Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Polypeptide Effect on Mg^{2+} Hydration Inferred from $CaCO_3$ Formation: A Biomineralization Study by Counter-Diffusion

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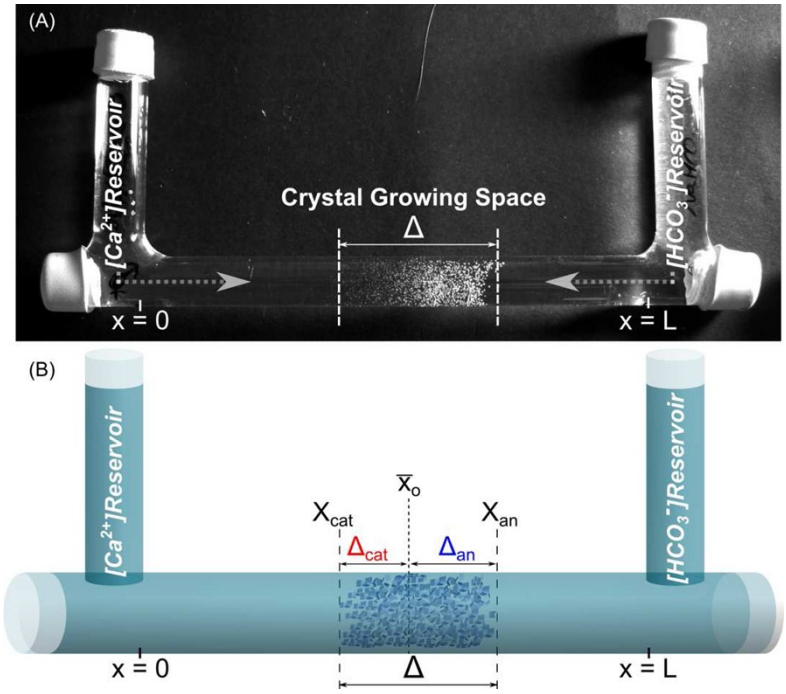

Figure SI1 (A) Camera picture of the U-tube set-up used for $CaCO_3$ crystallization experiments in CDS using agarose gels and viscous sols. (B) Schematic illustration of the measured crystallization parameters in the U-tube: x_o, the starting point of precipitation; Δ, the crystal growing space; x_{cat} and x_{an}, the boundaries of the crystal growing space close to the cationic and anionic reservoir, respectively; Δcat and Δan, the crystal growing space from the starting point xo to x_{cat} and x_{an}, respectively.

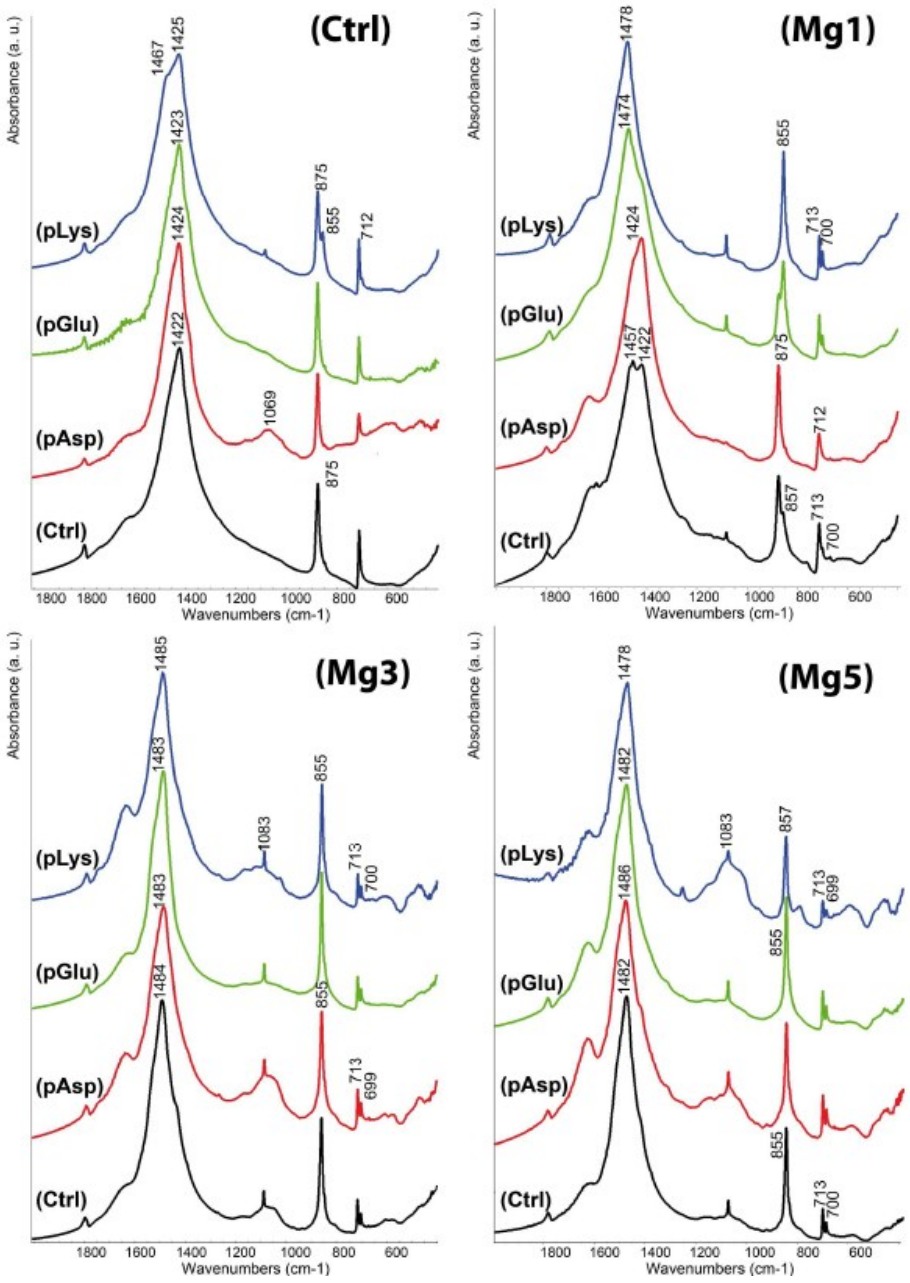

Figure SI2. FTIR spectra of $CaCO_3$ precipitated in agarose viscous sols entrapping pLys (blue), pGlu (green) or pAsp (red), and in additive-free experiments (black). Each set of spectra refers to experiments Mg2+-free (left-upper corner) or Mg^{2+}/Ca^{2+} molar ratios equal to 1 (right-upper corner), 3 (left-lower corner) or 5 (right-lower corner). The absorption intensities of the FTIR bands are reported in arbitrary units (a.u.). The salient features of infrared spectra of calcite are 1429, 877 and 713 cm^{-1}; and of aragonite, 1477, 1083, 858, 713 and 700 cm^{-1}. The peaks at 1477 and 1429 cm^{-1} correspond to the v_3 absorption band of carbonate ions; the peaks at 877, 858 correspond to v_2 and 713 and 700 cm^{-1} correspond to v_4 absorption bands of carbonate ions.

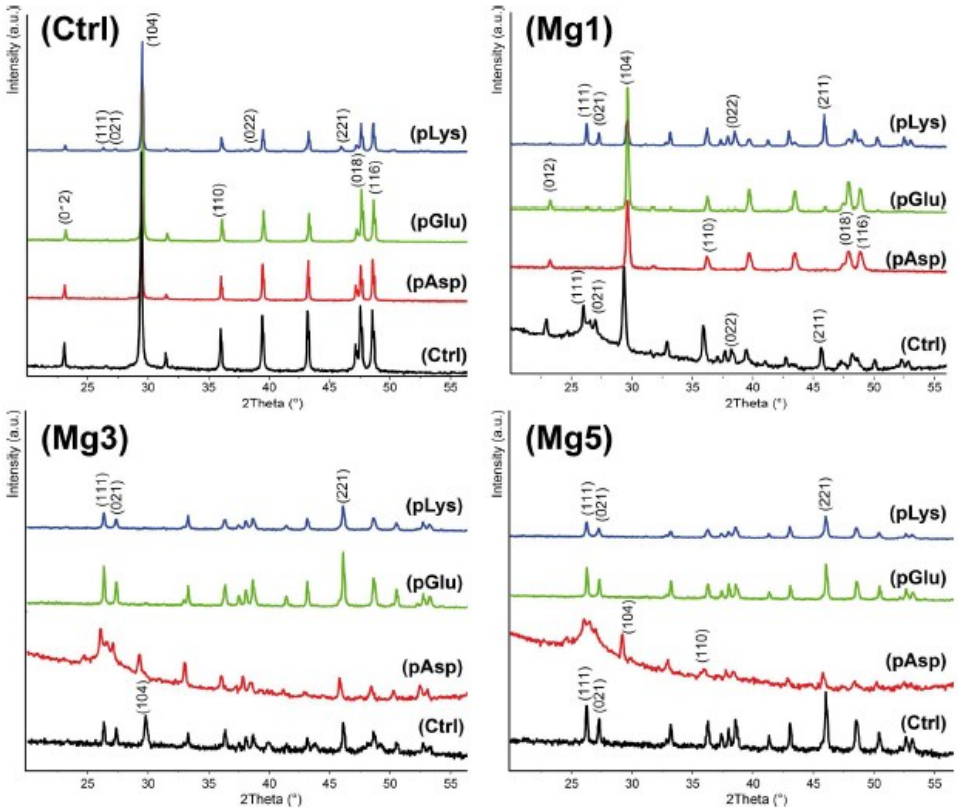

Figure SI3. X-ray powder diffraction patterns of the $CaCO_3$ precipitated in agarose viscous sols entrapping pLys (blue), pGlu (green) or pAsp (red), and in absence of additive (black). Each set of spectra refers to experiments carried out in Mg^{2+}-free (left-upper corner) or Mg^{2+}/Ca^{2+} equals to 1 (right-upper corner), 3 (left-lower corner) or 5 (right-lower corner). The main diffraction peaks for calcite, (012), (104), (110), (018) and (116), and aragonite (111), (021), (022) and (221), are indicated according to the reference patterns PDF-calcite 01-083-0587 and PDF-aragonite 01-077-0606. The diffractograms are shifted along the Y-axis that reports intensity in arbitrary units (a.u.).

Table SI1 Crystallization parameters measured in experiments of $CaCO_3$ precipitation in CDS using charged polypeptides entrapped in an agarose viscous sol and diffusing Mg^{2+}. Measured parameters are x_o, Δ_{cat}, Δ_{an}, t_w and d_c. From up to down the lines correspond to Mg^{2+}-free experiments (Mg0) in the cation reservoir and Mg^{2+}/Ca^{2+} molar ratio equal to 1(Mg1), 3(Mg3) and 5(Mg5), respectively. Each experiment was repeated at least 3 times and in parenthesis is reported the standard deviation.

		Δ_{cat}	x_o	Δ_{an}	t_w	d_C
Mg0	**Ref.**	0.10 (0.06)	0.66 (0.12)	0.16 (0.06)	~2	*l, m*
	pLys	0.11 (0.08)	0.68 (0.09)	0.18 (0.06)	~4	*l, m, h*
	pGlu	0.06 (0.07)	0.66 (0.08)	0.06 (0.05)	~2	*m*
	pAsp	0.02 (0.01)	0.64 (0.02)	0.03 (0.02)	~3	*h*
Mg1	**Ref.**	0.13 (0.05)	0.68 (0.04)	0.15 (0.04)	~4	*l*
	pLys	0.13 (0.07)	0.68 (0.12)	0.15 (0.05)	~3	*l, h, m*
	pGlu	0.07 (0.02)	0.65 (0.04)	0.11 (0.05)	~4	*m*
	pAsp	0.04 (0.02)	0.76 (0.02)	0.04 (0.03)	~4	*h*
Mg3	**Ref.**	0.19 (0.02)	0.60 (0.04)	0.12 (0.02)	2-3	*l*
	pLys	0.16 (0.07)	0.68 (0.10)	0.14 (0.09)	~5	*l*
	pGlu	0.09 (0.01)	0.74 (0.04)	0.09 (0.07)	~3	*m*
	pAsp	0.04 (0.08)	0.74 (0.08)	0.02 (0.09)	~6	*m*
Mg5	**Ref.**	0.16 (0.05)	0.42 (0.07)	0.12 (0.05)	~3	*l*
	pLys	0.14 (0.04)	0.70 (0.04)	0.11 (0.03)	~5	*l*
	pGlu	0.08 (0.04)	0.66 (0.03)	0.06 (0.05)	2-3	*l, m*
	pAsp	0.06 (0.14)	0.73 (0.14)	0.018	~8	*l*

The density of crystallization is indicated as low (l), medium (m) and high (h).