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# Effects of γ-Ray Irradiation on Colour and Fluorescence of Pearls

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The colour of cultured pearls of *P. fucata* can be changed by γ-ray irradiation, which has been applied to pearl processing. The effect of γ-ray irradiation on the colour and fluorescence of pearls was investigated experimentally. The experimental results show that a colour change of pearls to bluish-grey is mainly responsible for a decrease in the reflection factor of the nuclei. Furthermore, a significant change in the fluorescence spectra has been observed for pearls and nuclei. These changes are considered to be caused by the degradation of conchiolin contained in the nacre. Fluorescence from pearls is not affected by the nuclei, but the colour of pearls is affected. Thus, the fluorescence method is suitable for investigating the effect of γ-ray irradiation on the nacre.

**KEYWORDS: pearl, γ-ray irradiation, laser-induced fluorescence, colour change, optical reflectance**

## §1. Introduction

Pearls cultured by *Pinctada fucata* (Japan's Akoya Oyster), the most famous and important shellfish, have several different colours: pink, green, cream, white, gold, blue and so forth. In contrast to these natural colours, artificial colouring techniques have been introduced in order to increase the commercial value of cultured pearls. The γ-ray irradiation of low-grade pearls is one method for changing the colour to bluish-grey.

Studies on the γ-ray irradiation of pearls started in the 1950s in accordance with the "Atom-for-Peace-Program".[1)] In the 1960s irradiated pearls appeared in the pearl market. The mechanism of the pearl colour change caused by exposure to γ-rays is considered to be due to a colouring of nuclei resulting from oxidation of $MnCO_3$ which is contained in the nuclei as a minor component.[2)]

It has been shown that the spectral reflectance of pearls from *P. fucata* remarkably decrease over the visible region after exposure to γ-rays. This phenomenon depends not on the irradiation rate of γ-rays,[3)] but on the total irradiation dose.[4)] Spectral reflectances of the nacre of *P. fucata* hardly change upon γ-ray irradiation, while those of the nucleus considerably decrease with increasing irradiation dose.[3,5)]

Although the effect of γ-ray irradiation on the reflectance of pearls has already been studied (as described above), that for fluorescence has not yet been reported. In previous papers,[6-8)] we have reported that fluorescence from cultured pearls can be characterized by various organic components contained in the nacre, and have briefly mentioned that γ-rays affect the fluorescence from pearls; such spectral characteristics partly disappear upon irradiation.[6)] In this paper, we discuss the effect of γ-ray irradiation on the fluorescence of pearls of *P. fucata*. CIE tristimulus values and spectral reflectance curves were measured for pearls and nuclei as a means of assessing the colour change of these materials affected by γ-rays.

## §2. Experimental Procedure

Since a cultured pearl consists mainly of a spherical nucleus as a core, and nacre, the outer layer around the core, both were the object of our investigation. The pearls used in this study were from *P. fucata* without any preliminary chemical and/or physical treatment. These pearls had a spherical shape with a diameter of 6.7 to 7.0 mm. The

nuclei were made from the nacre of shells of freshwater bivalves, such as *Quadrule* species. The sizes of these nuclei, showing an absolute sphere, were about 6.5 mm in diameter. Pearls and nuclei were irradiated in air with γ-rays from $^{60}Co$ at room temperature using the irradiation apparatus of the Tokyo University of Fisheries in November, 1986. The dose rate of the γ-ray source was 3.0 x $10^4$ R/h. The total irradiation doses were 1.0 x $10^3$ R, 1.0 x $10^4$ R, 1.0 x $10^5$ R 1.0 x $10^6$ R and 1.0 x $l0^7$ R. Five pearls and two nuclei were examined for respective irradiation doses.

CIE tristimulus values of pearls and nuclei were measured with a colour and colour-difference meter (Nippon Denshoku Kogyo ND-1001DP). Spectral reflectance curves were measured with a double-beam spectrophotometer equipped with an integrating sphere (Japan Spectroscopic UVIDEC-610C); the reference was a small plate made of $Al_2O_3$. Laser-induced fluorescence spectra of pearls and nuclei were measured before and after irradiation with the following apparatus at 300 K (similar to those described in ref. 7). The excitation source was a pulsed $N_2$ laser (NDC JS-100L; $\lambda$ = 337.1 nm, pulse duration = 5 ns, repetition rate = 4 Hz). The laser beam was set at an angle of about $50^o$ off the normal incidence to the plane of a sample and was focused on a spot about 1 $mm^2$ in area by a quartz lens. The peak intensity of the laser light on the sample was about 50 $kW/cm^2$. Fluorescence was observed at $90^o$ to the laser beam and was focused on the entrance slit of a 50-cm monochromator (Oyo Bunko ASI-50S) by a glass lens. Time-integrated and time-resolved fluorescence spectra were measured with a monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator (NF Circuit Design Block BX-531) and a recorder.

## §3. Results and Discussion

It is commonly known that cultured pearls from *P. fucata* turn bluish-grey as a result of exposure to high-energy radiation, such as γ-rays, X-ray and neutrons.[1)] This phenomenon is caused mainly by a colour change of the nuclei. Nuclei, almost colourless before irradiation, turn grey or black according to the exposure to γ-rays. Since the manganese content is rich in the nucleus, the production of manganese oxidants, such as $Mn_2O_3$ or $MnO_2$, has accounted for the mechanism of colouring of the nuclei under γ-ray irradiation.[2)] Thus, colouring of the nuclei affects the colour of pearls,

since the nacre is translucent and a great part of the incident light is absorbed by the nuclei.

3.1 CIE tristimulus values and reflectance

In order to assess a quantitative change in colour, the CIE tristimulus values of pearls were measured with a colour and colour-difference meter. As shown in Fig. 1, the reflection factor for the nuclei ($Y_n$) are higher than those for the pearls ($Y_p$) before irradiation. The values of $Y_n$ significantly decrease after irradiation. On the contrary, only a feeble change occurs on $Y_p$ even when the decrease in $Y_n$ proceeds to about 50. Figure 2 shows spectral reflectance curves of pearls and nuclei before (solid curves) and after (dashed curves) exposure to γ-ray radiation. Before irradiation, the nuclei show a higher reflectance in the violet region than in the longer wavelengths, and a peculiar absorption resulting from protein is observed at 280 nm. The reflectance in the shorter-wavelength region decreases with an increasing irradiation dose; the 280 nm absorption disappears after irradiation of $1.0 \times 10^7$ R. On the contrary, a slight change is observed in the reflectance curves of the pearls after exposure, compared with those of the nuclei. However, the following noteworthy behaviours under γ-ray irradiation occurred for the pearls. Reflectance in the visible region decreases with γ-ray irradiation, especially at wavelengths longer than 500 nm. This indicates that these irradiated pearls show a bluish-grey colour. Furthermore, the dips at about 408, 436 and 460 nm, which characterize pearls from *P. fucata*. gradually disappear according to the exposure.[9] Figure 3 shows the changes in the CIE chromaticity of the pearls upon irradiation. A colour change cannot be detected until $10^4$ R of irradiation dose; at $10^5$ R that is observed. Moreover, the position on the chromaticity of the pearls tends to move from pale green (0~$10^4$ R) to pale bluish-purple ($10^7$ R). Thus, a significant change in $Y_p$ or the position on the chromaticity is observed for irradiated pearls.

The present experimental results are in agreement with those reported by Okamoto.[3] The results suggest that this phenomenon is mainly due to a considerable decrease in $Y_n$ caused by exposure to γ-rays. In Fig. 1, $Y_n$ decreases at $10^4$ R of the irradiation dose, while $Y_p$ decreases at $10^6$ R. Since a part of the light reflected from the nuclei is absorbed by the nacre, which is 0.2~0.3 mm in thickness, a faint colour change of the

nuclei hardly affects the colour of the pearls. The optical absorption by the nacre was estimated using the following procedure. The incident light was reflected and scattered at the nacre as shown in Fig. 4. Here, $Y_s$ is the reflection factor at the surface of the nacre, $Y_c$ is that at the crystals in the nacre, including scattering, $Y_i$ is that at the interface between the nacre and the nucleus and T is the transmittance of the nacre. The relation between the reflection factors is

$$Y_p = Y_s + kY_cT + Y_iT, \quad (1)$$

where k is a constant (k > l). Although the reflectance by the nacre slightly decreases with γ-ray irradiation,[4] $Y_s + kY_cT$ is considered to be almost constant. The value of $Y_i$ is different from $Y_n$, since the reflectance of the nucleus depends on the refractive index of the environmental medium of the nucleus: nacre for $Y_i$ and air for $Y_n$. However, the relative change in $Y_i$ is considered to be similar to $Y_n$. Thus, eq. (1) can be rewritten as follows:

$$Y_p = Y_s^* + Y_nT^*, \quad (2)$$

where $Y^* = Y_s + kY_cT$ and $Y_nT^* = Y_iT$. The value of $T^*$ includes the effect of replacement of $Y_i$ with $Y_n$. The value of $Y_p$ is calculated from $Y_n$ under the condition of constant values of $Y_s$* and $T^*$. The dashed curve in Fig. 1 is the calculated result for $Y_s^*$ = 32 % and $T^*$ = l7 %. The calculated curve is in agreement with the experimental results. This confirms that the change in the reflection factor of the pearls is caused by a decrease in that of the nuclei. The value of $T^*$ indicates that light reflected from the nuclei is considerably absorbed by the nacre.

### 3.2 Fluorescence

Figure 5 shows typical time-integrated fluorescence spectra of a γ-ray irradiated and nonirradiated pearl and nucleus; both were exposed to γ-rays of $1.0 \times 10^7$ R. The fluorescence peak for the pearl can be observed at 480 nm before irradiation; it is observed at 420 nm after irradiation. On the other hand, the fluorescence peak of the nucleus shifts from about 420 nm to about 440 nm after irradiation; apparently, this behaviour is quite different from that detected in the pearl. Although the spectral shape of a nonirradiated pearl is broader than that of an irradiated one, especially in the longer-wavelength region, a similar result was not obtained for the nucleus. As shown in

a previous paper,[7] fluorescence from aragonite ($CaCO_3$) was observed at about 420 nm, while that from conchiolin of *P. fucata* was detected at about 500 nm; the fluorescence from a mixture of aragonite and conchiolin (93:7, W/W) was very similar to that from pearls. In addition, the difference in the fluorescence spectra of a pearl and nucleus is considered to be due to a difference in the constituents of the organic matrix. Figure 6 shows the fluorescence peak wavelength of irradiated and nonirradiated pearls and nuclei as a function of the irradiation dose. In the pearls, a shift of the fluorescence peak occurs at about $10^5$ R of the irradiation dose; this shift seems to stop at about $10^7$ R. On the contrary, the fluorescence peak of the nuclei shifts from a shorter wavelength (about 420 nm) according to the γ-ray exposure. Changes in the fluorescence intensity of the pearls and nuclei upon γ-ray irradiation are shown in Fig. 7; the abscissa represents the intensity ratio of irradiated (I) to nonirradiated ($I_0$). The fluorescence intensity ratio of the pearls does not change, even at l.0 x $10^7$ R of the irradiation dose. On the contrary, the fluorescence intensity ratio of the nuclei decreases with an increasing irradiation dose. The irradiation-dose dependence of fluorescence for the nuclei is similar to that of the reflection factor in Fig. 1. This result indicates that fluorescence from the nuclei is reabsorbed by the colouring materials in the nuclei produced by the γ-ray irradiation. As discussed above, γ-rays affect the fluorescence from pearls and nuclei. It has been reported that a part of the constituted amino acids of the conchiolin of the nacre decreases as a result of irradiation.[10] The results, thus obtained, suggest that a change in the fluorescence of the nacre of pearls and nuclei, which are made from the nacre of shells of freshwater bivalves, is due to a degradation of the conchiolin. An essential difference is observed between the fluorescence behaviour of the pearls and that of the nuclei; therefore, we believe that the properties of the organic matrices are quite different from each other.

Figure 8 shows typical time-resolved fluorescence spectra of pearls before and after γ-ray irradiation. At the respective delay time (after t = -2 ns, 8 ns and 18 ns), the fluorescence peak position for an irradiated pearl is shorter in wavelength than that for a nonirradiated pearl. Moreover, it is observed that the fluorescence peaks for irradiated and nonirradiated pearls shift to a longer wavelength region with increasing delay time. We have reported that pearls possess 4~5 ns of decay time.[7] In this study, the irradiated

pearls have a similar decay time to the nonirradiated ones.

Both the changes in the fluorescence peak wavelength and the intensity of pearls are different from those of the nuclei, shown in Figs. 6 and 7. These results indicate that the fluorescence from the pearls is hardly affected by the nuclei. On the contrary, the reflectance of the pearls is affected by the nuclei (as described in §3.1). This difference may be due to a difference in the wavelength of the light source between fluorescence and reflectance measurements. Since the wavelength of the excitation light is shorter (337.1 nm) for fluorescence measurements, the light may be absorbed by the nacre. Therefore, the fluorescence from the pearls is that from the nacre and is hardly affected by the nuclei. On the other hand, the longer wavelength one for the reflectance measurement is partly absorbed by the nacre; therefore, the reflectance of the pearls is affected by the nacre.

## §4. Conclusion

Spectral reflectance curves and CIE tristimulus values were measured for pearls and nuclei in order to investigate the colour change of pearls under exposure to γ-rays. As a result, we found that this colour change depends chiefly upon a considerable decrease in the reflection factor of the nuclei. The colours of the irradiated pearls are considered to be determined by the colouring rate of the nuclei under exposure to γ-rays and the original colour of the nacre. The effects of γ-ray irradiation on the fluorescence from the pearls and nuclei were examined. It was found that under exposure to γ-rays, the peak wavelength of fluorescence from the pearls shifts to a shorter wavelength region, while that from the nuclei shifts to a longer one. Furthermore, changes in the spectral shape of the pearls were also observed. Although the fluorescence intensity of the nuclei decreases with increasing the irradiation dose, that of the pearls hardly changed. These results indicate that the fluorescence from the pearls is hardly affected by the nuclei and that it can be used to investigate the effect of γ-rays on the nacre. The time-resolved fluorescence spectra suggest that the transient characteristics of irradiated pearls are almost similar to those of nonirradiated ones, except for the fact that the irradiated pearls possess a shorter wavelength peak than that for nonirradiated ones. These changes in the fluorescence spectra are considered to be due to a degradation of the

conchiolin.

Acknowledgement

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**References**


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**Figure captions**

Fig. 1. Reflection factors for nuclei ($Y_n$) and pearls ($Y_p$) as a function of the irradiation dose of γ-rays. The dashed curve is the calculated result (see text). The values of $Y_p$ and $Y_n$ are averaged data at respective dose.

Fig. 2. Spectral reflectance curves of pearls and nuclei before (solid curves) and after (dashed curves) irradiation.

Fig. 3. Change in CIE chromaticity of pearls with irradiation.

Fig. 4. Schematic drawing of the light path in a pearl. $Y_p$ is the reflection factor of the pearl, $Y_n$, is that of the nucleus, $Y_s$, is that at a surface of the nacre, $Y_c$ is that at the crystals in the nacre and T is the transmittance at the nacre.

Fig. 5. Typical time-integrated fluorescence spectra of a pearl and nucleus before (solid curves) and after (dashed curves) irradiation. The irradiation dose was $1.0 \times 10^7$ R for both the pearl and nucleus.

Fig. 6. Fluorescence peak position of irradiated pearls and nuclei as a function of the irradiation dose. The peak wavelength position is averaged data.

Fig. 7. Fluorescence intensity of a pearl and nucleus as a function of the irradiation dose. The abscissa shows the intensity ratios of irradiated to nonirradiated ($I/I_0$).

Fig. 8. Typical time-resolved fluorescence spectra of a pearl before (solid curves) and after (dashed curves) irradiation. Peak intensity ratios are as follows: 0.9 (delay time t = -2 ns), 1 (8 ns), 0.3 (18 ns). The inset shows the transient characteristics of the laser pulse.

Fig. 1

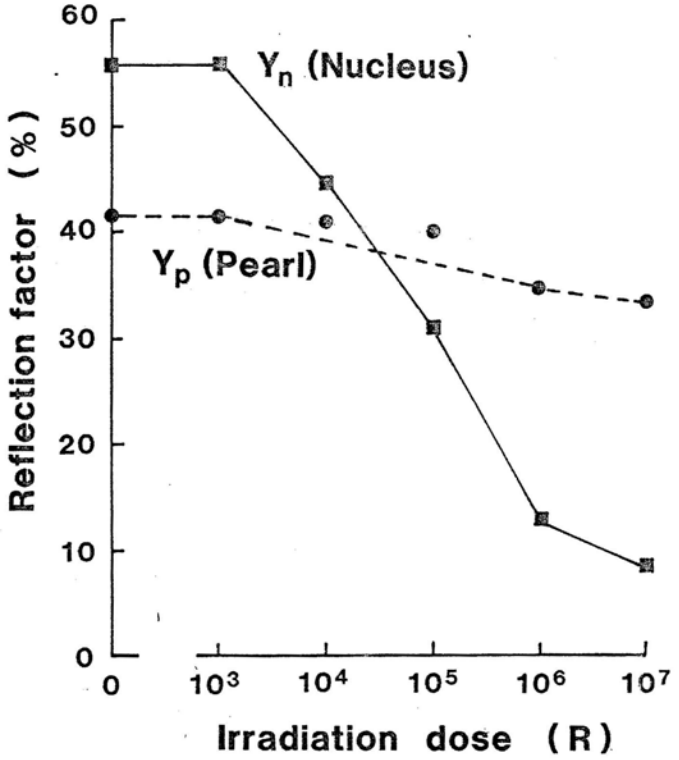

60
50
40
30
20
10
0
Reflection factor (%)
$Y_n$ (Nucleus)
$Y_p$ (Pearl)
0
$10^3$
$10^4$
$10^5$
$10^6$
$10^7$
Irradiation dose (R)

Fig. 2

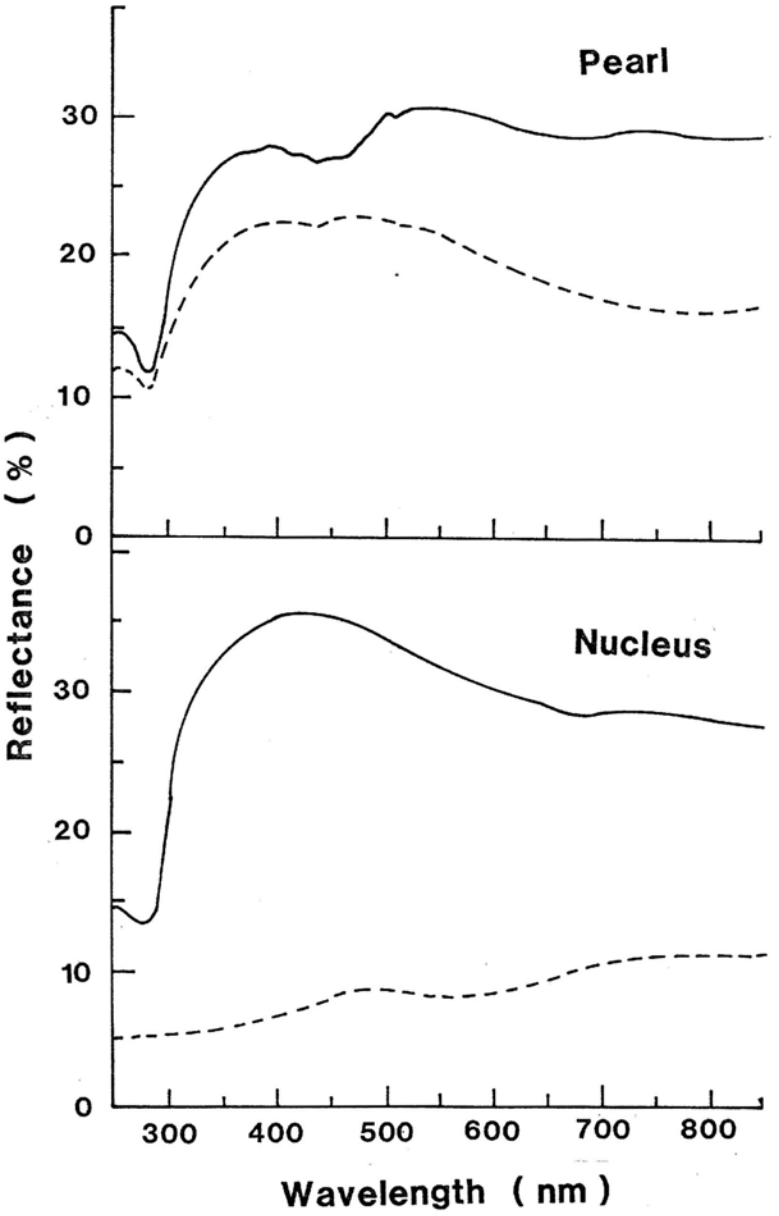

Pearl
30
20
10
0
Reflectance (%)
Nucleus
30
20
10
0
300
400
500
600
700
800
Wavelength (nm)

Fig. 3

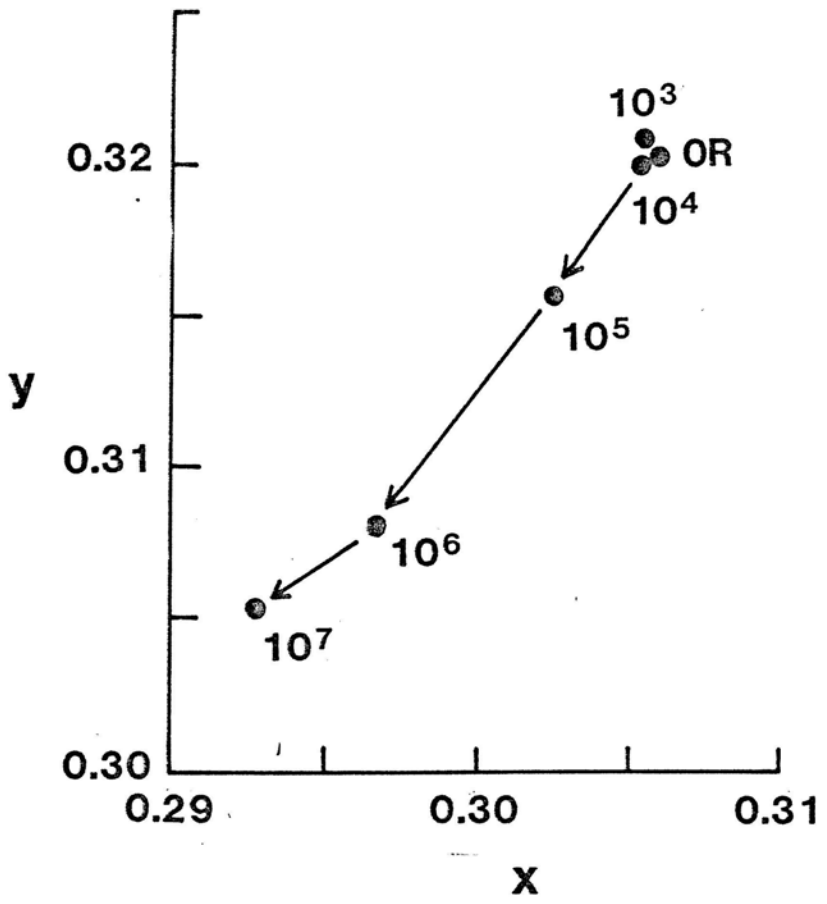

$10^3$
OR
$10^4$
$10^5$
$10^6$
$10^7$
0.32
0.31
0.30
y
0.29
0.30
0.31
x

Fig. 4

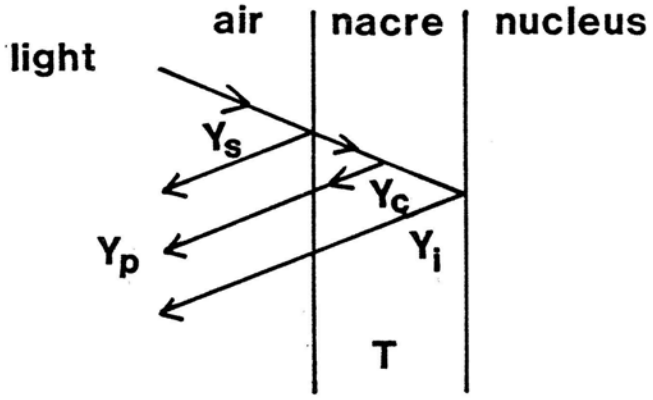

air
nacre
nucleus
light
$Y_s$
$Y_c$
$Y_p$
$Y_i$
T

Fig. 5

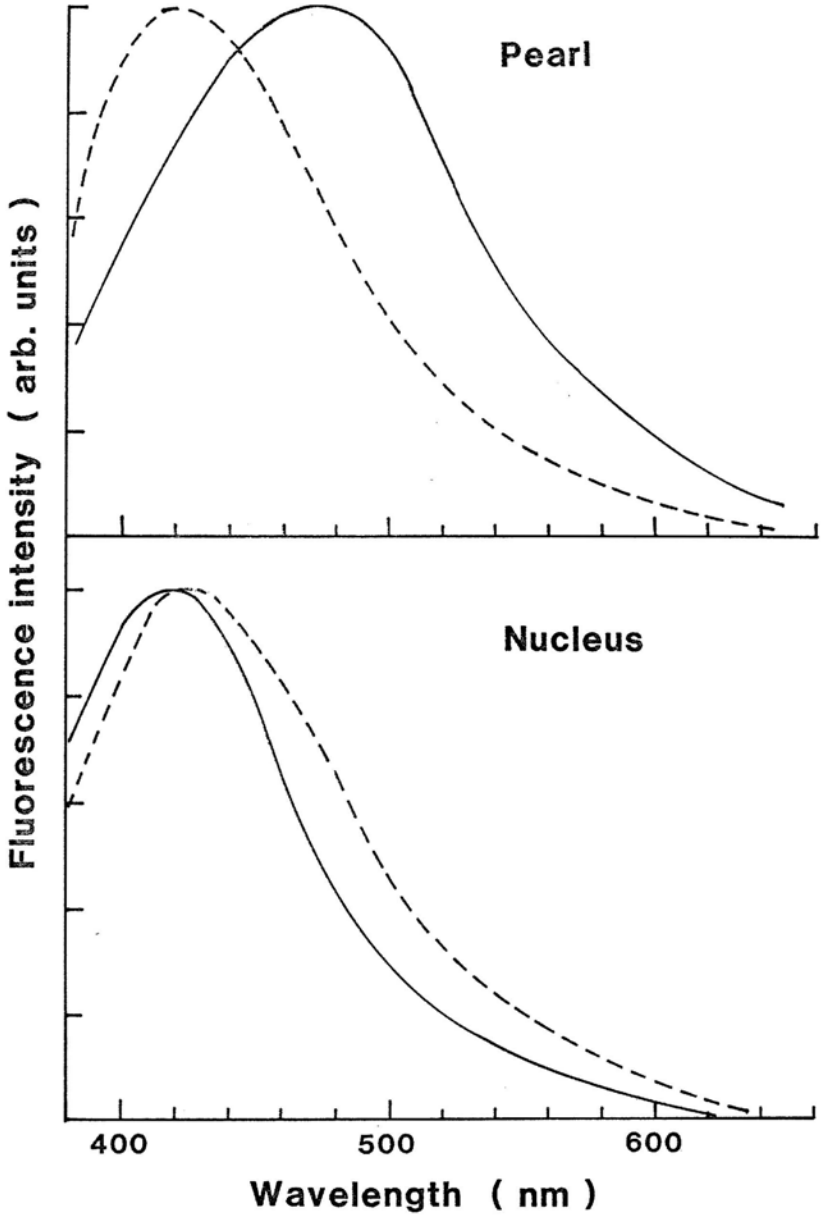

Pearl
Nucleus
Fluorescence intensity ( arb. units )
400
500
600
Wavelength ( nm )

Fig. 6

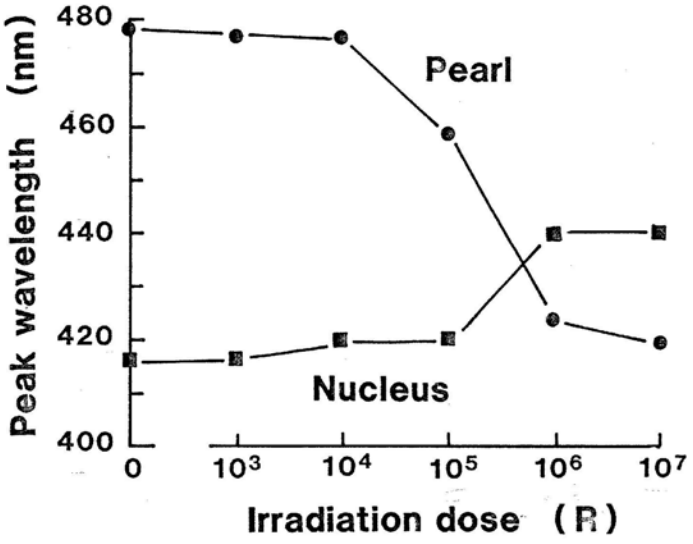

480
460
440
420
400
Peak wavelength (nm)
Pearl
Nucleus
0
10³
10⁴
10⁵
10⁶
10⁷
Irradiation dose (R)

Fig. 7

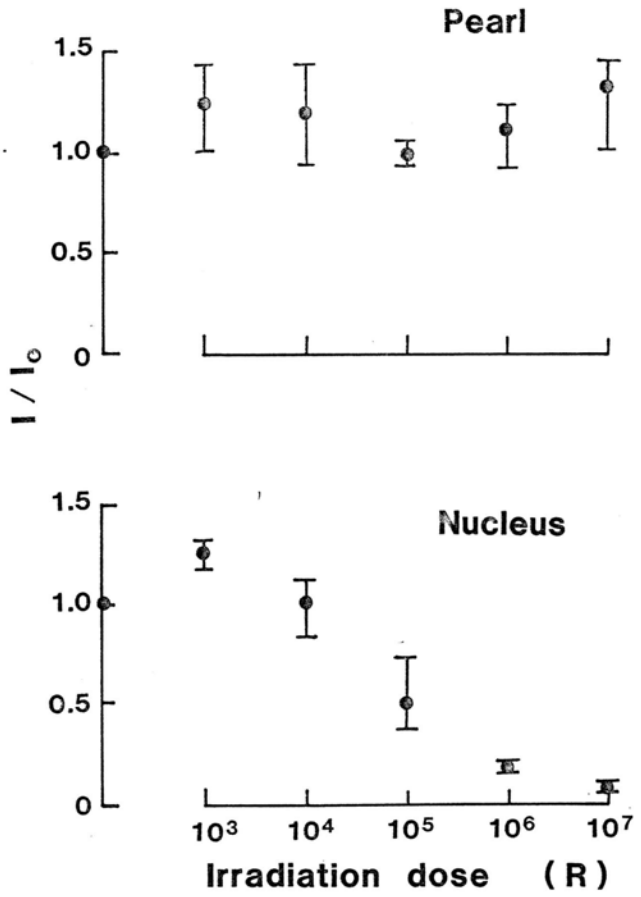
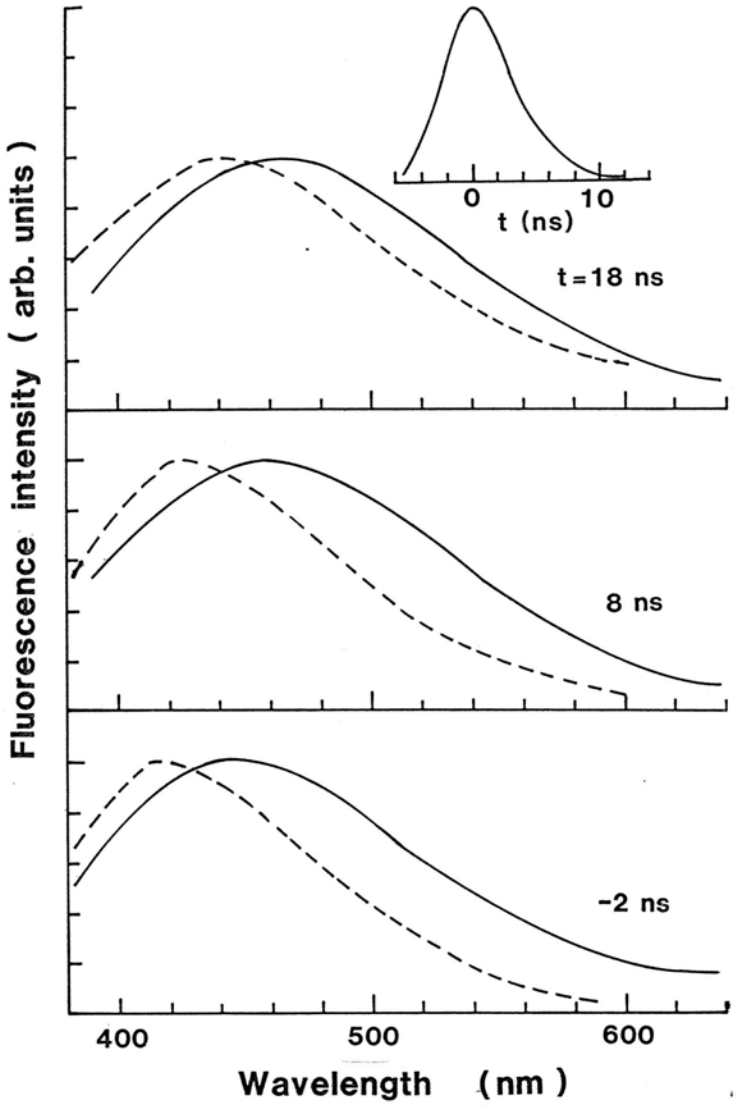

Pearl
1.5
1.0
0.5
0
I / I0
Nucleus
1.5
1.0
0.5
0
10³
10⁴
10⁵
10⁶
10⁷
Irradiation dose (R)

Fig. 8


Fluorescence intensity (arb. units)
0
10
t (ns)
t=18 ns
8 ns
-2 ns
400
500
600
Wavelength (nm)