

# Study of the dynamics of adsorption of branched and linear polysaccharides on calcite surfaces

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This project has been driven by the knowledge that organisms often use biomolecules to control the nucleation and growth of calcium carbonate through controlled biomineralisation. This control can produce remarkable crystal shapes, quite unlike those obtained by precipitation of the same mineral from solution. Several species of single-celled algae use polysaccharide molecules to control complex platelets of calcite known as coccoliths. Experimental studies<sup>1</sup> have shown that the chemical and physical composition of the molecule (e.g. branched vs linear, acidic vs non-acidic) has a noted impact on its effectiveness in controlling the growth of the mineral. This project is directed to understanding this relationship using simulations of a range of polysaccharide molecules absorbing onto various calcite surfaces in the presence of water. We have undertaken a study of the effect of differing chemical connectivity and acidity upon the adsorption of a number of polysaccharide decamers to flat, stepped, and kinked surfaces of calcite. Acidic and branched polysaccharides show stronger binding and reduced flexibility at the surface in comparison with linear, nonacidic species. The systems with the greatest relative stabilization with respect to pure calcite-water interface are those with high energy defects (kinks) and highly branched, acidic polysaccharides, suggesting that the known reduction in the growth rate of calcite crystals in the presence of these acidic, polysaccharides may be due to the effective coverage of high energy sites associated with calcite growth, blocking the growth mechanism during their residence. Additionally, a suggested metric for the estimation of polysaccharide to calcite binding energies, and thus their effectiveness at inhibiting calcite growth, is given, wherein the difference between the number of hydrogen bonding pairs present when the polysaccharide is in solution and in vacuo was shown to correlate strongly with overall binding energy.

[1] Nielsen *et al* (2012); *Cryst. Growth Des.* **12**, 4906–4910