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Laser-Induced Fluorescence of Pearls and Shells of Genus *Haliotis* and Their Comparison to Other Species Used in Pearl Culturing

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To determine the parentage of pearls nondestructively, the measurement of fluorescence spectra was applied to several kinds of pearls as well as shells. The fluorescence spectra of pearls and shells of genus *Haliotis* (abalone) were also measured together with those of other species of mother oysters used in pearl culturing. Experimental results indicate that some differences in the spectra make it possible for pearls of genus *Haliotis* to be distinguished from those of other mother oysters.

KEYWORDS: laser-induced fluorescence, pearl, abalone, nondestructive distinction

§1. Introduction

In pearl culturing, several species of mother oysters, including *Pinctada fucata* (Akoya oyster), *Pinctada maxima* (yellow-lip oyster), *Pinctada margaritifera* (black-lip oyster), *Pteria penguin* (Mabe), *Hyriopsis shlegeli* (Ikecho) and genus *Haliotis* (abalone), are used. Therefore, in pearl trading, the determination of the parentage of pearls is of much importance, and nondestructive methods for distinction need to be developed. In addition to the naked eye of an expert, several scientific methods can be employed. Analysis of the colour of pearls, which is caused partly by colouring materials, is especially effective. It is quite common for colouring materials to show peculiar peaks in fluorescence and/or reflection spectra, which are usually used for the distinction of pearls.

We previously investigated the fluorescence and reflection spectra of several of the above-mentioned kinds of pearls.[1-4] But pearls from genus *Haliotis* were excluded since they can be distinguished from pearls of other mother oysters in terms of nacreous structural differences by microscope; the nacreous structure of gastropods (genus *Haliotis*) is quite different from that of bivalves (other mother oysters).[5] To bring the fluorescence measurement method to completion, we have examined fluorescence from pearls and shells of genus *Haliotis*.

§2. Experimental Procedure

Time-integrated and time-resolved fluorescence spectra were measured at room temperature with an apparatus similar to that described in ref. 4. The excitation source was a pulsed N_2 laser (NDC JS-1000L, λ = 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 the sample and 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. The fluorescence spectra were measured with a monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator (NF Circuit Design Block BX-531) and a recorder. The transient characteristics of fluorescence were measured using a storage oscilloscope (Iwatsu

Electric TS-8123).

The materials used in this study were pearls of genus *Haliotis* and of other mother oysters. For genus *Haliotis* and *P. penguin*, the nacre of the shell and/or hemispherical nacre of the shell (usually called a "half pearl") were also used, since pearl, shell and half pearl seemed to be almost the same in their chemical compositions.

§3. Results and Discussion

Figures 1 and 2 show time-integrated fluorescence spectra for nacre of the *P. penguin* shell and the pearl of *P. margaritifera*, and for pearls of several mother oysters, respectively. As is shown in Fig. 1 by the existence of a peak in fluorescence spectra at 620 nm which is attributable to porphyrin, as confirmed by previous experimental results,[2,3] the samples are divided into two groups: those with and without porphyrin. Since pearls of genus *Haliotis* are considered to have no porphyrin as a chemical constituent, they are distinguishable from pearls of *P. margaritifera* and *P. penguin*.

Figure 2 shows that there are great differences among the fluorescence spectra of pearls, even though their appearance is almost the same.

As in the cases of other species, genus *Haliotis* also has pearls and/or nacre of shell with a wide colour range. But generally both are green, ranging from light to deep shades. This colour is considered to be due to several colouring materials, such as chlorophylls and carotenoids.[6,7] In order to examine the concentration effect of the colouring materials, time-integrated fluorescence spectra were measured for deep green hemispherical nacre from shells of genus *Haliotis*. At longer wavelengths, the fluorescence intensity of deep green nacre (Fig. 3) is relatively higher than that of a light green pearl (Fig. 2). This result suggests that fluorescence in the longer wavelength region may be due to the colouring materials in nacre.

Time-resolved fluorescence spectra were measured for the investigation of the properties of colouring materials in genus *Haliotis*. Figure 4 shows the time-resolved spectra of the nacre having a deep green colour. It is observed that fluorescence peak shifts to longer wavelengths as the delay time increases, which suggests a probable relationship between decay time and wavelength. The decay time as a function of fluorescence wavelength was also examined. Figure 5(a) shows the results. The decay

time was determined from the transient characteristics of fluorescence measured with the storage oscilloscope. The decay time becomes longer as the wavelength grows longer. This result is consistent with that of the time-resolved fluorescence measurement. It proves that the decay time of fluorescence depends on wavelength, and that the colouring materials of genus *Haliotis* fluoresce at a longer wavelength with a longer decay time.

Time-resolved fluorescence spectra and decay time were also measured for the pearl of genus *Haliotis*. The results are shown in Figs. 6 and 5(b), respectively. Peak wavelength for the pearl is slightly shorter than that for the nacre of the shell. This difference is considered to be attributable to the concentration of the colouring materials; the pearl may have a lower concentration of colouring materials than deep green nacre.

The spectral peaks of both pearl and nacre of genus *Haliotis* range in their wavelengths from 450 to 480 nm. As already reported,[1-4)] the spectral peaks of pearls from other mother oysters are as follows: *P. fucata* 460-490 nm, *P. maxima* 430-450 nm and *Hyriopsis shiegeli* 410-440 nm.[*] The range of genus *Haliotis* overlaps that of *P. fucata* or *P. maxima*, which makes distinction among these three difficult. However, when their spectral shapes are compared after normalization of their intensities, the differences are recognized in terms of full width at half maximum (FWHM); genus *Haliotis* has a broader FWHM than *P. fucata* and *P. maxima*. It also has a much higher fluorescence intensity in the longer wavelength region. The difference in spectral shapes may be derived from the variety of the colouring materials in pearls. These differences make distinction of these three species possible.

In summary, the fluorescence of pearls and nacre of shells of genus *Haliotis* and other mother oysters used in pearl culturing were measured. The differences in distribution of peak wavelength and spectral shape made it possible to distinguish pearls of genus *Haliotis* from those of *P. margaritifera*, *P. penguin*, *P. fucata*, *P. maxima* and *Hyriopsis shiegeli*.

Acknowledgement

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[*]Pearls of *Hyriopsis shlegeli*, except for those of brown colour, have fluorescence peaks within the wavelength from 410 to 420 nm. This wavelength range distinguishes pearls of *H. shiegeli* from those of *P. maxima*.

References

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Figure captions

Fig. 1. Time-integrated fluorescence spectra of nacre of shell of *P. penguin* and pearl of *P. margaritifera* at 300 K under N_2 laser excitation. Peak intensities are normalized.

Fig. 2. Time-integrated fluorescence spectra of pearls of several mother oysters. Peak intensities are normalized.

Fig. 3. Time-integrated fluorescence spectra of deep green shell of genus *Haliotis*.

Fig. 4. Time-resolved fluorescence spectra of deep green nacre of shell of genus *Haliotis*. Peak intensity ratios are as follows: 0.3 (delay time t = -4 ns), 1 (6ns), 0.3 (16ns). The inset shows transient characteristics of the laser pulse.

Fig. 5. Decay time of fluorescence as a function of wavelength of fluorescence for deep green nacre of shell (a) and light green pearl (b) of genus *Haliotis*.

Fig. 6. Same as Fig. 4 for light green pearl of genus *Haliotis*. Peak intensity ratios are as follows: 0.8 (delay time t = -4 ns), 1 (6 ns), 0.3 (16ns).

Fig. 1

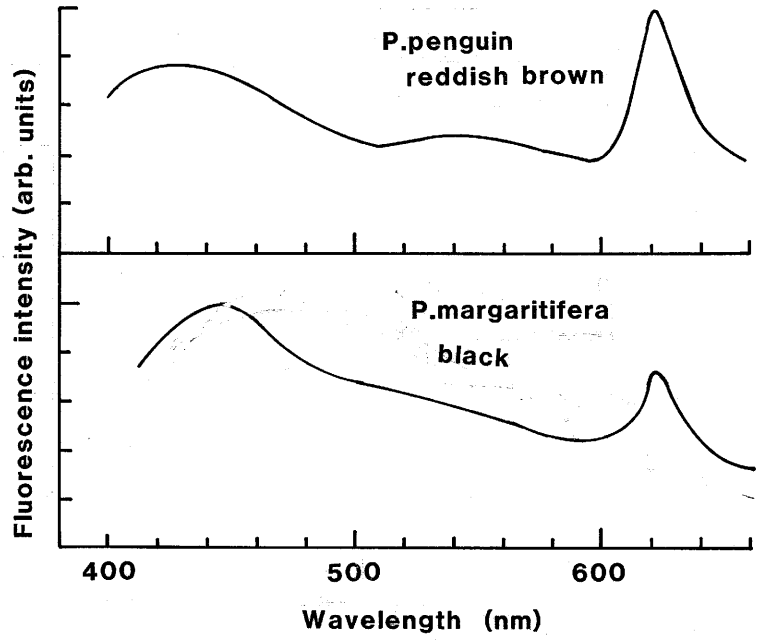

P.penguin
reddish brown
P.margaritifera
black
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)

Fig. 2

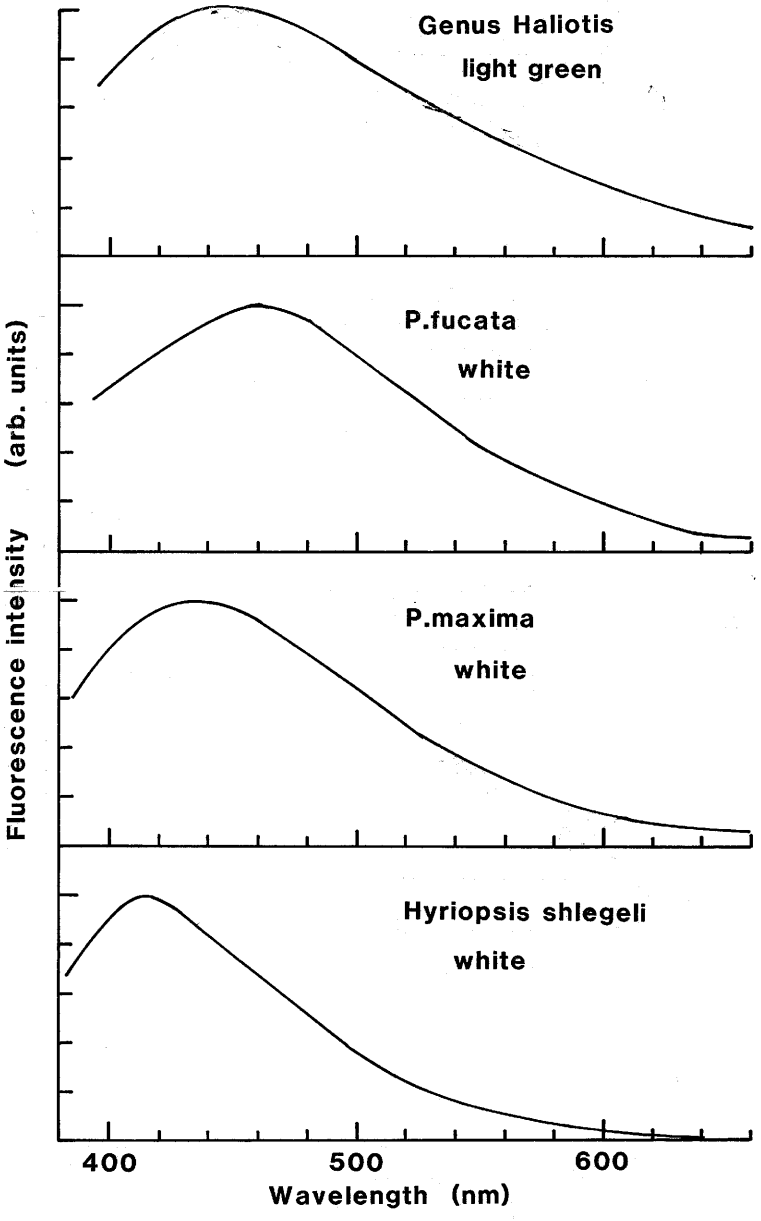

Genus Haliotis
light green
P.fucata
white
P.maxima
white
Hyriopsis shlegeli
white
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)

Fig. 3

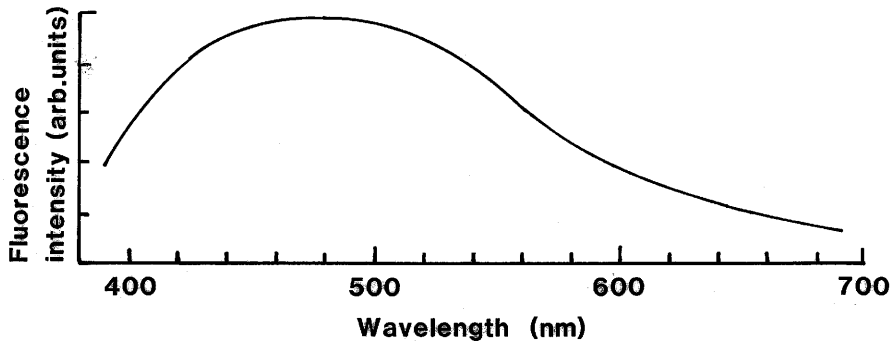

Fluorescence intensity (arb.units)
400
500
600
700
Wavelength (nm)

Fig. 4

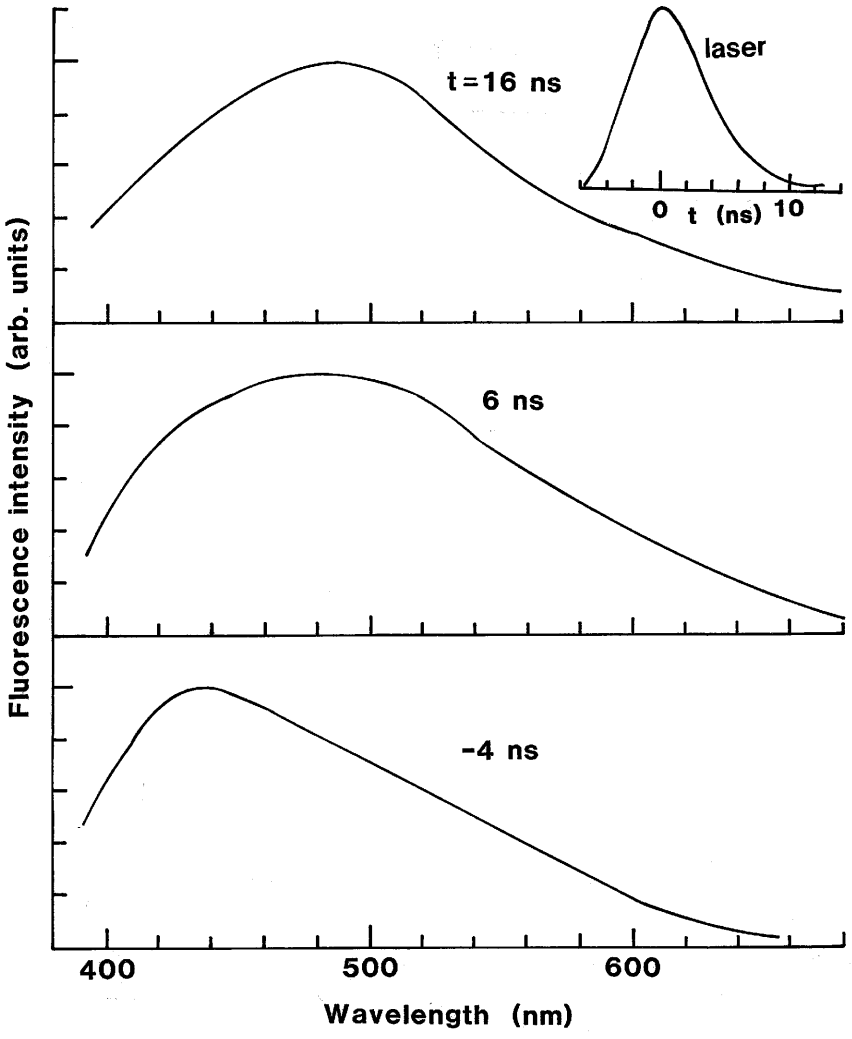

t=16 ns
laser
0 t (ns) 10
6 ns
-4 ns
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)

Fig. 5

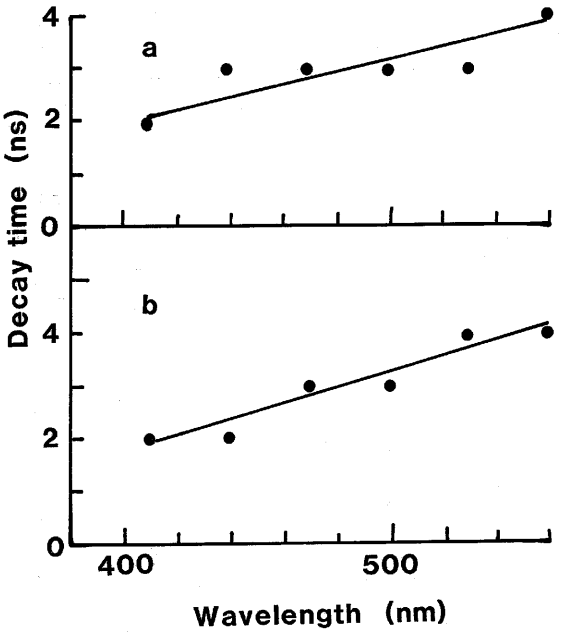
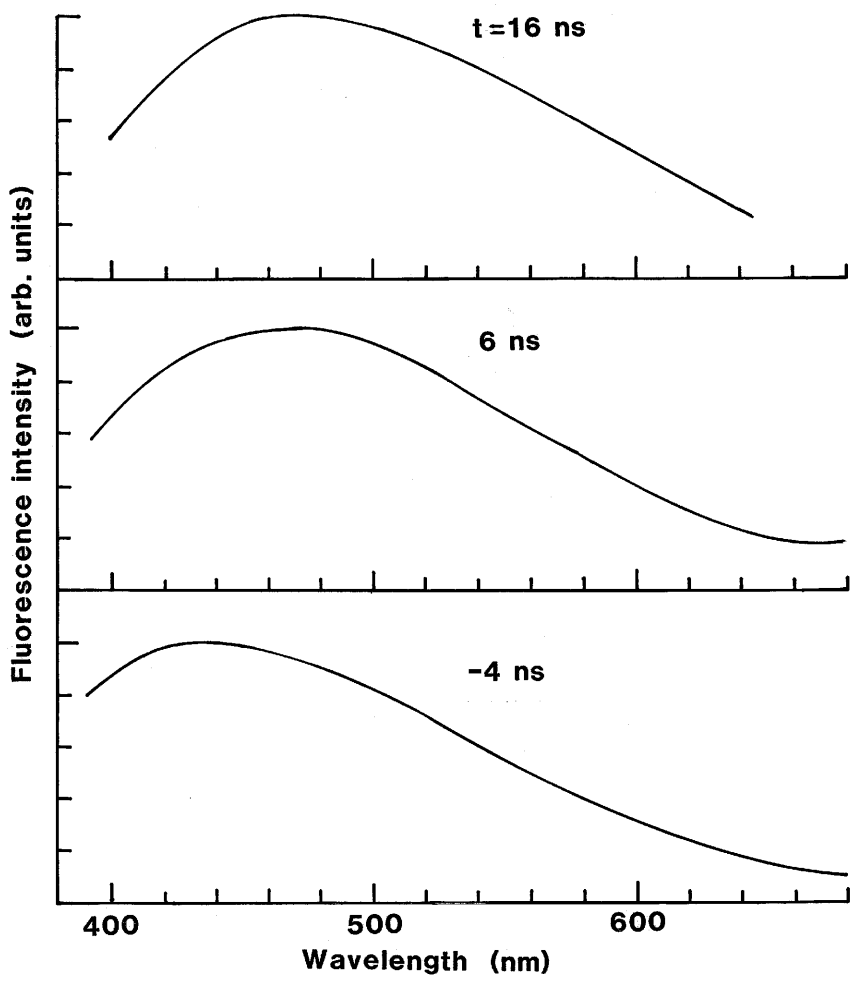

4
2
0
a
Decay time (ns)
b
4
2
0
400
500
Wavelength (nm)

Fig. 6


t=16 ns
6 ns
-4 ns
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)