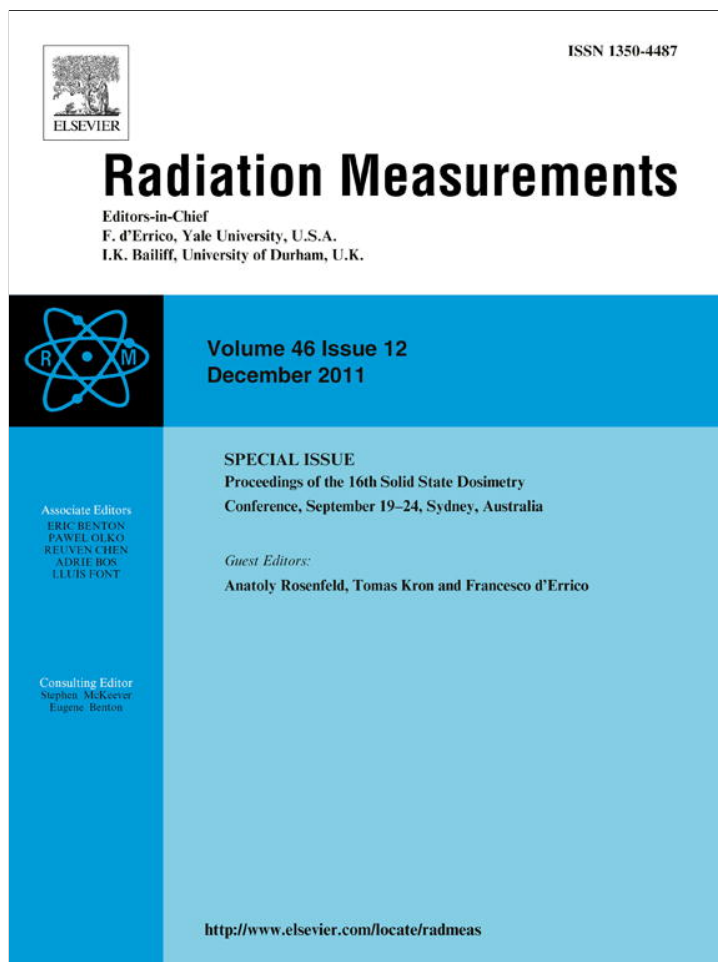


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Brazilian biominerals for high-dose dosimetry

Gustavo B. Vila, Linda V.E. Caldas*

Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, IPEN-CNEN/SP, São Paulo, Brazil

ARTICLE INFO

Article history:

Received 5 November 2010

Received in revised form

11 May 2011

Accepted 20 May 2011

Keywords:

Biominerals

High-dose dosimetry

Thermoluminescence

Optically stimulated

ABSTRACT

The thermoluminescent (TL) signal of biominerals was studied up to 400 °C. The glow curves present TL peaks at ~140 °C and 300 °C in the pellets (with Teflon) of coral reef, oyster shell and mother-of-pearl. The TL response to gamma radiation was found to be linear in the dose range of 10 Gy to 10 kGy, and the optically stimulated luminescence (OSL) response showed an increasing behavior in function of absorbed dose too. The TL lower detection limits of these materials were around 1.2 Gy, and the TL response reproducibility was 4.5%. The materials show a potential use for high dose dosimetry.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The study of the dosimetric properties of materials such as biominerals and coral reef samples has shown that they present good properties as promising materials for ESR dosimetric applications (Hassan and Sharaf, 2005; Sharaf and Hassan, 2004). These materials may be of interest for radiation dosimetry in radioprotection, medical diagnoses and nuclear medicine, and also for geological applications, such as dating. Different silicates have been studied by the Radiation Dosimetry Group of IPEN with results for application for high doses (Melo et al., 2007; Souza et al., 2007; Teixeira et al., 2008a,b).

Mother-of-pearl, oyster shell and coral reef are biominerals synthesized by bacteria in which composition almost 50% is water and organic materials. The thermoluminescent (TL) signal is dominated by isovalent ions e.g. Mn^{2+} (Anderle et al., 1998) and CO_3^{3-} formed by holes trapped at impurities, and the electrons are trapped at dislocations (Ikeya, 1993) and the high temperature peaks are correlated with SO_2^- (Engin et al., 1999).

The main compound of these biominerals is calcium carbonate ($CaCO_3$), which is found in three microcrystalline forms: calcite (rhombohedral), aragonite (orthorhombic), and vaterite (orthorhombic) (Ikeya, 1993; Hossain et al., 2009), although the calcite form is the most stable among the three forms. The TL measurement of aragonite is restricted to temperatures above 300 °C, because it is transformed into calcite between 300 °C and 400 °C

(Balmain et al., 1999). Among the constituents of the biogenic samples, there are traces of Mn^{2+} , Pb^{2+} , Ce^{3+} , $(UO_2)^{2+}$, Dy^{3+} , Sm^{3+} , Tb^{3+} , Nd^{3+} , Eu^{3+} , where Mn^{2+} and Pb^{2+} are responsible for the luminescence of calcite (Marfunin, 1979). Many of TL emissions in calcite are dominated by peaks at approximately 100 °C, 270 °C and 340 °C, and they are thought to be associated with a Mn^{2+} defect (Krbetschek et al., 1997) that acts as a recombination center (Medlin, 1963).

Some biogenic calcites for luminescence dating have been discussed by same researchers. In a recent study, Duller et al. (2009) suggested that biogenic calcites may be utilized as dosimeters for luminescence dating, showing that they present an increasing TL response up to high doses.

In the present work, the dosimetric thermoluminescent properties of gamma induced centers in marine coral reef, oyster shell and mother-of-pearl samples were determined and compared.

2. Materials and methods

The samples of coral reef, oyster shell and mother-of-pearl (or nacre) materials were powdered and sieved, retaining the 177 μm –74 μm size fraction. The powder was mixed with Teflon in a proportion of 2:1, at nitrogen temperature, to ensure the homogeneity in the mixing process. Pellets with 20 mg were sinterized at 300 °C/1 h and 400 °C/1.5 h, and kept in the environment until the TL measurements were performed (Fig. 1). For reutilization, the pellets and the powder samples were thermally treated at 300 °C/1 h. All samples were irradiated at room temperature using a ^{60}Co panoramic source of the Center for Radiation Technology/IPEN. For the TL fading study of all samples, they were previously irradiated

* Corresponding author.

E-mail addresses: gbvila@ipen.br, lcaldas@ipen.br (L.V.E. Caldas).

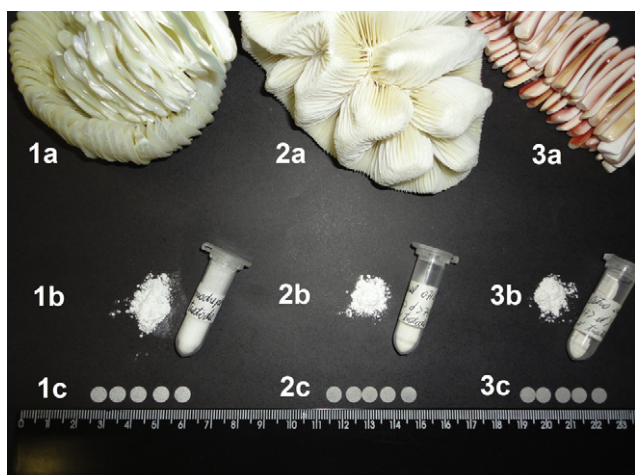


Fig. 1. 1a, 2a, 3a: natural mother-of-pearl (bracelet), coral reef and oyster shell (bracelet); 1b, 2b, 3b: same materials in powder form; 1c, 2c, 3c: same materials in pellets form.

and evaluated in intervals of one day and after a week. The TL measurements were taken using a Harshaw Reader TL, model 3500, in the range from 50° to 400 °C. All TL measurements were obtained with a linear heating rate of 10 °C/and in nitrogen environment.

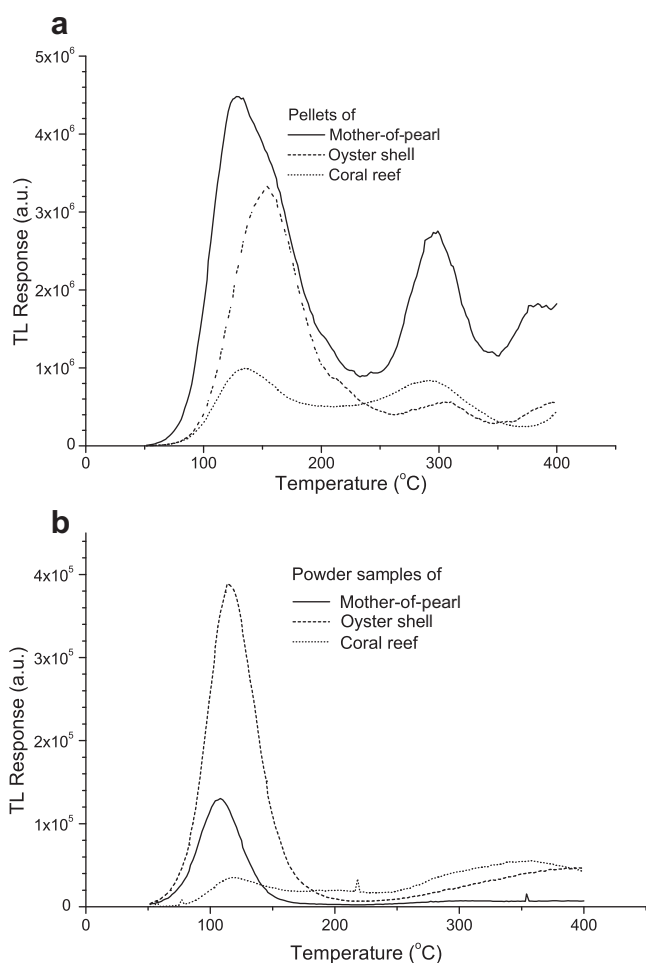


Fig. 2. TL glow curves of the biominerals in form of pellets (a) and powder (b) samples irradiated with ⁶⁰Co (500 Gy).

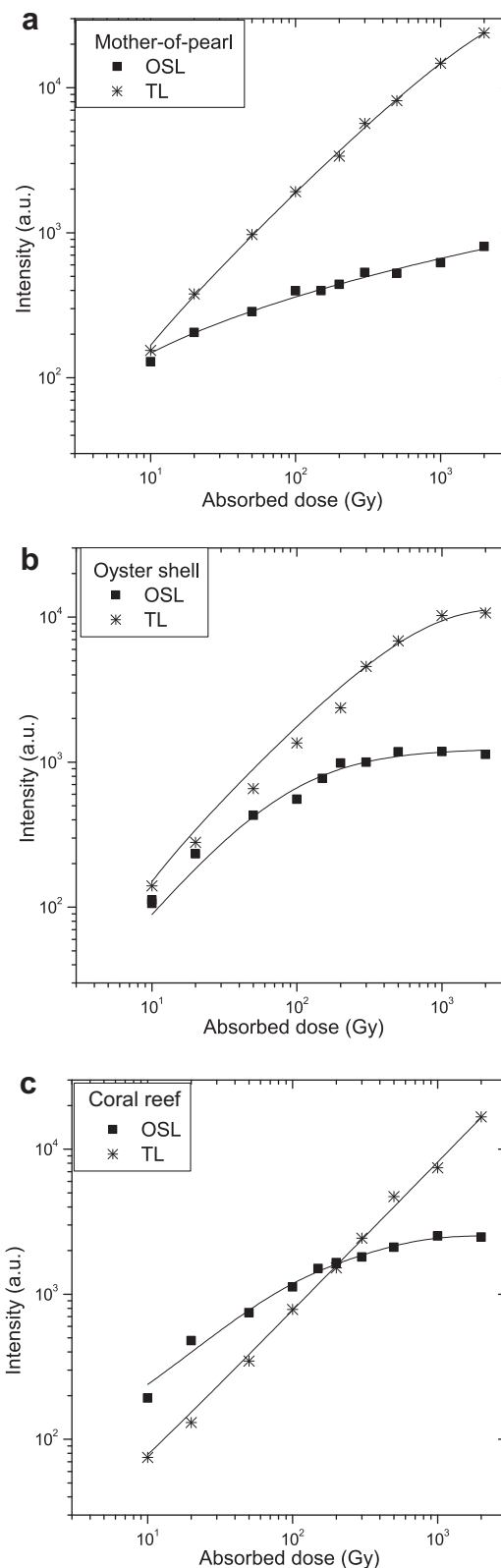


Fig. 3. OSL and TL dose–response curves for mother-of-pearl (a), oyster shell (b) and coral reef (c) in pellet form.

The OSL measurements were taken using a homemade system, with blue and green leds in a continuous mode. The system has a discriminator that allows the adjustment of the gain of the photomultiplier, keeping them for a good signal-noise ratio.

Table 1
TL and OSL characteristics.

	Sample	Mother-of-pearl	Oyster shell	Coral reef
TL	Lower limit detection (m Gy)	400	500	600
	Fading (35days) (%)	55.0	66.6	29.5
	Reproducibility (%)	4.5		
OSL	Lower limit detection (Gy)	1.2	1.0	1.5

Table 2
Neutron activation analysis of the biominerals.

Elements	Mother-of-pearl	Oyster shell	Coral reef
U (mg/kg)	34.2 ± 3.2	33.7 ± 3.2	32.0 ± 3.0
La (mg/kg)	3.08 ± 0.17	0.101 ± 0.003	0.102 ± 0.003
Ce (mg/kg)	0.41 ± 0.02	0.051 ± 0.001	0.0049 ± 0.010
Cr (mg/kg)	1.17 ± 0.02	<0.05	0.223 ± 0.001
Ba (mg/kg)	0.405 ± 0.011	0.247 ± 0.007	0.354 ± 0.010
Fe (mg/kg)	50 ± 1	3.31 ± 0.01	1.67 ± 0.05
Zn (mg/kg)	41.1 ± 0.2	<7	21.6 ± 0.1
	5.6 ± 0.5	5.5 ± 0.4	8.5 ± 1.5

3. Results

The thermoluminescent emission curves of the coral reef, oyster shell and mother-of-pearl pellets and of powder samples are presented in Fig. 2. The TL peak temperatures in the glow curves are around 150 °C and 300 °C for all samples with Teflon. All powered samples showed TL peaks around 140 °C and only the coral reef samples showed a low TL peak at 330 °C. The well defined TL peak of 300 °C of the mother-of-pearl pellets is very probably due to Teflon, which may show TL response for such high doses.

Fig. 3 shows the TL and OSL dose–response curves of the biominerals at room temperature over a range from 10 Gy to 1 kGy. The dose–response curves suggest an initial linear function, with a tendency to supralinearity and saturation. The maximum standard deviation for the dose–response curves was 5.8% for the mother-of-pearl samples.

The Teflon used as binder and the preparation of samples may have caused the dislocation of the TL peak to 200 °C. The TL fading was determined at samples irradiated in the dose of range 200 to 2 kGy; after 35days, a fading of 55.0% was observed for mother-of-pearl samples, 66.6% for oyster shell samples and 29.5% for coral reef samples.

These fading values are certainly due to the low temperature TL peaks. The maximum standard deviation was 4.5% for TL measurements. The OSL measurements show an increasing response in function of dose, although reaching the saturation in doses of 200 Gy for oyster shell sample, and 1 kGy for coral reef and mother-of-pearl samples.

The lower detection limits for the samples using TL and OSL techniques can be seen in Table 1.

A neutron activation analysis of these materials was provided by the Radiochemistry Department of IPEN, and it showed mainly elements of Ca, U, Fe and Zn (Table 2).

4. Conclusions

Although the neutron activation analysis did not detect the presence of Mn²⁺ or Pb²⁺ that are the main activators of the TL signal as suggested by other researchers, activators as Ce and U were found and may be responsible for the thermoluminescent signal in this case.

The preliminary results of the studies with mother-of-pearl, oyster shell and coral reef samples in this work show the possibility of their use for high dose dosimetry using the TL and OSL techniques.

Acknowledgments

The authors thank CNPq, CAPES and FAPESP, Brazil, for partial financial support.

References

- Anderle, H., Steffan, I., Wild, E., Hille, P., Bermanec, V., Sövegjarto, F., 1998. Detection and dosimetry of irradiated biominerals with thermoluminescence, radio-luminescence and electron spin resonance measurements: comparison of methods. *Radiat. Meas.* 29, 531–551.
- Balmain, J., Hannover, B., Lopez, E., 1999. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction analyses of mineral and organic matrix during heating of mother of pearl (nacre) from the shell of the mollusc *Pinctada maxima*. *J. Biomed. Mater. Res.* 48, 749–754.
- Duller, G.A.T., Penkman, K.E.H., Wintle, A.G., 2009. Assessing the potential for using biogenic calcites as dosimeters for luminescence dating. *Radiat. Meas.* 44, 429–433.
- Engin, B., Güvenb, O., Köksal, F., 1999. Thermoluminescence and electron spin resonance properties of some travertines from Turkey. *Appl. Radiat. Isot.* 51, 729–746.
- Hassan, G.M., Sharaf, M., 2005. ESR dosimetric properties of some biomineral materials. *Appl. Radiat. Isot.* 62, 375–381.
- Hossain, F.M., Murch, G.E., Belova, I.V., Turner, B.D., 2009. Electronic, optical and bonding properties of CaCO₃ calcite. *Solid State Commun.* 149, 1201–1203.
- Ikeya, M., 1993. *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*. World Scientific Publishing Company.
- Krbetschek, M.R., Götze, J., Dietrich, A., Trautmann, T., 1997. Spectral information from minerals relevant for luminescence dating. *Radiat. Meas.* 27, 695–748.
- Marfunin, A., 1979. *Spectroscopy: Luminescence and Radiation Centers in Minerals*. Springer, Berlin.
- Medlin, W.L., 1963. Emission centers in thermoluminescent calcite, Dolomite, Magnesite, aragonite, and Anhydrite. *J. Opt. Soc. Am.* 53, 1276–1284.
- Melo, A.P., Valerio, M.E., Caldas, L.V., 2007. Thermoluminescent characteristics of Actinolite-Teflon composites for gamma high-doses. *Phys. Status Solidi. C: Conf. Crit. Rev.* 4, 1052–1055.
- Sharaf, M., Hassan, G.M., 2004. ESR dosimetric properties of modern coral reef. *Nucl. Instrum. Methods Phys. Res. B.* 217, 603–610.
- Souza, D.N., Melo, A.P., Oliveira, M.G., Caldas, L.V., 2007. Dosimetric characterization of Wollastonite-Teflon composites. *Phys. Status Solidi. C: Conf. Crit. Rev.* 4, 1175–1178.
- Teixeira, M.I., Ferraz, G.M., Caldas, L.V., 2008a. Descalvado sand for high-dose dosimetry. *Radiat. Meas.* 43, 1163–1165.
- Teixeira, M.I., Costa, Z.M., Costa, C.R., Pontuschka, W.M., Caldas, L.V., 2008b. Study of the gamma radiation response of watch glasses. *Radiat. Meas.* 43, 480–482.