

## UV-INDUCED THERMOLUMINESCENCE OF NATURAL Ca-RICH CARBONATES

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The 400 nm-thermoluminescence (TL) emission of UV (254.7 nm) irradiated Ca-rich carbonates of inorganic (aragonite) and biogenic (mollusc exoskeleton) origin is here reported. The samples exhibit complex glow curves, but (i) acceptable TL sensitivity when exposed to ultraviolet C (UVC) irradiation and (ii) stability of the UV-induced TL signal with initial rapid decay (ca. 70% for the aragonite and 40% for the biogenic carbonate) while maintaining the stability from 75 and 150 hours onwards. The dose response shows a significant scattered behavior up to 8 hours of UVC exposure, which may be associated with a combination of the phototransfer TL mechanism, the bleaching process, and the partially ionizing effect of the UVC irradiation.

**Keywords:** thermoluminescence, ultraviolet radiation, calcium carbonate, dosimetry.

УФ-ИНДУЦИРОВАННАЯ ТЕРМОЛЮМИНЕСЦЕНЦИЯ  
ПРИРОДНЫХ КАРБОНАТОВ КАЛЬЦИЯV. Correcher<sup>1\*</sup>, C. Boronat<sup>1</sup>, M. D. Virgos<sup>1</sup>, J. Garcia-Guinea<sup>2</sup>

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Исследована термолюминесценция (ТЛ) в области 400 нм облученных УФ излучением (254.7 нм) богатых кальцием карбонатов неорганического (арагонит) и биогенного (экзоскелет моллюска) происхождения. Образцы имеют сложные спектры ТЛ; но показывают приемлемую чувствительность ТЛ к воздействию облучения в коротковолновом УФ С-диапазоне (УФС) и стабильность ТЛ-сигнала, вызванного УФ излучением, с начальным быстрым затуханием (~70% для арагонита и 40% для биогенного карбоната) при сохранении стабильности от 75 до 150 ч. Реакция на дозу демонстрирует значительный разброс до воздействия УФ излучения в течение 8 ч, что может быть связано с сочетанием механизма фотопереноса ТЛ, процесса обесцвечивания и частично ионизирующего эффекта УФС излучения.

**Ключевые слова:** термолюминесценция, ультрафиолетовое излучение, карбонат кальция, дозиметрия.

**Introduction.** Thermoluminescence (TL) properties of ceramic and natural materials including quartz feldspars, carbonates, phosphates, or halides, among others, have been usually employed in the fields of dating [1], detection of irradiated food [2], and personnel [3] or environmental retrospective dosimetry (focused on the assessment of the ionizing radiation) [4, 5] or defects characterization [6, 7]. TL is a process based on the emission of light from a solid dielectric sample (insulator or semiconductor) when heated after being irradiated (natural or artificially) by ionizing radiation (X-,  $\beta$ -, and  $\gamma$ -rays, or beams of electrons). During readout, the TL signal is detected by a photomultiplier tube and recorded as a function of temperature or wavelength. The resulting emission is called a TL glow curve, where both the luminescence intensity and the

shape are functions of the absorbed dose and the heating rate [8]. Such emission is associated with the presence of structural (planar, Frenkel, or Schottky) and point (impurities) defects, depending also on the crystalline phase that can be modified with the pressure and temperature of the formation. Particularly, carbonates exhibit TL emission that is associated with (i) non-bridging oxygen hole center (NBOHC) defects linked to the CO<sub>2</sub> groups, (ii) oxygen vacancies trapping two electrons (F<sup>0</sup> centers), (iii) self-trapped excitons (STE), (iv) presence of chemisorbed ions (H<sup>+</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, [Ca(OH)]<sup>+</sup>, and [Ca(HCO<sub>3</sub>)]<sup>+</sup>, etc.) distributed along the calcium carbonate lattice that are able to induce redox reactions [9], and (v) partial phase transitions of aragonite into calcite that can be produced at 400°C under atmospheric pressure [10].

Additionally to the ionizing radiation, the UV exposure is also able to induce TL emission that can be employed for UV dosimetric purposes, which have been mostly studied on synthetic materials (BeO [11], KCl:Eu<sup>2+</sup> [12], NaCl:Cu<sup>+</sup> [13], ZrO<sub>2</sub> [14], etc.), but scarcely investigated in natural materials where the efforts have been mainly focused on fluorite [15], borate (natural [16] or synthetic [17]), and limestone [18]. The assessment of the natural UV radiation is of great interest, since it can induce not only photochemical reactions or variations in the bacteria and yeast population [19], but can also correlate with global climate change; the increase in UV exposure is linked to the stratospheric ozone depletion and is directly involved in human health, in ocean warming, coral bleaching, etc. [20]. UV radiation (in particular, UVC) can produce a double-stage process that affects the luminescence emission concerning both (i) photo-transfer of charges from deeper to shallower traps upon illumination (photo-transferred TL (PTTL) process) [11] and (ii) partial bleaching of the TL signal [8]. According to [11], PTTL emission displays a glow curve due to UV exposure irradiation in a material that has previously absorbed ionizing radiation. Such ionizing radiation creates free charges that are hosted in the corresponding trapping states, and PTTL is observed when, during subsequent heating, the charge carriers are thermally released from shallower traps and recombine radiatively at luminescence centers. UVC is partially ionizing radiation and, consequently, is of enough energy to induce bond breaking (i.e., photodissociation process) giving rise to TL emission. An electron linked to an atom or molecule absorbing sufficient energy from an UVC source induces the release of the charge that was originally trapped.

To the best of our knowledge, the UV-Induce TL sensitivity of natural Ca-rich carbonates has never been reported before. This paper focuses on the study of the TL response of two Ca-rich carbonate samples (from inorganic (aragonite) and biogenic (mollusc exoskeleton) origin), which have been selected to determine their suitability in the field of UV retrospective dosimetry considering (i) sensitivity to the UVC exposure, (ii) the dose response and (iii) stability of the TL signal with the elapsed time.

**Materials and methods.** Ca-rich carbonates from different origin, (i) inorganic, aragonite from Minglanilla (Cuenca, Spain) and (ii) organic, winkle exoskeleton, from Vigo (Pontevedra, Spain) (five samples each) were here studied. The chemical analysis of the samples was carried out on a microscope ESEM XLS30 of the FEI Company, provided at 27 kV electron beam, using energy dispersive spectroscopy (EDS) where the semi-quantitative elemental-chemical composition is Ca (45.46%), Mg (1.40%), C (9.08%), and O (44.06%). The luminescence emission of the Ca-rich carbonate samples was characterized by means of TL performed using an automated Risø TL reader model TL DA-12 provided with an EMI 9635 QA photomultiplier. The emission was observed through a blue filter (a FIB002 of the Melles-Griot Company), where the wavelength (in nm) is peaked at 320–480 nm; FWHM is 80(16) nm and peak transmittance (minimum) is 60%. The TL reader is also provided with a <sup>90</sup>Sr/<sup>90</sup>Y source with a dose rate of 0.011 Gy/s calibrated against a <sup>137</sup>Cs photon source in a secondary standard laboratory. The sample was carefully powdered with an agate pestle and mortar to avoid triboluminescence. All the TL measurements were obtained using a linear heating rate of 5 °C/s from room temperature (RT) up to 500°C in a N<sub>2</sub> atmosphere. Aliquots of 5.0(1) mg were used for the TL measurements. The UVC radiation exposure on 50 μm powdered aliquots (from 1 to 8 h at RT) was carried out with an automated irradiator developed at CIEMAT that allows UV illumination with a TUV-6W Hg lamp (254.7 nm, UV irradiance value at 10 cm was 0.03 W·m<sup>-2</sup>) and controlled thermal treatments [21].

**Results and discussion.** Figures 1a,b displays two types of Ca-rich carbonates of different origin: organic (Littorina littorea exoskeleton) and inorganic (aragonite). The organic sample is characterized by the presence of structural holes of several sizes as appreciated in the left-hand figure where the mollusc is hosted. It exhibits an ovate, thick, and sharply pointed shape 3 cm in width and 5 cm in height on average with alternate spiral bands of pale and dark grey color. In the right-hand figure is a picture of a brown-reddish aragonite mineral that crystallizes in the orthorhombic system with crystals that are prismatic in habit but have pseudohexagonal twinned intergrowths which are indented angles and sutures along the composition

planes. The general microstructure (at 500  $\mu\text{m}$ ) of the biogenic sample observed under ESEM is characterized by bands containing a successive sequence of holes that is better appreciated in the bottom-left hand inset in Fig. 1c obtained at 40  $\mu\text{m}$ , which can be linked to the presence of layers of conchiolin protein that gives strength and flexibility to the shell. This structure has not been observed on the aragonite surface.

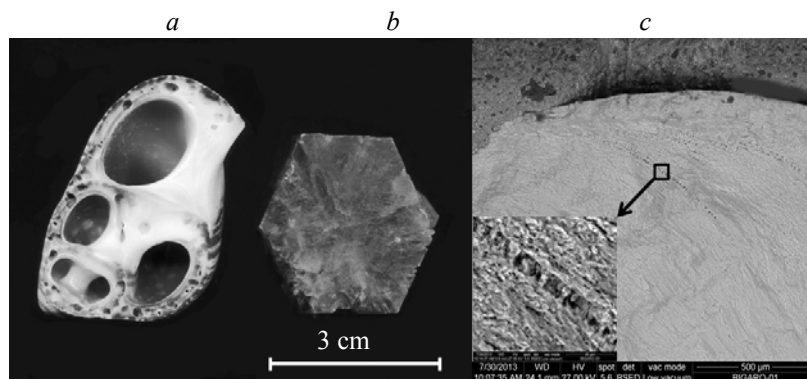


Fig. 1. Ca-rich carbonates of (a) biogenic and (b) inorganic origin and (c) an environmental scanning electron microscope (ESEM) image of the biogenic sample (*Littorina littorea* exoskeleton) observed at 500  $\mu\text{m}$ ; inset shows the ESEM image at 40  $\mu\text{m}$ .

As illustrated in Fig. 2, both natural TL emission (NTL, i.e., emission of the as received samples) displayed by aragonite (Fig. 2a) and biogenic samples (Fig. 2b) consist of complex curves with a broad signal peaked at 280°C with non-well-defined maxima with significant differences in shape and intensity. None of the curves could be successfully analyzed assuming first or second order kinetics since the figure of merit (FOM), which is the measurement of fit of the expression patterns for the clusters produced by the Levenberg–Marquardt algorithm [22], was higher than 2%. The NTL intensity corresponding to the biogenic Ca-rich carbonate is ten times smaller than the mineral sample due to the age of the sample that is of some decades, while the mineral one belongs to the Iberian Keuper geological facies (more than 200 million years ago). These complex UV-blue TL broad emission, in both aragonite and shell appearing at the same temperature, could be a consequence of continuous processes of successive breaking and linking of bonds (C=O, C–O, OH–Ca–OH, C–OH, etc.), as well as redox reactions. We herein show the preliminary studies concerning the TL properties of these UVC irradiated carbonates to determine the suitability of these materials to be potentially used as dosimeters in environments where non-conventional systems are available. In this sense, the samples have been analyzed considering three of the more important features that are required of a dosimeter, namely (i) radiation sensitivity, (ii) dose response, and (iii) fading effect.

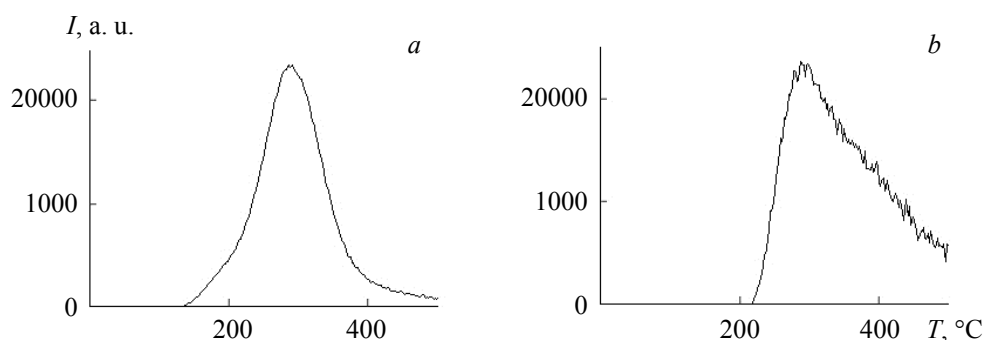


Fig. 2. Natural TL glow curves of (a) aragonite and (b) biogenic samples.

Thus, the dose response of the TL emissions from UV irradiated samples is displayed in Fig. 3. For such purpose, all the aliquots were consecutively (i) preheated up to 500°C (to remove its natural TL) and (ii) exposed to UVC radiation in the range of 10 min to 8 h. As shown in Fig. 3, one can distinguish how both Ca-rich carbonates show TL sensitivity when exposed to UV irradiation from at least 10 min, which means that

TL is a fast, simple, and reliable methodology to discriminate UV irradiated samples (very useful, for instance, in the field of detection of UVC irradiated food). The UV-induced glow emission of aragonite (Fig. 3a) and biogenic samples (Fig. 3b) measured under the same conditions show luminescence emission with a rather complex structure. Both curves consist of two groups of components that do not differ in the shape and intensity at (i) 110°C probably linked to oxygen vacancies in the calcium carbonate lattice [8] and (ii) at higher temperature, a non-well-defined structure peaked at 290°C that could be attributed to consecutive breaking and linking of bonds of Ca–O, C–O, C–OH, and OH–Ca–OH, including redox reactions involving the impurities [8], and also partial conversion of aragonite into calcite that, according to [10], is produced at temperatures higher than 400°C. However, the main difference is in the intensity of both maxima (at 110 and 290°C) where the ratio differs significantly with the time of exposure. Thus, the increase of the UVC illumination induces (i) intensities that are in a proportion of ~1:1 at shorter periods of time (up to 20 min); (ii) the second group of components increases the intensity relative to the first one in the range of 1–2 h; such behavior is meaningful in aragonite in contrast to the biogenic sample; (iii) the intensity of the first maximum predominates over the second one at higher exposures (up to 8 h). Both (i) and (ii) could probably be associated with the ionizing component of the UVC radiation and (iii), where the maximum peaked at 290°C decreases significantly the intensity and would be linked to a bleaching effect. The dose dependence considering the area under the UV induced TL glow curve in the range of 50–450°C is shown in Fig. 3c (for aragonite) and Fig. 3d (for biogenic sample).

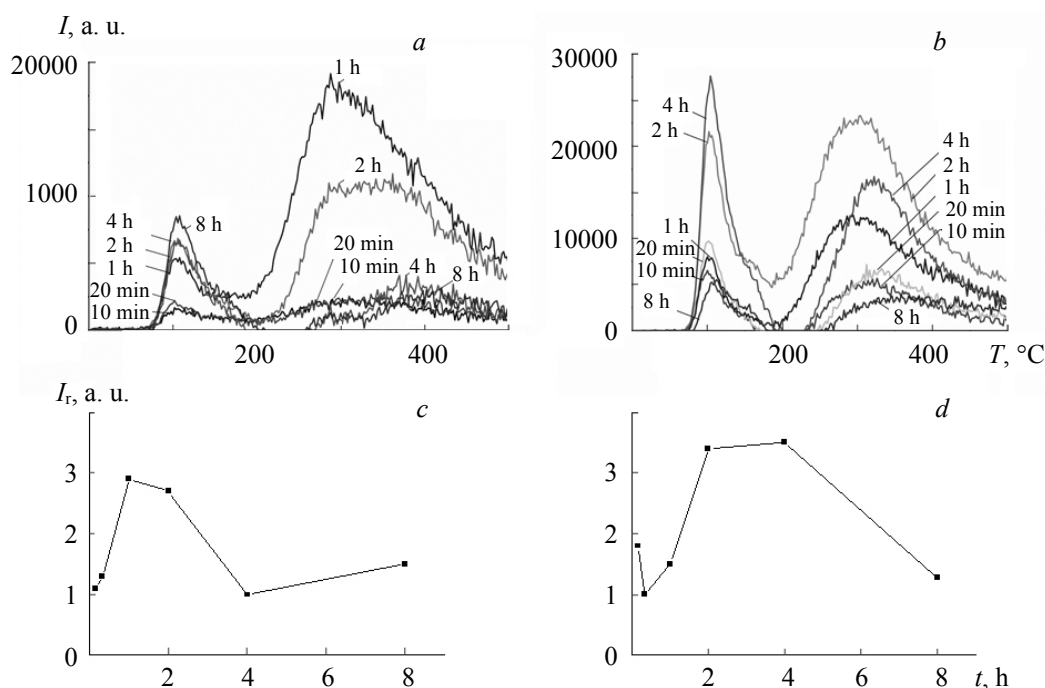


Fig. 3. UV-induced TL emission of (a) aragonite and (b) biogenic samples from 10 min to 8 h at RT; the dose response of the TL emission in the range of 50–450°C for the mineral and biogenic samples (c, d)

The relative intensity for each point was individually estimated referring the UV irradiated TL emission to an ionizing irradiated curve obtained from a calibrated beta source and performed on each aliquot, measured under the same conditions. The use of the ionizing radiation allowed us to determine the calibration factor associated with the radiation sensitivity of the Ca carbonate of each aliquot. As illustrated, both samples exhibit a similar behavior where the evolution of the relative intensity cannot be fitted to a mathematical equation since the obtained values are so scattered probably due to the combination of PTTL processes, bleaching effect, and the partially ionizing characteristic of the UVC irradiation [11].

The stability of the TL signal after increasing the storage of time (up to ~700 h) has been tested under red light at RT to prevent trapped electron releasing from semi-stable sites into the hole centers, including

luminescence centers (Fig. 4). The calculation of each point was calibrated individually for each aliquot (1 h UV-irradiated), referring to the direct delayed measurement (area of the glow curve in a range of 30–500°C) of the blue TL emission of aragonite (Fig. 4a) and the shell sample (Fig. 4b) to the 1 h UV induced prompt TL glow curve, in the same range of storage in darkness, thus avoiding the influence of the weight factor. The uncertainties ( $1\sigma$ ) represent the precision of the mean value of the luminescence response corresponding to the group of five aliquots. As can be seen, the temporal evolution of the TL emission from UVC irradiated aragonite (Fig. 4a) and exoskeleton sample (Fig. 4b) follows a similar behavior that consists of an initial rapid decay (up to 70% for the inorganic sample and 40% for the biogenic Ca-rich carbonate) maintaining the signal stability from ~75 and ~150 h onwards, respectively. Such fading could be linked to the probability of electron release from the shallower traps that occurs very fast at RT. The electron population decreases asymptotically by the  $X$ -axis, and the involved electrons are located in deeper traps; consequently, more energy is needed to leave their positions at RT. The number of trapped electrons depends on the time that the Ca-rich carbonate lattices need to reach stabilization after receiving the double treatment consisting of heating and UVC exposing. As appreciated, the physical process can be fitted to the first-order decay equation of the form  $y = y_0 + A\exp(-x/t)$ , where  $y$  is the relative intensity of the TL signal,  $x$  is the time after irradiation process, and  $y_0$ ,  $A$ , and  $t$  are coefficients of the equation that also have been observed in several polymineral and monophase materials [2, 23].

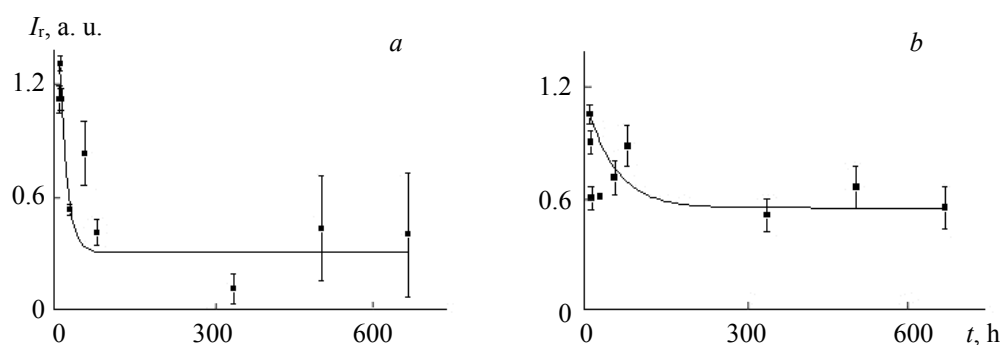


Fig. 4. Stability of the blue TL emission obtained from (a) aragonite and (b) biogenic carbonates, up to 700 h of storage at RT in darkness and fitted to an exponential first order decay equation of the sort  $y = y_0 + A\exp(-x/t)$ .

**Conclusion.** The study performed on the TL emission of Ca-rich carbonates, including aragonite and exoskeleton samples, indicates that both materials could be potentially employed in the field of UV dosimetry. The inorganic and the biogenic samples exhibit: (i) an acceptable radiation TL sensitivity and (ii) a reasonable stability information of the UV-induced TL signal after 700 h of storage, where both samples show an initial rapid decay (ca. 70% for the aragonite and 40% for the biogenic carbonate) maintaining the stability from 75 and 150 h onwards, respectively. However, both samples show a scattering behavior in the dose response (up to 8 h of UV exposure), although the irradiated and non-irradiated samples can be easily distinguished from a qualitative viewpoint. Nevertheless, further work is necessary to determine the influence of the combination of PTTL processes, bleaching effect, and the partially ionizing characteristic of the UVC irradiation.

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