Crystallographic Orientation of Biogenic Aragonite in Pearls

Ren Lu
GIA Laboratory, New York (April 8, 2009)

Pearls and shells consist of up to 99% biogenic calcium carbonates ($CaCO_3$) deposited over an organic substrate. Questions on their exact speciation (aragonite and/or calcite) and the origin of their wide variation in hardness (e.g., Fritsch and Misiorowski, 1987) have not been fully resolved. Recent research (Kamat et al., 2000; Soldati et al., 2009) indicates that these carbonates form growth patterns and sometimes complex interwoven orientations (lamellar structures) on a micrometer scale. Understanding microscopic structures sheds light on the appearance and characteristics (such as luster and hardness) of these materials.

Laser Raman spectroscopy is capable of sampling a few micrometers of material, making it ideally suited for the study of microscopic carbonates in pearls. The current study demonstrates the potential for material identification in pearls and for determining the orientation of their biogenic mineral growth (see Figures 1–3).

In summary, freshwater cultured pearls displayed well-crystallized aragonite characteristic of non-biogenic mineral aragonite. Spectroscopic data demonstrate that aragonite crystals in these pearls occur in an oriented arrangement: the pearl surface layers correlate to the ab- crystallographic plane of aragonite, and the radial direction to the c-axis of an aragonite crystal. The spectroscopic techniques used here are readily applicable to the study of a wider range of bio-mineralized materials such as nacreous and non-nacreous pearls, shells and corals.

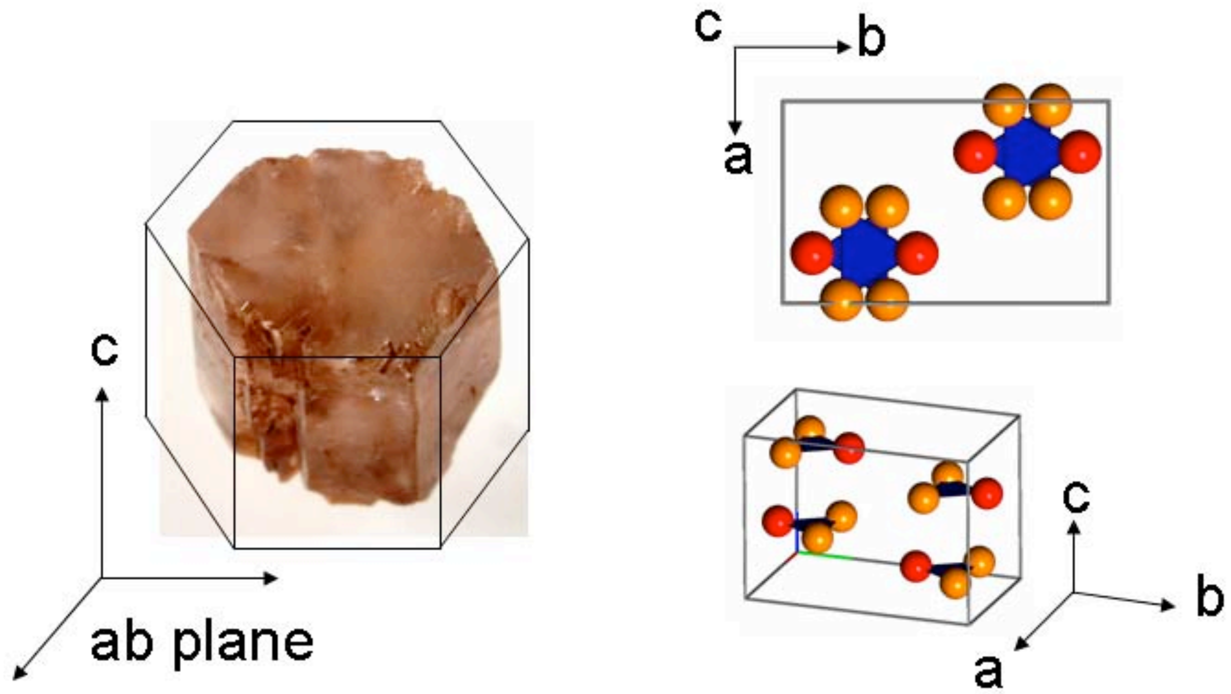

Figure 1. A single crystal of non-biogenic mineral aragonite ($CaCO_3$) on the left exhibits a typical pseudohexagonal crystal habit and natural cleavage planes relative to the crystallographic axes. Its crystal structure, shown in two crystallographic orientations on the right, consists of CO_3 units confined in planar triangles with a carbon atom in the center and three oxygen atoms at the corners. In the upper figure, two triangular layers overlap and form a hexagon when viewed down the c-axis. Contrasting spectroscopic behaviors are observed when light (from infrared or Raman spectroscopy) interacts with crystals within or orthogonal to the CO_3 plane, which helps determine the orientation of biogenic aragonite in pearls. Four calcium atoms associated with lattice modes have been omitted for visual clarity.

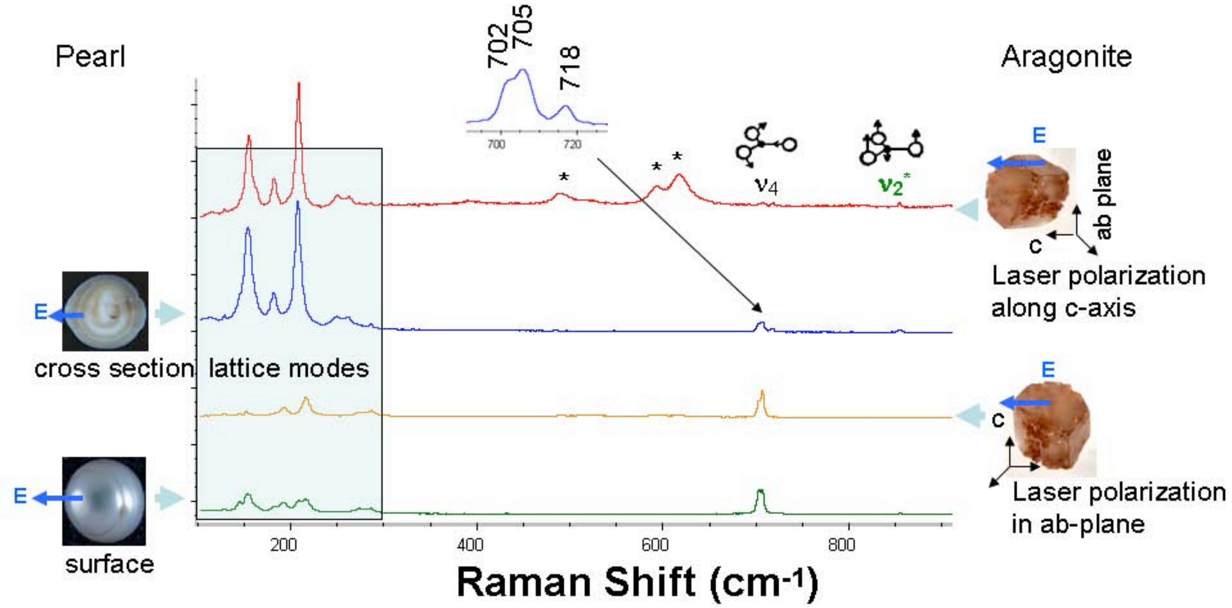

Figure 2. Raman spectra collected with 830 nm laser excitation demonstrate that the pearl surface behaves similarly to the ab-plane of an aragonite crystal, while the radial direction correlates to the c-axis of an aragonite crystal. The lattice region below 300 cm^{-1} and the in-plane bending vibration (ν_4) are indicative of crystallographic orientations of aragonite. Also note that the out-of-plane bending (ν_2) at 856 cm^{-1} is clearly present only when laser polarization (indicated by blue arrows) is along the c-axis (due to the CO_3 structural unit being confined in the ab-plane). Insert schematics next to spectral features illustrate atomic motions of the CO_3 unit. All spectra are normalized to the symmetric stretch mode (ν_1) at 1087 cm^{-1} (not shown). Asterisks in the aragonite spectrum (in red) indicate spectral features originating from fluorescence that are not Raman features. Orientation of the laser polarization is shown (blue arrows) in the small images of a freshwater cultured pearl (left images) and mineral aragonite (right images).

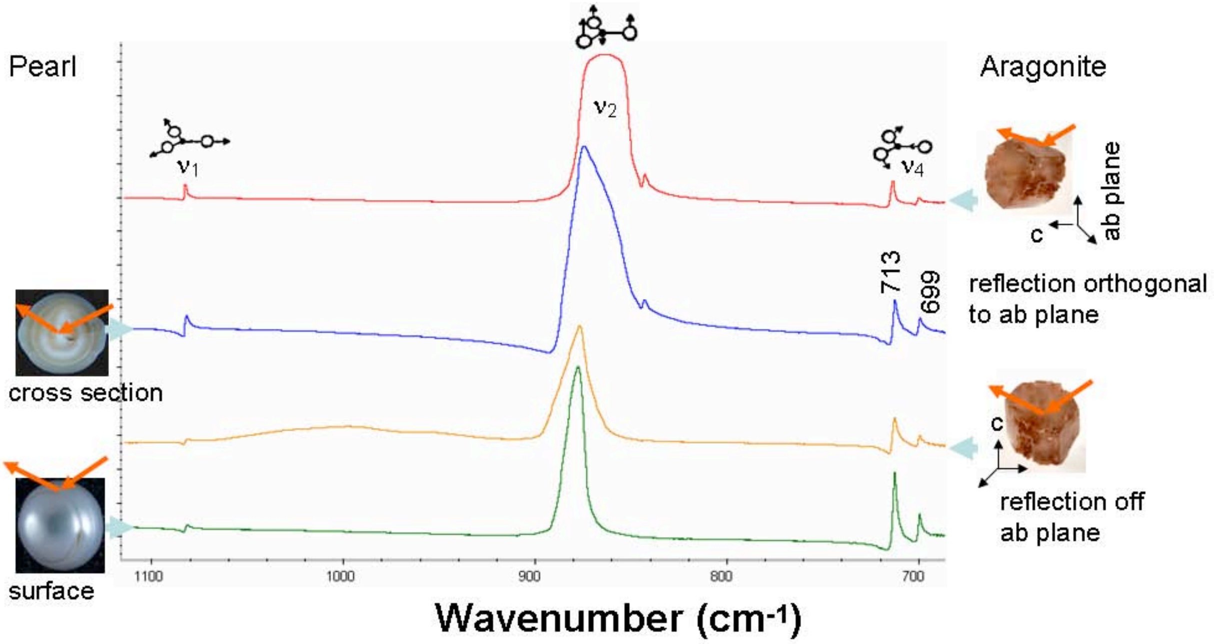

Figure 3. Infrared reflectance spectra further define the crystallographic orientation of aragonite with the contrasting band width (more than a factor of 2) and position in the out-of-plane bending mode (ν_2) between the pearl cross section and the surface. The symmetric stretch vibration (ν_1) is also noticeably enhanced for reflectance from the pearl cross section. Infrared reflectance, typically measured from a pearl surface, correlates to reflectance from the ab-plane of aragonite crystal. Calcite and aragonite, which have the same chemical composition but different crystallographic symmetry, can be easily differentiated by their spectroscopic features: a doublet for aragonite and a single band for calcite for the in-plane bending vibration (ν_4) near 700 cm^{-1}.

References

Fritsch E., Misiorowski E. (1987) The history and gemology of queen conch "pearls." *Gems & Gemology*, Vol. 23, No. 4, pp. 208–221.

Kamat S., Su X., Ballarini R., Heuer A. H. (2000) Structural basis for the fracture toughness of the shell of the conch *Strombus gigas*. *Nature*, Vol. 405, pp. 1036–1040.

Soldati A., Jacob D., Wehrmeister U., Hager T., Hofmeister W. (2009) Pearl micro- and nanostructure, mineralogy and composition: Factors affecting quality and provenance studies. The 2nd International Gem and Jewelry Conference, Bangkok, March 9–12, 2009.