Stabilization of amorphous calcium carbonate through controlled particle size

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SUPPORTING INFORMATION

- 1- Experimental setup
- 2- Light microscopy of calcium carbonate formed without additives
- 3- Radial integration of low-dose selected area electron diffraction
- 4- CryoEDX analysis of calcium carbonate particles

Experimental setup



Figure S1 Schematic representation of the CaCO₃ precipitation experiment setup.

CryoEDX analysis of calcium carbonate particles

Cryo-energy dispersive X-ray spectroscopy (cryoEDX) confirmed that the particles formed after 20 and 40 seconds of reaction were indeed composed of calcium carbonate.



Figure 3 CryoEDX analysis of ACC particles formed in 20 (a-b) and 40 seconds (c-d). (a) and (c) depict the spectra acquired, and (b) and (d) show the cryo-scanning-transmission electron microscopy (cryoSTEM) image of the corresponding areas whence the spectra was acquired (red squares). (e) and (f) show a background spectrum acquired on the carbon film without any particles (red square in f).

Radial integration of low-dose selected area electron diffraction

Table 1 Comparison of the radial integration of the diffraction patterns of the ACC particles, the amorphous ice layer at the background and and pure water. $\langle X \rangle$ is the average, σ ($\langle X \rangle$) is the sample standard deviation and N is the number of measurements. X_2 , first amorphous ring distance and X_1 , second amorphous ring distance.

	$< x_1 > \pm \sigma(< x_1 >)$	$< x_2 > \pm \sigma(< x_2 >)$	Ν
Background	$0.382 \pm 0.04 \text{ nm}$	$2.19\pm0.04~nm$	4
Pure water	$0.376 \pm 0.01 \text{ nm}$	$2.22 \pm 0.01 \text{ nm}$	3
ACC (5 s), no additives	$0.385 \pm 0.03 \text{ nm}$	$0.223 \pm 0.08 \text{ nm}$	3
ACC (20 s), no additives	$0.385 \pm 0.02 \text{ nm}$	$0.220\pm0.03~\text{nm}$	3
ACC (40 s), no additives	$0.384 \pm 0.02 \text{ nm}$	$0.220\pm0.04~\text{nm}$	2
ACC + pAsp (48 h)	$0.384 \pm 0.03 \text{ nm}$	$0.218 \pm 0.01 \text{ nm}$	5

To test whether the values obtained for ACC and the background are different from those of water, a t-test was performed. For the first amorphous ring (X₁) the t-test of all samples against pure water yielded a *p* value above 0.05, showing that there is no statistical significant difference between then. On the other hand, the shift in the second diffraction ring (X₂) in relation to that of pure water was significantly different for the background and all ACC particles (*p* value < 0.05). Therefore we can conclude that there is a real shift in the peaks due to the presence of amorphous material. The fact that the peaks of the background were also shifted in relation to that of water indicates the presence of pre-nucleation clusters in solution, as described¹.

¹ E. M. Pouget, P. H. H. Bomans, J. A. C. M. Goos, P. M. Frederik, G. de With and N. A. J. M. Sommerdijk, *Science*, 2009, 323, 1455-1458.

Optical microscopy of calcium carbonate formed without additives

When the mineralization experiment was allowed to proceed without additives, calcite crystals $2 \mu m$ in size were formed in 1 h, as observed by optical microscopy (fig. 2).



Figure 2. Optical microscope image of calcite formed in 1 h of reaction without polymer, average particle size was 2 μ m.