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ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>*Ostwald ripening of vaterite microspheres revealed by CDI* | **Experiment number**:<br>**CH-4568** |
| **Beamline**:<br>ID10 | **Date of experiment**:<br>from: 28 Oct. to: 1 Nov. | **Date of report**:<br>16.02.16 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>Thomas Beuvier | *Received at ESRF:* |

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## Report:

**Abstract :** The complex architecture of biominerals arises from their interactions with macromolecules [1]. Yet, little is known about the role of these macromolecules in directing precipitation and recrystallization. Here, by using coherent X-ray diffraction imaging (CXDI) [2], we investigate the self-transformation of biomimetic $CaCO_3$ microparticles formed in a matrix of polystyrene sulphonate (PSS) and reveal in details how a solid sphere can evolve into a hollow sphere. This work helps to understand the role of macromolecules in the precipitation and recrystallization of calcium carbonate but also to clarify the formation of core/shell and hollow structures by a self-transformation. Because such morphologies are encountered in many systems, the observed mechanism of formation may be relevant to other chemical systems such as ZnS [3], $Co_3O_4$, $TiO_2$ [4] and $Ca_8H_2(PO_4)_6.5H_2O$ [5].

**Sample Preparation:** The samples are prepared by quickly mixing an aqueous solution containing calcium ions and PSS (polystyrene sulfonate) with an aqueous solution containing $Na_2CO_3$. The solution is stirred during 1 min and then put at 70°C for different reaction times (from 30 min to 3 days). Then the suspension is filtered and dried at 60°C. The powders are then put on the $Si_3N_4$ membranes.

**Methods:** The measurements were performed at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a monochromatic x-ray beam of energy 7 keV.

**Results:** We analyzed 10 samples having different reaction times (from 30min to 3 days). The main results are summarized in Fig. 1. In A, B and C are shown the SEM images, the CXDI results and the TEM images, respectively.

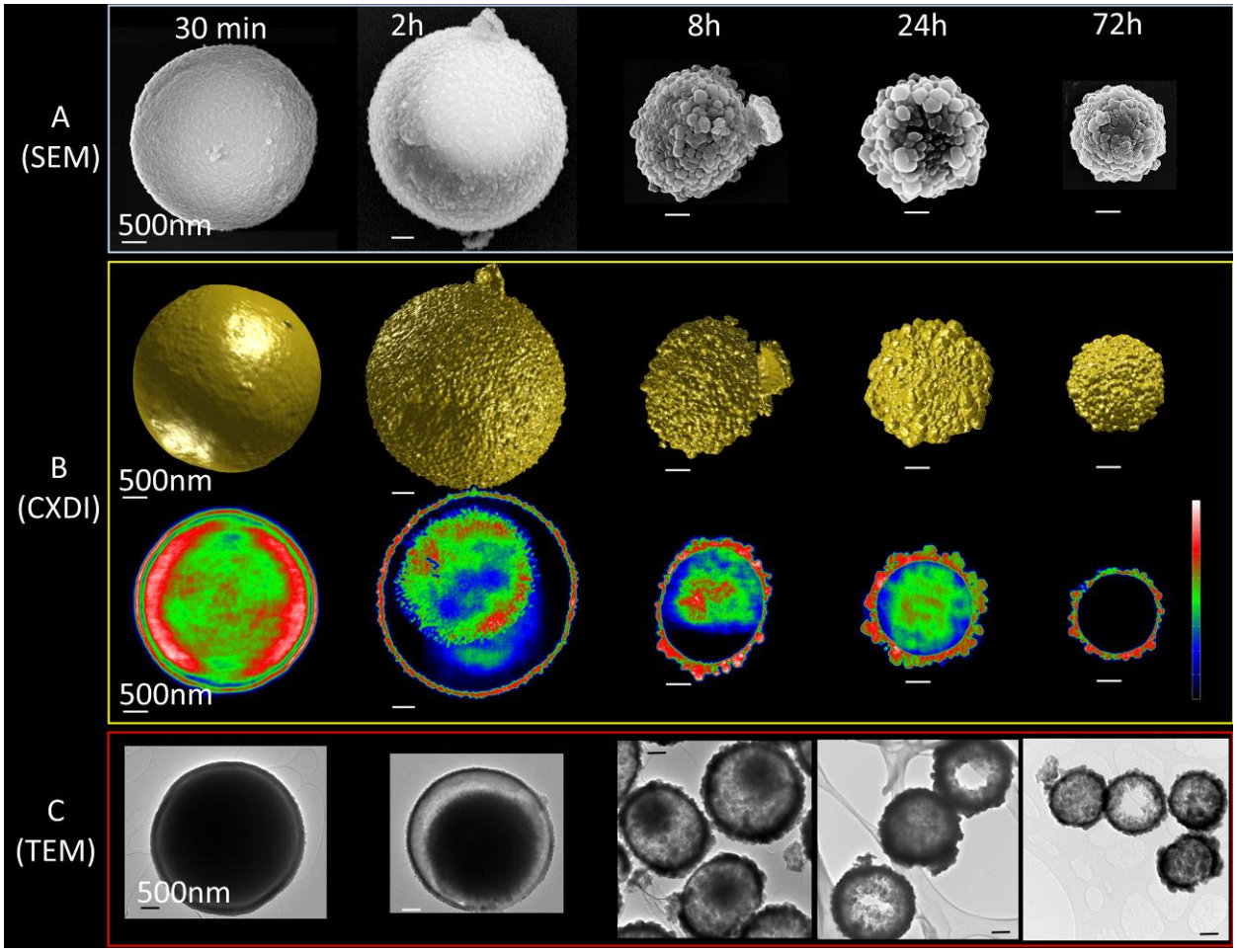


Figure 1 : Microspheres of $CaCO_3$ obained after different reaction times. (A) SEM images, (B) CXDI images with 3D views (upper part) and tomography slices (bottom) and (C) TEM images. Scale bar = 500nm

The good agreement between SEM and CXDI 3D views obtained on the same particles validate the CXDI reconstructions. We observed 2 important points from the 3D views. First, the crystals of vaterite grow on the surface of the microspheres. This may be due to the Ostwald ripening process for which small particles shrink, while larger particles grow. Secondly, we observed that the diameter of the microspheres decreases with time. This evolution is confirmed by SAXS done on ID02 (Fig.2).

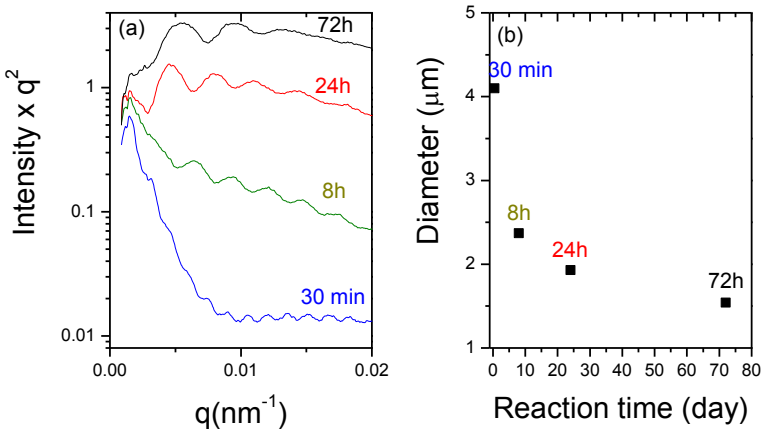


Figure 2 : (a) SAXS curves ($I*q^2$) obtained on ID02. In these experiments, the powders were put in glass capillaries. From the oscillations, we can extract the average diameters of the particles as shown in (b).

**Conclusion:** CXDI is particularly relevant to study such particles and to understand the growth mechanisms of vaterite. We highlight that the hollow particles result from a core-shell intermediate. In addition, the shell of the hollow and of the core-shell structures is interesting. The shell is made of 2 parts : a smooth inner part which acts as a template for the outward growth of vaterite crystals. This information is important not only in materials engineering but also to understand the growth of biogenic $CaCO_3$ for which the presence of soluble/insoluble membranes/templates is a key step in the design of the complex morphology.

**References**

[1] – F. C. Meldrum and H. Cölfen, Chem. Rev. **108**, 4332 (2008).
[2] - J. Miao et al, Science **348**, 530 (2015).
[3] – B. Liu, H. C. Zeng, Small **5**, 566 (2005)
[4] – H. G. Yang, J. Phys. Chem. B **108**, 3492 (2004)
[5] – A. Bigi et al, Ang. Chemie Int. Ed. 41, 2163 (2002)