

How do calcium carbonates form in microemulsions?

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Calcium carbonates, the most ubiquitous and functional biominerals in nature are formed in microorganisms through directed precipitation. The chemistry of these reactions underpins a vast array of Earth system processes, including the global C cycle. Being able to elucidate and mimic such biomineralization mechanisms, would not only increase our knowledge about important processes supporting a vast array of marine planktonic life forms, but would also provide us with a powerful tool to *nanoengineer* complex (bio)inorganic materials. We mimicked such processes through the use of water-in-oil microemulsions/micelles as they provide the reaction environments confined by polar-nonpolar interfaces. They offers ideal conditions for synthesis of nanoparticles of low polydispersity and well-defined shapes. Such micelle systems act as perfect bioinspired nanoreactors, in which reagents are dissolved in water nanodroplets, and react with each other upon droplet collisions.

We followed the development of a CaCO₃ precursor phase forming through a slow, but progressive agglomeration of the initially stable highly supersaturated ion-carrying microemulsion nanodroplets ($\varnothing < 10$ nm) into large spherical aggregates ($\varnothing > 250$ nm). We characterised this reaction by time-resolved, *in situ* SAXS and showed that the aggregates formed at the expense of the precursor ion-carrying water nanodroplets. The high stability of the aggregates led us to a hypothesis that they contained only liquid-like precursor CaCO₃ entities. Complementing this data with liquid-cell TEM characterisation allowed us to confirm that these liquid phase aggregates remained stable until intentional destabilization of the microemulsion interface lead to the very rapid transformation of their contents into solid and crystalline CaCO₃ phases. This demonstrates that biomineralization of CaCO₃ can be controlled in confinement by external chemical triggers, rather than depend only on supersaturation of ions in solution.