Coccolithophorid calcium carbonate dissolution in surface waters

J. Harlay[1], C. Koch[2], J.R. Young[2], N. Roevros[1], A.V. Borges[3], L.-S. Schiettecatte[3], C. van der Zee[1], S. Groom[4], L. Rebreanu[1], R. Godoi[5] & L. Chou[1]

[1]Université Libre de Bruxelles (ULB) - Océanographie Chimique et Géochimie des Eaux, Campus de la Plaine, Boulevard du Triomphe – B-1050 Brussels, B
[2]The Natural History Museum – Palaeontology Department, Cromwell Road, London SW7 5BD, UK
[3]Université de Liège (ULg) – Océanographie Chimique, Institut de Physique, Allée du 6 Août, 17 B5a) - B-4000 Liège 1, B
[4]Plymouth Marine Laboratory (PML)- Remote sensing Group, Prospect Place, The Hoe, Plymouth, UK
[5]University of Antwerp (UIA) – Micro and Trace Analysis Centre (MiTAC), Dept. of Chemistry, Universiteitsplein, 1,B-2610 Vilrijk-Antwerpen, B
Contact : jharlay@ulb.ac.be

In June 2004, a biogeochemical survey of a coccolithophore bloom in the Bay of Biscay was conducted onboard the *R.V. Belgica* in the framework of the Belgian Global Change Programme. This region is characterized by a steep continental slope that separates the open ocean from the wide continental shelf. Such a bathymetric feature induces vertical mixing that transports nutrient-rich deeper water to the photic zone, enhancing biological activity. Real-time remote sensing allowed us to pinpoint coccolithophore blooms located on the continental shelf and along the continental margin as shown by the high reflectance patches in Figure 1.

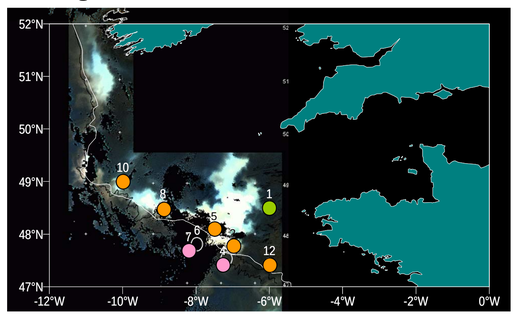

Figure 1: Reflectance satellite image on the 2nd of June. The white line indicates the isobath 200 m that separates oceanic waters from the continental shelf.

Biogeochemical context

The high reflectance patches spread along the 200 m isobath to the continental shelf. In June 2004, the coverage of the blooms extended from station 10 to station 12, representing respectively its north-western and south-eastern boundaries. Within the study area, surface waters were characterized by low nutrient levels ($[PO_4^{3-}]$ close to 0 μM at surface and [Si] < 2 μM). Sea-surface temperatures ranged between 13 and 15°C at the beginning of June, and reached 17°C at the end of the cruise (mid-June).
Chlorophyll-a (Chl-a) concentrations varied from 0.5 $\mu g\ .l^{-1}$ to 1.5 $\mu g\ .l^{-1}$. The production of $CaCO_3$ by coccolithophores led to a depletion in total alkalinity in surface waters (Figure 2). Nevertheless, the photic zone never became under-saturated with respect to calcite (Ω_{cal}>1).

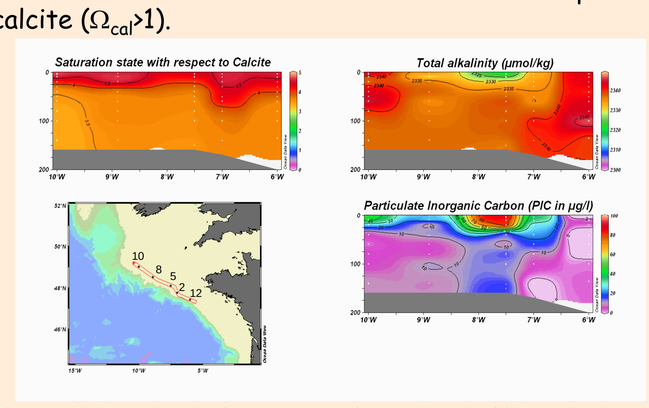

Figure 2: Longitudinal transect along the shelf-break showing Ω_{cal} (saturation state with respect to calcite), total alkalinity (in $\mu mol\ .kg_{sw}^{-1}$) and particulate inorganic carbon concentrations (in $\mu g\ .l^{-1}$).

Abundance of coccospheres and liths

SEM analysis of samples showed that the investigated area was dominated by the Prymnesiophyte *Emiliania huxleyi* (*E. huxleyi*), which could reach densities close to 10^7 cells $.l^{-1}$ (e.g. station 5, at 10m, Figure 3). The abundance of *E. huxleyi*, compared to other coccolithophores, was close to 65% at stations 10 and 8 and increased to more than 90% at stations 5, 2 and 7.

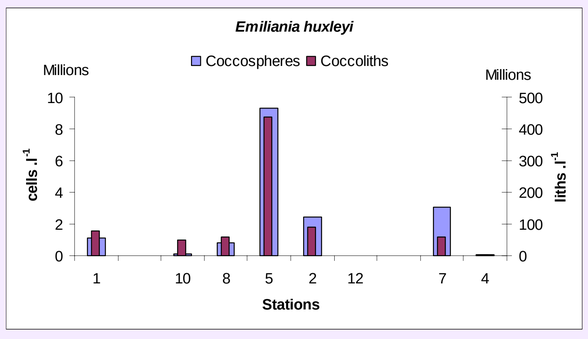

Figure 3: *E. huxleyi cells* (left Y-axis) and shed liths (right Y-axis) concentrations at 10 m depth for the continental plateau (station1), the shelf-break (Stations 10 to 12) and the slope (stations 7 and 4).

Primary production, calcification and bacterial density

Instantaneous daily rates integrated over the photic depth (based on ^{14}C incubations) ranged from 0.21 $gC.m^{-2}.d^{-1}$ and 0.68 $gC\ .m^{-2}\ .d^{-1}$ for net primary production and from 0.01 $gC\ .m^{-2}\ .d^{-1}$ to 0.14 $gC\ .m^{-2}\ .d^{-1}$ for calcification (Figure 4).

Bacterial density, measured by epifluorescence after DAPI staining, varied between 0.5x 10^6 cells $.ml^{-1}$ and 1.5x 10^6 cells $.ml^{-1}$ from surface to depth, during this survey. Relatively constant value of 0.5x 10^6 cells $.ml^{-1}$ was found below the Chl-a maximum. The higher density (> 3x 10^6 cells $.ml^{-1}$) was found in surface waters at station 5 (data not shown).

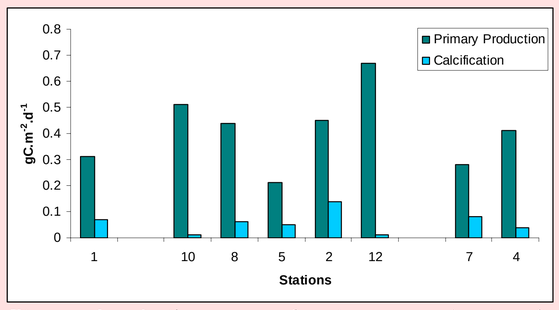

Figure 4: Daily rates of primary production (in green) and of calcification (in blue) integrated over the photic depth (in $gC.m^{-2}.d^{-1}$) for the continental plateau (station 1), the shelf-break (stations 10 to 12) and the slope (stations 7 and 4).

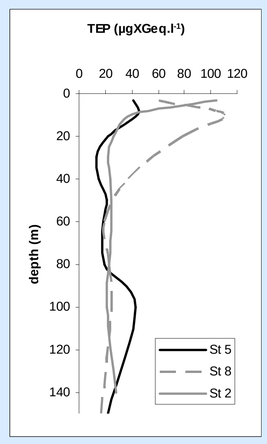

Figure 5: Vertical distribution of transparent exopolymer particles (TEP) within the high reflectance patch (stations 8, 5 and 2).

Transparent Exopolymer Particles (TEP)

TEP are formed from cellular releases during and after cellular growth. The aggregation of particles during the decay phase of a coccolithophore bloom (see poster of C. De Bodt *et al.*) is a mechanism that contributes to the export of particulate matter to depth and could lead to the formation of marine snow under certain conditions (Passow 2002b). The composition of the aggregates may be different if they come from cellular growth (labile) or bacterial growth (refractory) because bacterial polysaccharides are designed for sticking bacteria to their substrates (Azam *et al.*, 1999; Passow, 2002a).
TEP concentrations were measured colorimetrically (Passow & Alldredge 1995). The highest TEP concentrations were found in association with the highest Chl-a, at the top of the water column and could be attributed to phytoplankton. Variable concentrations (from 40 to >100 μg Xeq $.l^{-1}$) in surface waters were observed (Figure 5). TEP concentrations were lower at depth (±25 μg Xeq $.l^{-1}$) and appeared to be constrained by bacterial density.
In contrast to stations 8 and 2, station 5 displayed unexpectedly low TEP concentration in surface waters, which was associated with higher bacterial density and production (up to 25 $\mu gC.\ l^{-1}\ .d^{-1}$ in surface). This could be the result of the transformation of its labile fraction into a more refractory one and its export to depth. During this phase, the aggregation of particles, related to bacterial activity, may act as the microenvironments needed for biologically mediated dissolution of calcium carbonate above the chemical lysocline, according to Milliman *et al.* (1999).

SEM observation of $CaCO_3$ preservation

Various degrees of $CaCO_3$ preservation were observed by SEM in the cruise samples (Figures 6 and 7), but they globally appeared to be well preserved (good-4 stars- to excellent-5 stars). A contrario, bad preservation of coccoliths was encountered within the high reflectance patch, where 4 or 5 stars preservation index was rarely found in the top 40 meters of the water column. Such a low preservation may represent dissolution of $CaCO_3$ above the lysocline, as shown by Wollast & Chou (1998) in the same area.

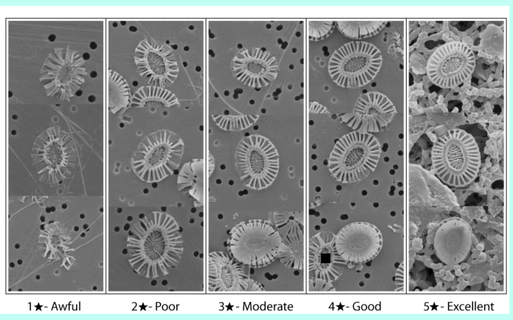

Figure 6: Index of coccolith preservation in samples based on morphological observations by SEM. Five stars correspond to intact coccoliths. Decreasing star numbers indicates a decrease in the preservation state of coccoliths.

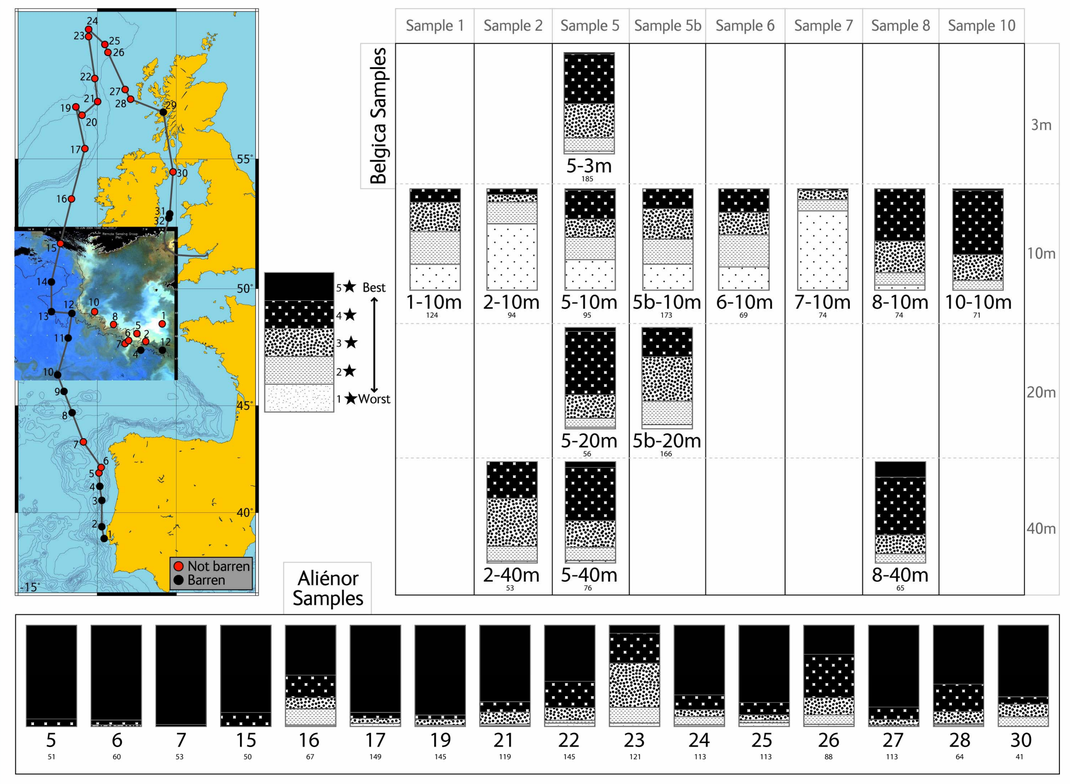

Figure 7: Diagram summarizing the degree of coccoliths preservation in seawater (see figure 6 for explanation of the preservation index). 'Aliénor Samples' refer to samples collected in surface waters during the Aliénor cruise (7th June to 17th June 2004). 'Belgica Samples' refer to samples collected at various depth (from 3m to 40m, sample number corresponds to station number) during the *Belgica* cruise 2004/13 (1st June to 17th June 2004). Small numbers below each sample indicate numbers of coccoliths graded.

CONCLUSIONS

In the light of these results, $CaCO_3$ dissolution may occur within coccolithophore blooms when nutrient limitation leads to the production of TEP. The continuum between the release of TEP precursors by coccolithophores and the export of particles to depth, through the formation and reworking of aggregates by bacteria (particularly from the Clade Roseobacter), is thought to constitute a mechanism through which coccolith preservation is altered. $CaCO_3$ dissolution contributes to the restoration of carbonate alkalinity and is a sink for dissolved CO_2 in seawater. Such a process in surface or intermediate waters counteracts the CO_2 fluxes of respiration and could act as a pump for atmospheric CO_2. It affects the exchange of CO_2 through the air-sea interface and the rain ratio of particulate matter to depth, and could thus play a potentially important role in the C cycle on the Global scale.

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