

CaCO₃ nucleation and growth at different {Ca²⁺}: {CO₃²⁻} ratios in aqueous environments

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CaCO₃ precipitation is an important process in industrial applications as well as in nature. However, its precipitation is usually impure and despite the ample amount of information available on this topic, the mechanisms playing a role during CaCO₃ precipitation are still not fully unraveled. We investigated the effect of stoichiometry on the new formation (nucleation) and subsequent growth of CaCO₃ over a large range of supersaturation with respect to calcite ($30 < \Omega < 200$; where $\Omega = \{Ca^{2+}\}\{CO_3^{2-}\}/10^{-8.48}$) and solution stoichiometries ($10^{-4} < r_{aq} < 10^4$; where $r_{aq} = \{Ca^{2+}\}:\{CO_3^{2-}\}$) at a pH of 10.5 ± 0.27 at ambient conditions. In stoichiometric solutions and $\Omega < 150$, dynamic light scattering (DLS) showed that ion adsorption onto preclusters (1 – 10 nm) was the dominant mechanism to form CaCO₃ particles of up to 300 nm in 15 hours. Contrary, aggregation of preclusters, forming particles of 100's of nm up to 2000 nm within 15 hours, was dominant at higher supersaturation levels. In non-stoichiometric solutions at $\Omega = 100$, preclusters remained smaller than 10 nm for up to 15 hours. Additional molecular dynamics (MD) simulations confirm that, at very high supersaturations ($\Omega \gg 1000$), stoichiometry effects the CaCO₃ formation substantially and observed trends closely match those observed with DLS. The CaCO₃ precipitation kinetics are more strongly affected by the absence of Ca²⁺ compared to the absence of CO₃²⁻. Our results imply that, besides Ω , stoichiometry effects initial precluster size and persistence, growth mechanism and ripening time towards μ m-sized crystals. Ultimately, our findings may help to improve future predictions of, or optimize the physico-chemical conditions for CaCO₃ formation in industrial and geo-engineering settings.