Supplementary Information

Aerosol based synthesis of pure amorphous calcium carbonate
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Experimental methods

Materials: 99.995% metal basis calcium hydroxide purchased from Sigma Aldrich was used for all the experiments as received. Nitrogen bubbled, 18.2 MΩ milli-Q water from laboratory-based purification system (Millipore, Milford, MA, USA) was used for all the experiments to ensure no dissolved CO₂ is present. All solutions were prepared in new low-density polyethylene bottles at standard pressure of 1bar and temperature of 297K. For each experiment, a fresh super saturated solution of calcium hydroxide (~23mM) was prepared by adding 2g of Ca(OH)₂ into 200ml milliQ and placing in an ultrasonic bath for 1 hour. The solution was then filtered using a syringe filtration unit Filtropur S 0.2 with filtration surface: 5.3 cm², pore size: 0.2 µm followed by subsequent dilution to the desired concentration.

Reference samples: Calcite and calcium hydroxide reference samples were purchased from Sigma Aldrich and used without further purification. Vaterite reference sample was synthesized by directly mixing 40mM ammonium carbonate solution (pH 9.0) with 40mM CaCl₂ solution. Immediately after mixing, the precipitate was filtered and washed several times using Buchner vacuum filtration with a glass fiber membrane (Whatman, 1820-025) then left to dry in a desiccator.

Particle size distribution: The particle size distribution was measured using an alcohol based condensation particle counter (CPC) model 3775 by TSI®. The Aerosol atomizer was coupled to the CPC where the aerosols emerging at the exit of the atomizer were drawn into the CPC by an internal pump. The inlet pressure of the CPC was 980.5mbars, the flow to the CPC was set to low flow with a sheath flow of 3L/min and aerosol flow of 0.3L/min going through the CPC saturator. The lower particle size...
limit was set to 22.9nm and the upper limit set to 1000nm. SMPS software was used for data collection. Fig S1 shows the aerosol particle size as a function of calcium hydroxide solution concentrations.

**Synchrotron based Ca K-edge XANES measurements:** All XANES measurements were done at the PHOENIX (Photons for the Exploration of Nature by Imaging and XAFS) beamline at the Swiss Light Source which is an undulator-based beamline, providing photons in the tender x-ray range between 0.3 and 8 keV with spot sizes between 3X3µm and 1X2 mm. For the Ca K-edge XANES measurements of calcium hydroxide, calcite, vaterite and dry ACCs, the samples are deposited on a carbon tape attached to a copper plate and mounted in a vacuum chamber maintained at about 10^{-5} -10^{-6} mbar for analysis. Spectra were collected both in total electron yield and in fluorescence, for fluorescence, a 4-element silicon drift diode (SDD) energy dispersive KETEK detector was used. For the in situ experiments, the freshly prepared dry ACCs were deposited directly on a vitreous carbon disc (Nano and more GmbH) which was then mounted in a vacuum tight in situ cell equipped with a 500nm silicon nitride window and connected to a humidification system equipped with humidity sensors at the entry and exit of the in situ cell. The cell was mounted into the PHOENIX end station vacuum chamber maintained at about 10^{-5} -10^{-6} mbar. The ACC sample was first measurement with no humidity (only dry He gas passing through the cell after which the humidity was switched on and set to 75% relative humidity at 800mbars pressure in the in situ cell. Continuous XANES measurements were done with each spectrum taking 15 minutes. A spot size of 0.4 by 0.6mm was used and data acquisition was done using a Roentec detector.

**SEM measurements:** For the SEM measurements, the aerosol ACCs were deposited on vitreous carbon support. The measurements were done using a Zeiss Merlin field emission SEM operated at an acceleration voltage of 6kV with a 100pA probe. The sample was coated with a 4nm thick iridium film to prevent charging. Additional SEM images of the aerosol ACCs are shown in Fig S2.
**IR measurements**: HYPERION 3000 FT-IR Microscope coupled to an INVENIO FT-IR Spectrometer was used for all the IR measurements. The measurements were done on reflection mode using 15X objective in the MIR region. Dry ACC samples were deposited on a polished steel mirror which was mountable in the in situ cell described above for *in situ* IR measurements. Data acquisition was done using a liquid nitrogen cooled focal array detector equipped in the FT-IR microscope and OPUS software was used for setting the experimental parameters, data acquisition and conversion. Background correction was achieved by measuring a region in the mirror with no sample and using it as the background. For the time resolved in situ measurement during humidity exposure, the sample was enclosed in the in situ cell equipped with the silicon nitride. Fig S3, shows the in situ IR measurements over the 8-day period of continuous 90% relative humidity exposure. The changes in the out-of-plane bending vibration (ν2) band at around 864cm⁻¹ are somewhat noisy due to the sharp absorption band of Si-N centered at about 840cm⁻¹.
Fig S1: *EDX elemental analysis of aerosol ACC deposited on vitreous carbon without the 4nm thick iridium film coating. Only carbon from the vitreous carbon support and calcium and oxygen from the ACC sample are detected*
Fig S2: particle size distribution as a function of calcium hydroxide concentration
Fig S3: SEM images of aerosol ACCs prepared from (a), (b) a 2mM Ca(OH)₂ solution and collected for 20 minutes (c), (d) a 20mM Ca(OH)₂ solution and collected for 10 minutes (scale bar 10µm)

Fig S4: Ca K-edge XANES spectra of Aerosol ACC, before and after 8 days of 90% relative humidity exposure.