



Synchrotron FT-IR analyses of microstructured biomineral domains: Hints to the biomineralization processes in freshwater cultured pearls.

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Recent investigations in freshwater cultured pearls (bio-carbonate) by micro-Raman spectroscopy (Wehrmeister et al., 2008; Soldati et al., 2008), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) imaging (Jacob et al., 2008) show that the pearl biomineralisation starts with a self assembling process in which an existing gel matrix of amorphous calcium carbonate (ACC) and organic substances reorganizes and conglomerates in small domains; these conglomerates then form prisms and mature nacreous tablets of aragonite or vaterite. Raman spectroscopy shows that the calcium carbonate polymorphs have decreasing luminescence in the order ACC>Vaterite>Aragonite, coinciding with decreasing quantities of S and P (related to the organic matrix) measured by Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) and Electron Probe Micro Analyzer (EPMA). Although little is known about the process of transformation of the ACC gel into vaterite and aragonite, it is speculated that this probably involves dehydration and change of the accompanying organic matrix. This is also supported by our laboratory FT-IR analysis. However, due to the small size of the areas of ACC (about 10 μ m) and the biogenic crystals an *in-situ* high spatially resolved IR-method is needed to record how the water content and organic matrix change in the biomineralisation sequence, to understand which processes take place in the self-organization. The beamline IR-1 at the ANKA synchrotron source (Karlsruhe, Germany) was used for this experiment.

Freshwater cultured pearls from China cultured in *Hyriopsis cumingii* mussels by tissue nucleation methods (so-called beadless pearls) as well as by bead implantation methods (aragonite nucleus) were studied. The pearls were cut in half with a diamond-plated saw and polished with diamond paste on a copper plate. Micro-Raman spectroscopy maps (Department of Geosciences, at the Johannes Gutenberg-University, Mainz) were generated to identify and pre-select those pearls containing ACC. Infrared absorption spectra were measured using a Ge ATR objective on 100-200 μ m thin sections and polished pearl sections. Attenuated total reflectance spectroscopy gives the opportunity to measure the infrared absorption in a reflectance mode directly without necessity to apply Kramers-Kronig transformation. The spectral range available is 650-5000 cm^{-1} when using a Ge ATR crystal with the MCT detector at the ANKA-IR microscope and allowed the detection of the ν_4 in-plane bending band (around 750 cm^{-1} in vaterite and 710 cm^{-1} in aragonite), the ν_1 symmetric stretching bands (1070-7085 cm^{-1} for vaterite⁴ and 1082-1084 cm^{-1} in aragonite⁵), the ν_2 out-of-plane bending vibration of the CO₃ groups (855 cm^{-1} for vaterite and 857-877 cm^{-1} in aragonite) and the ν_3 asymmetric stretching (1420-1490 cm^{-1} in vaterite and 1480 cm^{-1} in aragonite) respectively (Sato and Masuda, 1969; Yamoto et al., 1974). Water was detected by the presence of the O-H stretching at around 3500 cm^{-1} . Proteins and sugars included in the biogenic carbonates were recognized through the N-H and C-H bands, for example 1717-1575 cm^{-1} for aspartic acid, 1712-1558 cm^{-1} for glutamic acid, 1500 to 2000 cm^{-1} amide I and II (Dauphin et al., 2006).

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