Project 16 (WP4): Towards a better proxy calibration for improved T°C and pH reconstructions in corals' paleoclimatic studies: Case study of the impact of seawater acidification on coral larvae and boring microflora.

Project lead: Delphine Dissard, Aline Tribollet
Post-doctoral researcher: Henry Wu
Project Start/End : June 2015 – November 2016 (extension May 2017)

Position offer: The laboratory of excellence L-IPSL of the Institut Pierre-Simon Laplace offers a 18-months post-doctoral position to work on seawater acidification on coral larvae and boring microflora.

Context: Global climate change and ocean acidification are one of the most pressing issues in Earth Sciences today. This is supported by the growing scientific evidence that changes in ocean chemistry due to anthropogenic input are already occurring and will continue in the next decades to centuries at a rate that will depend on future CO_2 emissions. Temperature and carbonate chemistry of the oceans are critical parameters that not only control chemical and physical processes, but also a wide range of biogeochemical processes that are important for the development and survival of marine biota such as corals, which are the main framebuilders of coral reef ecosystems. These organisms are highly threatened by global change and ocean acidification, as well as the associated eco-systemic resources (1/15 of the world population depends on these resources). Recent studies suggest that net reef dissolution will occur by 2100 as corals will calcify less and one of the main agents of carbonate dissolution, the microboring flora, will be stimulated. It is therefore crucial to better understand and quantify the impacts of the rapid decrease in pH and increase in T°C on living corals from the early stages of calcification and the role of boring microflora on coral dissolution in order to predict the fate of reef ecosystems.

Geochemical proxies preserved in the carbonate skeleton of marine calcifying organisms such as corals provide a unique tool to reconstruct changes in seawater environmental parameters since the beginning of the industrial era. Many parameters however might impair high-resolution time-series (decadal to centennial) like vital effects and environmental stressors, which can bias geochemical signatures in corals and therewith paleo-reconstructions. It is thus essential to identify the biogeochemical processes involved in the incorporation of trace elements and isotopic signatures at the early stage of the aragonitic skeleton formation in corals as well as possible diagenesis effects. For this purpose, interactions between corals, microborers, and their environment need to be better assessed to fully constrain the reliability of coral skeletons as natural archives for climatic signals and better understand the impact of ocean acidification on boring microflora, one of the main agents of coral reefs dissolution.

Description of workwork: Here, we propose to develop a mechanistic understanding of elemental and isotopic composition of coral skeleton - with special emphasis on Li/Mg, Sr/Ca and $\delta^{11}B$ - at different stages of coral life cycles (i.e., post-larvae, and adults), in stressed and impaired corals (e.g., coral grown under ambient *vs* pCO_2 predicted for 2100) and to study the effects of pH on microboring flora development in living corals. *In fine*, this project will intend to derive knowledge from these experiments in order to establish simultaneously a temperature and pH record, and microboring flora successions, of a coral core from the western equatorial Pacific Ocean covering the last 600 hundred years. This core will therefore allow studying pre-industrial (low atmospheric CO_2) and post-industrial (high atmospheric CO_2) environmental impacts on coral skeleton (growth rate, geochemistry, diagenesis) and associated boring microflora (species, abundance, rates of dissolution).

Supervision team: The work will be conducted under the main supervision of D. Dissard and A. Tribollet (UMR LOCEAN) and in close cooperation with researchers from LSCE (E. Douville

and D. Blamart). Other scientists from LOCEAN, LSCE and GEOPS laboratory will also be involved in this research project. The analyses will be undertaken at LOCEAN and LSCE. The candidate will share his
time between the two laboratories involved.

Results:

This Postdoctoral project is currently divided into individual subprojects to thoroughly address the overarching scientific questions. The subprojects are organized in terms of individual peer-review papers as deliverables.

<u>Subproject I</u>: Boron isotope and trace elements incorporation in the *Acropora millepora* coral larvae under ocean acidification and thermal stress.

Increasing anthropogenic CO_2 emissions have a double impact on coral reefs: ocean acidification (OA) and increasing sea surface temperature (SST). It is thus important to understand how reef-building corals during the early-life stage will respond to climate change pressures. For this subproject, *Acropora millepora* larvae were raised in different experimental conditions of pCO_2 (390 and 750 ppm) and temperature (27 and 29°C). The subsequent coral larvae skeletal materials were examined by laser ablation ICP-MS and MC-ICP-MS for trace elements (Sr/Ca, Li/Mg, B/Ca, U/Ca) and boron isotope ($\delta^{11}B$) incorporation. Our results indicate that prolonged exposure to higher water temperature and decreasing pH conditions severely impacted coral skeletal morphology resulting in translucent appearance and brittle skeleton. The larvae $\delta^{11}B$ results cannot wholly support the use of this proxy as an accurate indicator of pH – at the larval stage – with significant impact due to water temperature variability (Figure 1). The commonly used paleo-SST proxies of Sr/Ca and Li/Mg ratios were significantly impacted by changes in OA (Figure 2). Taken together, the geochemical results suggest increasing OA and SST warming under future climate change scenario will lead to pronounced significant impact on the accuracy and precision of many commonly used coral-based climate proxies. The manuscript of this subproject is in the final phase of completion and is in the process of coauthor commenting, which will then be ready for submission to the journal *Biogeosciences* in November 2016.

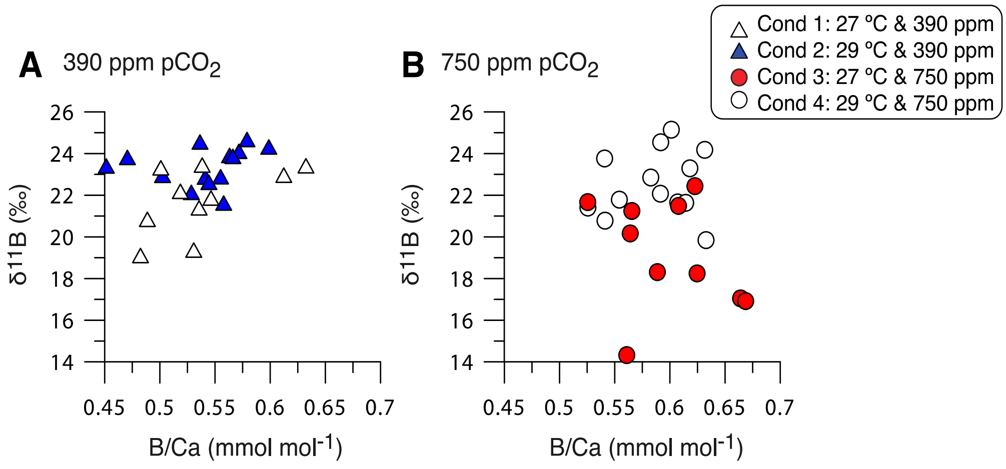

Figure 1. Significant impact of *Acropora millepora* larvae skeletal B/Ca and $\delta^{11}B$ results due to ocean acidification and decreasing seawater pH. (**A**) Coral cultured at 390 ppm with 27 ºC (condition 1, open triangles) and 29 ºC (condition 2, blue triangle). (**B**) Coral cultured at 750 ppm with 27 ºC (condition 3, red circle) and 29 ºC (condition 4, open circle).

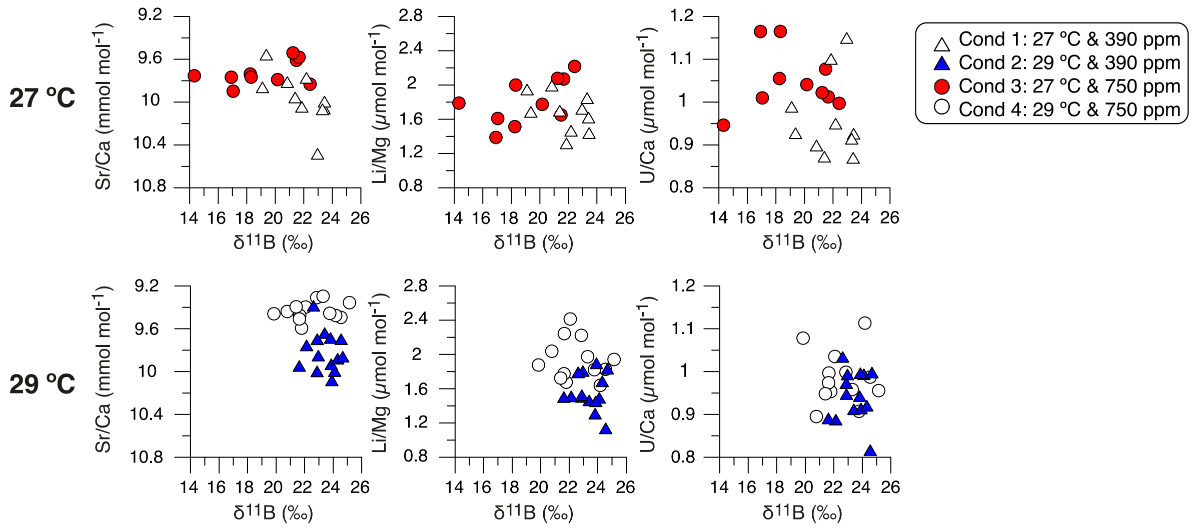

Figure 2. Significant impact on sea surface temperature proxies (Sr/Ca, Li/Mg, and U/Ca) in *Acropora millepora* larvae due to ocean acidification and decreasing pH. The plots are oriented starting at the top row with experimental conditions at 27 ºC for water temperature: Condition 1 (open triangles) and condition 3 (red circles). The bottom row plots are the experimental conditions at 29 ºC: Condition 2 (blue triangles) and 4 (open circles).

<u>Subproject II</u>: 320 years of sea surface pH and climate variability from South Pacific coral-based proxy records.

The aim of this subproject is to provide insight on the significant changes in South Pacific sea surface conditions (e.g. pH, SST, and others) over the past 320 years (1690-2010 CE) derived from a coral archive. To our knowledge, this is the very first continuous high-resolution record of δ^{11}B-based pH variability of over 300 years from our world's oceans. The climate proxy reconstruction records from this long-living *Diploastrea heliopora* coral will allow us to decipher past oceanographic changes in the South Pacific relative to modern-day conditions especially in light of our increasing atmospheric CO_2 concentration. Our coral displays an uninterrupted growth pattern over the last 320 years and has experienced three time intervals of interest such as the termination of the Maunder Minimum (ca. 1690-1715 CE), the beginning of the Industrial Revolution (ca. 1760-1830/1840 CE), and the modern instrumental/industrial era (1900 CE to present). The aragonite skeletal materials of the coral were analyzed at annual resolution for δ^{11}B, trace elements (Sr/Ca and Li/Mg), and stable isotopes (δ^{13}C and δ^{18}O) as recorders of sea surface pH, SST, δ^{18}O of seawater (or sea surface salinity), and atmospheric CO_2 changes. The most striking feature of our coral-based proxy reconstruction is the evidence of OA impact (decrease in sea surface pH) based on the depleting δ^{11}B ratio in the most recent part of the record. This long-term decrease in reconstructed pH appears to initiate ca. 1834-1835 in coherence with our coral-based Li/Mg-SST proxy revealing a significant warming trend (Figure 3). The long-term trend in the depletion of the coral δ^{13}C ratio with the same timing of onset is driven by the same increase in anthropogenic CO_2, termed the Suess Effect (Figure 4). Moreover, the coral-based proxy records indicate significant interannual to decadal-interdecadal variability in the South Pacific in terms of both SST and pH. Interestingly, the longer-term lower frequency variability of our proxy records indicate a tightly coupled anti-phase relationship between pH and SST with periods of higher SST and lower pH possibly reflecting a similar climatic driver. Post-analytical data analysis of this subproject is currently underway and the manuscript is in preparation. We expect the manuscript to be ready for submission to a high-impact journal in January/February 2017.

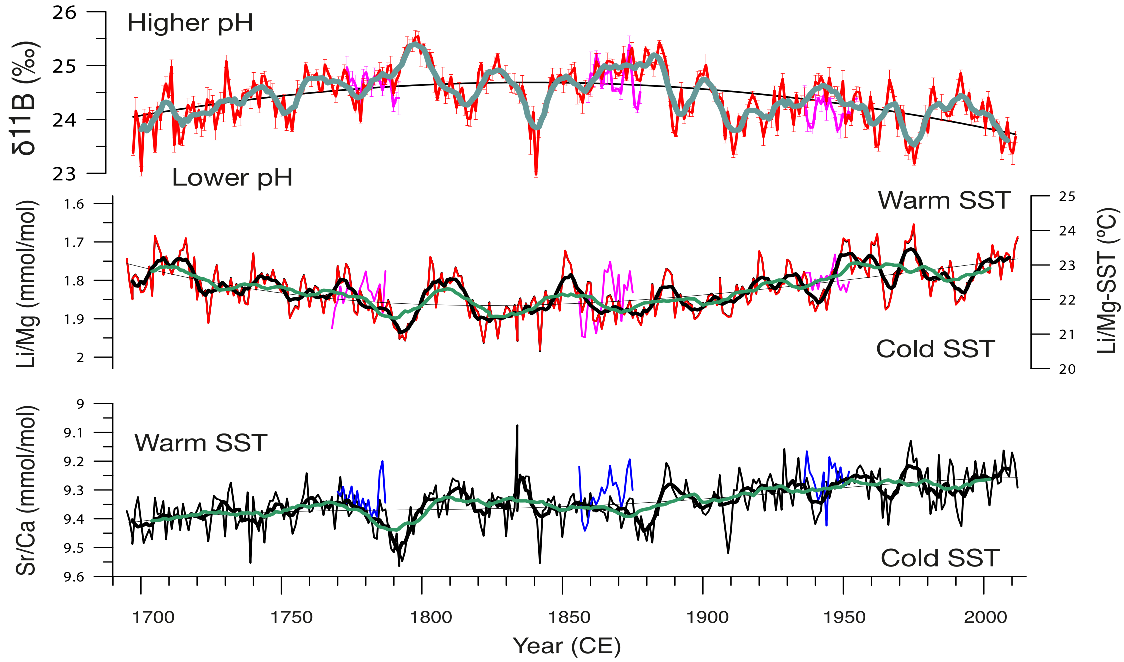

Figure 3. Annual resolution *Diploastrea heliopora* coral $\delta^{11}B$ ratio (**top**) indicating changes in paleo-pH from 1690-2010 CE shown with longer-term lower frequency variability. The trace element ratios of Li/Mg (**middle**) and Sr/Ca (**bottom**) indicating significant periods of cooling and warming in the South Pacific likely related to the interannual (El Niño Southern Oscillation) and decadal-interdecadal (Pacific Decadal Oscillation) variabilities. High inter-colony reproducibility of the climate signal are shown in magenta.

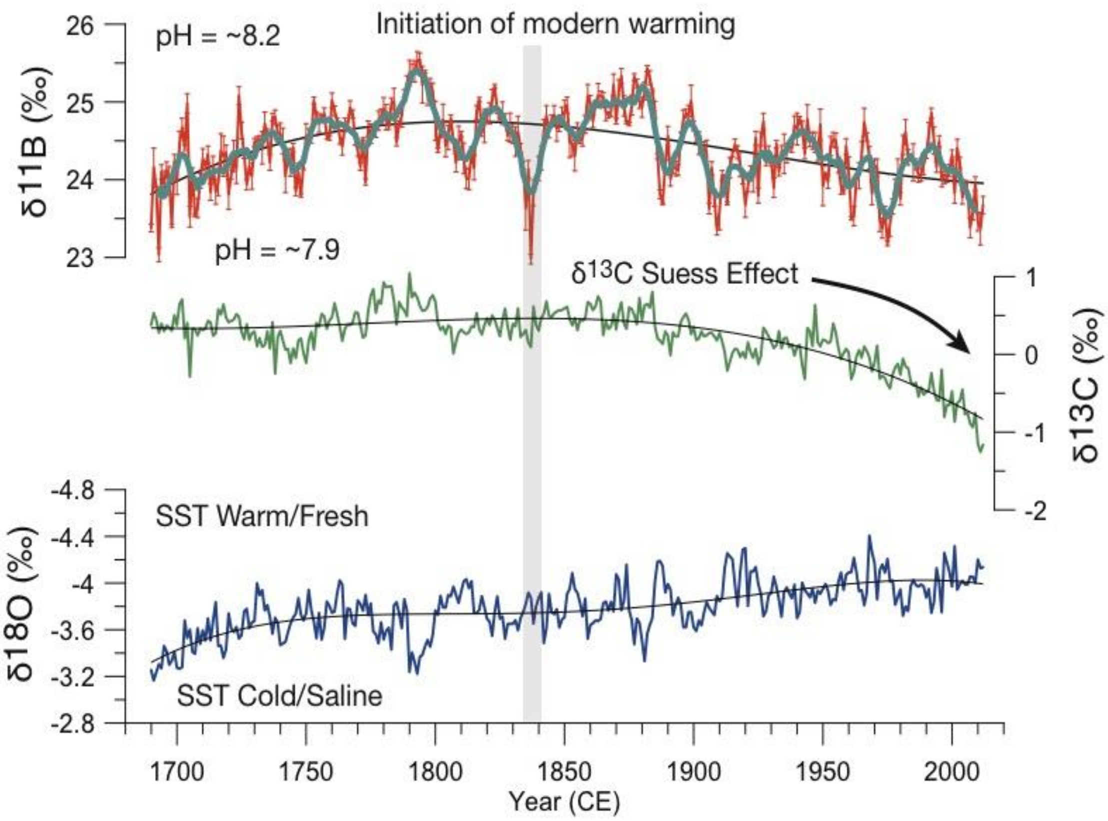

Figure 4. *Diploastrea heliopora* coral $\delta^{11}B$ results (same as Figure 3) indicating changes in paleo-pH from 1690-2010 CE (**top**). The rapid depletion of the $\delta^{13}C$ ratio (**middle**) in the recent part of the record indicates the increase in anthropogenic CO_2 taken up by the ocean. The initial warming (or freshening) signal of the South Pacific is indicated by the depleting $\delta^{18}O$ ratio (**bottom**) at the termination of the Maunder Minimum (1690-1750 CE) followed by the initiation of modern warming (~1834-1835 CE) of the industrial era warming.

<u>Subproject III</u>: Microborers of a New Caledonian massive coral colony and its relationship to environmental stress and pathology of coral biomineralization processes.

Microboring organisms are one of the main agents of carbonate dissolution in coral reef systems. Studies have recently documented the effect of ocean acidification on microborers colonizing dead coral skeletons under controlled and natural conditions. To confirm the trends obtained in previous studies in living corals and to better predict the fate of coral reefs by the end of the century, it is crucial to study *in situ* and over long periods of time, the effects of ocean acidification (combined to other factors such as global warming) on microborers. Using decalcified Scanning Electron Microscope (SEM) thin-sections, we will first study the microborers of a New Caledonian *D. heliopora* coral in terms of species, assemblages and galleries abundance and distribution. Preliminary results indicate the possible presence of multiple species of euendoliths (microborers) including *Ostreobium* sp., and fungi (Figure 5). Fungal hyphae were most probably interacting with coral tissues (parasitism/disease?) as calcified cones of defense were observed in several areas in the coral core. The abundance of the galleries and their distribution along the coral core can provide possible information on past bleaching or El Niño events as during thermal stress periods, coral growth slows down allowing microborers, especially phototrophic ones to bloom. To this end, the coral core is currently being systematically resampled for SEM thin-sections based on the parallel geochemical climate proxies from Subproject II. The prominent periods of high or low relative pH (SST) will aid in the identification of the effects on these micro-organisms. Due to pH decreases and rising temperatures, coral growth impairment may allow microborer filaments to bloom into the coral skeleton and potentially dissolve more calcium carbonate. Our approach will allow for a better understanding of the relationship between microborers and the coral holobiont, the impact of microborers on coral skeleton formation, and their relationship with environmental conditions. After completion of all analyzes, a manuscript will be prepared and submitted by the end of the project.

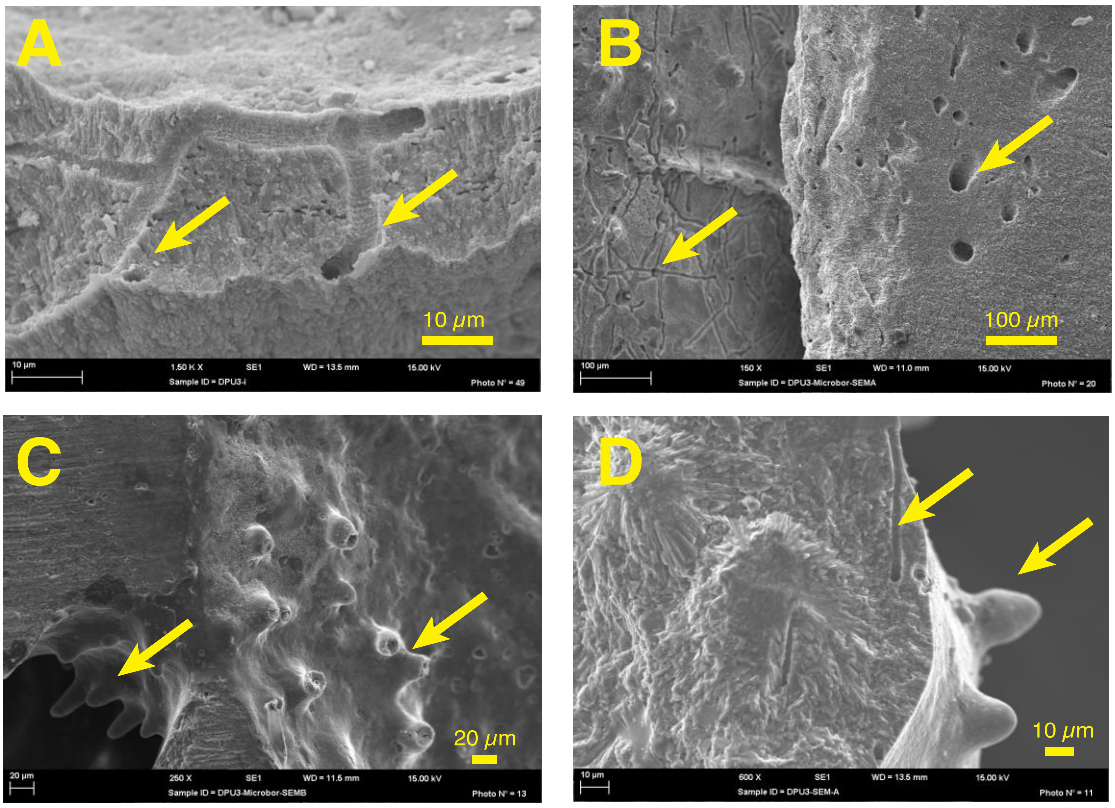

Figure 5. (**A and B**) Arrows indicate the presence of euendolithic microborer galleriess in a variety of shapes and sizes within the skeletal materials of *Diploastrea heliopora* coral. (**C and D**) Arrows indicate possible fungal attack on living coral and subsequent defense mechanism of coral depositing calcium carbonate nodulescones.

<u>Subproject IV:</u> South Pacific *Diploastrea heliopora* coral boron isotopes and trace elements systematics from high-resolution laser ablation MC-ICP-MS analyses.

This subproject will be completed at LSCE from December 2016 to January 2017 on the laser ablation coupled to the Quad-ICP-MS for trace elements and on the Multi-Collector ICP-MS for $\delta^{11}B$ ratios. Preliminary results indicate the ability of the *Diploastrea heliopora* coral to record highly detailed sub-seasonal changes of sea surface variability in its aragonite skeleton. We have observed sinusoidal patterns in some trace element ratios (e.g. Sr/Ca), which is directly related to the annual sea surface temperature cycle. Replicated and overlapping laser sampling profiles within different skeletal materials will enable us to distinguish the climate signal from the noise as well as test the reproducibility across distinct coral skeletal materials. These results will be the basis for our intra-colony reproducibility evaluation and provide a baseline for species-specific climate proxy calibrations from New Caledonia.

<u>Integration Project</u>: New coral-based calcium carbonate inter-laboratory calibration standard.

A new inter-laboratory calcium carbonate calibration standard is being produced from a previously collected *Porites* coral. This new standard will allow for trace elements, classical and other stable isotopes, and many other possibilities in both solution and laser ablation methods for the benefit of the geochemical community in Paris and Ile de France region (LSCE, LOCEAN-IRD, GEOPS). The coral sample is currently being pulverized to <100 µm in grain size and will be homogenized and distributed to the respective laboratories for analysis in February/March 2017.