RAMAN SPECTROSCOPY IN CORALS AND PEARLS. Laura Bergamonti, Danilo Bersani and Pier Paolo Lottici, Physics Department, University of Parma, Viale G.P. Usberti 7/a, 43124 Parma, Italy.
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Introduction: Corals and pearls are organic gem material used for ornamental purposes. Apart from black and gold corals, formed by hornlike organic matter, red to pink corals and pearls consist mainly of calcium carbonate in calcite or aragonite forms. The formation and nature of calcium carbonate have been largely investigated by means of Raman spectroscopy [1], [2], [3]. Raman scattering may be helpful to distinguish between coral and pearl species through the identification of their calcite or aragonite structure, or differences in the pigments.

Experimental: Here we report on the Raman spectra taken at 632.8 nm and at 473.1 nm with a micro-Raman Labram HORIBA Jobin-Yvon instrument equipped with 50x objective on a series of red to pink corals and on natural pearls.

Results: The Raman spectrum of coral identifies the biogenic calcium carbonate phase of the skeleton. The Raman spectrum of natural-color coral typically reveals additional peaks related to organic pigments. Pearls show the aragonite peaks at 206 cm^{-1}, 702-706 cm^{-1} and at 1086 cm^{-1}.

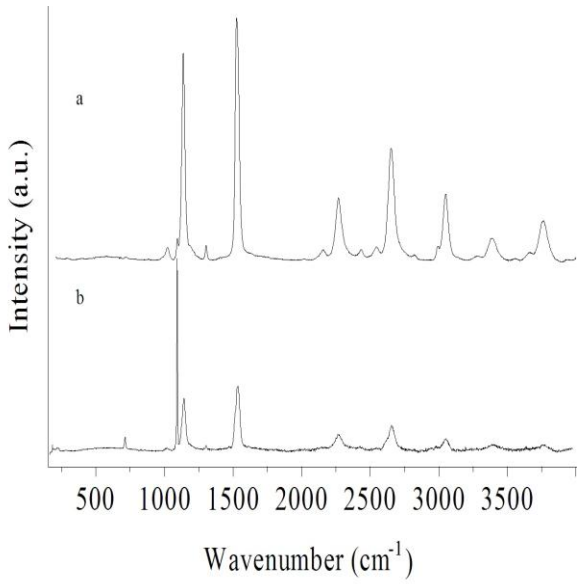

Fig.1 – Raman spectrum taken with 473.1 nm excitation showing the strong carotene features at 1132 cm^{-1} and 1523 cm^{-1} and a series of overtones and combination bands, in addition to characteristic peaks of $CaCO_3$: (a) Corallium rubrum (283, 713, and 1087 cm^{-1}, calcite); (b) pink cultured pearl (aragonite).

The nature of the dyes responsible for the natural color in pink-to-red corals and pearls has been largely investigated by means of Raman spectroscopy [4], but the scientific debate on their nature is still open [5]. Carotenoids or mixtures of polyenes [6] have been proposed. The presence of high intensity overtones and combination frequencies in the Raman spectrum taken with the "resonant" 473.1 nm line (Fig.1) enables the investigation of the characteristic C=C stretching vibrations, whose frequencies seem to depend on the polyenic chain length, and the C–C stretching vibrations, whose frequencies are more influenced by the presence of the $–CH_3$ substituting groups in carotenoids [6], [7], [8]. Here we report additional data on the vibrational frequencies and their combinations as found in the Raman spectrum of different corals and pearls.

Raman analysis can establish conclusively if the color of corals or pearls is natural or obtained by dyeing. The dyed coral samples do not exhibit the Raman spectrum associated with carotene (Fig.2). Some examples with both excitation lines are reported and the dyeing substance has been identified.

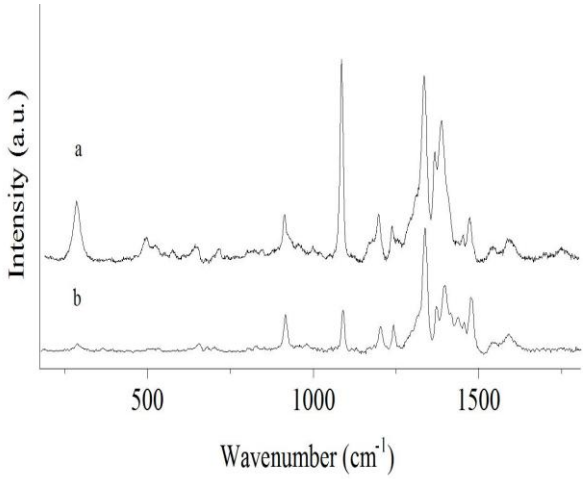

Fig.2 – Raman spectrum taken at 632.8 nm (a) and at 473.1 nm (b) of a dyed "red coral". No carotene features are present.

References: [1] Urmos J., Sharma S.K., Mackenzie F.T. (1991) *Am. Mineral., 76*, 641–646. [2] Kaczorowska B. *et al.* (2003) *Anal. Bioanal. Chem., 377*, 1032–1037. [3] Zakaria F.Z. *et al.* (2008) *J. Raman Spectrosc., 39*, 1204–1209. [4] Barnard W. and de Waal D. (2006) *J. Raman Spectrosc., 37*, 342–352. [5] Karampelas S. *et al.* (2009) *Gems Gemol., 45*, 48-52. [6] de Oliveira V.E. *et al.* (2010) *J. Raman Spectrosc., 41*, 642-650. [7] Fritsch E., Karampelas S. (2008) *Spectrochim. Acta A, 71*, 1627. [8] Karampelas S. *et al.* (2009) *Eur. J. Mineral., 21*, 85–97.