

## **Polysaccharide Chemistry and Ionic Strength Regulate Calcite Nucleation Barriers through Continuum of Competing Interfacial Forces**

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Researchers have long-postulated that living organisms utilize organic matrices to actively guide the formation of crystal structures. Calcified skeletons are produced within complex assemblages of proteins and polysaccharides whose roles in mineralization are not well understood. The timing and placement of these features are most easily controlled during nucleation. Our recent kinetic study of heterogeneous calcite nucleation found the energy barrier to formation is regulated by competing interfacial energies between the substrate, crystal, and liquid [1]. Chitosan presents a low energy barrier to nucleation because its near-neutral charge favors formation of a substrate-crystal interface, thus reducing interactions with water. Progressively higher barriers are measured for negatively charged alginates and heparin that favor contact with the solution over the formation of new substrate-crystal interfaces. These results showed calcite nucleation is controlled by substrate-crystal interactions but could not quantify the larger continuum of competing forces that must regulate calcite nucleation.

To determine these relationships, we measured the kinetics of homogeneous calcite nucleation in NaCl solutions that extend to seawater salinity (0.6 M). The data show the nucleation barrier and crystal-liquid interfacial energy are smaller in high ionic strength solutions. This supports recent findings that background electrolytes promote ion desolvation during nucleation. By applying this relationship to heterogeneous nucleation on chitosan and heparin, we quantify the relative contributions of substrate-crystal-liquid interfacial energies. The findings build a framework for how functional group chemistries of organic molecules regulate mineralization. Insights from this study suggest substrate chemistry and ionic strength provide additional means of tuning the energy barriers to calcite nucleation.

[1] Giuffre *et al* (2013), *PNAS* **110**, 9261-9266