

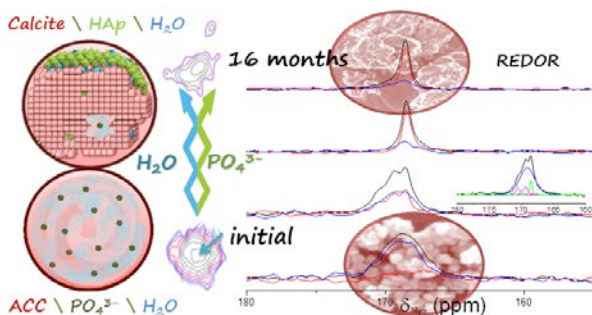
Molecular-Functional Insights into Biomimetic Pathways

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Amorphous materials and short-range order regions are of critical importance in materials science and in biomineralization. The lack of long range order poses a challenge for their structural characterization at the molecular level. Using dipolar-based solids NMR techniques I will review how directed incorporation of additives regulates the functional properties of calcium carbonate *biominerals* such as the construction of bioavailable calcium reservoirs (amorphous CaCO_3 , ACC, gastroliths in crayfish) or of complex skeletal scaffolds (calcitic coccoliths). Using *in vitro* model systems we show the interlinked thermodynamic-kinetic role of phosphate ions and water molecules in stabilizing ACC, or destabilizing it and inducing a 'programmed' phase separation and amorphous-to-crystalline transformations. Both pathways mimic primary strategies in biomineralization.



Solid state NMR, our primary tool (supported by XRD, FTIR, TGA, SEM), is shown most suitable to expose the molecular details that underlie the functionalities of these diverse systems. The emerging insight is directly connected with the understanding of fundamental principles of biomineralization/biomimetic pathways. Our findings are of immediate relevance to rational design of functional, bio-inspired materials.