



Experiment title: CaCO₃ and CaSO₄ crystallization within porous glass rods studied by XRD-CT

**Experiment number:
CH-5141**

Beamline: ID11	Date of experiment: from: 26 th September to: 3 rd October from: 20 th October to 23 rd October	Date of report: 27/10/2017
Shifts: 12	Local contact(s): Carlotta Giacobbe	<i>Received at ESRF:</i>
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Report:

During this experiment we used diffraction tomography (DCT) to study 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) containing pores that were 7 nm in diameter. CaCO₃ and CaSO₄ were precipitated within CPG rods by inserting the rod ends into glass tubes and injecting 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 a 40 KeV beam. During our last beamtime (experiment ch4778) we used CPG rods with 1 mm diameters and complemented the DCT data with information from absorption tomography. However, these rods were too fragile for the high reagent concentrations used, where they often fractured due to the force of the crystals forming within them. The current beamtime therefore investigated the crystallization of CaCO₃ and CaSO₄ within 2.8 mm diameter CPG rods, which prevented this fracture problem. We also investigated the crystallization of these solids in surface-modified CPG rods to investigate the influence of surface chemistry on the crystallization process.

(1) CaSO₄ crystallization in uncoated CPG rods and carboxylate-functionalised CPG rods:

Firstly, we followed CaSO₄ crystallization in nanopores by DCT for 24 h in uncoated rods at high (3M) and low (250 mM) concentrations. In both cases, we observed the formation of large bassanite crystals in the porous rods even at high solution concentrations. Bassanite is known to be very unstable in bulk solution at room temperature but was stable in the pores for over 24 h under the same reaction conditions. We also obtained new information about the mechanism of crystallization of CaSO₄. Amorphous calcium sulfate (ACS) was the first phase to be detected in the pores and transformed to bassanite over time. ***This is the first in situ study to show that ACS is a precursor to bassanite (figure 1).***

When modifying the surface chemistry of the porous rods with a carboxyl functionality, gypsum precipitation was induced and both gypsum and bassanite crystals nucleated in the pores. Again, a new understanding of this process was obtained. For the first time we saw that bassanite crystals did not redissolve in the presence of gypsum, but that both polymorphs coexisted (figure 2). This is entirely different behaviour to that seen in bulk solution and gives us new information about the role that confinement plays on crystallization. In bulk solution, crystallization processes are dynamic and every crystal nucleating is affected by other crystals nucleating in the same solution. This process does not appear to occur in confinement. Interaction between crystals forming in such restricted volumes (7 nm pores) was not observed in any of our experiments and gypsum did not grow at the expense of bassanite. ***These results have never been reported before and are extremely important to the formation of Ca sulfate in the environment.***

(2) CaCO_3 crystallization in non-coated CPG rods and in sulfonate and carboxylate terminated CPG rods:

In beamtime ch4778 we were able to detect large amounts of amorphous calcium carbonate (ACC), vaterite and calcite at different positions in uncoated CPG rods. We obtained similar results here, but also observed the formation of small aragonite crystals close to the carbonate reservoir. This is very interesting since aragonite is a metastable phase that is very difficult to obtain at room temperature without the use of additives. Once again confinement provided a way to stabilize metastable phases at room temperature. We did not observe any significant difference when crystallization took place in functionalised rods; calcite and vaterite were the main phases to form in the pores.

During this beamtime we confirmed the success of our methodology for studying our system. Indeed, as far as we are aware, synchrotron DCT is the only technique capable of identifying the phases of the crystals forming in-situ in the CPGs. No lab-based analysis has come close to the understanding gained here. During this beamtime we achieved new insight into the effects of confinement on crystallization. These studies could be now extended to other solids such as CaPO_4 and CaC_2O_4 , where both are highly important in healthcare issues.

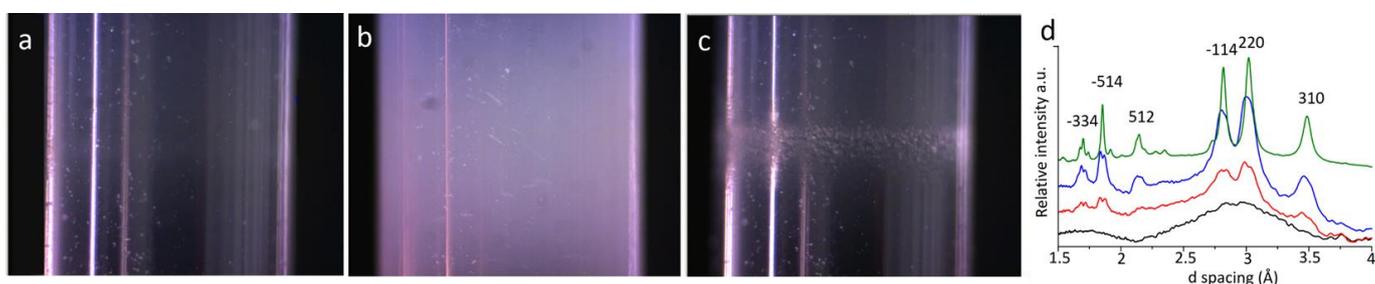


Figure 1: CPG rod after (a) 10 min, (b) 1h and (c) 2h from solution injection. (d) Diffraction patterns of the rod at different time points proving the existence of ACS after 1h (in black), which transforms to bassanite over time.

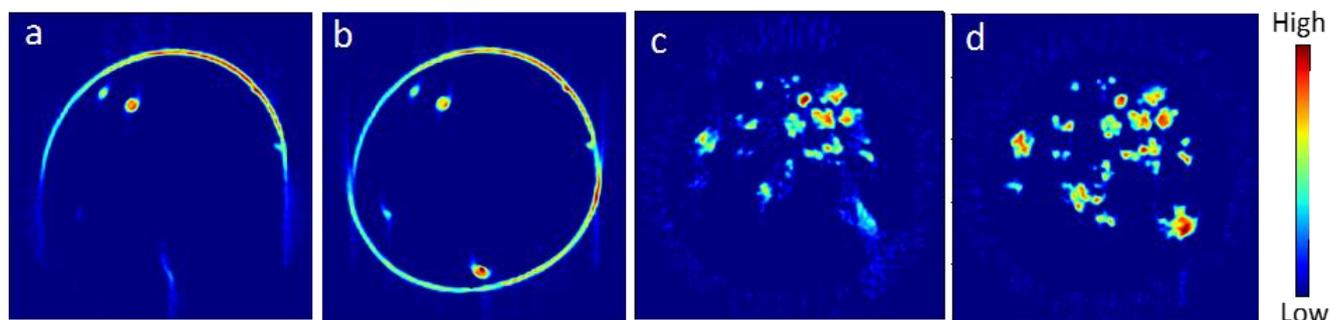


Figure 2: Diffraction 2D maps of bassanite (a,b) and gypsum (c,d) after 3 h (a,c) and after 13 h (b,d). Crystal growth is observed but no dissolution or transformation.

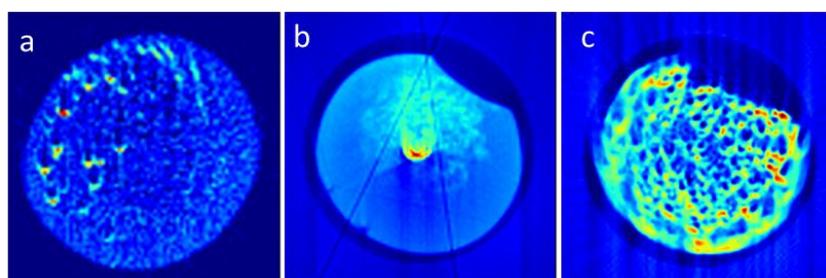


Figure 3: Diffraction 2D maps of aragonite (a), vaterite (b) and calcite (c) at different positions of a CPG rod, where aragonite nucleates close to de carbonate reservoir, calcite close to the calcium reservoir and vaterite in the middle.

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.