FINAL REPORT PROGRAM LEFE

Program LEFE-CYBER	proCOCA : calibration of proxies (pH and SSTs) in coccoliths	Years 2015 - 2017
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Context : Profound changes in marine ecosystems are already detected as a consequence of ocean acidification and warming at Anthropocene, but their effect on the biological carbon pump and pelagic calcification has not been evaluated yet. The coccolithophores are the most widely distributed calcite phytoplankton producers of the global ocean, whereas the geochemistry of the coccoliths has been relatively unexplored so far.

Objectives : The project aimed at developing new proxies of pH (B/Ca, and $\delta^{11}B$) and SST (Li/Mg) in coccoliths, and at jointly examining the effect of acidification on coccolithophores (growth, calcification, photosynthesis). Here, coccolithophores were considered as actor (changes in physiology) and witness (incorporation of proxies) of surface ocean changes to better assess recent-past and future evolution of their pelagic calcification under ocean acidification and warming.

Main results : A new analytical protocol has been developed, providing the first ever measurements of $\delta^{11}B$ in coccoliths (Delebecque *et al.,* in prep.). Naturally low- and high-calcifying strains of the most abundant coccolithophore, *E. huxleyi,* showed opposite trends for calcification under an acidification scenario simulated with elevated pCO_2 in culture experiments (Delebecque *et al.,* 2016). Calcification of the low-calcifying strains decreased in this scenario, as for $\delta^{11}B$ in their coccoliths like predicted by the thermodynamic equilibrium. This latter result suggested that there was no biological effect on the incorporation of B isotopes in calcite during biocalcification of these strains, and that $\delta^{11}B$ in their coccoliths can be used to estimate seawater pH (Delebecque *et al.,* in prep.). On the contrary, the increase of $\delta^{11}B$ in calcite of the high-calcifying strain at lower pH played against the thermodynamic equilibrium. In fact, this trend indicated an increase of pH in the internal vesicle where coccoliths are formed. Intra-vesicular pH regulation is favourable for the precipitation of calcite, which would explain why the calcification of this strain also increased despite the acidification of the water. In this case, $\delta^{11}B$ could thus reveal mechanisms of adaptation or resilience to acidification. Associated with these process studies, *in situ* relationships between the geochemistry of coccoliths buried in surface sediments (Figure 1) and sea surface pH and T were explored. A positive relationship was found between the B/Ca ratio of large sedimentary coccoliths (5-12 µm, mainly related to *C. leptoporus*) and the pH of surface waters (Figure 2), suggesting these biominerals could be used as an archive of surface acidification, similarly to the low-calcifying strains in cultures. Conversely, the relation was negative for those of small size (3-5 µm, essentially consisting of *E. huxleyi* and *G. oceanica*), as for the morphotype of *E. huxleyi* resilient to acidification (Boye *et al.,* in prep.). These works are an important step towards the calibration of B and its isotopes in coccoliths to reconstruct the pH of surface waters, and/or to explore biocalcification mechanisms that will help to better anticipate the evolution of the pelagic calcification in the High-CO_2 world.

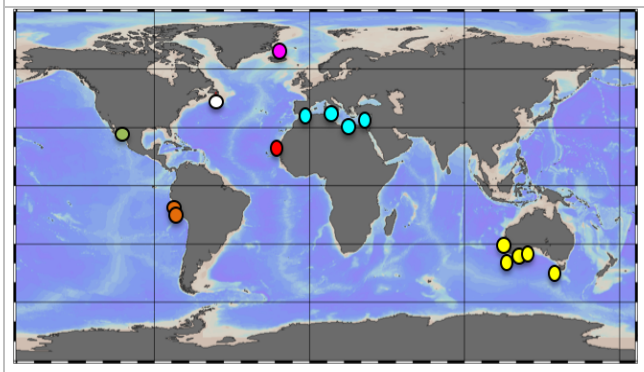

Figure 1: Location of the superficial sediments for extraction and

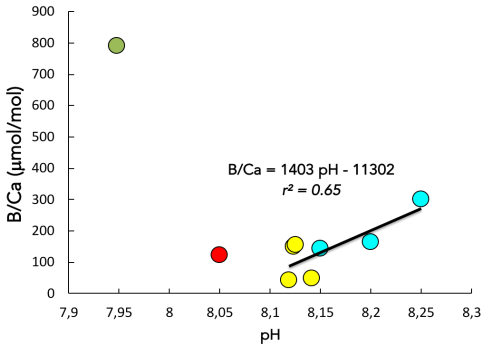

Figure 2: Variation of the B/Ca ratios in large size (5-12 µm) sedimentary

geochemistry of coccoliths.	coccoliths as a function of sea surface-pH (from GLODAP and SOCAT databases).

Future of the project : Ultimately, it is hope to use these calibrations and physiological studies to assess the anthropocene evolution of acidification, warming and pelagic calcification in key regions of the oceanic machine.

Publications, communications et thèses

- Delebecque, N., *et al.* (in prep.) $\delta^{11}B$ and B/Ca measurements in calcite of coccolithophore by MC-ICPMS and ICP-QMS. *Geochemistry, Geophysics, Geosystems (G^3).*
- Delebecque, N., M. Boye, D. De La Broise, E. Ponzevera, I. Probert, L. Beaufort, M.A. Sicre (2016) Investigating the change of pH in the internal vesicle of coccolith formation as a potential mechanism of adaptation of coccolithophores in the face of acidification. *4th International Symposium on the Ocean in a High-CO_2 World*, 3-6 May 2016, Hobart, Australia.
- Delebecque, N., M., Boye, I., Probert, J., Sutton, E., Ponzevera, G., Langer, M.A., Sicre (2017) The Possible future of coccolithophores in an acidifying ocean. *Goldschmidt 2017*, 13-18 August 2017, Paris, France.
- Delebecque, N. (2017) Etude de la biocalcification des coccolithophoridés dans un contexte d'acidification des océans. Calibrations de proxies (B/Ca et $\delta^{11}B$) du pH dans les coccolithes. *Thèse de Doctorat*, Université de Bretagne Occidentale, IUEM, Brest, 155 pp.
- Sabata i Vilardell, N. (2016) Géochimie élémentaire et isotopique des coccolithes sédimentaires : proxy du pH et de la T des eaux de surface ? *Master 2 thesis*, Université d'Aix-Marseille, Institut Pythéas, Océanographie Physique et Biogéochimie, Marseille.
- Melki, M. (2017) Réponses morphologiques des coccolithophoridés face à l'acidification des océans. *Master 1 thesis*, Mention Sciences de l'Univers, Environnement, Ecologie, Spécialité Océanographie et Environnements Marins, UPMC, Paris.