ESRF	**Experiment title:** **Time resolution extension of in-situ SAXS by combining microfluidics and stopped-flow-technique**	**Experiment number**: SC 3665
Beamline: ID02	**Date of experiment**: from: 17/06/2013 to: 21/06/2013	**Date of report**: 22/09/2014
Shifts: 9	**Local contact(s)**: Dr. Gudrun Lotze	*Received at ESRF:*

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Report:

The aim of experiment SC-3665 was to extend the time-resolution of in-situ SAXS by combining microfluidics, stopped-flow technique and microfucus SAXS. Using this approach we expected to cover the time range of kinetic investigations from µs to minutes for consolidating the (kinetic) results from microfluidic and standard stopped-flow experiments. As model system the formation of $CaCO_3$ nanoparticles was choosen due to the fact that the kinetic of this special reaction is already investigated by stopped-flow technique [1-2]. During the experiments we used a comercial stopped-flow device (BioLogic, SFM-400) and a standard micofluidic setup, e.g. a microchannel with mixing cross for hydrodynamic flow focusing made of UV-curable polymer (NOA81, Nordland Optical Adhesives) with a width of 250 µm and a height of 100 µm. During the microfluidc experiments the flow rates varied from 100-8000 µl/h to obtain a good temparally resolution. The chip itself was mapped by a large array ca. 6*10 (width/channel length) points.

To monitor the gowth kinetic exactly on the same samples (4 - 20 mM solutions of $CaCl_2$ and Na_2CO_3) we measured each sample under stopped flow and under microfluidic conditions. Figure 1 show exemplary some typical scattering patterns. After literature mixing of 9 mM solutions in stopped flow devices leads to the formation of highly monodisperse nanospheres growing to a final radius of about 200 nm in ca. 5 min. Indeed, under stopped flow conditions we found a rapid formation of primary, spherical and monodisperse $CaCO_3$ particles. No oscillations occurred in the scattering intensities using microfluidic focusing. Independent of the position in the chip a q^{-4} power law was observed, indicating the formation of very polydisperse spherical and huge particles. The corresponding 2D SAXS data showed a lot of streaks, indicating the presence of microcrystallites, mainly nucleating on the chip wall and filling the whole setup. Note, that we obtained similar patterns for all microfluidic experiments, even when we started with very low concentrated reagents. It seems that the continuous flow of reacting solutions lead to the very fast formation of crystallites at the channel walls due to the continuous supply of new reactants and their strong concentration gradient. The small channel dimensions in combination with continuous flow promotes the quick formation of $CaCO_3$ microcrystallites. Hence, the kinetic results obtained from both methods using the standard designs lead NOT to the same results.

The results obtained during that beamtime are very important concerning the construction of new microfluidic designs. We tested microfluidic devices with a standard single plane “2D”-design, which base on hydrodynamic flow focusing. In this standard setup, wall contact is unavoidable. As a consequence, the

combination of no-slip flow close to the walls with a continuously flowing supply of reactants leads to the strong deposition of material ($CaCO_3$) on the channel walls.

As a result of the experimental results of this beamtime, we created enhanced microfluidic devices with a multilayered- or "3D"-geometry. These devices are based on X-ray compatible materials and any contact of the reaction products with the wall is avoided. The question if kinetic results from microfluidic devices with "3D"-geometries are compatible with stopped flow measurement results is still unanswered.

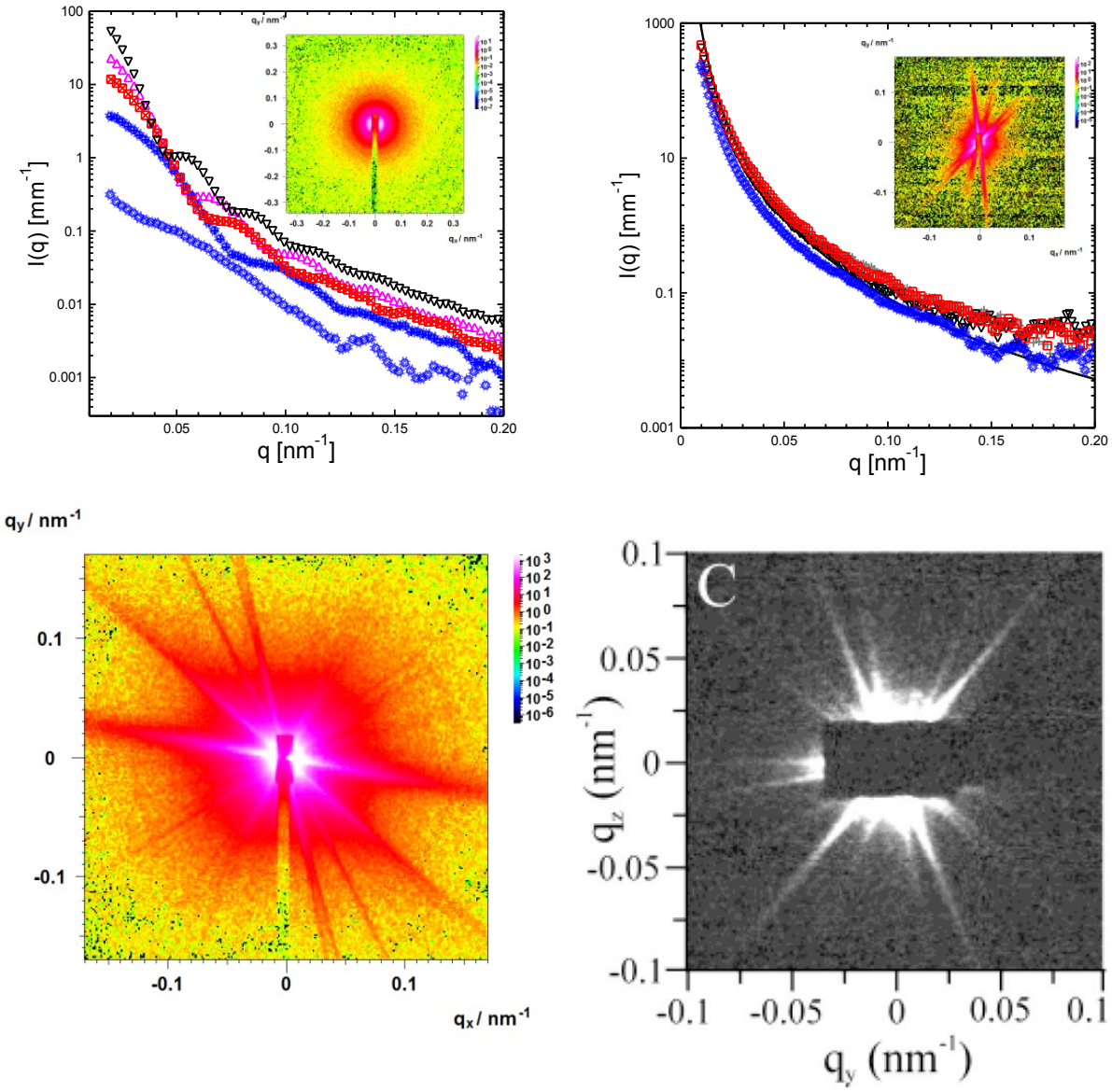

Fig.1 Time dependent scattering intensities obtained by studying the formation of primary $CaCO_3$ particles. Top: Typical intensities obtained by mixing 9mM $CaCl_2$ and Na_2CO_3 solutions in stopped flow device (left) and in the center flow of a microfluidic chip (right). The insets shows exemplarily 2D pattern, showing a spherical formfactor oszillation for one and a streaky pattern for the other method. Bottom: Left: 2D pattern obtained in the center region at the end of the microfluidic chip after mixing 9mM solutions. Right: SAXS pattern obtained 1h after mixing 50 mM reagent solutions (copy from lit. [2]). The authors reported that this pattern occurred to various crystalline modifications of calcium carbonate.

[1] J. Bolze, B. Peng, N. Dingenouts, P. Panine, T. Narayanan, M. Ballauff, Langmuir 18 (2002) 8364.
[2] D. Pontoni, J. Bolze, N. Dingenouts, T. Narayanan, M. Ballauff, J. Phys. Chem. B 107 (2003), 5133.