ESRF	**Experiment title:** Unveiling different phase transformation mechanisms in Calcite crystallization by Bragg ptychography	**Experiment number**: SC-5117
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Preliminary report:

Summary:

The aim of this experiment is to understand the phase transformation routes involved in the non-classical crystallization of calcite films under organic mediation. Theory describes solid-solid and dissolution-reprecipitation as possible crystallisation routes for the amorphous-to-crystal transformation and our in-vitro model allows us to choose the mechanisms based on the crystallization condition, irrespective of the initial film morphology. This experiment builds on the previous, succesful EV-394 experiment, where we investigated the two most extreme samples which showed markedly different crystalline properties.

In this experiment, we have chosen two different amorphous film morphologies by varying the polymer content and have subjected them to three different crystallization conditions, also resulting in morphologically different films. Our Bragg ptychography experiments shows that despite their different morphological appearance, the crystalline properties are largely determined by the crystallization conditions without major influence from the initial shape and polymer concentration of the amorphous films. Furthermore, our results shows that significantly different crystalline properties are observed, depending on the transformation pathway, i.e.,the solid-solid transformation or the dissolution/reprecipitation crystallization pathway.

Samples and setup:

Our sample set comprised in-vitro crystallized calcite films under various precursor and crystallization conditions. The aim was to complement the two most extreme conditions investigated during EV-394 experiment and systematically test our phase transformation hypothesis. In brief, based on preliminary analysis (from scanning electron microscopy), we are hypothesizing that the amorphous to crystalline transformation in our system is either happening along a solid/solid transformation or a dissolution/reprecipitation pathway and that we can selectively chose the transformation conditions via the crystallization pathway. With 3D Bragg ptychography (3DBP), we can test this hypothesis and investigate the resulting crystalline properties of the obtained single crystal, with high (~50nm) spatial resolution and high strain (10^{-3}) and orientation sensitivity (a few$1*10^{-3}$ degree).

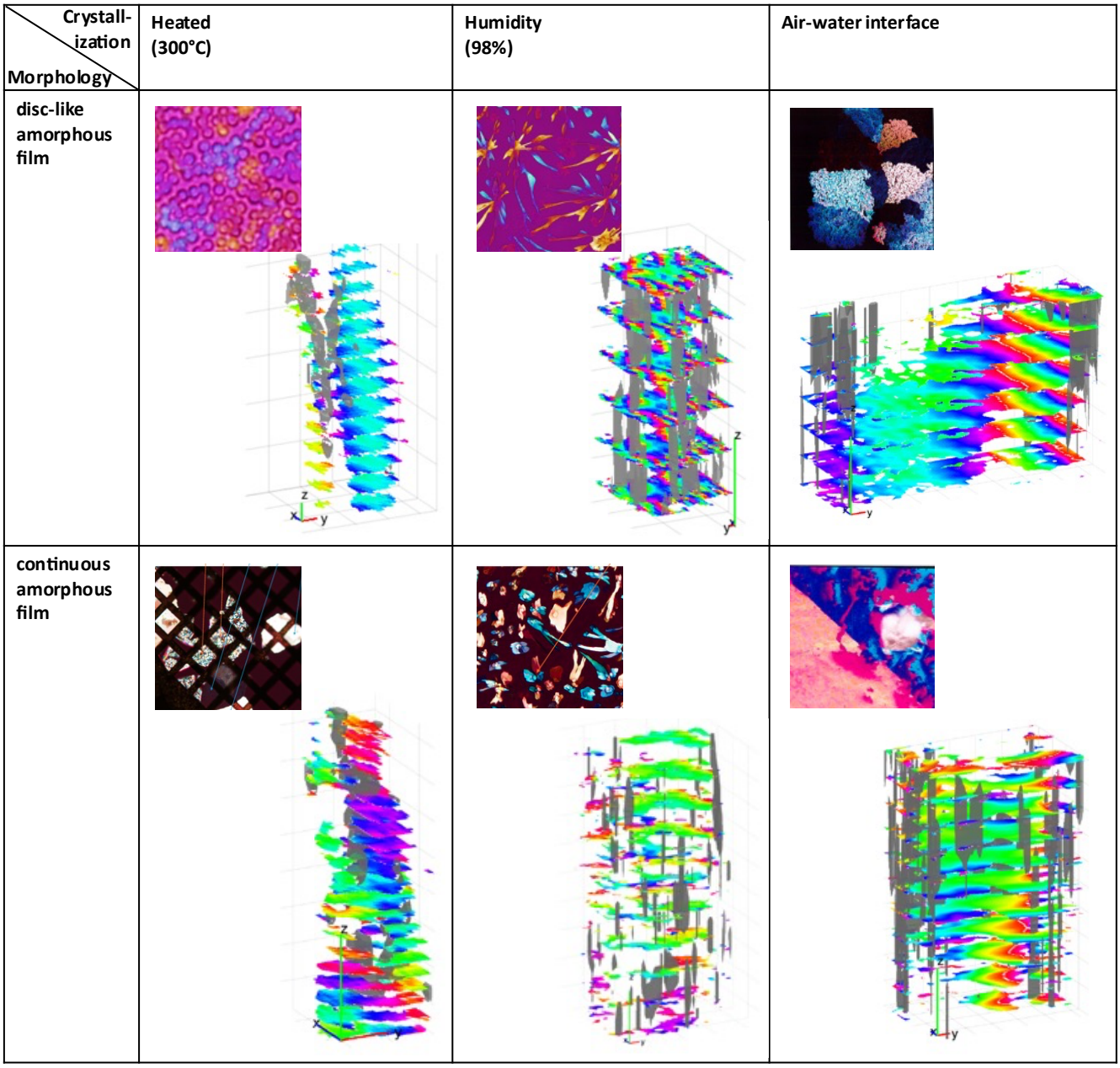

Figure 1 Overview of the different film morphologies and the strain extracted from the 3DBP inversions. The sample set comprised two different initial film morphologies of the amorphous precursor (disc-like and contionus) which is subsequently crystallized by three different routes (temperature, humidity and at the air-water interface of the initial liquid solution). From each crystallisation condition, two samples were characterized. The polarized light micrographs highlight the different morphologies of the resulting films while the bottom insets display the phase maps by showing several slices. Please note that the vertical direction (along the film thickness direction) is stretched to facilitate the visualization.

The experiments were carried out at the ID13 nanobranch (EH3), using a set of Si NFLs to produce a beam of ~ 250x300 nm^2 at 15.2 keV with a photon flux of 1.1 10^{11} ph/s. We note that we were the first users to use the EH3 with the new monochromator crystal and see clear evidence of a significant increase in the coherent beam quality. This configuration enabled us to collect at full 3DBP dataset in the range of 60-120 seconds, which is impressive compared to the few hours it took previously. While a detailed assesment is out of the scope of this report, it's a noteworthy observation. We have probed two samples (corresponding to two different amorphous films) for each of the three crystallising conditions, and several areas each time, to ensure some statistical robustness of our observations.

The diffracted signal was recorded using the Eiger 4M detector in the case of nanodiffraction maps or the maxipix for 3D Bragg ptychography. In either case, the XRF signal was recorded using a single element Vortex EM detector.

The experimental strategy comprised recording large nanodiffraction/rocking curve maps of the samples to search for suitable reflections in the horizontal plane, suitable for 3DBP. The newly installed motor system for

the detector table allowed for a extremly efficient peak selection and facilitated the experimental procedure greately. We have selected mostly the (104) calcite reflections in this study for their high intensity and high sensitivity along the c-axis of the crystal. In two cases (continous film/air-water interface and continous film/heater) we had to resort to the (012) and (113) reflections respectively.

Principal outcome:

The collected 3DBP datasets were all succesfully inverted using our own Bragg ptychography inversion codes. Figure 1 summarizes our main findings on the whole sample set. The final, crystallized film morphology is shown in the top-left of each panel and higlights that despite coming from similar amorphous films, the crystallized film exhibits very different morphologies depending on the crystallization route. The lower inset shows the phase from the 3DBP inversions after removing strain and tilt-induced phase ramps. To facilitate the presentation, the data has been stretched along the vertical direction and slices through the 3D volume are shown. The phase maps shows that the heated samples from both film morphologies exhibit a rather flat, homogenous phase map, corresponding to rather small iso-oriented domains (200-300 nm) and large strain distribution covering a range of about $5\text{-}8*10^{-3}$. In contrast to this, the humidity-crystallized (and liquid interface) samples exhibit a rather uneven phase map with much larger iso-oriented domains (0.5 - 2 μm) and much narrower strain distribution ($3*10^{-3}$). Remarkably, these behaviours are consistent for the two different precursor film morphologies.

Finally, with the in-vitro synthetic calcite film system, we are for the first time able to draw a direct conclusion on the crystallization kinetics. Furthermore, we are now able to contrast these findings with the crystalline signature of the biominerals we have characterized in the prismatic layer of Pinctada margaritifera shells. The crystalline properties of the biogenic crystals are very much resembling that of the air/water interface and the humidity crystallized sample, pointing towards the possibility that the biogenic crystal is formed by a dissolution/reprecipitation route.

Conclusions and further proceedings:

In conclusion, our experiment shows the presence of two different non-classical crystallization in our synthetic calcite films. The crystallization behaviour is not goverend by the structuring of the amorphous films but solely by the crystallization conditions of the amorphous/crystalline transformation. We found consistent and significantly different crystalline behaviors, depending on the crystallisation route. By comparing our findings on the synthetic crystals with the structure we obtained on biogenic calcite crystals in the prismatic layer of Pinctada margaritifera, we find that the crystalline properties of the biogenic crystal very much ressemble the humidity and air-water interface induced crystallisation. This indicates that the crystallisation in the biogenic crystal is likely driven by dissolution/reprecipidation.

With the data evaluation mostly finished, we are currently preparing a manuscript which reports these results.

We would like to express our thanks to the staff of ID13 for the continued efforts in improving the experimental setup and thus streamlining the data acqusition. On an experimental side note we want to mention that our 3DBP data collection time has plummeted from several hours before EBS to ~60 seconds and the fact that we are now limited by the detector speed of the Maxipix.