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Liquid-liquid phase separation of $CaCO_3$ revealed by in situ transmission electron microscopy

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Increasing evidence suggests that formation of mineral phases can occur via dehydration of an initial dense liquid phase or via nucleation within the dense liquid droplets. For example, nucleation of amorphous $CaCO_3$ (ACC) mineral has been shown to proceed by formation of a dense, disordered liquid droplet consisting of molecular precursors proposed to be either ion pairs or prenucleation clusters. However, the roles of water and additives, such as highly charged macromolecules that induce formation of a so-called “polymer-induced liquid precursor,” as well as the structural changes associated with the formation and transformation of the dense liquid phase, remain unclear due to limited studies on liquid-liquid phase separation. We directly captured the formation of the dense liquid phase in the presence of highly negatively charged proteins and observed multiple processes leading to the transformation into solid $CaCO_3$ phases. Liquid C-13 NMR and ATR-FTIR data record formation of the dense liquid phase and show that the protein has a stabilizing effect on it. Using in situ liquid cell transmission electron microscopy, we observed the early nucleation and growth stages of solid $CaCO_3$ from individual dense liquid droplets. These initial particles were identified as liquid through their liquid-like characteristics, such as rapid fusion, dependence of growth rate on time ($r(t) \sim t^{1/3}$), viscosity ($\sim 10^7$ Pa/s), density ($\sim$ 1.1 g/cm^3) and ratio of H_2O to $CaCO_3$ (~8). We also found that the liquid droplets can exhibit internal rearrangement to form a “core-shell-like” structure prior to dehydration to ACC and transformation to vaterite. Moreover, a network of the dense liquid phase was formed that was reminiscent of patterns of spinodal decomposition in polymer melts deep within a spinodal region. Generally, our investigations show that dense liquid phase appears to be a high viscosity fluid formed from initially supersaturated $CaCO_3$ solution through liquid-liquid phase separation. This liquid phase rearranges, dehydrates, and transforms into a less hydrated amorphous solid or crystal. These findings provide an in-depth view of $CaCO_3$ nucleation via liquid-liquid phase separation and highlight the role of charged proteins in orchestrating this complex pathway.