Experiment title: Reordering of the atomic structure of colored amorphous calcium carbonate samples during their crystallization using pair distribution function analysis

Experiment number: CH-6058

Beamline: ID15A

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Report:

Here we report on our total X-ray scattering experiments at ID15A on amorphous calcium carbonate (ACC) colored by different organic pigments (naphthazarin, lawsone and juglone). In this study we measured time-resolved series of ACC crystallization driven by in-situ heating. We used pair distribution function (PDF) analysis to follow structural changes in the mineral from short range to long range order via medium range order during the heat-induced crystallization of the colored ACC samples.

Experimental Procedure

Sample: 13 amorphous calcium carbonate (ACC) samples were synthesized at the ID15A lab, at pH=10.5 by the addition of $CaCl_2$ to a Na_2CO_3 solution using established methods [1]. ACC were prepared in the presence (or absence) of three organic pigments (naphthazarin, lawsone and juglone molecules) with four different concentrations from 0.1wt.% to 2.5wt%. One ACC sample with no pigment was synthesized at pH=12.5 by adding 40mM NaOH to the Na_2CO_3 solution. After precipitation, samples were filtered, rinsed with cold ethanol and dried for few minutes in a desiccator under vacuum. Powder samples were mounted on a cylindrical Cu-sample holder and placed inside a Linkam FTIR600 heating stage.

Methods: Measurements were performed at ID15A beamline, ESRF. Beam energy was set to 60KeV and beam-size was 0.15*0.15 mm^2 in cross-section. The calibration was performed with a CeO_2 powder standard. The Linkam FTIR600 heating stage temperature was increased from 30°C to 250-400°C at a rate of 5°C/min.

Data acquisition and evaluation: X-ray scattering data were acquired using a Pilatus CdTe 2M with 0.5-1 sec measurement time. Recorded 2D patterns were processed thanks to scripts provided by the beamline scientist to average, mask and integrate the 2D patterns. Pair distribution functions were produced with the PDFgetX3 [2] software and plotted using Origin software. Differential of the PDF data as a function of temperature (dPDF/dT) were calculated and plotted using python script developed by Luca Bertinetti (Center for Biomolecular Biology, Dresden).

Results: Figure 1-3 show the PDF results for 5 of the measured samples: pure ACC, ACC+0.5wt.% of naphthazarin, ACC+2.5wt% of naphthazarin, ACC+0.5wt.% of lawsone, and ACC+0.5wt.% of juglone. At room temperature, all 5 samples show very similar PDF exhibiting characteristic short and medium range order up to 10Å with typical positions for main maxima around 2.4Å, 2.9Å,

4.1Å and 6.2Å mainly containing contributions from Ca-O pairs, O-O pairs, Ca-O/Ca-Ca pairs (1st shell) and Ca-O/Ca-Ca pairs (2nd sell), respectively (Figure 1) [3,4].

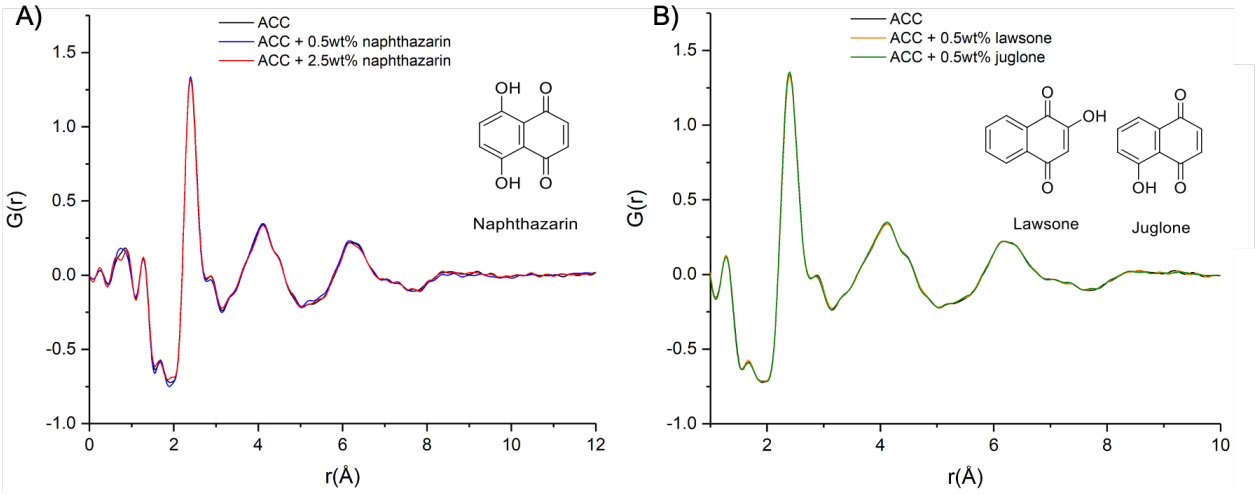

Figure 1: PDF calculated from X-ray scattering measurements at room temperature of pure ACC, ACC+0.5wt.% of naphthazarin and ACC+2.5wt% of naphthazarin and B) ACC+0.5wt.% of lawsone and juglone.

In order to mimic the solid-state crystallization mechanism occurring *in vivo*, ACC heat-assisted crystallization was chosen over humidity-induced crystallization, which was previously shown to lead to dissolution/reprecipitation mechanism instead [4]. In order to evidence small local ordering during the heat-induced ACC crystallization, dPDF/dT maps were generated (Figure 2). The most important changes in the dPDF/dT maps due to a sudden increase in the PDF intensities relate to the crystallization, which varies in terms of temperature onset and length according to samples. For pure ACC, crystallization starts at 180°C and last 30°C, whereas with the presence of 0.5wt.% lawsone and lawsone, it starts at 150°C/175°C and last 25°C, respectively. Interestingly, for ACC with 0.5wt.% naphthazarin, ACC crystallization starts at higher temperature (200°C) and last for more than 30°C. Regarding the local rearrangements, the different samples show small differences in the degree of SRO rearrangement before the crystallization. However, differences are observed in the MRO, especially around 6-7 Å, corresponding to the Ca-O/Ca-Ca pairs (2nd sell).

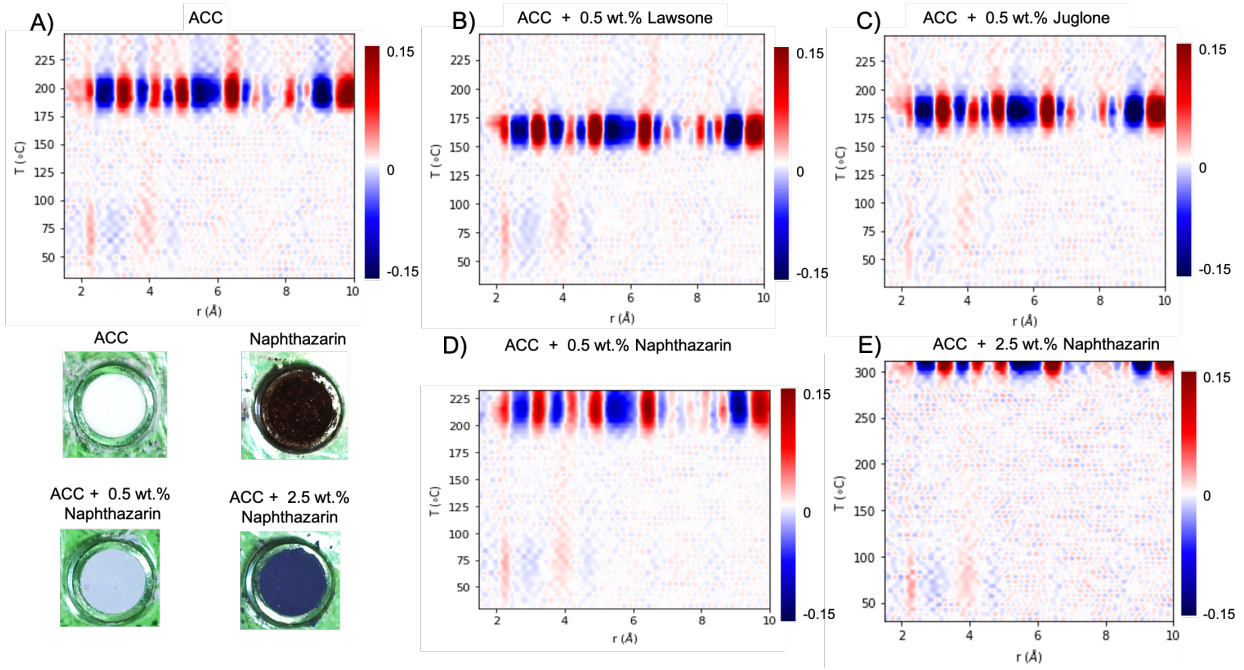

Figure 2: dPDF/dT maps upon heating of A) pure ACC, B) ACC+0.5wt.% of lawsone, C) ACC+0.5wt.% of juglone, D) ACC+0.5wt.% of naphthazarin and E) ACC+2.5wt% of naphthazarin.

Conclusions: *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 ID15A. The results show the effect of pigments on the temperature at which ACC transforms, namely a shift of the temperature of crystallization and different ordering at the MRO levels.

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References:

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