

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

Experiment number: CH- 3723

Beamline: ID11

Date of experiment: 03/07/2013 – 08/07/2013

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Local contact: Gavin Vaughan

Report:

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

Experimental Procedure

Synthesis: 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). The air dried powder samples were mounted on a cylindrical sample holder and placed inside a Linkam (300) heating stage. We performed two sets of in-situ measurements: in the first we increased the stage temperature from 25°C to 400°C at a rate of 2°C/min. In the second set of experiments the temperature was constant ($T=25^\circ C$), and the relative humidity was raised to a constant level of 85%. X-ray scattering patterns were acquired continuously with a 30 sec integration time.

Total-X-ray scattering: Measurements were performed at the first hutch of line ID-11, ESRF. Beam energy was set to 87KeV, using a beam-size with a 1*1 mm² cross section. Data was acquired using a Frelon2K and a Frelon4M detector with a 10-30 sec integration time. Recorded 2D patterns were processed making use of a series of scripts provided by the beamline scientist and the local contact Gavin Vaughan 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 and Sigmaplot software

Results

Figure 1 and 2 show a selection of data recorded at ID11 in July 2013. Figure 1 shows the total x-ray scattering data of 3 in-situ heating experiments corresponding to 3 synthetic ACC samples: ACC with no additives, ACC prepared in the presence of 5mole% PO_4^{3-} ions, ACC prepared in the presence of 10% Mg^{2+} ions and of an in-situ hydration experiment on additive free ACC at 85% relative humidity. Figure 2 shows 3 PDF maps obtained from the in-situ heating experiments and one PDF map (up to $r=10\text{\AA}$, the full data up to 25\AA is not

shown) of an *in-situ* hydration experiment at 85% relative humidity. During *in-situ* heating, ACC remains “amorphous”, i.e. does not possess long range order above 8\AA , even at a temperature where most of the structural water molecules are evaporated. On the other hand, during hydration experiments, loss of structural water seems to occur concomitantly with crystallization.

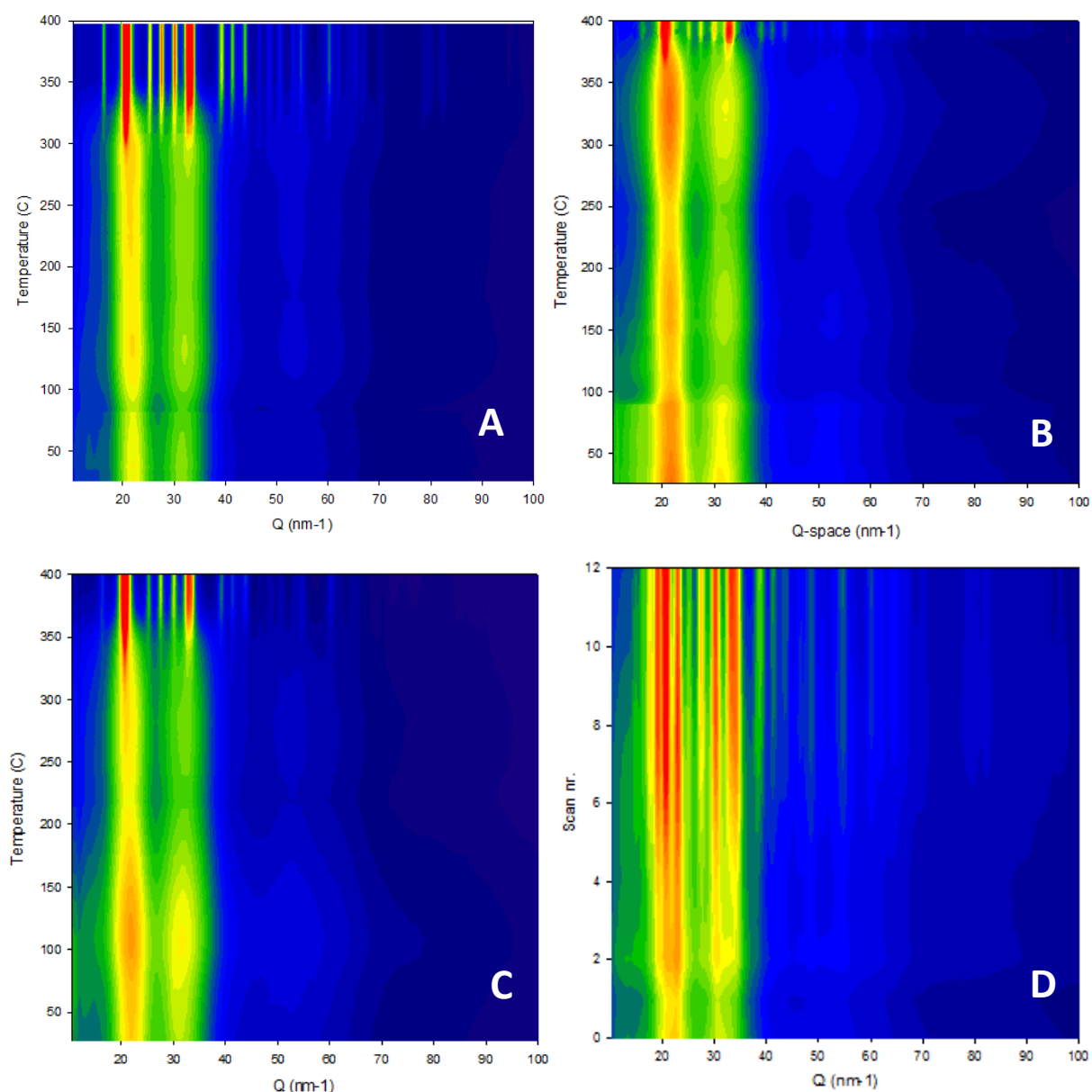


Figure 1: total x-ray scattering data obtained from 3 *in-situ* heating experiments (A-C, $2^{\circ}\text{C}/\text{min}$) and one *in-situ* hydration experiment at 85% relative humidity (D). (A) Synthetic ACC without additives (B) ACC with 5% phosphate ions (C) 10 % magnesium ions. (D) Synthetic ACC without additives, *in-situ* humidity driven crystallization experiment

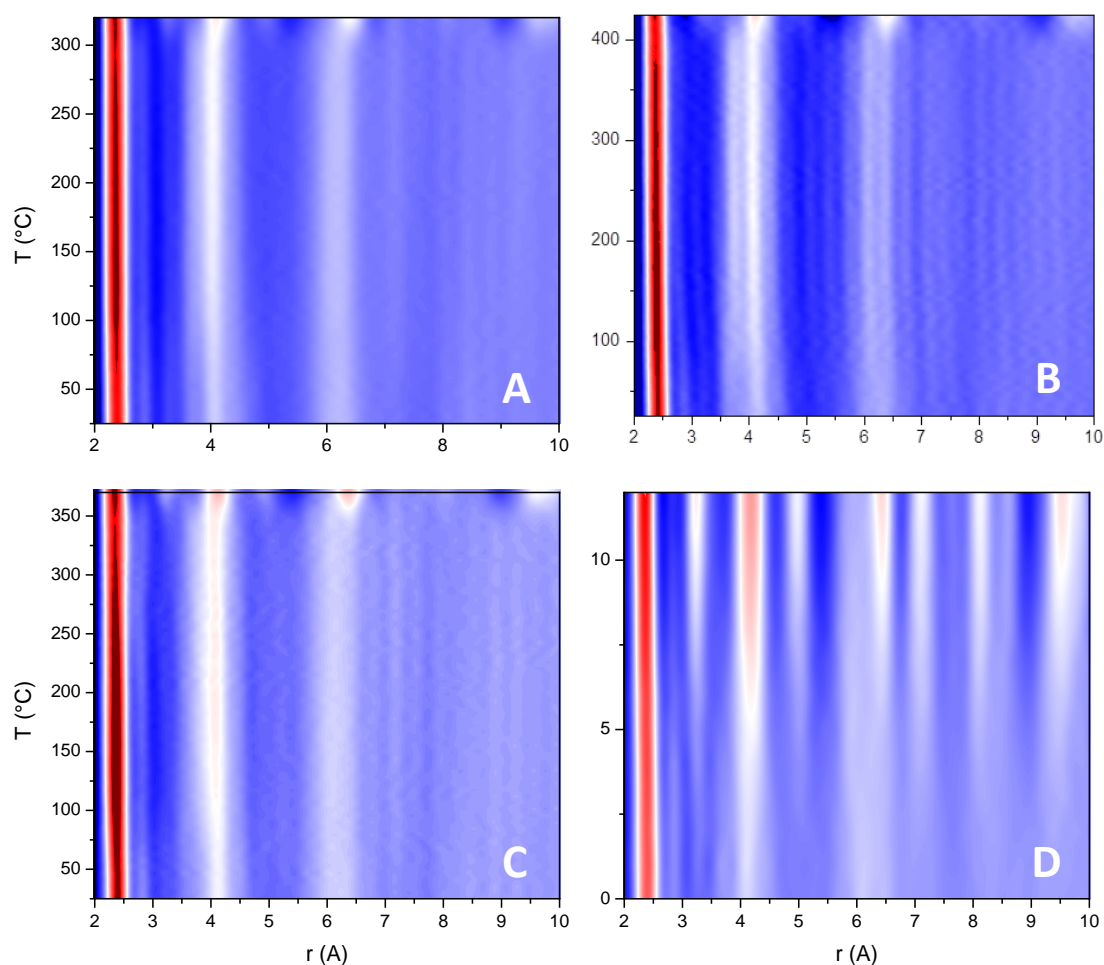


Figure 2: Pair distribution function maps (up to $r=10\text{\AA}$) of 3 *in-situ* heating experiments (A-C) and one *in-situ* hydration experiment at 85% relative humidity (D). (A) Synthetic ACC without additives (B) ACC with 5% phosphate ions (C) 10 % magnesium ions. (D) Synthetic ACC without additives, *in-situ* humidity driven crystallization experiment.

Conclusions and Outlook

Our results show the feasibility of performing such *in-situ* experiments at ID11 and, in addition, emphasize the importance of a comparison between both 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 at ID11. The results show the effect of the additive on the temperature induced transformation of ACC, which include different intermediates and the shifting of the temperature of the onset of crystallization. In addition, preliminary experiments of *in-situ* hydration induced crystallization show a distinctly different transformation mechanism. The effect of additives on this reaction is yet to be determined by further experiments. Further detailed data analysis is currently in progress. Specifically, we are currently working on a full characterization and analysis of the PDF data and combining it with TGA/DSC analysis in order to obtain a quantitative energetic and structural understanding of the crystallization reaction.

We would like to thank Gavin Vaughan for invaluable assistance in using beamline ID11 and help in critical online data evaluation.

References:

- [1] Koga N, Nakagoe Y, TanakaH(1998) Crystallization of amorphous calcium carbonate. *Thermochim Acta* 318:239–244
- [2] Hammersley AP. ESRF Internal Report, ESRF97HA02T, FIT2D: An Introduction and Overview, 1997
- [3] P. Juhás and T. Davis, C. L. Farrow, S. J. L. Billinge PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions, *J. Appl. Cryst.* **46**, 560-566 (2013)