Supplementary Material (ESI) for Integrative Biology

Supplementary materials

Method: Construction of supersaturation ratio profiles on-chip

The profiles of supersaturation ratio (S) on chip were calculated in the same approached as described previously.[1] Briefly, computational fluid dynamics software (Comsol) was used to construct the complete set of concentration profiles of CO_3^{2-} and Ca^{2+} ions on-chip. Supersaturation ratio was then calculated using Equation 1 with the activities estimated from the localized pH and the concentrations of Na^+, Ca^{2+}, CO_3^{2-} and Cl^- using Extended Debye-Hückel Equation. [2]

$$S = \sqrt{\frac{\gamma CO_3^{2-} \times \gamma Ca^{2+}}{K_{CaCO3}}} \qquad \text{(Equation 1)}$$

Where K_{CaCO3} is the solubility constant of calcium carbonate, γCO_3^{2-} and γCa^{2+} are the activities of CO_3^{2-} and Ca^{2+}, respectively. The solubility constant of calcite, 2.18×10^{-9} mol^2/dm^6, is used in the calculation.[3]

A 2D straight channel configuration was used for the computational simulation since the two sharp turns in the 10 mm long up channel have negligible effects. In contrast to previous non-buffered system, simulation of the MOPS buffered systems requires to take into account both the acid-base and MOPS equilibria at pH 7.5. These are listed in Table S1. The diffusion coefficients of ions and proteins are listed in Table S2.

Table S1. The acid-base and MOPS equilibria and the corresponding constant K at 25 °C.

Equilibrium	K	Reference
$H_2O \rightleftharpoons OH^- + H^+$	1.00×10^{-14} mol^2/dm^6	3
$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$	2.25×10^6 dm^3/mol	3
$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	2.13×10^{10} dm^3/mol	3
$MOPS^- + H^+ \rightleftharpoons MOPSH$	1.58×10^7 dm^3/mol	4

Table S2. Diffusion coefficients of ions and proteins in the calculation

Species	Diffusion coefficients (m^2 /s)	Reference
HCO_3^-	1.185×10^{-9}	5
CO_3^{2-}	9.23×10^{-10}	5
$H_2CO_3^*$	1.185×10^{-9}	5
H^+	9.31×10^{-9}	5

Na^+	1.33×10^{-9}	5
OH^-	5.27×10^{-9}	5
Ca^{2+}	7.92×10^{-9}	5
Cl^-	2.03×10^{-9}	5
$MOPS^{-}$ *	1.185×10^{-10}	5
MOPSH *	1.185×10^{-10}	5
BSA	6.21×10^{-11}	6
28KDa EP	8.20×10^{-11}	7

* This work assumes that the similarity in size of HCO_3^-, H_2CO_3, MOPS and MPOSH, compared to other components in the system, allows use of a similar diffusion coefficient in the numerical simulations.

Supplementary video:
Time lapse recording of the crystal formation from the 50 mM $CaCl_2$ and 50 mM Na_2CO_3 in MOPS in the absence of proteins.

Reference:

1. Yin, H. B.; Ji, B. Z.; Dobson, P. S.; Mosbahi, K.; Glidle, A.; Gadegaard, N.; Freer, A.; Cooper, J. M.; Cusack, M. *Analytical Chemistry* **2009**, *81*, 473-478.
2. Kelland, J. *J. Am. Chem. Soc.* **1937**, 59, 1675-1678.
3. Verdoes, D.; Kashchiev, D.;van Rosmalen, G.M. *J. Cryst. Growth*, **1992**, 118, 401-413.
4. Calculated from the pKa data provided by supplier, Sigma-Aldrich Co.
5. Handbook of Chemistry and Physics, Editor David R. Lide, 87th Edition, CRC press.
6. Meechai N.; Jamieson A.M.; Blackwell J. *Journal of Colloid and Interface Science*, **1999,** 218, 167-175.
7. Guiot E., Enescu M., Arrio B., Johannin G., Roger G., Tosti S., Tfibel F., Mérola F., Brun A., Georges P. and Fontaine-Aupart M. P. *Journal of Fluorescence*, **2000**, 10, 413-419.