# Experiment Report Form

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| | **Experiment title:** 3D-CXDI for CaCO3 microparticles for deciphering the nanoscale grains | **Experiment number**: MA-5103 |
| **Beamline**: ID 10C | **Date of experiment**: from: 27-Oct-2021 to: 02-November-2021 | **Date of report**: 11-09-2023 |
| **Shifts:** 18 | **Local contact(s)**: Yuriy Chushkin | *Received at ESRF:* |

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**Report:**

3D Coherent X-ray Diffraction Imaging (CXDI) in combination with tandem wide angle X-ray diffraction (WAXD) to study mineralisation of calcium carbonate ($CaCO_3$) under the presence of difference additives. The experiments were in continuance of an earlier beamtime at ID02 (MA5094) in order to systematically study the entire crystallisation process of $CaCO_3$ - from early-stage nucleation events leading to growth of crystals into a fully grown microparticles. The central goal of the proposal was to understand how nano-sized grains are packed in 3D in $CaCO_3$ particles thus unravelling the growth mechanism. Key questions are to understand transition from a flat hexagonal particle to a nested one and finally to spheroidal shapes with possibly spiky particles.

The upgrade of the CXDI detector to Eiger-4M at ID10C during 2021 allowed us to use 2D Pilatus detector as a WAXD detector instead of Mythen-1D detector. This detector now facilitated not only the studies on crystal structures of the sample particles but also the preferred orientation of the crystal planes within the particles. A total of 28 CXDI measurements were made as a function of three different additives NaCl (a regular table salt), Polystyrene Sulfonate (PSS) and Fetuin-A, using an 8.04 keV monochromatic beam of dimensions 10x10µm. Particles to image were mounted on sample stage on a $Si_3N_4$ membrane of 100nm thickness with the width and height of 3mm with sturdy frame spanning 10mm high and across. The far field specked diffraction pattern was collected on the Eiger-4M detector while WAXD data was captured on the 2D Pilatus detector. The precipitations experiments were done at the ESRF based on the same experimental protocols for MA-4673 and MA-5094.

Among several CXDI experiments done during the beamtime, two representative examples are shown in Figures 1 and 2. Figure 1 highlight the effect of three different additives NaCl, PSS and Fetuin-A on crystallization with 9mM of initial concentration of precursors. Effect of NaCl is well visible on the morphology as well where higher concentrations of $Na^+$ and $Cl^-$ has hindered the growth by slowing down on the attachment mechanism and has caused multiple nucleation sites giving rise to particles which at a later stage agglomerate into bigger structures as shown in image below. PSS has given rise to what appears to be an amorphous $CaCO_3$ whereas the Fetuin has resulted in formation of a calcite crystal growing in one dimension. The crystalline or amorphous phases are ascertained from the WAXD data.
Another set of data shown below in Figure 2 demonstrates the change in morphology and crystal structure upon doubling the concentrations of NaCl and PSS. We observe a transition from Calcite to vaterite with 18mM NaCl and amorphous $CaCO_3$ to crystalline vaterite with 18mM of PSS. With Fetuin-A the calcite polymorph of $CaCO_3$ is stabilised.

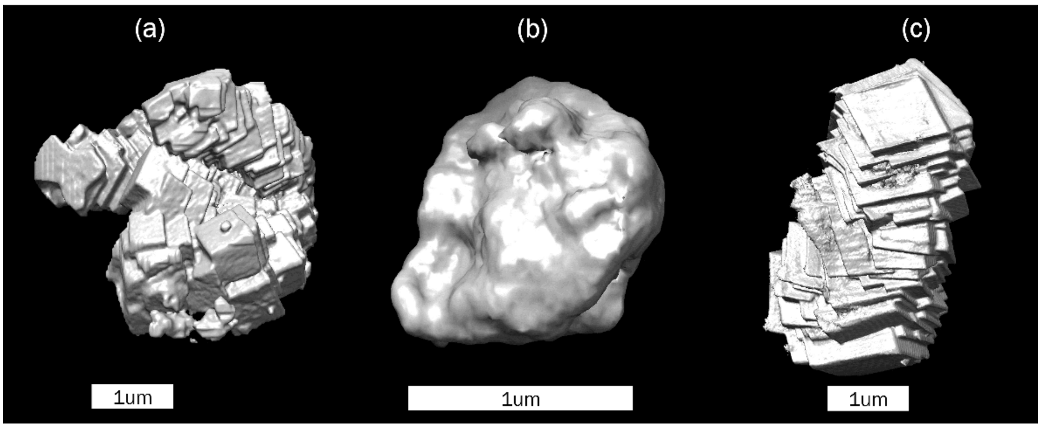

*Figure 1: Iso-surface mapping exhibiting morphology of Calcium Carbonate microparticles upon addition of (a) NaCl, (b) Polystyrene Sulfonate and (c) Fetuin-A prepared by 9mM each of initial precursors.*

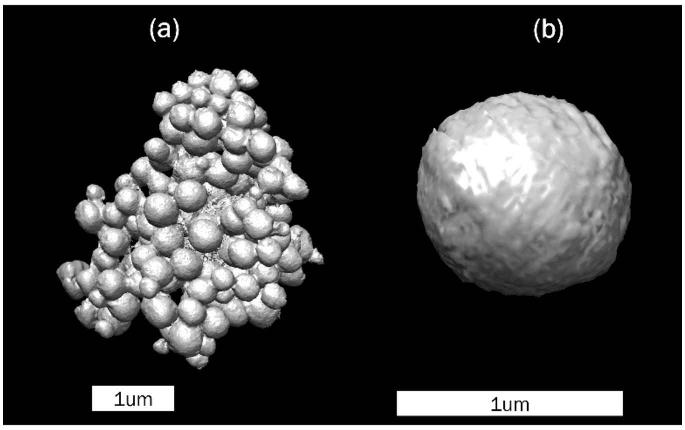


*Figure 2 : Iso-surface mapping exhibiting morphology of Calcium Carbonate microparticles upon addition of (a) NaCl, (b) Polystyrene Sulfonate prepared by 18mM each of initial precursors.*

The results from this experiment are being written up into manuscripts and will be submitted as the following set of publications.

1. Younas D. et al "*Coherent diffraction nanoscopy of additive controlled morphology of Calcium Carbonate microparticles.*", In preparation.

The results have also been presented in multiple conferences as both oral and poster presentations:

1. Younas, D. et al. (**2022**) 3D nanoscopy of $CaCO_3$ microparticles using coherent X-rays. *International Solvay Institutes* SOLVAY WORKSHOP ON "Nucleation: multiple pathways multiple outcomes" , Brussels 2022-12-07 - 2022-12-09. *Poster.*
2. Younas, D. et al. (**2023**) 3D visualization of calcium carbonate morphology as a function of different additives using coherent X-ray diffraction imaging. *International Union of Crystallography* 26h Congress and General Assembly of the International Union of Crystallography , Melbourne, Australia 2023-08-22 - 2023-08-29. *Oral.*
3. Younas, D. et al. (**2023**) Coherent X-Ray Diffraction Imaging to Study Effect of Additives on Crystallization of Calcium Carbonate Microparticles. *NTNU* TNNN Conference 2023 , University of South-Eastern Norway, Vestfold 2023-06-21 - 2023-06-23. *Oral.*

**Beamline Configuration:**

Beam height: 10 µm
Beam width: 10 µm
Energy: 8.04 keV
Wavelength: 1.52 Å
Detector: Eiger-4M. 2070 x 2167 pixels (horizontal × vertical), with a square pixel size of 75 µm
Sample-detector distance: 5.45 m