On the role of bicarbonate during the early stages of calcium carbonate precipitation

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In recent years, the important role of amorphous precursors and intermediates in crystallization has become obvious. While the advantage of such species for the generation of complex crystal morphologies in biomineralisation is known since the early 2000s, the underlying structural, thermodynamic and kinetic characteristics, as well as pathways involved towards the final crystal structures, often remain elusive.

Here, we present the newest insights into solute, liquid and solid amorphous precursors and intermediates and their role in crystallization. Thereby, we focus on calcium carbonate ($CaCO_3$), the most abundant biomineral, which is the major inorganic component in mollusk shells, corals or sea urchins —also addressing recent debates. One particular emphasis concerns the effects of near-neutral pH levels, which significantly influence $CaCO_3$ precipitation. The data shows that although calcium bicarbonate ion association is very weak, bicarbonate binding plays a distinct role during nucleation of the initial mineral phase at near-neutral pH. Solid-state nuclear magnetic resonance (NMR) results evidence that significant amounts of bicarbonate ions are incorporated into the structure of amorphous $CaCO_3$. Indeed, certain recombinant proteins from biomineralization show effects at physiological conditions, which are not evident at higher pH levels, and shed light on the biochemical mechanisms regulating mineral nucleation and growth. Since charge and structure of the proteins do not change in the investigated pH regime, this strongly suggests a role of the bicarbonate incorporation during mineral-protein interactions. 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.