UV-VIS-NIR REFLECTANCE SPECTROSCOPY OF NATURAL-COLOR SALTWATER CULTURED PEARLS FROM *PINCTADA MARGARITIFERA*

Stefanos Karampelas, Emmanuel Fritsch, Jean-Pierre Gauthier, and Thomas Hainschwang

Natural-color saltwater cultured pearls from *Pinctada margaritifera* were studied by diffuse reflectance UV-Vis-NIR spectroscopy to identify the absorption features associated with their various colors. Nine patterns observed in the visible range demonstrated that individual colors are caused not by one pigment but by a mixture of pigments.

Over the past 30 years, colored cultured pearls have become very popular (see Komatsu and Akamatsu, 1978; Shor, 2007; and references therein). Until the late 1990s, however, cultured pearl strands were marketed only in single colors: "golden," black, and so forth. Since that time, multicolored ensembles, some even using cultured pearls from different mollusks, began to see strong demand (figure 1; Elen, 2003; Shor, 2007; Shigley et al., 2010).

Saltwater cultured pearls (SWCPs) from the *Pinctada margaritifera* mollusk are principally grown in French Polynesia, but also in the Cook Islands, Fiji, and other localities (see Shigley et al., 2010). The vast majority of the SWCPs produced are bead-nucleated, and marketed as Tahitian, "black" South Sea, or simply "black" cultured pearls. They have a variety of bodycolors, most commonly black to light gray to white, as well as yellow to green, brown, gray-red, gray-blue, and gray-green. They can also contain strong overtones (i.e., secondary colors), including pink and purple. Combinations of bodycolors and overtones give *P. margaritifera* SWCPs a wide range of color appearances (again, see figure 1).

The origin of their color is still under investigation, and a better understanding will help separate natural-color cultured pearls from their treated-color counterparts. This study presents spectral characteristics in the ultraviolet/visible/near-infrared (UV-Vis-NIR) region of natural-color SWCPs from *P. margaritifera*, in an effort to better characterize the mechanisms of their coloration.

MATERIALS AND METHODS

For this study, we selected 21 undrilled SWCPs from *P. margaritifera* in a wide range of colors. The samples ranged from 9.3 to 13.4 mm in diameter (for details on their color and size, see table 1). They were obtained from reputable sources (see acknowledgments) and represented as natural color.

Diffuse reflectance UV-Vis-NIR spectra were obtained at the IMN (Institut des Matériaux Jean Rouxel) for the 250–1600 nm range (only 250–900 nm is presented here because this is the range containing color-related absorption bands) with a Cary 5G spectrometer fitted with a Varian diffuse reflectance accessory. The data sampling interval and spectral bandwidth of each measurement were set at 0.7 nm to achieve a high resolution, and the relatively slow scan rate of 60 nm/minute permitted a satisfactory signal-to-noise ratio. Matte black sample holders with various hole sizes (4–10 mm in diameter) were used so that the sample could be

See end of article for About the Authors and Acknowledgments.
GEMS & GEMOLOGY, Vol. 47, No. 1, pp. 31–35.

Figure 1. This bracelet features 32 multicolored round cultured pearls (represented as having natural color) from P. margaritifera, *~10 mm in diameter. Photo © Autore, Sydney, Australia.*

positioned for maximum exposed measurement surface (with as homogeneous a color as possible), producing a more intense signal. For samples with inhomogeneous color distribution (again, see table 1), separate spectra were taken from areas of different color. Before each measurement, background spectra were taken using white MgO powder (for 100% reflectance) and matte black card (0%) references. The measurements, which took about 25 minutes each, were repeated at least twice on each sample to confirm the repeatability of the results.

RESULTS

Figures 2 through 5 present the diffuse reflectance UV-Vis-NIR spectra of nine representative natural-color SWCPs. Each spectrum revealed a decrease in diffuse reflectance (i.e., increase in absorption) at about 280 nm, regardless of the sample's color. Figure 2 shows that nearly all the light from the visible part of the spectrum (390–780 nm) is transmitted, consistent with the samples' white bodycolor. Sample SK-208 showed weak absorptions at about 405 and 700 nm, while sample SK-224 had a small absorption from 330 to 460 nm (consisting of two different bands at 330–385 nm and 385–460 nm). However, these weak absorptions did not produce any eye-visible color. Sample SK-223 had small bands at 700 nm and at 330–460 nm (although less intense than in SK-224), as well as a weak absorption that gradually cut through the visible region with a maximum in the near-infrared region at ~820 nm. This absorption was responsible for the sample's very light gray coloration.

Figure 3 shows the UV-Vis-NIR spectra of the inhomogeneously colored SWCP SK-206, in the grayish yellow and black parts of the sample. As

TABLE 1. Color and size of saltwater cultured pearl samples from *P. margaritifera* used in this study.

Sample no.	Bodycolor	Size (mm)
SK-205	Light gray	9.6
SK-206	Grayish yellow/Black	11.0
SK-207	Green-yellow/Yellow	10.2
SK-208	White	10.2
SK-209	Black	13.0
SK-210	Blue-black/ Green-blue-black	13.4
SK-212	Green-black	10.9
SK-213	Grayish green-yellow	11.7
SK-214	Red-black	13.2
SK-216	Gray-green/Gray-red	11.0
SK-217	Orange-red-black	10.5
SK-218	Gray-blue/Gray-red	9.3
SK-219	Gray-blue/ Gray-green-yellow	10.0
SK-220	Grayish green-yellow	12.3
SK-221	Grayish greenish yellow	11.4 × 9.2
SK-223	White (slightly gray)	11.6 × 10.5
SK-224	White	12.6 × 8.5
SK-228	Dark gray	10.0
SK-230	Green-black	10.4
SK-231	Red-black	9.6 × 9.4
SK-232	Gray-green-yellow	10.2

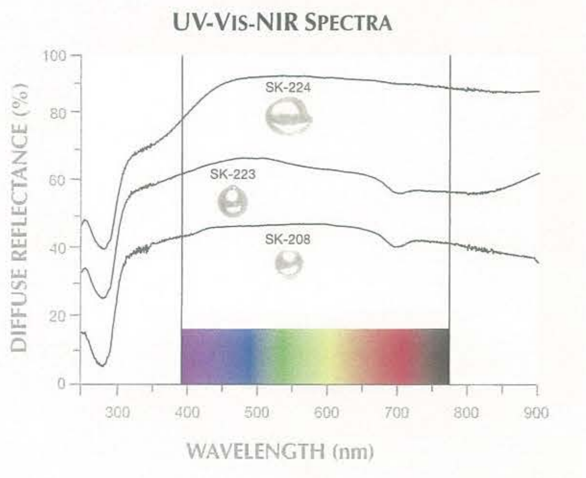


Figure 2. These diffuse reflectance spectra are from three P. margaritifera *SWCPs with a white or very light gray bodycolor. A weak continuous absorption that extends through the visible region with a maximum in the near-infrared region (at about 820 nm) is responsible for sample SK-223's slight coloration; none of the bands in the other spectra produce visible hues. The spectra of SK-223 and SK-208 are shifted down by 15% and 35% for clarity.*

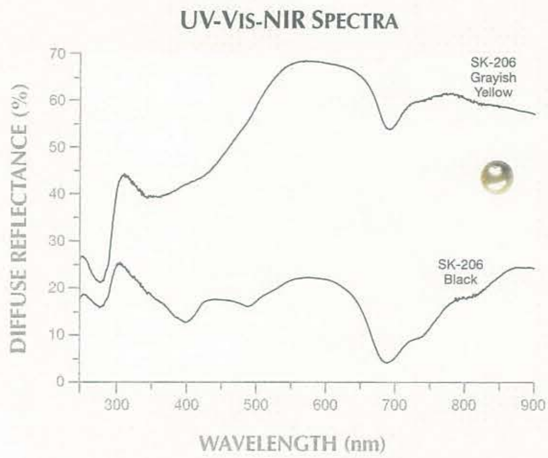


Figure 3. The grayish yellow part of SK-206 shows an intense absorption from 330 to 460 nm, as well as other weak bands and continuous absorption with a maximum at about 820 nm. The black part of the sample (spectrum shifted downward 5% for clarity) shows the same absorptions as the yellow part, and has an additional band at about 530 nm. The absorptions have equal intensity, giving the sample its black color.

expected, the two spectra were different in the visible range. The grayish yellow part had a band from 330 to 460 nm, as well as at 405 and 700 nm, and continuous absorption with a maximum in the near infrared at ~820 nm, similar to the spectra in figure 2. These features were more intense than those of the whitish samples in figure 2. Two additional weak bands at 495 and 745 nm were observed. The yellow color is due to the relatively stronger absorption from the UV-to-blue range; a grayish color is probably due to the continuous absorption. The spectrum from the black part of the sample shows the same bands observed in the yellow area, as well as an additional absorption at about 530 nm. The black color occurs because all the absorptions are equally intense.

The spectra of black (SK-209) and dark gray (SK-228) cultured pearls are presented in figure 4. The same absorptions seen in the black portion of sample SK-206 are observed, along with two additional barely visible bands at about 585 and 625 nm. The two spectra taken from black surface areas presented in figures 3 and 4 vary due to the different relative intensities of the same bands.

Figure 5 shows the spectra of three natural SWCPs of other colors: the blue-black portion of SK-210, orange-red-black sample SK-217, and red-black sample SK-231. Bands occur at the same wavelengths as in the previous spectra, but with different relative intensities. The spectrum taken from the blue-black sample showed a spread of absorptions across the visible range that produced the black color. A diffuse reflectance maximum (i.e., transmission maximum) was also observed in the blue range

NEED TO KNOW

- Reflectance spectra collected from natural-color *P. margaritifera* cultured pearls show various absorptions according to bodycolor.
- The diversity of absorptions suggests that the cultured pearls' coloration is due to combinations of several pigments.
- Uroporphyrin has been confirmed as one of the pigments, but additional research is needed to identify the exact nature of the others.

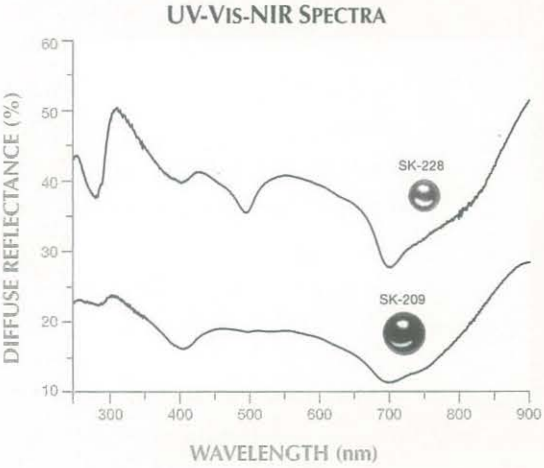
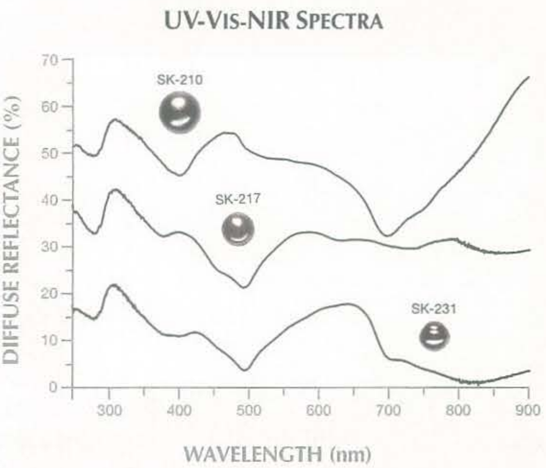


Figure 4. The diffuse reflectance spectra of a a dark gray (SK-228) and black (SK-209) SWCP from P. margaritifera *are similar to those of the black portion of SK-206. The absorptions from the black bodycolors (SK-206 and SK-209) are more intense than those observed in the dark gray sample (SK-228). The SK-209 spectrum is shifted downward by 5% for clarity.*

from ~450 to 490 nm. The spectrum taken on the orange-red-black SWCP showed absorptions across the visible range that are responsible for the black coloration. The bands in the orange-red portion, from about 580 to 780 nm, are less intense than elsewhere in the spectrum, and this caused the orange-red coloration. The spectrum on the red-black sample showed bands across the visible range causing the black coloration, and a diffuse reflectance window in the red portion with a maximum at about 650 nm that caused the red bodycolor.

Figure 5. A series of absorptions in the reflectance spectra for the blue-black portion of sample SK-210, orange-red-black SK-217, and red-black SK-231, at the same wavelengths as in the previous spectra, explains their black coloration.



DISCUSSION

Nine visible-range absorption features were observed in the spectra of natural-color SWCPs from *P. margaritifera*: a continuous band extending through the visible range with a maximum in the near infrared (at ~820 nm), an absorption from the ultraviolet to blue portion of the spectrum (330–460 nm, consisting of two bands at 330–385 nm and 385–460 nm); two others in the blue region (at 405 and 495 nm); three absorptions in the green-yellow-orange region (at 530, 585, and 625 nm); and two in the red (at 700 and 745 nm).

Some of these bands have been documented previously in natural-colored SWCPs from *P. margaritifera*: those at 405, 495, and 700 nm (Cuif et al., 1993; Dauphin and Cuif, 1995; Elen, 2003; Huang, 2006; Wang et al., 2006) and from 330 to 460 nm (Elen, 2003). Slight differences in band position between the present study and earlier ones are probably due to the different parameters we used for the measurements (i.e., higher-resolution spectra). In other studies, some of the bands seen in SWCPs from *P. margaritifera* were also found in similarly colored SWCPs from *Pteria sterna* (Kiefert et al., 2004). However, some bands present in spectra from *P. margaritifera* are absent from those of *P. sterna*, and vice versa (authors' unpublished research).

The particular color shown by SWCPs from *P. margaritifera* depends on the relative intensity of several absorptions, which are probably due to various combinations of pigments. Applying a tentative simplified approach, there should be as many absorptions bands as there are pigments in any sample (i.e., up to nine). To our knowledge, only the cause of the 405 nm band has been identified; it is attributed to a kind of porphyrin called uroporphyrin (Iwashi and Akamatsu, 1994). Porphyrins are a type of tetrapyrrole, composed of four modified pyrrole (C_4H_4N) rings interconnected via methine bridges. A combination of melanins (Caseiro, 1993) as well as other tetrapyrroles could produce some of the other patterns observed in the visible region of the spectrum. A study of the precise relationship between the samples' optical absorption and photoluminescence characteristics and a comparison with isolated natural pigments is ongoing.

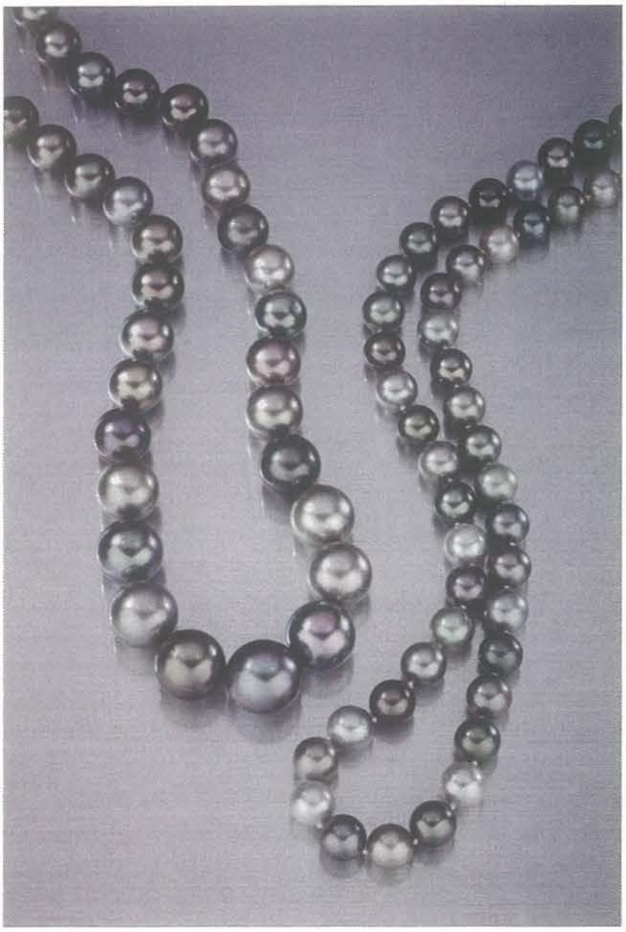


Figure 6. These two necklaces show the diversity of color (here represented as natural) in cultured pearls from P. margaritifera *(10–14 mm in diameter on the left, and 8–9 mm on the right). Courtesy of Armand Asher Pearls, New York; photo by Robert Weldon.*

CONCLUSION

SWCPs from *P. margaritifera* feature a variety of natural bodycolors (figures 1 and 6). UV-Vis-NIR spectroscopy reveals that their specific color is due to the relative intensity of several absorption features (probably up to nine). Uropor-phyrin is the only pigment that has been conclusively identified so far. Further research using other spectroscopic methods on different natural-color SWCPs from *P. margaritifera* and on isolated natural pigments is needed to identify other factors involved in their coloration.

ABOUT THE AUTHORS

Dr. Karampelas is a research scientist at the Gübelin Gem Lab, Lucerne, Switzerland. Dr. Fritsch is professor of physics at the University of Nantes, Institut des Matériaux Jean Rouxel (IMN)-CNRS, Team 6205, France. Dr. Gauthier is a former professor of crystallography at the University of Lyon, France. Mr. Hainschwang is one of the two managing directors of the GGTL Gemlab–Gemtechlab Laboratory located in Balzers, Liechtenstein, and Geneva, Switzerland.

ACKNOWLEDGMENTS

The authors thank the Ecole de Greffe (school of pearl farming techniques), Rangiroa, French Polynesia, and the ADEQUA program (Service de la Perliculture) and IFREMER (French Research Institute for Exploration of the Sea), French Polynesia, for providing the study samples.

REFERENCES

Caseiro J. (1993) La Nacre Noire de Polynésie. PhD thesis, Université Claude Bernard, Lyon, France, 386 pp.

Cuif J-P., Dauphin Y., Stoppa C., Beeck S. (1993) Forme, structure et couleurs des perles de Polynésie. *Revue de Gemmologie a.f.g.*, No. 115, pp. 9–11.

Dauphin Y., Cuif J-P. (1995) Trichromatic characterization of the "black pearls" from aquaculture centers of French Polynesia. *Aquaculture*, Vol. 133, No. 2, pp. 113–121.

Elen S. (2003) Identification of yellow cultured pearls from the black-lipped oyster *Pinctada margaritifera*. *G&G*, Vol. 38, No. 1, pp. 66–72.

Huang Y.L. (2006) Visible absorption spectrum representation of Tahitian black pearls and treated pearls. *Journal of Gems and Gemmology*, Vol. 8, No. 1, pp. 5–8.

Iwahashi Y., Akamatsu S. (1994) Porphyrin pigment in black-lip pearls and its application to pearl identification. *Fisheries Science*, Vol. 60, No. 1, pp. 69–71.

Kiefert L., Moreno D.M., Arizmendi E., Hänni H.A., Elen S. (2004) Cultured pearls from the Gulf of California, Mexico. *G&G*, Vol. 40, No. 1, pp. 26–39.

Komatsu H., Akamatsu S. (1978) Differentiation of black pearls. *G&G*, Vol. 16, No. 1, pp. 7–15.

Shigley J.E., Laurs B.M., Janse A.J.A., Elen S., Dirlam D.M. (2010) Gem localities of the 2000s. *G&G*, Vol. 46, No. 3, pp. 188–216.

Shor R. (2007) From single source to global free market: The transformation of the cultured pearl industry. *G&G*, Vol. 43, No. 3, pp. 200–226

Wang W., Scarratt K., Hyatt A., Shen A.H.-T., Hall M. (2006) Identification of "chocolate pearls" treated by Ballerina Pearl Co. *G&G*, Vol. 42, No. 4, pp. 222–235.