# Solid State Crystallization of Amorphous Calcium Carbonate Nanoparticles Leads to Polymorph Selectivity

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**Figure S1:** X-ray diffraction spectra of (a) AOT microemulsion ACC and (b) calcite particles produced on heating the microemulsion ACC particles at 10  $^{\circ}$ C min<sup>-1</sup> to 70  $^{\circ}$ C, followed by isothermal incubation at 70  $^{\circ}$ C for 12 hours (c) vaterite particles produced on heating microemulsion ACC particles at 1  $^{\circ}$ C min<sup>-1</sup> to 70 $^{\circ}$ C, followed by isothermal incubation at 70  $^{\circ}$ C for 12 hours.



**Figure S2:** Thermogravimmetric analysis (TGA) data for dry AOT microemulsion ACC, obtained at a heating rate of  $5^{\circ}$ C min<sup>-1</sup> and showing the temperatures at which water is lost from the sample.



**Figure S3:** X-ray absorption spectra showing pre-edge and XANES regions of "high pH" ACC precipitated in bulk solution and AOT microemulsion ACC (AOT-ACC).



**Figure S4:** IR spectra of (top) high pH ACC samples and (bottom) high conc ACC samples before and after heating. The samples were produced by heating at 10  $^{\circ}$ C min<sup>-1</sup> to either 70  $^{\circ}$ C or 350  $^{\circ}$ C, followed by isothermal incubation at 70  $^{\circ}$ C for 12 hours and 350  $^{\circ}$ C for 3 hours, respectively. Both samples remained as ACC after heating at 70  $^{\circ}$ C, but crystallised to calcite after heating to 350  $^{\circ}$ C.



**Table S1:** Raman peak broadening data for ACC precipitated in Na-AOT microemulsions (AOT-ACC), heat-treated AOT-ACC and control calcite samples. The ACC samples were all precipitated within microemulsions. A full width half maximum (FWHM) analysis on a Gaussian fit of the carbonate internal symmetric stretch peak at 1085 cm<sup>-1</sup> shows a broadening of the peak with reduced crystallinity.

Sample	Product	FWHM Ratio $\times$ 10 <sup>4</sup>
Unheated AOT-ACC	-	5370
Laser Heating	Vaterite	969
1 °C min <sup>-1</sup> ramp rate to 70 °C, maintained for 12 hrs	Vaterite	548
10 °C min <sup>-1</sup> ramp rate to 70 °C, maintained for 12 hrs	Calcite	26.2
Commercial Nanocalcite	-	24.5
Synthetic Calcite	-	7.73