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Controlling $CaCO_3$ particle size with $\{Ca^{2+}\}$:$\{CO_3^{2-}\}$ ratios in aqueous environments

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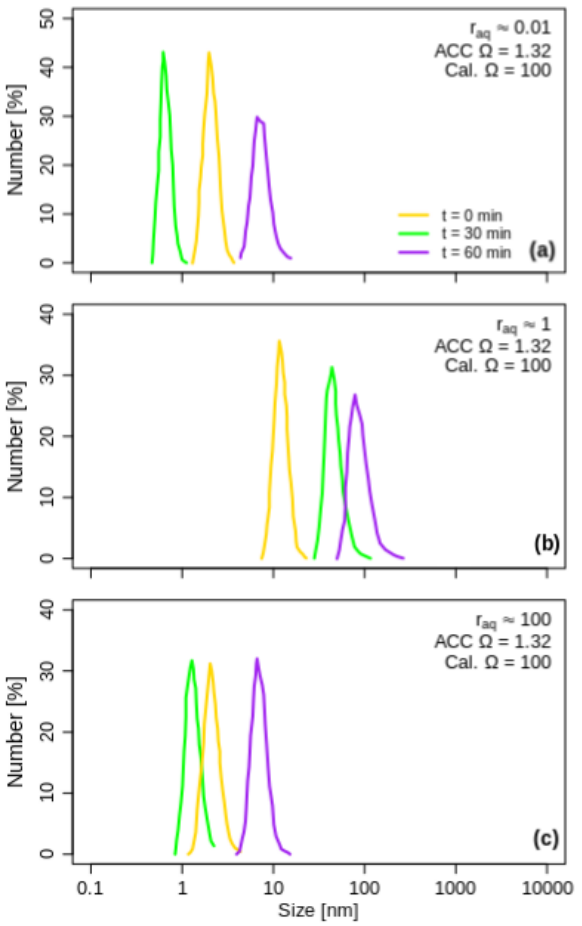
The impact of stoichiometry ($r_{aq} = \{Ca^{2+}\}:\{CO_3^{2-}\}$) on the new formation and subsequent growth of $CaCO_3$ is important, as most natural waters and industrial crystallization processes proceed nonstoichiometrically. Therefore, we investigated in a broad range ($10^4 < r_{aq} < 10^{-4}$) the effect of solution stoichiometry at various, initially constant degrees of supersaturation ($30 < \Omega_{cal} < 200$; where $\Omega_{cal} = \{Ca^{2+}\}\{CO_3^{2-}\}/K_{sp}$), pH of 10.5 ± 0.27, and ambient temperature and pressure [1]. At $r_{aq} = 1$ and $\Omega_{cal} < 150$, dynamic light scattering (DLS) showed that ion adsorption onto nuclei (1 - 10 nm) was the dominant mechanism. At higher supersaturation levels, no continuum of particle sizes is observed with time, suggesting aggregation of prenucleation clusters into larger particles as dominant growth mechanism. At $r_{aq} \neq 1$ ($\Omega_{cal} = 100$), prenucleation particles remained smaller than 10 nm for up to 15 hours. Cross-polarized light in optical light microscopy was used to measure the time needed for new particle formationand growth to at least 20 μm. This precipitation time depends strongly and asymmetrically on r_{aq}. Complementary Molecular Dynamics (MD) simulations confirm that r_{aq} affects $CaCO_3$ nanoparticle formation substantially. At $r_{aq} = 1$ and $\Omega_{cal} >> 1000$, the largest nanoparticle in the system had a 21 - 68% larger gyration radius after 20 ns of simulation time than in nonstoichiometric systems. Our results imply that, besides Ω_{cal}, stoichiometry affects particle size and persistence, growth and ripening time towards μm-sized crystals. Our results help to improve understanding, prediction and formation of $CaCO_3$ in geological, industrial and geo-engineering settings.

[1] Seepma, Ruiz-Hernandez, Nehrke, Soetaert, Philipse, Kuipers & Wolthers (2021), Accepted for publication in *Crystal Growth & Design*. DOI: 10.1021/acs.cgd.0c01403



Caption Figure: The relative number of particles plotted against the size of particle at different stoichiometric conditions at an $\Omega_{cal} = 100$ for the first hour of the precipitation reaction (adapted from [1])