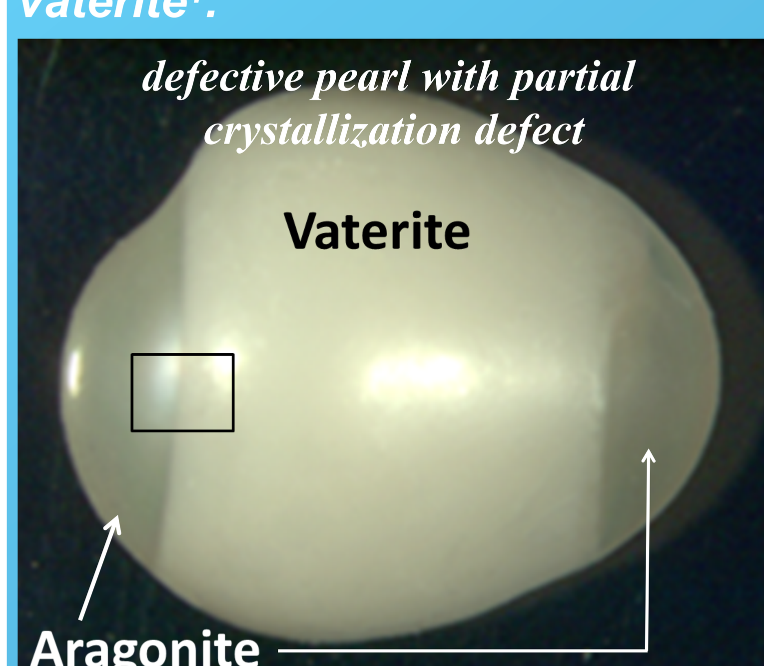
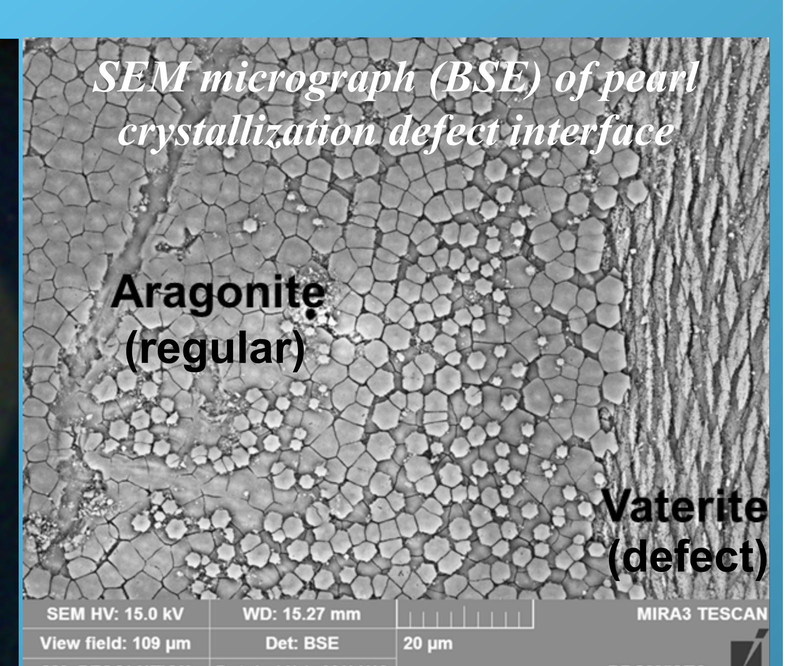
PEARLS DEFECTS EVIDENCED BY EPMA, EDS AND COUPLED SEM-MICRO-RAMAN SPECTROSCOPIES

Fresh water pearls (Hyriopsis cumingii) are produced from a natural biomineralisation process controlled by organic molecules. These pearls originate from mussels cultured in Zhuji, China . Pearl biocrystal is a hybride composite organic / mineral (3 % / 97 %). The regular form of pearl mineralization is aragonite, an orthorhombic polymorph of $CaCO_3$. This biocarbonate shape is a stack of nanometric thickness hexagonal plates stacked along the c-axis of the aragonite crystal. This mineralization produces well-known shiny and 'pearly' aspect.

The 'milky' pearls defect of pearls

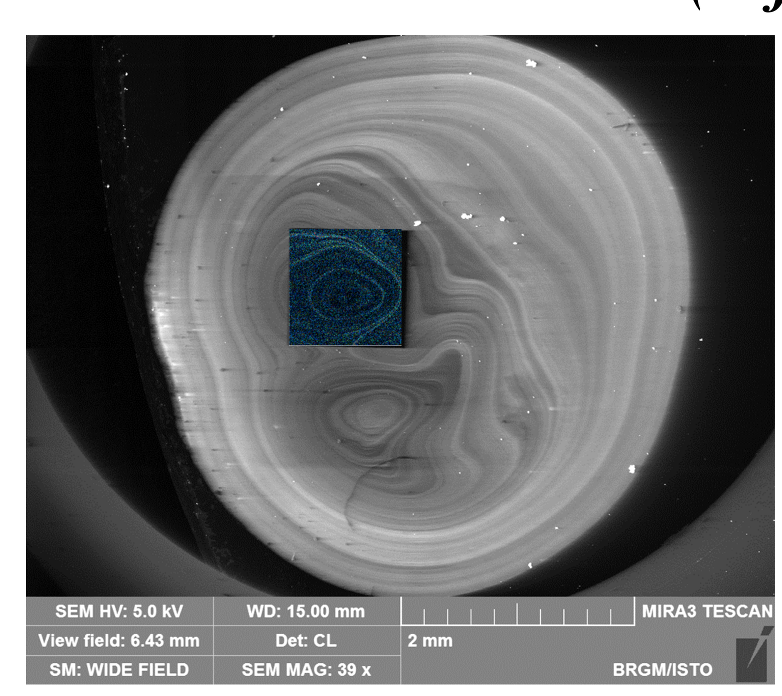
A major growth defect of pearls is related to the formation of hexagonal vaterite instead of orthorhombic aragonite during the biomineralisation growth process . Defective pearls are characterized by a lack of shine also called 'milky pearl'. It has been established that this defects is related to the change in mineralization form from orthorhombic aragonite to hexagonal vaterite[1].

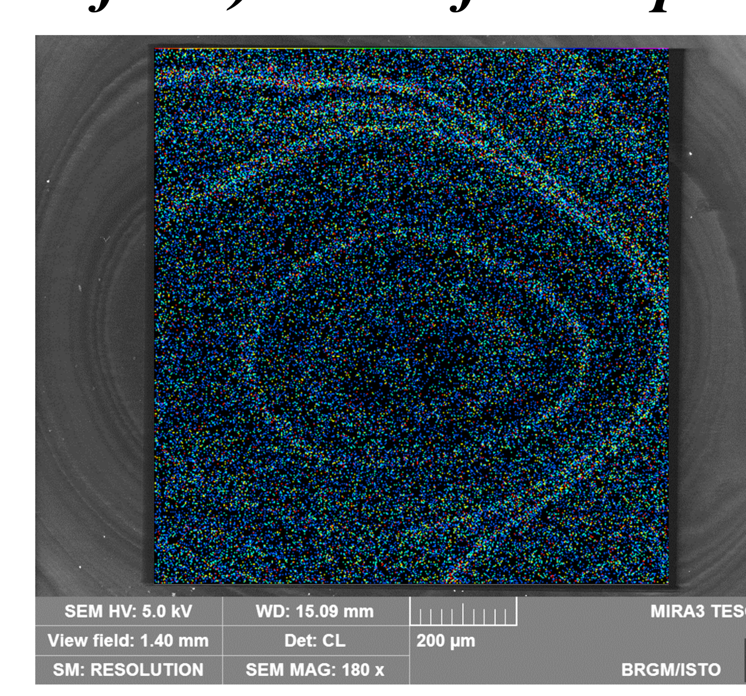




[1] Bourrat et al., J. Mat. Char. 72 (2012), p. 94-103

Cathodoluminescence and Manganese content in Vaterite (defect form) in a defective pearl



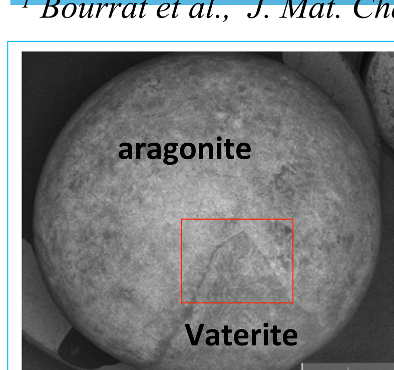


Left : Growth rings (related to a daily alternation) evidenced by cathodoluminescence (inset : EPMA Mn mapping)

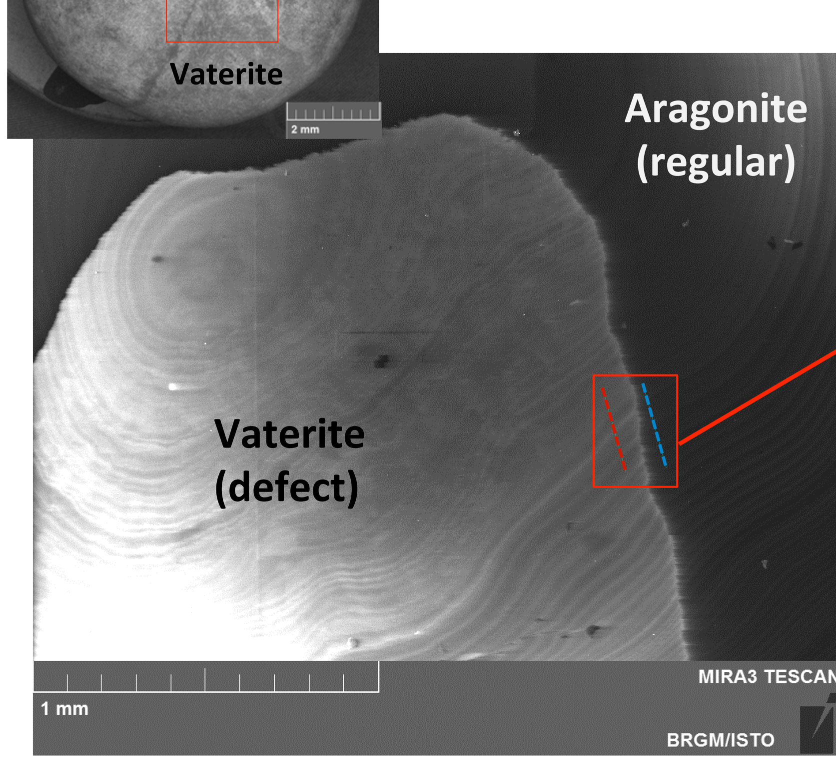
Right : EPMA Mn mapping appears to be strongly connected to CL signal, therefore to the growth rings.

CL : Tescan Mira 3 XMU - Panchromatic CL detector (350 – 650 nm) @ 5 kV
Mn Kα mapping : Cameca SX50 - LiF - 15 kV / 20 nA

Comparison of cathodoluminescence signal related to Manganese content in aragonite (regular form) and Vaterite (defect form) in a partly defective pearl

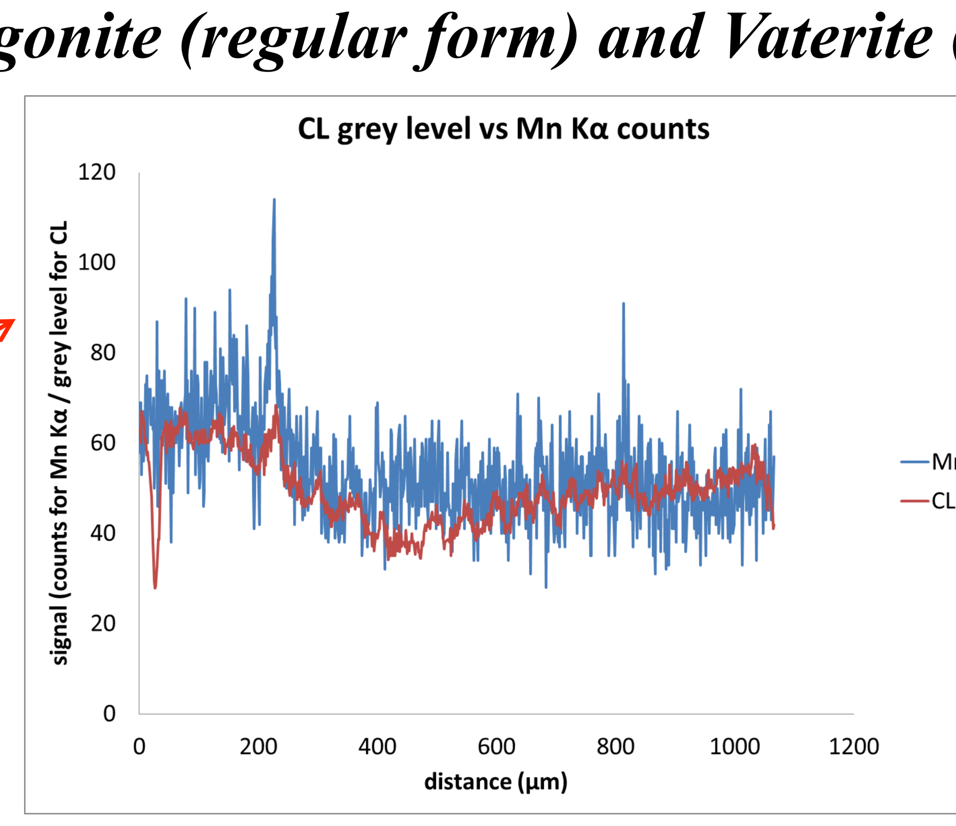


BSE image of a defect in a pearl

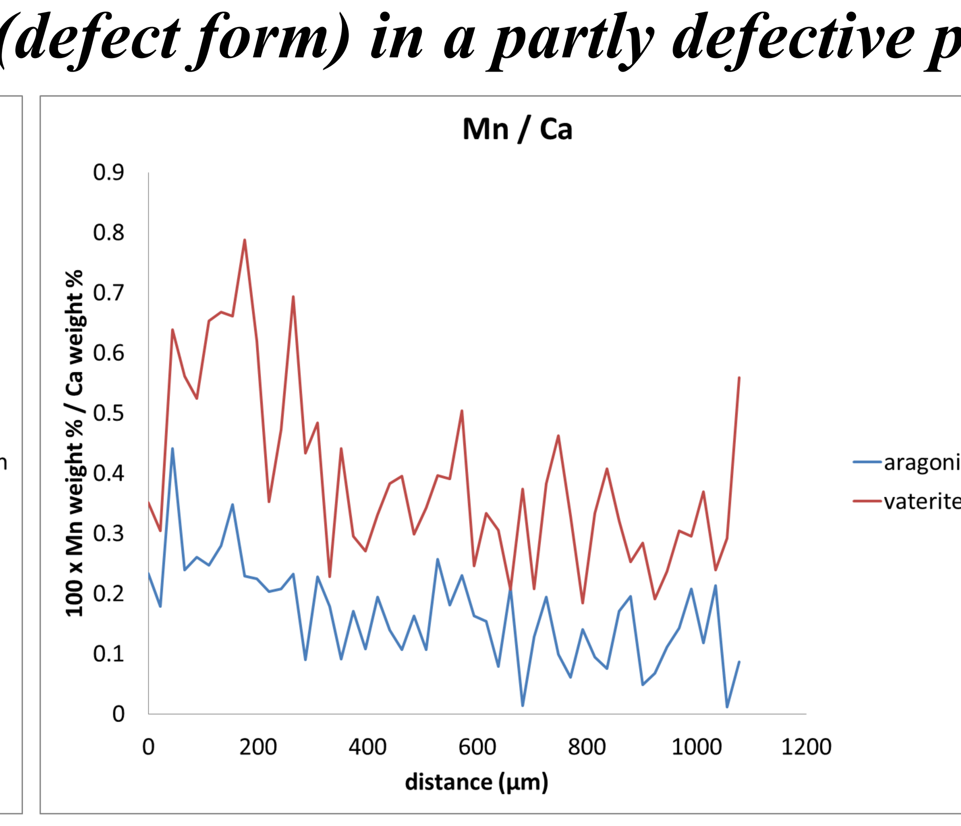


CL image of vaterite defect in a pearl

(polished section of the pearl presented at the top left)



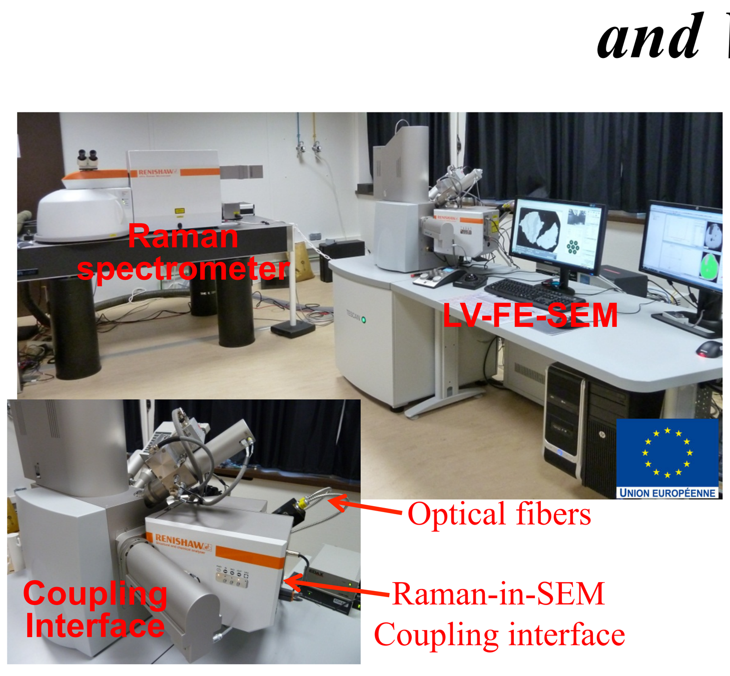
CL signal (blue : grey level) compared to Mn signal (red : counts on LiF) in vaterite defect

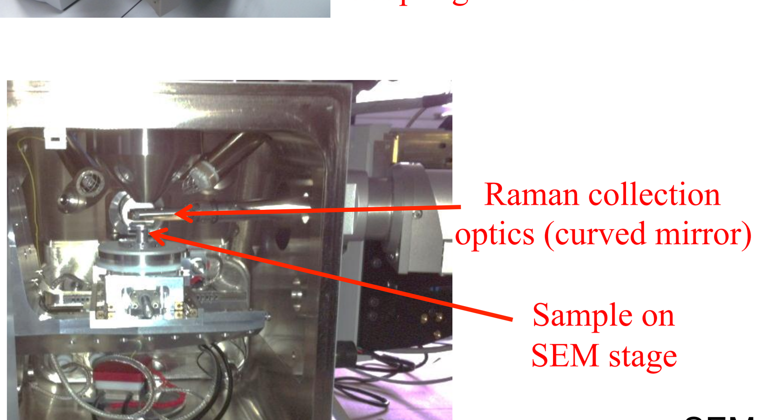


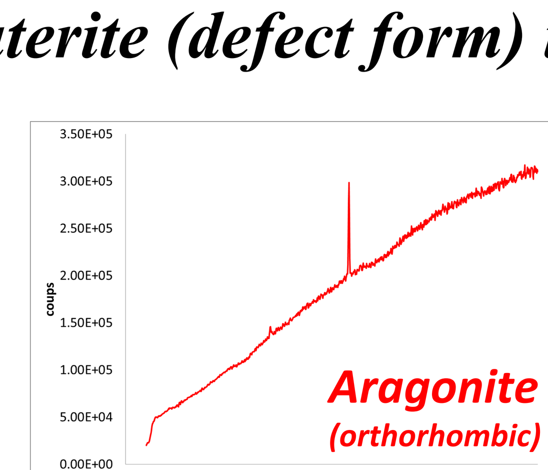
Mn / Ca ratio (100 x) in regular aragonite and defect vaterite zones on either side of the defect interface

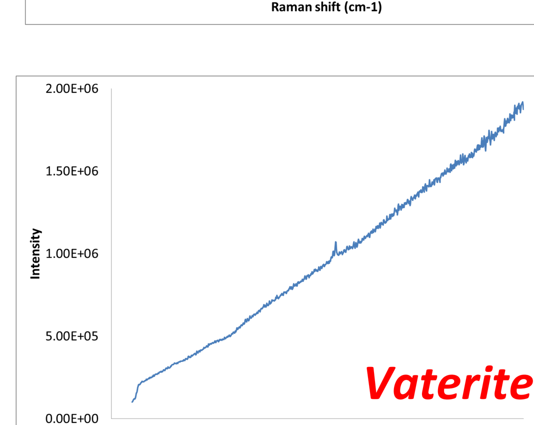
SEM : Tescan Mira3XMU - BSE : LV on non-coated sample / CL : Panchromatic CL detector (350 – 650 nm) @ 5 kV
EPMA : Cameca SXFive - 5 spectrometers - 15 kV / 20 nA - Mn on LiF / LLiF

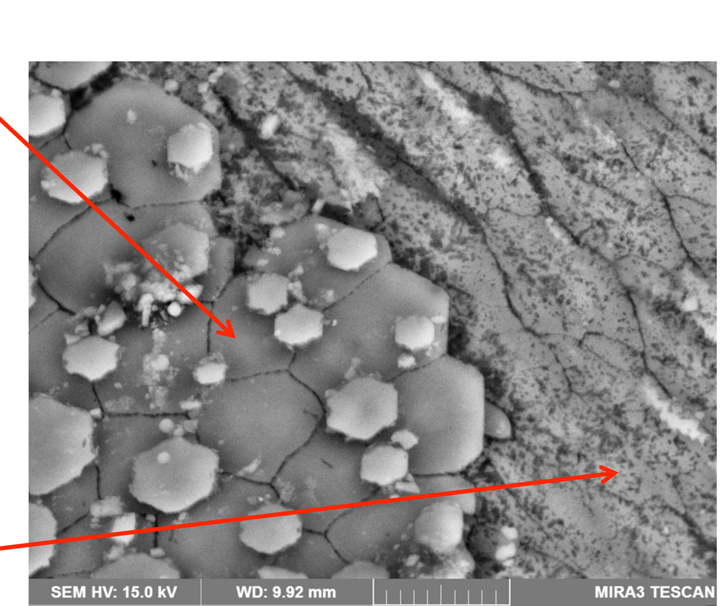
Raman-in-SEM spectroscopy in aragonite (regular form) and Vaterite (defect form) in a partly defective pearl











SEM : Tescan Mira3XMU - BSE @ 15 kV - LV on non-coated sample (BSE detector)
Raman : Renishaw SemSca coupling interface connected to Renishaw InVia - λ = 514 nm

CONCLUSIONS

- *Growth rings evidenced by CL signal, strongly connected to Mn content.*
- *Mn : evidenced to be much higher in Vaterite (up to 0.4%) than in Aragonite*
- *Significant contribution from Raman-In-SEM : coupled SEM-microRaman system allows to precisely characterize specific zones of the sample i.e. regular and defective areas, at micrometric scale.*

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