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A MULTIMODAL MICROCHARACTERIZATION OF TRACE-ELEMENTS IN DEFECTIVE PEARLS BY SEM-CL, EPMA, µ-XRF AND CONFOCAL RAMAN-IN-SEM IMAGING

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Pearls are greatly valued by the jewelry industry as shiny organic gems. Their glossiness, results of a defense mechanism against foreign particles. Pearls (Hyriopsis cumingii) are produced from a natural biomineralization process controlled by organic molecules. Pearl biocrystal is a hybrid composite: organic / mineral (3 % / 97 %). The regular form of pearl mineralization is aragonite, an orthorhombic polymorph of calcium carbonate. Each biocarbonate plateletis a polygranular composite of aragonite nanograinsstuck by proteins. It diffracts as a single crystal and is so called mesocrystal. Platelets have a polygonal shape, few hundreds of nanometersthick, whichstack along the c-axis with chitin organic 'cement'. This layered structure produces the well-known 'pearly' aspect. Sometimes, pearls show a biomineralization defect characterized by a lack of shine (also called 'milky pearl'). It has been established that this defect is related to the change in crystallization form: from orthorhombic aragonite to hexagonal vatérite [1].

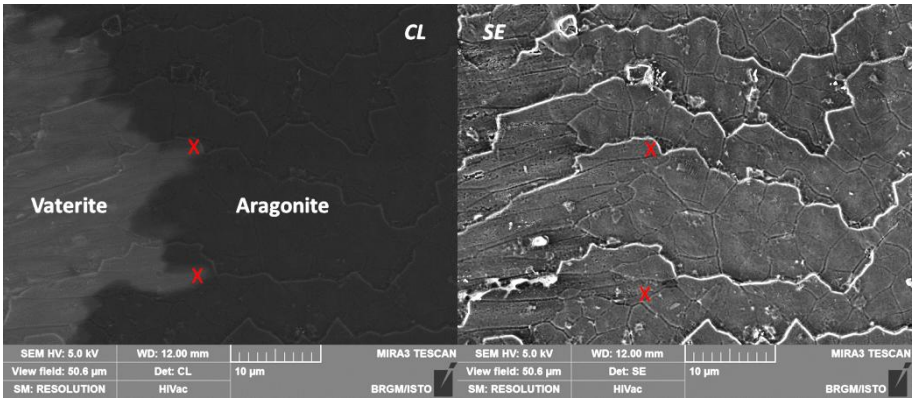

Fig. 1: SEM observation of the interface: same area as seen with cathodoluminescence (CL, left) and in secondary electron mode (SE, right)

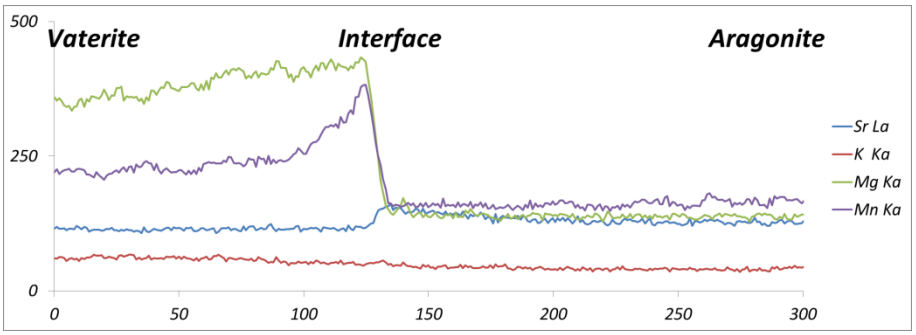

Fig. 2: Trace elements distribution on both side of the interface by EPMA (vaterite: left, aragonite: right)

The transition from 'regular' aragonite to 'defective' vaterite has been investigated by SEM-CL (fig. 1), EPMA (fir. 2), micro-X-ray Fluorescence and confocal Raman-in-SEM imaging [2]. Crossing the results of these different microcharacterization methods is neededfor understanding the control on this crystallization process. The distribution of the trace elements on each side of the interface was highlighted. During a synchronous deposition, vaterite shows a higher concentration of magnesium and manganese, whenaragonite is characterized by a near-absence of magnesium and manganese (fig. 2). Variation in the low wavenumber Raman bands on the aragonite phase next to the interface are noticed, pointing out subtle variations at the crystallographic level.

[1]Bourrat X. et al., *origin of growth defects in pearl*, 2012, Materials Characterization**72**94-103

[2] Jiruse J. et al.,*Integrating focused ion beam–scanning electron microscope with confocal Raman microscope into a single instrument*,2014,Journal of Vacuum Science & Technology B**32** 06FC03