

NUCLEATION OF CaCO_3 , LINKING RATES AND MECHANISMS

WOLTERS, Mariette (Department of Earth Sciences, Utrecht University, The Netherlands)

FERNANDEZ-MARTINEZ, Alejandro (ISTerre, CNRS & University Grenoble Alpes)

NEHRKE, Gernot (Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany;

Outline

The overall aim was to study the mechanism(s) and kinetics of Amorphous Calcium Carbonate (ACC) formation and ACC transformation into calcite *in situ* in relation to solution stoichiometry. Experiments were performed in kapton capillary, while calcium and carbonate bearing solutions were individually pumped towards and mixed just before the entrance to the capillary. While we varied the carbonate to calcium activity ratio $r_{\text{aq}} = \{\text{CO}_3^{2-}\}/\{\text{Ca}^{2+}\}$, we kept degree of supersaturation, pH and temperature constant. We focused the beam at one point along the flow path, as close to the mixing point as possible, observed particle formation and transformation at the kapton capillary wall with time.

Results

At $r_{\text{aq}} 2.6$, rapid formation of a "WAXS amorphous" scattering phase was observed in the time-resolved SAXS patterns (Fig. 1A), which we know is ACC. This phase disappears just before appearance of the dominant calcite peak in the WAXS pattern (red line Fig. 1B). Nucleation of this ACC phase is instantaneous in the current experimental set-up: the measurements started prior to mixing, but the first 1s scan after mixing started was identical to the next few scans. This means that ACC formed within less than 1s. A next set of experiments will be aimed to resolve ACC formation kinetics at millisecond time scales using a stop-flow set-up. ACC formation and transformation into calcite were much slower at $r_{\text{aq}} 0.015$, while at $r_{\text{aq}} 91$ a strongly scattering phase persists throughout the 83 minutes of the experiment while calcite peaks appear and intensify (green line in Fig. 1B).

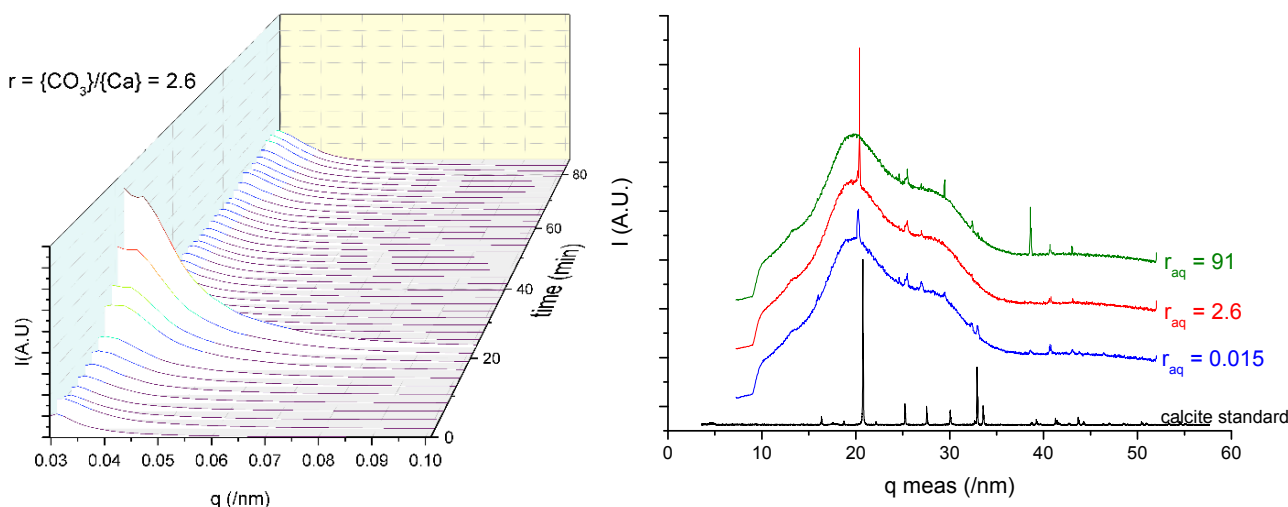


Fig. 1. (A) Time-resolved SAXS patterns at $r_{\text{aq}} = 2.6$. Only one scan per 20 scans obtained is shown for visibility. (B) WAXS patterns obtained after 85 minutes of experiment time at three different solution stoichiometries compared to calcite standard (RRFUFF 040070).

In the WAXS patterns a small peak is observed from ~ 40 min into the experiment at $r_{\text{aq}} 2.6$. This peak is the [10-14] d-spacing of calcite and becomes more intense with time (highest peak in red line, Fig. 1B.). Several other d-spacings of calcite appear in the WAXS pattern, with different intensity ratios to standard randomly ordered calcite powder obtained using XRD (black line, Fig. 1B), suggesting the calcite formed in these experiments is either preferentially ordered at the kapton capillary or is of slightly different morphology. At $r_{\text{aq}} 0.015$, the intensity ratios of the various calcite d-spacings, deviates more strongly than at $r_{\text{aq}} 2.6$. Besides, peaks are broader, suggesting small sized calcite (nano)crystals have formed. At $r_{\text{aq}} 91$, the most striking observation is the missing peak for the [10-14] d-spacing, which is usually the dominant cleavage plane. Given the narrow width of other WAXS peaks, crystalline calcite formed of a particular morphology with a strong preferential ordering at the capillary wall.

Conclusions

The results suggest that rates of ACC formation and transformation depend on solution stoichiometry. Furthermore, calcite formed varies in particle size, morphology and potentially degree of crystallinity. Further analysis of SAXS (particle size and morphology) and WAXS data is currently underway to detail formation kinetics, mechanisms and morphologies in relation to solution stoichiometry.