



	Experiment title: CaCO₃ crystallization within porous glass rods studied by XRD-CT	Experiment number: CH-4778
Beamline: ID11	Date of experiment: from: 12 th December to: 16 th December	Date of report: 24/2/2017
Shifts: 12	Local contact(s): Jon Wright	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): C. Anduix-Canto* and F. C. Meldrum, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK.		

Report:

Aims of Project: The aim of this experiment was to investigate – using imaging and diffraction tomography - the effect of confinement on the crystallization of CaCO₃ and CaSO₄. This was achieved by investigating the precipitation of these minerals within commercial Controlled Porous Glass rods (CPGs), which have sponge-like internal structures, and pores in the range of 2-100 nm. Over the last 5 years we have shown that confinement can have significant effects on crystallization, affecting polymorphism, crystal orientation and single or polycrystalline character of inorganic compounds²⁻⁷. However, we still have a poor understanding of the origins of these effects. The goal of this project is to generate new understanding of the crystallization of inorganic solids in nanopores, where combined absorption and diffraction tomography were used to observe the formation of different polymorphs with time, and how these are determined by the ion concentrations and positions within the CPG rod. This is the first study of crystallization in-situ in nanopores, and will provide a new understanding of processes such as weathering and biomineralisation. It will ultimately enable us to use confinement to control crystallisation processes in a predictable way.

Experimental Methods: CaCO₃ and CaSO₄ were precipitated within CPG rods with 7 nm pores by inserting the rod ends into glass tubes and injecting the CaCl₂ and Na₂CO₃/(NH₄)₂SO₄ solutions into the glass tubes. Counter diffusion of the ions through the rods results in precipitation of the inorganic salt. At ID11, the system was mounted onto M4 screws and placed parallel to the beam. A beam energy of 40 KeV was used. After mounting and aligning the samples, we took tomograms and diffraction maps of the regions of interest. This required us to keep changing the detectors so that we could obtain maps of crystallite formation (polymorph and morphology) within the rod. The first crystal system investigated was CaCO₃ at 1M followed by CaSO₄ 3M and 250mM (initial concentrations). Both systems gave good results. However, we had some evaporation problems during the first day which were fixed by surrounding our system with a kapton film.

Results Obtained: During the second day we were able to (1) follow the crystallization of CaCO₃ over 24h in CPGs, observing dendritic growth of the crystals along the pores and interesting effects such as Ostwald ripening by tomography (figure 1). We also observed (2) significant stabilisation of metastable phases such as amorphous calcium carbonate (ACC) and vaterite. Both polymorphs were present in high amounts in the pores after 24h. Further, calcite is the polymorph usually found in bulk after a few minutes but we did not find any in the pores after 6 h. We also observed that (3) calcite is formed preferentially at high concentrations of calcium (figure 2). Phase identification along the CPG rods was possible using diffraction tomography at ESRF. We had not had any success with lab-based diffraction tomography.

The third and fourth day we focused on the crystallization of CaSO₄ at high and low concentrations and obtained very interesting results. We observed that the rods were too fragile for high reagent concentrations and that they fractured due to the force of the crystals forming. However, at lower concentrations, we observed the formation of large crystals in the porous rod by tomography. These crystals were shown by diffraction tomography to be Bassanite, which is known to be very unstable at room temperature. Bassanite was seen to be stable in the pores for longer than 24 at room temperature and without additives. **This result**

is unprecedented in the literature and is extremely important to the formation of Ca sulfate in the environment.

The advantage of using diffraction tomography was that we were able to map the entire rod, and were therefore able to conclusively demonstrate that every crystal within the rod was bassanite. Gypsum (the stable polymorph at room temperature) was never found in the pores unless the rod was broken. Breakage of the rod caused the immediate formation of gypsum (stable polymorph of CaSO_4) or mascagnite ($(\text{NH}_4)_2\text{SO}_4$) crystals at the fracture surface (where the crystals were no longer confined). The results obtained at this beamtime are unique and relevant for chemists and physics studying crystallization mechanisms as well as geologists studying weathering and structural problems. Further beamtime will be needed to complete the study of CaCO_3 at low concentrations. We would also like to extend our study to investigate the influence of surface chemistry and pore size, where this will provide us with a more complete understanding of confinement effects on crystallization. Having confirmed the success of this technique using our system, we also intend to extend these studies to other solids such as CaPO_4 and CaC_2O_4 , where both are highly important in healthcare issues.

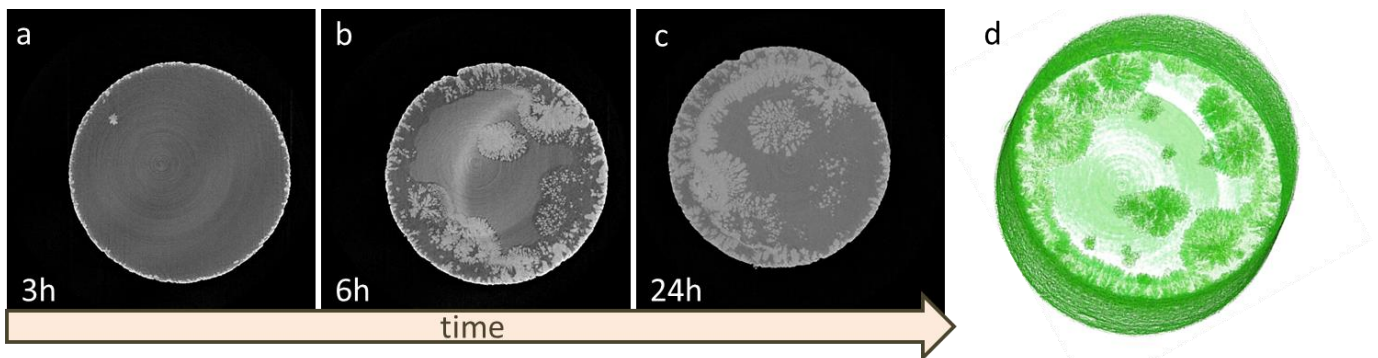


Figure 1: Crossed sections of the CaCO_3 crystals nucleating and growing over time (a-c) and 3D tomogram of the crystals in the CPG rod. After 6 h we observe dendritic vaterite crystals and ACC precipitating along the pores.

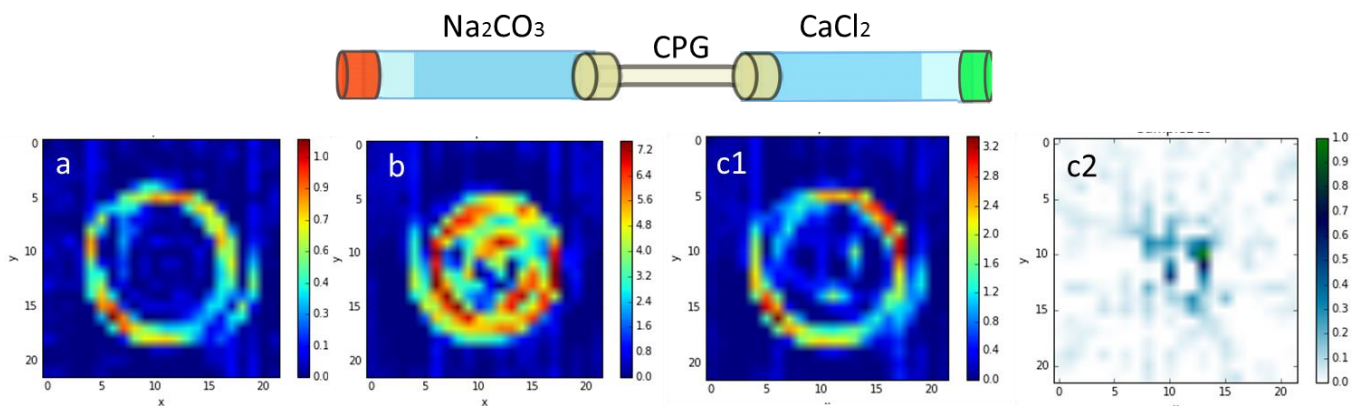


Figure 2: Diffraction 2D maps of vaterite (a,b,c1) and calcite (c2) showing the proportion of crystals and their position. Map (a) is a slice situated close to the CO_3^{2-} ion reservoir, (b) is a slice at the centre of the rod and (c1 and c2) is a slice close to the Ca^{2+} ion reservoir. The amount of vaterite is higher at the centre and the calcite closer to the Ca^{2+} ions.

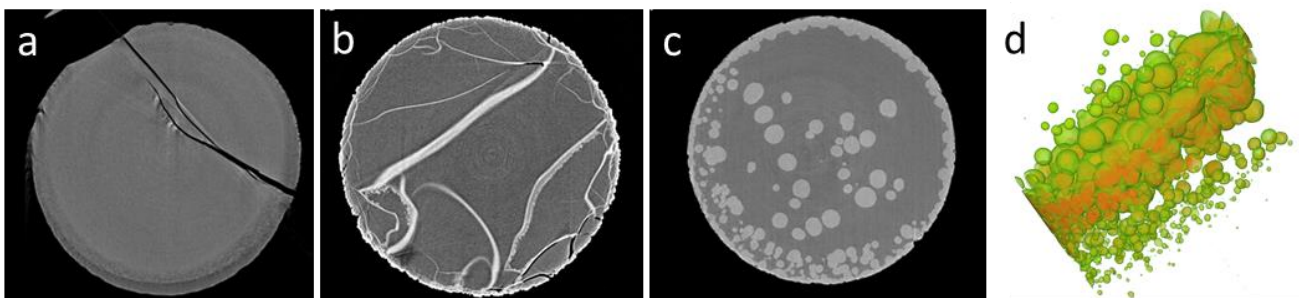


Figure 3: Crossed sections of CPG rods after CaSO_4 crystallization where the crystals in (a) are mascagnite, (b) gypsum and (c) bassanite. (d) 3D tomogram of bassanite crystals in the rod.

References: [1] Jiang, Ward, *Chem. Soc. Revs.* 2014, **43**, 2066. [2] Stephens, Meldrum et al, *Adv. Funct. Mater.*, 2010, **20**, 2108. [3] Wang, Meldrum et al *Chem Mater.* 2014, **26**, 5830. [4] Wang, Meldrum et al, *Adv. Funct. Mater.*, 2013, **23**, 5615. [5] Cantaert, Meldrum et al, *Chem Eur J.*, 2013, **19**, 14918. [6] Ihli, Meldrum et al *Chem. Mater.* 2015, **27**, 3999. [7] Loste, Meldrum et al, *Adv. Func. Mater.* 2004, **14**, 1211.