

Experiment title: Time resolved study on the crystallization of biogenic and synthetic amorphous calcium carbonate induced by in-situ heating, by pair distribution function analysis

Experiment number: CH- 4144

Beamline: ID11

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Report:

Here we report on our total X-ray scattering experiments at ID11 on synthetic amorphous calcium carbonate (ACC) and biogenic ACC (sea urchin spines). In this study we measured time-resolved series of ACC crystallization driven by in-situ heating or hydration. We used pair distribution function (PDF) analysis to follow structural changes in the mineral from the short range (SRO), via- medium range order (MRO) to full crystallization.

Experimental Procedure

Sample: Amorphous calcium carbonate was synthesized at pH=10 using established methods [1], in the presence (or absence) of inorganic additives (Mg^{2+} , PO_4^{3-} ions). Sea urchin spines were cut 4 days before the beamtime and stumps had been left to regenerate in order to have newly formed spine of 4 days. The regenerated spines had been severed from the animal just before the measurement. The air-dried powder samples as well as the sea urchin spines were mounted on a cylindrical sample holder and placed inside a Linkam (300) heating stage (Fig. 1.).

Methods: Measurements were performed at the first hutch of line ID-11, ESRF. Beam energy was set to 88KeV, using a beam-size with a $1 \times 1 \text{ mm}^2$ cross-section for synthetic ACC and $50 \times 50 \mu\text{m}^2$ for the newly formed sea urchin spines. After having acquired several (up to 600) x-ray scattering patterns of each sample, we performed two sets of in-situ measurements: in the first we increased the stage temperature from 25-30°C to 400-500°C at a rate of 2°C/min. In the second set of experiments the temperature was constant ($T=25^\circ\text{C}$), and the relative humidity was raised to a constant level of 85% with a self-build humidity controller (Fig. 1.).



Figure 1: Set up of CH-4144 experiments at ID 11 Hutch 1.

Data acquisition and evaluation: Data was acquired using a Frelon2K detector with a 5-30 sec integration time. Recorded 2D patterns were processed thanks to scripts provided by the beamline scientist to average, mask and integrate the 2D patterns, together with the Fit2D software [2]. Pair distribution functions were produced with the PDFgetX3 [3] software and plotted using Origin software.

Results

Figure 2 shows the different PDF maps upon heating experiments for ACC without additives and with different concentrations from 5mM to 100 mM as well as for ACC with additives (5mol% PO_4^{3-} and 10% Mg^{2+}) at 40 mM. Figure 3 shows the different PDF maps of in-situ hydration experiments at 85% relative humidity.

The samples show small differences in the degree of SRO rearrangement during in-situ heating, before the crystallization stage in which significant rearrangement at the MRO and long-range order can be seen (Fig. 2). ACC is stable until a certain temperature, which varies depending on the sample. As ACC concentration increases, the temperature of the beginning of the transformation into calcite increases from 150°C to 320°C. The use of additives also plays a role on the temperature of crystallization with little preliminary reordering (Fig. 2).

During hydration experiments, continuous reordering is observed for all samples, where from the initial stage reordering of long range order is observed (above 10 Å) (Fig. 3). For ACC without additive (5 mM) the transformation into calcite starts very soon and ends after one hour, whereas in the presence of 5% PO_4^{3-} the transformation starts later, meaning that PO_4^{3-} stabilizes ACC. In the presence of 10% Mg^{2+} the transformation starts immediately but lasts longer than without additive.

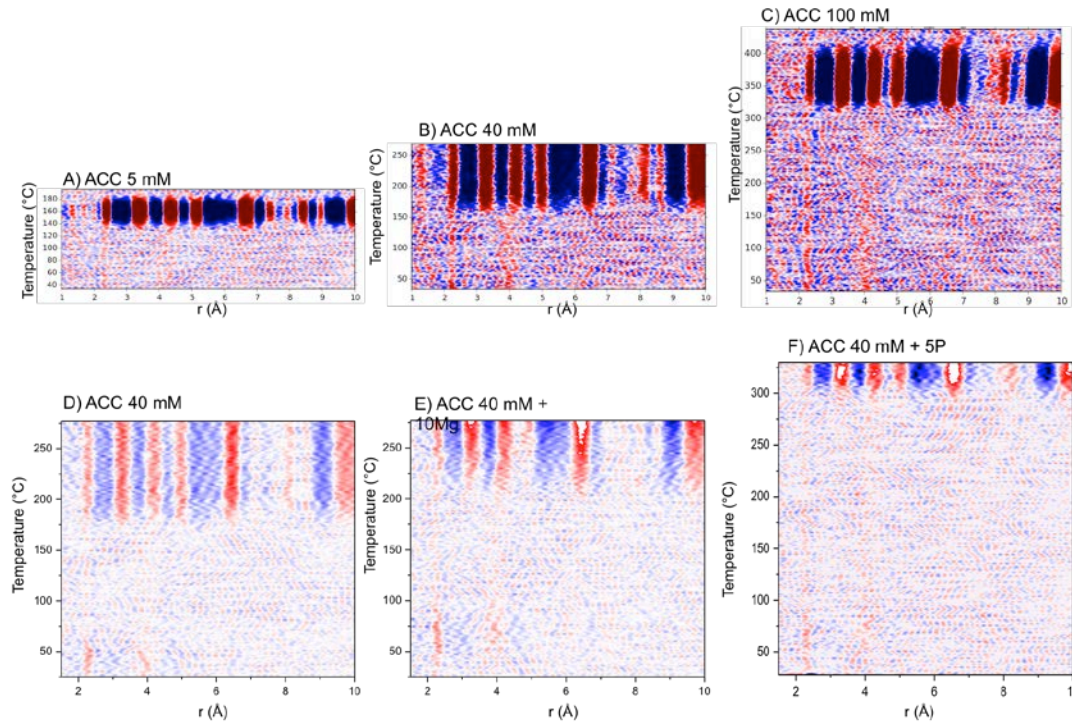


Figure 2: Different Pair Distribution Function (PDF) maps upon heating ($dPDF(T)/dT$) of different concentrations synthetic ACC without additives and particle size (A-C). A) Synthetic ACC at 5mM with the biggest particle size, B) synthetic ACC at 40mM with the intermediate particle size and C) synthetic ACC at 100mM with the smallest particle size. $dPDF(T)/dT$ of D) ACC 40 mM without additive, E) ACC 40 mM with 10% magnesium ions and F) ACC 40 mM with 5% phosphate ions.

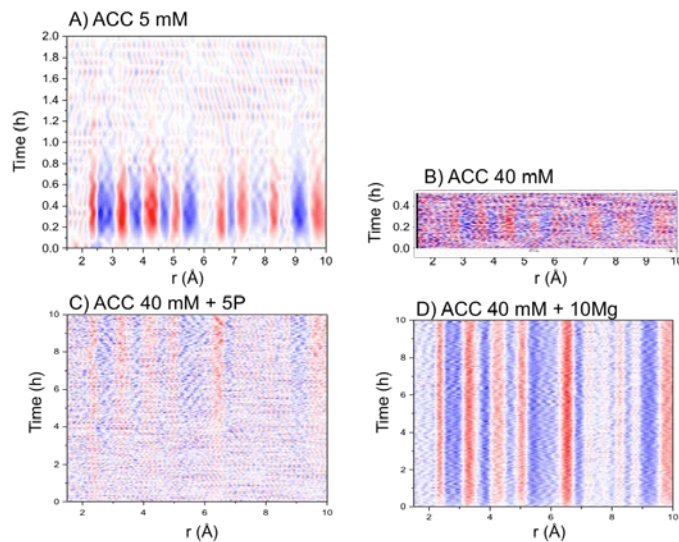


Figure 3: Different Pair Distribution Function (PDF) maps during hydration of A) synthetic ACC at 5mM with the biggest particle size, B) synthetic ACC at 40mM with the intermediate particle size, C) ACC 40 mM with 5% phosphate ions and D) ACC 40 mM with 10% magnesium ions.

Conclusions and Outlook

Our results show the feasibility of performing in-situ experiments at ID11 and, in addition, emphasize the importance of a comparison between heating and hydration time resolved measurements for the full understanding of the mechanism of transformation. In situ time resolved measurement by X-ray scattering and PDF analysis were performed with good signal to noise ratio and high temporal resolution. The results show the effect of the additive on the ACC transformation, namely the presence different intermediates with different ordering and the shift of the temperature of crystallization. In addition, preliminary experiments of in-situ hydration induced crystallization show a distinctly different transformation mechanism from the one induced by heating. The results of this and a previous beamtime at ID11 are summarized in a manuscript soon to be submitted.

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References:

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