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IDENTIFICATION OF THE ENDANGERED PINK-TO-RED *STYLASTER* CORALS BY RAMAN SPECTROSCOPY

Stefanos Karampelas, Emmanuel Fritsch, Benjamin Rondeau, Aude Andouche, and Bernard Métivier

All corals within the Stylasteridae family (including the *Stylaster* genus) are listed in Appendix II of CITES; this means they are protected and their trade requires an export permit, unlike corals from the *Corallium* genus, which include most pink-to-red corals used in jewelry. Raman scattering demonstrates that corals from the *Stylaster* genus contain carotenoid pigments (polyenic pigments substituted with methyl groups), whereas those from the *Corallium* genus are colored by unmethylated polyenic pigments. Additionally, *Stylaster* corals are made of aragonite, whereas those from *Corallium* are composed of calcite. Through Raman scattering analysis, the fully protected *Stylaster* pink-to-red corals may be distinguished from this other type of gem coral.

In June 2007, delegates from 171 countries convened at The Hague to decide which species to include under the CITES (Convention on International Trade in Endangered Species of Wild Fauna and Flora) agreement. The aim of CITES is to ensure that international trade in plant and animal specimens does not threaten their survival. The species covered by the convention are listed in three appendices, according to the degree of protection they need. Appendix I includes species threatened with extinction, where trade is permitted only in exceptional circumstances. Species in Appendix II are not necessarily threatened with extinction, but their trade must be controlled to avoid use that would threaten their survival. Appendix III contains species that are protected in at least one country that has asked other CITES parties for assistance in controlling the trade.

The gemological significance of this triennial meeting is that corals from the *Corallium* genus, the most impor-

tant of all gem coral species, were being considered for protection under Appendix II (CITES, 2008a). Ultimately, it was decided not to include them. More recently, on April 8, 2008, China, which now has domestic laws to protect these species, requested that CITES include four *Corallium* species (*C. elatius*, *C. japonicum*, *C. konjoi*, and *C. secundum*) under Appendix III (Fish and Wildlife Service, 2008). Meanwhile, the Stylasteridae family, which includes all *Stylaster* gem corals (e.g., figure 1), remained listed under Appendix II of CITES (as of January 18, 1990), which means a certificate issued by the management authority from the country (or state) of export is required (CITES, 2008b).

Pink-to-red corals have been used for ornamental purposes for about 10,000 years (Liverino, 1989). According to Rolandi et al. (2005), there are two classes, Hydrozoa and Anthozoa, within the Cnidaria phylum (i.e., cnidarians) that have skeletons durable enough for use in gem materials and carvings. These two classes each contain a family (Stylasteridae and Coralliidae, respectively) that together yield the majority of pink-to-red coral species used for ornamentation (Pienaar, 1981; Rolandi et al., 2005; Smith et al., 2007). Most corals found in the

Figure 1. These orangy pink cabochons (12 × 12 × 5 mm) were fashioned from *Stylaster* coral. No evidence of dye or impregnation was detected in these specimens. Photo by B. Rondeau.

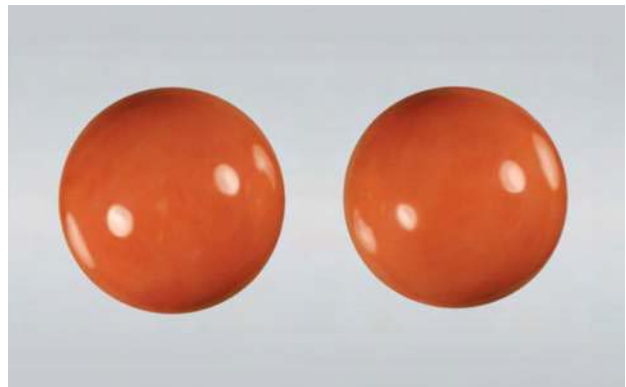




Figure 2. This early 15th century Portuguese reliquary holding a fragment of the Holy Cross features red *Corallium* coral. The piece measures 53.2 cm tall and 20.0 cm wide. Courtesy of Museu Nacional de Machado de Castro, Coimbra, Portugal; collection no. MNMC 6036, © DDF/IMC.

market today are from the *Corallium* genus, including the prized “ox-blood” (dark red; figure 2) and “angel-skin” (light pink; figure 3) colors.

Corals from the *Corallium* genus are found in waters throughout the world—notably the Mediterranean Sea and the Atlantic, Pacific, and Indian Oceans—as are corals from the *Stylaster* genus (e.g., Pienaar, 1981; Rolandi, 1981; Rolandi et al., 2005; Smith et al., 2007; CITES, 2008a). *Stylaster* corals (sometimes referred to as “lace” corals; figure 4) are typically impregnated and/or dyed and may be used as a substitute for *Corallium*—mostly as beads and cabs. In such forms, it is sometimes difficult to precisely identify any coral by routine gemological examination. *Stylaster* corals are also found with natural purple and violet coloration (e.g., *S. californicus* and *S. subviolaceus*).

Careful observation of the structural features found in the *Stylaster* and *Corallium* genera may be useful in identifying the particular species of a coral jewel. *Stylaster* corals typically contain surface pores (again, see figure 4) that are arranged in circular patterns called cyclo-systems (Pienaar, 1981; Rolandi, 1981; Rolandi et al., 2005). Corals from the *Corallium* genus typically have striated or scalloped structures (Smith et al., 2007).

The specific gravity of coral ranges from 2.37 to 2.75, and it is strongly dependent on the porosity of the individual piece. The refractive indices of both calcitic and aragonitic corals are a function of their calcium carbonate configuration. RI is also influenced by the magnesium content of calcitic corals and the strontium content of aragonitic corals (Rolandi et al., 2005). Because corals from these two genera can be difficult to separate using only classical

Figure 3. The pink *Corallium* coral in this 6-cm-tall clip is set with emerald, amethyst, and diamond. Courtesy of Van Cleef & Arpels.





Figure 4. Corals of the Stylasteridae family, such as this pink specimen of the species *Stylaster roseus* (sample no. 1; other portions of this same specimen were red) are protected by CITES. Note the distinctive surface pores of this “lace” coral. Courtesy of MNHN, Paris (Collection no. MNHN-Hyd.0000-0001); photo by S. Karampelas, image width 9 cm.

gemological methods, the present study explores their identification based on Raman scattering analysis.

Materials and Methods. This study was carried out on seven pink-to-red coral specimens from the collections of the Muséum National d’Histoire Naturelle (MNHN; National Museum of Natural History) in Paris and the Centre de Recherche Gemmologique (CRG; Center for Gemmological Research) in Nantes. Two of the samples (nos. 1 and 2) belong to the *Stylaster* genus, and the other five (nos. 3–7) to the *Corallium* genus. See table 1 for their

detailed taxonomy, color description, and geographic origin. All seven specimens were represented as being of natural color, and this was verified by standard gemological examination (i.e., microscopic observation and fluorescence to UV radiation). Note that we could not obtain a group photo of the samples because we did not have access to all of them at the same time.

We recorded Raman scattering spectra with a Jobin Yvon T64000 spectrometer coupled with an Olympus microscope at the University of Nantes. The study used an excitation laser emitting at 514 nm (argon ion laser), with a power of 2 mW and a resolution of 1 cm^{-1} at room temperature. A low-power laser was selected to avoid destroying the corals’ fragile organic matter. For samples with varying color distribution, spectra were taken in different-colored areas as identified by the spectrometer’s microscope (50 \times magnification). The analyzed areas measured about $2 \times 2 \mu\text{m}$. Measurements were repeated at least twice in the same area to ensure reproducibility. Exposure time was 240 seconds.

Results and Discussion. Raman spectra of two light pink corals of different species, *Corallium secundum* and *Stylaster sanguineus*, in the 1600–600 cm^{-1} range are presented in figure 5. In the *C. secundum* spectrum, two bands at ~ 1088 and 714 cm^{-1} correspond to the ν_1 symmetric and ν_4 in-plane bending of carbonate ions (CO_3^{2-}) in calcite, respectively (Urmos et al., 1991). The two bands at ~ 1520 and 1130 cm^{-1} are characteristic of unmethylated polyenic pigments; they are assigned, respectively, to C–C (ν_1) and C=C (ν_2) stretching (Merlin and Delé-Dubois, 1986; Karampelas et al., 2007).

Polyenes (or polyacetylenes, cited here as *unmethylated polyenes*) are organic compounds that contain several sequences of alternating double and single carbon-carbon bonds (i.e., a polyenic chain). Polyenic molecules can have

TABLE 1. Taxonomy^a, color range, and geographic origin of the seven coral samples.

Sample no.	Class	Order	Family	Genus and species	Color range	Geographic origin	Collection ^b
1	Hydrozoa	Anthoathecatae	Stylasteridae	<i>Stylaster roseus</i>	Light pink to red	Unknown	MNHN
2	Hydrozoa	Anthoathecatae	Stylasteridae	<i>Stylaster sanguineus</i>	Light to dark pink	Pacific Ocean (Hawaiian Islands)	MNHN
3	Anthozoa	Alcyonacea	Coralliidae	<i>Corallium rubrum</i>	Light to dark red	Mediterranean Sea (southern France)	CRG
4	Anthozoa	Alcyonacea	Coralliidae	<i>Corallium rubrum</i>	Light to dark red	Mediterranean Sea (southern France)	CRG
5	Anthozoa	Alcyonacea	Coralliidae	<i>Corallium rubrum</i>	Light to dark pink	Unknown	MNHN
6	Anthozoa	Alcyonacea	Coralliidae	<i>Corallium rubrum</i>	Light to dark red to orange	Atlantic Ocean (Republic of Senegal)	MNHN
7	Anthozoa	Alcyonacea	Coralliidae	<i>Corallium secundum</i>	Light to dark pink	Pacific Ocean (Hawaiian Islands)	MNHN

^aTaxonomy follows the Integrated Taxonomic Information System, www.itis.gov (Phylum: Cnidaria).

^bMNHN = Muséum National d’Histoire Naturelle (Paris); CRG = Centre de Recherche Gemmologique (Nantes, France).

various substitutions at their terminations. The general chemical formula of these compounds is $R-(\text{-CH=CH-})_n\text{-R}'$ (where n = number of double bonds, and R and R' = end groups; Merlin and Delé-Dubois, 1986; Karamelas et al., 2007). We obtained similar results for different areas in all the samples within the *Corallium* genus (ν_1 : $1130 \pm 5 \text{ cm}^{-1}$; ν_2 : $1520 \pm 10 \text{ cm}^{-1}$). Raman peaks at the same positions have been documented in the spectra of other *Corallium* species (see Merlin and Delé-Dubois, 1986; Urmos et al., 1991; Kaczorowska et al., 2003; Rolandi et al., 2005; Smith et al., 2007; and Fan and Yang, 2008).

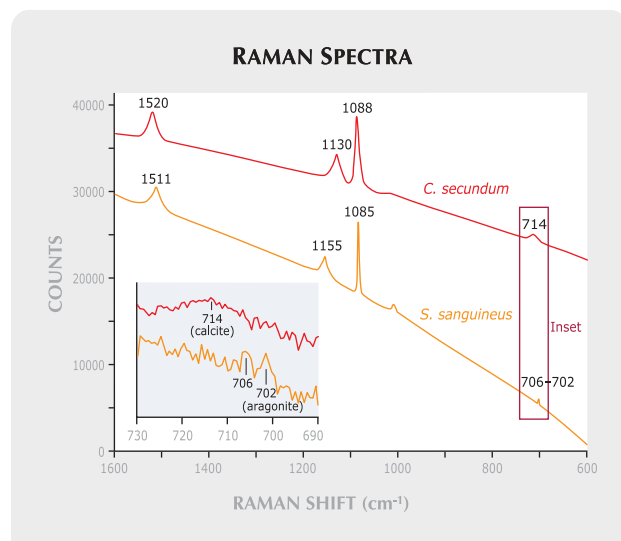
In the spectrum of *S. sanguineus*, we observed a band at about 1085 cm^{-1} and a doublet at 706 and 702 cm^{-1} (see inset to figure 5); the band and doublet correspond to the ν_1 symmetric and ν_4 in-plane bending of CO_3^{2-} ions in aragonite, respectively (Urmos et al., 1991). Two additional peaks at ~ 1511 and 1155 cm^{-1} are characteristic of carotenoid pigments (Merlin and Delé-Dubois, 1986). Carotenoid pigments are also polyenic molecules, with various substitutions on their terminal ends and an additional

four methyl groups attached to their polyenic chain. In carotenoids, the ν_1 vibration is modified by the presence of additional methyl (CH_3) groups in the polyenic chain (methyl in-plane bending modes); hence, the Raman peak is shifted $25 (\pm 10) \text{ cm}^{-1}$ (Okamoto et al., 1984). This difference (1130 vs. 1155 cm^{-1} in figure 5) is substantial enough to separate unmethylated polyenes (corals of the *Corallium* genus) from carotenoids (corals from *Stylaster*) unambiguously.

The position of the other peak related to polyenic chains, at $1520 \pm 10 \text{ cm}^{-1}$ (under 514 nm excitation), is dependent on the number of carbon double bonds in the chain. Thus, for a given number of double bonds, this particular Raman peak is in the same position for a carotenoid and an unmethylated polyenic molecule (Okamoto et al., 1984). In different areas of the two *Stylaster* corals, we obtained similar results for each of the two peaks ($1155 \pm 5 \text{ cm}^{-1}$ and $1520 \pm 10 \text{ cm}^{-1}$). Rolandi et al. (2005), again, measured peaks at the same positions for other species within the *Stylaster* (stated as “*Allopora*”) genus. Destructive studies on extracted pigments from *Stylaster* corals also demonstrated that they contain carotenoids (Ronneberg et al., 1979).

Moreover, a recent study has shown that the different colors seen in some corals are actually due to mixtures of several types of carotenoids (e.g., orange *Stylaster*) or unmethylated polyenes (e.g., pink *Corallium*; Karamelas et al., 2007). Thus, the natural colors of pink-to-red *Stylaster* and *Corallium* corals result from the nature and relative proportions of several carotenoids and unmethylated polyenes, respectively.

Figure 5. In the Raman spectrum of *Corallium secundum* (red line; sample no. 7), bands due to calcite are observed at $\sim 1088 \text{ cm}^{-1}$ and 714 cm^{-1} . The two bands at ~ 1520 and 1130 cm^{-1} are due to unmethylated polyenic pigments. In the spectrum of *Stylaster sanguineus* (orange line; sample no. 2), aragonite bands are observed at ~ 1085 , 706 , and 702 cm^{-1} (see inset). Two sharp bands at ~ 1511 and 1155 cm^{-1} are due to carotenoids. Among corals of gemological interest, only the *Stylaster* genus appears to contain aragonite and carotenoid pigments. Note that the spectra are normalized to the major Raman peak of carbonate ($\sim 1088 \text{ cm}^{-1}$ for calcite and 1085 cm^{-1} for aragonite). The spectra have been stacked and shifted vertically for clarity.



Conclusion. Gem corals from the *Stylaster* genus are protected by Appendix II of CITES, and a certificate issued by the management authority of the country (or state) of export is required for any new material released (import/export of a *Stylaster* coral from old stock is permitted; for more information about the legal framework of importing/exporting species protected by Appendix II, consult CITES, 2008c). Currently, there are no such restrictions on corals of the *Corallium* genus.

This study showed that pink-to-red *Stylaster* corals contain carotenoid pigments and are aragonitic, while those from the *Corallium* genus contain unmethylated polyenic pigments and are calcitic, so they can be separated on this basis using Raman spectroscopy. A review of the literature indicates that *Stylaster* is the only pink-to-red gem coral that contains carotenoid pigments. Thus, if a coral from the *Stylaster* genus cannot be distinguished by its surface features, it can be identified non-destructively using Raman scattering. Raman spectra of additional natural-color coral specimens from these and other genera need to be collected to refine this criterion. Raman spectroscopy may also prove useful to gemologists in detecting other materials protected by CITES, such as ivory and pearls.

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