Supplementary materials

Insights into the amorphous calcium carbonate (ACC) → ikaite → calcite transformations

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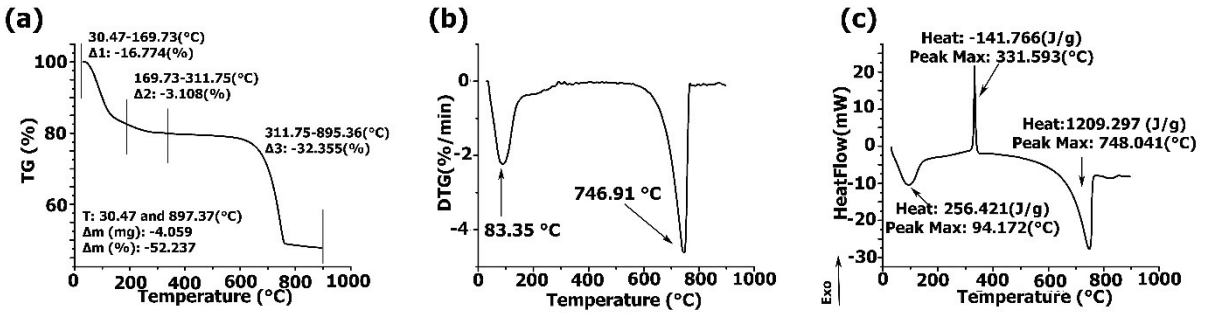

Figure S1. Thermal analysis of ACC (I) between 25 and 900 °C. (a) TG, (b) DTG and (c) DSC data.

Supplementary Note 1

Ikaite-precursor ACC was synthesized following Zou et al.30 by mixing 0.5 ml of 1 M $CaCl_2$ solution and 49.5 ml of 20.2 mM Na_2CO_3 solution at 2 °C with constant stirring. A white opaque solution formed after the addition of $CaCl_2$. A portion (20 ml) of this solution was immediately vacuum filtered onto Whatman Cellulose acetate filter paper with 0.2 µm pore size and washed with 10 ml absolute ethanol to remove the surface water. Approximately 2 mg of this product was immediately removed from the filter paper and a diffraction pattern acquired the Rigaku DMax RapidII Micro X-Ray diffractometer. Approximately 1 min passed between the mixing of the solutions and the starting of the XRD measurement. The diffraction pattern, acquired for 5 minute, showed ACC and ikaite (Fig. S1). We repeated the experiment and filtered the entire solution (50 ml), which lasted for 2 min. According the XRD analysis the 5 mg material was pure phase ikaite (Fig. S2).

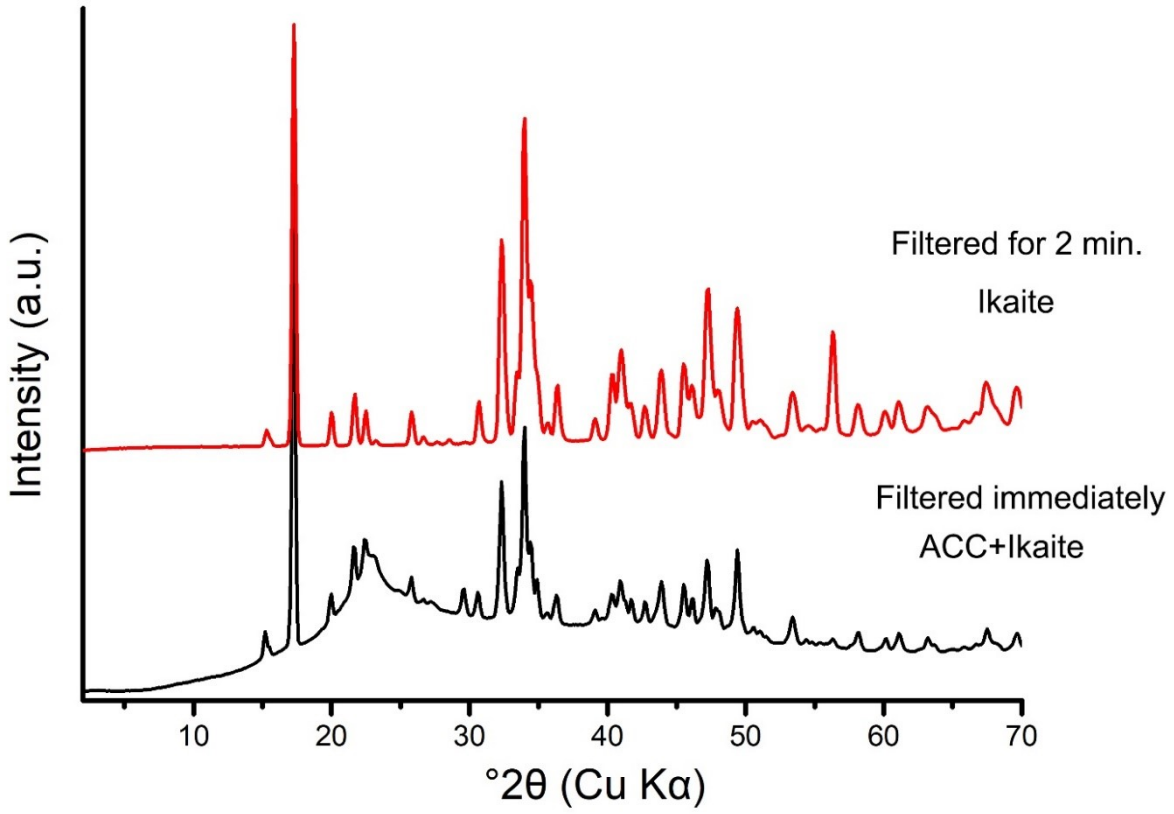

Fig. S2. XRD patterns of the precipitates obtained by following the experimental route of Zou *et al.* [30] for synthesizing ikaite-precursor ACC.

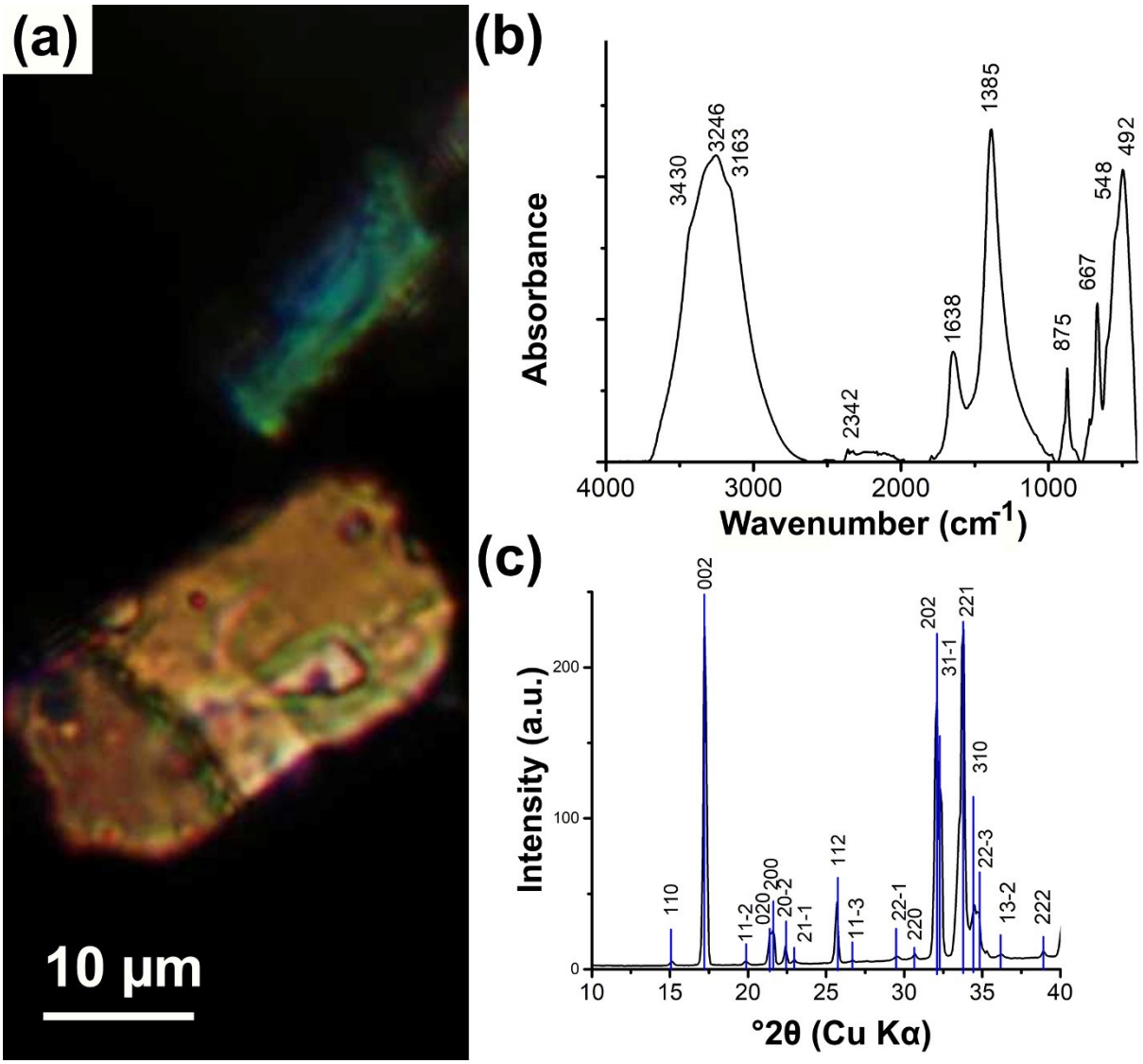

Figure S3. Morphology and structure of ikaite (M1). (a) optical microscope image, (b) FTIR spectrum and (c) XRD pattern.

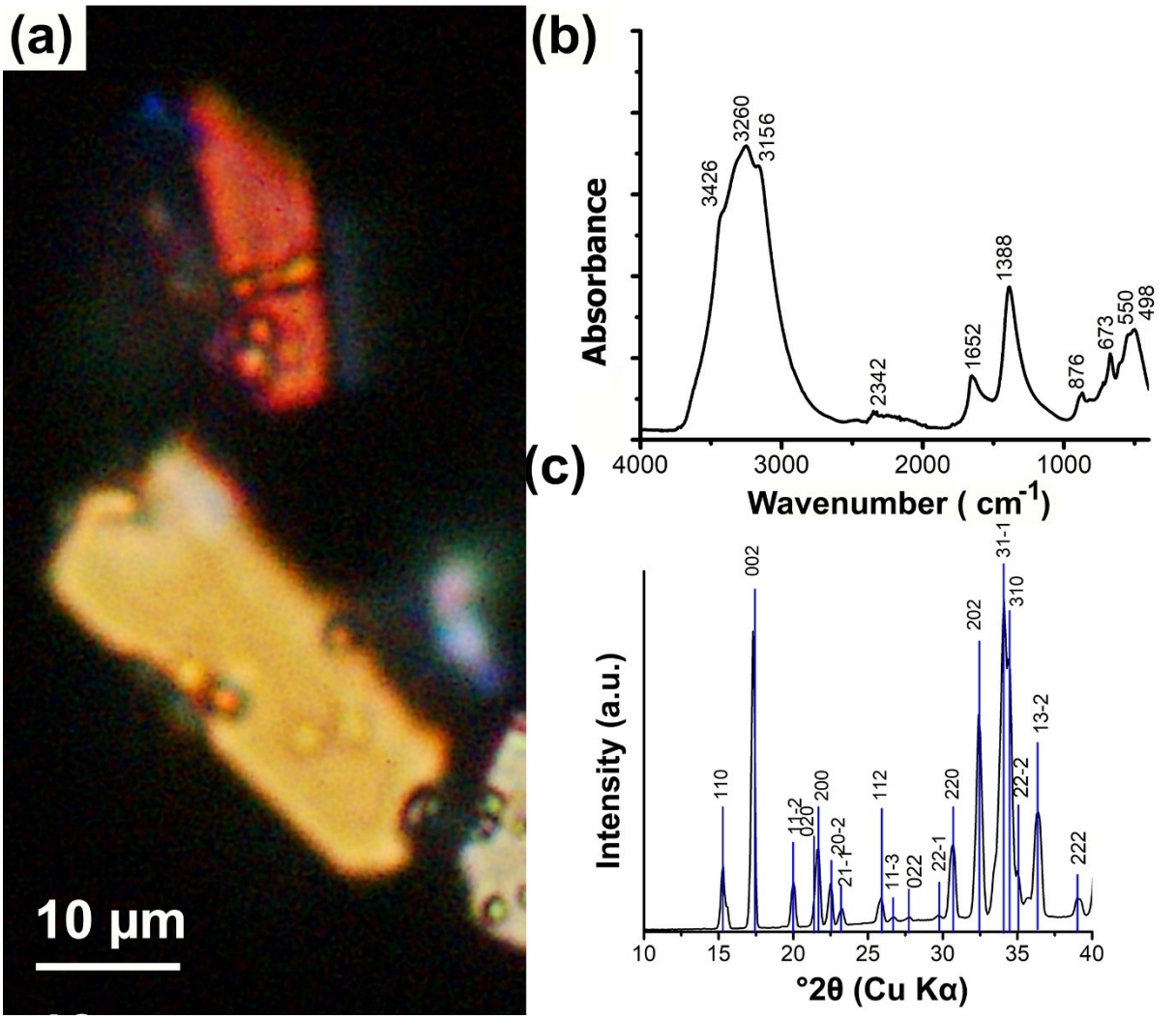

Figure S4. Morphology and structure of ikaite (M2). (a) optical microscope image, (b) FTIR spectrum and (c) XRD pattern.

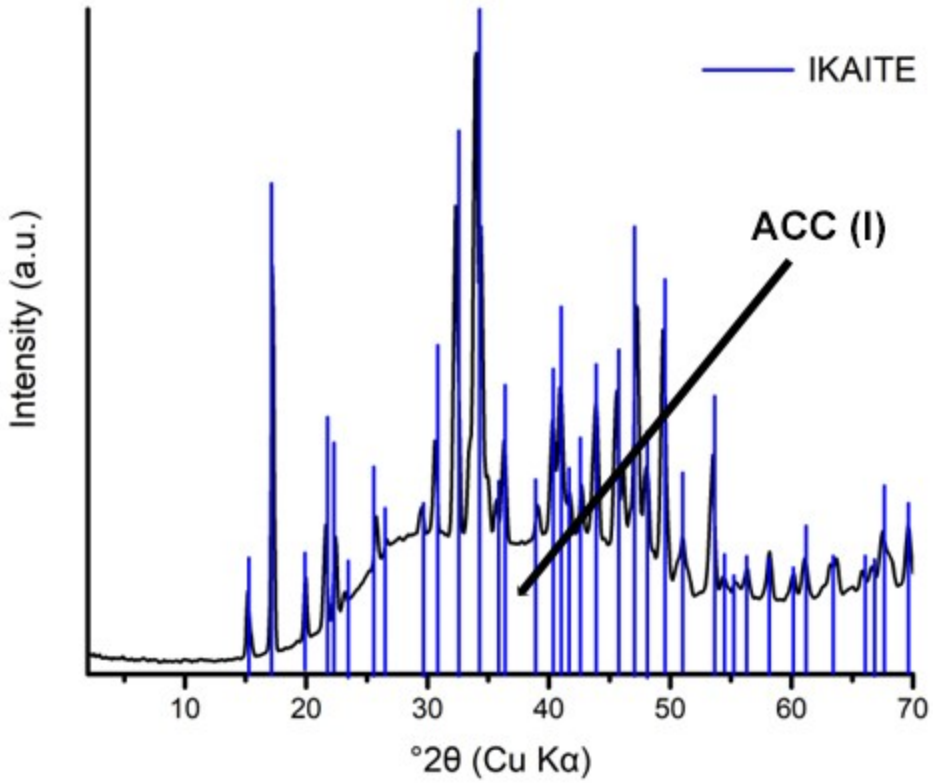

Figure S5. XRD diffractogram of the material prepared by rapid mixing of the solutions following the procedures of Johnston *et al.* [52].

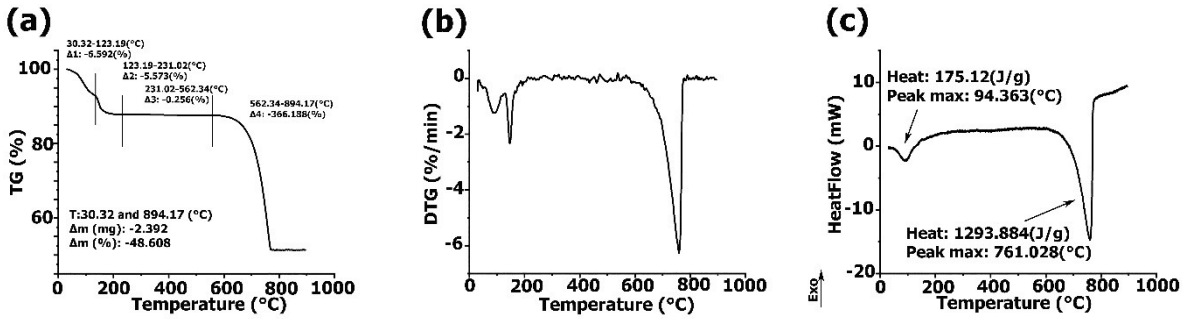

Figure S6. Thermal analysis of ACC (II) between 25 and 900 °C. (a) TG, (b) DTG and (c) DSC data.

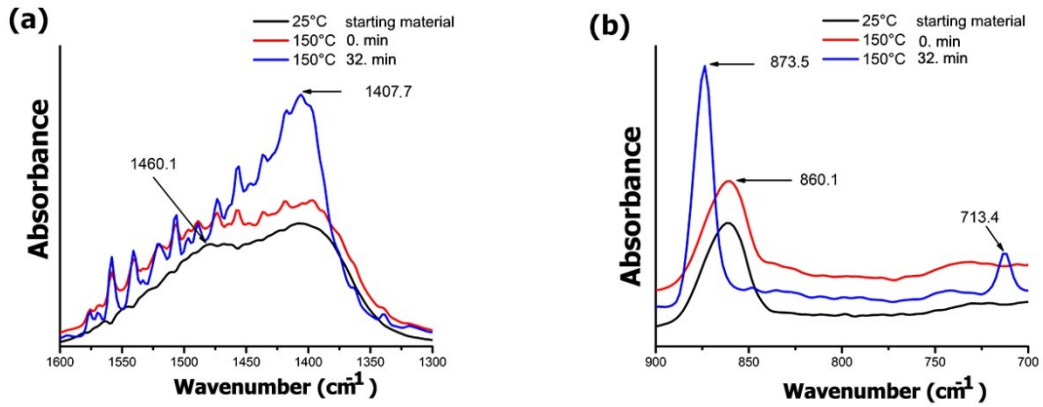

Figure S7. FTIR spectra of the ACC (II) → calcite transformation at 150 °C between (a) 1600 and 1300 cm^{-1} and (b) 900 and 700 cm^{-1} regions. Heating of the sample to 150 °C was performed in contact with the ATR crystal.

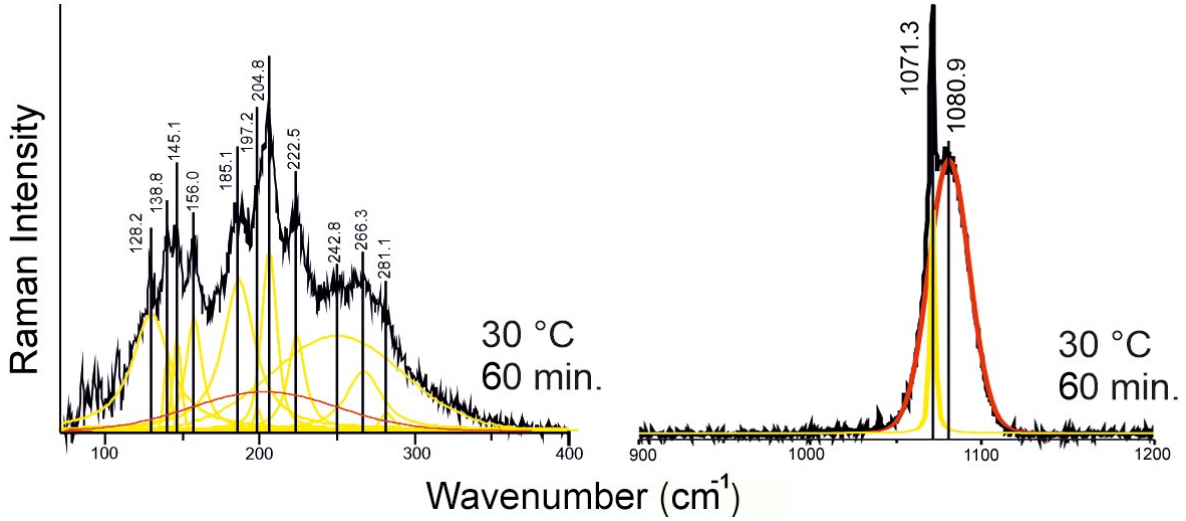

Figure S8. Raman spectra of ikaite (M2) in the lattice and ν1 (C-O) vibration regions after heating to 30 °C at the 60th minute,. Yellow and red lines correspond to the characteristic Raman bands of ikaite (M2) and ACC (II), respectively

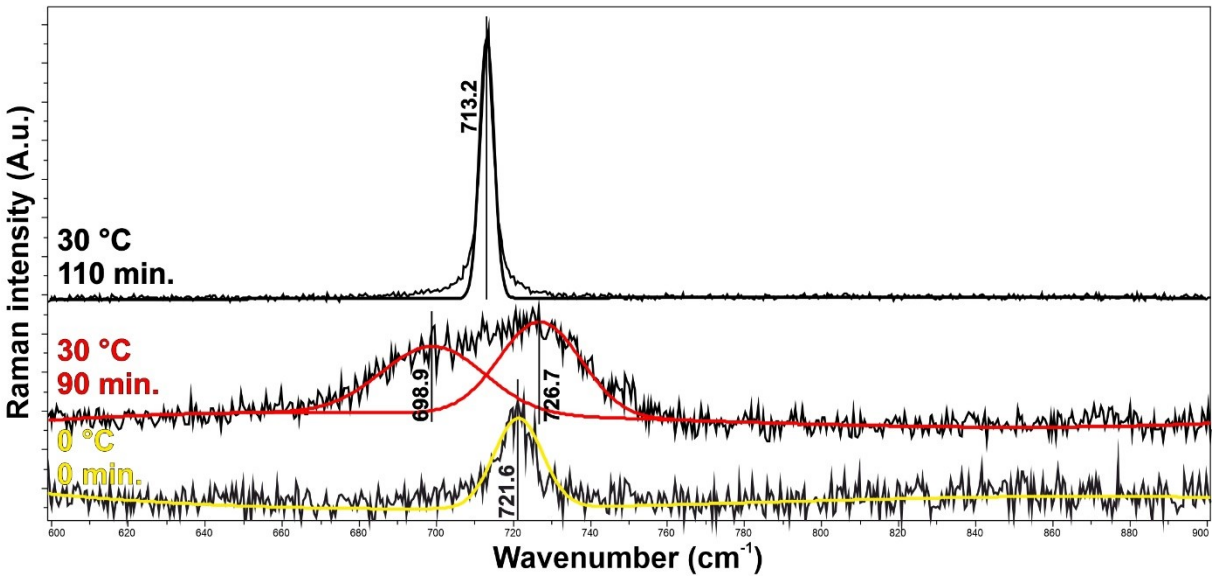

Figure S9. Ikaite (M2) → ACC (II) → calcite transformation process followed with Raman spectroscopy in the ν4 (C-O) vibration region. Yellow, red and grey curves correspond to the characteristic Raman bands of ikaite (M2), ACC (II) and calcite, respectively.