



The Role of Bicarbonate in Calcium Carbonate Mineralization

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Calcium carbonate (CaCO_3), the most abundant biomineral, is the major inorganic component in mollusk shells, corals and sea urchins. Although the pH level significantly influences CaCO_3 precipitation, the assessment of physiological, i.e. near-neutral pH has not yet been explored quantitatively. In this study, we implemented a quantitative titration assay to fill this gap. The data strongly suggests that although calcium bicarbonate ion association is very weak, bicarbonate binding plays a distinct role during nucleation of the initial mineral phase, at least at near-neutral pH. Solid-state nuclear magnetic resonance (NMR) results evidence that bicarbonate ions are incorporated into the structure of amorphous CaCO_3 . The titration methodology further shows the effects of recombinant proteins on mineralization at physiological conditions, which are not evident at higher pH levels, and shed light on the biochemical mechanisms regulating mineral nucleation and growth. Altogether, our work suggests that biomineralization encompasses bidirectional processes involving; (i) biomolecules that modulate nucleation and crystallization behavior of inorganics; and (ii) inorganics that tune the self-association of biomolecules.