ESRF	**Experiment title:** Understanding $CaCO_3$ nucleation using reactors	**Experiment number**: CH-4155
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Report:

Aim of the experiment: In the experiment we aimed to quantify the nature and structure of $CaCO_3$ clusters confined in the 4-5 nm nano-droplets of water of water-in-oil microemulsions. This reaction is an analogue model system for biomineralization reactions e.g., coccolith frustules produced within the organic cell vesicles of coccolithophores. The process involved the reaction between two separate initially clear microemulsions, one containing solely Ca^{2+} and the other CO_3^{2-} ions dissolved in the water pools. Our extended preliminary studies by means of time-resolved and in situ small angle X-ray scattering and liquid-cell electron microscopy showed that upon mixing of the aforementioned microemulsions relatively large (Ø ~ 1 μm) particles developed (further referred to as "blobs"), which were amorphous. We hypothesized that internally those large particles were composed of small micelle cores (or other surfactant-based aggregates), containing supersaturated solution of $CaCO_3$ precursor, stabilised through confinement.

Practical arrangements: Our SAXS investigations made us realise that the direct characterisation of the "blobs" and drawing definitive conclusions about their **internal composition** was challenging, because of the **majority contribution** of water-micelles in the scattering data. We expected that this issue would also afffect the HEXD experiments. Essentially, independent of the $CaCO_3$ precipitation mechanism, water will constitute a majority phase forming micelles. Therefore, during the HEXD measuremnts we spent a considerable amount of time on various tests with sample preparation methods in which the actual volume fraction of "blobs" was increased through centrifugation.

<u>*Experimental details:*</u> *Generic synthesis of $CaCO_3$ in microemulsions:* The water-in-oil microemulsion system was based on 0.1M solution of NaAOT in isooctane, with molar water/surfactant ratio, W = 5, 10 and 15. Within this W-range water droplets were spherical with the water-pool diameter ranging from 3 to 5 nm and polydispersity of ca. 20%, as based on SAXS measurements. $CaCO_3$ precursor phase was obtained by mixing two distinct microemulsions: (1) containing Na_2CO_3 dissolved in the water pools, and (2) containing $CaCl_2$. The concentrations of salts dissolved in the water-pools were 0.10M, 0.15M and 0.20M and the reaction took place after mixing of equimolar systems (1) and (2) leading to the formation of white colloidal particles ("blobs") within 1-4 hours depending on conditions. In the next step, the microemulsions containing the white colloids were centrifuged at 14000 RPM in order to separate the colloidal phase from the remaining microemulsion, after which the 98% of the supernatant was removed, hence yielding presuming primarily $CaCO_3$-containg species. Various centrifugation times were used to evaluate the influence of centrifugation onto the stability and the expected volume fractions of the "blobs" (5 min – 120 min).

Measurement conditions: The as-prepared samples were transferred to 1 mm Kapton capillaries, from which the diffraction was measured. The HEXD were performed at the wavelength of 0.14383 Å, which allowed to collect scattering in the Q-range of up to ~25 $Å^{-1}$. 2D diffractions/scattering patterns were collected using MARCCD165 detector (pixel size 150x150 μm) in Debye-Scherrer geometry according to ID15B guidelines. The sample-to-detector distance was 234.4 mm and was calibrated using CeO_2 standard in 1 mm Kapton capillary. Due to the expected relatively low signal-to-background from the measured samples, we used long counting times (up to 200 s, typically 100 s) and collected multiple frames (up to 300 per sample, typically 20), which were later averaged together. The detector dark-current image was measured every 5-10 frames. Dark current was corrected for automatically by the acquisition software. Furthermore, various background and reference samples were measured under similar conditions, and included among others, an empty Kapton capillary and a capillary containing pure isooctane. The as obtained 2D images were further processed to 1D curves using Fit2D. The atomic pair distribution functions were obtained from the 1D curves using PDFgetX3 software package. The background and Compton scattering subtractions were also performed using the same software package.

<u>*Results:*</u> Figure 1 presents a PDF obtained from the pure-water microemulsion (i.e. without $CaCO_3$ as-synthesized, not centrifuged), a PDF from the aged and centrifuged $CaCO_3$-containing microemulsion and the finally a PDF of the isooctane phase with 0.1M AOT surfactant, but no water. In all three cases an empty Kapton capillary was used as a background. All three samples share certain characteristic distances primarily at 1.5 and 2.5 Å, which we attributed to the structure of isooctane. On the other hand, the PDFs from the microemulsion samples contain additionally characteristic distances at 0.55 and 2.2 Å, and exhibit a broad bump for $3 < r < 5$ Å. The aforementioned structural features can be attributed to the molecular structure of the constituent compound forming the microemulsion. However, as it can be observed, there is practically no difference between the presented PDFs of the microemulsions. despite ageing and centrifugation of the as forming colloidal phase. This may indicate two things. The signal from the as-grwoing $CaCO_3$ amorphous component is too weak in comparison with the components constituting the microemulsion. Indeed, the used concentration of dissolved ions amounts to at maximum 0.1M of $CaCO_3$ but in a volume of water (which is only < 2% of the total volume fraction). However in that case the

centrifugation should improve the signal-to-noise ratio from $CaCO_3$ if it actually forms. Therefore, the second explanation accounts for the fact that Ca^{2+} and CO_3^{2-} ions may remain dissolved within the structure of the microemulsion due to the confinement, and hence such a morphology would appear nearly identical (at the local scale probed by HEXD) to the one of the pure-water microemulsion. Further experimental evidence is required, however.

Publications resulting from work: Beamtime was in December 2014 and thus so far no publications are available.

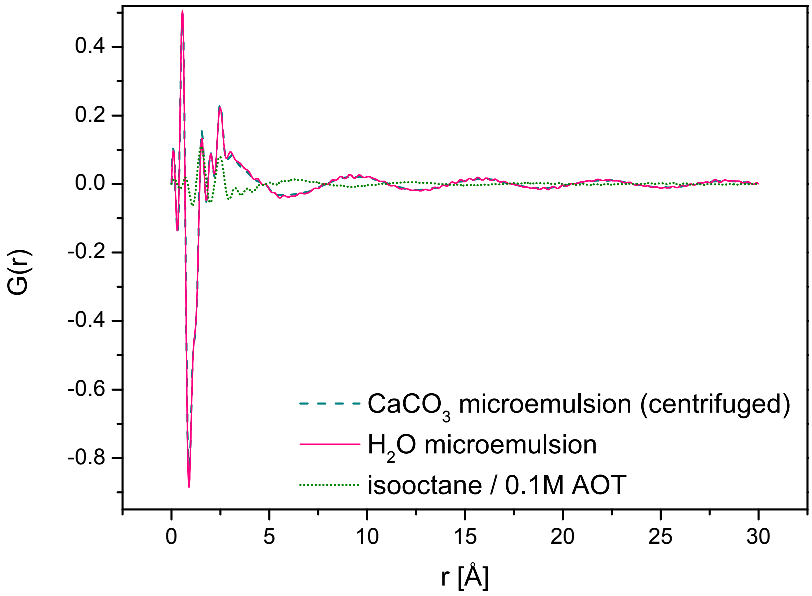

Figure 1. Selected PDFs from the microemulion samples.