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CULTURED PEARLS FROM THE GULF OF CALIFORNIA, MEXICO

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Black pearls have been found in Mexico's Gulf of California since the area was settled more than 2,000 years ago. Attempts at culturing pearls in this area have met with varying success over the past century. Today, a pearl farm in Guaymas is producing commercial quantities of mabe as well as bead-nucleated full-round cultured pearls from the indigenous pearl oyster *Pteria sterna*. This article provides an overview of the history of natural and cultured pearls from Mexico, describes pearl culturing at the Guaymas farm, and focuses on the properties of bead-nucleated cultured pearls from *P. sterna*. These cultured pearls have a brown or gray to dark gray bodycolor with various interference colors caused by the stacking of platy aragonite crystals and organic matter. One indication of their natural color (and their Mexican provenance) is a red fluorescence to long-wave UV radiation.

The history of pearls from the Gulf of California is as fascinating as the pearls themselves (figure 1) and has been described by various authors over the years (e.g., George, 1971; Cariño and Monteforte, 1995; Strack, 2001; McLaurin Moreno, 2002; McLaurin Moreno and Arizmendi Castillo, 2002). Therefore, only a brief historical summary, based on these sources, is given here.

The first European to visit the "Sea of Pearls" (another name for the Gulf of California) was Captain Fortun Jiménez, a Spanish explorer sent by famed *conquistador* Hernán Cortés, who in 1533 observed native people wearing large dark pearls. From that time until the early 20th century, the history of Baja California was closely connected with the recovery of these pearls, which for decades were more important exports than gold, silver, or spices.

For more than 300 years, European and Mexican entrepreneurs harvested fine dark natural pearls from the Gulf of California with rudimentary diving techniques. The introduction of the diving suit in the late 19th century made it possible to reach new pearl oyster beds at greater depths. Eventually, though, overfishing led to the total depletion of the beds and brought pearl fishing to a halt.

In 1903, Gastón Vivès founded the first pearl farm on the Baja California peninsula in the bay of La Paz. The oysters and equipment were either confiscated or destroyed in July 1914, as a consequence of the Mexican Revolution. The company harvested approximately 1.5 million pearl oysters (*Pinctada mazatlanica*) in each of the last three years of its operation (Cáceres-Martinez and Chávez-Villalba, 1997), 9–11% of which yielded natural pearls.

By the 1930s, the oyster beds in the Gulf of California had recovered sufficiently that pearls could again be found. However, these oysters were not *P. mazatlanica* but rather the rainbow-lipped *Pteria sterna*, which produced smaller pearls of unusual color. Then, in 1936, virtually all the oysters began inexplicably dying off, starting in the north. To protect the remaining beds, the Mexican government banned pearl fishing in 1939, but unfortunately this did not stop the death of the oysters. The die-offs would remain a mystery for another

See end of article for About the Authors and Acknowledgments.

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Figure 1. Attractive cultured pearls are now commercially available from the Gulf of California. The cultured pearls shown here range from 9.5 to 10.5 mm in diameter. Courtesy of Colombia Gem House; photo © GIA and Harold & Erica Van Pelt.

three decades, until it was suggested that the construction of the Hoover Dam in early 1936 had held back enough of the Colorado River to deplete the nutrients flowing into the Gulf of California and greatly disturb its salinity (Alvarez-Borrego, 1983). In recent years, there have been only a few reports of natural pearls from this area (e.g., Crowningshield, 1991; Hurwit, 1992; Wentzell, 1995).

Around 1966, two pearl farms in the Gulf of California began cultivating both *P. mazatlanica* and *P. sterna* with the aim of producing cultured pearls. However, it is only in the past 10 years that two commercial pearl farms have opened. The more significant of these, Perlas del Mar de Cortez (Pearls from the "Sea of Cortez," as the gulf is also known), is located in Guaymas (see Ladra, 1998). This pearl farm has the larger production and is the more technically advanced. To the best of our knowledge, it is the only facility in Latin America that cultures full-round pearls. One of the authors visited this farm in 2000 (see Kiefert, 2002). With the assistance of two staff members (DMM and EA), we have prepared this description of the farm and, primarily, its full-round cultured pearls, as well as obtained new gemological and spectroscopic data that enable them to be distinguished from Tahitian and treated-color cultured pearls. This study concentrates on the full-round cultured pearls from *P. sterna*, since they are much more valuable than the mabe product and because *P. mazatlanica* production is currently for research purposes only; cultured pearls from this oyster are not available commercially.

BACKGROUND OF THE SEA OF CORTEZ PEARL

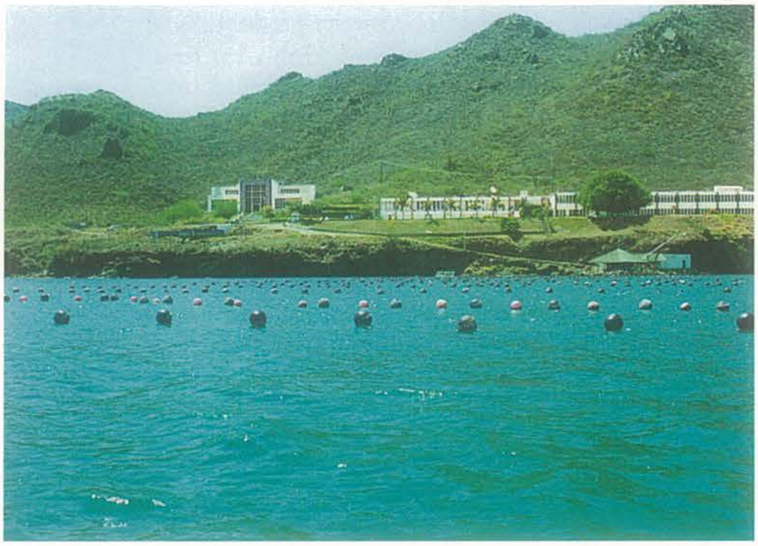
Pearl Oyster Biology. Pearl oysters are mollusks belonging to the family *Pteriidae*, which includes two genii capable of producing high-quality mother-of-pearl shell: *Pinctada* and *Pteria*. There are fewer than 40 species of pearl oysters worldwide (Shirai, 1994), and of these just three are responsible for about 99.9% of the world's production of saltwater cultured pearls: the Akoya (*Pinctada fucata martensii* or *Pinctada imbricate*), the black-lipped oyster *Pinctada margaritifera*, and the silver/gold-lipped oyster *Pinctada maxima*. Another saltwater oyster commonly used for commercial pearl production is the mabe-gai or penguin-wing oyster *Pteria penguin*, which is used solely for the production of mabe or half-round blister pearls.

Pearl oysters have separate sexes (although any individual oyster may change sex, known as *protandric hermaphrodism*) and breed by external fertilization. Clouds of gametes, sperm, and eggs are released into the water, so fertilization occurs randomly. Once fertilization takes place, several free-swimming larval stages develop; eventually, the juvenile will settle on an appropriate hard substrate (rock, coral, or shell). This entire process takes 18–34 days depending on water temperature and other factors. Once the juveniles settle, growth is rapid. During the first year, an oyster can reach 7 cm in length. It takes 18–24 months for the oysters to reach 8.5–10 cm, which is the desired size for pearl seeding (McLaurin Moreno and Arizmendi Castillo, 2002).

Figure 2. The Perlas del Mar de Cortez pearl farm in Guaymas, Sonora, is located on Bacochibampo Bay in the Gulf of California.

Pearl oysters usually grow in colonies from the low-tide mark to depths of 20 m and attach themselves to the substrate by a tuft of strong fibers (called the byssus). They feed by continuously filtering minute particles and organisms with their gills (branchia), which are adapted to both breathing and feeding (McLaurin Moreno and Arizmendi Castillo, 2002).

Figure 3. The pearl farm is situated on coastline owned by the campus of the Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM) in Guaymas. Buoys mark the location of "long lines," from which the oyster cages are suspended. Photo by Lore Kiefert, © SSEF.



Within the Gulf of California, there are two species of native pearl oysters: the Panamic black-lipped pearl oyster *Madreperla* (*P. mazatlanica*) and the rainbow-lipped pearl oyster or *Concha Nácar* (*P. sterna*). Both species inhabit the Sonora coastline as a part of their natural distribution, but both can also be found along Mexico's Pacific coast, except that *P. mazatlanica* is not present on the western side of southern Baja California. *P. mazatlanica* can reach lengths of 20 cm, and has long been considered by many authors to be a variety or subspecies of *P. margaritifera*, the black-lipped oyster of the Indo-Pacific (Shirai and Sano, 1981). *P. sterna* can reach lengths of 16 cm, and has a more concave shell than either *P. mazatlanica* or *P. margaritifera*. The nacre of *P. sterna* has a more iridescent multicolored hue, with a metallic sheen unequalled by any other pearl oyster. It belongs to the "winged oyster" variety, thought by some (e.g., Shirai and Sano, 1981) to be unable to produce full-round (bead-nucleated) cultured pearls. While Perlas del Mar de Cortez has produced full-round cultured pearls from both oyster species, the commercial production is entirely from *P. sterna*, which yields richer and more varied colors than *P. mazatlanica*.

Location and Access. The Perlas del Mar de Cortez farm is located in Bacochibampo Bay, some 8 km from the port town of Guaymas, Sonora (figure 2), on coastline owned by the Guaymas campus of the Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM; figure 3). This privately owned and operated technological university has campuses across Mexico. Guaymas may be reached by air (a direct flight from Phoenix, Arizona); by land (a four-hour drive from Nogales, Arizona), or an eight-hour ferry ride from Santa Rosalia, on the Baja California peninsula. Once in Guaymas, any taxi can take the visitor to the university (known locally as "Tec de Monterrey"). The pearl farm is open to visitors, who may take a free tour of the facilities. Eight thousand visitors, most of them from the U.S., come every year.

Bacochibampo Bay is a typical marine bay, with little influence of freshwater (consisting mainly of rainfall runoff). The bay has a diversity of ecological niches: sand, gravel, and rocky bottoms provide a rich environment. Most of the bay is shallow (average depth 7 m), but near its mouth it deepens abruptly (to 20 m), creating yet another marine environment.

Because of the Gulf of California's subtropical climate, summer months (June to September) are usually hot and dry, with an average water temperature of 29°C (84.2°F), a range of 27–32°C (80.6–89.6°F), with considerable evaporation. Winter months are characterized by much cooler average water temperatures of 19°C (66.2°F), with a range of 15–25°C (59–77°F), due primarily to the strong northwest winds that create upwelling along the Sonoran coastline. This movement of cold, nutrient-rich water masses from the deep ocean to surface levels allows for the high production of chlorophyll, which is necessary for the survival of pearl oysters.

Company Structure and Facilities. In 1993, ITESM researchers Sergio Farell, Manuel Nava, and two of the present authors (DMM and EA) began developing an economically and technically feasible pearl culture methodology. This group subsequently was responsible for the first commercial harvest of cultured mabe pearls in North America (in 1995) and the production of the first bead-nucleated cultured pearls utilizing *P. sterna*. Increased funding from ITESM in 1996 led to a project known as ITESM/Perlas de Guaymas, which served mainly to assist with pearl culture in Mexico and promote the resulting products in the local and world markets. In 2000, this branch of the aquaculture department was converted into a separate private company, Perlas del Mar de Cortez, which is still linked to the university.

The pearl farm encompasses a lagoon of 2 hectares (5 acres) for collecting spat and culturing the pearl oysters. A thatched-roof structure, or *palapa*, houses the land-based operations, and a small pearl-culture structure shelters the seeding operations and an X-ray apparatus. Pearl oyster production depends solely on juveniles gathered from "spat collectors" (mesh bags on which pearl oyster larvae settle) deployed within the bay. The abundance of pearl oyster larvae in Bacochibampo Bay is largely a result of the adult oysters in the pearl farm, since they are able to release their eggs and sperm directly into the sea where fertilization takes place. Thus a positive cycle develops where the more adult pearl oysters there are under culture, the more juveniles can be collected. Wild adult pearl oysters also contribute to larvae production but are never removed from the natural beds, since the 1939 Mexican federal fishing ban (mentioned above) remains in effect.

Figure 4. Juvenile P. sterna *oysters are cultivated in various types of cages, according to their age. Photo by Lore Kiefert, © SSEF.*

The oysters are housed in various cages according to their age and size (figures 4 and 5); these are hung from buoy-supported surface "long-lines." The cages are suspended at depths of 3–4 m. The largest number of oysters being cultivated at any one time is approximately 250,000. At the time of this writing, there were no plans to expand the size of the operation, although short-term plans are to increase the yield of cultured pearls, using the same number of oysters, through technical improvements.

Pearl seeding operations take place from October to early March, when the water temperature is below 25°C. As many as five seeding technicians can work simultaneously, using nuclei made from the shells of *Unionidae* family freshwater mussels from the Tennessee River.

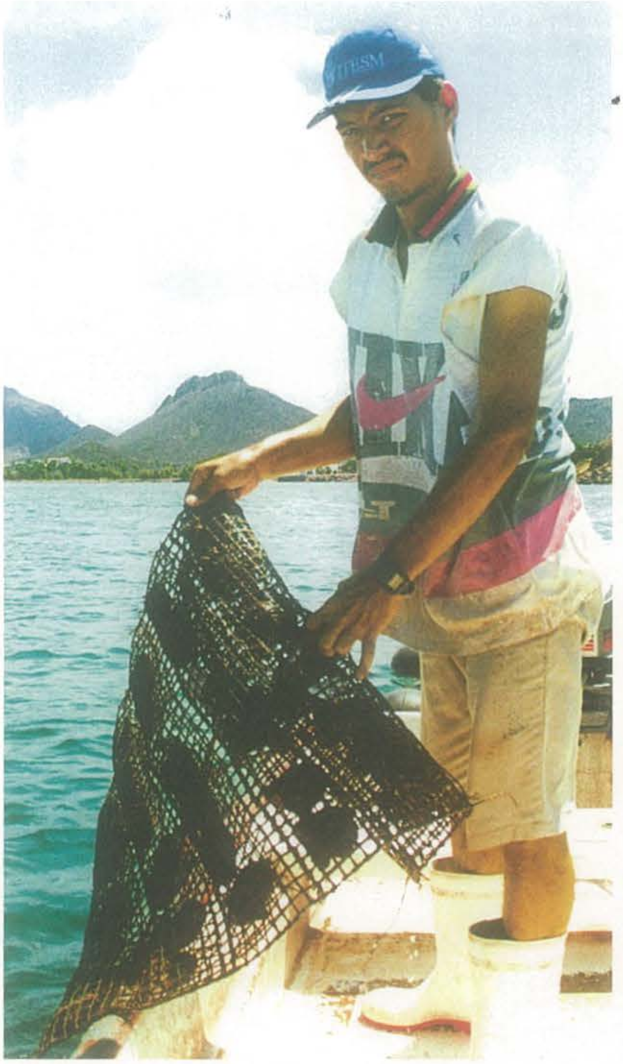


Figure 5. After bead nucleation, the oysters are suspended in flat cages. Photo by Lore Kiefert, © SSEF.

Harvesting and Production. The results of the pearl culturing operation are unpredictable. There are no reliable methods to predetermine quality of the product, although Perlas del Mar de Guaymas uses two methods to monitor it. The first is X-ray examination of all the oysters, eight weeks after implantation. With this method, one can ensure that the oyster has not rejected the bead, and that the bead is located in the correct area of the animal's body. Oysters not meeting these criteria are considered "rejects," but they can be used to culture mabe pearls by opening the shell, pushing back the mantle, and attaching a mabe implant with cyanoacrylate ("super glue"). The second method involves several random samplings in order to better evaluate the development of the cultured pearls.

There is only one harvest per year, which takes place 18–20 months after seeding, typically in June when the water temperature rises. While other pearl oysters are sometimes reseeded with a larger bead, *P. sterna* oysters are shucked (their flesh removed) at the first harvest. This is because reseeding is very difficult and the resulting cultured pearls are, although larger, not as lustrous or colorful (Nava et al., 2000). Natural pearls and "keshi" (beadless cultured pearls formed due to rejected beads or injured mantle tissue) are occasionally found; both are used in jewelry. The shell is fashioned into buttons, while the oyster meat is sold locally.

P. sterna "keshi" are small (2–8 mm) and typically have baroque shapes (figure 6). Natural pearls usually are caused by drill-worms and worm-cysts. These pearls tend to be smaller and rounder than the "keshi." They can be distinguished during harvest because most grow within a very thin and delicate pearl sac found in the oyster's mantle. Typically, a half-dozen to a dozen good-quality natural pearls are obtained yearly.

The first dozen experimental full-round cultured pearls were shown during the February 1996 Tucson gem show. Since then, production has grown to about 4,000 cultured pearls per year, with improvements in size, shape, and surface quality evident each year. In the 2001 harvest, the average size was 7.5 mm, and only 5% were round or near-round; the other 95% were baroque. By 2002, average size had increased to 8.9 mm and some 25% were round or

Figure 6. A variety of shapes is seen in these "keshi" cultured pearls (up to 8 mm long) from the rainbow-lipped oyster P. sterna. Photo by Lore Kiefert, © SSEF.

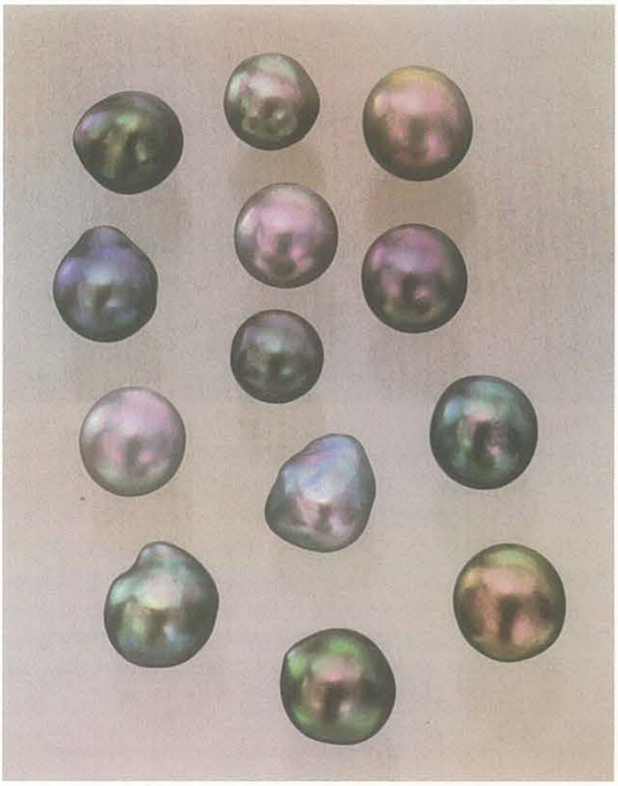


Figure 7. These cultured pearls (9.0–11.5 mm in diameter) illustrate the range of colors and shapes that are commercially available from Mexico's Gulf of California. Courtesy of Columbia Gem House; photo © GIA and Harold & Erica Van Pelt.

near-round. Starting in 2005, production is expected to stabilize at 10,000 cultured pearls (10 kg) per year.

Processing and Marketing of the Sea of Cortez Pearl. After harvesting, the full-round cultured pearls are placed in containers of fresh water, then drained and washed several times under running water. They are patted dry in a soft cotton towel and placed in a receptacle with mineral oil for about six hours, after which they are removed and blotted with a paper towel.

Approximately half of the cultured pearl production is mounted in jewelry by Mexican artisans and sold at the farm site and other tourist destinations. The marketing of these cultured pearls is managed primarily by the producing company, but the main distributor in the U.S., Columbia Gem House (Vancouver, Washington), is becoming a leading participant. The main goal of the marketing effort is to highlight differences between Mexican and Tahitian black cultured pearls. The Mexican product exhibits a greater diversity of color (figure 7), and prevailing colors may vary from year to year. Future goals include development of a stable price structure with wholesalers, while avoiding overproduction.

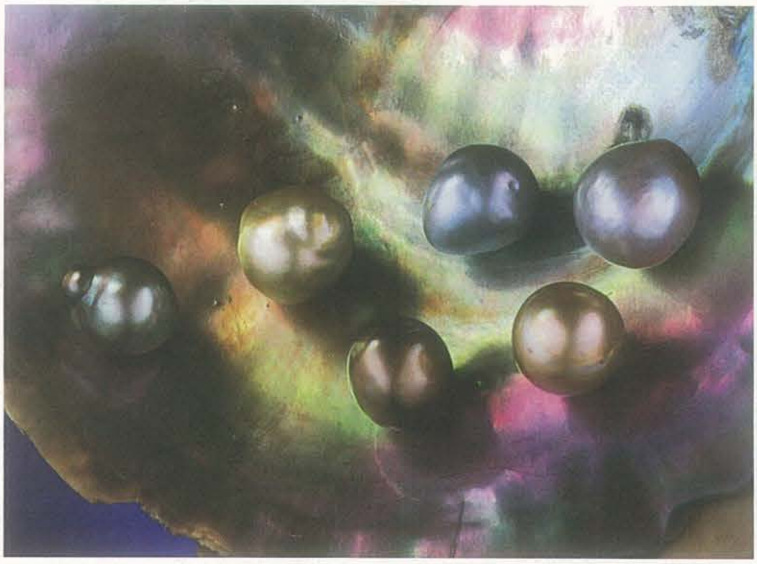
MATERIAL AND METHODS

For this study, 20 shells, 50 full-round cultured pearls (approximately 7–12 mm), and 11 "keshi" (4.5–8.3 mm long), all from *P. sterna* and farmed by Perlas del Mar de Cortez, were examined at SSEF. Additionally, two *P. sterna* shells and three full-round cultured pearls from the same farm were studied at GIA for comparison (figure 8). All of the samples tested were obtained in 2000. The samples consisted of various colors and qualities; 10–15% represented the commercial quality seen in the jewelry trade, whereas the others were rejects due to thin nacre layers and surface blemishes.

Forty-two of the full-round cultured pearls and 10 of the "keshis" were X-rayed using a Hewlett-Packard X-ray unit and Agfa Industrex X-ray film. Specific gravity of 20 cultured pearls was determined hydrostatically. All the cultured pearls were tested for reaction to both long- and short-wave UV radiation with a System Eickhorst UV lamp.

Scanning electron microscopy of five shell sections was performed at the University of Basel

Figure 8. Three of the P. sterna *cultured pearls shown here were analyzed at GIA (i.e., the "golden," gray, and dark brown samples in the center, 6.7–8.2 mm in diameter). Note the similarity in their colors to portions of the* P. sterna *shell (GIA Collection no. 30488). Photo by Maha Tannous.*



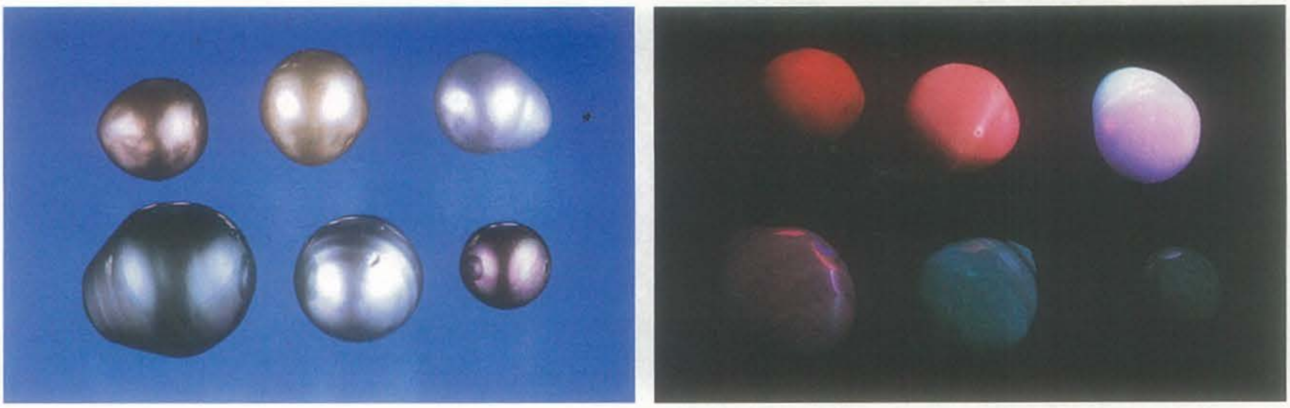


Figure 9. When exposed to long-wave UV radiation, the Mexican cultured pearls (top row; 6.7–8.2 mm in diameter) typically showed a weak to distinct red fluorescence. In contrast, the Tahitian cultured pearls examined (bottom left and center) fluoresced bluish gray and slightly reddish brown, and the dyed Akoya cultured pearl (bottom right) was inert. Natural Mexican pearls have fluorescence reactions similar to their cultured counterparts. Photos by Maha Tannous (left) and Shane Elen (right).

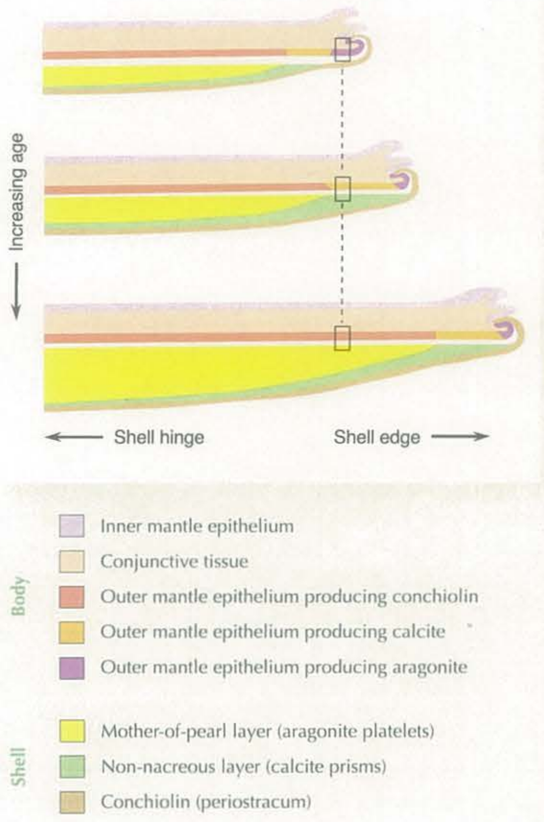
(ZMB SEM laboratory) with a Philips ESEM XL 30 FEG instrument, and the surface of one cultured pearl was imaged with the camera connected to a Raman microscope.

Reflectance spectra of 12 cultured pearls and one piece of shell were acquired in the visible and UV range (between 290 and 800 nm) with a Hitachi U4001 spectrophotometer at SSEF. Three cultured pearls and one piece of shell were characterized at GIA with the same type of instrument; luminescence spectra were also collected at GIA with an SLM Aminco AB2 luminescence spectrometer, using 360 and 400 nm excitation.

The chemical composition of six cultured pearls was determined qualitatively with a Tracor Spectrace 5000 energy-dispersive X-ray fluorescence spectrometer (EDXRF) at SSEF.

Raman spectra of six other cultured pearls and a piece of shell were recorded at SSEF with a Renishaw Raman System 1000 spectrometer, equipped with a CCD-Peltier detector and argon-ion laser (514 nm).

Figure 10. This drawing shows the succession of materials (conchiolin, calcite prisms, aragonite platelets) that are deposited by the oyster's mantle tissue. Within a particular location (as indicated by the boxes) the production of the various materials changes with the passage of time. Mother-of-pearl (aragonite platelets) is the last material to form. © SSEF, 2004.



RESULTS

Physical Properties. The colors observed in the Mexican cultured pearls consisted of a brown or gray to dark gray bodycolor with overtones of violet, blue, yellow, and green, also called orient. The size of the cultured pearls depended mainly on the size of the implanted bead, and varied between approximately 7 and 11 mm. The larger samples often contained a cavity, occasionally with a loose bead. X-ray images showed the same pattern as for Akoya and other cultured pearls (Hänni, 1995, 1997, 2002; Strack, 2001): The round bead, which

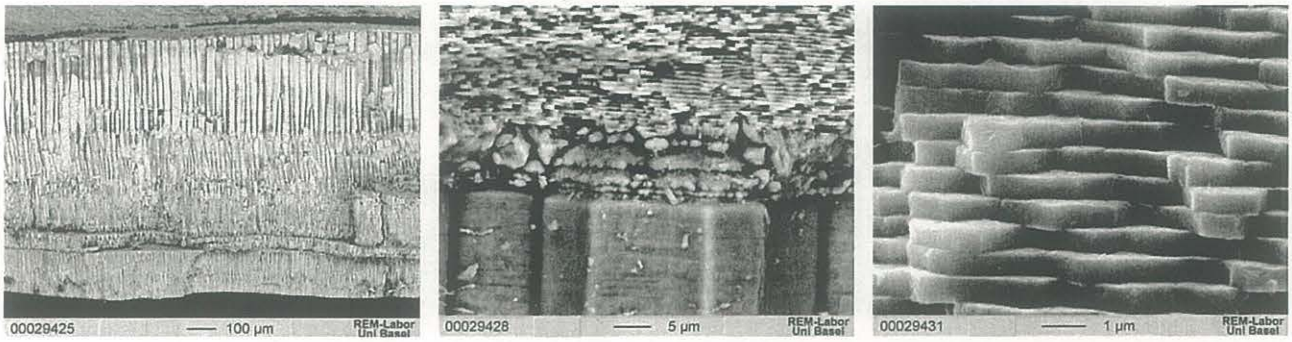


Figure 11. These SEM images show the microstructure of a shell section from P. sterna. *As seen in the image on the left, most of the shell is composed of columnar calcite with subordinate tabular growth (aragonite). At higher magnification (center) the transition from columnar to tabular growth is plainly visible; the left side of the aragonite shows a more irregular growth pattern than the right side. The image on the right provides a closer look at the stacked aragonite "tiles" of the nacre, which are approximately 500 nm thick.*

usually appeared lighter in the image, was surrounded by a concentric, somewhat darker layer of nacre. Nacre thickness of the commercial-quality cultured pearls X-rayed at SSEF varied between 0.8 and 1.2 mm. For the irregular and larger cultured pearls (semi-baroque or baroque), a dark, mostly irregular layer was visible on the X-ray image between the bead and the nacre, which indicated either a cavity or a layer of organic material.

For the most part, the "keshis" were baroque shaped and had a gray bodycolor with vivid overtones of violet, blue, yellow, and green. As with most "keshis," the X-ray images of these samples frequently showed an irregular cavity in the center, which was surrounded by a relatively thin layer of nacre.

The full-round cultured pearls without a cavity had a specific gravity between 2.45 and 2.76, while the S.G.'s of those with a cavity were much lower, between 1.54 and 2.17. These values are below that of pure aragonite (2.94) and varied according to the presence of organic matter and/or cavities.

The vast majority (about 95%) of the cultured pearls analyzed showed a weak to distinct red fluorescence to long-wave UV radiation (figure 9).

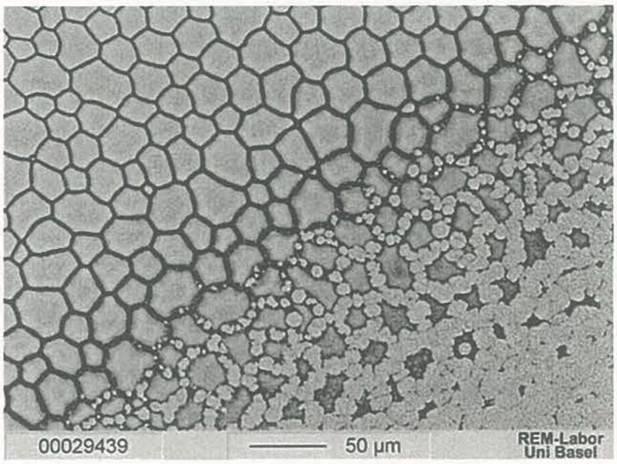
Microstructure. Shell sections from *P. sterna* were used to study the construction of the strongly iridescent nacre in a manner similar to that used later by Liu et al. (2003). SEM images revealed that the shell showed the same succession of $CaCO_3$ components from outside to inside as other *Pinctada* and *Pteria* shells (Wise, 1970; figure 10): Columnar calcite was overlain by tabular aragonite (figure 11), and this was confirmed by Raman spectroscopy. A transition from columnar calcite to tabular aragonite also could be seen on the surface of the shell's interior (figure 12), with the aragonite tiles initially deposited at the ends of the calcite columns.

The microstructure of *P. sterna* nacre is shown in figure 11 (center and right). The average thickness of the aragonite tablets was 500 nm, which is comparable to the wavelength of green light.

The scales of aragonite tiles that form the nacre surface of a cultured pearl are shown in figure 13. In places, the aragonite scales revealed spiral arrangements (figure 14).

Reflectance Spectroscopy. The top spectrum in figure 15 shows a typical UV-Vis reflectance spectrum of the Mexican *P. sterna* cultured pearls. An absorption band appears at around 400–405 nm, which can be attributed to porphyrins (Britton,

Figure 12. This SEM image of a P. sterna *shell's inner surface shows the polygonal pattern created by columnar calcite (upper left), which is overgrown by tabular aragonite (lower right).*



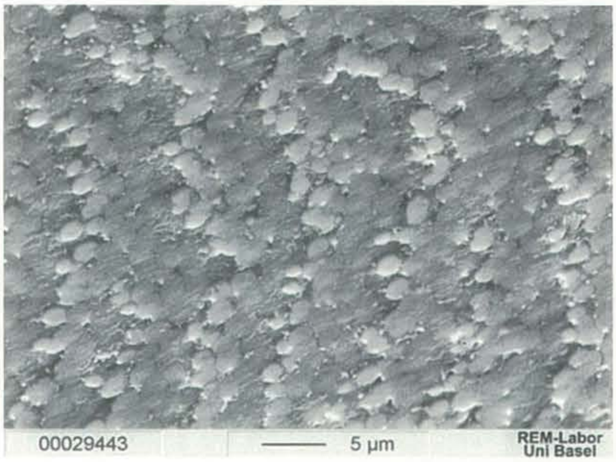


Figure 13. The aragonite tiles shown in this SEM image of the surface of a cultured pearl are responsible for the gritty sensation when it is rubbed against a tooth.

1983). This absorption is also present in black Tahitian cultured pearls (see bottom spectrum in figure 15). However, the distinctive absorption maximum at 700 nm in the Tahitian product is not present in the UV-Vis spectrum of Mexican cultured pearls. There are other more subtle differences in these spectra, as well.

Luminescence Spectrometry. Luminescence spectrometry of a cultured pearl revealed a broad fluorescence feature at 618 nm and a weaker one at 678 nm (figure 16). These features are the source of the red fluorescence, and are stronger than those recorded in dark-colored *P. margaritifera* cultured pearls (Elen, 2001). In the latter, the weaker peak at 678 nm is often not present (again, see figure 16).

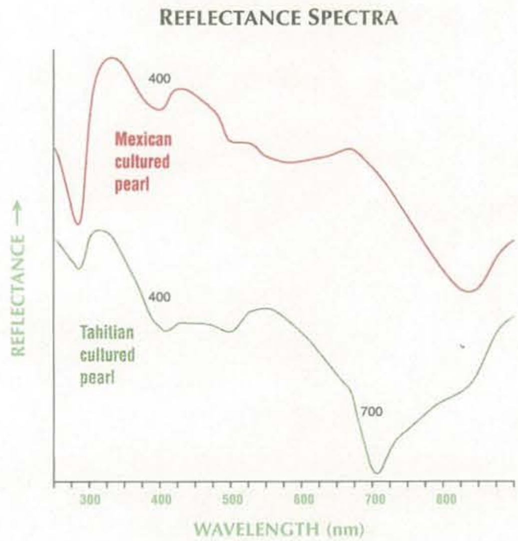
Chemical Composition. The chemical composition of the Mexican cultured pearls resembled that of other saltwater cultured pearls, with Ca as the main element and traces of Sr. The Mn content was below the detection limit of EDXRF analysis, which is expected for saltwater cultured pearls (Gutmannsbauer and Hänni, 1994).

Raman Spectroscopy. Raman spectra of the *P. sterna* shell and the cultured pearls showed a strong increase in fluorescence from 1000 cm^{-1} toward higher wavenumbers, with aragonite bands at 210, 705, and 1084 cm^{-1} that were weak due to the overall high fluorescence of the samples. Between 1100 and 1800 cm^{-1} were several broad bands centered at approximately 1260, 1320, and 1565 cm^{-1}, which are attributed to various types of organic matter such as conchiolin and porphyrin (figure 17, top).

Figure 14. Note the spiral patterns formed by the aragonite layers on the surface of this Mexican cultured pearl. Photomicrograph by Lore Kiefert, © SSEF; magnified 100×.

The intensity of these bands increased with the intensity of the color. The Raman spectrum of a black Tahitian cultured pearl shows similar features (figure 17, bottom).

Figure 15. The UV-Vis reflectance spectrum of a Tahitian P. margaritifera *cultured pearl (bottom) shows a typical absorption feature at 700 nm, which was absent from the Mexican* P. sterna *cultured pearls studied (top).*



DISCUSSION

Cause of Color. A dark bodycolor in cultured pearls is produced by layers of conchiolin (and porphyrin) that are found between the layers of aragonite (cf. Wentzell, 1998). The iridescence has been attributed to the microstructure (i.e., layering) of the aragonite tiles and organic matter (Wada, 1981; Gauthier and Ajaques, 1989; Liu et al., 2003). The violet, blue, yellow, and green iridescent overtones seen in the Mexican cultured pearls are produced by interference, as light passes through and is reflected from the alternating thin layers of aragonite and conchiolin (Fritsch and Rossman, 1988). The iridescent colors exhibited by our samples are very similar to those of natural pearls from the Gulf of California (Cariño and Monteforte, 1995) and, in some cases, comparable to the colors of natural abalone pearls (e.g., Wentzell, 1998).

The calcite and aragonite constituents are produced by the same external mantle tissue, but at different times. This observation and explanation is in agreement with Lowenstam and Weiner (1989), Gutmannsbauer and Hänni (1994), and Hänni (2002). Figures 11 and 12 illustrate how the first aragonite tiles were deposited at the ends of the calcite columns. Scanning electron micrographs of the *P. sterna* shell sections revealed that the average thickness of an aragonite tablet was 0.5 μm (or 500 nm), which is comparable to the wavelength of green light. Thus, the layers are spaced appropriately to cause interference phenomena and produce iridescence. The aragonite layers are mostly parallel, but there are also areas that are slightly irregular (figure 11). This wavy structure has been observed previously in abalone shells, which also show very strong iridescence (Hänni, 2002). It is therefore possible that this structure may provide an additional cause of iridescence in shell and cultured pearl samples from *P. sterna*.

As mentioned above, both the shells and the cultured pearls contained a certain amount of conchiolin and porphyrin. Conchiolin is a fibrous protein, and porphyrins are naturally occurring tetrapyrrole pigments. While such organic network structures are essential for the formation of the individual aragonite tiles, we could observe no traces of them in our SEM images. This is probably due to the high water content of this organic material, which dries out and shrinks when removed from the water. Porphyrin occurrence in mollusk shell can often be detected by a red, pink, or reddish brown fluorescence to long-wave UV radiation or blue light (Comfort, 1949), which also produces a fluorescence emission around 620 nm (Miyoshi et al., 1987a,b). Similar red fluorescence was documented in our samples.

The presence of porphyrin and conchiolin was also evident in the Raman spectra of the cultured pearls, where several broad bands centered at approximately 1260, 1320, and 1565 cm^{-1} can be observed. Reference spectra of one type of porphyrin (i.e., uroporphyrin) taken by one of the authors (SE)

Figure 16. With 365 nm excitation, the luminescence spectrum of a typical P. sterna *cultured pearl from Mexico shows features at 618 and 678 nm due to porphyrins. The luminescence spectrum of a typical* P. margaritifera *cultured pearl taken under similar conditions reveals a much weaker emission at 618 nm and no evidence of the 678 nm feature.*

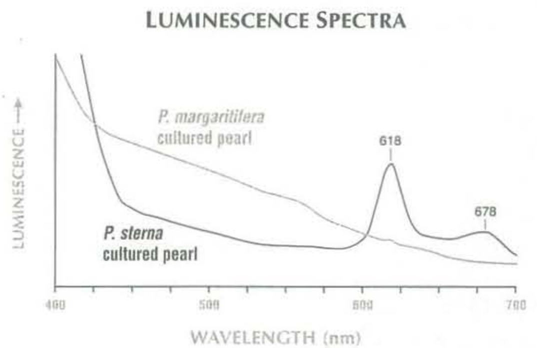
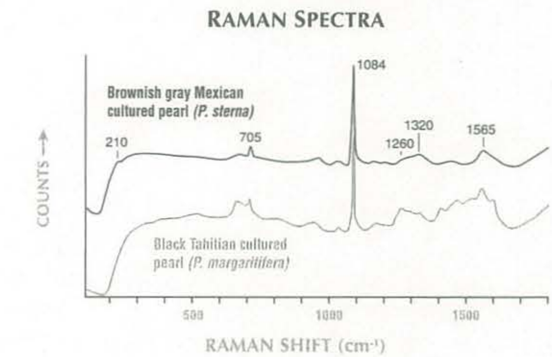


Figure 17. The similarity in the Raman spectra of Mexican cultured pearls (top) and black Tahitian cultured pearls (bottom) is the result of the presence of porphyrin as a coloring pigment in both. The spectra have been baseline-corrected to eliminate the fluorescent effect.



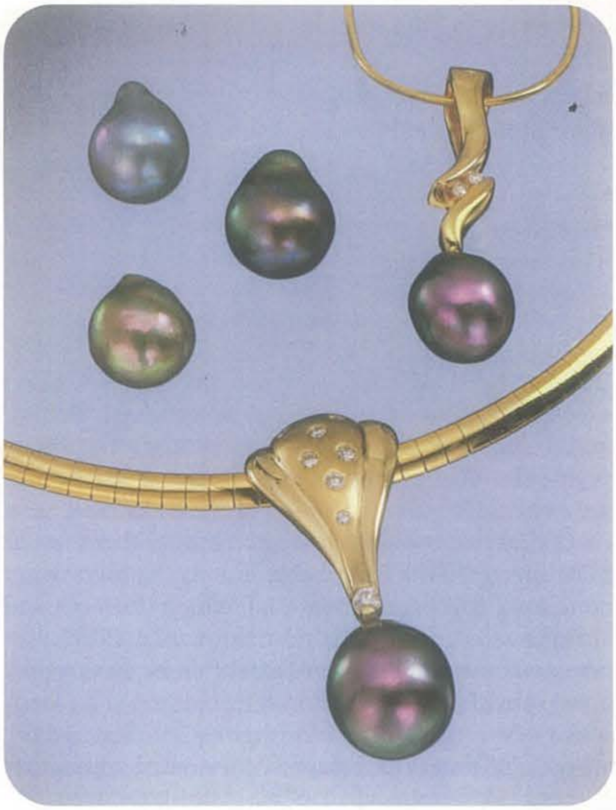


Figure 18. The cultured pearls produced in Mexico by the rainbow-lipped oyster P. sterna *show brown or gray to dark gray bodycolors and attractive iridescence. Interesting baroque shapes as well as spherical products are available, as shown by these cultured pearls shown loose (up to 12.5 mm long) and in 18K gold jewelry. Courtesy of Columbia Gem House; photo © GIA and Harold & Erica Van Pelt.*

contain these bands, but other organic materials also have such features in the same region. The bands attributed to organic matter increased with the intensity of the bodycolor. Porphyrin has been described as a coloring pigment in Tahitian cultured pearls from *P. margaritifera* (Gauthier and Ajaques, 1989; Iwahashi and Akamatsu, 1994) as well as for *P. sterna* (S. Akamatsu, pers. comm., 2003). This explains the similarity between the Raman spectra of these two varieties of cultured pearls (figure 17).

Separation from Tahitian Cultured Pearls. The red long-wave fluorescence shown by the Mexican cultured pearls is not seen in Tahitian cultured pearls, which are typically inert to slightly reddish brown (Elen, 2002; figure 9). Porphyrins are among the most highly fluorescent compounds in nature (Guilbault, 1990), and according to Hurwit (1992; 2000), red fluorescence is a characteristic feature of pearls from the Gulf of California.

Usually the presence of porphyrins also results in an intense absorption feature between 390 and 425 nm, depending on the exact structure of the porphyrin present. This absorption is known as the B band, or Soret band, after its discoverer (Britton, 1983). In the case of *P. sterna* from Mexico, it was observed that this absorption feature appears around 400–405 nm, and exposure to this wavelength of light will produce strong fluorescence from the porphyrin in the shell or cultured pearls.

The most significant difference in the reflectance spectra of *P. sterna* and *P. margaritifera* is the absence of the 700 nm absorption feature for *P. sterna*. This absorption is characteristic of *P. margaritifera* (figure 15; see also Goebel and Dirlam, 1989; Iwahashi and Akamatsu, 1994; and Elen, 2002).

Separation from Artificially Colored Black Pearls. Since the full-round cultured pearls from the Sea of Cortez are similar in size to Akoya cultured pearls and are also bead-nucleated (unlike black dyed or irradiated Chinese freshwater cultured pearls), it is important to identify their color authenticity. Attempts to produce black colors in Akoya cultured pearls with silver nitrate were undertaken as early as the 1930s in Japan (Strack, 2001). This treatment is still being done, although a number of other methods of artificial coloration have been developed (McClure and Smith, 2000; Strack, 2001). Silver nitrate treatment is relatively easy to detect, either through X-ray imaging, where a white line due to the absorption of X-rays by the silver nitrate is visible between the bead and the nacre, or through X-ray fluorescence, where silver is detected. Another method of identifying silver nitrate treatment is Raman spectroscopy, which reveals a band at 240 cm^{-1} (Kiefert et al., 2001) that does not occur in black cultured pearls of natural color (see figure 17).

Other treatments, such as irradiation or organic dye, are much harder to identify. One identification tool is the fluorescence to long-wave UV radiation. The red fluorescence typical of natural (Cariño and Monteforte, 1995) and cultured pearls from the Gulf of California is not seen in those artificially colored by organic dye or irradiation, which are either inert or display a weak white fluorescence.

CONCLUSIONS

As a commercial source of black cultured pearls, the Gulf of California is relatively unknown compared to Tahiti. Natural pearls from the Gulf of California have been highly valued since the times of the Spanish conquerors, but they have been extremely rare for many decades. At the end of the 1990s, pearl culturing in the Gulf of California achieved commercial status for the first time. The full-round cultured pearls from this area are produced by the rainbow-lipped oyster *P. sterna*, and possess an attractive brown or gray to dark gray bodycolor with various overtones (figure 18). They are marketed directly through sales offices in Mexico and at the Tucson gem show; the main U.S. distributor is Columbia Gem House. Since these cultured pearls are similar in size to Akoya cultured pearls, which are often artificially colored black, it is important to know their distinguishing features.

As in other dark-colored cultured pearls, the bodycolor of those from the Gulf of California is produced by layers of conchiolin (and porphyrin) between the layers of aragonite, while the various hues and overtones are a product of light passing through and reflecting from alternating layers of aragonite and organic matter (mostly conchiolin, but also some porphyrin). Compared to black Tahitian cultured pearls, those from the Sea of Cortez have a wider variety of overtones, sometimes similar to colors found in abalone pearls.

The porphyrin present in the *P. sterna* cultured pearls produces a clearly visible red fluorescence when observed with long-wave UV radiation, while such strong red fluorescence is not observed in Tahitian cultured pearls. Another difference lies in the UV-Vis spectrum, with Tahitian cultured pearls exhibiting a strong absorption feature at 700 nm that is absent from Mexican cultured pearls. The presence of conchiolin and porphyrin may be detected with Raman spectroscopy, where bands between 1100 and 1800 cm^{-1} can be observed. These bands, as well as the red fluorescence, are not present in the spectra of artificially colored cultured pearls and therefore are indicative of natural color.

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REFERENCES

Alvarez-Borrego S. (1983) Gulf of California. In B.H. Ketchum, Ed., *Estuaries and Enclosed Seas*, Elsevier Science, Amsterdam, pp. 427–449.

Britton G. (1983) *The Biochemistry of Natural Pigments*. Cambridge University Press, Cambridge.

Cáceres-Martinez C., Chávez-Villalba J. (1997) The beginnings of pearl oyster culture in Baja California Sur, Mexico. *World Aquaculture*, Vol. 28, No. 4, pp. 33–38.

Cariño M., Monteforte M. (1995) History of pearling in La Paz Bay, South Baja California. *Gems & Gemology*, Vol. 31, No. 2, pp. 88–105.

Comfort A. (1949) Acid-soluble pigments of shells. I. The distribution of porphyrin fluorescence in molluscan shells. *Biochemical Journal*, Vol. 44, pp. 111–117.

Crowningshield R. (1991) Gem Trade Lab Notes: Pearls from Baja California. *Gems & Gemology*, Vol. 27, No. 1, p. 42.

Elen S. (2001) Spectral reflectance and fluorescence characteristics of natural-color and heat-treated "golden" South Sea cultured pearls. *Gems & Gemology*, Vol. 37, No. 2, pp. 114–123.

Elen S. (2002) Identification of yellow cultured pearls from the black-lipped oyster *Pinctada margaritifera*. *Gems & Gemology*, Vol. 38, No. 1, pp. 66–72.

Fritsch E., Rossman G.R. (1988) An update on color in Gems. Part 3: Colors caused by band gaps and physical phenomena. *Gems & Gemology*, Vol. 24, No. 2, pp. 81–102.

Gauthier J.P., Ajaques J.M. (1989) La perle au microscope électronique. *Revue de Gemmologie a.f.g.*, No. 99, pp. 12–17.

George C. D. (1971) The black pearls. History and development. *Lapidary Journal*, Vol. 25, No. 1, pp. 136–147.

Goebel M., Dirlam D.M. (1989) Polynesian black pearls. *Gems & Gemology*, Vol. 25, No. 3, pp. 130–148.

Guilbault G.G. (1990) *Practical Fluorescence*, 2nd ed. Marcel Dekker, New York.

Gutmannsbauer W., Hänni H.A. (1994) Structural and chemical investigations on shells and pearls of nacre forming salt- and fresh-water bivalve molluscs. *Journal of Gemmology*, Vol. 24, No. 4, pp. 241–252.

Hänni H.A. (1995) A short synopsis of pearls: Natural, cultured, imitation. *Journal of the Gemmological Association of Hong Kong*, Vol. 18, pp. 43–46.

Hänni H.A. (1997) Über die Bildung von Perlmutter und Perlen. *Gemmologie: Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 46, No. 4, pp. 183–196.

Hänni H.A. (2002) *Pearls*. SSEF Tutorial 1, Modern Gemmology.

CD-ROM, SSEF Swiss Gemmological Institute, Basel.

Hurwit K. (1992) Gem Trade Lab Notes: Black pearl from Baja California. *Gems & Gemology*, Vol. 28, No. 2, p. 126.

Hurwit K. (2000) Black cultured pearls from Baja California, Mexico. *GIA Insider*, Vol. 2, Issue 6, www.gia.edu/newsroom/issue/2798/1002/insider_newsletter_details.cfm#2.

Iwahashi Y., Akamatsu S. (1994) Porphyrin pigment in black-lip pearls and its application to pearl identification. *Fisheries Science*, Vol. 60, pp. 69–71.

Kiefert L. (2002) Zuchtperlen vom Golf von Kalifornien, Mexiko. *Gemmologie: Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 51, No. 2–3, pp. 121–132.

Kiefert L., Hänni H.A., Ostertag T. (2001) Raman spectroscopic applications to gemmology. In I.R. Lewis and H.G.M. Edwards, Eds., *Handbook of Raman Spectroscopy*. Marcel Dekker, New York, pp. 469–489.

Ladra D. (1998) Mexico revives pearl production. *Colored Stone*, Vol. 11, No. 6, pp. 38–41.

Liu Y., Hurwit K.N., Tian L. (2003) Iridescence of a shell of *Pteria sterna* (Gould 1851): An optical and structural investigation. *Gemmologie: Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 52, No. 4, pp. 145–150.

Lowenstam H.A., Weiner S. (1989) *On Biomineralization*. University Press, Oxford.

McClure S.F., Smith C.P. (2000) Gemstone enhancement and detection in the 1990s. *Gems & Gemology*, Vol. 36, No. 4, pp. 336–359.

McLaurin Moreno D. (2002) Mexico's pearling history. *Pearl World*, Vol. 10, No. 1, pp. 1–16.

McLaurin Moreno D., Arizmendi Castillo E. (2002) Five centuries of Mexican pearls. *Australian Gemmologist*, Vol. 21, No. 5, pp. 190–201.

Miyoshi T., Matsuda Y., Komatsu H. (1987a) Fluorescence from pearls to distinguish between mother oysters used in pearl culture. *Japanese Journal of Applied Physics*, Vol. 26, No. 4, pp. 578–581.

Miyoshi T., Matsuda Y., Komatsu H. (1987b) Fluorescence from pearls and shells of black-lip oyster, *Pinctada margaritifera*, and its contribution to the distinction of mother oysters used in pearl culture. *Japanese Journal of Applied Physics*, Vol. 26, No. 7, pp. 1069–1072.

Nava M., Arizmendi E., Farell S., McLaurin D. (2000) Evaluation of success in the seeding of round pearl nuclei in *Pteria sterna* (Gould 1851) a new species in pearl culture. *SPC Pearl Oyster Information Bulletin*, Secretariat of the Pacific Community, New Caledonia, December, pp. 12–16.

Shirai S. (1994) *Pearls & Pearl Oysters of the World*. Marine Planning Co., Nagano, Japan, 108 pp.

Shirai S., Sano Y. (1981) Report on the pearl resources, pearl oyster grounds and pearl culture around La Paz in Baja California, Mexico. *Journal of the Pacific Society*, October, pp. 5–23.

Strack E. (2001) *Perlen*. Rühle-Diebener Verlag GmbH & Co. KG, Stuttgart, 696 pp.

Wada K. (1981) Pearls. *Journal of the Gemmological Society of Japan*, Vol. 8, pp. 151–158.

Wentzell C.Y. (1995) Gem Trade Lab Notes: Blister pearl attached to shell. *Gems & Gemology*, Vol. 31, No. 1, pp. 55–56.

Wentzell C.Y. (1998) Cultured abalone blister pearls from New Zealand. *Gems & Gemology*, Vol. 34, No. 3, pp. 184–200.

Wise S.W. (1970) Microarchitecture and mode of formation of nacre (mother-of-pearl) in pelecypods, gastropods and cephalopods. *Eclogae Geologicae Helvetiae*, Vol. 63, pp. 775–797.