MS18 Biomineralogy and bioinspired materials

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The concomitant role of amorphous precursors and organic molecules in forming colourful single crystalline biominerals with convoluted porous structures

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Abstract

Some biomineralized structures with intricate shapes and morphologies, such as the colourful skeletal elements of sea urchins grow via the deposition of hydrated amorphous calcium carbonate (ACC) that subsequently transforms in anhydrous ACC and finally crystallizes into single-crystalline calcite. Applying the heat-stimulated crystallization of remnant anhydrous ACC and destruction of intra-crystalline organic molecules in those biominerals, we evidenced by HR-XRD, calcite lattice distortions originating in strong atomic interactions at the organic-inorganic interfaces and showed by *in situ* heating SAXS measurements, the evolution of nano-pores, which likely compensate mineral volume shrinkage during ACC crystallization and organics removal.

Our results suggest that ACC crystallization proceeds as far as organics can serve as space-filling and accommodate for density changes due to the amorphous to crystalline transformation. Beyond that point, crystallization is hindered and ACC kinetically trapped within the biominerals in the form of thin layers. We propose that ACC thin layers are adjacent to the organic/inorganic interfaces and may serve as buffer layers between intracrystalline organics and crystalline calcite with elastic energy stored in the form of lattice strains.

In addition, studying *in vitro* ACC systems with pair distribution function analysis during heat induced crystallization we showed that water governs the local structural rearrangement prior to crystallization.

Finally, we are recently extending our approach to study the role of organic pigments in the biomineralization pathways of these colourful biominerals in which polyhydroxylated naphthoquinones are entrapped and may very well be involved in shaping these large single crystalline biominerals.

References

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