SUPPORTING INFORMATION

Non stoichiometric hydrated magnesium-doped calcium carbonate precipitation in ethanol

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EXPERIMENTAL DETAILS

Calcium carbonate was precipitated by direct addition of Ca^{2+} and CO_3^{2-} in absolute ethanol solution in the presence of Mg^{2+}. Precursor reagents used for the synthesis were anhydrous $CaCl_2$ (Sigma Aldrich, purity >99%), anhydrous $(NH_4)_2CO_3$ (Acros Organics, for analysis ACS) and anhydrous $MgCl_2$ (Sigma Aldrich, powder, purity>98%). Reagents were put in a desiccator with P_2O_5 for several days in order to dry them completely. After that, they were stored in a closed desiccator with P_2O_5 until usage. 0.1 M solutions of $CaCl_2$ and $(NH_4)_2CO_3$ and several solutions with different concentrations (see Table SI1) of $MgCl_2$ in absolute ethanol (Sigma Aldrich, for HPLC, purity >98%) were prepared stirring the previously dried salts overnight. The solutions were filtered with 0.2 μm filters before use. Then, 5 mL of both $CaCl_2$ and $(NH_4)_2CO_3$ solutions were injected with syringe pumps (rate 7.5 mL/h, era pump system inc.) into 5 mL of different $MgCl_2$ alcoholic solution to reach the desired Ca/Mg ratio.

The whole synthesis process was conducted in a sealed vessel using 3 different custom-made setups to prevent the diffusion of water in ethanol:

   A. Synthesis without any probe in a vessel with 2 holes on the top for tubes to add solutions;
   B. Synthesis with turbidity sensor in a vessel with 4 holes on the top: 2 for the tubes, 1 for the turbidity sensor and 1 for a glass stick necessary to assure the perfect filling of optical path of the probe;
   C. Synthesis with turbidity and conductivity sensors in a vessel with 4 holes on the top: 2 for the tubes, 1 for the turbidity sensor and 1 other for the conductivity sensor.

All the probes are suitable and calibrated for use in ethanol solutions.

The presence of water in the ethanol used for the experiments was assessed both by refractive index and density-based methods.

To follow the kinetics of nucleation and precipitation, two different probes were used. A turbidity sensor associated to a spectrophotometer (Ocean optics 2000+ UV-Vis lamp with Ocean optics USB-DT CCD) was used to see the effective beginning of precipitation measuring the scattering of light by particles precipitated in solution. All these data were treated with a customized software, edited by the research group of prof. Helmut Cölfen in Konstanz (Germany). A conductivity sensor (Metrohm plug-in head G) was used to confirm turbidity data.

To evaluate particle dimensions and their size distribution before centrifugation, dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano ZS instrument equipped with a 633 nm laser diode. Samples were transferred to disposable polystyrene cuvettes of 1 cm optical path length without diluting them. The values were taken averaging three different runs.

When a precipitate was formed, it was separated by centrifugation at 4500 g for 10 minutes. The precipitate was then dried in an oven at 60 °C overnight. Samples were then kept in a closed desiccator with P_2O_5.

Fourier transform infrared (FT-IR) spectra were acquired by using a PerkinElmer Spectrum 100 instrument equipped with an attenuated total reflection (ATR) accessory and recorded with spectral resolution of 1 cm^{-1} in the range of wavenumbers 4000–650 cm^{-1}. FTIR spectra of samples in KBr pellet were collected by using a FT-IR Thermo Scientific Nicolet iS10 spectrometer equipped with a

"Smart Omni-Transmission" module working in the range of wavenumbers 4000–400 cm^{-1} at a resolution of 1 cm^{-1} with 64 scans.

Transmission electron microscopy (TEM) and electron diffraction (ED) were performed by using a Zeiss Libra120 instrument working at 200 keV, in the nano.lab of the University of Konstanz after depositing a few drops of the calcium carbonate suspension on the TEM grid and letting them evaporate without further processing. More than 50 particles have been measured with the software Image-J to determine the average size of the particles.

X-ray Powder diffraction (XRPD) measurements were performed with a D8 Discover X-Ray diffractometer (Cu, K$_\alpha$) with a VANTEC-500 detector from Bruker (Karlsruhe, Germany) or a PanAnalytical X'Pert Pro diffractometer equipped with X'Celerator detector with Cu K$_\alpha$ radiation. In addition to this equipment, an Anton-Paar TTK450 was used to carry out XRPD measurements with different temperatures in the range 25-320°C in vacuum.

Thermogravimetric analysis (TGA) was performed using an SDT Q600 instrument (TA Instruments). Analytical ultracentrifugation was performed on an Optima XL-I (Beckman-Coulter) using the Rayleigh interference optics as detection system. The samples were investigated in 12 mm Ti double sector cells (Nanolytics) at 20 °C and 60000 rpm.

SEDFIT (http://www.analyticalultracentrifugation.com/) was used for the evaluation of the data using discrete species fits to the Lamm equation and g(s) sedimentation coefficient distributions. The particle size was determined from the diffusion coefficient using the Stokes-Einstein equation.

Magnesium content in the precipitate obtained with starting Mg/Ca=2 has been measured with flame atomic absorption spectroscopy (Ametek Spectro, Arcos, Kleve, Germany). The Mg content has been obtained by dividing the Mg quantified via flame atomic spectroscopy by the amount of precipitate used for the analysis.

ADDITIONAL CHARACTERIZATION

Table SI1. Experimental cconditions used for $CaCO_3$ precipitation in ethanol in the presence of Mg^{2+}.

[Ca] : [Mg]	$[Ca^{2+}] = [CO_3^{2-}]$ (mM)	$[Mg^{2+}]$ (mM)	Result
∞	33	0	Precipitated and analyzed
1	33	33	Precipitated but dissolved during stirring
2	33	16	Precipitated but dissolved during stirring
3	33	11	Precipitated and analyzed
5	33	6	Precipitated and analyzed
10	33	3	Precipitated and analyzed
30	33	1.1	Precipitated and analyzed
50	33	0.6	Precipitated and analyzed
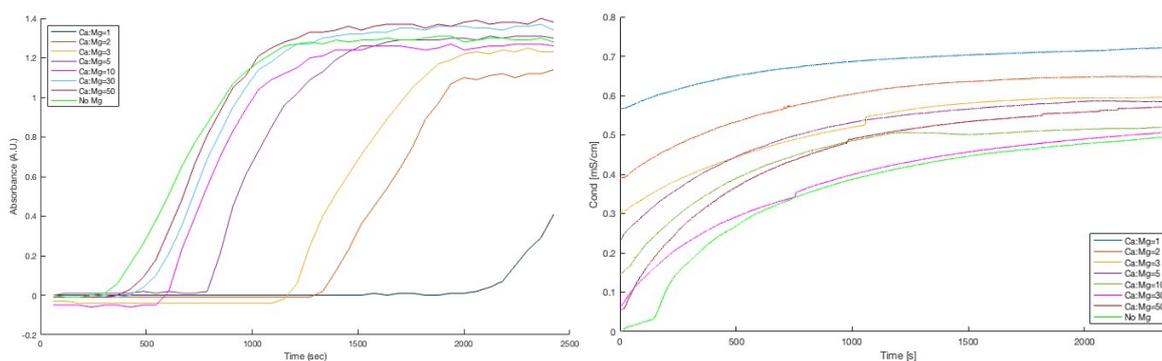
Figure SI1. (a) Turbidity and (b) conductivity data of syntheses of $CaCO_3$ at different Ca/Mg molar ratio.

These data show that the time necessary for the precipitation to start increases with the increase of the concentration of Mg^{2+}. Conductivity data, which measure the free ion content in the solution, show similar trends during synthesis reaching a "plateau" when precipitation occurs.
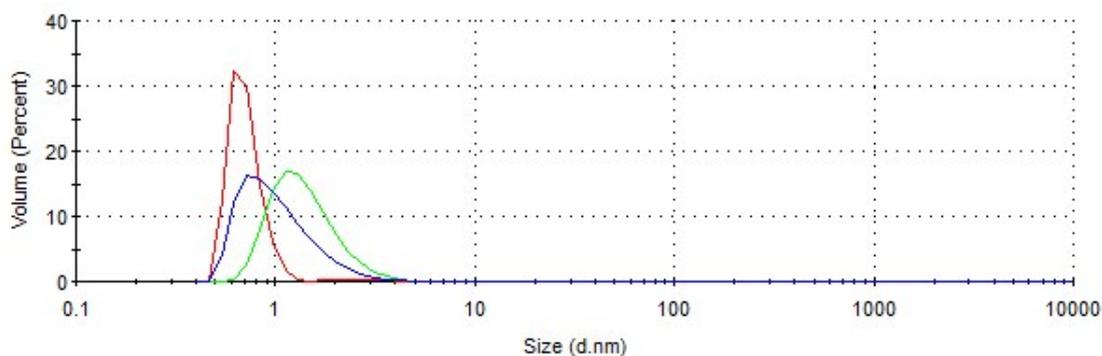
Figure SI2. DLS measurements of Ca/Mg molar ratio = 1 samples after 23 h (red), after 22 h (green) and after 21 h (blue) with Size Distribution weighted by volume.
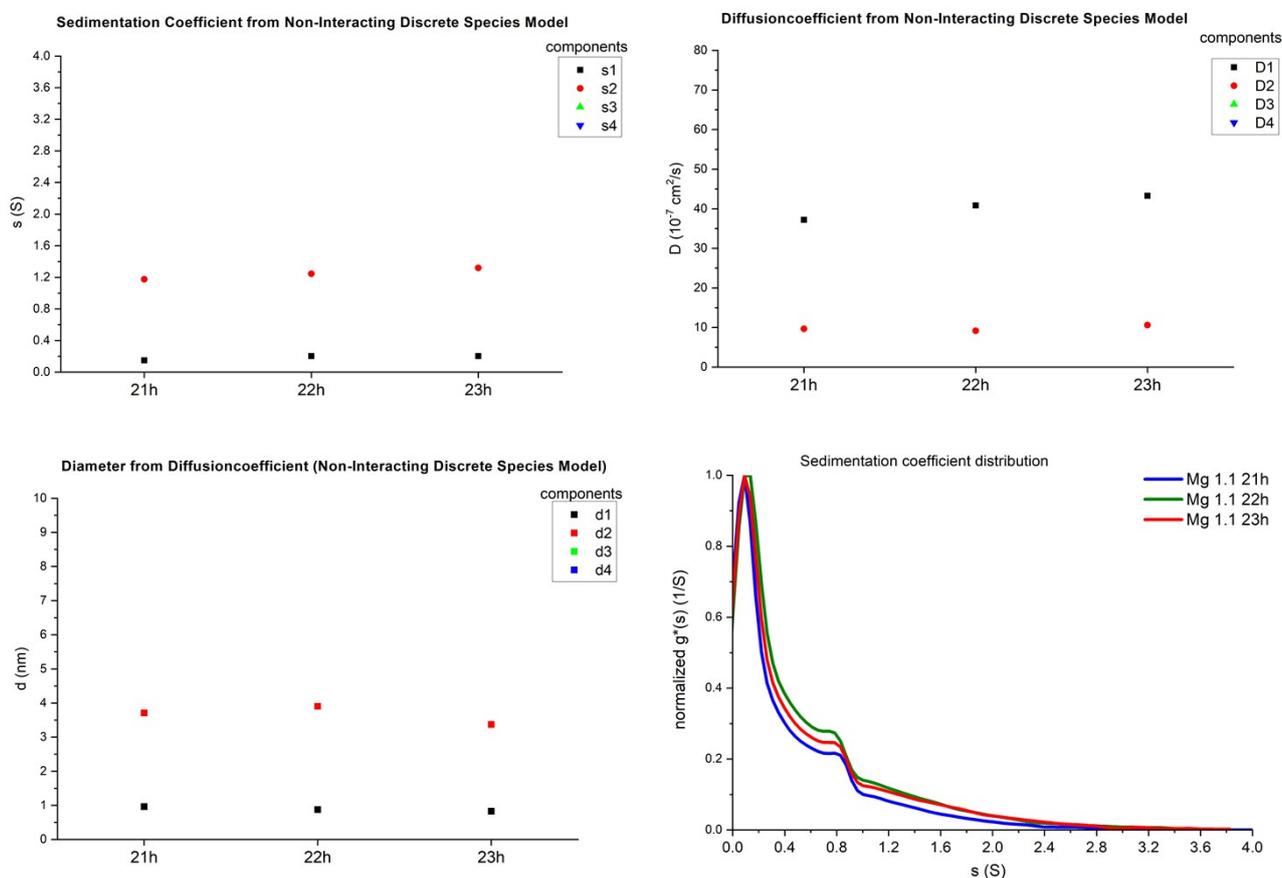
Figure SI3. Sedimentation coefficient, diffusion coefficient, diameter of species and sedimentation coefficient distribution from Ca/Mg molar ratio = 1 samples after different stirring times.
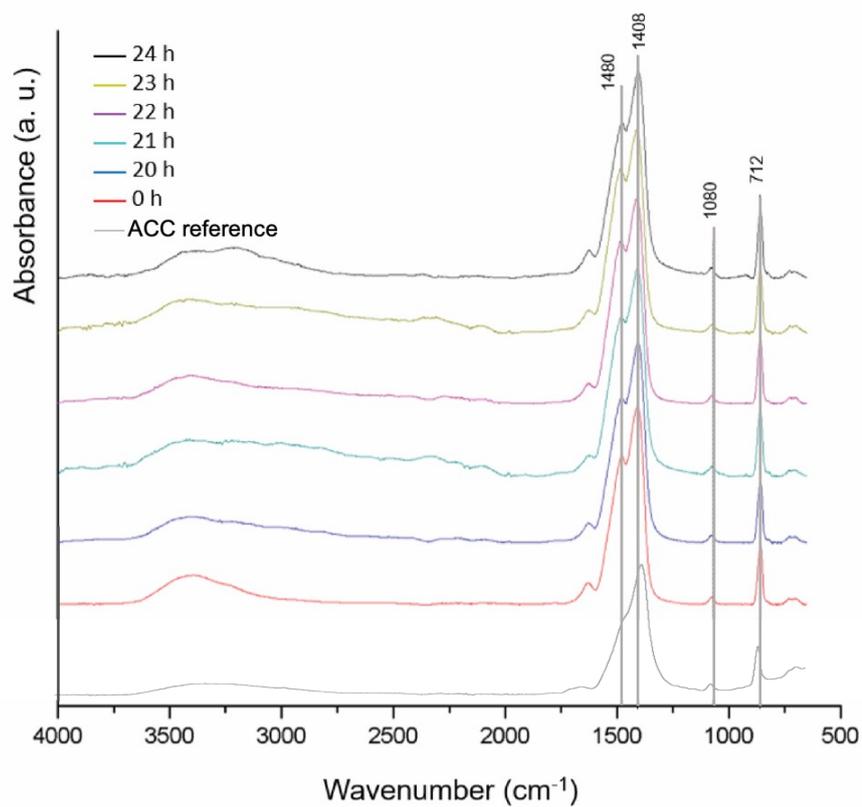
Figure SI4. FTIR spectra after different times with Ca/Mg molar ratio = 2.

ACC reference spectra found in:

- Gebauer, V. Oliynyk, M. Salajkova, J. Sort, Q. Zhou, L. Bergström, G. Salazar-Alvarez, Nanoscale 2011, 3, 3563-3566;

- M. Farhadi Khouzani, D. M. Chevrier, P. Güttlein, K. Hauser, P. Zhang, N. Hedin, D. Gebauer, CrystEngComm 17, 4842-4849, 2015.
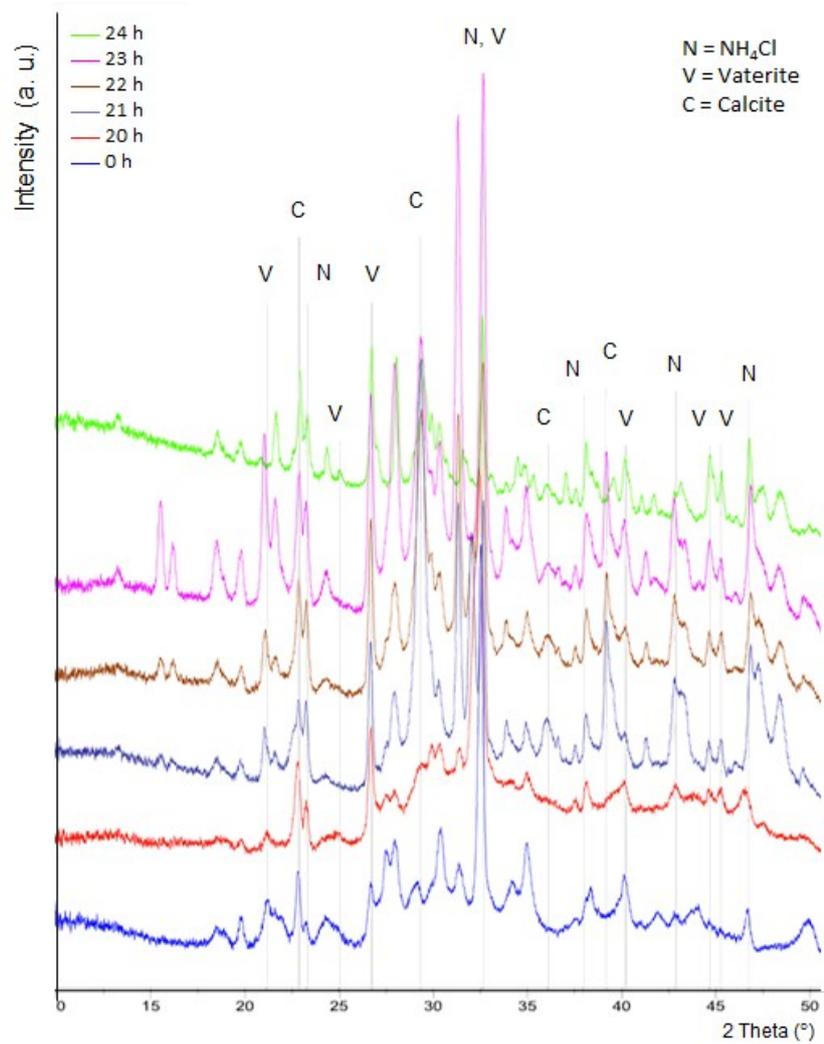
Figure SI5. XRPD patterns after different times with Ca/Mg molar ratio = 2.