

## Correlative NanoSIMS and Atom Probe Study of Nacre: Toward Understanding Polymorphism Effects in a Chinese Pearl

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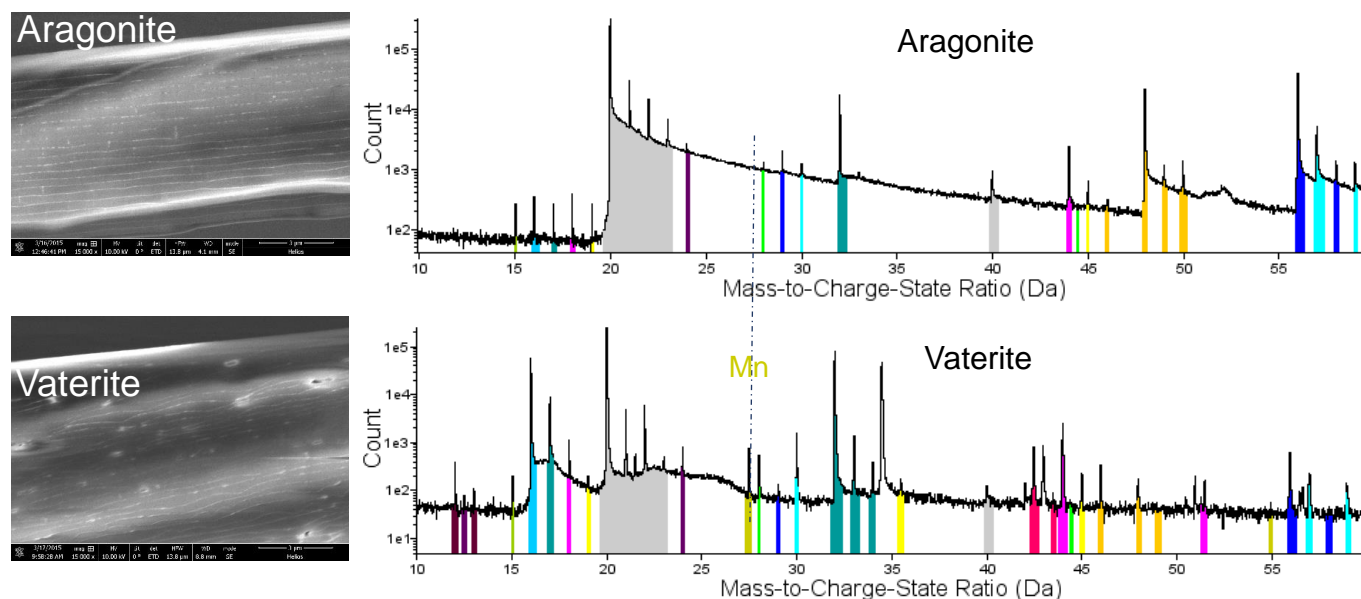
Mineralized tissues are naturally synthesized in the biological world for optimizing mechanical performances required for specially defined functions. For instance nacre (mother of pearl), which is the internal layer of some mollusk shells, has evolved to reinforce the mechanical toughness and self-healing of the exoskeleton. When a crack occurs in the shell, calcium carbonate nano-grains (NG) are secreted by hemocytes and used for healing [1]. Mother Nature uses a strategy based on the assembly of organic molecules for controlling mineral growth and texture [2]. A protein network controls the arrangement of mineral NG under the form a 'mesocrystal', shaped as platelets [3]. At a higher level, the organic network controls the stacking of platelets with the well-known 'brick and mortar' bivalve model [3]. This current study aims at understanding how the crystal lattice modifies its network depending on the calcium carbonate polymorphism. Can this re-organization be explained by pure thermodynamic aspects such as enthalpy of formation or could the answer come from the intervention of an organic mediator? The *Hyriopsis cumingii* Chinese pearl, exhibits synchronous co-growths consisting of Aragonite and Vaterite areas, in direct contact with each other. Unfortunately, Vaterite is a defect in Nacre, highly non-desirable from an economic point of view, as it alters the shiny aspect of the pearl.

A correlative microscopy study by NanoSIMS (NS) and Atom Probe Tomography (APT) shows that the most likely mechanism responsible for this polymorphism variation occurs through forcing lattice distortion by mineral trace elements. NS has shown that if similar Ca, C and O content in both phases were found, mineral traces (especially Mn, Al and Mg) are much more abundant in the Vaterite phase (see Figures 1 and 2). These results, confirmed at the atomic level by APT, are important as they demonstrate that Mn-rich NG adopt the hexagonal structure of Vaterite and aggregate in the form of needle platelets. On the other hand, Mn-poor NG would have an orthorhombic structure and aggregate the orthorhombic neighboring platelets (Aragonite). When the level of Mn contamination increases in the extrapalleal fluid, the winning mechanism tends to create a hexagonal structure, supported by a substitution of Mn present in higher levels. An even more damaging mineral hexagonal phase for pearl due to its pink coloration also known as Rhodochrosite ( $\text{MnCO}_3$ ), has not been identified in these samples.

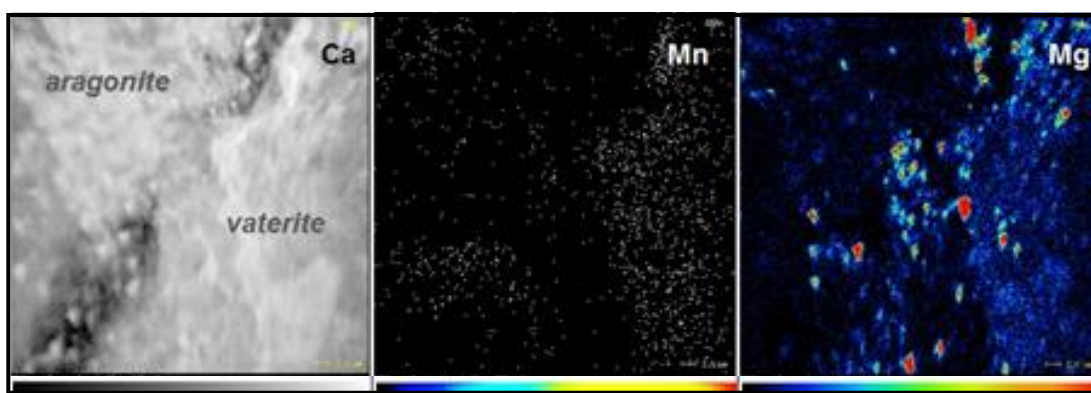
Finally, the Vaterite structure itself is still the subject of controversy due to its biogenic character and its limited crystal size. A recent Cs aberration-corrected Transmission Electron Microscopy (TEM) study depicted Vaterite as a mixture of two interspersed crystalline structures, mostly hexagonal [4]. Other works involve a micro-twinning mechanism [5]. Our collaborative work continues using TEM and APT, and will focus on resolving this controversy.

## References:

- [1] Andrew S. Mount *et al*, *Science* **304** (2004) p. 297.  
 [2] M. Rousseau *et al*, *Journal of Structural Biology* **165** (2009) p.190.  
 [3] M. Rousseau *et al*, *Biomaterials* **26(31)** (2005) p. 6254.  
 [4] Lee Kabalah-Amitai *et al*, *Science* **340** (2013) p. 454.  
 [5] A. Le Bail, S. Ouhenia, and D. Chateigner, *Powder Diffraction* **26** (2011) p. 16.



**Figure 1.** Electron micrographs of Aragonite and Vaterite phases along with their respective mass spectra as acquired by APT, showing differences in physical and compositional aspects.



**Figure 2.** NanoSIMS mapping at the interface between Aragonite and Vaterite: Mg is the trace element with the most enriched regions being Vaterite.