Biomineralization pathways of regenerated sea urchin spines

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Biomineralization of marine carbonates play an important role in the carbon cycle, which contributes to both climate change and ocean acidification. In order to understand better the impact of biomineralization on the environment, first we need to understand crystallization pathways. Here, we propose to study the crystallization mechanism of sea urchin (SU) spines. SU's are good marine fossil records, which are successfully survived to present, and are therefore widely studied. It has been recently shown that SU are able to resist long-term moderate ocean acidification [1]. SU spines are Mg2+ rich single crystals of calcite, which regenerate after fracture. Regenerated SU spine formation starts with the acquisition of the inorganic ions from the seawater, which then form a disordered hydrated amorphous calcium carbonate (ACC). Finally it transforms into calcite, possibly via a transient ACC [2-4]. However, the nature of the transient ACC and the interface between amorphous, crystalline and organic fractions are yet unknown. Here, we address these questions by using cryo-scanning electron microscopy observations of the evolving spine morphology and x-ray photoemission electron microscopy to determine the chemical and structural nature of the transient ACC. Small angle x-ray scattering analysis was used to investigate the structure of the amorphous-crystallineorganic interface.

[1] Moulin *et al.* (2015) Mar Environ Res **103**, 103-114. [2]
Weiner and Addadi (2011) Annu. Rev. Mater. Res. **41**, 21-40.
[3] Politi *et al.* (2004) Science **306**, 1161-1164. [4] Politi *et al.* (2008) PNAS **105** (**45**), 17362-17366.