DOSIMETRIC PROPERTIES OF BIOMINERALS APPLIED TO HIGH-DOSE DOSIMETRY USING THE TSEE TECHNIQUE

Gustavo B. Vila[1,2] and Linda V. E .Caldas[1]

[1]Instituto de Pesquisas Energéticas e Nucleares
Comissão Nacional de Energia Nuclear, IPEN-CNEN/SP
Av. Prof. Lineu Prestes, 2242, 05508-000, São Paulo, Brazil

[2]Universidade Nove de Julho, UNINOVE
Rua Vergueiro, 235/249, 01504-001, São Paulo, Brazil
gbvila@ipen.br and lcaldas@ipen.br

Abstract

The study of the dosimetric properties such as reproducibility, the residual signal, lower detection dose, dose-response curve and fading of the thermally stimulated emission exoelectronic (TSEE) signal of Brazilian biominerals has shown that these materials present a potential use as radiation dosimeters. The reproducibility within ± 10% for oyster shell, mother-of-pearl and coral reef samples showed that the signal dispersion is small when compared with the mean value of the measurements. The study showed that the residual signal can be eliminated with a thermal treatment at 300 °C/1h. The lower detection dose of 9.8 Gy determined for the oyster shell samples when exposed to beta radiation and 1.6 Gy for oyster shell and mother-of-pearl samples when exposed to gamma radiation can be considered good, taking into account the high doses of this study. The materials presented linearity at the dose-response curves in some ranges, but the lack of linearity in other cases presents no problem since a good mathematical description is possible. The fading study showed that the loss of TSEE signal can be minimized if the samples are protected from interferences such as light, heat and humidity. Taking into account the useful linearity range as the main dosimetric characteristic, the tiger shell and oyster shell samples are the most suitable for high-dose dosimetry using the TSEE technique.

Keywords: Brazilian Biominerals; High-Dose Dosimetry; TSEE Technique; Gamma Radiation; Beta Radiation.

1.- INTRODUCTION

The thermally stimulated exoelectronic emission or exoemission (TSEE) is the emission of low energy electrons that appears on the surface of many ionic crystals for temperatures below those at which the thermionic emission occurs. This phenomenon, also known as Kramer effect, previously observed in the nineteenth century, was systematically studied by Kramer in 1949 (Crase, 1971), Becker (1973) and others. Since then, some other researchers have used the technique for the study of low penetrating radiations such as: Caldas (1980) showed that, BeO and $\alpha\beta$-Al_2O_3 samples based on graphite are useful dosimeters for beta radiation; Herbaut *et al.* (1983) studied LiF with graphite samples for beta and gamma radiation dosimetry; Melo *et al.* (2008) measured the TSEE spectrum emission of actinolite, tremolite, diopside and rhodonite samples, and showed that the samples present dosimetric properties at high doses in the range of 2 Gy to 20 kGy; and Rocha (1997) developed a system for TSEE measurement in the group of Radiation Metrology of IPEN, which was used in this work.

The TSEE phenomenon occurs in a very thin layer on the order of 10^{-4} mm and 10^{-3} mm from the material surface with strong influence of surface defects. Therefore, it is expected that exoemission is very sensitive to variations in the surface structure of material to defects and also to the presence of impurities in the material. Depending on the depth of the electron traps, the exoemission may occur at temperatures ranging from -240 °C for KBr up to 500 °C for α-Al_2O_3 (Glaefeke, 1979). The exoemission electrons located at the surface and in the bulk material traps probably follow different kinetics. The exoemission occurring on the surface of the material probably does not require the involvement of the conduction band; however, for issuing traps located in the material bulk, it is considered that the electrons are first excited to the conduction band, and they are able statistically to reach the material electron affinity (Becker, 1973).

The materials studied in this work are compounds formed by the activity of bacterias, therefore are they called biominerals. They are formed by main calcium carbonates and found in nature in two main polymorphic forms: calcite and aragonite. Due to the natural formation of calcium carbonate, they present several impurity elements as Mn, La, Ba, Fe, Na, Zn and other. Some biominerals have already been studied as dosimetric materials using the thermoluminescence technique by Vila and Caldas (2011), Carmichael *et al*. (2002), Duller *et al*. (2009) and Zaragoza *et al*. (2012) and the electronic paramagnetic resonance technique by Seletchi and Duliu (2007), Sharaf and Hassan (2004), Hassan and Sharaf (2005) and Köseağlu *et al* (2004), mainly for datation and medical applications.

In the present work the reproducibility, residual signal, lower detection dose, dose-response curve and fading of the TSEE signal of some Brazilian biominerals from the family of calcium carbonates were studied.

2.- MATERIALS AND METHODS

The materials studied in this work, all from the calcium carbonate family, known as oyster shell (OST), coral reef (COR), mother-of-pearl (MAD) and tiger shell (CON) (Figure 1), usually used for decoration, were obtained at a market of Recife city originating from the northwest coast of Brazil.

Figure 1. Biomaterials: a) As obtained; b) Pellets of powdered samples with Teflon; and c) Powdered samples.

All samples were powered and sieved retaining the 177 µm – 74 µm size fraction. The powder was mixed with Teflon to a proportion of 1:2, respectively, obtaining pellets of 20 mg with dimensions of 6 mm of diameter and approximately 1 mm of thickness. In the sinterization process the samples were pre-heated at 300 °C for 30 minutes; soon afterwards they were thermally treated during 1.5h at a temperature of 400 °C.

After the sinterization process, the pellets were thermally treated at 300 °C/1 h, in order to guarantee that there was no remaining signal, and kept in dark until their irradiation and TSEE measurements. The pellets were irradiated using a ^{60}Co panoramic and a Gamma Cell sources of the Centre for Radiation Technology (IPEN) and in the case of beta radiation they were exposed to a ^{90}Sr/^{90}Y source of the TL/OSL Risöe system, TL/OSL-DA-20 model. All irradiations were performed at room temperature, and the pellets were sandwiched in Lucite plates with 3.5 mm thickness to guarantee the electronic equilibrium during their exposure at gamma radiation. The TSEE measurements were taken using a home-made system developed at the Radiation Metrology Group of IPEN in the range from ambient temperature to 300 °C. The TSEE measurements were obtained with linear heating rates (10 ºC/s) in a P-10 continuous gas flow.

3.- RESULTS

The biomineral pellets were irradiated with 1 kGy and 100 Gy to gamma and beta radiations, respectively. The TSEE emission curves showed two characteristic peaks for OST samples when exposed to gamma radiation (Figure 2a) at approximately 200 °C and 285 °C, and when exposed to beta radiation only one TSEE peak was observed at 200 °C.

For COR samples (Figure 2b), when exposed to gamma radiation, one main peak was observed at 175 °C, approximately, and when exposed to beta radiation two peaks at 125 °C and 175 °C could be seen. After exposure to gamma radiation, two peaks were observed for MAD samples (Figure 3a) at 130 °C and 195 °C, approximately, and when exposed to beta radiation, as well, two peaks were observed at 130 °C and 210 °C.

For the CON samples exposed to gamma radiation (Figure 3b) one main TSEE peak was observed at 245 °C with a broad tail at lower temperatures, probably due to the presence of one peak approximately at 175 °C; when exposed to beta radiation, two TSEE peaks were observed at approximately 150 °C and 220 °C.

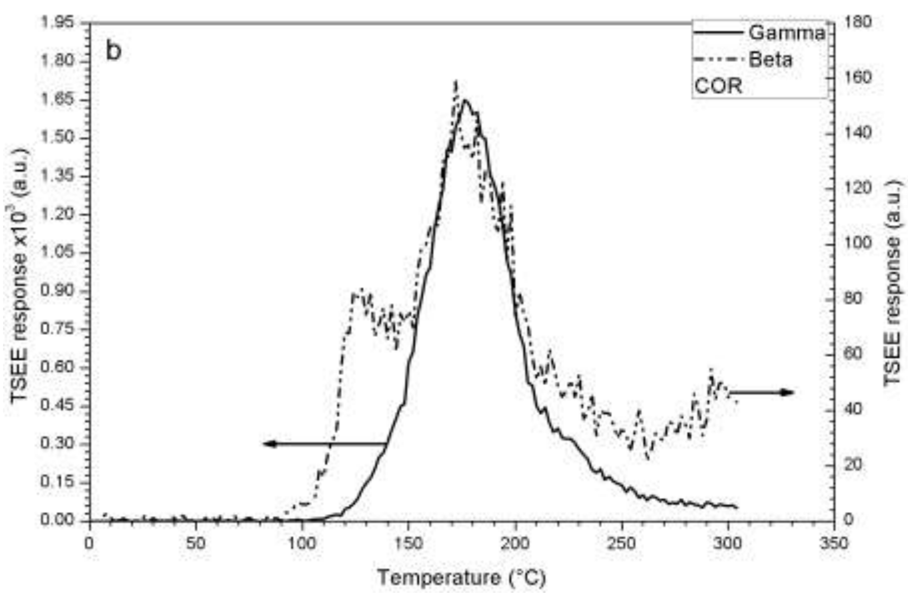

Figure 2. - TSEE emission curves of OST (a) and COR (b) samples exposed to gamma and beta radiations with doses of 1 kGy and 100 Gy, respectively.

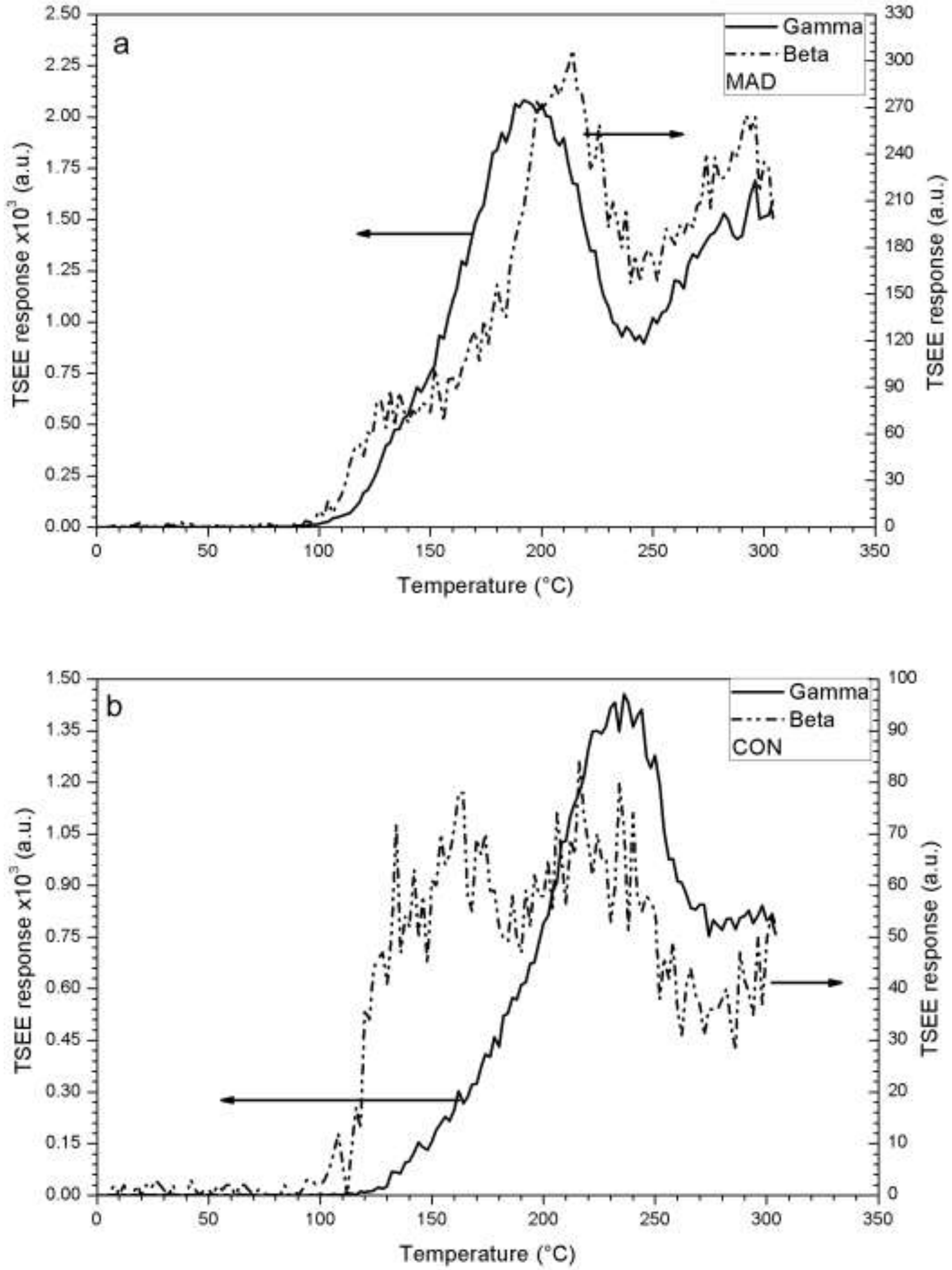

Figure 3. - TSEE emission curves of MAD (a) and CON (b) samples exposed to gamma and beta radiations with doses of 1 kGy and 100 Gy, respectively.

The reproducibility tests of the TSEE response were performed on samples submitted to the thermal treatment of 300 °C/1 h and subsequently irradiated with a dose of 1 kGy to gamma radiation and 20 Gy to beta radiation. The reproducibility is given by the coefficient of variation (CV%), which is equal to the ratio between the standard deviation and the mean of the TSEE measurements of each sample. The coefficient of variation (CV), determined for the samples taking into account the radiation type, showed the lowest CV for MAD samples after gamma irradiation and the lowest CV to COR samples when exposing them to beta radiation (Table 1).

Table 1. - TSEE response reproducibility (%) of Brazilian biominerals.

Radiation	OST	COR	MAD	CON
Gamma	6.1	4.9	3.8	4.4
Beta	9.3	6.1	7.5	6.7

For the determination of the residual signal, the pellets were irradiated and then two measurements were carried out in sequence. The second measurement was taken to verify if the TSEE signal had been completely zeroed after the first measurement. The residual signals of biomineral samples are summarized in Table 2.

Table 2. - Residual signal of the biomineral samples.

Sample	Residual signal (%)
OST	6.6±1.5
COR	7.8±1.6
MAD	5.6±1.1
CON	10.5±0.7

As can be seen in Table 2, the values demonstrate the need for a heat treatment for reuse of the samples. The highest value among the biomineral samples was observed for the CON samples and the lowest residual signal was observed for the MAD samples. Therefore, the thermal treatment of 300 °C/1 h was always performed for the materials reutilization.

For the determination of the lower detection limits (D_{LDL}), using the TSEE technique the procedure described by Pagonis et al. (2006) was followed. As can be seen in Table 3, the D_{LDL} is different when comparing the results obtained of each sample for different radiation types. The lowest D_{LDL} value was obtained for CON samples when exposed to gamma radiation and for MAD samples when exposed to beta radiation (Table 3).

Table 3. - Lower detection limits (Gy) for Brazilian biomineral samples exposed to gamma and beta radiations, using the TSEE technique.

Radiation	Samples			
	OST	COR	MAD	CON
	D_{LDL} (Gy)			
Gamma	1.6	2.3	1.6	1.0
Beta	9.8	2.9	0.8	3.7

As can be seen in Figures 4 and 5, the dose-response curves show an increasing behavior with the absorbed dose, and a tendency toward saturation, when exposed to gamma radiation. For the OST samples (Figure 4a) a linear behavior over the dose range of 5 Gy to 20 Gy, when exposed to beta radiation, was observed, and for COR samples (Figure 4b) over the dose range of 5 Gy to 50 Gy. The MAD samples (Figure 5a) showed a linear behavior between 20 Gy and 500 Gy when exposed to gamma radiation and sublinear behavior when exposed to beta radiation. The CON samples (Figure 5b) exposed to gamma radiation showed linearity in the range from 1 Gy to 1 kGy, and a sublinear performance when exposed to beta radiation.

The fading of the TSEE response of the Brazilian biomineral samples was studied after an exposure to gamma and beta radiations with doses of 1 kGy and 100 Gy, respectively, and at certain intervals from 0h to 720 h, as can be seen in Table 4. The highest fading was obtained for the CON samples when exposed to gamma radiation and for the MAD samples when exposed to beta radiation.

Table 4. – Fading (%) of the TSEE response of Brazilian biomineral samples exposed to gamma and beta radiations.

Radiation	Gamma	Beta	Gamma	Beta	Gamma	Beta	Gamma	Beta
Time (h)	OST		COR		MAD		CON	
0	100±3	100±2	100±2	100±1	100±2	100±5	100±6	100±9
24	94±3	92±14	95±4	67±5	91±8	64±8	50±10	92±3
72	82±10	79±15	88±7	57±8	78±12	51±14	33±4	81±10
120	76±6	75±3	83±8	51±11	67±7	42±8	24±5	68±9
168	74±3	74±9	79±9	45±12	64±8	39±3	21±7	58±5
720	72±4	71±9	70±9	40±8	62±9	35±3	18±7	40±6

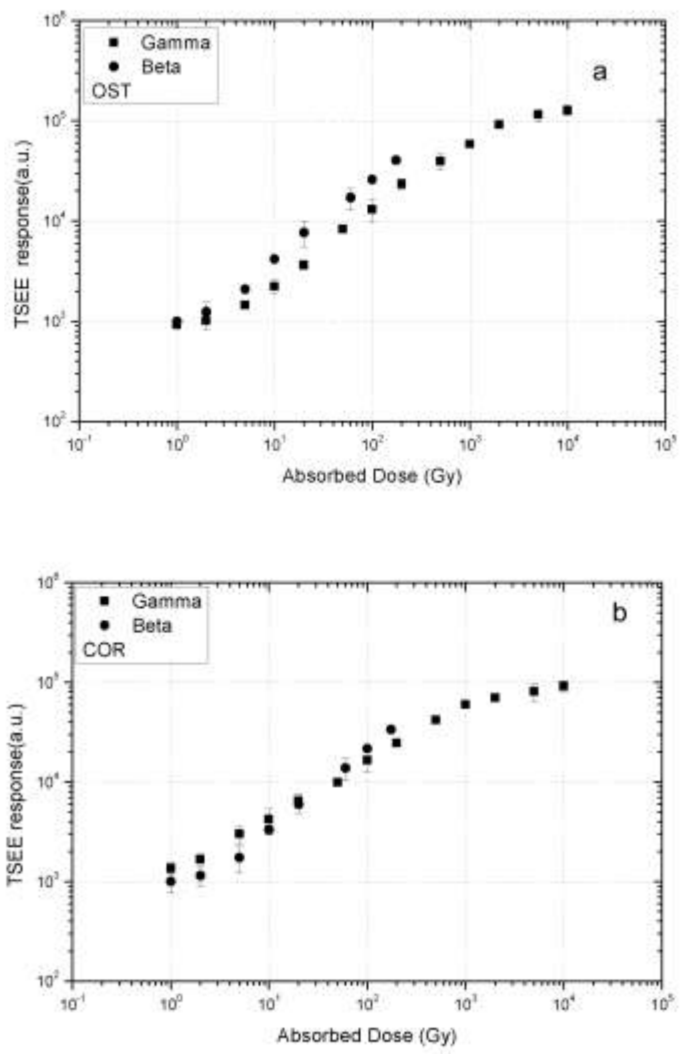

Figure 4. - Dose-response curves for OST (a) and COR (b) samples exposed to gamma and beta radiations.

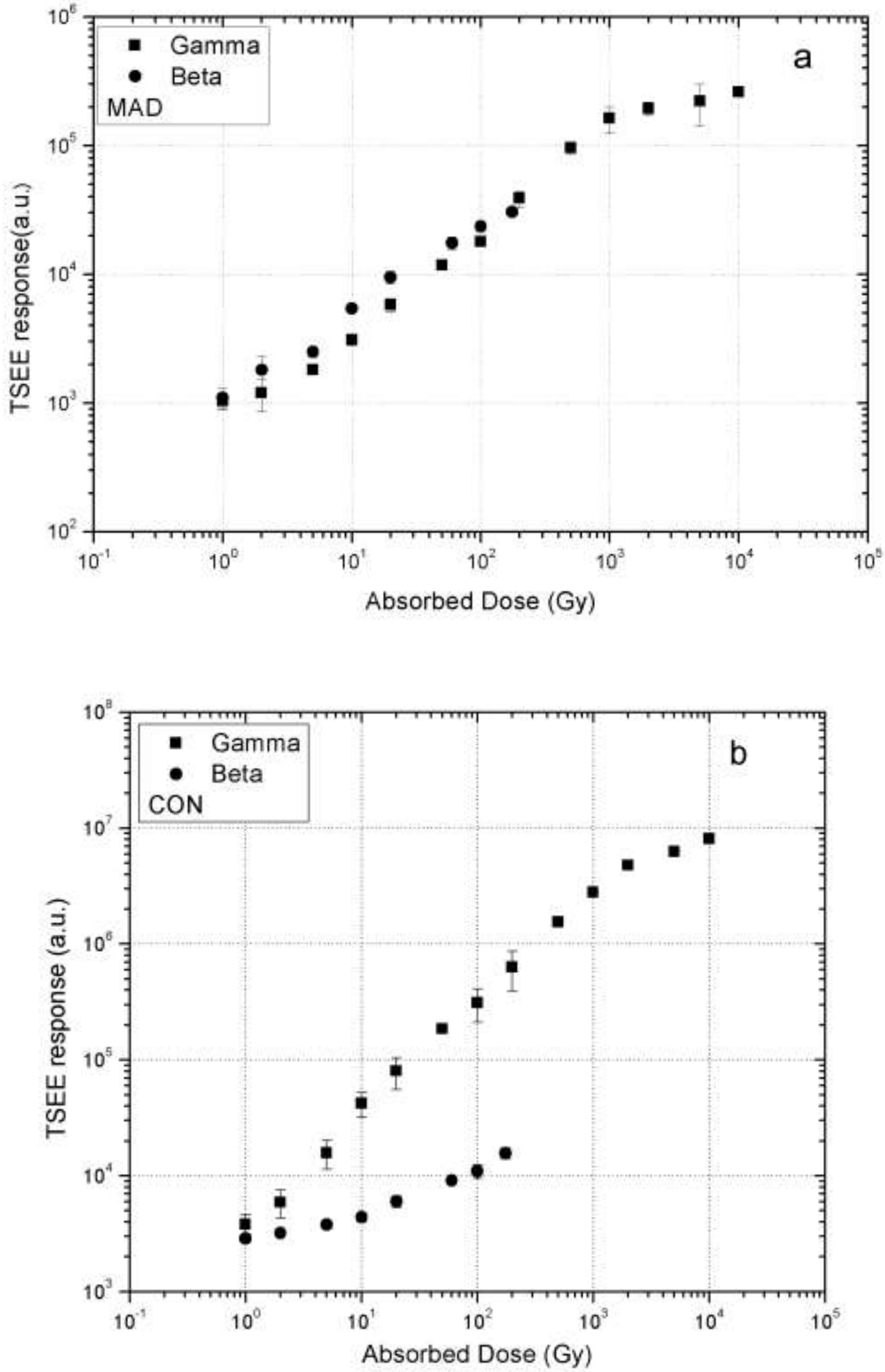

Figure 5.- Dose-response curves for MAD (a) and CON (b) samples exposed to gamma and beta radiations.

4.- DISCUSSION

The study of the TSEE emission curves of the samples showed a superposition of peaks; the kinetic order of the emission may be greater than first order, suggesting that the kinetics of the electrons in the exoemission takes place with the participation of the surface and bulk electrons.

The reproducibility tests, despite presenting values above 3.5 % for all samples, may still be considered satisfactory in the case of high doses, because there are no regulating parameters that may contradict these results.

The residual signal values demonstrated the need of a thermal treatment of 300 °C/1 h for reuse of the samples.

The lower detection doses showed values from 0.8 Gy to 9.8 Gy; they may be considered satisfactory, when the materials are used for high-dose dosimetry.

Although the TSEE response of the biominerals did not show linearity for all studied samples, the dose estimative is still possible with an appropriate mathematical model for each material and each radiation type used in this work.

The fading study of the TSEE response showed that the signal loss can be avoided by protecting the samples from light, heat and moisture.

5.- CONCLUSIONS

The results of the studies with the Brazilian biominerals as oyster shell, mother-of-pearl, coral reef and tiger shell samples show the possibility of their use for high-dose dosimetry using the TSEE technique. Taking into account the range of linearity, the CON samples exposed to gamma radiation and the OST samples exposed to beta radiation are the most suitable for application in high-dose dosimetry.

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REFERENCES

Becker K. (1973). *SOLID STATE DOSIMETRY*. Cleveland, CRC Press.

Caldas LVE. (1980). *Some calibration methods and dosimetry of beta radiation*. PhD Thesis, University of São Paulo. Brazil. (In Portuguese)

Carmichael LA; Sanderson DCW; Ni Riain S (2002). *Thermoluminescence measurements of calcite shells. Radiation Measurements* **23**: 455-463.

Crase KW. (1971). *Parameters affecting the radiation induced thermally stimulated exoelectron emission from ceramic beryllium*. PhD Thesis, University of Tennessee. USA.

Duller G; Penkman K; Wintle A (2009). *Assessing the potential for using biogenic calcites as dosemeters for luminescence dating*. Radiation Measurements **44**: 429-433.

Glaefeke H. (1979). *Exoemission*. In: Topics in Applied Physics. Thermally Stimulated Relaxation in Solids. Edited by Bräunlich, P. Berlin: Springer, **37**: 225-272.

Hassan GM; Sharaf M (2005). *ESR dosimetric properties of some biomineral materials*. Applied Radiation and Isotopes **62**: 375-381.

Herbaut Y; Rodriguez NA; Petel M; Portal G. (1983). *Thermally stimulated exoelectron emission from lithium fluoride for beta and gamma dosimetry*. Radiation Protection Dosimetry **4**: 140 -143.

Köseağlu R; Kösal F; Çiftci E (2004). *EPR study of radicals produced by gamma-irradiation in marine mollusc (Venus sp.) fossils*. Radiation Effects and Defects in Solids **159**: 497-502.

Melo AP; Teixeira MI; Caldas LVE (2008). *TSEE response of silicates of the jade family in gamma radiation beams*. Radiation Measurements, **43**: 397-400.

Pagonis V; Kitis G; Furetta C. (2006). *NUMERICAL AND PRACTICAL EXERCISES IN THERMOLUMINESCENCE*. New York, Springer.

Rocha FDG. (1997). *Development of a system of thermally stimulated emission exoeletrônica for application in dosimetry*. PhD Thesis, Instituto de Pesquisas Energéticas e Nucleares, University of São Paulo. Brazil.

Sharaf MA; Hassan GM (2004). *ESR dosimetric properties of modern coral reef*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **217**: 603-610.

Seletchi ED; Duliu OG (2007). *Comparative study of ESR spectra of carbonates*. Romanian Journal of Physics **52**: 657-666.

Vila GB; Caldas LVE (2011). *Brazilian biominerals for high-dose dosimetry*. Radiation Measurements **46**: 1900-1902.

Zaragoza CE, Marcazzó F, Della Monaca S, Boniglia C, Gargiulo R, Bortolin E (2012). *Thermoluminescence analysis of irradiated oyster shells*. Applied Radiation and Isotopes **71**: 18-22.