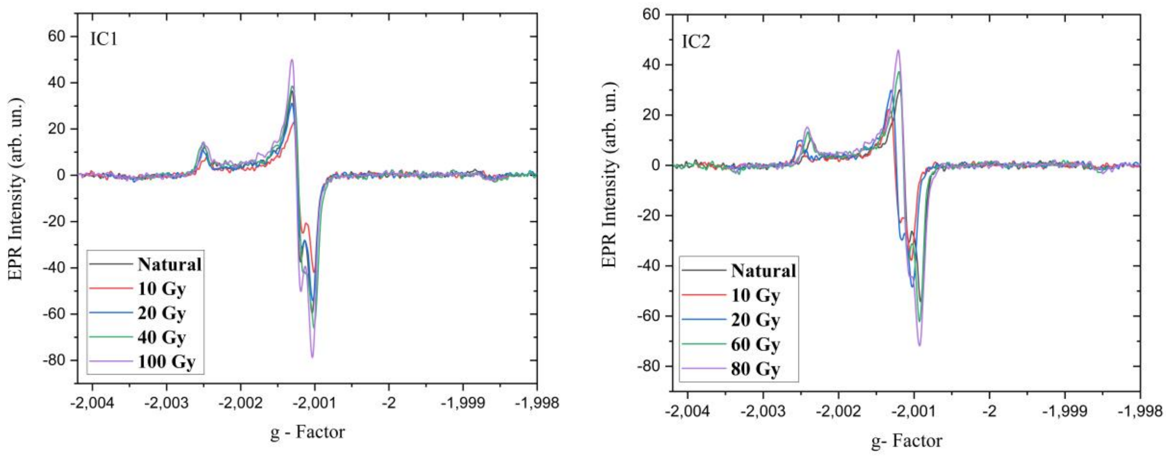
Thermal treatment studies define the temperature that stabilizes the defect of E'1, according to the protocol used previously mentioned, therefore calibration curve was constructed, observed in Figure 7 (a) and (b) the graphs of samples IC1 and IC2, respectively.

The peak-to-peak intensity of the EPR spectrum observed was used to building the calibration curve to determine AD using the Ikeya [11] equation. The dose interpolation was performed to obtain the AD of samples.

Figure 7: *Paramagnetic species observed for (a) IC1 natural and gamma irradiated with 10, 20, 40, and 100 Gy radiations absorbed doses; and (b) IC2 natural and gamma irradiated with 10, 20, 60, and 80 Gy radiation absorbed doses.*

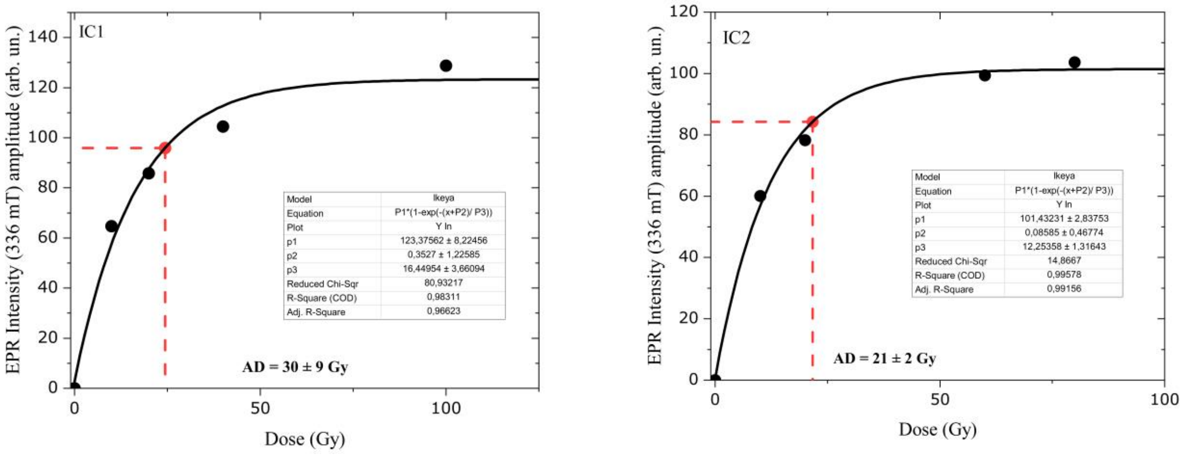


(a) *(b)*

The peak-to-peak intensity was used, building the curve calibration and determine D_{ac} using the Ikeya [19] equation, and with the dose interpolation was done to obtain the accumulated dose of each sample as shown in Figure 8.

In this paper, additive dose technique for the stable EPR signal at g= 2.00179 is used to construct a growth curve and to obtain the accumulated dose (Dac) for four carbonate samples. The growth curve of this signal shows the typical saturation type pattern.

Figure 8: *Calibration curve accumulated doses with the EPR intensity of the samples IC1 and IC2.*



(a) *(b)*

Table 2 shows the concentrations of the ^{238}U, ^{232}Th and ^{40}K sediment samples obtained by gamma-spectrometric analysis. The sediment in the local is in constant disintegration of radionuclides, which through the contents in ppm of ^{238}U, ^{232}Th and percentage of ^{40}K is found the external dose in which the sediment has been submitted in years [19].

The content of the radionuclides ^{238}U, ^{232}Th and ^{40}K for Dan (annual dose) was calculated. The parameters are those mentioned in the item of experimental.

Table 2: *Radioisotopes concentrations of Samples IC1 and IC2.*

Samples	**^{238}U (ppm)**	**^{232}Th (ppm)**	**^{40}K (%)**
IC1	0.62 ± 0.04	3.55 ± 0.19	0.20 ± 0.01
IC2	0.47 ± 0.03	1.34 ± 0.07	0 ± 0

In this paper the DRAC program was used to have greater precision in the age of the sediments [22]. Table 3 shows also the moisture contents of the sample and cosmic radiation, other parameters such as depth and geographical coordinates were taken into account. The values of radionuclide concentration contents are used in the calculation of the sediment annual dose, in table 4 the values of Accumulated Dose are shown.

Table 3: *Moisture contents % and cosmic radiation for each sample collected.*

Sample	Moisture contents %	Cosmic radiation (Gy)
IC1	9.37	0.28
IC2	1.8	0.28

The ages obtained of the samples IC1 and IC2 with the mentioned parameters are shown in the table 4 below The samples ages can be related to the lower Pleistocene period, which is in accord with the ages in literature as mentioned.

Table 4: *Values EPR from regenerative method and sediment ages.*

Samples	$D_{ac} \pm \sigma$ (Gy)	Age (Ka)
IC1	31 ± 9	38 ± 12
IC2	22 ± 3	46 ± 7

4. CONCLUSION

EPR technique it is possible to correlate the number of E'_1 center of quartz and the age of the sediment found. The E'_1 center to be stabilized with thermal treatment, the signal g-factors being 2.00179. it is conclude that of the thermal treatment, with around 320 ºC stabilizes reaches the highest intensity, and the multiple-aliquot regenerative-dose (MAR) was used for samples under treatment at 450 ºC eliminated the E'_1 center.

In the past, the occurrence of currents may have been like the present, where winds come and deposit sediment, in turn, the opposite river elements do not would leave the dispersion of these sediments. The age obtained approximately for EPR is consistent with the period of the Pleistocene and the period in which fluctuations in the level of the In the state of São Paulo, the terrace can be considered part of the Barrier II due to its age about 38,000 ± 1 2 ,000 and 46,000 ± 7,000 years (BP).

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