

CaCO₃ precipitation confined in microemulsion nano-droplets of water

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Reverse microemulsions are thermodynamically stable water-in-oil suspensions (i.e., micelles stabilised by an interface surfactant). Such water-in-oil droplets are typically 1-10 nm in diameters and each can carry dissolved salt ions and exchange their contents upon collisions. Thus, they are ideal for mimicking mineral precipitation in highly confined volumes at the polar/non-polar interface. Here we present results from a study where we used such microemulsions as analogue model systems for biomineralization (e.g., coccolith frustules produced within the organic cell vesicles of coccolithophores). We followed the reaction between two separate initially clear microemulsions, one containing solely Ca²⁺ and the other CO₃²⁻ ions and quantified the gradual development of a white precipitate using *ex situ* and *in situ* high-resolution imaging, diffraction and scattering.

The *ex situ* results revealed stabilised nano-sized ($\emptyset \sim 10$ nm) particles of low-polydispersity forming larger aggregates ($\emptyset \sim 250$ nm). However, the morphology of the particles as determined *in situ* (with the liquid phase present) was considerably different. Time-resolved and *in situ* small angle X-ray scattering demonstrated that the particles grew through a slow but progressive agglomeration of ion-carrying micelles to larger mass-fractal-like stable structures of high fractal dimension ($\emptyset \sim 100$ nm, $D_f > 2.8$). The *in situ* scattering in conjunction with liquid-cell TEM results suggested that upon destabilization of the mass-fractal-like structures, a transformation from initially stable micelle-sized structural units to larger particles took place.

By combining these results with the fact that an individual micelle can accommodate in its water core only a limited number of reacting ions, we hypothesize that these micellar mass-fractal-like aggregates likely contain only liquid-like CaCO₃ complexes stabilised by the confinement and interfaces and not CaCO₃ solid particles *per se*.