Akoya Cultured Pearls with Corallium Species Bead Nuclei
含珊瑚珠核的日本阿古屋(Akoya)養珠

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Fig. 1 From the left “Sango” cultured pearls (3), Akoya cultured pearls (3), freshwater cultured pearls (3)
左起：珊瑚(Sango)養殖珍珠(3)，阿古屋(Akoya)養殖珍珠(3)，淡水養殖珍珠(3)

日本的松本珍珠有限会社已經成功地培育出一種名為“Sango珍珠”，日文名為“珊瑚”的珍珠，並使用粉紅色至紅色的珊瑚作為珠核。作者選取“Sango珍珠”，阿古屋(Akoya)養珠和紫色淡水養珠以及粉紅色珊瑚作鑑證比對。

The colour and quality of nucleus used in pearl culture affects the colour of the pearls, showing through the nacreous layers consisting of transparent aragonite especially where the pearl coating is thin. Therefore, white nuclei with no brown spots are used for light coloured cultured pearls (CP). On the other hand, producers have tried a variety of methods to give pearls a unique colour, such as using dyed/coloured nuclei or injecting organic dyes into the internal organs of a host mollusk during the aquaculture process. Recently, it has been reported that the Matsumoto Pearl Co. Ltd. of Japan has successfully cultivated an Akoya cultured pearl being sold as “Sango pearls”, the Japanese for “coral” pearls, using a pink-to-red coloured coral as the nucleus. Some “Sango pearls” were obtained and their characteristics compared with Akoya CP (pinked) and purple freshwater cultured pearls (natural colour) which exhibited similar colours. To determine the materials and treatment of the nuclei used in “Sango pearls”, we also investigated pink-to-red corals.

Materials and Methods

First, we compared comparatively similar Akoya CP (pinked) with purple freshwater CP (natural colour) to see the difference between the “Sango pearls” and other CP. The nine samples in total consisted of 3 samples of each (Sango, Akoya, freshwater CP) ranging in size from 6.5~8.5mm. All samples had drill holes (Fig. 1). In order to identify the substances and treatment of the nuclei used in “Sango pearls”, we additionally studied pink-to-red corals, specifically corallium rubrum and corallium elatius of the species corallium and melithaea ochracea (sponge coral). We also, inspected dyed bamboo coral, of the family Isididae.

A 60x microscope objective was used to observe an inner nucleus through the drill holes and surface features of pearls. We observed the fluorescence reaction of pearls in long (365nm) and short wave (254nm) UV. UV-Vis reflectance spectra were recorded in the 200~850nm range using JASCO V-660 at a scan time of 400nm/min. Using a Renishaw In Via Raman microscope, we measured the surface area of “Sango pearls”, Akoya CP (pinked), purple freshwater CP, corallium rubrum, corallium elatius, melithaea ochracea, and bamboo coral (dyed) as well as the exposed section of nucleus around the perforation in the “Sango pearls”. All Raman spectra were recorded in the 100~2000cm^{-1} range using a spectral acquisition time of 10 seconds, objective lens magnification 50x, laser focusing diameter 2μm with 532nm laser excitation (Nd:YAG Laser).

Chemical analysis, qualitative and quantitative (fundamental parameters), was performed on nine samples of “Sango pearls”, Akoya CP (pinked), and purple freshwater CP (natural colour) with a Shimadzu EDX-8000. The thickness of nacre and characteristic nuclei of the nine pearls were investigated using a micro CT equipped with KIGAM (Korea Institute of Geoscience and Mineral Resources). The internal structures of corallium elatius, melithaea ochracea, and bamboo coral were also compared.

Results

General Observations

The body colour of the “Sango pearls” was a strong reddish pink that was different from the Akoya CP (pinked) and freshwater cultured pearls, and its lustre was stronger than other pearls. On the surface, observed with a microscope, “Sango pearl” showed some pits. The nucleus of the “Sango pearl”, observed through the drill hole, was reddish while that of the Akoya CP was white. The Akoya CP showed a pinkish colour between the nucleus and the nacre, that might have be due to pinking. It was difficult to determine the presence of the nucleus in the purple freshwater CP but the inside of the pearl showed a reddish hue similar to the “Sango pearl” (Fig. 2). In UV testing, “Sango pearls” showed a chalky blue fluorescence, weaker than in the Akoya CP and stronger than in the freshwater CP. Under short wave, a chalky green was shown of a similar strength to that observed under long wave (Fig. 3).

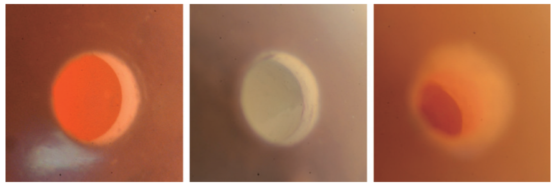

Fig. 2 The colour of the nucleus observed through the perforation (from the left “Sango pearl”, Akoya CP, freshwater CP).
從珠孔觀察：左起“Sango珍珠”、Akoya養珠、淡水養珠的珠核顏色

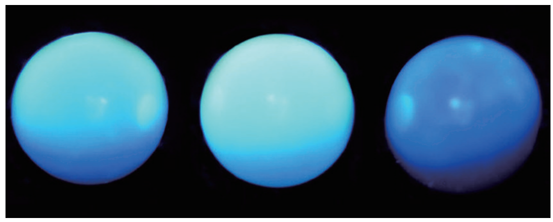

Fig. 3 Long wave UV fluorescence reaction (from the left “Sango pearl”, Akoya CP, freshwater CP)
紫外光長波熒光反應：左起“Sango珍珠”、Akoya養珠、淡水養珠

UV-Vis Spectra

Fig. 4 shows the UV-Vis spectra of pearls and corals in the region of 250~800nm. The absorption bands of “Sango pearls”, Akoya CP, and purple freshwater CP were different.

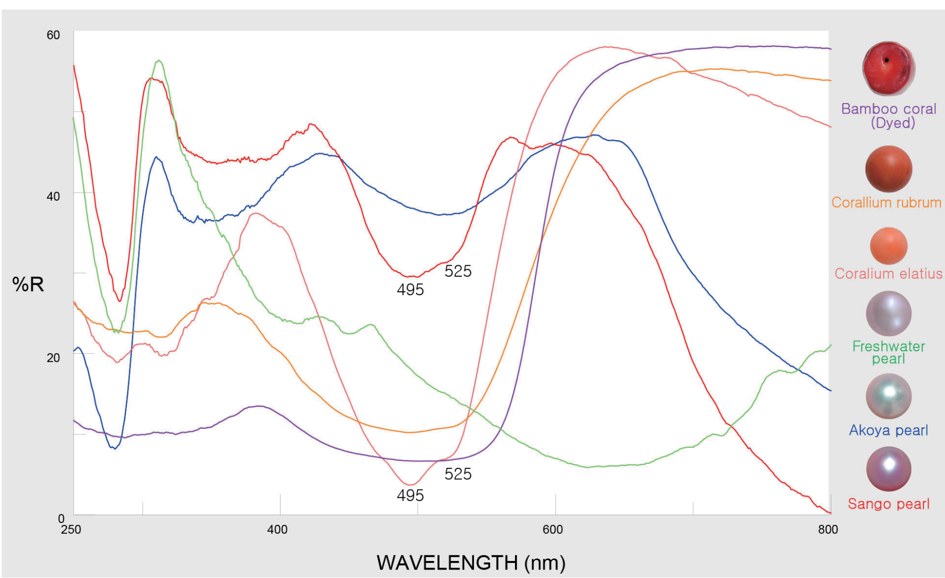

Fig. 4 The UV-Vis spectra of the “Sango pearl” and corallium elatius showed the gradual absorption at 495, 525nm.
“Sango珍珠”和桃紅珊瑚的紫外 - 可見光譜顯示在495, 525nm處逐漸被吸收

The "Sango pearl" had a weak absorption at 495 and 525nm. This absorption was fairly similar to corallium elatius but was not detected in corallium rubrum and dyed bamboo coral. The absorption at 495 and 525nm was detected in the pale reddish pink corals and was not detected in the reddish corallium rubrum (Fu et al., 2011). "Sango pearl" and corallium elatius had a similar absorption at 495 and 525nm, revealing that corallium elatius might be associated with the nucleus of "Sango pearls".

Raman Spectroscopy

There are various kinds of pink to red precious corals such as paracorallium japonicum, corallium rubrum, corallium elatius, corallium secundum etc. There are also red stylaster coral and melithaea to organic pigments. Many corals coloured by organic pigment have been studied. Karampelas et al. (2007, 2009) reported that the colour of both corallium genus and purple freshwater CP was ochracea, which are not categorized as precious corals. Bamboo coral is also dyed to imitate red precious coral. The colour of the natural pink to red-coloured corallium species is known to be due to unmethylated polyenic pigments and the pink to red colour of stylaster corals was caused by carotenoids. The molecular structure of these pigments was linear polyenic chains with alternating single and double bonds. In Raman spectra, peaks of C=C (v_1) and C-C (v_2) were observed near 1500cm^{-1} and 1130cm^{-1}, respectively. Carotenoids were structures in which four methyl groups were attached to the linear polyene structure, but unmethylated polyenes did not contain these methyl groups. Due to these differences, carotenoids had the C-C (v_2) peak at around 1155cm^{-1} and unmethylated polyenes were 1130cm^{-1} (Okamoto et al., 1984; Karampelas et al., 2007, 2009).

In order to determine the presence of pigments and to identify the substance used for the nucleus in the "Sango pearls", Raman spectroscopy was used (see Figs. 5 and 6). Fig. 5 showed the Raman spectra measured on the surface of the test pearls ("Sango pearl", Akoya CP, and purple freshwater CP). All samples had 701, 705 and 1085cm^{-1}, known as vibrations of the carbonate ions in the aragonite (Urmos et al., 1991). In the freshwater CP, 1511cm^{-1} (v_1) and 1127cm^{-1} (v_2) peaks related to the unmethylated polyene pigment were detected (Fig. 5).

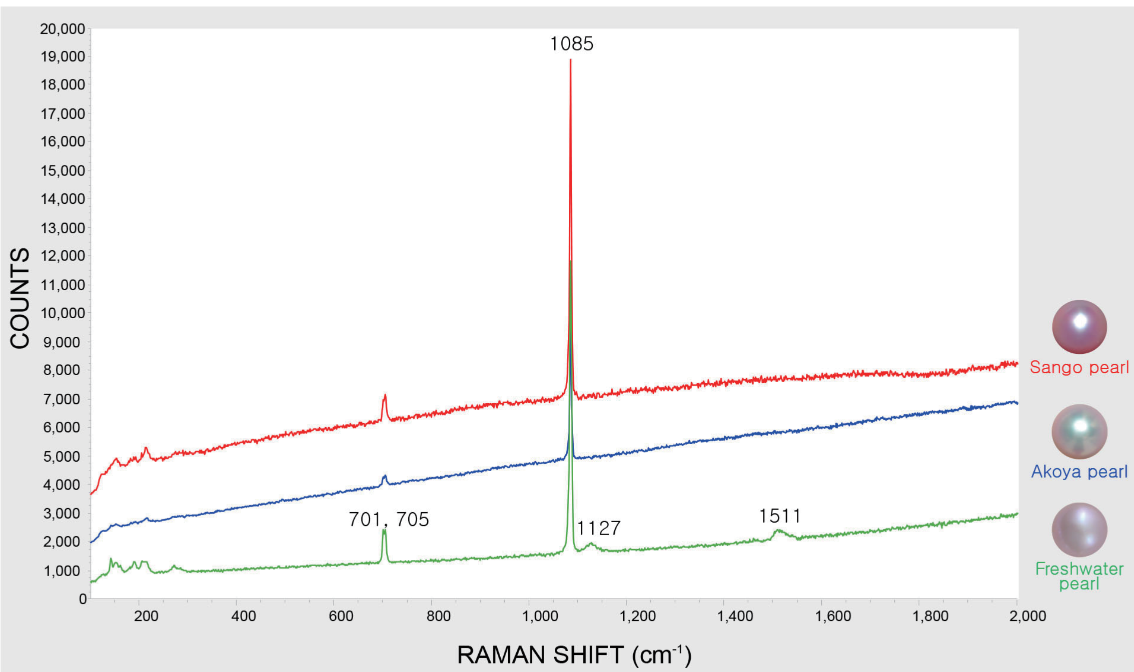

Fig. 5 Raman spectra of "Sango", Akoya, and freshwater CP. The "Sango pearl" only shows aragonite-related peaks in the surface area measurement.
"Sango珍珠"，Akoya和淡水養珠的拉曼光譜。"Sango珍珠"只在表面積測量中顯示與文石相關的吸收峰

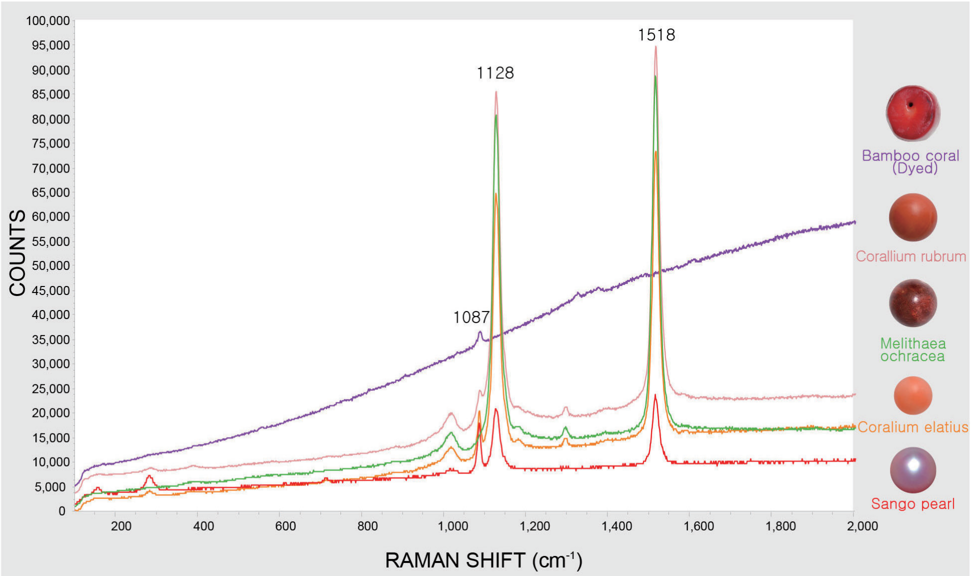

Fig. 6 Raman spectra of "Sango pearl", bamboo coral (dyed), corallium rubrum, melithaea ochracea, and corallium elatius. Organic pigment-related peaks were observed at 1128 and 1518cm^{-1} in the nucleus of the "Sango pearl"
"Sango珍珠"，竹狀珊瑚（染色），深紅珊瑚，紅扇珊瑚和桃紅珊瑚的拉曼光譜。在"Sango珍珠"的珠核中，於1128和1518cm^{-1}處觀察到與有機色素相關的吸收峰

Fig. 6 showed the Raman spectra of the exposed section of nucleus around the drill hole of the "Sango pearl", dyed bamboo coral, corallium rubrum, melithaea ochracea, and corallium elatius. Except for the dyed bamboo coral, all other samples had peaks at 1518cm^{-1} (v_1) and 1128cm^{-1} (v_2), related to unmethylated polyene pigment. A peak of 1087cm^{-1}, related to carbonate ions in calcite, was detected in all samples except melithaea ochracea. These results indicated that the nucleus used in the "Sango pearls" was similar to natural corallium rubrum and corallium elatius, and the red colour origin of "Sango pearl" was closely related to natural organic pigments.

Chemical Composition

EDXRF analysis detected the major element Ca, and trace amounts of Na, Mg and Sr in "Sango", Akoya and freshwater CP. There was no Mn in "Sango" and Akoya CP and Mn in freshwater

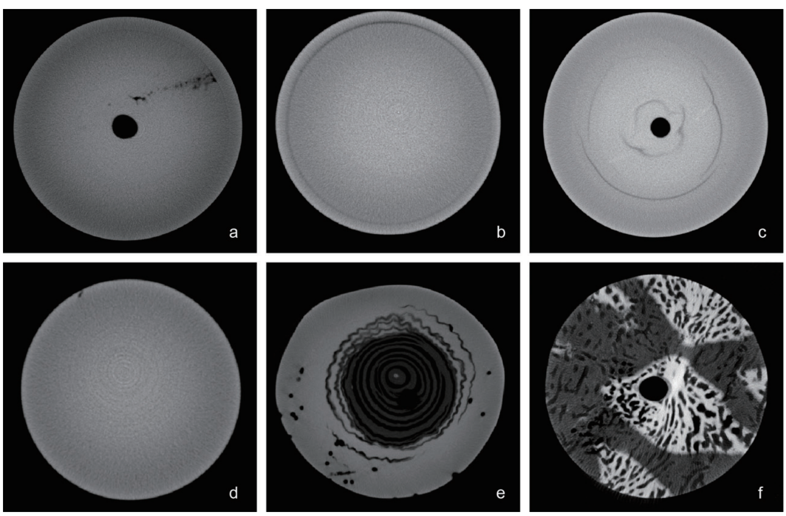

Fig. 7 "Sango pearl" (a) had a spot-like shadow partially in the nucleus, but this was not found in the Akoya CP (b), and the freshwater CP (c) was non-nucleated. Corallium elatius (d), bamboo coral (e), and melithaea ochracea (f) showed a distinct internal structure.
"Sango珍珠"(a)在珠核中有部分斑點狀的影子，但在Akoya養珠(b)中未有發現，而淡水養珠(c)未見珠核；桃紅珊瑚(d)、竹狀珊瑚(e)、紅扇珊瑚(f)顯示出獨特的內部結構

pearls. The concentration of Sr in the "Sango" and Akoya CP was higher than in the freshwater CP and the Ca/(Sr+Mg) ratio in the "Sango" CP was lower than in Akoya CP.

Internal Structures

The results of micro CT scanning of the "Sango", Akoya, and freshwater CP showed that the nacre of the "coral pearl" was about 0.35mm at the thinnest part and 0.50mm at the thickest part, which was thicker than Akoya CP (0.25~0.40mm). The peculiar thing was that there were many spot-like shadows in the "Sango pearl" not found in the Akoya CP. This was presumably due to the cavities commonly found in coral (Fig. 7). The CT image of the nucleus inside the "Sango pearl" was distinctly different from that of the bamboo coral, melithaea ochracea. In particular, the melithaea ochracea had a porous structure with a remarkable difference in shade. If bamboo coral or melithaea ochracea were to be used as the nucleus for CP, the CT scan would be an effective method of identifying the nucleus (Fig. 7).

Conclusion

In the gemmological observations made, the "Sango pearl" showed a stronger reddish pink body colour than the other pearls, and the nucleus observed through the drill hole showed redness. The strength of UV fluorescence of the "Sango pearl" was about halfway between the Akoya and freshwater CP. However, these characteristics alone could not be a decisive criterion for distinguishing these pearls. Analytical characteristics were investigated using various analytical instruments. In EDXRF analysis, the Ca/(Sr+Mg) ratio of the "Sango pearl" was lower than that of the Akoya CP. Sr in the "Sango pearl" was higher than that in the freshwater CP and Mn was not detected. This meant that the "Sango pearl" was a marine pearl. In UV-Vis spectroscopy, the "Sango pearl" and corallium elatius had the characteristic broad band at around 495, 525nm, which was not observed in other pearls. This suggested that the beads used for the nucleation of "Sango pearl" were similar to corallium elatius. Also, Raman spectroscopic analysis confirmed calcite, which was the main component of coral and the colour origin of pink to red corallium was related to the organic pigments (1128, 1518cm^{-1}), so it could be assumed that it was a natural red coral. In the internal nuclear observations using micro CT, we could see that the shadows of the "Sango pearl" were different from the shades of bamboo coral and melithaea ochracea. Therefore, it could be concluded that the nuclei used in "Sango pearl" were the natural pale red corallium species.

The Raman study was the most effective in determining the material and treatment of the nuclei used. However, Raman spectroscopy only provides analysis several micrometers deep on the surface, it was therefore difficult to analyze the inner nucleus surrounded by nacre. This "Sango pearl" could be analyzed because there was a slightly exposed nucleus around the drill hole, but in some cases a destructive analysis may be necessary. It is undesirable to destroy and analyze submitted gemstones, and this is a problem to be solved in the future.

[One might ask if it is necessary to support the destruction of endangered species such as red corals to produce pearl bead nuclei. Ed]

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