

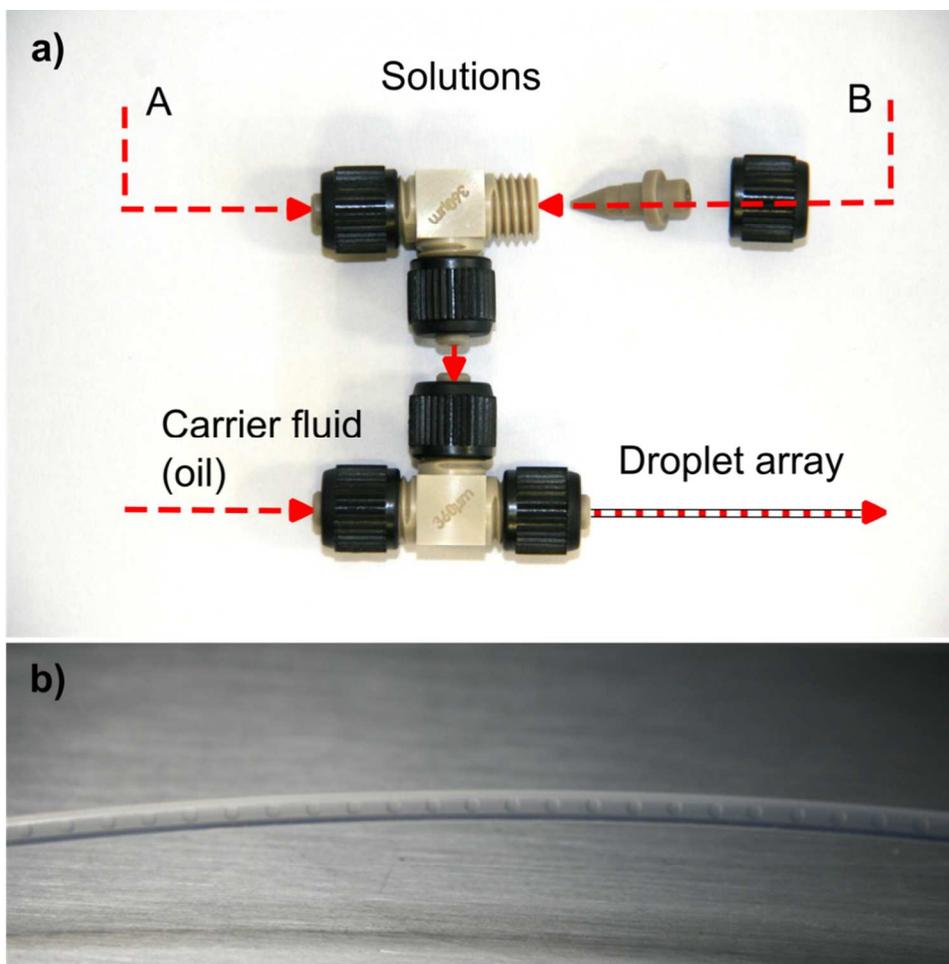
# Transient calcium carbonate hexahydrate (Ikaite) nucleated and stabilized in confined nano- and picovolumes

*I. Rodríguez-Ruiz<sup>1</sup>, S. Veessler<sup>2</sup>, J. Gómez-Morales<sup>1\*</sup>, J. M. Delgado-López<sup>1</sup>, O. Grauby<sup>2</sup>, Z.  
Hammadi<sup>2</sup>, N. Candoni<sup>2</sup>, J. M. García-Ruiz<sup>1</sup>*

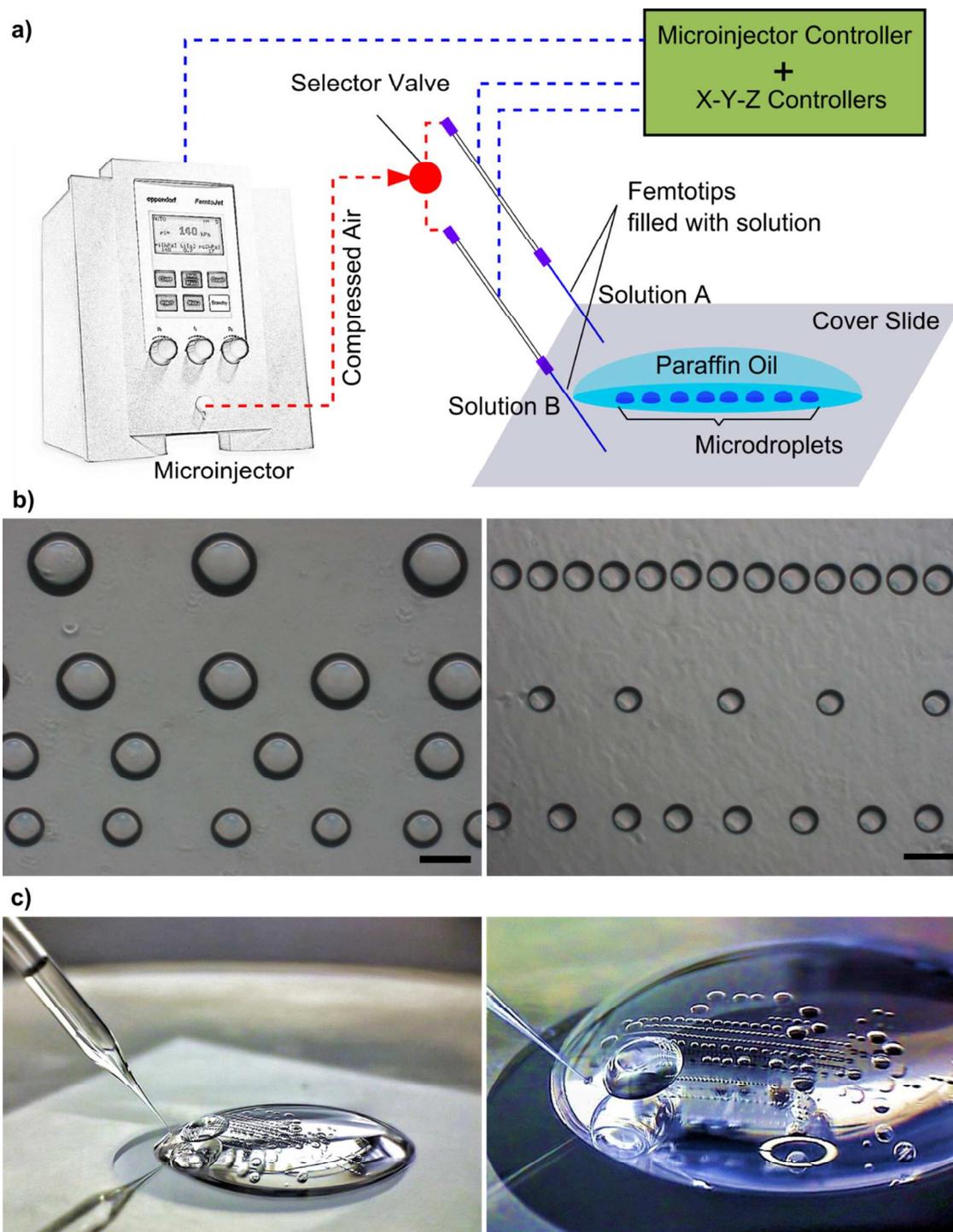
<sup>1</sup> Laboratorio de Estudios Cristalográficos, IACT (CSIC-UGR). Avda. de las Palmeras, 4.  
18100 Armilla, Granada, Spain. <sup>2</sup> CINA-M-CNRS, Aix-Marseille Université, Campus de Luminy  
F-13288 Marseille, France.

\*Corresponding author: J. Gómez-Morales (jaime@lec.csic.es)

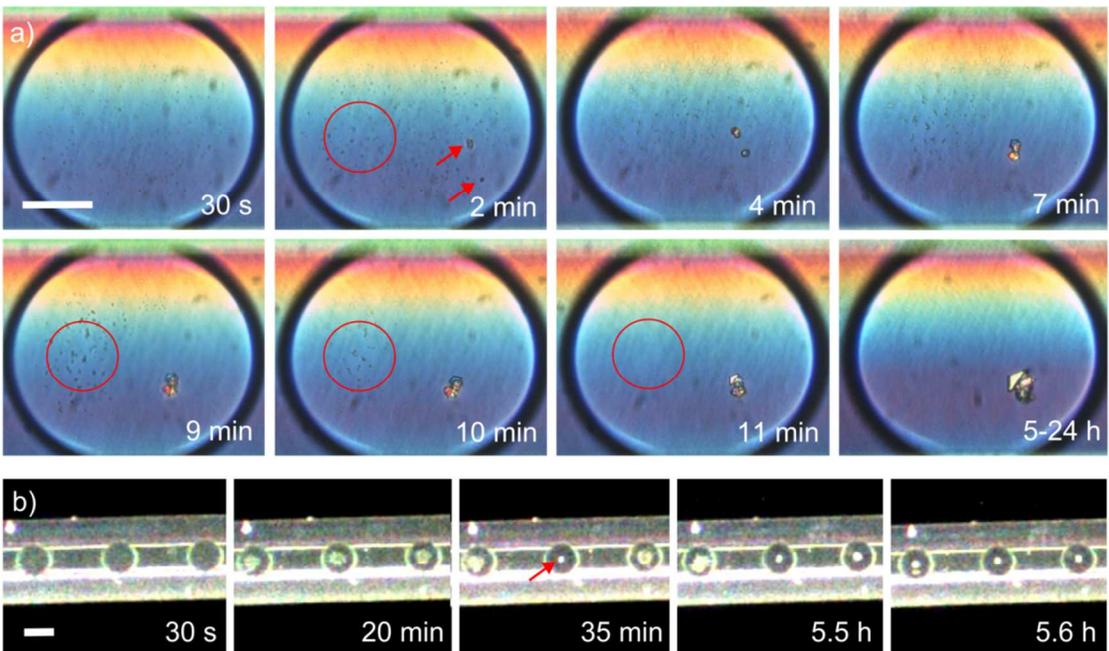
## Supporting Information



**Figure S1.** a) Schematic representation of the plug factory; b) Array of 2 nL droplets generated inside a 150  $\mu\text{m}$  internal diameter teflon capillary.



**Figure S2.** a) Schematic representation of the microinjection set up b) Array of different sized sitting droplets generated by microinjection. Scale bar = 100  $\mu\text{m}$ ; c) Femtotip injecting under a 30  $\mu\text{L}$  paraffin oil droplet.



**Figure S3.** Time evolution of  $\text{CaCO}_3$  precipitation in nanodroplets generated in microfluidic setup: a) evolution in a 3 nL droplet containing 50 mM  $\text{CaCl}_2$  and 50 mM  $\text{Na}_2\text{CO}_3$  (nominal IAP  $5.25 \times 10^{-6} \text{ mol}^2 \cdot \text{L}^{-2}$ , S.I. = 3.18). Red arrows show the appearance of two calcite crystals. Inside the red circle it is observed the presence of micron-sized particles that dissolve while the 2 calcite crystals grow. Scale bar = 50  $\mu\text{m}$  b) Evolution of  $\text{CaCO}_3$  precipitation in three droplets of 2 nL containing 30 mM  $\text{CaCl}_2$  and 30 mM  $\text{Na}_2\text{CO}_3$  (IAP  $1.35 \times 10^{-6} \text{ mol}^2 \cdot \text{L}^{-2}$ , S.I. = 2.59) Scale bar = 150  $\mu\text{m}$ . Red arrow in figure at 35 min shows the transformation of the first precipitate in a single faceted calcite crystal.

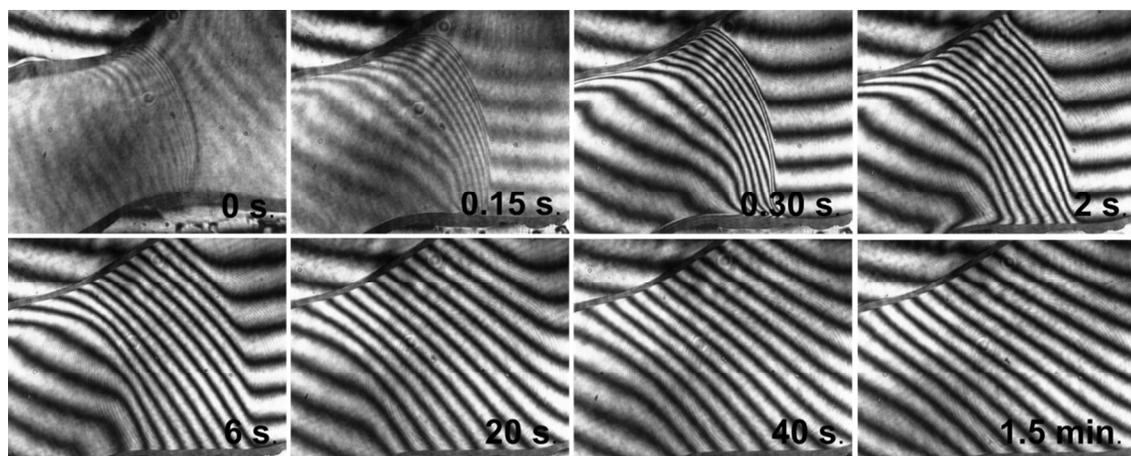
Figure S3a shows a sequence of images corresponding to a time resolved precipitation experiment. The images were recorded in a 3 nL droplet at S.I.=3.18 and 1:1 ( $\text{CaCl}_2$ : $\text{Na}_2\text{CO}_3$ ) molar ratio. The formation of a first precipitate is initially observed and then its dissolution while a second crystalline precipitate appears and grows. In the initial moments (from 30 s to 2min) a sol composed of ultrafine particles that showed a brownian motion appears in the droplets (red circle at  $t=2\text{min}$ ). At 2 min, 2 small crystals (lately morphologically characterized

as calcite) appeared (red arrows at  $t=2\text{min}$ ) and merged into an aggregate ( $t=7\text{min}$ ) that grew while the first precipitate dissolved (from 9 to 11min, red circles at  $t=9, 10$  and 11min). The period for this transition was increased from few minutes to several hours as the initial S.I. was decreasing from 3.18 to 0.9. Figure SI3b shows the evolution with time of 3 nanodroplets (2 nL each, S.I.= 2.74 and molar ratio 1) of a total of 50 composing an array in the microfluidic setup. The precipitation occurred instantaneously just after mixing the reactant solutions in the capillary. Once the nanodroplets formed the precipitates showed birefringence under crossed polarisers from the very beginning of the experiment, increasing their intensity during the first minutes. After 35 min, in one of the droplets, the precipitate transformed into a faceted calcite crystal (pointed with a red arrow), clearly identified by its morphology. Later, after 5.6 h, the precipitates in the three droplets were no longer observed because all of them were transformed into calcite. In few droplets ( $\sim 5\%$  of the total), in addition to the faceted calcite crystals, polycrystalline spherulitic aggregates of different sizes were also found.

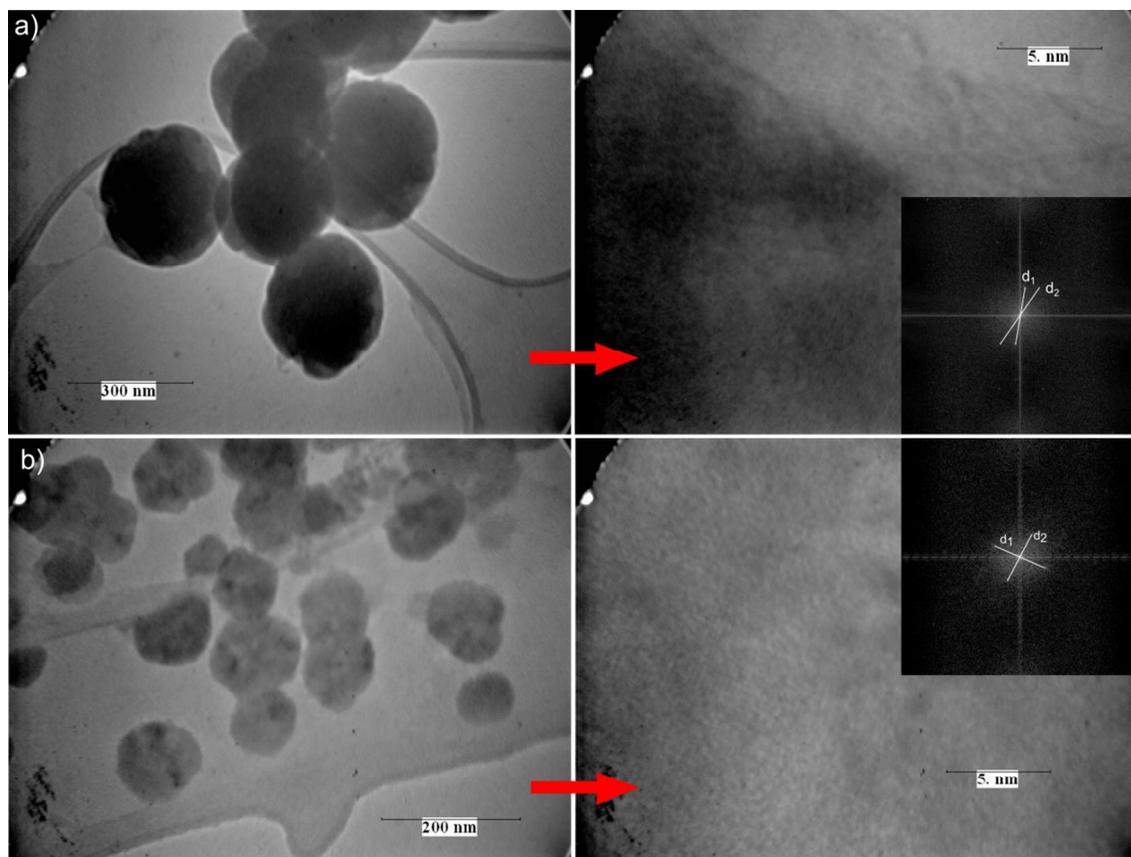
**Table S1.** Obtained XRD d-spacings, averaged over 10 measurements, and possible assignments to calcium carbonate phases

d(Å)	Calcite <sup>a)</sup>	Monohydrocalcite <sup>b)</sup>	Ikaite <sup>c)</sup>
3.17 ± 0.02		(2 1 1) = 3.15	
3.04 ± 0.02	(1 0 4) = 3.035	(3 0 0) = 3.05	
2.845 ± 0.005	(0 0 6) = 2.845		
2.74 ± 0.02			(-3 1 2) = 2.733
2.17 ± 0.02		(4 0 1) = 2.1899 (2 2 2) = 2.1665	(1 1 4) = 2.178
1.99 ± 0.02		(4 1 0) = 1.9968	(-3 3 2) = 1.992 (-4 0 4) = 1.992 (2 2 3) = 2.004
1.94 ± 0.02	(0 2 4) = 1.927	(3 0 3) = 1.9447 (4 1 1) = 1.9308	(3 3 0) = 1.9509 (-4 0 4) = 1.9509 (-1 3 4) = 1.9433 (-4 2 1) = 1.9345 (-2 2 5) = 1.9235
1.79 ± 0.02		(1 1 4) = 1,7823	(-4 2 4) = 1.7926

a) d-spacings assigned according to PDF card file 050586; b) d-spacings assigned according to PDF card file 290306; c) d-spacings assigned according to PDF card file 370416



**Figure S4.** Series of eight frames selected from the interferometric experiment (time scale, 7 frames/s) corresponding to the dilution of a  $1\mu\text{L}$  droplet  $0.5\text{ M Na}_3\text{Cit}$  in a  $1\mu\text{L}$  water droplet. Clear interferometric bands are seen, depicting the diffusion of solutions through the mixing front in a total period of 1.5 min. It can be also seen the higher number of interferometric bands along the mixing interface in the first moments, revealing a maximum concentration gradient of citrate, which is diffusing from left to right, from the more to the less concentrated droplet.



**Figure S5.** TEM images of spherulitic particles. Fourier transform over lattice resolution magnifications confirms they are IK particles: a)  $d_1$  and  $d_2$  correspond to 1 1 1 (4.63 Å) and 0 2 1 (3.82Å) IK reflections; b)  $d_1$  and  $d_2$  correspond to 1 1 1 (4.63 Å) and 0 0 2 (5.17Å) IK reflections.