



	<b>Experiment title:</b> <b>Deciphering the ocean chemistry during Jurassic times from calcareous microalgae (180-160 Myrs)</b>	<b>Experiment number:</b> <b>EC-811</b>
<b>Beamline</b> ID22NI	<b>Date of experiment:</b> from:18 June to:23 June 2011	<b>Date of report:</b> 10.10.15
<b>Shifts:</b> 12	<b>Local contact(s):</b> R. Tucoulou Tachoueres	<i>Received at ESRF:</i>
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#### Report:

The aim of the project was to trace ancient ocean chemistry thanks to the coccoliths elemental composition. Coccoliths are calcite platelets produced by unicellular algae called coccolithophores which are abundant in modern oceans and present in the sedimentary record for more than 200 Ma. Coccoliths are about 5  $\mu\text{m}$  large and composed of several crystals of calcite (Fig. 1).



Fig. 1: Coccolith of the species *Watznaueria britannica* from the Jurassic (from Bown, 1998).

We designed a new picking method (Suchéras-Marx et al., in prep) to extract them from the sediment (Fig. 2). Basically, rock powder is deposited on a cover slide and observed under polarized microscope at x400 magnification. Once a coccolith is selected, it is picked with Si capillary thin down to  $\sim 10\text{-}15\ \mu\text{m}$  (Fig. 2A). The coccolith is then deposited on a  $\text{Si}_3\text{N}_4$  TEM membrane by detaching the coccolith in an ethanol microdrop. From 1 to 4 coccoliths were deposited per TEM membrane depending on sample and species characteristics. Finally, the TEM membrane is pictured under  $\lambda$  polarized microscope at x100 magnification (Fig. 2B). This procedure clearly reduced the sample research during the experiment to its minimum, maximizing time for analysis.

During the experiment, 20 coccoliths were analyzed from 3 species (*W. britannica*, *Discorhabdus striatus* and *Crepidolithus crassus*) with various resolution. Most of them were mapped with a 100 nm x 100 nm resolution at 17 keV incident excitation beam with 3 s integration time per pixel. Fourteen elements were identified and mapped in coccoliths calcite, namely Sr, Rb, Br, Zn, Cu, Fe, Mn, Cr, V, Ti, Ca, K, Cl, S (Fig. 3).

The first results on this experiment focus on the element maps and set up an interpretation scheme of coccolith element maps (Suchéras-Marx et al., accepted). We observed that the elements can be classified in 3 groups: i) element concentrations following crystalline organization (Fig. 4); ii) homogenous concentration of the elements and iii) elements concentrated on the border and in the central area cavity.

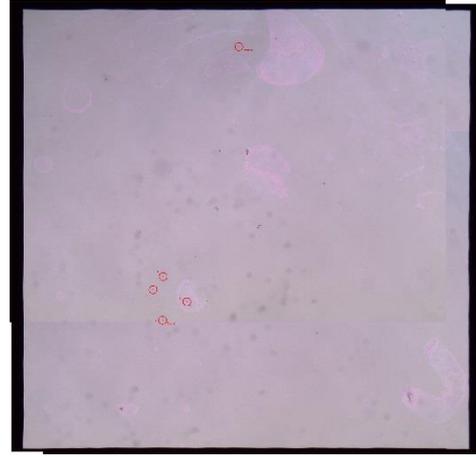


Fig. 2: A. Left, picking a coccolith with a Si capillary. B. Right, picture of a TEM mebrane after coccolith deposition. Red circles correspond to coccoliths.

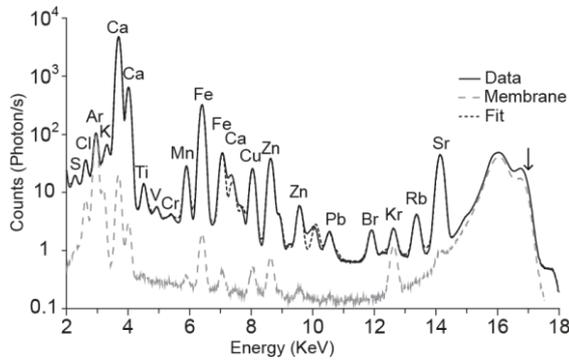


Fig. 3: XRF spectrum (cps) of a *W. britannica* with identified elements in the calcite.

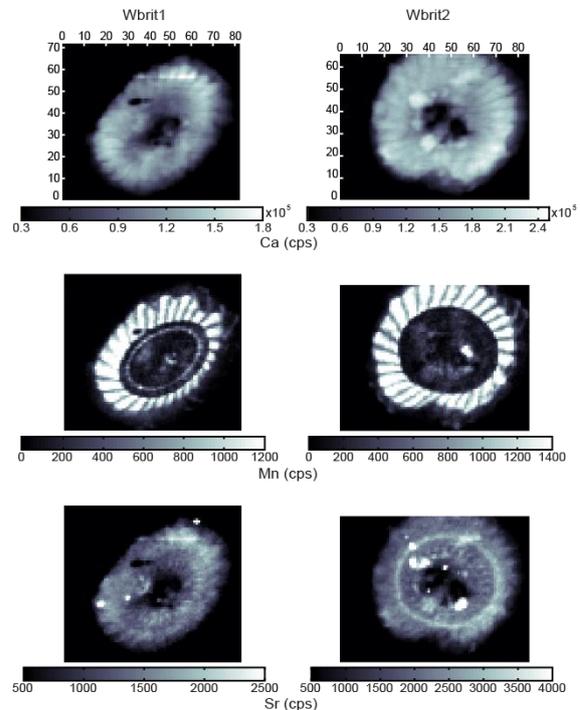
Within the first group of elements, Ca is base of coccolith crystallography defining the primary organization produced by the cell. Sr is quite similar to Ca by interchange between both elements. Conversely, Mn is more complex, its organization partially follows crystals organization. Further studies are needed to propose a clear scheme for Mn.

Fig. 4: Ca, Mn and Sr maps (cps) of a *W. britannica*.

The second group of elements is composed of S, Cl, and Br which are naturally in seawater in the form of anions. Those elements seem to be incorporated by passive diffusion in the coccolith during its formation. Cl is particularly interesting because it may be link to seawater salinity. This results need experiments on cultured specimen in a controlled environment to be confirmed.

Finally, the third group of elements (K, Ti, V, Cr, Cu, Zn, Rb) are related to clay contamination and calcite overgrowth during diagenesis.

We used our final shift to test 3D mapping. The resolution was 100 nm x 100 nm x 475 nm with only 200 ms integration time per voxel. This reconstruction helped to propose the interpretations presented above but still need improvements especially because the z axis of analysis has a low resolution and because the kapton holding the coccolith partly melted during the experiment.



## **Perspectives:**

This experiment worked perfectly thanks to a good sample preparation and set up at ID22NI. But there are still questions to be addressed and especially two of them retains our attentions

- The presence of Mn and its organization need further analysis to be understood. Mn may be related to secondary overgrowth of the calcite or, more interestingly, to photosynthesis; Mn being at the base of H<sup>+</sup> acquisition by H<sub>2</sub>O reduction for photosynthesis.
- The 3D produced need to be replicated on few other individuals with different crystalline organization. This is particularly critical for Sr and Cl because Sr/Ca is used as an environmental proxy by paleoceanographers and Cl/Ca may become one in the future. Different incorporation of Sr or Cl linked to crystal growth direction and shape could explain the disequilibrium in Sr and the discrepancy observed between modern species (Stoll and Ziveri, 2004).

## **References:**

- Bown, P.R., 1998. Calcareous nannofossil biostratigraphy. Chapman and Hall (Kluwer Academic Publishers), Dordrecht.
- Stoll, H.M., Ziveri, P., 2004. Coccolithophorid-based geochemical paleoproxies, in: Thierstein, H.R., Young, J.R. (Eds.), Coccolithophores: From molecular processes to global impact. Springer, Verlag, pp. 529-562.
- Suchéras-Marx, B., Giraud, F., Simionovici, A., Daniel, I., Tucoulou, R. Accepted. Prospects for new heterococcolith geochemical proxies from high resolution X-ray fluorescence mapping. *Geobiology*.
- Suchéras-Marx, B., Giraud, F., Lena, A., Simionovici, A., Daniel, I. In prep. Picking nannofossils: How and why? *Journal of Micropalaeontology*.