

## **Biomacromolecules in *Arctica islandica* shells: molecular signatures of a bivalved Methuselah at micron and submicron scale**

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*Arctica islandica* (Bivalvia, Linnaeus, 1767) is the ‘Methuselah of the sea’, living to ~400-500 years, and is now used as an established paleoenvironmental archive for the boreal North Atlantic [1]. Despite that, organic matrix that controls the formation of its complex nanoarchitecture is still poorly characterized. It is expected that the shell matrix exerts a great degree of crystallographic control over the nucleation and growth of inorganic phases, and that a significant fraction of the organic phase is composed of hydrophobic biopolymers. However, much of our knowledge about shell biomolecules is restricted to nacreous shells such as *Hyriopsis cumingii*, where the biopolymer primarily consists of silk-like protein fibre and form a complex with a minor chitin component. Less attention has been devoted to the proteinaceous motifs and their possible interactions with other components in shells with other architectures. Hence, we conducted detailed structural and molecular analyses of the key components of organics in modern and subfossil *A. islandica* shells, which predominantly consist of crossed-acicular microstructures.

Large shell pieces that mainly consist of aragonite were decalcified in 6N HCl as described previously [2]. We analysed intact shells and their water insoluble acid extracts. Submicron optical photothermal infrared (O-PTIR) identified chitin and a collagen-like matrix as the predominant protein in the inter-crystalline and intra-crystalline matrix of modern and subfossil *A. islandica* shells. Micro-Raman, transmission micro-FTIR and solid-state NMR validated this observation, which was further complemented with ATR-FTIR, fluorescence microscopy, FEG-SEM, elemental and stable isotope analyses and chemical analysis. The results of element and light stable isotope analysis ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) of organic extracts are consistent with the shallow marine environment where these organisms lived. We further show that submicron grains of calcium carbonate crystals permeate the framework of polysaccharide chitin fibrils coated with proteins, which control

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crystallization and architecture. This study shows that O-PTIR is a promising technique for submicron scale organo-mineral interactions, and further our understanding regarding the compositions of shell macromolecules, both in modern and subfossil bivalve shells.

[1] Schöne BR (2013), *Global and Planetary Change* 111, 199–225. [2] Agbaje et al (2021), *Biochemistry and biophysics reports*, 26, p.100939.