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Biological control on calcite crystallization: AFM investigation of coccolith polysaccharide function

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Abstract

Calcite crystals grown by organisms can be elaborate and enigmatic. One of the best examples is the tiny calcite shields known as coccoliths that are produced by unicellular algae. Coccoliths consist of interlocking single crystals of highly modified morphology, and complex organic molecules called CAPs (coccolith associated polysaccharides) are known to be intimately associated with their formation. Here, we show how a CAP can regulate crystal morphology to enhance precipitation of specific faces, a crucial aspect of the biomineralization process.

Using atomic force microscopy (AFM), we investigated the interaction of CAP from the species *Emiliania huxleyi* with the calcite surface during dissolution, precipitation, and dynamic equilibrium. We were able to see the polysaccharide adsorbed to the surface and observe its impact on mineral behavior. These experiments demonstrate that CAP preferentially interacts with surface sites defined by acute, rather than obtuse, angles and blocks acute sites during dissolution and growth. Therefore, CAP makes the calcite face that is most stable in the pure system, $\{10\bar{1}4\}$, extend preferentially on the obtuse edges, promoting development of faces with lower angles to **c**-axis. AFM images of *E. huxleyi* at micrometer and atomic scales established that this is precisely the type of faces that define the morphology of the coccolith crystals. Therefore, we propose that crystal shape regulation by CAP is a fundamental aspect of coccolith biomineralization, and that preferential growth inhibition by site-specific functional groups is the mechanism causing CAP functionality.