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# Ornaments in radiation treatment of cultural heritage: Color and UV–vis spectral changes in irradiated nacres

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## HIGHLIGHTS

- Radiation induced changes of nacres color were investigated with FORS.
- Nacres darken at high doses while the color component depends on the nacre type.
- Observable changes occurred at larger doses than needed for cultural heritage.
- For samples irradiated to high doses carbonate radical anion absorption appeared.

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## ABSTRACT

Cultural heritage objects that are radiation treated in order to stop their biodegradation often contain ornamenting materials that cannot be removed. Radiation may produce unwanted changes to such materials. Nacre is a common ornamenting material so this is an attempt to assess the impact of gamma-radiation on its optical properties. Two types of nacre (yellow and white) were obtained from a museum and subjected to different absorbed doses of Co-60 gamma irradiation under the same conditions. The radiation induced changes of nacres color were investigated with fiber optic reflectance spectroscopy (FORS). Colorimetry in CIE Lab space revealed that in both nacres the lightness shifted to darker grey hues at high doses while the color component's (red, green, yellow and blue) behavior depended on the nacre type. Observable changes occurred at doses much above the dose range needed for radiation treatment of cultural heritage objects that are often ornamented with nacre.

In UV–vis reflectance spectra of samples irradiated to high doses carbonate radical anion absorption appeared.



## 1. Introduction

Cultural heritage (CH) objects of organic origin such as wood, leather, paper and textiles, are subject to biological attack and subsequent degradation. Radiation methods have been proven to be very effective in saving CH objects (Katušin-Ražem et al., 2009). The dose ranges for treatment are based on experience in radiation treatment of food, pharmaceutics and medical devices and they are selected according to the biodegradant type. This is the reason why most of the published research on the subject of CH treatment using gamma irradiation has also been done from the microbiological point of view (Bletchly and Fisher, 1957, Briški et al., 2001, Petushkova et al., 1988). To comply with restores criteria it is necessary to confirm no irreversible change occurred in the treated object. Considering the constituent materials radiation effect on wood (Despot et al., 2012, Divos and Bejo, 2006, Pointing et al., 1998) and wood consolidation are mainly studied. Recently an increased number of publications appeared on the research on the influence of irradiation on pigments (Manea et al., 2012, Negut et al., 2012, Rizzo et al., 2002). To our best knowledge no research has been published on the influence of gamma irradiation on various properties of materials that by themselves need not be irradiated but are decorating CH objects and cannot be removed. In that case the personnel of the radiation facilities are compelled to work according to their own judgment and expertize if they have one. The experience gathered on radiation treatment of various CH objects that is performed at the Radiation Chemistry and Dosimetry Laboratory, Ruđer Bošković Institute for over 30 years (Katušin-Ražem et al., 2009) prompted us to investigate some of the materials that may be found on CH objects.

Nacre or mother-of-pearl is a tough biomineral produced by numerous kinds of mollusks. Like pearls it consists of about 95% of

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highly oriented aragonite crystals embedded in an organic matrix composed of proteins and chitin that forms a lamellar structure (Xie et al., 2011) giving it its special optical properties. The colors of nacre vary naturally and may be enhanced by one of the common treatments like bleaching and heating (Elen, 2001). It can be found in a variety of colors and practically no two samples of nacre look the same. It is commonly used for decoration of various CH objects, particularly those made of wood that are often radiation treated. Removing the ornaments is rarely feasible so the question arises whether it is acceptable to irradiate nacre-containing CH objects at all and if yes up to which doses. Because of that this study focuses on how nacre's color is affected by irradiation. There is a study on changes in pearls irradiated to modify their color (Kim et al., 2012) but without colorimetric and/or spectroscopic analysis but no research on irradiation effects on nacre color was published. Because of that this study focuses on how nacre's color is affected by irradiation.

## 2. Experimental

### 2.1. Test material and samples

The nacre samples have been obtained from the conservation stock of Museum of Arts and Crafts in Zagreb since such are likely to occur on CH objects. The origin of nacres is unknown as well whether they were treated in any way. In Fig. 1 two types of nacre that were studied are shown, a white one (in text referred as “white nacre”) and the other with a yellowish tone (referred as “yellow nacre”). Relatively large pieces were cut to appropriate dimensions for FORS measurements, i.e. roughly $1 \times 1\ \mathrm{cm}^2$ (thickness 2–3 mm).

### 2.2. Gamma irradiation

Irradiation was performed at a Co-60 γ-source of Radiation Chemistry and Dosimetry Laboratory, Division of Materials Chemistry, Ruđer Bošković Institute at room temperature, in contact with air, the dose rate was 0.32 kGy/h.

A separate sample of each nacre and an ECB-system dosimeter (to confirm the dose) were irradiated to a selected absorbed dose. The dose range included doses common in CH treatment: 0.5, 1, 2, 6, 10 kGy; and much higher doses: 22 and 54 kGy to ensure development of radiation induced effects (all doses are expressed as absorbed dose in water). During the post-irradiation period the samples were kept in the dark at room temperature. A reference sample of each type of nacre was left unirradiated.

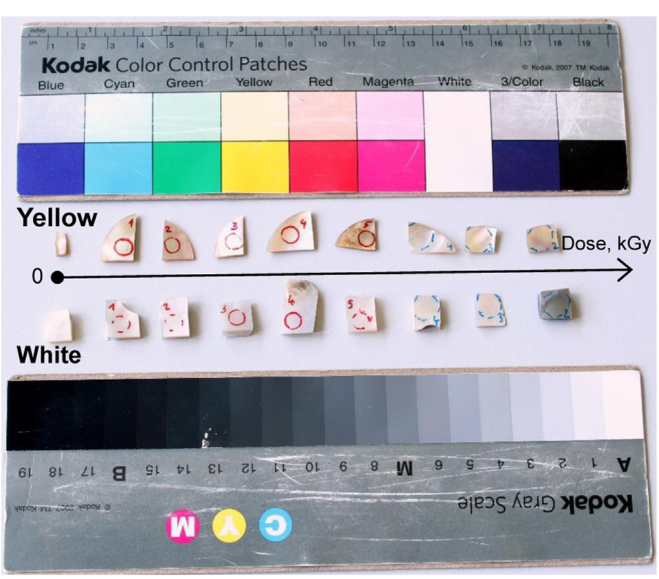


**Fig. 1.** Unirradiated and irradiated samples of nacre arranged according to the increasing absorbed dose: 0, 0.5, 1, 2, 6, 10, 22 and 54 kGy in comparison with color and gray scales. The marks on samples indicate positions for FORS measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 2.3. Methods and analysis

Fiber optic reflectance spectroscopy (FORS) measurements were done under a 45°/45° geometry using Ocean Optics USB4000 spectrometer with a HL-2000 halogen source connected via fiber optics. Before each set of measurements calibration of the spectrometer was performed using a PTFE optical diffuse reflectance standard. The exact position and orientation were marked on each sample (Fig. 1) and the measurements were performed the same way each time. The colorimetric properties and reflectance spectra of each sample were taken prior to irradiation (referred as “unirradiated”), the day after irradiation (“immediately”), 30 days after irradiation (“one month”) and 60 days after irradiation (“two months”). To ensure reproducibility the spectra of unirradiated reference samples of each nacre were taken each time the radiation effects were monitored.

The radiation induced color change in studied nacres was monitored using CIE colorimetry, in the CIE 1976 Lab $L^*a^*b^*$ (CIE, 1978) system. CIE Lab is a color specification system for quantitative interpretation of the color developed by the Commission Internationale de l’Eclairage (CIE). It provides a standard method for describing the stimulus of a color, under controlled light and viewing conditions, based on the average known response of the human visual system (Schanda, 2007). Parameter $L^*$ represents the lightness of a color, known as the CIE 1976 psychometric lightness. The scale of $L^*$ is from 0 (black) to 100 (white). The chromaticity of a color is represented in a two-dimensional diagram where axis $a^*$ determines the ratio of green (negative) to red (positive), and axis $b^*$ specifies the ratio of blue (negative) to yellow (positive).

Widely used measure for overall color change is the CIE 1976 $L^*a^*b^*$ color difference, that is simply calculated as the Euclidean distance in CIELAB space. For colors specified by [$L_1^*$, $a_1^*$, $b_1^*$] and [$L_2^*$, $a_2^*$, $b_2^*$] parameters the difference, $\Delta E^*$, is calculated as follows:

$$\Delta E^*_{a,b} = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \tag{1}$$

The interpretation of color differences is not straightforward. The observer will perceive a difference in color only after a certain amount, equal to the Just Noticeable Difference (JND). The JND value varies for different materials that are observed and thus different values are found in literature (Hardeberg, 2001). The value of JND $\Delta E^*_{a,b}=1$ is often mentioned in literature (Kang, 1997), but Mahny et al. introduced the value $\Delta E^*_{a,b}=2.3$ (Mahy et al., 1994) since this is the value below which not even a trained observer's eye can notice the difference.

When two colors are shown side by side $\Delta E^*_{a,b}$ is according to Hardeberg (Hardeberg, 2001) interpreted as: $\Delta E^*_{a,b}<3$ the effect is *hardly perceptible*, $3<\Delta E^*_{a,b}<6$ *perceptible, but acceptable* and $6<\Delta E^*_{a,b}$ *not acceptable*.

## 3. Results and discussion

Several factors contribute to nacre color appearance. Diffraction of the light on its lamellar structure (Liu et al., 1999) and iridescence (Snow et al., 2004) give it its structural colors. Depending on the mollusk type and origin, pigments like carotenoids and