X-ray luminescence, a valuable test in pearl identification

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Abstract: *The increasing similarity of structures encountered in natural pearls and beadless freshwater cultured pearls requires one or more additional criteria for their differentiation. The majority of natural pearls are from saltwater oysters; in contrast, most beadless cultured pearls come from freshwater mussels. For some time it has been known that freshwater pearls produce luminescence under X-rays, whereas pearls grown in saltwater do not. The reason is because freshwater nacre contains traces of manganese. By using a sensitive camera this visible luminescence can be recorded and displayed on a monitor. The beads (from freshwater nacre) in Japanese saltwater cultured pearls (Akoya) also react to the X-ray excitation and may shine through the cultured overgrowths that are relatively thin. The method is used as an additional test and is not an alternative for X-radiograph images.*

Keywords: *freshwater nacre, Mn in aragonite, pearl identification, X-ray luminescence*

Pearl identification

Natural and beaded cultured pearls

In testing pearls, natural and cultured pearls are usually differentiated using X-ray shadow graphs (Lorenz and Schmetzer, 1986). X-ray shadowgraphs provide the most meaningful images to enable identification. Drill hole investigation by endoscope is now a historic method as needles for this technique are no longer available. A modern successor to the endoscope has been produced in a few prototypes (Atalay, 1994) and works with a red laser light. The proof for a bead in a cultured pearl is most efficiently detected by good radiography. With small beads and thick overgrowths, however, an X-ray shadowgraph will rarely show evidence of a bead. The Laue method is then a supplementary method when the presence of a nacre bead should be checked (Barnes, 1944). The method depends on interpreting the patterns obtained from unfiltered X-ray radiation directed on a bead consisting of well ordered layers of aragonite platelets (Barnes, 1944; Hänni, 1983). Six-spot patterns or four-spot patterns (Webster, 1994, p.547) may appear, depending on the direction of the ray with respect to the layers of an aragonite bead nucleus. Should the bead be of amorphous or unordered crystalline material, the

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pattern obtained would have no definite point structure, e.g. it may have a blurred halo or ring. A recent bead material manufactured form the giant clam shell (*Tridacna*), produces haloes on lauegrams when the X-ray beam is parallel to the growth layers. Perpendicular to the growth layers, clear four point patterns are visible. In any case, direct radiography (X-ray shadow method) is the preferred method to distinguish natural pearls from cultured pearls with a bead, either on fine-grained film or by digital imaging.

The growth structures of natural pearls as seen on X-radiographs have been known for many years; they reflect the individual growth development of each pearl (Alexander, 1939; Hänni, 2002). Characteristically there is an approximately round central body (formed by conchiolin-rich columnar calcite) coated by a more or less thick overgrowth of nacre formed by minute scales of tabular aragonite in concentric array. The X-radiographs of the aragonite coating can show concentric or bow-shaped lines.

Most natural pearls (all oriental pearls) derive from marine oysters, and the majority of beadless cultured pearls form in freshwater mussels. When there is no indication of a bead, a first separation of the two types can thus usually be made on the basis of whether nacre is saltwater or freshwater. A number of authors have already reported that freshwater nacre has an elevated concentration of manganese compared to saltwater nacre (Komatsu, 1987; Gutmannsbauer, 1992, 1994). Mn-doped calcium carbonate, including aragonite, possesses a characteristic luminescence when excited with X-rays or cathode rays (Waychunas, 1998). Freshwater nacre shows a characteristic fluorescence in whitish yellow (Lorenz and Schmetzer, 1985). In a recent publication Hänni *et al.* (2004) have demonstrated the usefulness of Mn-related X-ray luminescence in pearl identification.

Beadless cultured pearls

In the past the identification of beadless cultured pearls was straightforward because their radiography showed clear indications of their origin. The distinctive features on the film consist of a curved fine line or tangle of lines in the centre of the pearl, being the image of a complex central cavity, often empty or containing brown organic material. Note that the organic material is not the tissue transplant, as often reported. The tissue transplant grows into the pocket which is later the pearl sac, producing and containing the cultured pearl. However, these central features in older freshwater beadless cultured pearls are no longer as clear and large in the newer Chinese freshwater beadless cultured pearls. Smaller tissue parts are being transplanted and more years are allowed for the growth of the pearl. Because of the smaller graft the first pocket on whose surface the calcium carbonate is precipitated is also smaller. Any resulting cavity in the cultured pearl would be minute and would most probably be eliminated by the drilling process. Other growth features in the near-round to round Chinese freshwater cultured pearls may exist but are not always clearly visible in a random position of the pearl, although wavy growth lines or dividing lines have been shown by Scarratt *et al.* (2000). Beadless saltwater cultured pearls may show central cavities, too. Two cases may be discussed:

1. If the oyster has expelled the first bead, but the tissue graft still forms a pearl sac, a beadless cultured pearl can result. In the trade, beadless cultured saltwater pearls (South Sea and Tahiti) are often called 'Keshi'. There is no need and it is rather incorrect to call these products 'Keshi'. Originally Japanese Keshi cultured pearls were mantle pearls produced by accidental injury to the mantle of Akoya oysters. The term should definitely not be used for cultured pearls in gonad-grafted oysters.
2. If, after the first pearl crop, a second bead is inserted and the oyster expels it, the pearl sac, ready for further production, collapses, with nothing there to support it. Consequently, the shape of the second cultured pearl is very baroque, usually flattened. There is no need to call it 'Keshi' either, it is just a beadless cultured pearl. This kind of beadless Tahiti or South Sea cultured pearl is relatively simple to identify with an X-radiograph.

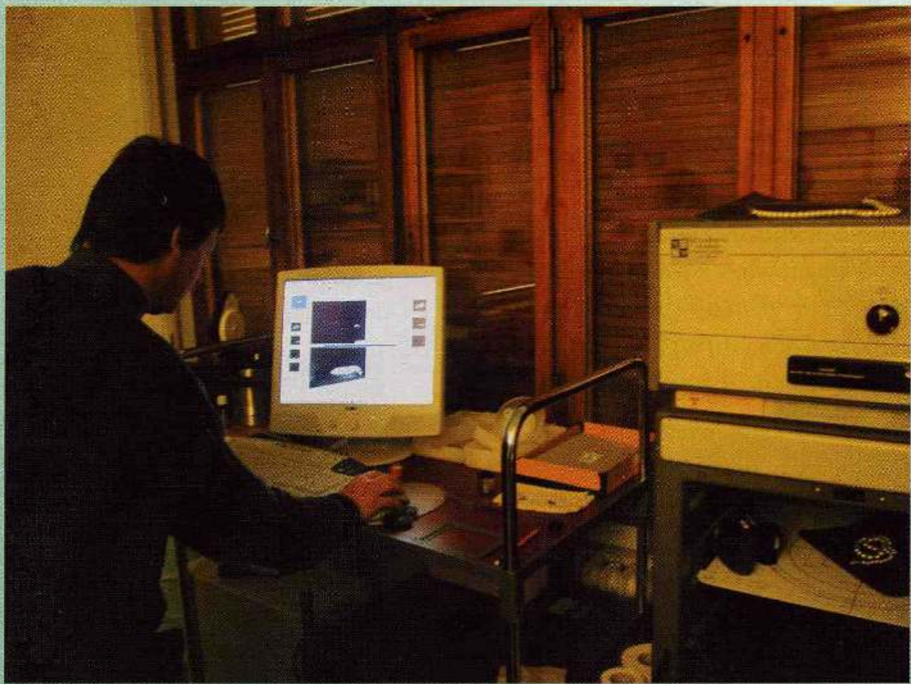

Figure 1: Working situation with X-ray apparatus, CCD camera and screen. A pearl necklace is ready in the X-ray chamber, the camera F-View II is visible. Photo H.A. Hänni © SSEF Swiss Gemmological Institute.

Investigation of the X-ray luminescence of nacre

For the observation of X-ray luminescence it could be sufficient to look at the objects in the dark when they are under X-ray excitation were it not for health and safety requirements. Since X-rays scatter and reflect off surfaces, it is absolutely necessary that the observer is protected from any of the rays which might reach the body. The excitation has thus to be made in a conventional X-ray cabinet, i.e. a conventional device for X-radiography with an observation window of lead glass. Safety is then guaranteed. The tungsten tube is operated at 95 kV and 4 mA. Instead of just looking at the effect, we propose here the use of a very sensitive digital camera system which records the luminescence pictures. The low intensity light emitted requires a special CCD camera and a computer programme (AnalySIS) which manages the recording. Preliminary experiments have proven the validity of the commercially available viewing system 'F-View II' by Soft Imaging Systems (*Figure 1*). The camera is equipped with a Peltier element that cools the detector. This provides low noise and the signals produce excellent pictures. The software allows easy control of the system and picture management (*Figure 2*). Since the camera is very sensitive to light, only low light is

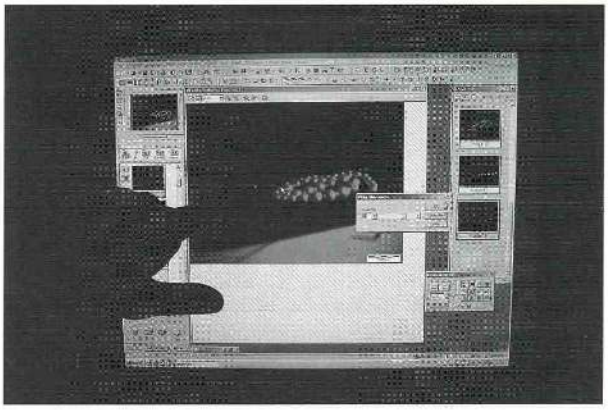

Figure 2: A pearl necklace, ready in the X-ray chamber, is pictured in room light and shown on the screen. The management and recording of images are done with a special programme. Photo H.A. Hänni © SSEF Swiss Gemmological Institute.

Figure 3: *A strand of South Sea cultured pearls from Australia (right) and a strand of freshwater cultured pearls from China (left) in the weak room light supplied by a diode. Photo P. Giese © SSEF Swiss Gemmological Institute.*

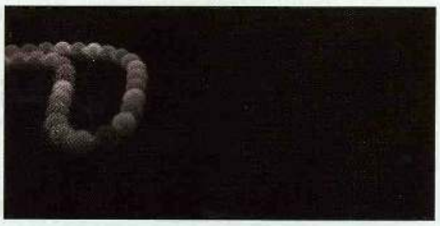

Figure 4: *The same necklace as in* Figure 3 *under X-ray excitation. The South Sea cultured pearls (from saltwater) do not show any luminescence while the freshwater cultured show clear luminescence. Photo P. Giese © SSEF Swiss Gemmological Institute.*

needed to provide the first reference picture, and a diode was chosen, already fixed in the sample room. A second picture of the pearls in the same position was then taken under X-rays. *Figures 3* and *4* show a strand of Australian saltwater cultured pearls with thick overgrowths on the beads, next to a strand of beadless Chinese freshwater cultured pearls for comparison.

When Akoya cultured pearls are tested it becomes apparent that the bead which is made of shell grown in freshwater, also gives a luminescence reaction to the X-ray excitation. Depending on nacre thickness and the amount of organic material on each bead, different amounts of light may be registered (see *Figures 5* and *6*). The luminescence reaction may also be inhibited when pearls are dyed with dark colours or beaded cultured pearls have naturally pigmented overgrowths as e.g. from Tahiti or Mexico – although even in these examples, response can be variable.

No luminescence reaction appears with *Tridacna* (giant clam shell) beads, since this shell material grows in saltwater and does not contain the Mn which causes the luminescence.

Conclusions

X-rays cause weak luminescence in freshwater nacre or pearls. This effect is due to a weak concentration of manganese. Since nacre or pearls from saltwater are free of manganese, luminescence does not occur. The luminescence is only visible in the dark, either by the naked eye or with a sensitive CCD digital camera. This is an additional means of differentiation between freshwater and saltwater pearls and cultured pearls where X-ray features are not sufficient. Since Chinese freshwater cultured pearls are taking an increasing share of the market, possibilities of mixing them up with South Sea

Figure 5: *An Akoya cultured pearl necklace (freshwater nacre beads with saltwater nacre overgrowth) in room light, ready in the X-ray apparatus for a luminescence picture. Photo P. Giese © SSEF Swiss Gemmological Institute.*

Figure 6: *The Akoya cultured pearl necklace shown in* Figure 5 *recorded under X-ray radiation. Depending on the thicknesses of the overgrowths, a different luminescence is visible in different pearls, indicating that Mn is present in the beads. Photo P. Giese © SSEF Swiss Gemmological Institute.*

cultured pearls or with natural marine pearls are growing. Since pearl identification may be increasingly problematic, especially when only X-radiographs are considered, the observation of X-ray luminescence will be most useful for testing strands with a mixture of different types of pearls, and the attribution of pearls of a different type within a strand can be made with more confidence. The method is limited when nacre is rich in colouring pigment which generally suppresses the luminescence. This can occur with naturally coloured as well as with dyed pearls.

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