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| | Experiment title: X-ray fluorescence microscopy on hybrid CaCO ₃ microspheres | Experiment number: CH-4916 |
| Beamline: ID16A-NI | Date of experiment: from: 02 nov2016 to: 08 nov.2016 | Date of report: 24.02.17 |
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Report:

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. Recently, by using coherent X-ray diffraction imaging (CXDI) on ID10 [2], we have investigated the self-transformation of biomimetic CaCO₃ microspheres formed in a matrix of polystyrene sulphonate (PSS) and we checked the reconstructions by SEM and TEM analysis. One interesting result was the formation of a core-shell intermediate. The fact that the core dissolves with time reveals a higher solubility of the core compared to the shell. This can be explained either by a less crystallized state (nanoparticles are more soluble than bigger particles according to the Ostwald ripening process) or by a heterogeneities in the spatial concentration of PSS. **The objective of this work was to measure on ID16A the fluorescence spectrum of the microspheres to determine the local concentration of PSS and to know whether the concentration of PSS is higher in the core than in the shell.** This work should help 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], Co₃O₄, TiO₂ [4] and Ca₈H₂(PO₄)₆.5H₂O [5].

Results:

In this run we have tried to image a series of CaCO₃ core/shell microstructures containing PSS. As expected, we were able to evidence in 2D and 3D elemental analysis the presence of sulfure, and as a consequence the presence PSS in higher concentration at the center than in the shell (Fig. 1). Note that in 3D experiments, the voxel size was 65×65×65 nm³ which was enough to localize correctly the PSS.

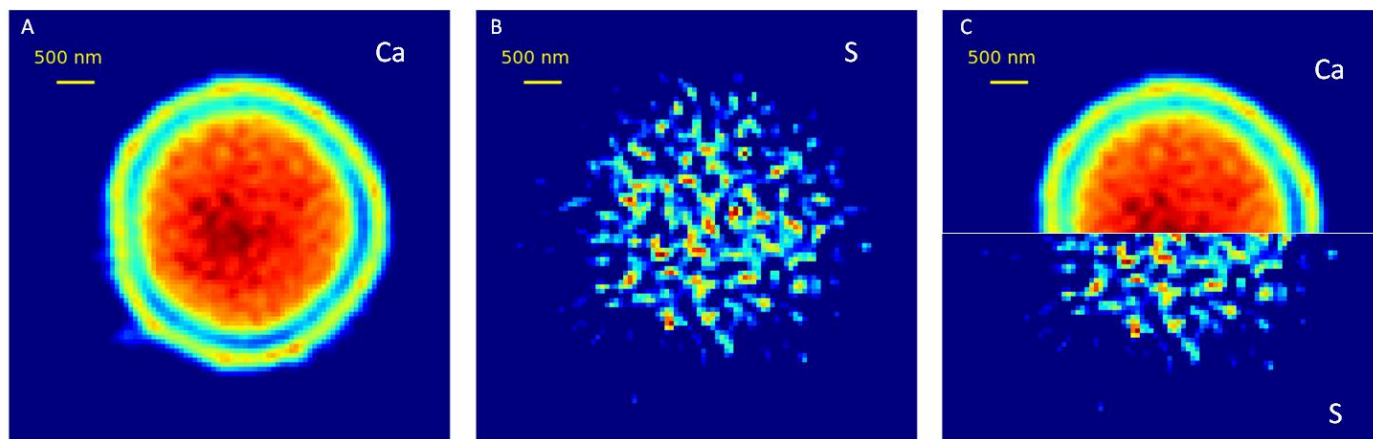


Figure 1 : 2D slices extracting from a 3D analysis of a CaCO₃ core/shell microparticle and showing the fluorescence of (A) calcium, (B) sulfure . In (C), we combine half of the two previous cartographies.

In addition, holomography was successfully done on the same microparticles to stress on the packing of the nanoparticles. Even though some important results were obtained, we encountered many problems during the 3D fluorescence measurements which should be mention here. First, the size of the nanobeam on the sample was measured to be close to 40×40 nm². With such flux and even by adding attenuators, we observed that as soon as the beam went through the sample, the core of the microparticle vibrated and broke the shell. We resolved this problem by metalizing the sample with a carbon coating of 5-10 nm thick. This is an important point concerning the preparation of the sample. They have to metallize the sample to evacuate the charges. Note that to do 3D elemental analysis, the samples of around 2-4 μm size were attached at the top of a silica tip of around 5-10μm size. Now, we have the experience of mounting such particles. Secondly, we observed also that during the 3D elemental analysis, the sample moves progressively during the rotation of the samples. This drift was not due to a bad alignment of the center of rotation but may be originate from thermal fluctuations. We basically lost one day due to this problem. Thirdly, one of the beryllium window brokes.

References

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