ESRF	**Experiment title:** **Formation and function of coccoliths by Manganese elemental mapping and XANES**	**Experiment number**: **ES-113**
Beamline ID21	**Date of experiment**: from: 15 November to: 19 November 2013	**Date of report**: 18.11.15
Shifts: 12	**Local contact(s)**: Camille Rivard	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

SUCHERAS-MARX Baptiste (UU), SIMIONOVICI Alexandre (ISTerre), GIRAUD Fabienne (ISTerre), DANIEL Isabelle (UCBL)

UU: Uppsala Universitat, Sweden; ISTerre : Université Grenoble Alpes, France; UCBL: Université Claude Bernard Lyon1, France

Report:

The aim of the project was to map Mn in coccolith and explain its organization in this algal calcite. 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 µm large and composed of several crystals of calcite (Fig. 1).

Fig. 1: Coccolith of the modern species Calcidiscus leptoporus *(from Nannotax3).*

We used the new picking method designed for EC-811 (Suchéras-Marx et al., in prep) to extract them from the sediment (Fig. 2). Coccolith picked were deposited between two thin ultralene films hold with a special sample holder designed for ID21 set up.

During the experiment, 12 coccoliths were analyzed from 8 modern and fossil species (*C. leptoporus*, *C. pelagicus*, *H. carteri*, *G. oceanica*, *W. barnesiae*, *D. striatus* and *D. araneus*) with various resolution. Most of them were mapped with a 400 nm x 400 nm resolution at 7.5 keV and 3.15 keV incident excitation beam with 3 s integration time per pixel. Twelve elements were identified and mapped in fossil coccoliths calcite, namely Na, Mg, Al, Ca, S, Cl, K, Ca, Ti, V, Cr, Mn and Fe and, among them, only 8 elements were found in modern coccoliths (Fig. 3).

The first phase of the experiment focused on mapping the chemical composition with an incident excitation beam at 7.5 keV of coccoliths allowing us to identify the zone with Mn and to compare the Mn repartition between fossil (Suchéras-Marx et al., accepted) and modern coccoliths. We observed that Mn is more concentrated in fossils than in modern coccoliths suggesting that Mn is rather linked to post-depositional processes of crystallization.

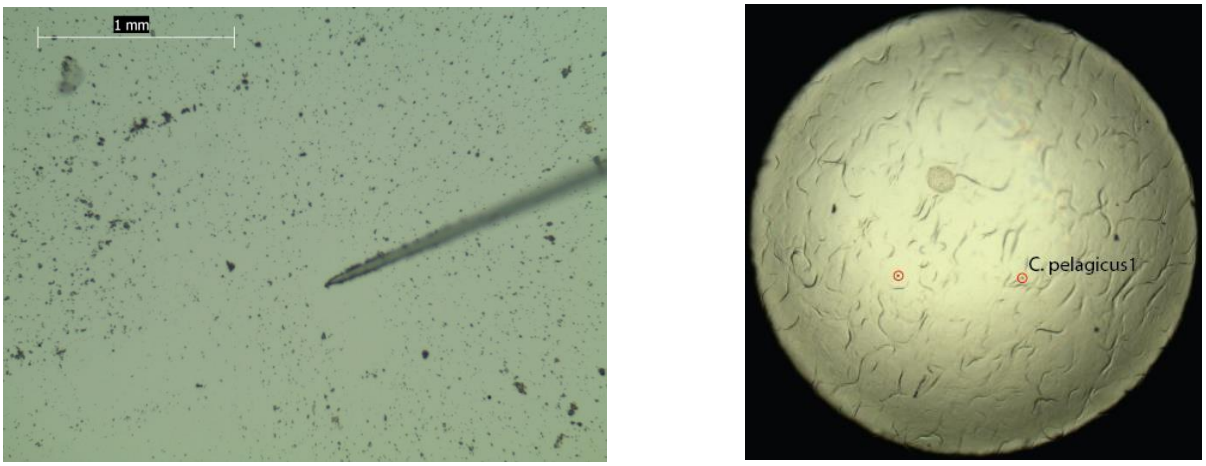

Fig. 2: A. Left, picking a coccolith with a Si capillary. B. Right, picture of the ultralene membrane after coccolith deposition. Red circles correspond to coccoliths.

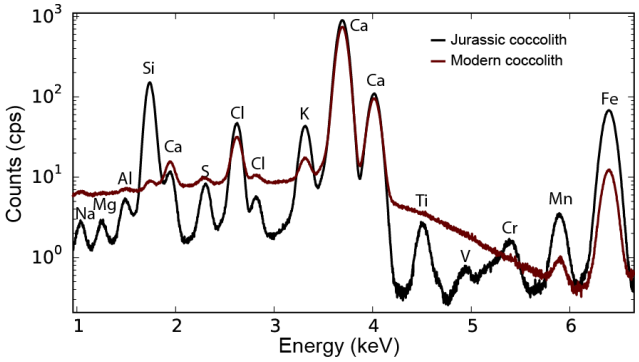

Fig. 3: XRF spectrum (cps) of a fossil and a modern coccolith *with identified elements in the calcite.*

In the coccolith parts with enough Mn we have performed XANES on Mn (Fig. 5). Three standards were analyzed and 3 coccoliths, 2 fossils and a modern. Based on the Mn XANES, the Mn in coccoliths is likely on the form of $MnCO_3$.

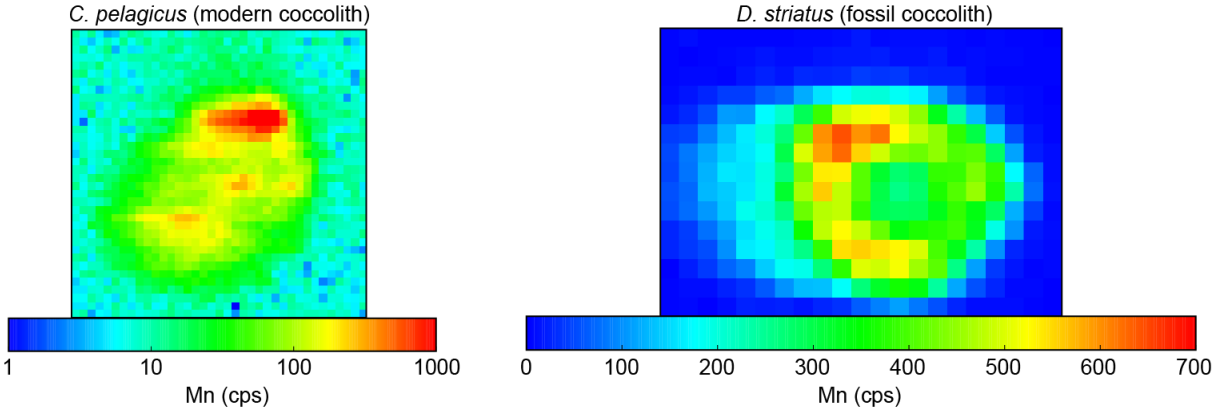

Fig. 4: Mn maps (cps) of a C. pelagicus and D. striatus.

The second phase of the experiment consisted on mapping 12 coccoliths aiming on Cl, Mg and Na at 3.15 keV. Those elements are of a primary interest in coccolith calcite because i) Mg is very low in comparison to most other marine calcite producers and ii) Na and Cl may be indicators of the seawater salinity (Suchéras-Marx et al., accepted; Wit et al., 2013).

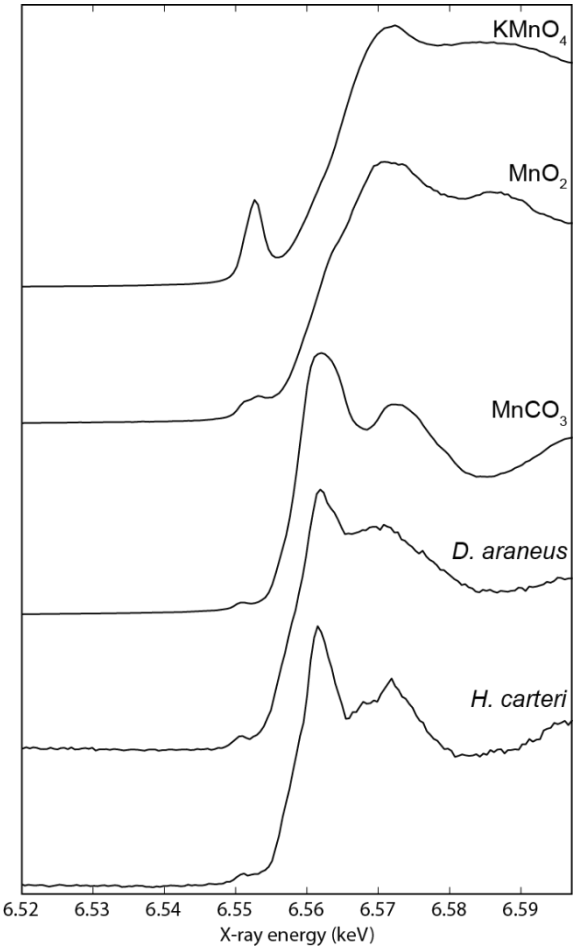

Fig. 5: Mn XANES spectra with $KMnO_4$, MnO_2 and $MnCO_3$ standards and D. araneus *and* H. carteri.

Conclusion and perspectives:

The experiment ES-113 perfectly worked at ID21. Unfortunately, there were less Mn in modern coccolith than supposed based on fossil results (EC-811) limiting the XANES analysis planned.

We conclude that Mn was likely present in coccolith in the form of $MnCO_3$ that results from secondary crystallization during the early diagenesis.

The new low energy maps opened to new perspectives on the potential development of salinity proxy on Cl and Na and highlight the scarcity of Mg in the coccolith calcite

References:

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