	Experiment title: ***In situ* coupled GISAXS/QCM studies of crystallization processes at surfaces relevant to construction materials**	**Experiment number**: CH-4937
Beamline: ID10	**Date of experiment**: from: November 29th 2016 to: December 6th 2016	**Date of report**: February 20th 2017
Shifts: 21	**Local contact(s)**: Andrei Chumakov	*Received at ESRF:*

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Introduction

A new, costum designed setup to study surface induced precipitation (i.e. heterogeneous nucleation) of solid phases from supersaturated aqueous solutions, developed in a collaboration between ISTerre (CNRS & Univ. Grenoble Alpes) and BASF (Germany), was installed and tested for the first time at ID10. This setup allows simultaneous *in situ* GISAXS & quartz crystal microbalance (QCM) measurements. GISAXS provides information about the size and shape of the formed particles, and their evolution over time. The information obtained from the QCM measurements is highly complementary: it allows not only to quantify the deposited mass on the substrate, but also gives information about the elastic properties of the precipitates.

Results

The first two days were devoted to the installation of the setup, including beamline (vacuum tube) and beamstop adjustments as well as integration and optimization of the wet chemistry ancillary equipment (connection to peristaltic pump system for flow-through experiments,

preparation of stock solutionsetc.). Incident X-rays with an energy of 22 keV were selected in order to cover an appropriate *q*-range and to have enough transmission through the ~12 mm thick liquid cell. Two photos of the setup are shown in Figure 1.

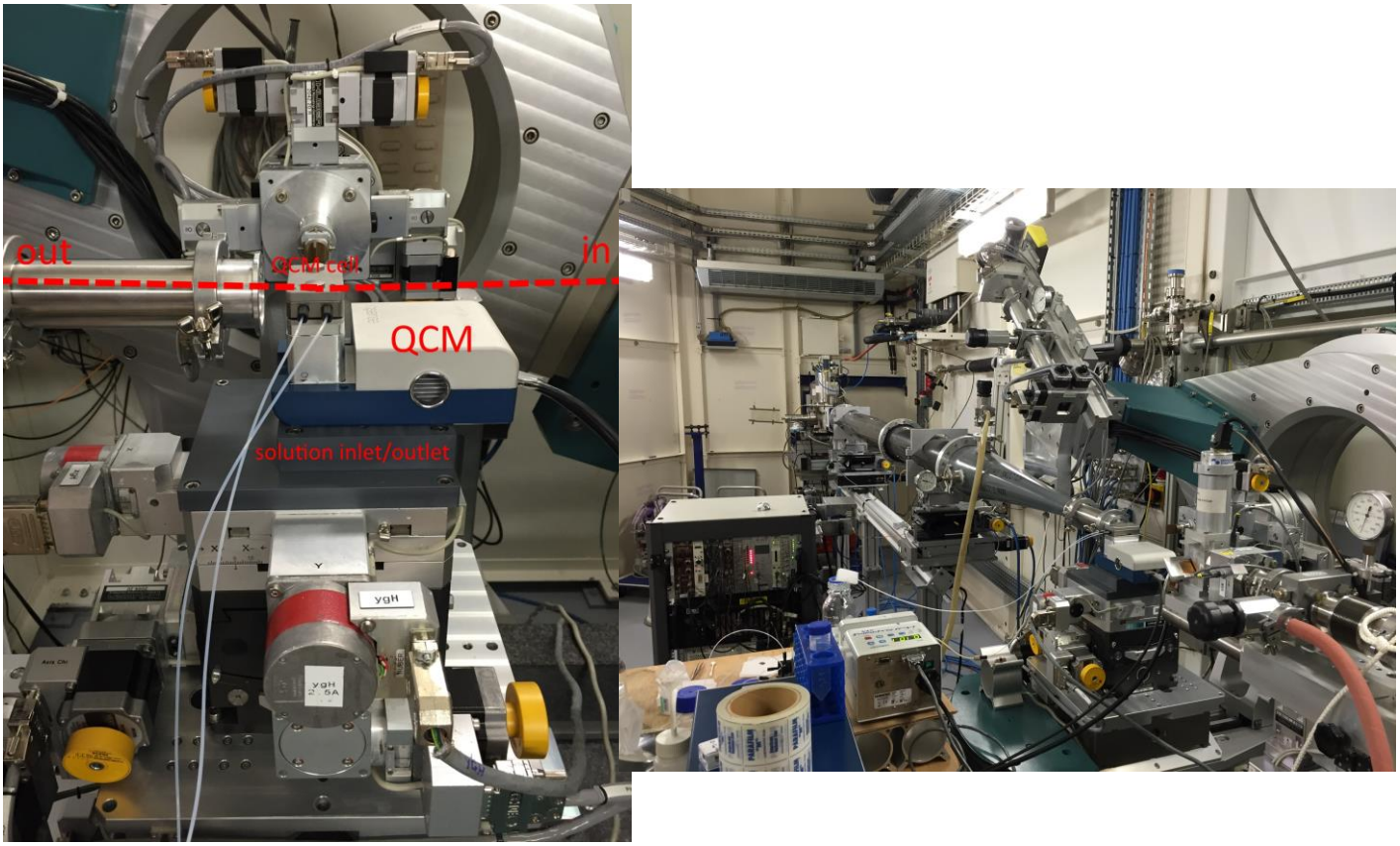

Figure 1. *<u>Left</u>: side view of the setup installed at ID10. <u>Right</u>: view along the flight path tube with the Pilatus detector placed at the end.*

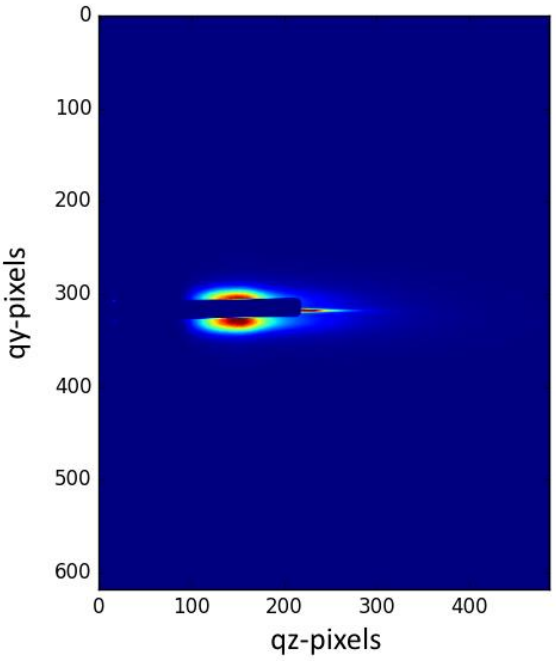

Figure 2. *Scattered X-rays at the 2D detector. The reflected beam is elongated along q_z due to substrate bending.*

First tests with the whole system running were performed to observe $CaCO_3$ nucleation on bare gold substrates (commercial QCM sensors). A 2D image of X-rays scattered from the substrate and detected by the used Pilatus detector is shown in Figure 2.

The QCM setup contains a liquid cell, which is tightened using a home-made kapton gasket allowing transmission of the X-ray beam. Supersatured solution is flown through the liquid cell using a peristaltic pump and a Y-mixer to combine two stock solutions (e.g. $CaCl_2$ and $NaHCO_3$). Several technical problems were detected during days 3 and 4, related to (i) a misfunctioning of the Y-mixer (the stock solutions were not mixed in a 1 to 1 ratio), (ii) to the bending of the QCM sensors upon fixation into the fluid cell, and (iii) the need to optimize the beamstop position in order to

protect the detector from the reflected beam. Addressing this last issue allowed us to increase our experimental sensitivity to successfully study poorly scattering systems such as$CaCO_3$ in water. All other problems were also solved or taken into account in data analysis (for example, substrate bending leads to a slightly higher direct beam image on the detector). Note that most of the measurements were performed without one or two of the attenuators, in order to take advantage of a large part of the high flux available at ID10 from the three in-line undulators. This highlights the need of a high-flux beamline such as ID10 for the targeted kind of experiments.

From day 4, a good correlation between QCM and GISAXS data evolution was observed. Subsequently, a series of experiments were performed to study heterogeneous $CaCO_3$ nucleation (a system previoulsy studied by our group using in situ GISAXS) at different solution conditions (e.g. different levels of supersaturation) and on a variety of substrates with different surface chemistry. These include pure Au, thiol-functionalized Au, and silica substrates. Both solution conditions and surface properties were found to have a strong influence on the kinetics (and mechanisms) of heterogeneous nucleation (as expected).
A typical result is highlighted in Figure 3, where an increase of scattering intensity is observed with time for thiol-functionalized Au substrates. The corresponding change in resonance frequency recorded by the QCM is shown in Figure 4.

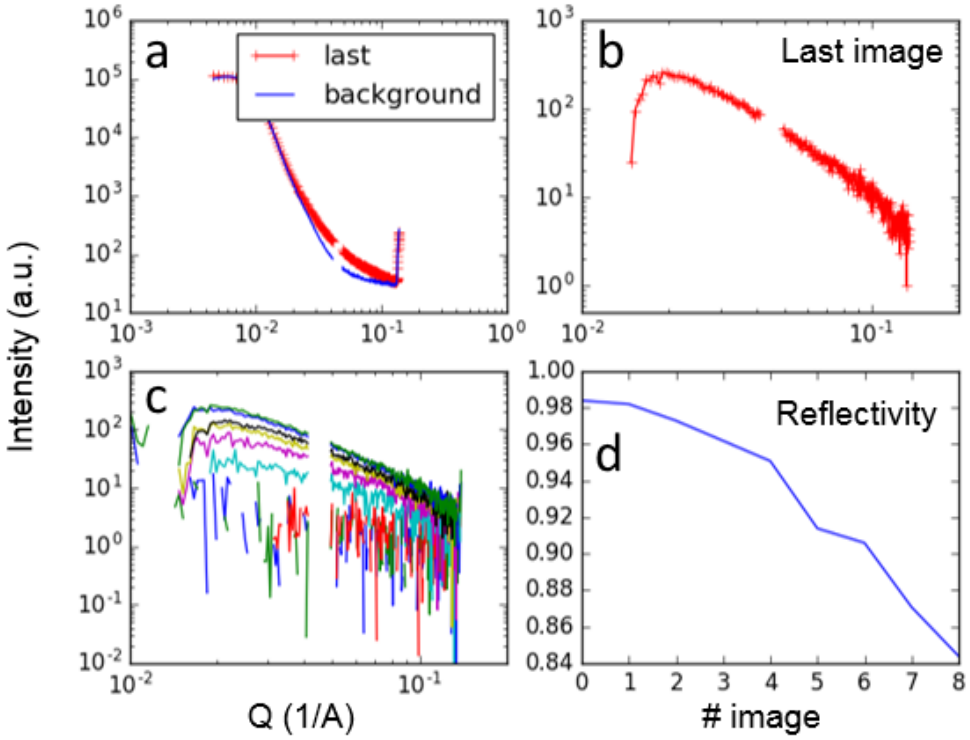

Figure 3. *GISAXS data collected during nucleation of a 10mM $CaCO_3$ solution on a thiol-functionalized Au substrate. (a) The scattering pattern obtained at the end of the experiment is shown together with the background image. (b) Background corrected last image. (c) Time evolution of the background-corrected intensity. (d) Evolution of the reflected intensity with time. The decrease is due to the increase of the substrate roughness with time. All intensity cuts are made along the q_y direction at the Yoneda wing position.*

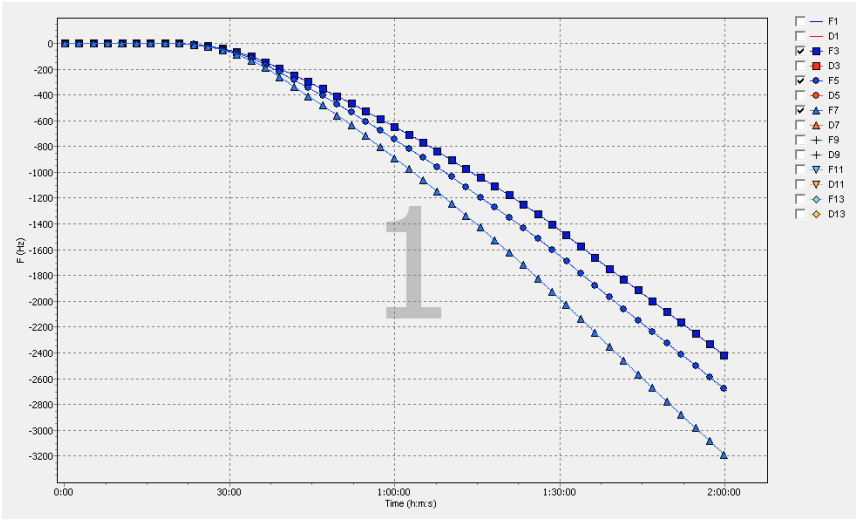

Figure 4. *Monitoring heterogeneous $CaCO_3$ nucleation by QCM: changes in resonance frequency as a function of time for three different harmonics in the same experiment as shown for GISAXS in Figure 2.*

After this first successful test, a new series of experiments will be designed in order to systematically study heterogeneous nucleation rates for relevant mineral systems such as $CaCO_3$, $CaSO_4$ and silica. Currently, work is in progress to avoid substrate bending and to improve the mixing of stock solutions. Data analysis of QCM and GISAXS is in progress.