ELECTRON SPIN RESONANCE AND THERMOLUMINESCENCE FOR ASSESSMENT OF COLOR CHANGES IN IRRADIATED NACRES

Irina Pucić, Katarina Marušić, Željka Knežević, Nadica Maltar-Strmečki

Ruđer Bošković Institute, Zagreb, Croatia

INTRODUCTION

Radiation treatment is an advantageous method of biodecontamination of cultural heritage (CH) objects [1]. Its possible side effects need to be assessed for any material that may be included. Nacre or mother-of-pearl is a common ornament material in CH objects and it often cannot be removed prior to radiation treatment. Nacre is a natural biocomposite composed of calcium carbonate in crystalline form of aragonite embedded in a protein matrix. Proton induced X-ray emission (PIXE) was used to determine composition and concentration of trace elements present in nacre. Some radiation induced color changes of selected irradiated nacre samples were detected by color assessment in CIELAB space and by UV-VIS reflectance. **The goal of this research was to identify the nature of color centers formed upon irradiation of nacres and to determine the cause of difference in changes between the nacres.** The color centers formed are assumed to arise of electronic excited states, various species containing unpaired electrons and free radicals so the electron spin resonance (ESR) and the thermoluminscence (TL) methods were used.

EXPERIMENTAL

Two different types of nacre, one white and the other yellow, intended for restoration purposes were obtained from Museum of Arts and Crafts in Zagreb. Separate sample of each nacre was prepared for a particular dose (0, 1, 2, 6, 10 kGy and 54 kGy). The samples were irradiated at ^{60}Co irradiation facility of Radiation Chemistry and Dosimetry Laboratory of RBI at a dose rate 0.32 kGy/h, at room temperature, in air. The samples for all measurements were irradiated simultaneously.

For ESR measurements the nacres were cut into 20 mm x 2mm x 2mm rods and ESR spectra taken prior to and a day after the irradiation. Some selected samples were additionally irradiated. Continuous wave (CW) ESR spectra were recorded on Varian E-109 X-band (9.5 GHz) spectrometer equipped with Bruker ER 4111 VT variable-temperature unit with a flow of N_2 gas. A Bruker standard reference, "strong pitch" (g=2.0028) was used to calibrate the absolute values of the integrated intensity, EPR and to obtain accurate g-values of the samples.

For TL measurements nacre samples were cut into 5mm x 5 mm x 0.5 mm platelets. The readout of samples was carried out using a modified manual TOLEDO 654 (Vinten) reader. The glow curves were measured using linear ramp rate of 10°C/s to a maximum temperature of 300°C.

UV-VIS spectra were recorded using Ocean Optics USB4000 spectrometer with a HL-2000 halogen source and test probe connected via fiber optics.

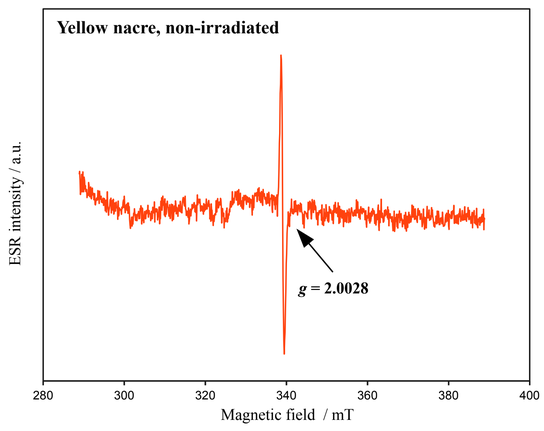
RESULTS

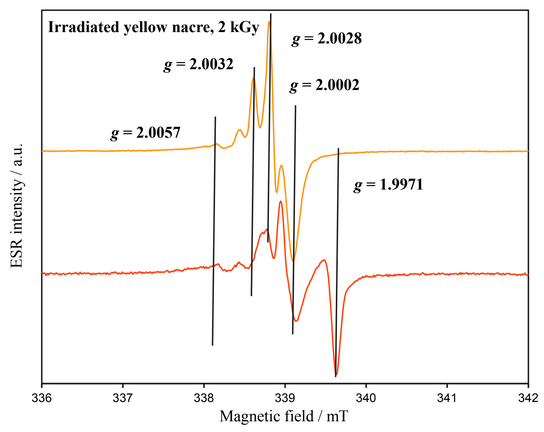
PIXE analysis

Element Z	Sym	White nacre Conc. ppm	White nacre LOD ppm	Yellow nacre Conc. ppm	Yellow nacre LOD ppm
11	Na	4789.6	498.2	1667.6	463.9
12	Mg	257.5	247.2	205.6	227.3
13	Al	1254.4	168.9	400.6	169.2
14	Si	2695.3	175.4	0	226.3
16	S	664.7	137.0	0	202.5
17	Cl	410.8	75.5	29.9	77.8
20	Ca	364197.0	240.1	354910.5	230.2
25	Mn	14.6	24.6	521.6	25.1
26	Fe	17.5	25.1	0	48.2
29	Cu	0	24.7	7.6	21.9
30	Zn	14.3	9.3	3.9	16.6
32	Ge	13.4	10.7	0	35.2
38	Sr	858.4	262	113.7	36.7

Of all the numerous trace elements that were detected in nacre samples by PIXE, manganese atoms play an important role in formation of color centers.

ESR analysis





NON-IRRADIATED NACRES

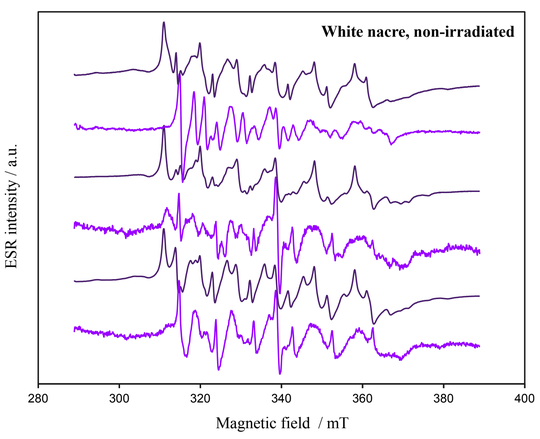
A single peak at g=2.004, line width 0.8 mT, in the ESR spectrum of non-irradiated yellow nacre (left) can be attributed to carbonate free radicals [2], that often exist in natural carbonates especially of marine origin. There is no evidence of Mn^{2+} paramagnetic ions. Manganese in yellow nacre is most likely in Mn^{3+} (S= 0), state that is EPR inactive, therefore yield no EPR signals.

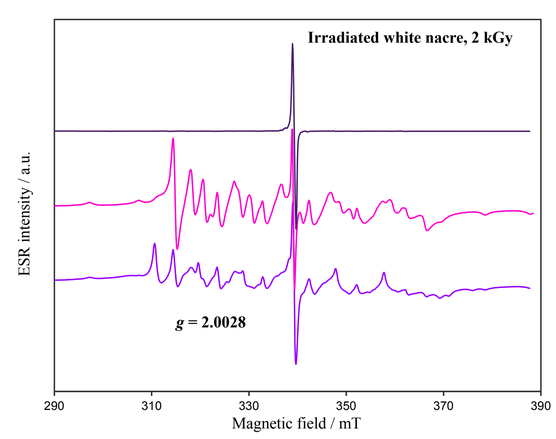
Every ESR spectra of non-irradiated white nacre (right) corresponds to a different location (sample) on the same nacre. In a naturally very non-homogeneous structure of nacre, ESR spectra of each Mn^{2+} paramagnetic ion show different spectral features depending on variations in their distribution across the sample and of the $CaCO_3$ structural forms.

IRRADIATED NACRES

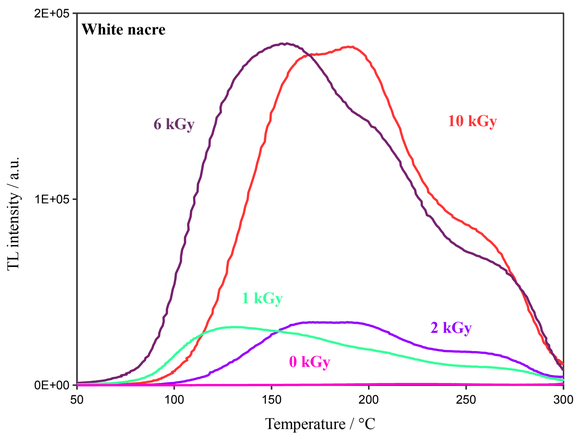
In irradiated yellow nacre (left) a complex ESR spectra appeared and their shapes depend on the location in the sample. The signals arise of free rotating CO_2^- (g=2.0002), orthorombic CO_2^- (g_{min}=1.9971), free rotating SO_2^- (g=2.0057) and isotropic SO_3^- (g=2.0032) radicals [3,4].

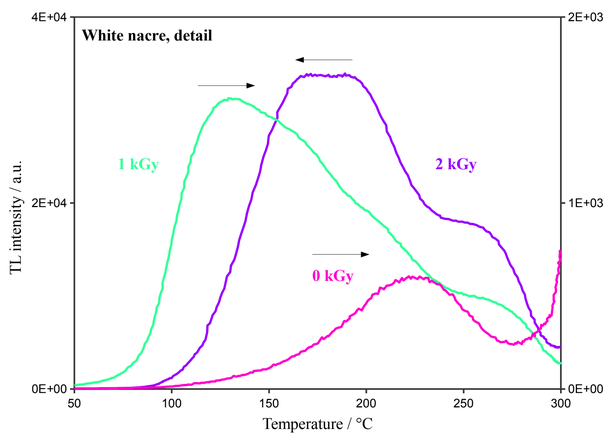
Upon irradiation in all ESR spectra of white nacre (right) additional line at g=2.0028 appeared. The lines coming from Mn^{2+} in different local environments remained, but Mn^{2+} concentration decreased in comparison to the same positions in the non-irradiated samples. In some cases oxidation state of all manganese changed to ESR inactive Mn^{3+} resulting in a complete loss of Mn^{2+} ESR signal (upper spectrum). These parts of the nacre did not change the color after irradiation, indicating that oxidation of manganese under gamma-irradiation may control the sample coloration. This is in agreement with results reported in [4] where color change was in a part associated with increase of radicals with irradiation dose. That was confirmed by an increase of CO_2^- line that can be attributed to carbonate-derived radical on additional irradiation of selected previously irradiated samples.





TL analysis





Both non-irradiated nacres sample emitted weak TL signals.

WHITE NACRE

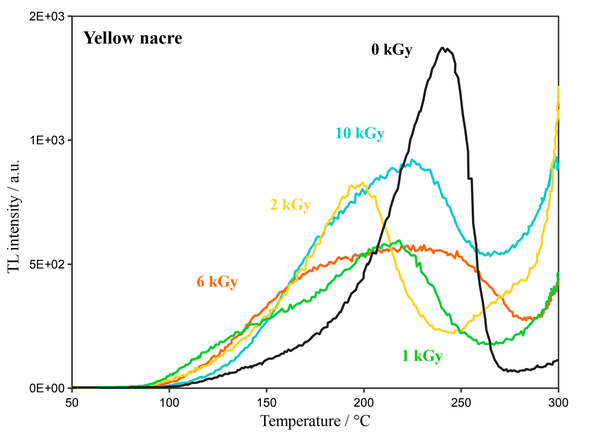
In non-irradiated white nacre peak temperature was around 225°C. Upon irradiation (left figures) TL signals significantly increased and 225°C peak obviously merged with radiation induced low and high temperature emissions. At the highest dose the peak at 220°C becomes the strongest emission again. The two radiation induced peaks, at about 150 °C and at about 250°C are characteristic of mollusc aragonite that contains traces of Mn^{+2} [5]. The low temperature peak is particularly strong and shifts to higher temperatures at higher doses. The higher temperature peak appeared at a constant temperature and its intensity increased with dose differently from that of the lower temperature peak. At the highest dose the peak TL intensity was almost 500x greater than in non-irradiated nacre.

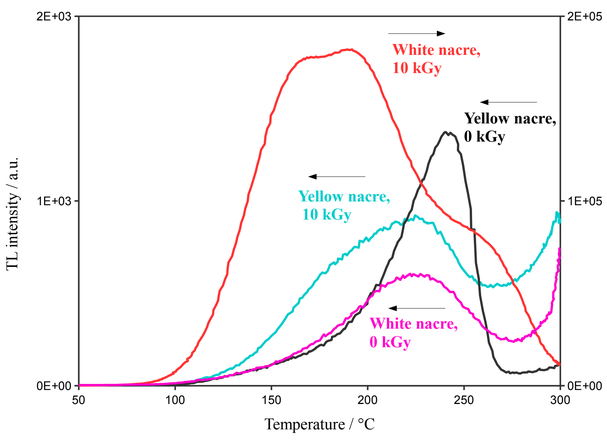
The glow curve of the white nacre irradiated to 10 kGy is of completely different shape and the TL intensity is 2 orders of magnitude higher than in the non-irradiated white nacre (right lower figure).

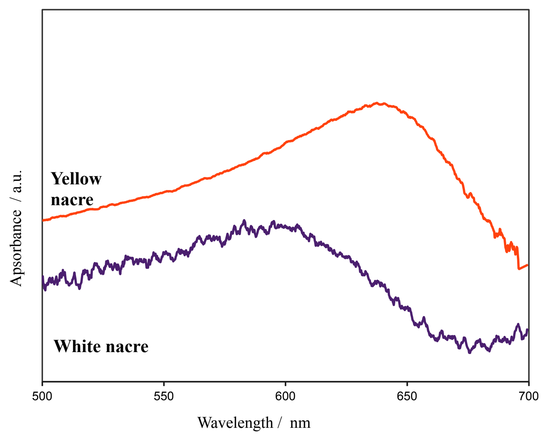
YELLOW NACRE

The TL signal of non-irradiated yellow nacre (right upper figure) is almost three times higher than that of non-irradiated white nacre. Upon irradiation TL intensity does not increase and the differences in the glow curves are a result of non-homogeneity of natural nacre. The dose of 10 kGy in yellow nacre caused an apparent decrease of TL intensity (right lower figure) suggesting that the pre-irradiation treatment affected electronic states responsible for TL.

UV-VIS







In order to discern radiation induced changes a sample of each nacre was irradiated to a high dose of 54 kGy. In difference UV-VIS spectra increased absorption is observed in vicinity of 600 nm that is characteristic absorption of carbonate radical anion.

CONCLUSIONS

- **Due to highly non-homogeneous composition of nacre it is very difficult to determine the nature of all color centers formed upon irradiation.**
- **According to ESR and UV-VIS results main color centers in nacre arise of anion radicals, predominately carbonate anion radical.**
- **In white nacre oxidation of Mn^{+2} to Mn^{+3} involves reactions with radical anions and thereby increases color stability of that nacre.**
- **Despite much higher concentration of manganese, color centers in irradiated yellow nacre due to carbonate radical anions predominate. Due to a proposed previous heat treatment to enhance the color and gloss the manganese was oxidated and so it could not reduce formation of color centers. The structural effect of the heat treatment resulted also in loss of the TL response to irradiation while the intensity of TL glow curves in irradiated white nacre increased with dose.**

REFERENCES

[1] B. Katušin-Ražem, D. Ražem, M. Braun, Radiat. Phys. Chem. 78, (2009), 729-731.
[2] V. Vongsavat, P. Winotai, S. Meejoo, Nucl. Instrum. Meth. 243, (2006), 167-173.
[3] P. Fattibene, F. Callens, Appl. Radiat. Isotopes, 68, (2010), 2033-2116.
[4] H.-Y. Kim , Y. Hanifehpour , A. N. Banerjee , B.-K. Min , S. W. Joo , W.-G. Jung, Radiat. Eff. Defect S. 168, (2013), 696-704.
[5] I. A. Bhatti, J. Lee, Y.D. Jang, K.S. Kim, J.H. Kwon, Radiat. Phys. Chem. 77, (2008), 663-668.