Supporting Information

Role of CaCO$_3^o$ neutral pair in calcium carbonate crystallization

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SI1: Experimental methods

Counter-diffusion experiments were carried out within U-tubes (Triana S&T). Reservoirs containing 0.5 M solutions of the two reagents, sodium hydrogen carbonate (NaHCO₃, Fluka Biochemika) and calcium chloride (CaCl₂·2H₂O, Sigma-Aldrich), were separated by an agarose gel column, allowing diffusion of two reagents into the gel from opposite ends. The 3% (w/w) agarose gel was previously loaded with the pH-fluorescent dye (8-hydroxypirene-1,3,6-trisulfonic acid trisodium salt (SF); Aldrich H1529). The time evolution of the pH was obtained from time-lapse series pictures (Figure 1).

The horizontal part of the U-tube (Triana S&T) was filled with a sol of agarose prepared by heating a 3% m/v solution of agarose powder in water. This sol was allowed to set by cooling after adding a pH-fluorescence dye under stirring. After setting the gel, the vertical arms of the U-tube were filled with [0.5 M solutions of sodium hydrogen carbonate and calcium chloride (CaCl₂·2H₂O) respectively. All solutions were prepared with ultrapure water (0.22 µS, 25°C, MilliQ©, Millipore).

The fluorescence photographs were observed with a custom-assembled instrument shown in Figure 1. The sample tube was excited with a homogeneous illumination beam from a 500W Xenon arc lamp selected with a bandpass filter (bandpass 450nm, Oriel Corp. Scorpio Optics), while the fluorescence signal was selected with a cut-off filter (cut-off 495nm Oriel Corp. Scorpio Optics, to collect fluorescence and get rid of the excitation light and collected by a CCD camera (Basler scA640-70gc) equipped with a M1214-MP Computer objective (12mm, F/1.4), each pixel yielding a fluorescence intensity signal in a precise spatial point to be elaborated for further analysis. All videos were analysed by means of custom developed Matlab code. Two references were taken to correct for non-ideal illumination conditions: an average of first 100 frames was taken as the reference for non-homogeneities in the beam profile, and used to normalize the rest of the video frames, assuming that beam profile has no dependence on time. To correct for instabilities of the lamp power (oscillation of total intensity in time), a region in the tube displaying constant fluorescence (very close to the anionic reservoir, constantly basic pH) was taken as the reference for the maximum emission intensity in the rest of the images. The analyses were carried out on the central row of pixels of the U-tube.

SI2: Simulation methods

The simulation reported in the paper includes computation of the speciation, mass transport and precipitation. The simulation was run using the Phreeqc code (version 3.1.4) [Parkhurst, D.L., and Appelo, C.A.J., 2013]. Species activities were calculated using ion-association with thermodynamic data from the phreeqc.dat database. Precipitation mass balance was computed using thermodynamic data for condensed phases from the same database. One-dimensional, multicomponent diffusion of the different species, accounting for
Electrical neutrality was also computed using the same code. Full details on the simulation setup can be checked in the input file that follows:

```
DATABASE phreeqc-3.1.4-8929/database/phreeqc.dat
TITLE CaCO3 precipitation in U-tubes (50mm) (HCO3)
SOLUTION 1-40 # Ca Repository
  pH 5.8
  -units mg/L
  Ca 20039
  Cl 17725
END
SOLUTION 141-180 # HCO3 Repository
  pH 8.15
  -units mg/L
  Na 11495
  C 30508 as HCO3;
END
SOLUTION 41-140 # Agarose segment
  pH 6.5
END
EQUILIBRIUM_PHASES 1-180
Calcite 0.0 0.0
SELECTED_OUTPUT
  -file hco3.sel
  -simulation false
  -state false
  -distance true
  -time true
  -pe true
  -ionic_strength true
  -charge_balance true
  -activities H+ OH- H2O CH4 CO2 CaHCO3+ HCO3- CaCO3 CO3-2
             Ca+2 CaHCO3+ CaOH+ CaCO3 Cl-
             NaCl- NaHCO3 Na+ NaCO3- NaHCO3 NaOH
  -molalities H+ OH- H2O CH4 CO2 CaHCO3+ HCO3- CaCO3 CO3-2
              Ca+2 CaHCO3+ CaOH+ CaCO3 Cl-
              NaCl- NaHCO3 Na+ NaCO3- NaHCO3 NaOH
  -si calcite
  -equilibrium_phases calcite
TRANSPORT
  -cells 180
  -shifts 259200
  -time_step 1 sec
  -flow_direction diffusion_only
  -boundary_conditions closed closed
  -lengths 0.5e-3
  -print_cells 1-180
  -print_frequency 300
  -punch_cells 1-180
  -punch_frequency 300
```
SI3: Wavelength spectra and filtering

The experiment is illuminated using a fraction (around 450 nm) of the spectrum produced by a Xe lamp. This fraction is selected using the excitation bandpass filter (pink rectangle). The fluorescence emitted by the ink in the solution (green) has a wavelength distribution centred around 510 nm. An emission cut-off filter (orange rectangle) in front of the camera select this fluorescence for quantification. The plot shows the absorbance (dashed lines) and emitted intensity (solid lines) of both the protonated (red) and deprotonated (blue) ink and how the excitation and emission filters were selected to maximize the pH-dependent signal.
SI4: Fluorescence intensity vs. solution pH calibration

Calibration used to quantify the pH in the solution from the fluorescence intensity. Dots correspond to experimental determinations. The solid line is a sigmoidal fit of these experimental data.

SI5: Space/Time maps for additional solution species

This section includes maps for the evolution in time of the concentration along the tube of the following species: H\(^+\), OH\(^-\), Cl\(^-\), Na\(^+\), Ca\(^{2+}\), CO\(_2\)(aq), HCO\(_3\)\(^-\), CO\(_3\)^{2-}, CaHCO\(_3\), CaCO\(_3\), CaOH\(^+\), NaCO\(_3\), NaHCO\(_3\) and NaOH(aq). The amount of precipitated solid (calcite) is also shown. For all of them the map to the left shows the evolution during the experiment and the plot to the right concentrates on the evolution of the given value at the point where precipitation first occur (marked by the vertical dotted line in the map). The vertical dotted line in the plot to the right indicates the time of first nucleation.
SI6: Time evolution of pH, CaHCO$_3^+$, CaCO$_3^0$

Video animation of 576 plots showing the time evolution of pH and activity of the two solution species discussed in the text (CaHCO$_3^+$ and CaCO$_3^0$) along the tube. These plots are the full animated sequence of figure 3 in the article.