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# High-resolution climatic reconstruction in the tropical Pacific based on biocarbonate archives

Claire E. Lazareth

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# MÉMOIRE D'HABILITATION À DIRIGER DES RECHERCHES

UNIVERSITE PIERRE ET MARIE CURIE

École doctorale des Sciences de la Terre et de l'Univers

## High-resolution climatic reconstruction in the tropical Pacific based on biocarbonate archives



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## RÉSUMÉ

Dans le contexte actuel du changement climatique et la nécessité de fournir des prédictions du climat futur aussi précises que possible, il est primordial de connaître au mieux notre système climatique. L'Océan Pacifique est un compartiment important de ce système, lieu d'interactions océan-atmosphère fortes et où naît l'Oscillation australe El Niño (ENSO), dont les impacts sont catastrophiques pour l'environnement et les populations. Nos connaissances de ce phénomène sont basées en partie sur des observations, qui restent cependant limitées dans le temps. Pour pallier le manque de données et mieux comprendre la variabilité naturelle du climat, des données supplémentaires sont acquises pour des périodes passées à partir de différentes archives. Comme les occurrences ENSO sont liées à la variabilité saisonnière et durent quelques mois, il est nécessaire d'obtenir des données de l'environnement à haute résolution temporelle.

Dans ce manuscrit je montrerai comment j'ai tenté de développer, puis d'appliquer, différents traceurs présents au sein d'archives biocarbonatés (mollusques et coraux) pour obtenir des données de la température de surface de l'eau (SST) et de la balance précipitation/évaporation à une échelle mensuelle à infra-mensuelle. Je montrerai que les diminutions de croissance des coquilles du bivalve *Protothaca thaca* (Pacifique Est) indiquent des occurrences d'événements El Niño. Dans l'ouest du Pacifique, les variations d'épaisseur des incréments journaliers des coquilles de *Tridacna maxima* et *Hippopus hippopus* (Tridacnidae) sont liées aux changements de SST mais dépendent également de l'état physiologique des animaux. Alors que certains traceurs géochimiques (Sr/Ca,  $\delta^{18}\text{O}$ ) au sein du squelette de *Porites* sp. peuvent être utilisés avec une certaine confiance, ce n'est pas toujours le cas pour les coquilles de mollusques. Je montrerai que l'utilisation du rapport Mg/Ca comme traceur de la SST dépend de l'espèce considérée et que la physiologie et la diagenèse très précoce sont un obstacle à l'utilisation de ce proxy. Au sein de *T. maxima* and *H. hippopus*, le  $\delta^{18}\text{O}$  peut être utilisé comme traceur des variations de SST et de la balance précipitation/évaporation. Pour reconstruire les variations passées de ces paramètres, des archives fossiles sont utilisées. Je montrerai comment différents types de diagenèse impactent la microstructure, la géochimie, et les paramètres environnementaux reconstruits. Je proposerai également des hypothèses concernant les processus diagénetiques eux-mêmes. A partir d'archives datant de l'Holocène moyen, je montrerai que la remontée des SSTs, après la dernière époque glaciaire, était terminée à partir de 6.5-6 ka BP dans le Sud-ouest Pacifique, que l'influence de la zone de convergence du Pacifique Sud était très probablement réduite, la circulation de Hadley plus importante, et la variabilité ENSO réduite. Les travaux faits à partir de Tridacnidae de sites Lapita (3 ka BP) confirment que la migration Lapita a été favorisée par une augmentation de la variabilité climatique.

Le dernier chapitre est consacré aux futures directions que j'aimerais donner à mes travaux de recherches qui incluent entre autres de i/ mieux comprendre les processus d'incorporation des proxies au sein des coquilles de mollusques et ii/ tenter de proposer des solutions pour une gestion durable des écosystèmes tropicaux en utilisant les archives biocarbonatés comme enregistreurs de l'environnement et de ses perturbations.



## ABSTRACT

In the current context of global change and the associated need to provide forecasts on the future evolution of the climate as precise as possible, it is crucial to have a deep understanding of the earth climate system. Pacific Ocean is an important compartment of this system. It is the place of strong ocean-atmosphere interactions and the birthplace of the El Niño Southern Oscillation (ENSO), the impacts of which are catastrophic for the environments and the populations. The current knowledge on ENSO partly relies on observations which are however limited in time. To increase this dataset and understand the natural climate variability, additional data are acquired for past periods, based on various type of archives. Because ENSO occurrences are connected with the seasonal variability and last several months, high temporal resolution information, are necessary.

In this manuscript I shall describe how I tried to develop, and to apply, environmental proxies from biocarbonate archives in the tropical Pacific Ocean to reconstruct the monthly or infra-monthly variability of the sea surface temperatures (SSTs) and the evaporation/precipitation balance. To do that, I focused my works on the mollusk shells and *Porites* sp coral skeleton. These archives contain various tracers (growth and geochemical variations) of the sought environmental variables. I will show that the thicknesses of growth decreases of the *Protothaca thaca* bivalve shells (East Pacific) indicate occurrences of El Nino events. In the Western part of the Pacific basin, changes in daily increment thicknesses in two Tridacnidae species, *Tridacna maxima* and *Hippopus hippopus* are related to SST changes but also depend on physiological condition of the animals.

While certain geochemical tracers (Sr/Ca,  $\delta^{18}\text{O}$ ) within *Porites* sp. Skeleton can be used with a certain confidence, this is not always the case for the mollusk shells. I will show that the use of Mg/Ca as a SST proxy depends on the species and that physiology and very early diagenesis are obstacles in the use of this proxy. In *T. maxima* and *H hippopus*,  $\delta^{18}\text{O}$  can be used as a tracer of SST and of the evaporation/precipitation balance. To reconstruct variations of these parameters during the Mid-Holocene, I worked on fossil giant clams and corals, after diagenesis assessment. I will show how various types of diagenesis impact the microstructure, the geochemistry, and the reconstructed environmental parameter. I will also propose hypotheses on the diagenesis process itself.

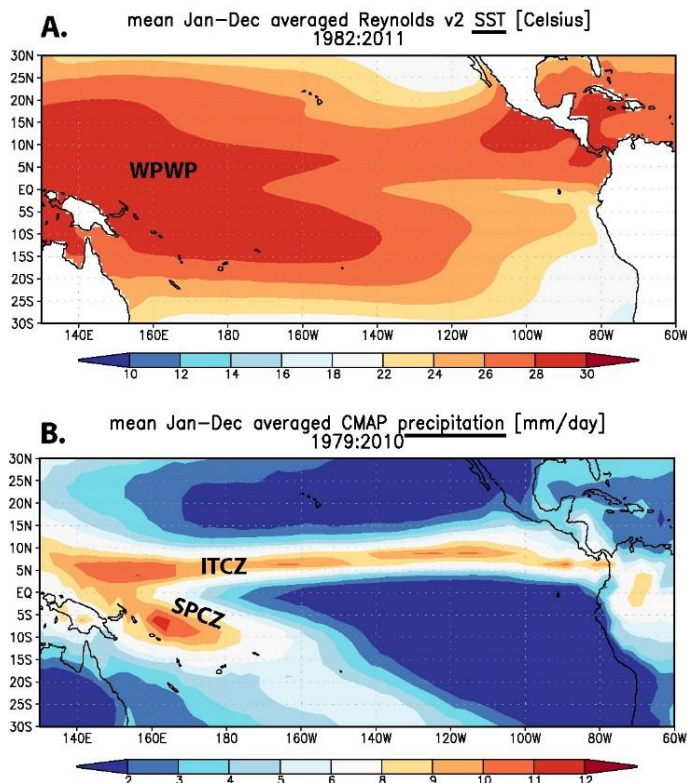
Based on results obtained from Mid-Holocene archives, I will show that the post-glacial SST rise was reached at around 6.5-6 ka BP in the Southwest Pacific, that the South Pacific Convergence Zone influence was more probably reduced, the Hadley circulation enhanced, and that ENSO variability was probably reduced. The work done on Lapita (3 ka BP) Tridacnidae confirmed that the Lapita migration has probably been favored by an increase in climatic variability.

The last chapter deals with the future directions I would like to give to my research that include i/ better understand the incorporation of proxies in mollusk and ii/ try to propose solution for sustainable management of tropical ecosystems based on the use of biocarbonate as recorder of the environment and its disturbances.

## I / GENERAL INTRODUCTION AND MANUSCRIPT STRUCTURE

## 1.1 The tropical Pacific Ocean: a major component of the climate system

The Pacific Ocean covers 1/3 of the planet and is the largest body of water on Earth. It is a place where strong ocean/atmosphere interactions take place due to various specific features. The main atmospheric circulation at the basin scale is the Walker circulation. This is a large zonal equatorial circulation with ascending air in the western part of the Pacific and descending air in the eastern part. The Pacific basin also hosts the largest pool of warm waters, the Western Pacific Warm Pool (WPWP), located in the western part of the basin and geographically constrained considering waters above 28.5°C (Fig. 1). This WPWP alimnts strong atmospheric convection that transfers large amounts of heat and humidity from the tropics to the poles via the Hadley cells. Two bands of clouds are accumulated by the easterlies and delimit zones of high precipitations. These convergence zones are the Intertropical and the South Pacific Convergence Zones (from now ITCZ and SPCZ). The ITCZ is located at around 5-10°N, with an east-west orientation (Fig. 1B). The SPCZ, which splits from the ITCZ in the western part of it, is inclined south-eastward and extends until the French Polynesia (Fig. 1B). The WPWP and the convergence zones play an important role in the seasonal and interannual climate variability in the tropical Pacific Ocean but also at worldwide scale.



**Fig. 1: Main ocean-atmospheric features in the tropical Pacific. Average position of A. the Western Pacific Warm Pool (WPWP; SST>28°C) and B. the two convergence zones, the Intertropical and the South Tropical ones (ITCZ and SPCZ). Maps from Climate Explorer site; Data: CMAP and Reynolds and Smith; 2002.**

The positions and area of these features vary, at the seasonal and interannual scales, participating in the climatic variability of the tropical Pacific Ocean. During the austral summer (Dec-Jan-Feb), the WPWP extends southward and the SPCZ is larger and extends more south-eastward; the opposite occurs during the austral winter (June-July-Aug; Fig. 2). At the

interannual scale, the variability is dominated by the El Niño Southern Oscillation (ENSO) with ENSO-related events occurring on average every 2-7 years and lasting several months. This phenomenon, which has worldwide impacts, is related to a decrease of the easterlies strength that allows the WPWP to extend more eastward than at normal. This leads to a change in the inclination of the thermocline providing colder waters to the west and warmer ones to the east part of the Pacific basin, which in turn shift the position of the convergence zones (Fig. 3). At the basin scale, the ENSO-related changes in the water temperatures and convergence zone positions lead to dryer climate in the west and wetter one in the east during the El Niño phase. Consequences are dramatic for populations and environment, particularly in the tropical Pacific. While the western part of South America endures inundations, and its corollary impacts on agriculture and landscapes, and coastal production decrease related to sea surface temperature (SST) increase for several months, countries in the western part of the basin (e.g., Australia, Indonesia) face drought and fires. Impacts of ENSO events are not restricted to the Pacific basin and teleconnections lead to droughts/heavy rains in some places in East Africa, heavy rains in South Brazil, fire in Canada, etc. (e.g., Gamoyo et al., 2015; Xu and van Kooten, 2014)

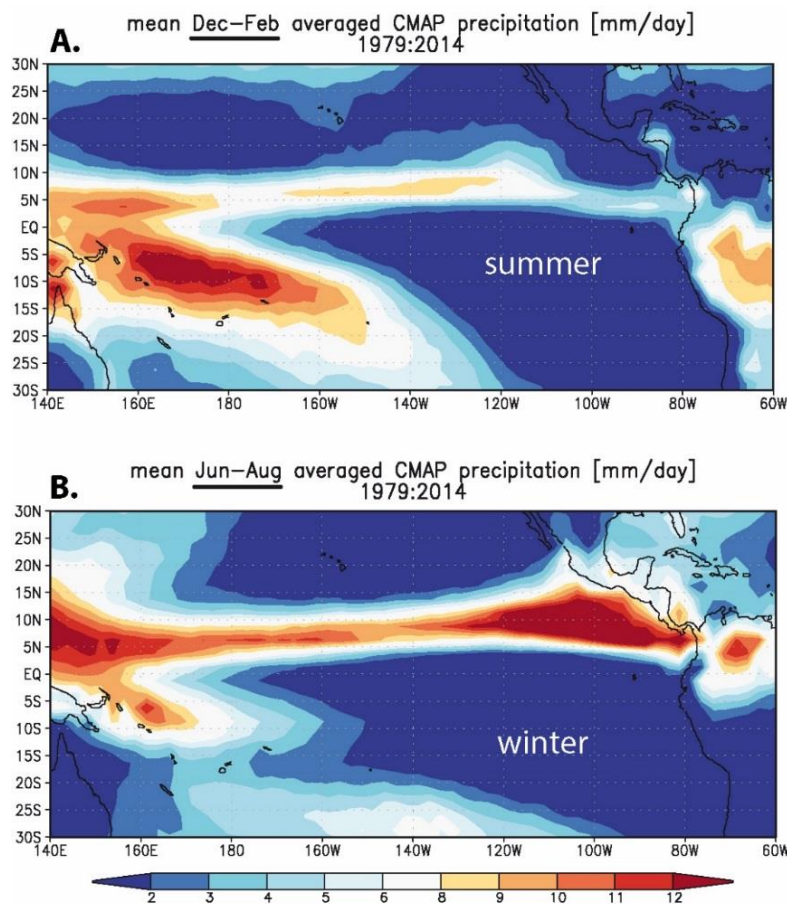


Fig. 2: Average summer (A. Dec-Jan-Feb) and winter (B. June-July-Aug) position of the ITCZ and SPCZ. Data CMAP (Xie and Arkin, 1997). Maps done using the KNMI Climate explorer website (<http://climexp.knmi.nl/start.cgi?id=someone@somewhere>).

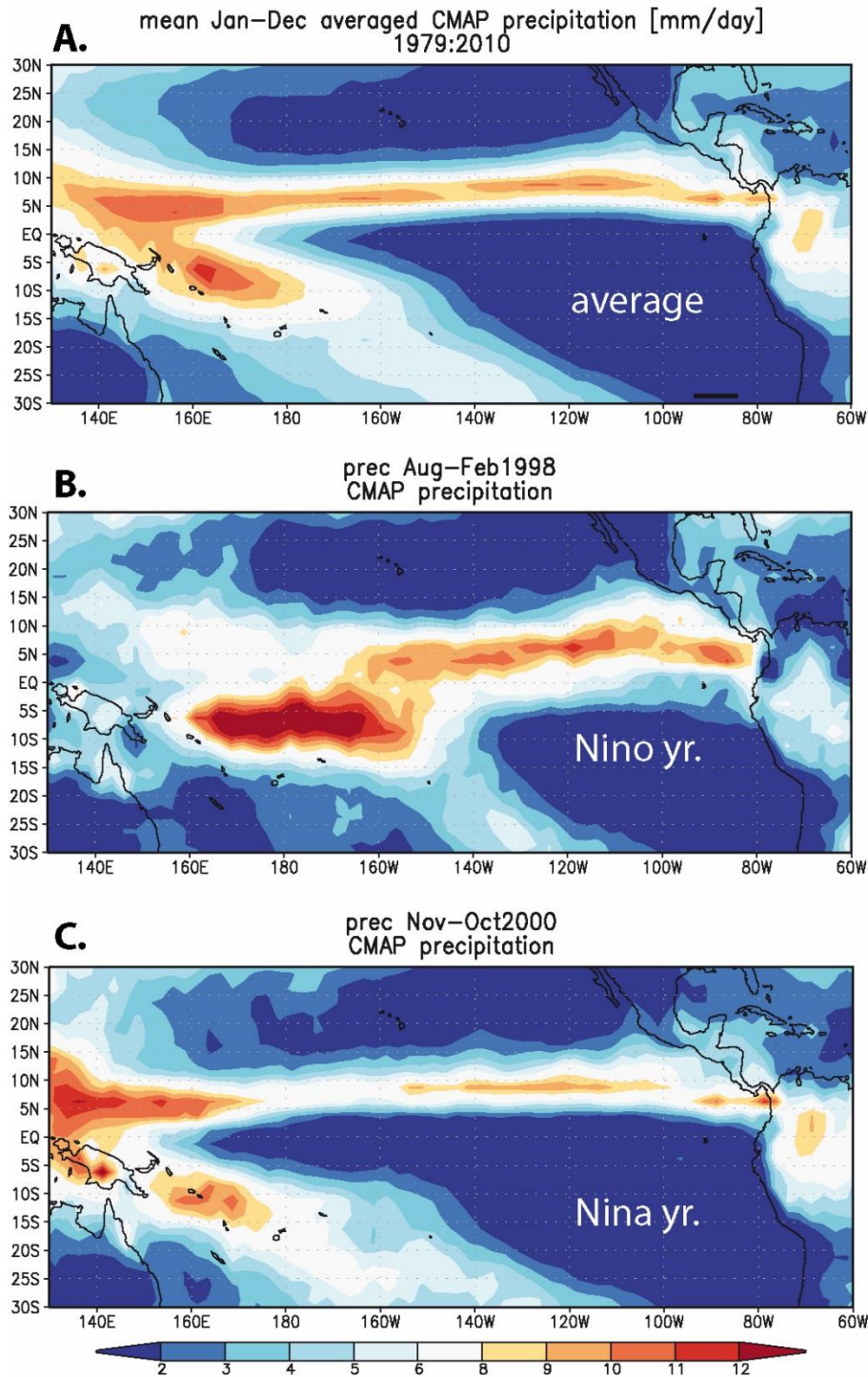


Fig. 3: ITCZ and SPZC locations. A. "normal"; B. El Niño events and C. La Niña conditions. Data from CMAP (Xie and Arkin, 1997); maps done using the KNMI Climate explorer website (<http://climexp.knmi.nl/start.cgi?id=someone@somewhere>).

Better understand ENSO is thus crucial, all the more in the context of actual and future climatic change where ENSO frequency might increase. Such understanding will allow to better predict its occurrences and to mitigate economic and human consequences. One way of improving predictions of future ENSO episodes is to use climate model simulations. Such models are based on physical laws and on *in situ* observations like those obtained from the ARGO program

for ocean temperature and salinity (<http://www.argo.ucsd.edu/index.html>; started in 2000) and are used to simulate current and future climate under various scenarios. Nevertheless, depending on the model used, answers in terms of ENSO occurrences are different. Concerning the convergence zone positions, and more particularly for the SPCZ, model simulations still failed to reproduce them with accuracy (Brown et al., 2013; Saint-Lu et al., 2015). The measurements of climate-related parameters, essential for model development and validation, began at around 1850, with an increase in the number and quality of data since 1950. Nevertheless, such measurements include the anthropic external forcing on climate, the dominant forcing for the last three decades global changes (IPCC, 2013). Hence, it is difficult to untangle human's activities-related impact on the climate system from the natural climate variability. To improve the knowledge of the latter, and thus better understand and qualify the role of human's activities on the climate system, it is necessary to extend our knowledge on the natural climate system.

## 1.2 High-resolution proxies from biocarbonate archives

To extend our knowledge on natural climate variability and better understand the current evolutions, climate-related data for past periods, i.e., in the absence of such important anthropogenic forcing, are necessary. Such data can be obtained from numerous archives. Each of these archives has its specificities, in terms of temporal resolution, type of provided information, precision, etc. (Fig. 4).

Considering the tropical Pacific Ocean climate variability, high temporal resolution information on specific climate parameters like sea surface temperatures (SSTs) and sea surface salinities (SSSs), or on the evaporation/precipitation balance, are necessary. Indeed, "the seasons have a strong influence on the activity and zonal/latitudinal position of the convergence zones (Delcroix and Henin, 1991; Delcroix et al., 1996; Meehl, 1987; Vincent, 1994). Since El Niño events generally start at the end of the calendar year (this is termed "phase locking"), the seasonal cycle plays a critical role in the ENSO dynamic (An and Wang, 2001; Tziperman et al., 1997). The underlying mechanisms are, however, complex and still debated (An and Wang, 2001; Lengaigne et al., 2006; Tziperman et al., 1997; Yan and Wu, 2007)." *Extract from Lazareth et al. (2013b)*. Reconstructions of past SST and precipitation variations in the tropics are mainly based on proxy data obtained from biocarbonates like coral skeleton, foraminifera, or mollusks. Because of their high accumulation/deposition rate, these archives should allow to obtain high-resolution paleo-environmental reconstructions, possibly at an infra-seasonal to infra-monthly resolution.

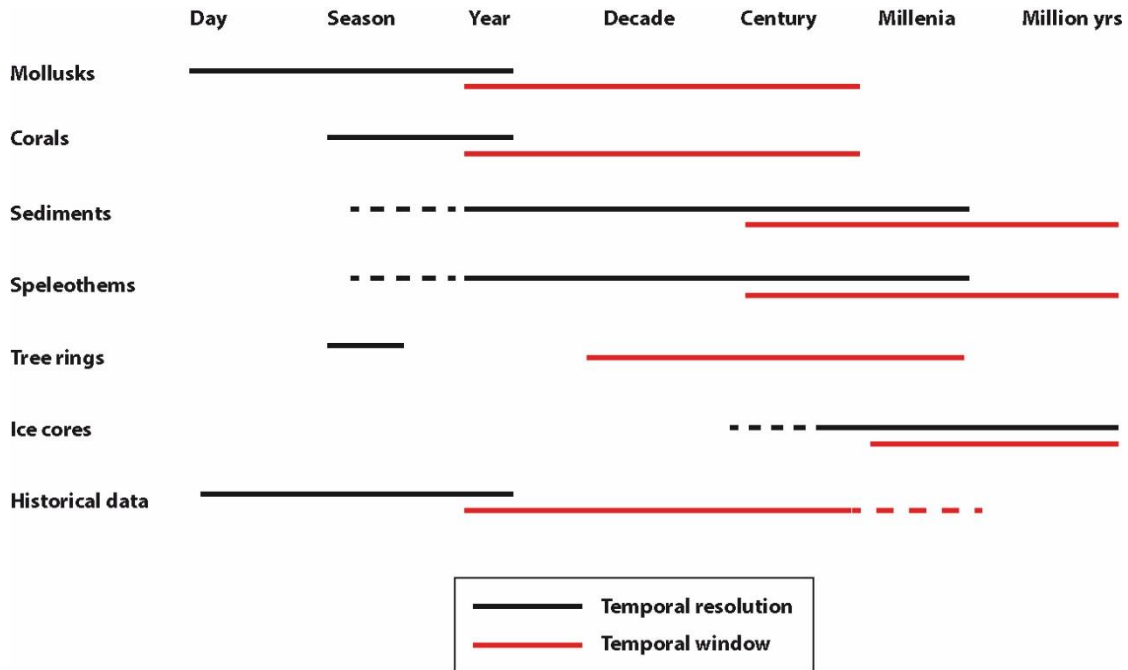


Fig. 4: Temporal resolution and window for environmental reconstructions using some commonly-used archives. Dotted lines represent potential resolution that could be obtained; this depending on various parameters like the species, the localization, etc.

Among those high-resolution archives, the molluscan shells arouse the scientific interest for several reasons. Mollusks live in a very large array of environments, including marine and freshwater ones, going from the surface to the deep oceans, and from the tropics to the high latitudes. In addition, many of them are edible and shells can thus be recovered on archaeological sites or shell mounts also human-related (Bērziņš et al., 2014; Gernet et al., 2014; Macario et al., 2014). This provides the opportunity to obtain environmental data on periods and places not available when working on other archives like corals for example. Mollusks' lifetime's encompasses a few years to several centuries, providing hence a temporal resolution from day to year and several proxies can potentially be used to reconstruct environmental variations. Indeed, shell growth variations, stable isotopes, trace elements can potentially be used to reconstruct environmental variations like SST, precipitations, and upwelling events.

The shell growth variations through time can be used to reconstruct life-traits and/or environmental changes the animal went through. The study of the deposition rhythm and thickness changes of shell growth increments, i.e., sclerochronology, is likely to bring information on the variations of the environmental conditions of mollusks while also dating events in the shell (cf. Lutz and Rhoads, 1980; Richardson, 2001). Indeed, the mollusk shell settles layer by layer, the length-growth takes place at the edge of the shell and its thickening on the whole inner shell. This incremental deposition is governed both by the metabolism of the animal (reproduction, nutritive inputs, etc.) and by environmental parameters, often cyclic (SSTs variations, tides, day/night alternation, for example) which act on the "biological clock" of the organisms. This peculiar growth results in a succession of lines and increments (portion between two lines) observable either at the surface and/or in cross section (or both) of the shell, depending on the species. In the following, I will use the term sclerochronology strictly for the

study of the rhythm of increment deposition and of increment thickness changes, here applied to mollusk shells, as recommended in Gröcke and Gillikin (2008).

In an attempt to document on the SST rise for several weeks characteristic of El Niño events and thus better understand present and past El Niño occurrences in the East Pacific, I investigated the potential of using *Protothaca thaca* daily growth increment thickness changes as a SST proxy (Chap. II, § 2.1.1, p. 19). This common Peruvian-Chilean bivalve inhabits coastal areas along the Peruvian-Chilean coasts, a region severely impacted by ENSO events. This species is particularly interesting as a potential environmental recorder because it can survive strong El Niño events thanks to an elevated thermal tolerance (Urban, 1994); providing thus potential archive of such events; and it is commonly found in Holocene archaeological deposits and Pleistocene terraces (Moore, 1991; Ortlieb et al., 1996; Ortlieb et al., 1992; Reitz, 1988). Because ENSO impact the whole Pacific Ocean, I also focused on mollusks from the Western Pacific. I thus worked on the growth of mollusks from the Tridacnidae family because their growth rate, at around 1 cm per year, is also particularly appropriate to obtain monthly to daily-resolution records of environmental variations (e.g., Aubert et al., 2009; Sano et al., 2012; Watanabe and Oba, 1999; Yan et al., 2013; Chap. II, § 2.1, p. 21).

In addition to sclerochronology that can be used to reconstruct environmental changes at an infra-annual resolution, and more specifically SST modifications, the shell geochemistry can also provide information on environmental parameters through various proxies. Indeed, "Many [...] studies tackled SST (and/or sea-surface salinity) tracers through variations in the elementary [...] or stable isotope ( $\delta^{18}\text{O}$ ) composition within mollusk shells" (e.g., Dodd, 1965; Freitas et al., 2005; Klein et al., 1996; Lorens and Bender, 1980; Takesue and van Geen, 2001; Thébault et al., 2007; Yan et al., 2015). "Since Epstein et al. (1953) pioneering work,  $\delta^{18}\text{O}$  has been the most commonly used proxy in attempts to infer SST from mollusk shell analyses (e.g., Andreasson and Schmitz, 1998; Chauvaud et al., 2005; Schöne et al., 2004). *Slightly modified extract from Lazareth et al. (2007)*. Considering the need of obtaining high-resolution environmental data in the Western Pacific and the several advantages in developing the use of Tridacnidae shells as environmental recorders, I thus tried to establish the link between shell  $\delta^{18}\text{O}$  and SST, taking into account the  $\delta^{18}\text{O}_{\text{sw}}$  variations. Indeed, even if "The potential of bivalve's  $\delta^{18}\text{O}_{\text{shell}}$  records as a proxy for SST has been investigated in more than 20 bivalve species in the past 40 yr. (e.g., Aharon and Chappell, 1983; Carré et al., 2005; Hong et al., 1995; Ullmann et al., 2010), few species specific relationships linking  $\delta^{18}\text{O}_{\text{shell}}$  and  $\delta^{18}\text{O}_{\text{sw}}$  values to SST are available, and most of the above studies rely on three calibrations produced by Böhm et al. (2000), Aharon and Chappell (1983), and Grossman and Ku (1986). Although these calibrations are robust, considering the wide range of SST and SSS included and the diversity of species involved, the relationship between  $\delta^{18}\text{O}_{\text{shell}}$  records,  $\delta^{18}\text{O}_{\text{sw}}$ , and SST may vary at the genus or even at the species level due to different vital effects (Bemis and Geary, 1996; Böhm et al., 2000; Dunbar and Wefer, 1984; Rahimpour-Bonab et al., 1997; Wefer and Berger, 1991; Ziveri et al., 2003)." *Extract from Duprey et al. (2015)*. I thus conducted experiments to establish  $\delta^{18}\text{O}_{\text{shell}}$ -SST equations for two giant clam species, *Hippopus hippopus* and *Tridacna maxima* (§ 2.2.2, p. 28).

Nevertheless, oxygen stable isotope fractionation in biocarbonate is dependent on both the SST and the  $\delta^{18}\text{O}_{\text{sw}}$  (Aharon, 1991; Epstein and Mayeda, 1953; McConnaughey, 1989; Weber and Woodhead, 1969), this last one depending on the precipitation/evaporation balance with most of the time a direct relationship between  $\delta^{18}\text{O}_{\text{sw}}$  and SSS (Craig, 1965). Such dual dependency implies that interpretations must consider potential salinity variations; this being critical in some locations as estuaries; and that, ideally,  $\delta^{18}\text{O}_{\text{sw}}$  must be known, directly or via its relation with SSS. Consequently, to obtain potentially direct SST records in the absence of  $\delta^{18}\text{O}_{\text{sw}}$  data, I focused on Mg/Ca because this elemental ratio could provide such information. I indeed observed a good relationship between SST and Mg/Ca in my first study of bivalve shells as archive of SST changes (Lazareth et al., 2003; § 2.2.2, p. 28) and try to establish if such a link exists in two South American molluscan species, *Protothaca thaca* and *Concholepas concholepas* (Chap. II, § 2.2.2, p. 28).

Besides mollusks, in the tropics, the chemical composition of massive coral skeleton is one of the most-used geochemical tool to reconstruct environmental variations at a high temporal resolution. *Porites* sp is the commonly used species. It has an average growth rate of 1 cm per year and its study using the current analytical techniques allows to reach monthly to infra-monthly temporal resolution. As *Porites* sp. can grow for several decades to centuries it can provide long records of past environmental changes. In addition, *Porites* sp. specimens are found on various uplifted reefs, opening windows on more distant past (e.g., Ayling et al., 2006; Inoue et al., 2010; Sun et al., 2005a). "The incorporation of various trace elements and of the Oxygen (O) and Carbon (C) stable isotopes in its (*i.e.*, *Porites* sp.) biogenic aragonite skeleton depends on environmental conditions and may thus document on both past climates and anthropogenic disturbances. Numerous studies using element/Ca ratios as SST-related proxies were published. Magnesium/Calcium (Mg/Ca) ratio has tentatively been used for SST reconstructions (Mitsuguchi et al., 1996; Wei et al., 2000) but the Mg/Ca-SST relationship is strongly questioned, if not dismissed (Inoue et al., 2007; Mitsuguchi et al., 2008; Yu et al., 2005). The Uranium/Calcium (U/Ca) can also be used to reconstruct past sea surface temperatures (SSTs) (Corrège, 2006; Corrège et al., 2000; Emiliani et al., 1978; Felis et al., 2009; Gagan et al., 2000; Min et al., 1995; Weber, 1973). Nevertheless, the element/Ca ratio the most used to reconstruct past SST from *Porites* sp. colonies is certainly the Sr/Ca (e.g., Ayling et al., 2006; Azmy et al., 2010; Corrège et al., 2000; McCulloch et al., 1996). Indeed, even if some limitations about the relationship between Sr/Ca and SST have been pointed (de Villiers et al., 1995; de Villiers et al., 1994; Sun et al., 2005b), the Sr/Ca in coral skeleton remains the more robust SST-proxy (e.g., Beck et al., 1992; Corrège, 2006; Fallon et al., 2003), with a high inter-colony reproducibility (DeLong et al., 2011; DeLong et al., 2007; Inoue et al., 2007; Stephans et al., 2004)." *Extract from Lazareth et al. (2013b)*.

In corals, another widely used proxy to reconstruct SSTs, SSSs, precipitation, or specific climatic indices variations is the oxygen stable isotope ratio ( $\delta^{18}\text{O}$ ). As stated above, oxygen stable isotope fractionation in biocarbonate depends on both the SST and the  $\delta^{18}\text{O}_{\text{sw}}$  (Aharon, 1991; Epstein and Mayeda, 1953; McConnaughey, 1989; Weber and Woodhead, 1969), this last one depending on the precipitation/evaporation balance with often a direct relationship



between  $\delta^{18}\text{O}_{\text{sw}}$  and SSS (Craig, 1965). Consequently, the interpretation of *Porites* sp.  $\delta^{18}\text{O}$  signature will depend on the environmental setting where it lives and on the time resolution considered, seasonal vs. interannual. Indeed, depending on the locus, either SST or SSS can be the dominant seasonal or interannual signal (Linsley et al., 2006). To better understand a key-period of the past, the mid-Holocene, I worked on fossil coral colonies from the South-west Pacific to obtain high-resolution records of environmental changes, mainly SST and the precipitation/evaporation balance (Chap. I, § 1.4, p. 17 and Chap IV, p. 59).

### 1.3 The diagenesis issue

Modifications of the skeleton/shell can occur after its secretion and deposition; those processes are grouped under the term diagenesis. These modifications can occur very shortly after biocarbonate formation, while the organism is still living, or after the organism death. It has been shown that diagenesis can modify the original geochemical signal enclosed in the skeleton/shell, which distorts the result regarding environmental reconstruction. For example, if "geochemical analyses of corals have become a standard means to assess environmental variability in the tropical surface oceans (Beck et al., 1992; Corrège, 2006; Gagan et al., 2000) [...], recent works have pointed out that their aragonitic skeleton may have been affected by marine and freshwater diagenesis so that the geochemical data, and their interpretation in terms of sea surface temperature (SST) and related climatic features, must be sometimes regarded with caution (Enmar et al., 2000; Hendy et al., 2007; Lazareth et al., 2013b; Lazareth et al., 2016; McGregor and Gagan, 2003; Müller et al., 2001; Quinn and Taylor, 2006) (Chap. III, p. 41)." *Extract from Aubert et al. (2009)*. While preservation assessment on fossil corals and on other biocarbonate archives becomes a standard before paleo-environmental reconstructions (reference above and Chap. III, § 3.2, p. 47), diagenesis studies on the biocarbonate skeleton/shell of live-collected specimens are rarely done because one makes the assumption that such alteration cannot occur, or is very rare, while the organism is still alive. In our attempt to calibrate SST proxies from *Protothaca thaca* shells, we observed geochemical signatures inconsistencies between young and old shell (Chap. II, § 2.2.1, p. 28). Consequently, the study on the shell preservation at the specimen level was essential (Chap. III, § 3.1.1, p. 39). Concerning Tridacnidae shells, even if they are hard and dense, diagenesis alteration cannot be ruled out. For example, shells left by humans, usually after flesh consumption, might have been cooked or left in conditions partially exposed to weathering which might be inadequate for a proper preservation through time. Diagenesis on living coral colonies has also been observed (Houck et al., 1975; Nothdurft et al., 2007). In our case, while willing to establish the Sr/Ca paleotemperature equation from *Porites* sp. in the Vanuatu, a high percentage of calcite was measured in the aragonite skeleton of the live-collected colony. The impact of such calcite on the geochemistry of the skeleton was studied on currently-used (ex., Sr/Ca, Mg/Ca, etc.) and less currently-used (ex., Li/Mg,  $\delta^{11}\text{B}$ , B/Ca) proxies (Chap. 3, § 3.1.2, p. 41). In each of these studies I tried to understand the diagenetic process(es) and suggested hypotheses to explain the observed modifications. In any case, when studying (paleo-)environmental conditions based on

geochemical proxies in biocarbonate archives, a prerequisite is to identify any diagenesis on the studied archive (Chap. III, p. 38).

#### 1.4 The Holocene time-period

The Holocene spans the last 10 000 yrs.; it began at around 11 500 yrs. cal BP after the last glacial maximum. Modern human societies developed during this Holocene period. Even if climate variations during the Holocene were not as large as those encountered before, significant variations occurred. "The transition from the early Holocene to the Mid-Holocene (~7.0–6.0 ka BP) was accompanied by a progressive, but significant, change of the climate mean-state which took place at the millennial timescale. The early Holocene, that started at around 11 ka BP, was characterized by a cold post-glacial climate that warmed progressively until reaching temperature higher than modern ones during the Holocene Thermal Maximum, at around 9.0–5.0 ka BP [see the review proposed by Renssen et al., 2012] [...] Early Mid-Holocene climatic changes present the same order of magnitude as the ongoing climate changes. Documenting such changes will provide thus invaluable clues to understand the mechanisms involved in the climate dynamic. However, the spatial and the temporal resolution of the early Mid-Holocene paleoclimatic reconstructions are still insufficient". *Extract from Duprey et al. (2012).*

The Mid-Holocene is a key climatic period during which difference in Earth's orbital parameters, compared to our current setting, results in a different insolation regime and seasonality timing (Kutzbach and Guetter, 1986). In terms of inter-annual climatic variability, the paleoclimatic studies in the tropical Pacific showed that after a period characterized by La Niña-like conditions (Clement et al., 2000; Koutavas and Joanides, 2012; Koutavas et al., 2002; McGregor and Gagan, 2004), the current ENSO periodicity would have been established from c. 5500-5000 years BP (e.g., Cane, 2005; Donders et al., 2008), as confirmed by some model simulations (Zheng et al., 2008). However, the modalities of this Mid-Holocene transition are still very controversial. Furthermore, SST and/or SSS high resolution data at c. 6000 BP in the Southwest Pacific are limited to Australia and Papua New Guinea (Gagan et al., 2004; McGregor and Gagan, 2004) while in Vanuatu and in New Caledonia, under the influence of the SPCZ, they are scattered (Montaggioni et al., 2006). It is thus essential to acquire such data in this region to understand better the modalities of ENSO, the influence of the spatial and temporal fluctuations of the SPCZ at c. 6000 BP, and to provide data for model simulations like that issued from the Paleoclimate Modelling Intercomparison Project (PMIP) dedicated partially to this period (Chap. IV, § 4.1, p. 59). This was done through reconstructions of SST and precipitation/evaporation balance based on geochemical analyses of corals and giant clams from New Caledonia and Vanuatu, dated between ~ 7 - 5.5 ka BP (Chap. IV, p. 59).

Another key-period of the Holocene is at c. 3000 yr. BP. At around this date a rapid climatic change (RCC) occurred (Mayewski et al., 2004), associated to cultural changes around the world (Anderson et al., 2007b; Dalfes et al., 1997). In the Pacific, this RCC was characterized by an intensification of El Niño occurrences (e.g., Gagan et al., 2004; Moy et al., 2002; Tsonis, 2009) that, for example, might have led to the abandonment of Initial Period temples in Peru

(Sandweiss et al., 2001; Sandweiss et al., 2007). An intensification of the El Niño activity has also been recorded in Australia and Papua New Guinea (PNG) at this period (Gagan et al., 2004). Moreover, it corresponds to the onset of the colonization of the remote South-west Pacific islands by the Lapita people (Anderson et al., 2007a; Kirch, 1997). Because this colonization occurred very lately compared to the first settling in Australia and PNG (~ 60-40 ka BP), and because Lapita spread in Remote Oceania in a short period (less than 300 yrs.), scientists wondered about the triggers of this incredible migration. Some authors advance that the “relative” reduction in the sea level, following the 6000 yr. BP optimum, would have returned the coasts of the islands more favorable to human colonization by providing livable coastal spaces (Dickinson, 2003; Nunn, 2007). However, this reduction was only very weak and the explanation could be rather found in modification of the climatic variability. Among the numerous edible molluscan species, the Tridacnidae are often found in archaeological sites in the Southwest Pacific (Asami et al., 2014; Clark et al., 2006; Galipaud and Kelly, 2007) and the isotopic signature of such archaeological shells from Vanuatu and New Caledonia was studied to investigate further the link between the Lapita settlement on Remote Oceania island and ENSO (Chap. IV, § 4.2, p. 65).

## Manuscript structure

The manuscript is built around 3 main topics, the potentiality of using of bivalves as environmental recorders, that includes calibration studies (Chap. II, p. 18), assessment and impact of diagenesis on bivalve and coral archives and proposals on the causes of the diagenesis (Chap. III, p. 38), and Holocene paleo-environmental reconstructions that derive from those archives (Chap. IV, p. 59). The last chapter deals with the future directions I would like to give to my researches (Chap. V, p. 71) while a resume of my scientific carrier, including the various aspects of it, from C.V. to publications and students' supervisions are in the appendices.

The scientific questions that directed my studies are resumed below:

- Can molluscan shells be good recorders of SST?
- Can we use bivalves to reconstruct climate variability in the East Pacific, including El Niño Southern Oscillation (ENSO)?
- What are the effects of diagenesis on the geochemical signature of biocarbonate and can diagenesis processes be proposed?
- What were the climatic characteristics in the South-west Pacific at around 6 ka?
- What climate prevailed during the Lapita colonization?

## 2.1 Sclerochronology as a tool for environmental variability reconstruction

### 2.1.1 *Protothaca thaca* and ENSO

"Environmental variations can be recorded in bivalve shells and this proxy information can be crucial for paleoceanographic studies in regions where other archives (e.g. corals) are absent. We present the first sclerochronological study of *Protothaca thaca* (Mollusca, Veneridae), a common upper subtidal bivalve, characterized by a high temperature tolerance, from the SE Pacific Ocean (12 to 45° S). *P. thaca* is present in archaeological deposits and Holocene marine terraces, making it a potentially useful paleo-environmental recorder, particularly in respect to El Niño Southern Oscillation (ENSO) reconstructions." *Extract from Lazareth et al. (2006).*

#### Main questions:

- What is the shell increment deposition rhythm in *Protothaca thaca*?
- Can we use sclerochronological profiles obtained on *Protothaca thaca* shell to reconstruct SST or SST variations as a tracer of ENSO occurrences?

#### Work done:

- Sclerochronological study on several Peruvian and Chilean *Protothaca thaca* specimens, including the methodological development for shell preparation,
- Interpretation of the sclerochronological profiles in terms of environmental changes.

#### Methodology in brief

To observe and study shell growth increments, "the [...] shell sections were polished and acetate peel replicates were made after etching with 10% acetic acid for 30 s. Microstructural growth units and growth anomalies were identified by combining diffused and transmitted light microscopic observations of thin sections and acetate peels<sup>1</sup> and SEM imaging (Philips 505). The width of each thinnest growth increment was measured on the acetate peel replicates [...] under an optical microscope with a precision of 5 µm. [...] The thinnest clearly bounded growth increments have a width of 10 to 120 µm and are limited by a 3 to 5 µm thick line of organic matter (black in transmitted light, etch-resistant). [...] The beginning/end of each cycle are characterized by a small groove on the surface of the shell, as reported in other bivalves (e.g. *Chione cortezi*: Schöne et al., 2002); this cyclic pattern is thought to coincide with tidal cycles. As tidal mode here is semidiurnal with a diurnal inequality (see Dirección de Hidrografía y Navegación; <http://www.dhn.mil.pe>), the microgrowth increments defined above can thus be interpreted as 'daily' growth increments." *Extract from Lazareth et al. (2006).* In addition to daily increments, growth stops or anomalies were identified in all the *Protothaca thaca* shell studied. "Growth anomalies in *Protothaca thaca* shells consist of an organic-rich layer associated with a depression on the surface of the shell (Fig. 1B; here **Fig. 5 B & D**). Relatively thin growth anomalies, 5 to 40 µm thick (Fig. 1D; here **Fig. 5 B**), which are irregularly distributed

<sup>1</sup> Acetate peels: "replicas of etched surfaces embedded in sheets of cellulose acetate." Wilson & Palmer (1989)

in the shell are interpreted as short non-periodic stress events like storms, predation attempts, etc. These irregular growth anomalies might also be related to spawning events, as *P. thaca* reproduction can occur in various months of the year (Henríquez et al., 1981). Major growth anomalies (MGAs) are characterized by organic-rich layers of 50 to 400  $\mu\text{m}$  thickness and a more conspicuous groove at the surface of the shell (Figs. 1B & 2; here Fig. 5 D & Fig. 9). The microgrowth increment width is drastically reduced in MGAs (Fig. 3; here Fig. 9).

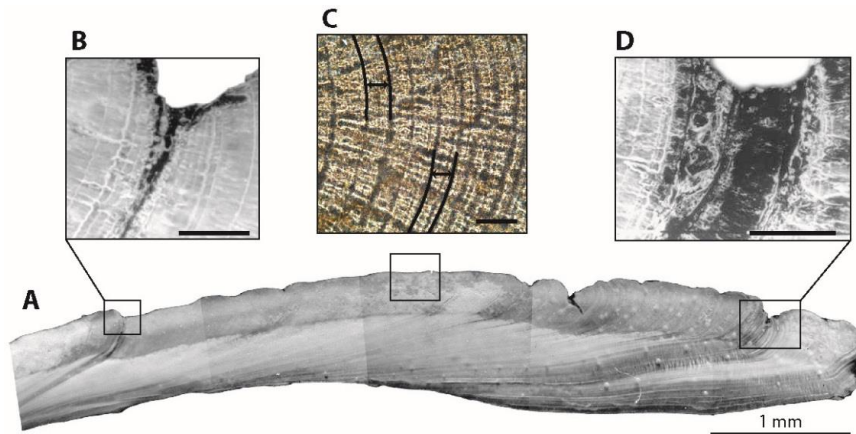


Fig. 5: Daily growth increments and growth anomalies in a *Protothaca thaca* shell. A. Polished thick section of a shell (diffused light). B. Sporadic growth anomaly (retro-diffused electron SEM image). C. Daily growth increments. Arrows: growth rings of 1 day (acetate peel replicate, transmitted light). D. Major growth anomalies (retro-diffused electron SEM image). Scale bars for B.–D. = 100  $\mu\text{m}$ . Modified from Lazareth et al., 2006.

#### Main results:

**What is the shell increment deposition rhythm in *Protothaca thaca*?** The *Protothaca thaca* shells grow at a daily pace but for growth stops evidenced by the occurrence of growth anomalies, as it has been observed in many other bivalve species (e.g., Beukema et al., 1985; Cardoso et al., 2012; Chauvaud et al., 2005; Lutz and Rhoads, 1980; Rhoads and Pannella, 1970).

**Can we use sclerochronological profiles obtained on *Protothaca thaca* shell to reconstruct SST or SST variations as a tracer of ENSO occurrences?** Measuring daily increments on acetate peels replicates, it was shown that daily growth increment thickness changes in *P. thaca* shells cannot be related to SST via an empirical equation. However, growth decreases or even stops occur during summers characterized by temperatures above 18°C ('summer check'-SC). Such growth anomalies are particularly thick when related to an El Niño occurrences, synonym of elevated SSTs in this region (Fig. 6). Conversely, SC can be absent under La Niña conditions due to lower SST and enhanced productivity.

Later work done on this species concludes that these El Niño-growth anomalies we observed were most probably due to a combination of both elevated temperature and food availability decrease during such events (Riascos et al., 2012). Nevertheless, measuring the thickness of

fossil *P. thaca* shell growth anomalies to identify MGA might be a way to obtain qualitative information on SST and climate variability over the studied period.

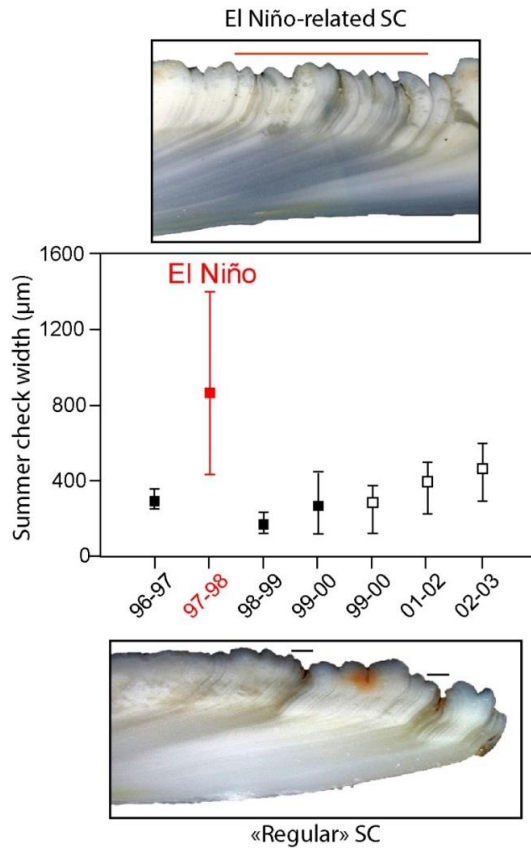


Fig. 6: *Protothaca thaca* summer check's thickness. Means, minima, and maxima of 'summer check' (SC) widths in shells (mean and range; n = 42 SC). Filled squares: El Lenguado - Chile (N = 6). Empty squares: Pocoma - Peru (N = 7). Picture above: El Niño related summer check (horizontal red line represents the measured thickness); Picture below: Summer checks (black horizontal lines) resulting from more regular summer with temperature above 18°C for short periods. Images from polished sections (optical microscope). Modified from Lazareth et al. (2006).

### 2.1.2 The daily increment thickness of giant clam shells and the SST

The sclerochronological potential of two giant clam species, *Tridacna maxima* and *Hippopus hippopus*, was investigated. *Tridacna maxima* was chosen because "This species is particularly interesting as *T. maxima* is generally dominant in geological and archaeological fossil assemblages in the Indo-Pacific region (Moir, 1986 Faylona et al., 2011) where paleoclimatic reconstructions are scarce. Moreover, today, *T. maxima* has the largest distribution area compared to that of the other giant clam species (Bin Othman et al., 2010). Fossil and modern specimens of *T. maxima* provide thus an invaluable opportunity to access past and present environmental records within the same species in different locations around the world. In addition, this species can live more than 30 yr., making it interesting as a paleoclimatic archive of environmental information." *Extract from Duprey et al. (2015)*. *Hippopus hippopus* shells or shell parts are also abundantly found in archeological settings, being sometimes the sole Tridacnidae species remnant from a crucial past period in the western Pacific; the Lapita one (Seeto et al., 2012; § 4.2, p. 65). In addition, both species can be found on the same sites (Faylona et al., 2011). Thus, having potentially two paleo-environmental archives on the same site for the same period would allow to i/ increase the possibilities of environmental reconstitution in the event of shell alteration (see Chap. III, p. 38) and ii/ cross the obtained information when relevant.

#### Main questions:

- What is the frequency of *T. maxima* and *H. hippopus* shell deposition?
- Which environmental parameter (or parameters) influences shell increment thickness changes?

#### Work done:

- Monitoring of living specimens growth including labeling experiment and environmental characterization,
- Combination of valvometry and sclerochronology (pioneer study),
- Establishment of optimal shell preparation on both species,
- Interpretation of shell growth pattern in terms of environments and/or specimen life-traits.

#### Methodology in brief:

Before relating shell daily growth to daily SST, the existence of daily increment has to be assessed. This was done experimentally by labeling the shell of 8 living giant clam specimens using a fluorochrome (calcein) and then following up their growth. This was done both on *T. maxima* and *H. hippopus* specimens. After recovery of the experimentally grown specimens, shells were cut from the umbo to the margin, following the axis of maximum growth (Fig. 7).

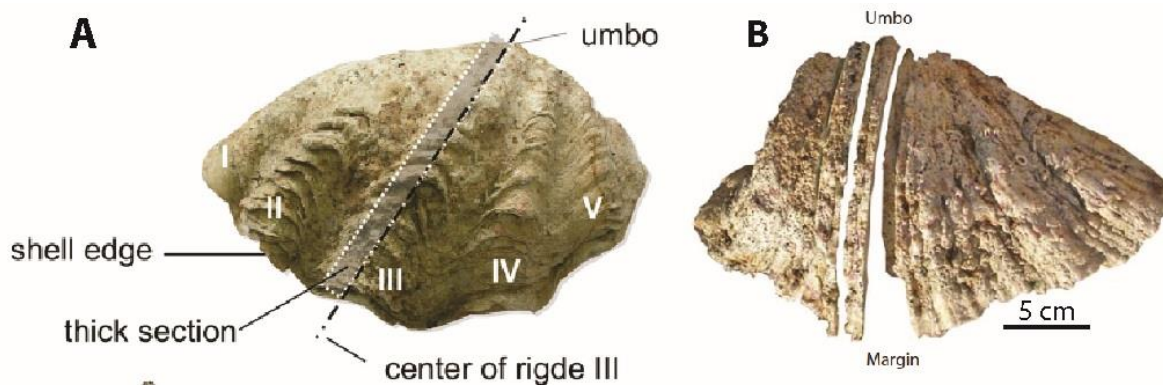


Fig. 7: Localization of the section used for A. *Tridacna maxima* and B. *Hippopus hippopus* shell studies. Scale bar valid for both shells. Modified from Duprey et al. (2015) and Aubert et al. (2009).

For *Tridacna maxima*, the sclerochronological work was done in the outer shell layer because this layer is deposited at a higher rate than the other ones (Fig. 8 and Fig. 20, p. 42). The optimal shell preparation for this species and this layer was thin sections. Three *T. maxima* specimens were studied. In *Hippopus hippopus*, the outer shell layer is almost always heavily bioeroded that precludes any continuous sclerochronological work in this layer. Consequently, the sclerochronology work was done in the inner shell layer. The increments were better observed in this layer following a specific etching technique that involves a slightly modified version of the Mutvei's solution (compare Fig. 9 and Fig. 10).

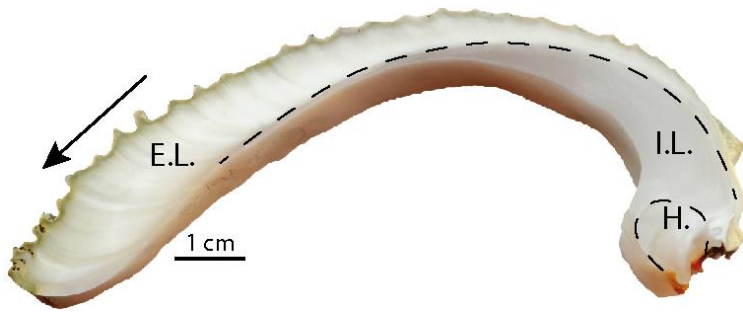


Fig. 8: Cross-section of a *Tridacna maxima* shell with the organization of the different layers. E.L.: external layer; I.L.: inner layer; H.: hinge area. The arrow represents the growth direction.

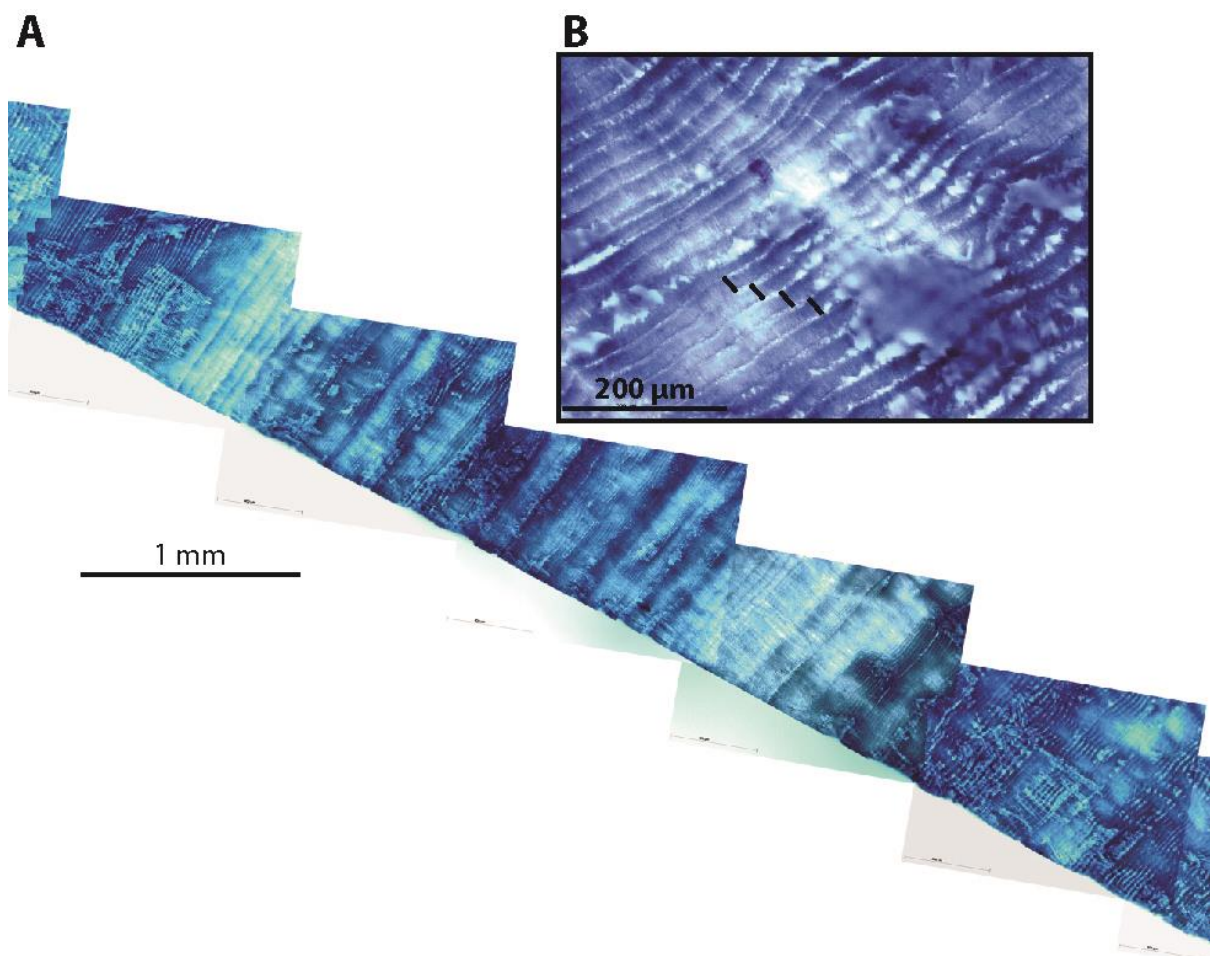


Fig. 9: Daily increments in *Hippopus hippopus* inner shell layer such as revealed after Mutvei's solution etching. A. Succession of daily increments in part of the inner layer. B. Enlargement showing the daily increments (black bars). Aubert (2007)



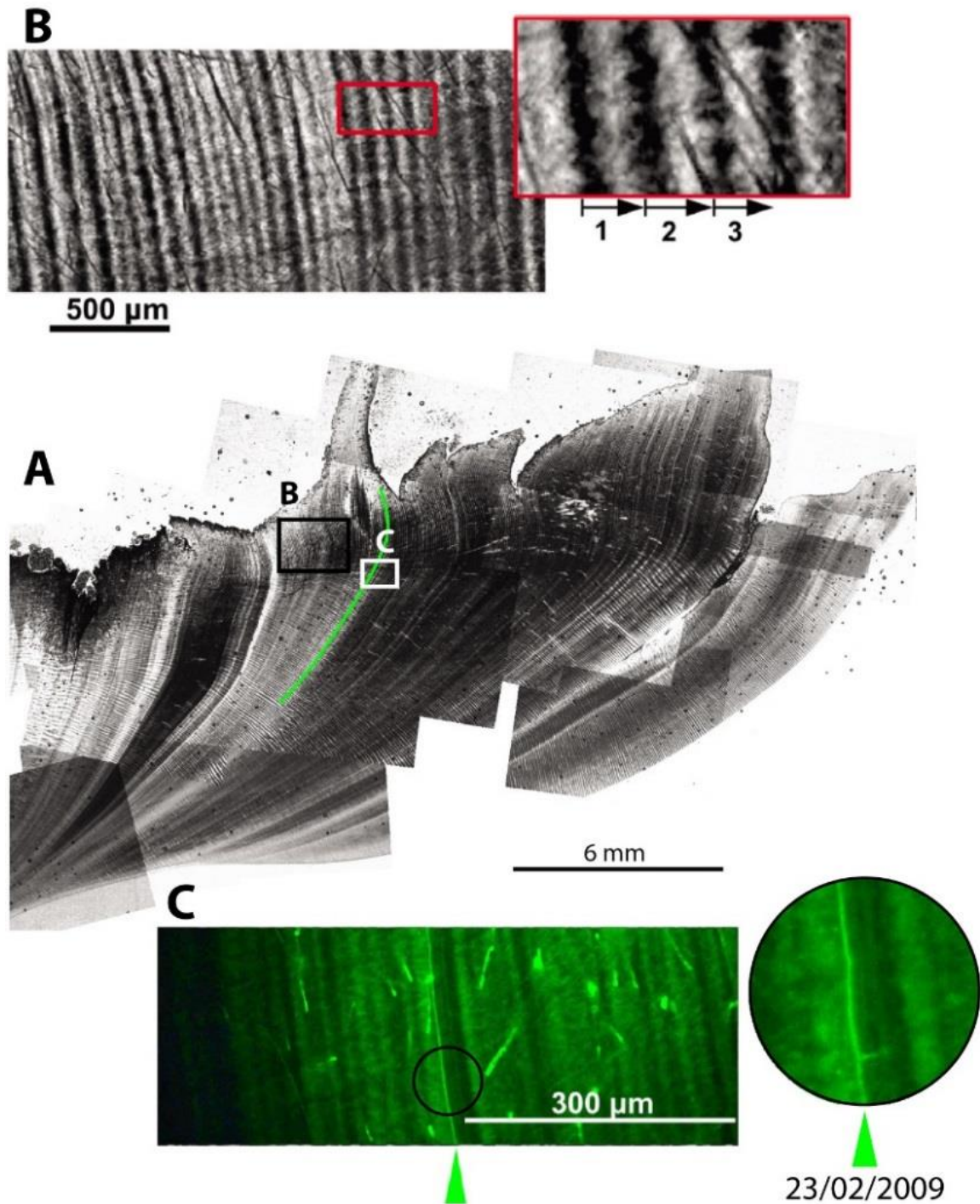


Fig. 10: Identification of daily growth increments in *Tridacna maxima* shell. A. Thin section viewed under transmitted light and reconstructed from different pictures using the Quantum-GIS software. The location of the calcein labeling is shown by the fluorescent green line (optical microscope, transmitted light). B. Successive daily growth increments. Three daily increments (one increment = a doublet of one dark and one light band) are enlarged in the red inset (right; optical microscope, transmitted light). C. Detail showing the location of the calcein labeling (green triangles; optical microscope, reflected UV light). Modified from Duprey et al. (2015).

To go one step further and to better understand the daily shell growth changes of *Hippopus hippopus* and their relationships with environment and physiology, the gaping behavior<sup>2</sup> of the animal was studied using high-frequency noninvasive valvometry (HFNI). Fifteen living specimens were instrumented with electrodes, one on each valve, and their gaping behavior registered for one year (Fig. 11; see complete methodology in Schwartzmann et al., 2011) and 5 of these specimens were studied via sclerochronology.

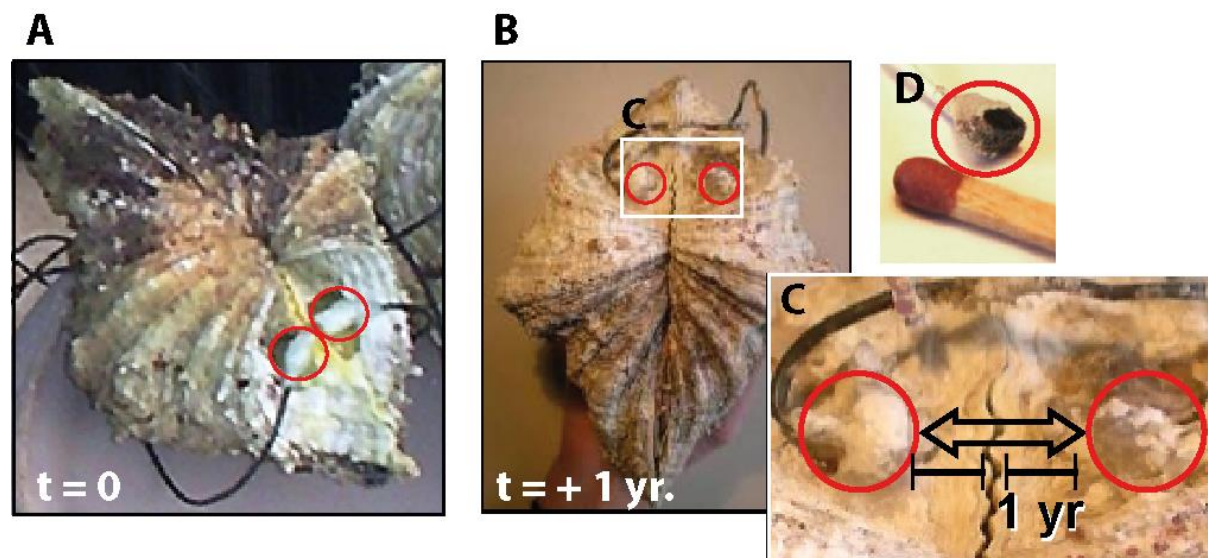


Fig. 11: *Hippopus hippopus* valvometry experimental protocol. A. View of the electrodes at the beginning of the experiment. B. and C. View of a shell after one year of growth showing the spacing between the electrodes due to shell growth. D. Close-up of an electrode. Modified from Schwartzmann, 2009.

#### Main results and conclusion:

**What is the frequency of *T. maxima* and *H. hippopus* shell deposition?** The two Tridacnidae studied species deposit daily growth increments. For *Tridacna maxima*, "The temporal resolution of the growth increment was validated by counting the number of growth increments between two tie-points clearly identifiable in the shell. [...] that confirmed that *Tridacna maxima* growth increments were deposited on a daily basis. [...]" *Extract from Duprey et al. (2015)*. Reduced shell growth was observed on some *T. maxima* sclerochronological profiles while others presented "scars" potentially due to shell growth stops (Duprey, 2012). For *Hippopus hippopus*, we use for the first time sclerochronological in concert with valvometry. Both techniques confirmed the existence of daily growth increments in the inner layer of this species. Additionally, the shell growth of *H. hippopus* is continuous all year long, every day a new shell increment is deposited (see fig. 3 in Schwartzmann et al., 2011). This result means that it may be possible to obtain records of environmental parameters whole year-long because the shell growth continues even in case of extreme SST.

<sup>2</sup> The way bivalves open and close their valves.

### Which environmental parameter (or parameters) influences shell increment thickness changes?

The main driver of daily growth increment thickness changes for these two Tridacnidae species is the SST. In *Tridacna maxima*, "The sclerochronological profile obtained showed that daily growth increment thickness presented well-marked seasonal variations, being higher in summer  $55.3 \pm 14.0 \mu\text{m d}^{-1}$  (January–March) and lower in winter  $30.5 \pm 8.3 \mu\text{m d}^{-1}$  (July–September)." *Extract from Duprey et al. (2015)*. Two other sclerochronological profiles confirmed the seasonal trend in daily increment thickness changes (Fig. 12; N. Duprey; unpublished data). Nevertheless, individual differences were observed. At present, it is not possible to establish a linear relationship between monthly-averaged daily growth and monthly SST. Analysis on several years of growth should be done to confirm this relationship. The origin of growth decreases for short period as well as of growth stops remains unknown for the studied specimens.

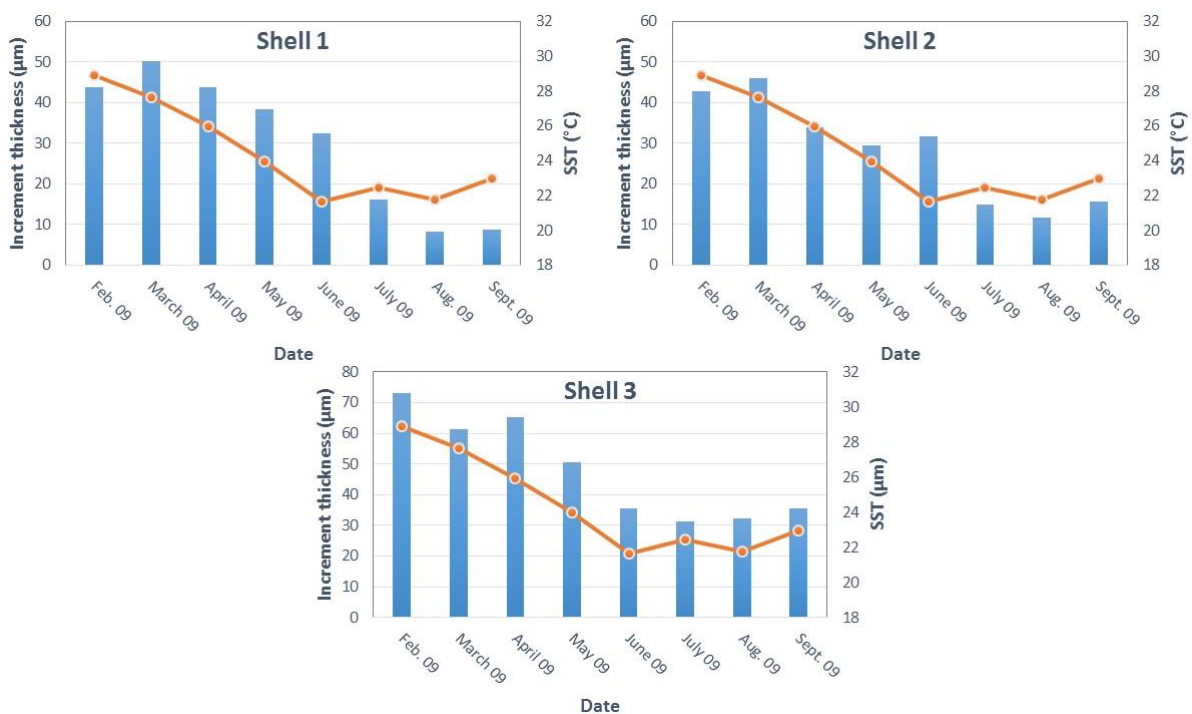
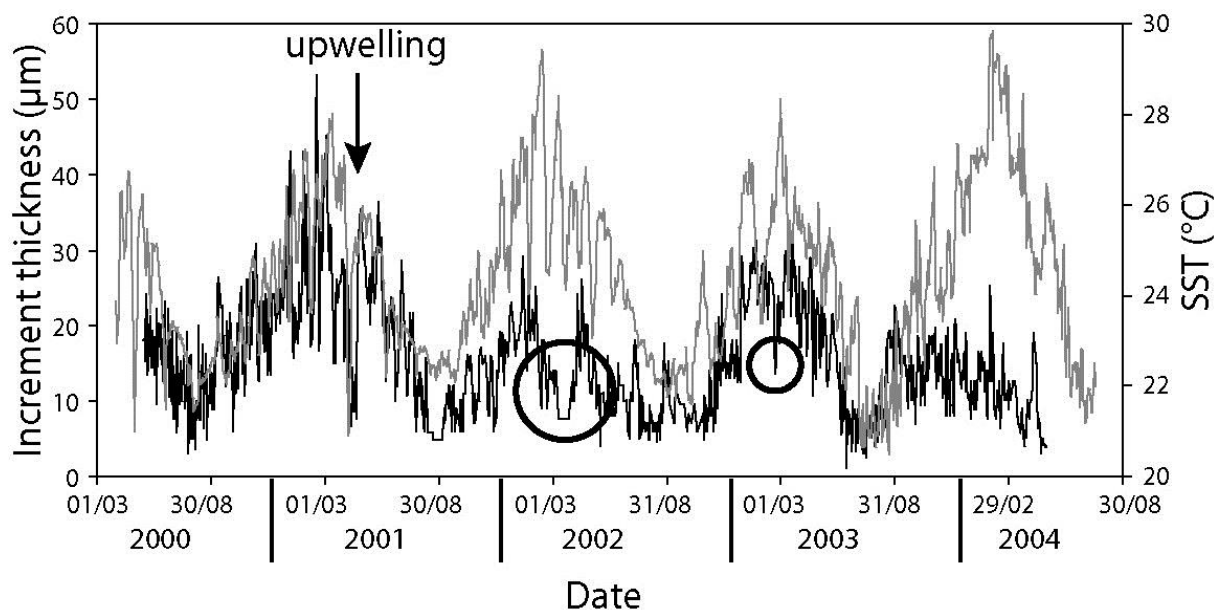


Fig. 12: Relationship between New Caledonian *Tridacna maxima* daily growth, averaged month by month, and monthly averaged SST. (N. Duprey, unpublished data).

Other parameters than SST, either environmental- or physiological-related, have an impact on shell growth. This is evidenced here on *Hippopus hippopus*. Indeed, even if a relationship between daily growth increment thickness changes and SST was established for this species, the relationship is not linear; it is disrupted by both physiological event, like reproduction, and short-term and abrupt environmental change, like upwelling (Fig. 13).



**Fig. 13:** *Hippopus hippopus* daily shell growth increment thickness change (black) and SST instrumental record (grey). The daily growth increment thickness changes are seasonal and roughly follow the SST. The abrupt and short growth decrease in 2001 is related to an upwelling. The growth decreases shown in the circles are non-climatic-related and could be linked to intrinsic or extrinsic factors (reproduction event, disease, predator, etc.) Modified from Aubert et al. (2007).

The absence of a continuous relation between daily increment thickness and SST was confirmed, and its origin specified, by the study of the 5 specimens for which both valvometry and sclerochronological records were obtained over one year of growth. The drop in correlation coefficient between SST and daily growth increment thickness is concomitant to erratic gaping behavior. This erratic behavior, indicator of a stress endured by the animal, is probably a result of both elevated temperature and solar irradiance which have brought the animals close to their upper thermal limit of life (Schwartzmann et al., 2011). Unless the daily growth of *Hippopus hippopus* is better understood, the use of daily growth increment thickness as a direct proxy for SST reconstruction is precluded. Such sclerochronological study should thus rather be used qualitatively.

All the studied shells of Tridacnidae display daily growth increments (Aharon and Chappell, 1986; Duprey et al., 2015 for a review; Pätzold et al., 1991; Watanabe and Oba, 1999) but our two studies are the only ones that attempted to relate the thickness changes of these increment to SST variations in an empiric way. If one wish to obtain quantitative SST data at a monthly or infra-monthly resolution, such sclerochronological studies must be pursued since, at the moment, no other proxy of SST exclusively has been found. Indeed, paleotemperature equations based on oxygen stable isotopes need oxygen isotope ratio of the seawater (see § 2.2.1) to be known and no other paleotemperature equation exists.

## 2.2 The potential of shell geochemistry to reconstruct SST changes

### 2.2.1 Magnesium content and SST: does it work?

If the  $\delta^{18}\text{O}_{\text{shell}}$  as a proxy for SST seems robust for Tridacnidae and most aragonitic mollusks, it remains that "In biogenic carbonates,  $\delta^{18}\text{O}$  is however dependent on both temperature and salinity variations (Epstein and Mayeda, 1953). Because it is difficult to obtain independent information on  $\delta^{18}\text{O}_{\text{SW}}$  or on paleosalinities, complementary geochemical proxies of SST have been actively sought in biogenic carbonates. Variations in Mg/Ca ratios might provide such independent information on (paleo)SST (Bougeois et al., 2016 and reference therein; Bougeois et al., 2014; Klein et al., 1996; Lazareth et al., 2003; Mouchi et al., 2013; Takesue and van Geen, 2004; Ullmann et al., 2013)". *Slightly modified extract from Lazareth et al. (2003)*. In the following I will present studies I undertook to establish if a direct link exists between shell Mg/Ca and SST in three molluscan species, i.e., *Isognomon ehippium* from Kenya, and *Protothaca protothaca* and *Concholepas concholepas* from South America.

#### Main question:

- Is the Mg/Ca ratio in molluscan shells a (reliable) proxy for SST reconstructions?

#### Work done:

- Validation of high-resolution analyses of magnesium in mollusk shells,
- Investigation of the potential link between shell magnesium variations and SST changes.

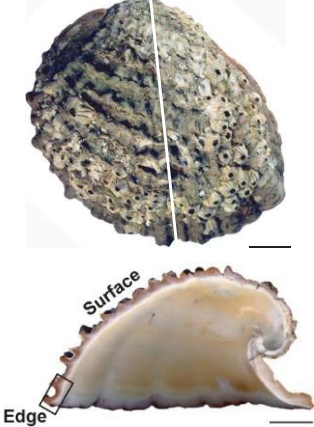
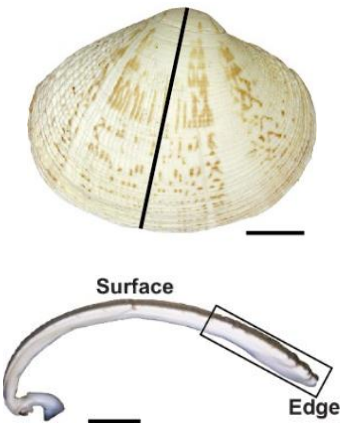
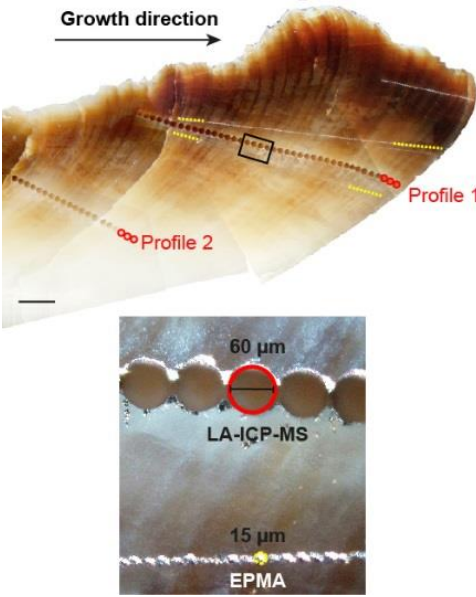
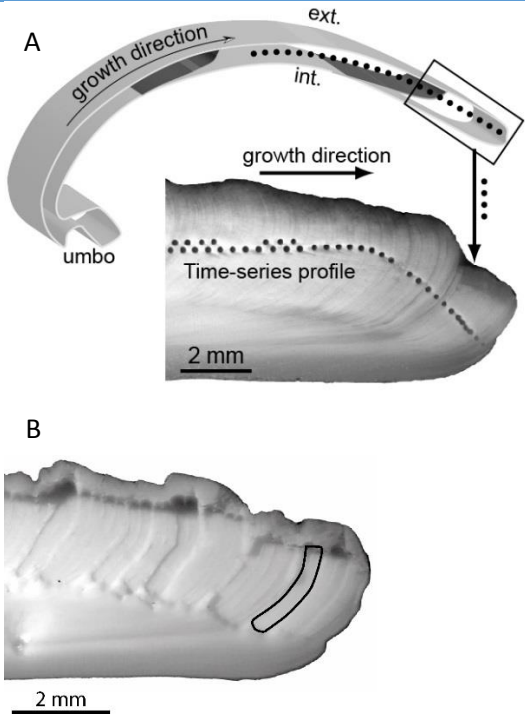
#### Methodologies in brief:

In the followings geochemical studies on *Isognomon ehippium* (Kenya), *Concholepas concholepas*, and *Protothaca thaca* shells (South America), time-series profiles were obtained using laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). As an assessment for the LA-ICP-MS quantitative results, the LA-ICP-MS was completed using electron probe microanalyses (EPMA) for *C. concholepas* and using solution ICP-MS for *P. thaca*. The methodologies are resumed in **Table 1** (for complete description, refer to the cited references). The methodology used to obtain the *I. ehippium* Mg/Ca profiles using LA-ICP-MS is similar to the one used for *P. thaca* ones (details in Lazareth et al., 2003).

#### Main results and conclusion:

In general, the variations of magnesium content in the shells were similar whatever the analytical technique used, LA-ICP-MS, EPMA, or SN-ICP-MS (Lazareth et al., 2007; Lazareth et al., 2013c). Hence the three techniques we used enable to measure Mg content variations in mollusk shell with accuracy, the main difference being the spatial, and thus temporal, resolution (SN-ICP-MS>LA-ICP-MS>EPMA).

Table 1: Resume of the methods used for Mg/Ca studies in the shells of the *Concholepas concholepas* gastropod and the *Protothaca thaca* bivalve.

	<i>Concholepas concholepas</i>	<i>Protothaca thaca</i>
<b>Shell preparation</b>		
The line represents the direction of cut; the box represents the studied shell part. (scale bar: 1 cm)		
<b>Analytical protocol</b>		
Geochemical profiles were obtained by using A. LA-ICP-MS and B. Solution ICP-MS (SN-ICP-MS). In this last case, samples were obtained using a microdrilling device.		

Is the Mg/Ca ratio in molluscan shells a (reliable) proxy for SST reconstructions? The use of Mg/Ca to reconstruct SST is highly species-dependent, and probably also site-dependent. In our studies on 3 different species, 3 distinct behaviors of Mg content shell variations were observed.

In Kenya, *Isognomon ehippium* shells were collected in three creeks along the coast (see fig. 1 in Lazareth et al., 2003). For the 4 shells, Mg concentration varies in a more or less sinusoidal mode. Because the shells collected in the Tudor creek have the clearest seasonal pattern, we tentatively related Mg content variations to SST changes. Despite the overall increase in Mg/Ca value through time, most probably related to ageing of the specimens, a clear main control of SST on Mg/Ca incorporation was observed for those two shells (Fig. 14). However, the relationship between Mg and SST is not that clear for the shells sampled in the two other settings. This indicates that other factors, such as ageing of the specimens but also physiological factors, could influence the Mg incorporation and distribution in the shell. In addition, an empirical equation relating Mg shell content and SST for this species remains to be established.

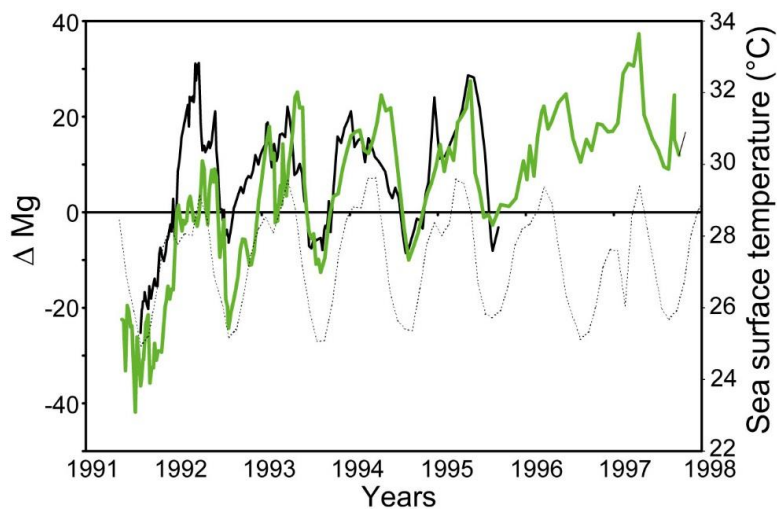
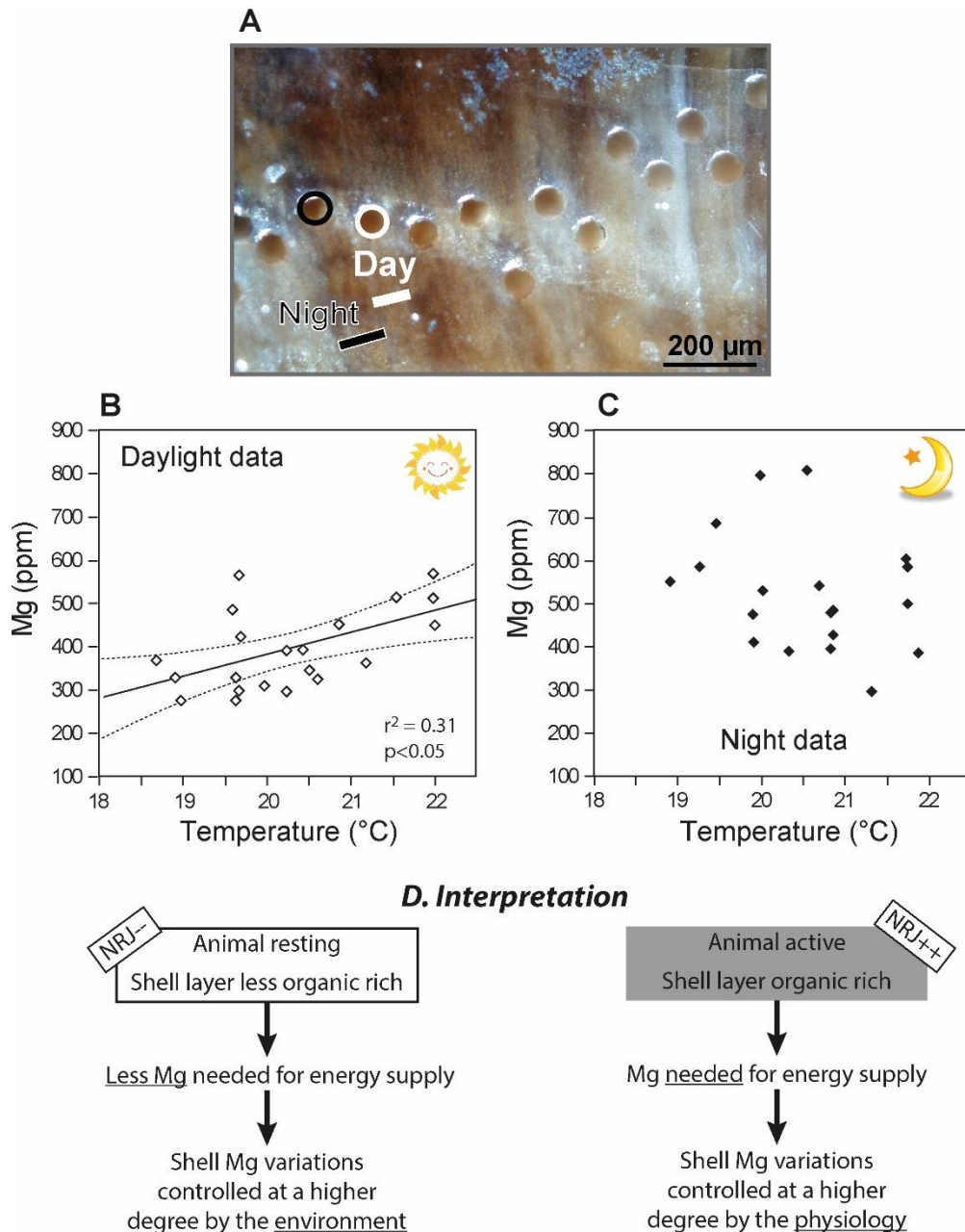


Fig. 14: Relationship between Mg/Ca ratios from Kenyan *Isognomon ehippium* shells (green and black line) and SST (thin dotted line after Reynolds and Smith, 1994). Mg/Ca ratios are expressed as % of variation around the mean (= zero) of each profile, modified from Lazareth et al. (2003).

In *Concholepas concholepas* and *Protothaca thaca* shells, no relationship was observed between Mg/Ca variations and recorded SST. For *Concholepas concholepas*, we made the hypothesis that the lack of correlation between Mg and SST is related to distinct animal behavior between day and night. Indeed, when splitting day and night Mg data, we observed that mean Mg flux into the shell is lower during the day than during the night and that a weak relationship links  $[Mg]_{\text{day}}$  and  $SST_{\text{day}}$ , unlike the  $[Mg]_{\text{night}} - SST_{\text{night}}$  (Fig. 15). These differences were related to the animal activity; resting during the day, moving and feeding during the night. This has consequences on Mg utilization by the animal. Indeed, Mg is used as a cofactor in reactions that involve adenosine triphosphate (ATP), the molecule used to provide energy to the animal, so here potentially more needed during nighttime. In addition, because the shell layer formed during the night is richer in organic matrix (darker, see Lazareth et al. 2007 for more details), this again involves mobilization of more energy for such shell layer to be secreted compared to a shell layer less rich in organics (such as that during daylight). Consequently, during the night, Mg is more specifically allocated to physiological needs of the animal, so its incorporation into the shell is less controlled by the environment conversely to the day pattern

(Fig. 15). "This is the first time that such differences between day and night shell formation and shell composition are found. The complexity of these metabolic processes (yet to be fully understood) should not be forgotten when Mg variations within mollusk shells are investigated with the aim to reconstruct paleo-SST. These processes might account for the inconsistencies reported in the literature regarding the use of Mg as a paleo-SST proxy in other mollusk species." *Extract from Lazareth et al., 2007 (Table 2).*



**Fig. 15: Relationship between Mg and SST in the *Concholepas concholepas* shell depending on the period of the day the shell is secreted. A. Close-up of the subdaily growth pattern of the *C. concholepas* shell, of laser craters, and how they were attributed to daylight or night shell secretion. The black bar highlights the shell layer secreted during nighttime, the white one that secreted during daytime. B. and C. Relationship between Mg and temperature for analyses covering mainly shell deposited during A. daylight and B. the night. B. and C. NRJ - -: energy less needed; NRJ ++: more energy needed. Modified from Lazareth et al. (2007).**



In *Protothaca thaca*, to try to explain the lack of relationship between Mg/Ca and SST variations, we investigated the geochemical homogeneity of layers secreted at a given time; what we named "isochronous profiles". This was done in recent and in old part of different shells and in young ( $n = 2$ ) and older specimens ( $n = 4$ ). The observed Mg/Ca distributions were highly reproducible (Fig. 16). The observed fluctuations of the Mg/Ca ratios along isochronous layers goes against what could be expected when considering that an isochronous layer is deposited at a given - almost instantaneous - moment, corresponding thus to a specific composition of the secreting extra-pallial fluid (EPF; see Appendix A).

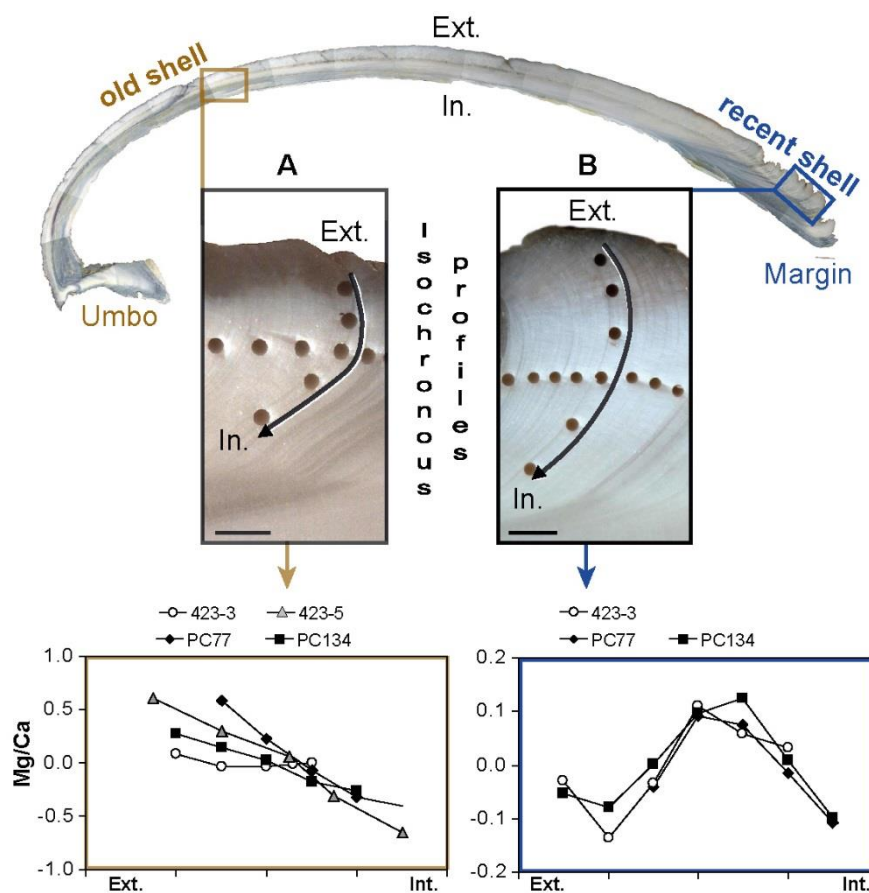
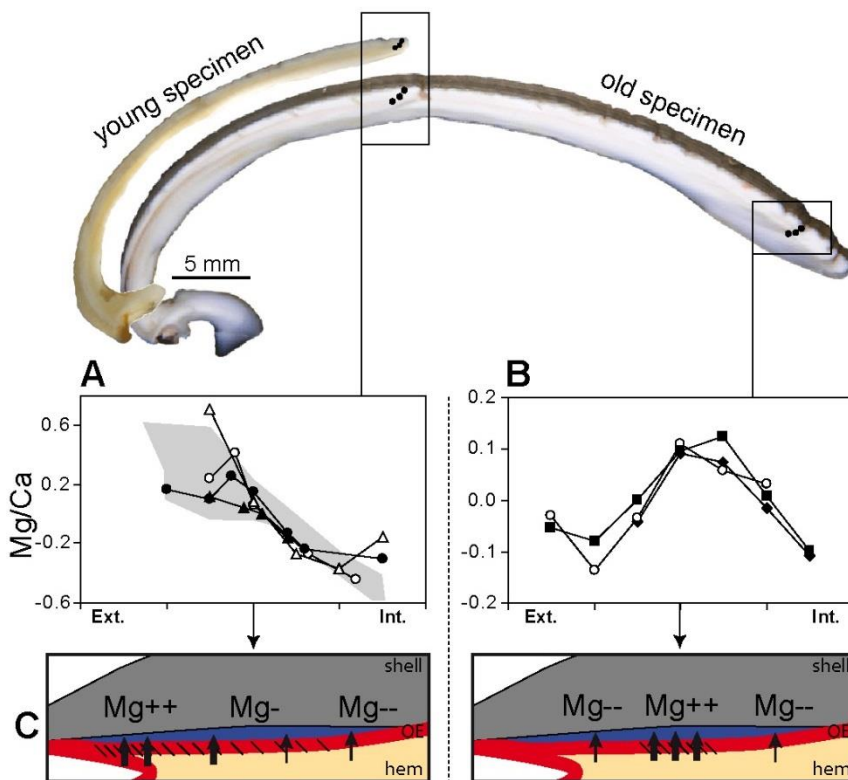


Fig. 16: Protocol followed to study intra-shell Mg/Ca homogeneity along isochronous layers (upper part) and Mg/Ca distribution obtained (lower part; centered data). A. Location and results obtained in old shell part (i.e., close to the umbo) and B. Location and results obtained in recent shell part (i.e., close to margin/shell edge). Mg/Ca is presented as centered element/Ca ratio. "Ext." and "Int.": external and internal side of the outer shell layer.

In addition, patterns are different depending on the location of the isochronous profile within the same shell (Fig. 16). Scanning electron microscopy observations of old vs. recent shell of a same individual collected alive revealed shell alteration in the oldest part (see § 3.2., p. 39). This shell alteration, corresponding to very early diagenesis, might have changed the Mg repartition in the shell, particularly close to the natural environment (external part of the shell). But early diagenesis by itself is not sufficient to explain the isochronous patterns observed as we also found differences in Mg distribution along isochronous profiles between young and old specimens. Indeed, "the isochronous Mg/Ca distributions and ranges at the ventral margin of the young specimens (PC173 and PC180) differ from those observed close to the ventral margin

of the older specimens (Fig. 3a, Table 1), but are similar to the isochronous profiles done far from the ventral margin of the older specimens (Fig. 3; here Fig. 17)." *Slightly modified extract from Lazareth et al. (2013c)*. Without excluding a possible role of very early diagenesis, we suggested that the Mg distributions in the studied *Protothaca thaca* specimens reflect a regionalization of the biomineralizing tissue (i.e., mantle), favoring or not the Mg incorporation in the shell, at a specific location and at a given moment. This mantle regionalization might evolve with the animal ageing (Fig. 17).



**Fig. 17:** Schematic representation of the mantle regionalization hypothesis and of the resulting Mg distribution along isochronous growth layer in *Protothaca thaca* shells. Ext. external side of the shell; Int.: Internal side of the shell. At the top: Picture of a young and of an older *Protothaca thaca* shell section (common scale). A. Mg/Ca distribution observed in old specimens far from the growing edge (grey area) and in young specimens close to the growing edge. B. Mg/Ca distribution observed in old specimens close to the growing edge. C. Corresponding hypotheses in term of mantle zonation and Mg transport from the hemolymph to the shell. Hem: hemolymph; OE: outer epithelium; in blue: extrapalleal fluid. Arrows represent the amount of Mg going through the external epithelium to the EPF and shell. Black slashes on the outer epithelium represent the hypothetical mantle zonation; the more they are tightened, the more there is magnesium in the shell. Modified from Lazareth et al. (2013c).

While a rather good fit between Mg and SST was obtained for some Kenyan *Isognomon ephippium* shells, no relationship between Mg and SST was observed for the South American species *Concholepas concholepas* and *Protothaca thaca*. This observation is probably due to strong physiological impacts. This confirms the complexity of using Mg content in molluscan shells as a proxy for SST and ties with conclusions reached for many other molluscan species (Table 2). Indeed, the possibility of using Mg/Ca as a SST proxy is restricted to a limited number of species, with still some restrictions for some of them. These studies also point out the necessity of improving our knowledge on biomineralization processes, in particular in regards with geochemical proxies' incorporation in the studied biocarbonate.

Table 2: Data on the "validity/invalidity" of using Mg/Ca in marine and estuarine bivalves as a proxy for SST reconstructions. The Mg/Ca ratio was considered as "valid" when a quantitative relationship between Mg/Ca and SST was established. Nevertheless, even if the case of validity of using Mg/Ca for SST reconstruction, restrictions where noted in some cases, reported in the "Remark / Cause" column. In case the Mg/Ca cannot be used for SST reconstruction, the cause is noted in the "Remark / Cause" column. For additional information, please refer to the mentioned references. The column "mineralogy" stands for the mineralogy of the shell layer studied; C: calcite; A: aragonite; Juv.: juvenile; †: fossil. Data from our studies are highlighted in blue.

	Species	Mineralogy	Remark / Cause	Reference
Valid	<i>Ensis siliqua</i>	A		Pearce and Mann, 2006
	<i>Crassostrea gigas (juv.)</i>	C		Mouchi et al., 2013
	"	C	Shell layer dependent	Ullmann et al., 2013
	<i>Crassostrea virginica</i>	C		Surge and Lohmann, 2008
	<i>Isognomon ephippium</i>	C	Ontogenic trend, site dependent	Lazareth et al., 2003
	<i>Ostrea edulis</i>	C	High growth rate	Mouchi et al., 2013
	<i>Patella rustica</i>	C		Ferguson et al., 2011
	<i>Pecten maximus</i>	C	Inner shell layer	Freitas et al., 2009
	<i>Pina nobilis</i>	C	Early growth phase only	Freitas et al., 2005; Richardson et al., 2004
<i>Sokolowia buhsii</i> (†)	C		Bougeois et al., 2014	
Invalid	<i>Chione subrugosa</i>	A		Carré et al., 2006
	<i>Concholepas concholepas</i>	C	Nyctemeral variations (maybe valid for daylight layers)	Lazareth et al., 2007
	<i>Corbula amurensis</i>	A		Takesue et al., 2008
	<i>Hippopus hippopus</i>	A		Yoshimura et al., 2014
	<i>Mesodesma donacium</i>	A		Carré et al., 2006
	<i>Mya arenaria</i>	C	Ontogeny	Strasser et al., 2008
	<i>Mytilus californianus</i>	C	Growth rate, intertidal position	Ford et al., 2010
	<i>Pecten maximus</i>	C	Outer shell layer	Freitas et al., 2009; 2008
	<i>Protothaca staminea</i>	A		Takesue and van Geen, 2004
	<i>Protothaca thaca</i>	A	Shell layer heterogeneity	Lazareth et al., 2013c
	<i>Ruditapes philippinarum</i>	A	Metabolism control	Poulain et al., 2015
	<i>Tridacna gigas</i>	A	Shell layer dependent, ontogeny impact	Elliot et al., 2009; Warter et al., 2015
	<i>Trachycardium procerum</i>	A	SST threshold proxy	Pérez-Huerta et al., 2013
Not conclusive	<i>Diplodon chilensi</i>	A		Soldati et al., 2009
	<i>Phorcus lineatus</i>	A+C		Garcia-Escarzaga et al., 2015
Controversial	<i>Arctica islandica</i>	A	Crystal fabric controlled, organic-matrix	Foster et al., 2008; Schöne et al., 2013; Schöne et al., 2010; Shirai et al., 2014
	<i>Mytilus edulis</i>	C		Freitas et al., 2009; Freitas et al., 2008; Rosenberg and Hughes, 1991; Rosenberg et al., 2001; Vander Putten et al., 2000; Wanamaker Jr. et al., 2008



### 2.2.2 Calibration of $\delta^{18}\text{O}$ in Tridacnidae shells

Because of the potential use of Tridacnidae for environmental reconstitutions and to establish the link between shell  $\delta^{18}\text{O}$  and SST, I tried to calibrate the relationship between  $\delta^{18}\text{O}_{\text{shell}}$ ,  $\delta^{18}\text{O}_{\text{sw}}$ , and SST for two giant clam species, *Hippopus hippopus* and *Tridacna maxima*, in relation to SST, SSS or  $\delta^{18}\text{O}_{\text{sw}}$  (or both) of the surrounding environment.

#### Main question:

- Which equation relates  $\delta^{18}\text{O}_{\text{shell}}$  and SST for *Tridacna maxima* and *Hippopus hippopus* species?

#### Work done:

- Follow up of growth of living *H. hippopus* and *T. maxima*, with environmental monitoring,
- Isotopic analyses of the shells and establishment of the  $\delta^{18}\text{O}_{\text{shell}}$ -SST relationship.

#### Methodology in brief

The studied "*Tridacna maxima* / ***Hippopus hippopus*** / specimen were collected on September 22, 2008, at 2.5 meters depth, on the outer crest of the barrier reef surrounding the main island of New Caledonia (Fausse Passe de Uitoé, 22°17'S; 166°11'E - Fig.1) **and at 2 m water depth, at Ducos Island in the Bay of Saint Vincent in New Caledonia (166°E, 21°60S)**. The specimen was then placed in an open-air, i.e., no roof and non-shaded, seawater-fed tank for a 1.5 year-long / **14.5 months** / experiment at the Aquarium des Lagons, Nouméa, New Caledonia (Fig.1; here **Fig. 18**). The water level in the tank was kept constant (~ 80 cm) during the experiment." *Slightly modified extract from Duprey et al. (2015)*.

During the period of specimen growth in aquarium, SST was measured using a data-logger. For SSS, this parameter was measured using a data-logger in the case of the first experiment, established for *H. hippopus*. Seawater sampling for SSS and  $\delta^{18}\text{O}_{\text{sw}}$  measurements; at a weekly resolution; were added for the *T. maxima* experiment. Shells were prepared as described previously (§ 2.1.2, p. 21) and the inner layer for *H. hippopus* and the outer layer for *T. maxima* were sampled for isotopic analyses using a microdrilling device (Micromill, Merchantek®).

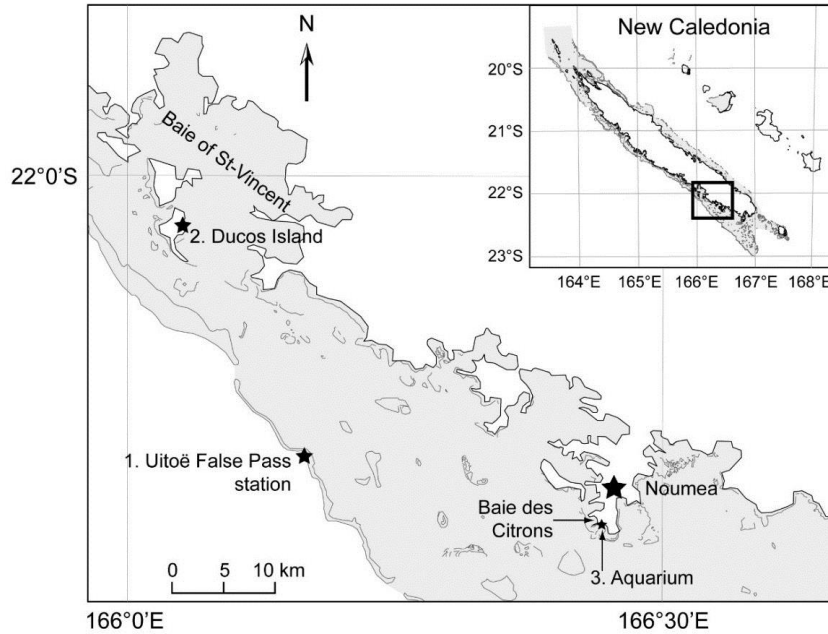


Fig. 18: Localization of *in situ* giant clam specimens collection (1.: *Tridacna maxima*; 2.: *Hippopus hippopus*) and of the Aquarium des Lagons (3.). Modified from Aubert et al., 2009.

#### Main results and conclusion:

Which equation does relate  $\delta^{18}\text{O}_{\text{shell}}$  to SST for *Tridacna maxima* and *Hippopus hippopus*? Based on the previous sclerochronological work, the shell isotopic measurements were placed along time that permitted to attribute a SST and  $\delta^{18}\text{O}_{\text{sw}}$  value to each shell sample. The shell growth rate variations through time were also considered to average the SST data (acquired at an infra-daily resolution) for each microdrilled sample (see Aubert et al., 2009; Duprey et al., 2015 for details). The resulting paleo-temperature equations, together with previous ones from the literature, are gathered in Table 3.

Even if SST is the main driver for  $\delta^{18}\text{O}_{\text{shell}}$  changes, the obtained  $R^2$  are below or equal to 0.70. This is quite low, moreover for our studies where environmental data were mostly measured beside the specimens and for which  $\delta^{18}\text{O}_{\text{sw}}$  were available in the case of *T. maxima*. In addition to the short period of studied shell growth in the case of Watanabe and Oba (1999) and Duprey et al. (2015) studies, various parameters can explain these relatively low  $R^2$ . In the case of the *H. hippopus* calibration, the environmental data were not all available beside the specimens, therefore differences between real environment and used environmental data might have occurred. Additionally, environmental data are rarely acquired at the same resolution than shell isotopic samples (or inversely). Consequently, some environmental data had to be averaged (e.g., SST data) or, conversely, others were missing (e.g.,  $\delta^{18}\text{O}_{\text{sw}}$  measurements were non-continuous). Nevertheless, "Overall, the temperature reconstructed with Eq. 2 yielded reliable values and reproduced nearly 70 % of the temperature seasonal amplitude. This equation provides thus a way to reconstruct SST values from giant clam species for which no SST =  $f(\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{sw}})$  equation is available: *Tridacna gigas*, *T. squamosa*, *T. crocea*, *T. derasa*, [...]. This equation also offers the

opportunity to standardize paleoclimatic reconstructions based on giant clam isotopic records by obtaining comparable SST datasets." *Extract from Duprey et al. (2015).*

**Table 3: Parameters of the transfer functions available for giant clams. The linear model used is:  $\Delta\delta^{18}\text{O} = a \text{ SST} + b$ , where SST is the sea surface temperature in Celsius degrees and  $\Delta\delta^{18}\text{O}$  is the difference between the stable oxygen isotope ratio of the shell and of the seawater ( $\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{sw}}$ ) expressed in ‰ VPDB. *Tm, Tg* and *Ts* stand for *Tridacna maxima*, *Tridacna gigas* and *Tridacna squamosa*, *Hh* for *Hippopus hippopus*; HR: high resolution sampling. N: number of specimen; Var.: for the Aharon and Chappelle (1983) study, the number of specimen differs according to temperature. L.: length of shell growth period studied. n.a.: not available. Modified from Duprey et al. (2015).**

	Genus	Sampling	n	L.	a	b	R <sup>2</sup> #	1 $\sigma$ *	Source of the datasets	
									SST	$\delta^{18}\text{O}_{\text{sw}}$
<i>Aharon and Chappelle, 1983</i>	<i>Tm, Tg, Ts</i>	bulk	Var.		-4.42	21.30	n.a.	n.a.	<i>in situ</i>	n.a.
<i>Watanabe and Oba, 1999</i>	<i>Hh</i>	HR	1	11 months	-3.91	22.40	0.70	1.36	8 km away	8 km away**
<i>Aubert et al., 2009<sup>1</sup></i>	<i>Hh</i>	HR	1	3 yrs	-2.87	21.40	0.67	0.91	in tank / 40 km away	25 km / 40 km away**
<i>Equ. 1 (this study)</i>	<i>Tm</i>	HR	1	8 months	-3.96	20.12	0.63	1.44	<i>in situ</i>	<i>in situ</i>
<i>Average equation for giant clams (Equ. 2)</i>	<i>Tm, Tg, Ts, Hh</i>	-	31		-3.79	21.31	-	-	-	-

<sup>1</sup>the giant clam specimen used in this study grew *in situ* and in a tank.

#SST vs.  $\Delta\delta^{18}\text{O}$

\*standard deviation of residuals

\*\*reconstructed from SSS

### III / DIAGENESIS ASSESSMENT: AN ESSENTIAL STEP

As stated in the Chap. I (§ 3), the molluscan shell or the coral skeleton microstructure and geochemical composition are not necessarily stable through time. Because environmental reconstructions are done based on the link between geochemistry and the environment at the time the considered animal build its skeletal structure, any ulterior (post-secretion) change will thus not reflect anymore the environment in which they grew. While studying various biocarbonates as potential archives of environmental changes, I thus pay a specific attention to any microstructural and geochemical modifications and propose hypotheses to explain observed diagenesis features.

### 3.1 Molluscan shell alterations

#### 3.1.1 Diagenesis on mollusk shells from specimen collected alive

Peruvian and Chilean *Protothaca thaca* shells were studied both in terms of sclerochronology (§ 2.1.1, p. 19) and geochemistry. Different geochemical signatures were obtained depending on the location of the isochronous profiles done; in recent or past secreted shell (§ 2.2.1, p. 28). Because shell diagenesis can alter the pristine geochemical signature, the possible occurrence of such process was investigated.

##### Main question:

- Is there a microstructural difference between old and recent secreted shell?
- If such microstructural difference exists, could this difference be related to different geochemical signatures observed?

##### Work done:

- SEM observations on recent and old secreted shell pieces of same specimens.

##### Main results:

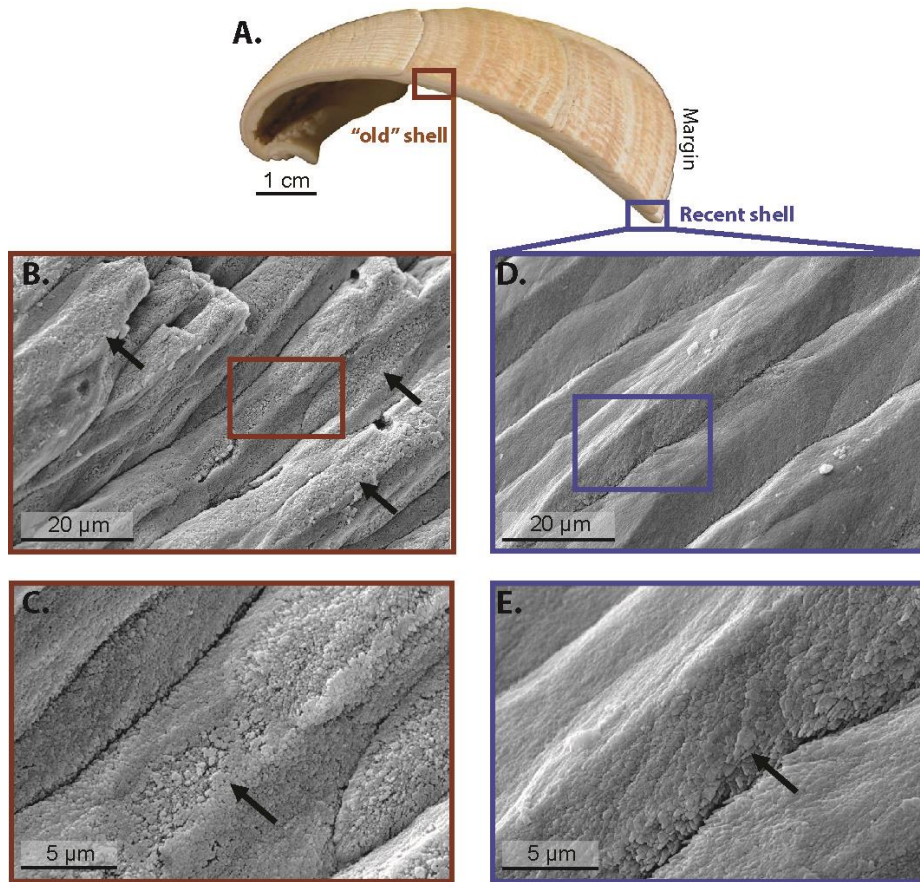
**Is there a microstructural difference between old and recent secreted shell?** The examination of the microstructure of recent and old secreted parts of *Protothaca thaca* shells revealed that "The surface of the prisms close to the ventral margin was relatively smooth, constituted by micrometer-sized scales (Fig. 6a & c; [here Fig. 19 D & E](#)). Older prisms showed an altered surface; the scale edges seemed to have been slightly dissolved and the surface of the prisms was granular (Fig. 6b & d; [here Fig. 19 B & C](#)). All specimens examined presented the same patterns. [...] The shell microstructure of old shell part (far from growing ventral margin) was altered with slight dissolution of the prisms, even on specimens collected alive (early diagenesis). Pyritization was observed at the surface and inside living shells collected in marshes (Clark and Lutz, 1980). Inside the shells, the pyrite was located in specific places where the shells were weak (e.g., holes, fractures, zones rich in organic matter)." *Extract from Lazareth et al. (2013c).*

**If such microstructural difference exists, could this difference be related to different geochemical signatures observed?** "This shell alteration might indeed have favored some balancing of the shell composition with the surrounding seawater, the external part of the old shell becoming relatively enriched in trace elements ([Fig. 16, p. 32](#)). The occurrence of such early diagenesis, and of its



consequences in terms of geochemical signature of the shell, should be evaluated on other molluscan species, in particular on long-lived ones." *Extract from Lazareth et al. (2013c)*.

"Nevertheless, we also observed similar trace element distribution for isochronous profiles far from the ventral margin in old altered shell (PC77 and C00-423-3) and closer to the ventral margin in more recent shell with no clear microstructure alteration (PC134; C00-423-5). Therefore, early diagenesis alone is insufficient to explain the different trace element distribution along isochronous profiles done close to and far from the ventral margin." *Extract from Lazareth et al. (2013c)*.



**Fig. 19:** Live-collected *Protothaca thaca* shell diagenesis study. **A.** Half-shell view showing the shell parts observed under scanning electron microscope. **B to E.** Scanning electron microscope images of recent and old outer (prismatic) layer of *Protothaca thaca* shell (specimen PC77). **B. and C.** Prisms far from the ventral margin; i.e., old shell. The surface of the prisms is granular because of slight dissolution (arrows). **D. and E.** Prisms close to the ventral margin; i.e., recent shell. The surface of the prisms is regular and composed of micrometer scales (arrow in E). The white spots on the picture D are small remains from the preparation.

The fact that shell of a living specimen can be subjected to dissolution is new and very important since such modification could alter the geochemical composition. An accurate screening of biocarbonate integrity remains a prerequisite before undertaking geochemical studies.

### 3.1.2 The dense shell of Tridacnidae: not always devoided of diagenesis

Among the numerous edible molluscan species, the Tridacnidae are often found in archaeological sites in the south-west Pacific (Asami et al., 2014; Clark et al., 2006; Galipaud and Kelly, 2007). In addition to the fact that Tridacnidae bivalves are commonly consumed, their shell, thanks to its hardness, was used as tools like axes and adzes or ornaments (Haslam and Liston, 2008; Kinch, 2008; Szabó et al., 2007; Weisler and Marshall, 2001). Nevertheless, such shells left by humans, usually after flesh consumption, might have been cooked and left in conditions that might be not adequate for a proper preservation through time. In this context, two giant clam shells from the Philippine were studied to investigate if such shells were sufficiently well preserved to reconstruct environmental conditions around the Mid-Holocene, a key period of the past (Chap I, § 1.4, p. 17).

Another key periods is the Last Interglacial (LIG), between ~130-118 ka BP, also named MIS5e. This climatic stage is characterized, at a global scale, by temperatures and a sea level higher than today (Kukla et al., 2002). Here I will present essentially some characteristics of the diagenesis observed in New Caledonian and Kenyan *Tridacna gigas* fossils from that period as well as preliminary results on its impacts on geochemistry.

To ease the reading of the following paragraph, I briefly present the structure and the microstructure of Tridacnidae shells. The aragonitic Tridacnidae shell is made of three main zones: the hinge area, the external and the inner layer (Fig. 20). The hinge area and the external layer have a crossed-lamellar microstructure while the inner shell layer is prismatic (Fig. 20). The external layer has the higher growth rate, therefore it is the best choice to obtain environmental reconstitution at a high resolution. In *Hippopus hippopus*, this shell layer is however often highly bioeroded, precluding geochemical analyses in this part. Consequently, analyses in *H. hippopus* shells are done in the inner layer. In *Tridacna gigas* shells reconstruction are also generally obtained from analyses in the inner shell layer. In *T. maxima*, analyses are done in the external layer since the inner layer is too thin to obtain sufficiently high-resolution data.

#### Main questions:

- Which kind of diagenesis can affect giant clam shells?
- Can the studied fossil shells be used for environmental reconstructions?

#### Work done:

- Micro-FTIR analyses and SEM observations on *Hippopus hippopus* and *Tridacna maxima* shells, XRD analyses and SEM observations on *Tridacna gigas* shells.

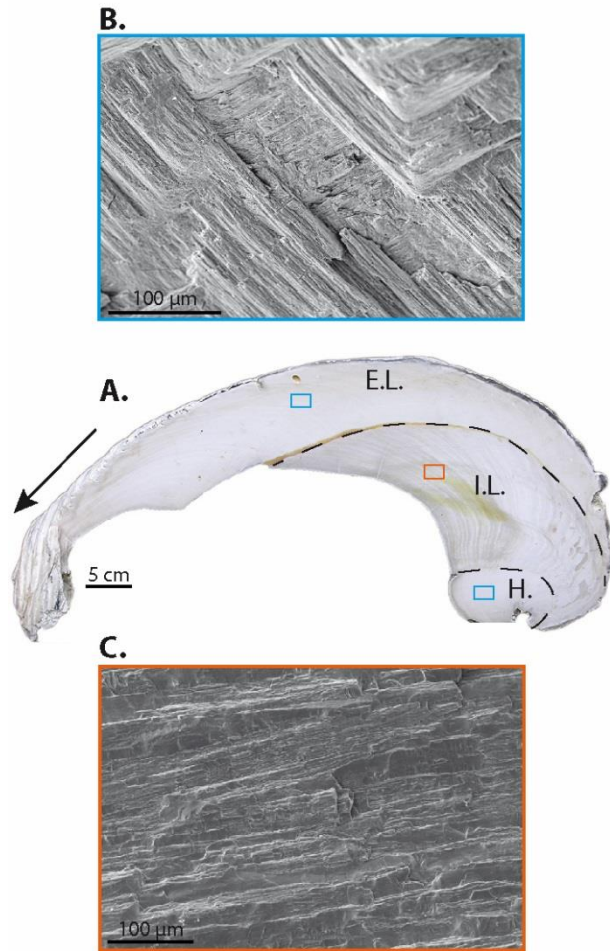


Fig. 20: Tridacnidae shell organization and microstructure. A. Cross-section of a *Tridacna maxima* shell with the organization of the different layers. E.L.: external layer; I.L.: inner layer; H.: hinge area. The blue and orange rectangles refer to the scanning electron microscope (SEM) images in B. and C. The arrow represents the growth direction. B.: SEM view of the crossed-lamellar microstructure representative of the external layer and hinge area. C. SEM view of the prismatic microstructure representative of the inner layer.

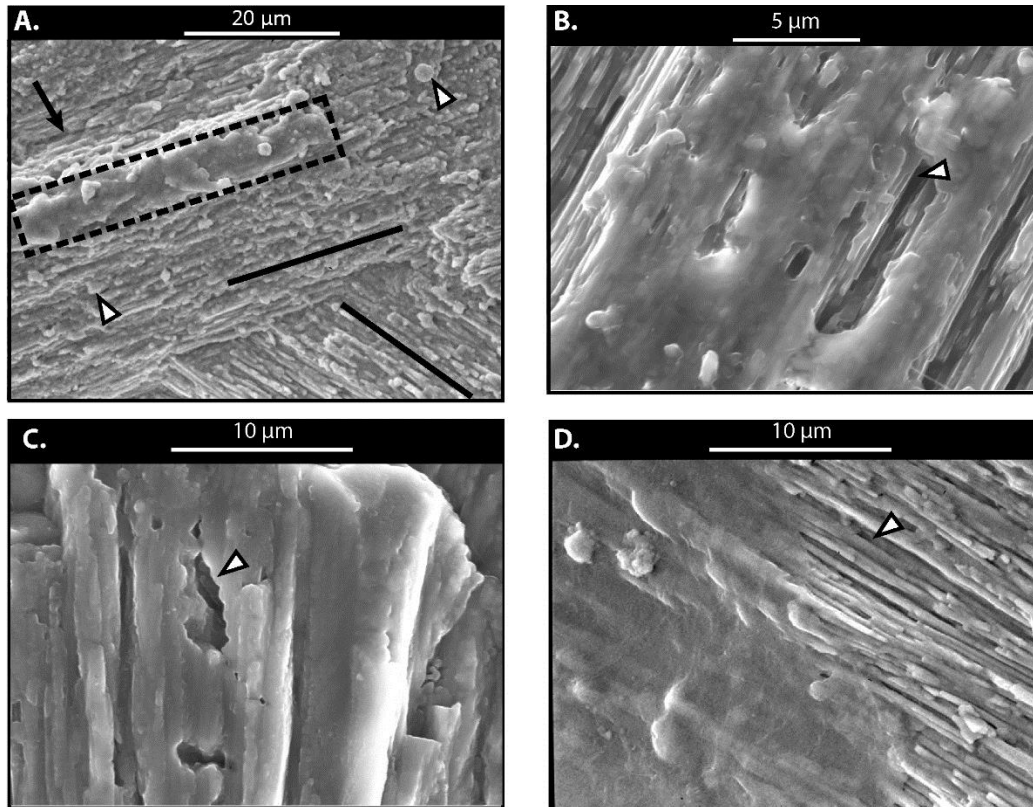
#### Methodology in brief:

Micro-Fourier Transform Infrared (micro-FTIR) analyses were done on polished cross-sections of the selected shells. This technique allows to obtain the mineralogical composition at a high spatial resolution (20-350 µm). Scanning electron microscope observations were done on broken pieces of the shells. To preserve potential dissolution features related to diagenesis alteration, the shell (or coral) pieces were not etched before SEM observations.

#### Main results:

**Which kind of diagenesis can affect giant clam's shells?** In the archaeological shells, "even if the shells are still aragonitic, their microstructural arrangements have been altered. [...] In the crossed-lamellar layer of the *Tridacna maxima* shell, even if the two directions of the shell's microstructure remained unchanged, the elongated crystals were not visible (Fig. 6a) and the lamellae of the crossed-lamellar microstructure were dissolved (Fig. 21 A and B). Moreover, some parts seemed like "melted" (Fig. 21 B). The prisms of the inner layer were dissolved and started to recrystallize in a

similar way as that observed in the external shell layer. [...] *At a high magnification, the crystals of the Hippopus hippopus external shell layer are partly dissolved. In the inner layer, gulfs of dissolution and "melted" aspects were observed on the prisms (Fig. 21 C and D).*" Modified extracts from Faylona et al. (2011). Dissolution features were also observed in the other studied species, with some variety in the dissolution patterns (Fig. 22).



**Fig. 21:** Characterization of the shell preservation of the Tridacnidae shells studied (SEM images). A. Example of a *Tridacna maxima* altered crossed-lamellar microstructure (external shell layer) with dissolution pattern between aragonite crystals (black arrow) and loci of recrystallization (white arrows); the black lines mark orientation of elongated aragonite crystals and the dotted box outlines a "melted" texture. B. Enlargement of a "melted" part of the crossed-lamellar microstructure. C. and D. Altered prismatic microstructure of the inner shell layer of a *Hippopus hippopus* specimen with dissolution in C. (white arrow) and dissolution (white arrow) and "melted" part in D. Modified from Faylona et al. (2011).

Alteration visible to the naked-eyes is present on some *Tridacna gigas* and *Hippopus hippopus* shells (Fig. 23). These patches are made of calcite (micro-FTIR), those calcite crystals being easily recognizable via SEM observations since they present a mineralogical habitus of calcite such as that of geological calcites (

Fig. 24). Magnesium calcium carbonate, most probably dolomite, was also detected in a *T. gigas* shell.

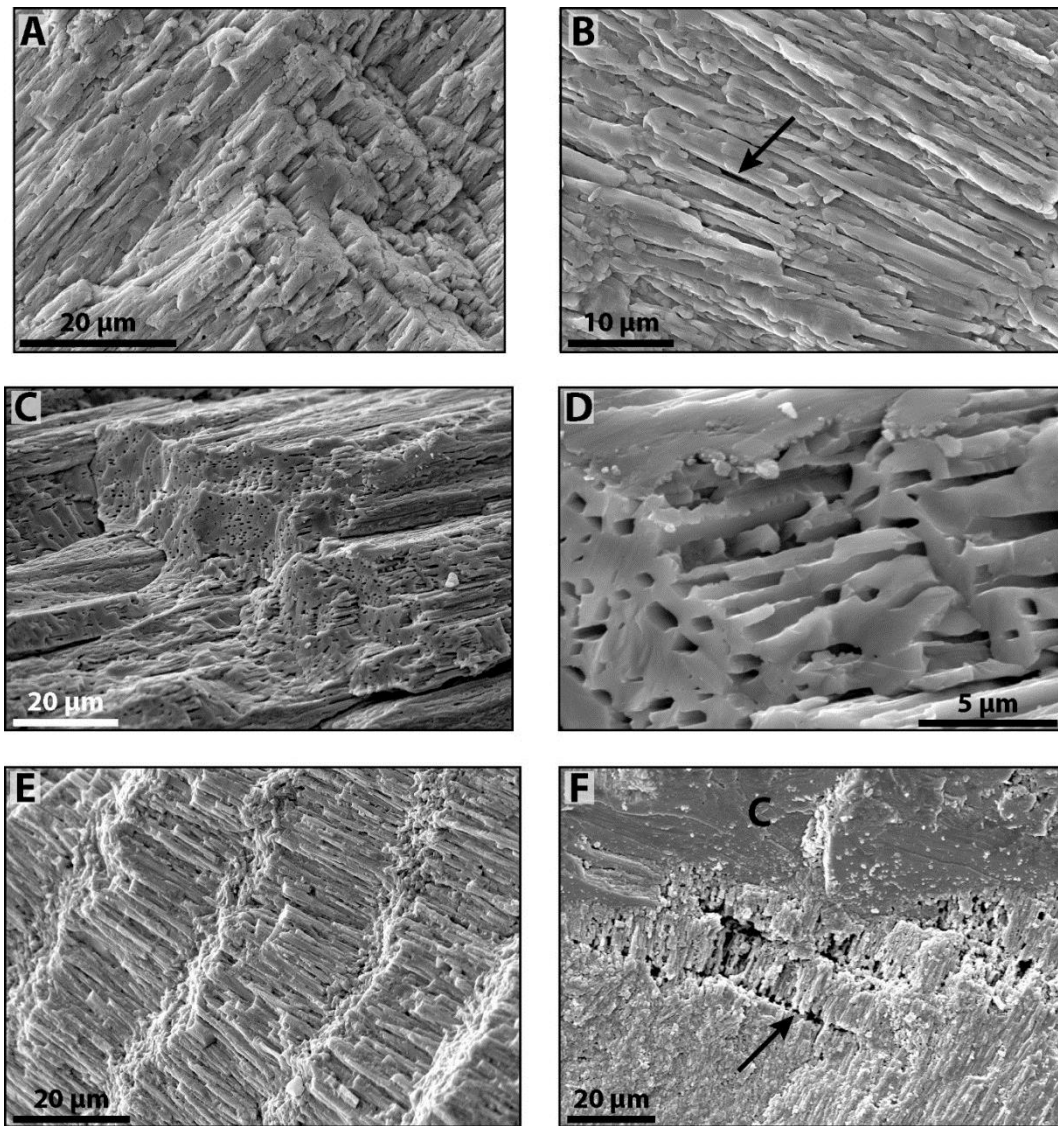


Fig. 22: Dissolution patterns observed in various archeological and fossil Tridacnidae shells. A., B. Slight dissolution of the prismatic layer of *Hippopus hippopus* (A.) and *Tridacna gigas* (B.) with the prisms starting to be disjoined (arrow in B.). C., D. Significant dissolution in the prismatic layer of a *T. gigas* specimen. The dissolution led here to the appearance of more or less connected channels, parallels to the longest prism's axis. E. F. Dissolution located more specifically along growth lines (arrow in F.). This led to the stair-like appearance in E. In F., some parts are more dissolved and the upper part is already in calcite (C). (Lazareth et al., unpublished data).

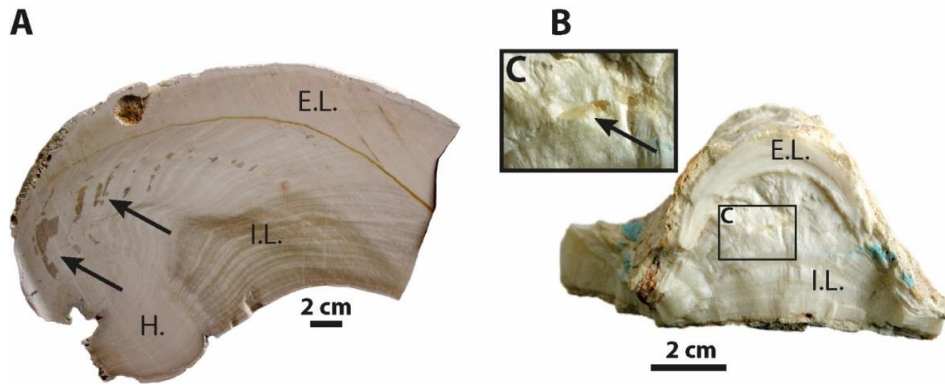


Fig. 23: Macroscopic view of two of the studied *Tridacna gigas*. A. Section of a *T. gigas* from New Caledonia, longitudinal cut, growth of the inner layer goes down. B., C. Piece of a *T. gigas* from Kenya, transversal cut (shell growth toward the reader). Arrows point the altered portions. E.L.: external layer; I.L.: inner layer; H.: hinge area. Lazareth et al. (unpublished data).

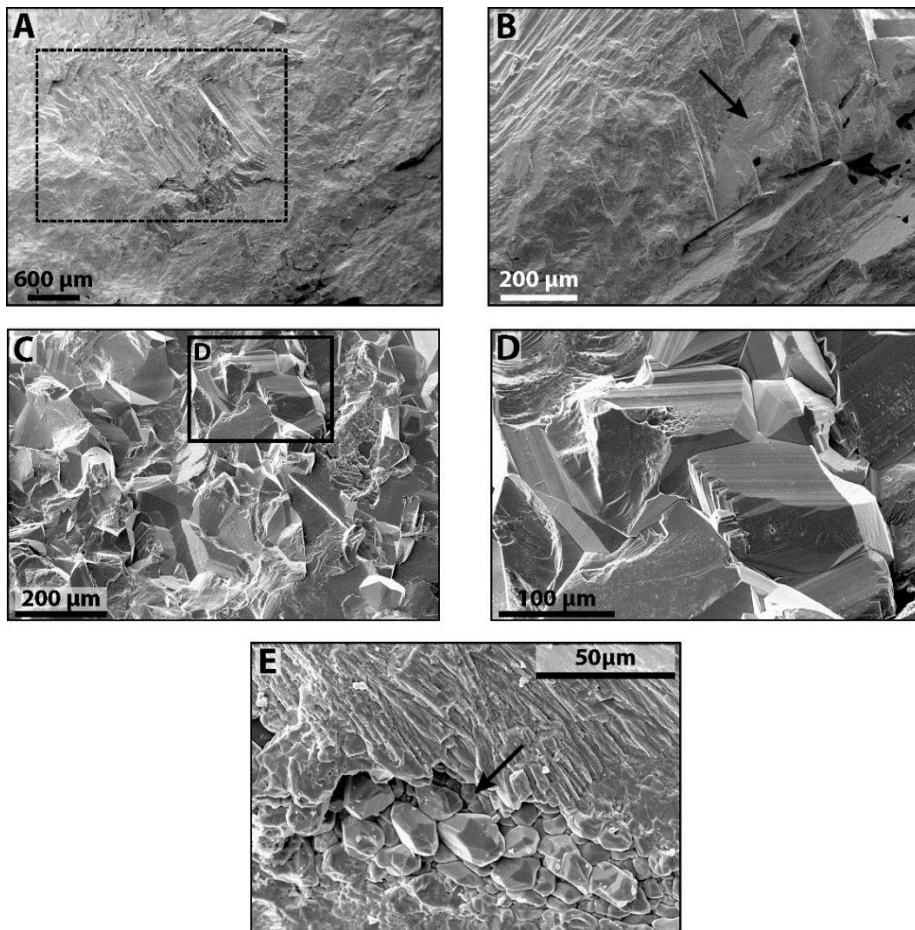


Fig. 24: Examples of calcite crystals present in altered aragonitic shell layer of Tridacnidae. A., B. Massive calcite crystals in the inner layer of a Kenyan *Tridacna gigas*. Dotted-line rectangle in A. surrounds the calcite patch. The arrow in B. points a massive calcite crystal face. C., D. Massive calcite crystals in the inner layer of a New Caledonian *T. gigas*. E. Calcite crystals filling a void, probably left after dissolution, in the inner layer of a New Caledonian *T. gigas* (Lazareth et al., unpublished data). Note the difference in habitus of the crystals between the Kenyan and the New Caledonian shell.

Can the studied fossil shells be used for environmental reconstructions? The presence of dissolution features in Tridacnidae shells should "exclude any geochemical studies for paleo-environmental reconstructions [...]. Indeed, it was shown that the dissolution and the degradation of the biocarbonates organic matrix change their geochemical composition (Buchardt and Weiner, 1981; Cuif et al., 1997; Hendy et al., 2007). Geochemical studies on the *dissolved* shells of Tridacnidae could provide anyway information on the mobility of chemical elements during *such* diagenesis. For paleo-environmental reconstructions based on giant clam geochemistry, better-preserved shells have to be found. *Concerning archaeological settings*, such shells could occur in sites less subjected to the percolation of meteoric waters. Moreover, larger shells should also offer a better material because the diagenesis may not have (completely) affected the inner shell layer." *Slightly modified extract from Faylona et al. (2011)*. The "melted" parts observed in some shells (Fig. 22) were interpreted at first as diagenesis features. Afterwards, many additional SEM observations on other shells, or corals, make me think that these microstructural aspects are rather organics, either that of the shell - the organic matrix - or that of micro-organisms that can colonize shells (bacteria, micro-algae, fungi; e.g., Radtke and Golubic, 2005; Tribollet and Golubic, 2011; Fig. 25). A study to determine if there were geochemical differences between more or less colonized substrata was realized on corals (Brahmi et al., 2014). This study did not show major differences between samples. However, possible biases in the methodology does not allow to end definitively on this point. Because Tridacnidae shells often contain numerous micro-bioeroders, the potential impact of these bio-eroders on the geochemical signature should be investigated or, at least, such bio-eroded zones should be carefully avoided while analyzing shells for environmental reconstructions.

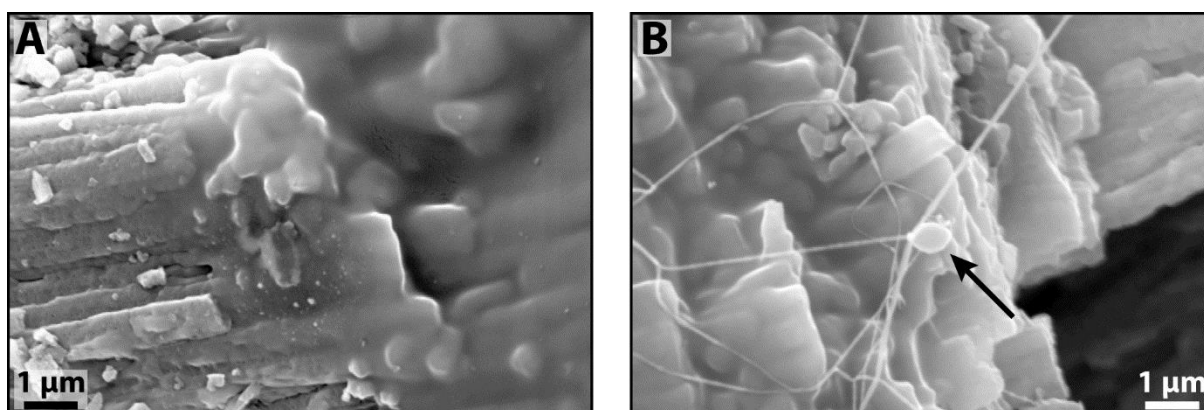


Fig. 25: Organics in the external layer of an archaeological *Tridacna maxima* (SEM views) A. Organic layer recovering crystals. B. Organic layer recovering crystals (left of the picture) and filaments, probably endolithic fungi (Golubic et al., 2005; Grange, 2015). Lazareth et al. (unpublished data).

Because dolomite is a magnesium calcium carbonate, apart if one can avoid sampling the shell areas containing such secondary crystallization with certainty, it is probably imperative to rule out such samples for environmental reconstructions based on geochemistry. Concerning calcite, its presence does not necessarily preclude any geochemical studies since the patches are easily

identifiable, but care must be taken and each case carefully studied. Indeed, in a preliminary geochemical study of fossil *Tridacna gigas* from New Caledonia, the geochemical signature of the calcite;  $\delta^{18}\text{O} = -4.45 \pm 0.44 \text{ ‰}$ , was found to be very different than that of the pristine aragonite,  $\delta^{18}\text{O} = -0.29 \pm 0.37 \text{ ‰}$  (Fig. 26). If calcite was not observed everywhere on the surface of the sample, it was sometimes all the same present slightly below and sampled anyway. The geochemical signature of such samples represented a mixture between the aragonite and the calcite one. Environmental reconstructions based on such samples would thus have been biased.

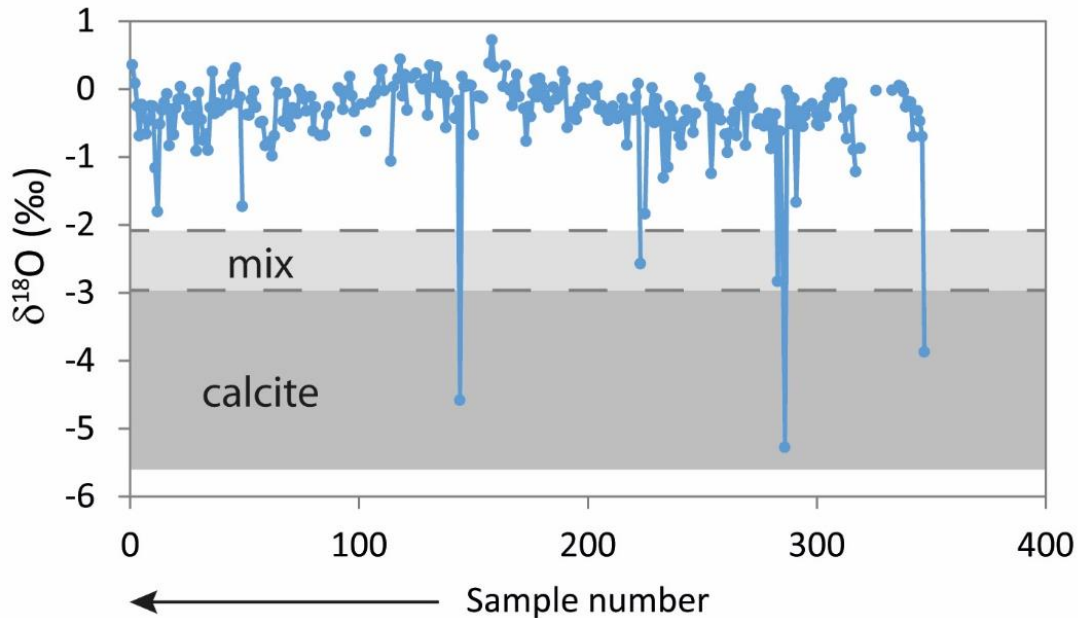


Fig. 26: Effect of the presence of calcite patches on the  $\delta^{18}\text{O}$  signature in a fossil *Tridacna gigas* shell. The  $\delta^{18}\text{O}$  profile was done along the shell growth (growth direction indicated by the arrow). Most samples have a pristine signature (above -2 ‰), others, clearly collected on calcite patches, have very low  $\delta^{18}\text{O}$  values (calcite), and some are intermediary (mix). The limits between calcite-mix and mix-aragonite in terms of  $\delta^{18}\text{O}$  value cannot be fixed with certainty. (Lazareth et al., unpublished data).

To conclude, if calcite/dolomite patches can easily be identified in Tridacnidae shells, one should still take care at the geochemical interpretations even if the line along which analyses were done avoids such patches. In addition, I observed that dissolution features are quite abundant in archaeological and fossil Tridacnidae shells, whatever the considered shell layer. Since dissolution impacts the pristine geochemical signature of the studied biocarbonate (references above and § 3.1, p. 47), a preliminary screening, and evaluation of the degree of dissolution, in the shells should be systematically done. This is not currently the case and most papers presenting paleo-reconstitutions based on fossil Tridacnidae shells either do not screen for diagenesis or only rely on aragonite preservation (e.g.; Batenburg et al., 2011; Yan et al., 2015; Yan et al., 2014).

### 3.2 Coral skeleton diagenesis and its impact on geochemical tracers



In the tropics; besides recent studies that use Tridacnidae shells; the main archive used to obtain infra-annual data on recent and past SST and SSS is the coral skeleton, mainly the massive *Porites* sp.. *Porites* sp. can grow for several decades to centuries and the skeleton it leaves can thus provide long records of past environmental changes (Beck et al., 1992; Corrège, 2006; Gagan et al., 2000; Smith et al., 1979; Weber, 1973). The incorporation of various trace elements (Sr, Mg, U, rare earth elements, etc.) and of the oxygen (O) and carbon (C) stable isotopes in the biogenic aragonite skeleton depends on environmental conditions and may thus document on both past climates and anthropogenic disturbances (Al-Rousan et al., 2007; Alibert and McCulloch, 1997; Carriquiry and Horta-Puga, 2010; Corrège, 2006; Corrège et al., 2004; Tudhope et al., 2001). However, the skeleton of corals is porous and fragile that renders it more prone to diagenesis alteration than other biocarbonates more compact and dense like the giant clam shell (Fig. 27).

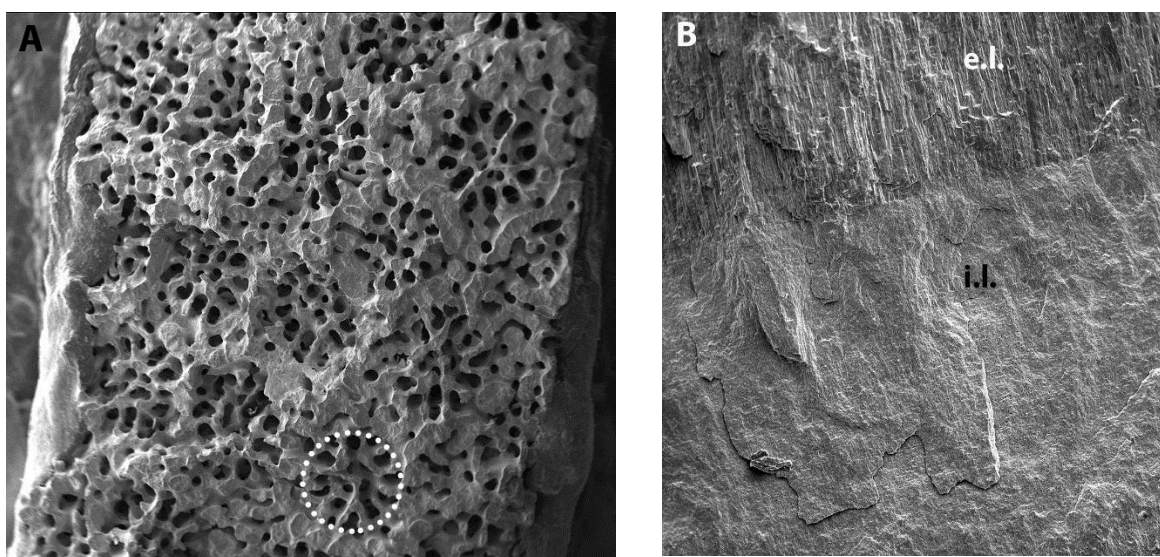


Fig. 27: Comparison between coral skeleton and giant clam shell. A. *Porites* sp. skeleton (secondary electron microscope-SEM image, 3 mm) where the corallite is visible (circle), together with the porosity. B. giant clam shell (*Tridacna maxima*, SEM image, 2 mm). The two layers that constitutes the compact shell are visible: the external (e.l.) and the inner layer (i.l.).

"Submarine<sup>3</sup> and freshwater diagenesis can affect the coral skeleton microstructure and chemistry. The submarine diagenesis is mainly characterized by the occurrence of secondary aragonite (MacIntyre, 1977) and the freshwater diagenesis is characterized by skeleton's aragonitic dissolution and low-magnesian calcite precipitation (Pingitore, 1976). Both diagenesis types affect both the trace element ratios and the stable isotope values of the coral skeleton (e.g. Allison et al., 2007; Bar-Matthews et al., 1993; Hathorne et al., 2011; Hendy et al., 2007; McGregor and Gagan, 2003; Zazo et al., 2002). Therefore, environmental reconstructions based on such diagenetically-

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<sup>3</sup> For coral colonies that stayed in contact with seawater essentially.

altered skeleton are false (Allison et al., 2007; Bar-Matthews et al., 1993; Hendy et al., 2007; McGregor and Gagan, 2003; Quinn and Taylor, 2006). Negative SST anomalies reconstructed from Sr/Ca, U/Ca, Mg/Ca, and  $\delta^{18}\text{O}$  data were indeed observed within corals presenting secondary aragonite and dissolution (Allison et al., 2005; Allison et al., 2007; Enmar et al., 2000; Hendy et al., 2007; Müller et al., 2001; Quinn and Taylor, 2006)" *Extract from Lazareth et al., 2013b*. Accordingly, while studying paleo-environmental conditions based on the geochemical compositions of coral, we have carefully sought for any diagenesis, by looking in particular at the microstructure of the coral skeleton.

We studied a 5.5 ka BP fossil coral from New Caledonia to obtain high resolution data for this key-period (Chap. IV, p. 59). Despite the overall good preservation of the skeleton of this sample, as assessed by the radiography, XRD analyses, and SEM observations, dissolution features were observed in a restrained part of the colony with specific impact on some geochemical tracers.

To calibrate environmental proxies in *Porites* sp. from Vanuatu, we studied a colony collected alive in 2009. The preservation state of the skeleton of modern coral colonies is rarely checked prior geochemical studies. Nevertheless, the studied Vanuatu *Porites* sp. was found to contain calcite, reaching more than 30 % in some places. We thus "investigated the impact of intra-skeletal calcite on trace elements concentration and boron isotope composition in a modern, live-collected, *Porites* sp. coral. A possible origin of the intra-skeletal calcite is proposed." *Extract from Lazareth et al. (2016)*.

#### Main questions:

- Depending on the diagenesis feature(s), how are the geochemical tracers, and thus environmental reconstructions, impacted?
- What processes could have led to the observed diagenesis features?

#### Work done:

- XRD analyses and SEM description of the coral skeleton states,
- Geochemical analyses of the colonies, including relatively news tracers like boron isotopes (pH) and Li/Mg (SST) in the modern colony,
- Attempt to explain the diagenesis process.

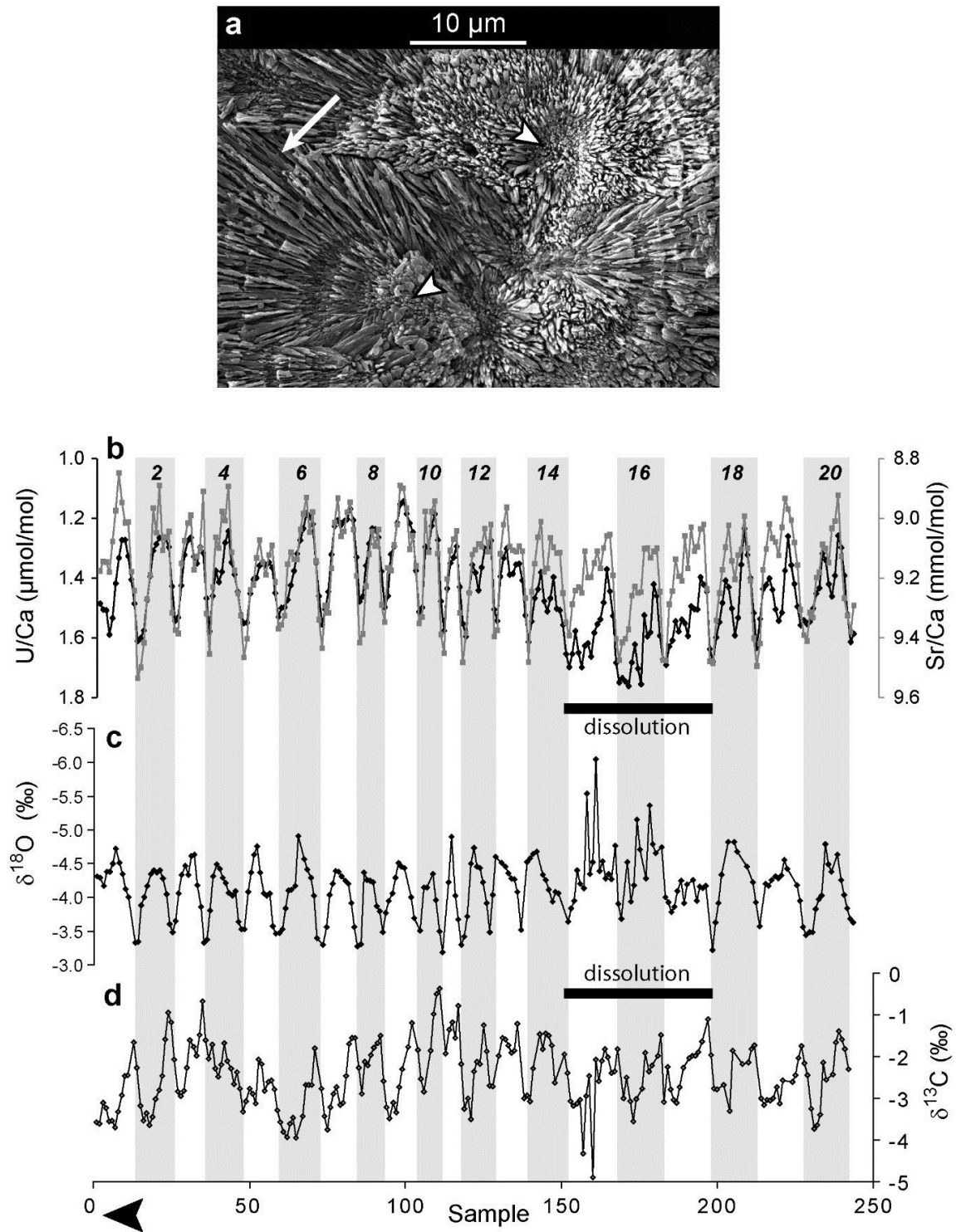
#### Methodology in brief:

For both corals, "1 cm-thick slab along the maximum growth axis was sampled, rinsed in deionized water in an ultrasonic bath, and dried overnight. An X-ray radiography of the slab was taken to identify the density bands and determine the growth axis along which the geochemical analyses were conducted. [...] The percentages of aragonite vs. calcite were determined, on powdered skeleton fragments collected in recent and oldest parts of the colony by X-ray diffraction. [...] Then, coral fragments ( $\sim 1\text{--}2\text{ cm}^2$ ) were sampled [...] and prepared for scanning electron microscopy

(SEM) observations. [...] A micro-sampling system was used to collect ~ 1 mg powders for trace element analyses [...] with a step size of 0.8 mm allowing for a monthly resolution. [...] Element concentrations were then measured using an Inductively Coupled Plasma Quadrupole Mass Spectrometer. [...] *For the modern Vanuatu colony*, to determine the isotopic composition of boron ( $\delta^{11}\text{B}$ ), at a yearly timescale approximately, seven large samples were collected parallel to the high resolution profile. [...] The measurements of boron isotopes were performed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) using a multi-collector ICP-MS. The LSCE's batch protocol was used to purify and extract boron in final 0.1 N nitric acid solutions as previously described (Douville et al., 2010; Dissard et al., 2012)." *Slightly modified extract from Lazareth et al. (2016).*

#### *Main results and conclusion:*

Depending on the diagenesis feature(s), how are the geochemical tracers (Table 5), and thus environmental reconstruction, impacted? In the 5.5 ka BP coral, altered zones are characterized by strongly dissolved aragonite fibers. They can be as thin as 0.2 mm while in pristine coral they are  $0.5 \pm 2$  mm thick (Holcomb et al., 2009; Spiro, 1971; Fig. 28). "U/Ca and stable isotopes departures from the average annual cycle are observed between the years 15 and 17, with no disturbances on the other tracers (Fig. 2c, e / here Fig. 28)." *Extract from Lazareth et al. (2013b).* Because  $\delta^{18}\text{O}$  signature in coral skeletons is widely used for SST/SSS reconstruction and can be modified via dissolution processes, a special emphasis must be given to such diagenesis features. Hendy et al. (2007) observed cool artefacts in their modern corals using Mg/Ca, Sr/Ca and U/Ca proxies. However, the characteristics of the dissolution they observed are completely different than ours. Such dissolution probably has different effects on geochemical proxies, depending on the process. Note that I observed similar features to those noticed by Hendy et al. (2007) in several modern corals, without any geochemical imprint. Moreover, sometimes the coral walls are smooth, sometimes the aragonite bundles are more visible, even in the same area of the skeleton (Fig. 29). Consequently, I would interpret the aragonite bundles such as those described in Hendy et al. (2007) rather as "normal" skeleton than dissolved one and would interpret the occurrence of both types (smooth and not smooth skeleton) as different steps of growth, but this remains to be confirmed.



**Fig. 28:** Impact of dissolution on the skeleton and geochemical signature observed on a 5.5 ka BP coral colony from New Caledonia. **A.** Typical dissolution pattern observed in some part of the skeleton. Arrow heads: center of calcifications; arrow: voids left by dissolution of the aragonite needles. **B-D.** Raw geochemical profiles of the geochemical proxies impacted by dissolution of the skeleton. In **B.** Sr/Ca is added as a reference of non-impacted ratio (grey). Arrow points the living part of the skeleton. Numbers of years are indicated above. modified from Lazareth et al. (2013b).

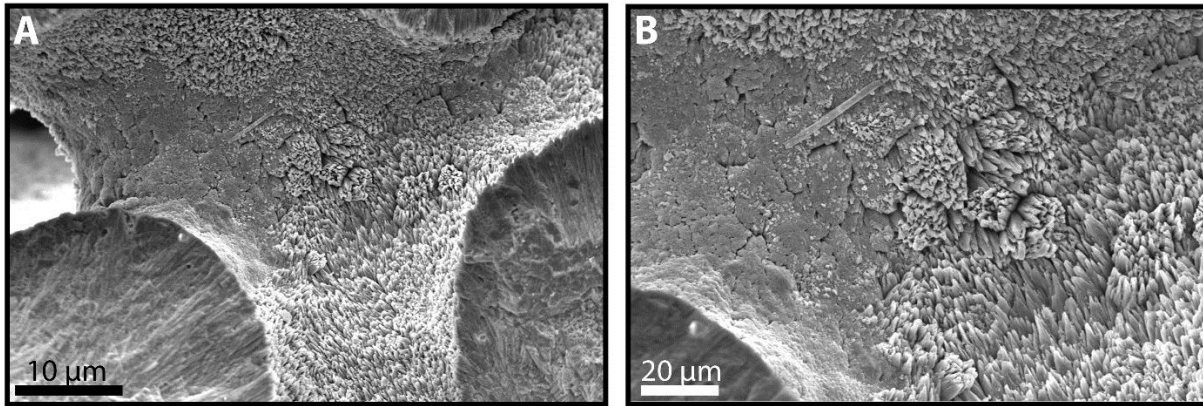


Fig. 29: Modern *Porites* sp. coral skeleton where both smooth and not smooth coral wall aspects are observed on the same locus (SEM images; Lazareth et al., unpublished data; images acquired during A. Boudeau and E. Milleret training, 2016; Boudeau, 2016; Milleret, 2016).

The modern coral colony collected alive in Vanuatu has two parts separated by a dark line, each characterized by a specific calcite percentage. The oldest part of the skeleton contains systematically less than 3% of calcite ("no-calcite" skeleton) and the most recent (last 5 years of growth) has a particularly high calcite percentage, ranging from 8 to 32% ("with-calcite" skeleton; Fig. 30). This calcite replaces, in part or completely, the centers of calcification (COCs) and has a sparry habitus (Fig. 31).

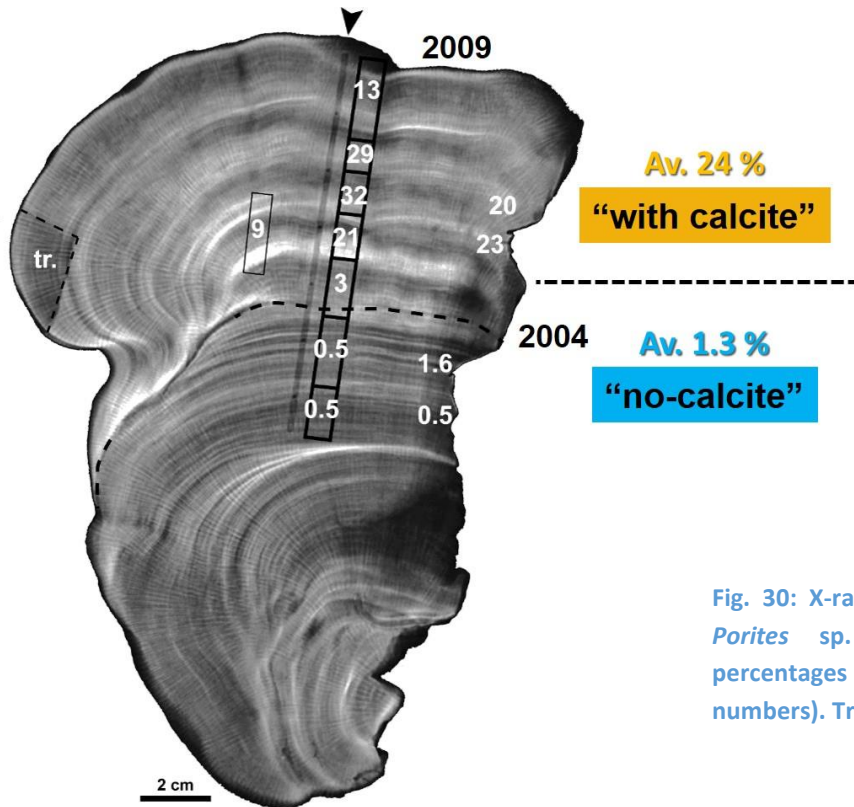
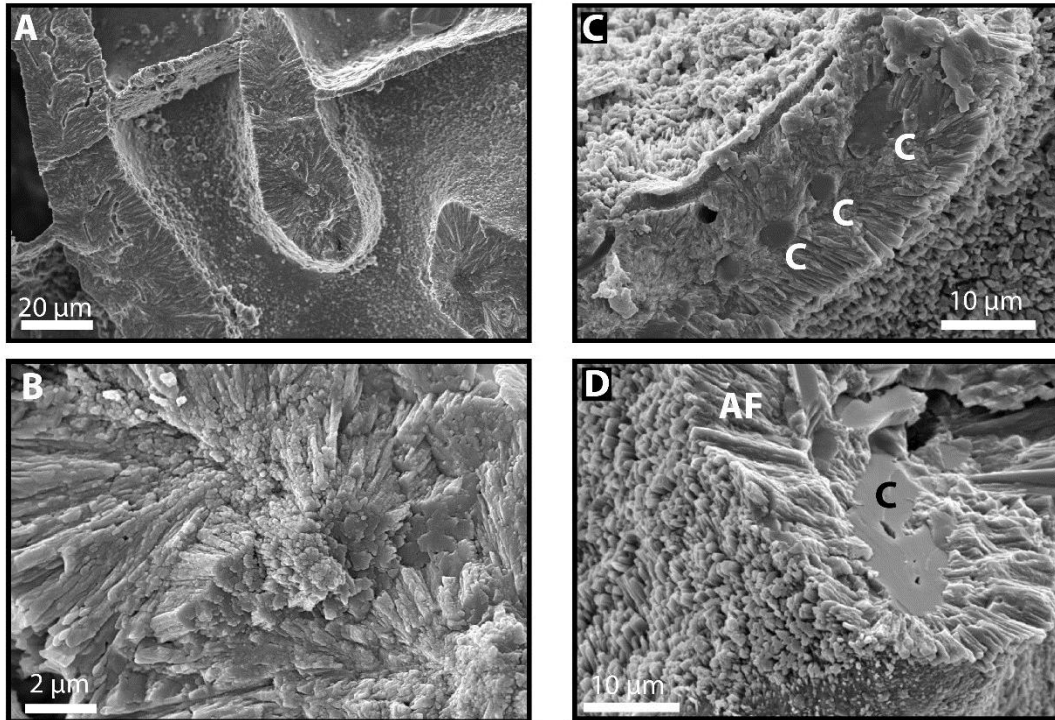


Fig. 30: X-ray radiography of the Vanuatu *Porites* sp. colony with the calcite percentages measured using DRX (white numbers). Tr.: traces; Av.: average.



**Fig. 31: Microstructure features of the A.-B. "no-calcite" vs. C.-D. the "with-calcite" coral skeleton (SEM pictures).** A. Overview of the coral skeleton showing the well-preserved skeleton with empty pores. B. Enlargement of a center of calcification (COC) showing the well-preserved microgranular and fibrous structure of aragonite crystals. C. Section of a septum in the "with-calcite" part of the skeleton. The aragonite fibers are very well preserved, i.e., without any dissolution features. Patches of calcite occur along the center of calcification (COC) line (black arrows + letter C). D. Section of a septum in the "with-calcite" part of the skeleton. The COC are completely replaced by calcite here (letter C), the aragonite fibers (AF) are again very well preserved. Modified from Lazareth et al., 2016; 2014a.

From the "no-calcite" to the "with-calcite" parts, all elements/Ca ratios and the  $\delta^{11}\text{B}$  are clearly impacted by the presence of calcite (Fig. 32 and Table 4). In terms of environmental reconstitution, the impact of the calcite presence is of  $+0.14 \pm 0.03^\circ\text{C}$  and  $+0.17 \pm 0.04^\circ\text{C}$  per calcite-% based on the Sr/Ca and Li/Mg proxies, respectively (Lazareth et al., 2016).

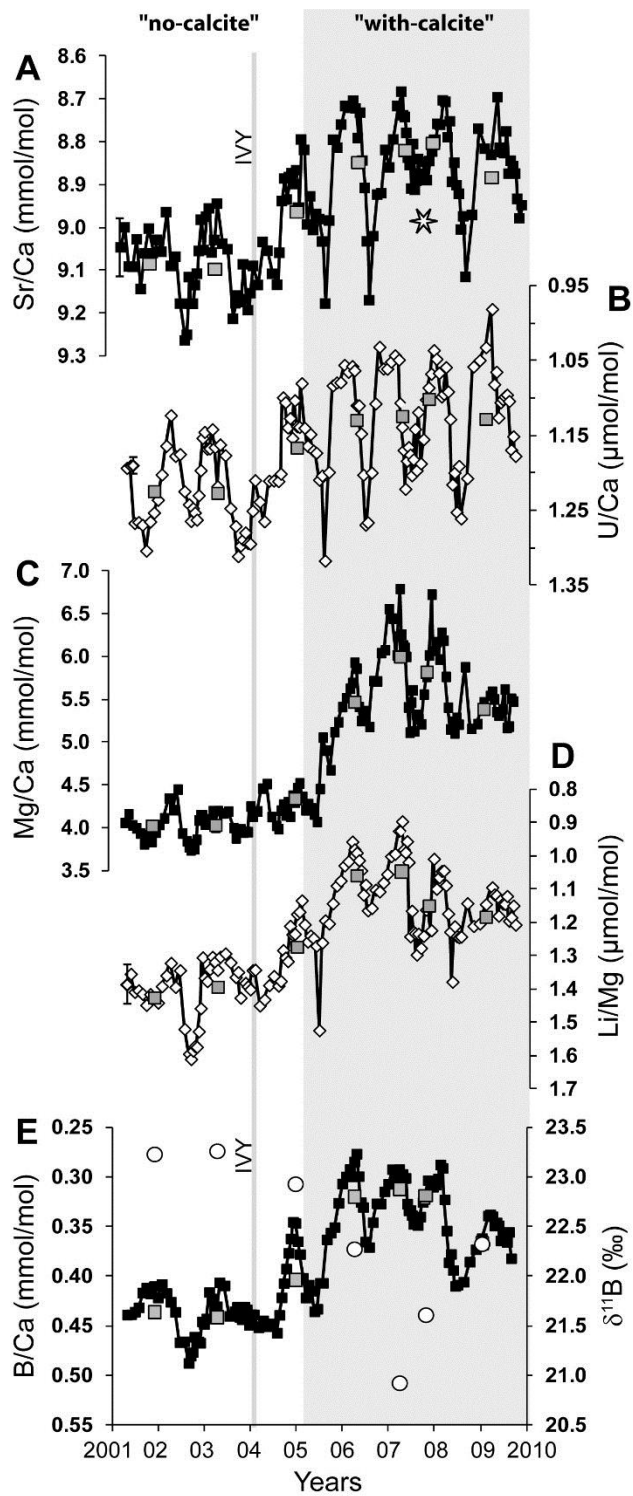


Fig. 32: Geochemical record obtained from the Vanuatu Epi colony. The grey squares represent the yearly data (samples taken at a yearly resolution). The  $1\sigma$  precision on the element/Ca ratio is shown for the seasonal data. When not visible, this error is smaller than the symbol. The grey area underlines the “with-calcite” part of the skeleton. The grey line materialized the date when the Ivy Cyclone passed above Vanuatu. A. Sr/Ca. The star represents the 2007–08 La Niña event. B. U/Ca. C. Mg/Ca. D. Li/Mg. E. B/Ca and  $\delta^{11}\text{B}$  at the monthly resolution (black squares) and B/Ca and  $\delta^{11}\text{B}$  at the yearly resolution (grey squares and white circles respectively). Modified from Lazareth et al. (2016).

**Table 4: Elemental (left) and isotopic (right) ratios measured in the "no-calcite" and "with-calcite" skeleton in the Vanuatu *Porites* sp. collected alive. Mean: first row of each tracer, bold; standard deviation: second row, italic. All isotopes are expressed in per-mill. n: number of sample analyzed. For  $\delta^{11}\text{B}$ , this number is indicated in brackets after the mean.**

Element ratios	"no-calcite"	"with-calcite"
<b>n</b>	57	74
<b>Sr/Ca</b> (mmol/mol)	9.05	8.86
	0.11	0.11
<b>Mg/Ca</b> (mmol/mol)	4.10	5.51
	0.20	0.56
<b>Ba/Ca</b> ( $\mu\text{mol/mol}$ )	3.27	2.89
	0.54	0.42
<b>U/Ca</b> ( $\mu\text{mol/mol}$ )	1.21	1.13
	0.06	0.07
<b>B/Ca</b> (mmol/mol)	0.43	0.34
	0.03	0.04
<b>Li/Ca</b> ( $\mu\text{mol/mol}$ )	5.63	6.19
	0.35	0.45
<b>Li/Mg</b> ( $\mu\text{mol/mol}$ )	1.37	1.13
	0.10	0.11

Isotopes	"no-calcite"	"with-calcite"
<b>n</b>	46	61
$\delta^{13}\text{C}$	<b>-1.53</b>	<b>-0.82</b>
	0.47	0.69
$\delta^{18}\text{O}$	<b>-4.76</b>	<b>-4.17</b>
	0.26	0.41
$\delta^{11}\text{B}$	<b>23.14 (4)</b>	<b>21.78 (3)</b>
	0.18	0.66

"Looking now at the reconstructed SST in terms of variability, one can note that the SST seasonal cycles are preserved in the "with-calcite" skeleton but with different amplitudes than that of the gridded-SST ones (Fig. 7a; here Fig. 33). This might reflect an increasing amount of calcite, and potential environmental effects as discussed above, during the summer season. Nevertheless, it is interesting to notice that for the Sr/Ca ratio, the year-to-year relative seasonal amplitude changes are maintained. Indeed, a moderate La Niña (as defined using the Ocean Niño Index) occurred in 2007-2008. In the Vanuatu region, this resulted in a winter with warmer SST than usual (star on Fig. 5a and 7a). This warmer winter is still observable on the Sr/Ca profile, even if located in the skeleton part containing almost 30% of intra-skeletal calcite". So if intra-skeletal calcite is observed, "i) SST reconstructions using Sr/Ca can only be done when less than 5% of intra-skeletal calcite is present, and temperature reconstructed from Li/Mg ratio appears more impacted by the calcite presence than Sr/Ca temperature; ii) qualitative data, e.g., seasonal amplitude changes, can be obtained using the Sr/Ca ratio changes even if 32% of intra-skeletal calcite is present; it remains thus possible to obtain climate-like reliable information such as Niño or Niña year's occurrences." *Extract from Lazareth et al. (2016).*



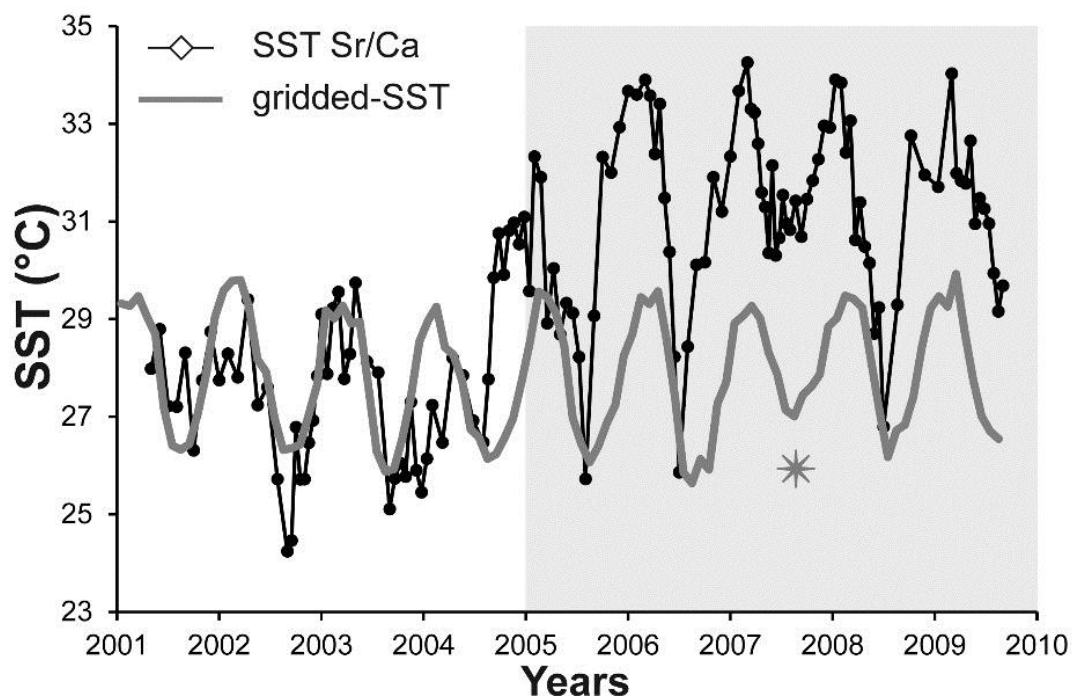


Fig. 33: Comparison between time series for the reconstructed SST based on the Sr/Ca profile from the Vanuatu coral and that of gridded SSTs. Gridded-SST was obtained for a box centered on 168.5E– 16.5S (IGOSS, Reynold and Smith 02). Grey area: “with-calcite” skeleton part (see text for details). The star represents the 2007–08 La Niña event. Modified from Lazareth et al. (2016).

For pH, the effect of the presence of calcite is also pronounced with potentially  $-0.011 \pm 0.002$  unit-pH per calcite-% for the computed seawater pH. "Such impact is particularly pronounced and can strongly limit the use of  $\delta^{11}\text{B}$ -pH proxy for corals, especially if the objective is to reconstruct the recent anthropogenic pH changes of the ocean. For illustration, 5% of calcite in *Porites* sp. skeleton will decrease the reconstructed seawater pH by  $\sim 0.055$  pH-unit whereas surface ocean acidification over the last two centuries due to industrial era for tropical areas is about 0.05-0.09 pH-unit (Pelejero et al., 2005; Sabine et al., 2004). [...] Consequently, the paleo-pH technique based on boron isotopes has to be applied on tropical corals, here a massive *Porites* species, free of calcite." *Extract from Lazareth et al. (2016).*

Our studies on impact of diagenesis on geochemical signature of coral skeleton add new insight into this problematic (Table 5). Each type of diagenesis is characterized by a specific imprint on the skeleton chemistry, the impacts remaining difficult to quantify. Furthermore, diagenesis alterations can be local which means that they do not affect the whole studied colony; making complicated the use of altered coral skeletons for environmental reconstructions.

**Table 5: Main impacts of different diagenesis types on *Porites* sp. coral skeleton geochemistry.** ↗ (↘; =): increase (decrease; no impact) of the tracer relative to its pristine value. † (L): observed on fossil (living) colony. Note that in the presence of brucite-[Mg(OH)<sub>2</sub>] (observed in *Porites* sp.; Nothdurft and Webb, 2009; Nothdurft et al., 2005), the Mg/Ca ratio will increase (Buster and Holmes, 2006). Data from our studies are highlighted in blue. Concerning the intra-skeletal calcite, we observed the same trends than other works but added other proxies.

	Dissolution	2 <sup>de</sup> aragonite	2 <sup>de</sup> calcite		
		Cement	Intra-skeletal	μ-borer filling	Cement
<b>U/Ca</b>	↗; summer-†; L	↗ †; L	↘ L		
<b>δ<sup>18</sup>O</b>	↘; summer-†	↗ †; L			
<b>Sr/Ca</b>	= †; ↗ L	↗ †; L	↘ L	↘ L	↘ †
<b>Mg/Ca</b>	= †; ↘ L	↘ †; L	↗ L	↗ L	↗ †; L
<b>Li/Mg</b>			↘ L		
<b>δ<sup>11</sup>B</b>			↗ L		
	Hendy et al., 2007; Lazareth et al., 2013b	Allison et al., 2007; Hendy et al., 2007	Houck et al., 1975; Lazareth et al., 2016; Rabier et al., 2008	Nothdurft et al., 2007	Nothdurft and Webb, 2009; Rabier et al., 2008

**What processes could have led to such diagenesis features?** To better understand the diageneses impacts on the geochemical tracers used for environmental reconstructions, I tried to understand the causes of the observed changes. However, only hypotheses can be moved forward. Reports on impact of dissolution on coral skeleton geochemistry are rare. If we consider that the changes in U/Ca and δ<sup>18</sup>O in our skeleton are related purely to the dissolution process (see Lazareth et al., 2013b for another hypothesis) only "Hendy et al. (2007) reported, in a living *Porites* sp., an increase of Sr/Ca and U/Ca and a decrease of Mg/Ca in dissolved areas of the skeleton. They proposed "incongruent dissolution" to explain the element/Ca changes they observed. In our case, incongruent dissolution would be hardly conceivable since only one element/Ca ratio is affected by the dissolution. An increase in uranium content in the coral skeleton itself, i.e., not in secondary crystals, during diagenesis has been noted (Gallup et al., 1994; Shen and Dunbar, 1995). Uranium uptake has also been observed in modern coral plunged in uranium-enriched seawater (Swart and Hubbard, 1982). Uptake of <sup>234</sup>U by the coral skeleton has been related to U decay by means of the alpha-recoil processes which have been modelled for U-series dating improvements (e.g., Henderson et al., 2001; Robinson et al., 2006; Villemant and Feuillet, 2003). Such uptake however generally requires a U-source. In our case, the only potential source would be the coral organic matrix itself, as no particularly intensive microborings were observed in the dissolved part of the skeleton. If the organic matrix of the skeleton is rich in U, its degradation could be the source of both the U-enrichment and the particularly negative δ<sup>18</sup>O, such a link between δ<sup>18</sup>O depletion and the degradation of the organic matrix having been observed by Cuif et al. (1997). [...] The fact that the anomalies are preferentially observed during the summer could be related to skeletal specificities in link with seasonal growth bands. Clearly, further work is needed to improve our

knowledge on vital and diagenetic bias on geochemical coral proxies." *Extract from Lazareth et al. (2013b)*.

Calcite replacing corals skeleton without pore cementation (at least in the first steps of diagenesis) such as the one observed in our lived-collected colony "is characteristic of the freshwater vadose and phreatic zone<sup>4</sup> (James James, 1974; Longman, 1980; Pingitore, 1976; Sorauf, 1980). Two main processes for the aragonite-calcite transformation, via dissolution/ precipitation, in such environments were proposed. In the vadose zone, the zone of dissolution/precipitation has a width of 1  $\mu\text{m}$  (or less) where an immobile water film, termed "thin film" or "messenger film", is present (Pingitore Pingitore, 1976; Rabier et al., 2008). The dissolution/precipitation process in this case occurs in a closed or semiclosed system and precipitation is concomitant to dissolution (James, 1974; Pingitore, 1976; Rabier et al., 2008). In the phreatic zone, the calcite formation occurs via a zone of chalky aragonite of several millimeters wide (James, 1974; Pingitore, 1976). In this case, the calcitization process occurs in an open system. In our study, no chalky zone was observed; the calcite crystals are in neat contact either with the remaining unaltered COC part or with the surrounding aragonite fibers in case of total COC replacement (Fig. 4). This feature strongly resembles what was described in the case of subaerial freshwater vadose diagenesis, such as for example in James (1974) (p. 12 and fig. 8d). Because only COCs are (partly) replaced, what we observe might be the very first stage of such subaerial freshwater vadose diagenesis". We thus assume that the coral colony, collected in a shallow setting "could have been subjected to occasional relative water freshening, related to rainwaters. Precipitations may have acted here in a similar way than freshwater does in subaerial vadose setting. Looking at the reconstructed SST using Sr/Ca, the winter values are similar to the gridded ones while the summer values are higher (Fig. 7A). In Vanuatu, rainfall is more abundant during the summers than during the winters. Consequently, the skeleton accretion during summers would have been more impacted by rainfall-related freshwaters than during winters, resulting in a higher calcite concentration, and thus geochemical modification, during summers." Concerning the absence of calcite in the oldest part of the skeleton, we suggest that the colony had first lived in an 'open Oceanic' environment (deeper) and that it has been moved up during the passage of cyclone Ivy to the shallow environment where it was collected. "We therefore interpret all the observed features, i.e., partial change in coral growth direction, presence of the skeletal dark line, and appearance of intra-skeletal calcite in the last years of coral growth, as the consequence of a displacement of the colony, related to the Ivy cyclone, from deep to shallow environment where it would then have been more impacted by rainfall than previously". *Extracts from Lazareth et al. (2016)*.

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<sup>4</sup> The vadose zone is comprised between the land and the groundwater surface (also named water table). The freshwater phreatic zone is below the groundwater surface and above the zone where fresh- and marine-water are mixed (e.g., Longman, M.W. (1980) Carbonate diagenetic textures from nearsurface diagenetic environments. *Am. Assoc. Petrol. Geol. Bulletin* **64**, 461-487.).

It remains difficult to identify and understand the processes that led to structural and geochemical modifications of coral skeletons. The results obtained in this study combined to our current knowledge on biomineralization and mineralogy can however allow proposing hypotheses on the coral's skeleton history. To improve our knowledge in these diagenetic processes it could be interesting to combine both biomineralization and mineralogical studies, in particular by conducting specific experiments dedicated to this subject.

## IV / HOLOCENE PALEO-ENVIRONMENTAL RECONSTRUCTIONS

Studying past climates offers the opportunity to extend our knowledge on climate variability and on climate processes beyond the instrumental period. In addition, this allows studying the mechanisms behind climatic variability in different configurations than the current one (e.g., in terms of terrestrial orbital characteristics, insolation, human impacts, etc.). Efforts in climate reconstructions are thus focused on some key-periods, like the Mid-Holocene, ~ 6 ka BP.

### 4.1 The Mid-Holocene period

"The Mid-Holocene climate is characterized by an insolation seasonality decrease in the Southern Hemisphere [...] *and* coupled ocean-atmosphere models forced by the Holocene insolation change show that ENSO [...] amplitude and/or frequency was reduced during the early- to Mid-Holocene period (Cane et al., 2006; Clement et al., 2000; Liu et al., 2000; Otto-Bliesner et al., 2003; Zheng et al., 2008). Paleoclimate data indicate that ENSO was indeed reduced during that period (Koutavas et al., 2006; McGregor and Gagan, 2004; Moy et al., 2002; Rodbell et al., 1999; Tudhope et al., 2001). Various hypotheses are advanced to explain this ENSO damping: an increased heating of the western equatorial Pacific in boreal summer and autumn (Clement et al., 1999; Clement et al., 2000), a general warming of the equatorial Pacific (Rodbell et al., 1999), an interaction with the Asian Monsoon (Liu et al., 2004; Marzin and Braconnot, 2009 Luan et al., 2012), or a northward shift of the ITCZ (Koutavas et al., 2006). To our knowledge, monthly-resolved proxy data on Mid-Holocene are rare, or at least not used neither in studies dealing with Mid-Holocene ENSO or in studies describing the mean climatological state for that period. More data on Holocene tropical Pacific Ocean, including seasonal data, are thus needed. [...]. For most proxies, it is difficult to distinguish between seasonal and inter-annual variability." *Extract from Lazareth et al. (2013b)*. Analyses of coral skeleton from *Porites* sp. species enable to recover such data. Consequently, to obtain information on paleoceanographic parameters in the southwest tropical Pacific, where climatic variations are related to SPCZ displacements and ENSO, we worked on New Caledonia

and Vanuatu fossil corals dated from the early- to the Mid-Holocene and compared our Mid-Holocene results to PMIP2 model simulations.

*Main question:*

- What were the climatic characteristics at around 6 ka, in terms of SST, position and seasonal variability of the SPCZ, and ENSO variability?

*Work done:*

- Fossil collection, dating, and diagenesis assessment,
- Reconstructions of SST and  $\delta^{18}\text{O}_{\text{sw}}$  at a monthly resolution from geochemical analyses (Sr/Ca and  $\delta^{18}\text{O}$ ) of New Caledonian and Vanuatu fossil corals,
- Comparison of SST seasonality obtained from the New Caledonian coral with that obtained from PMIP model simulations.

*Methodology in brief:*

"Fossil samples were dated using conventional  $^{14}\text{C}$  measurements and dates were calibrated using the Marine09 database [Reimer et al., 2009]. The DeltaR value used for the Vanuatu area was  $29 \pm 28$  years according to [Petchey et al., 2008]. The coral samples and the fossil giant clam shell were screened for their mineralogical composition and micro-structure preservation before geochemical analysis to ensure they were well-preserved. Mineralogical analyses were carried out using X-ray diffraction (XRD) [...]. The preservation state of the fossil specimens was evaluated by comparing SEM images of modern and fossil specimens of coral and giant clams." *Extract from Duprey et al. (2012)*. The ~ 1 cm-thick coral slabs were then "continuously sampled at 1-mm steps, providing on average one sample per month of coral growth." *Extract from Lazareth et al. (2013a)*. The trace element contents were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent 7500cx<sup>®</sup>). "The oxygen stable isotope samples of the modern *Porites* sp. (VA-EPI), and the fossil *Porites* sp. (Psp-07-09) were analyzed on a GV IsoPrime<sup>®</sup> mass-spectrometer at LOCEAN (Paris 6 University), whereas fossil *Porites* sp. Psp-06-09 was analyzed on a GV Optima<sup>®</sup> mass-spectrometer at EPOC (Bordeaux I University). Both instruments were coupled to a Multiprep carbonate Gilson<sup>®</sup>. [...] The  $\delta^{18}\text{O}$  profiles of the modern coral of Kilbourne et al. (2004) and of the continuous fossil coral record Psp-06-09 were band-pass filtered as described by Tudhope et al. (2001). This process extracts the 2.5- to 7-yr frequency of the signal (i.e., the dominant mode of modern ENSO - [Trenberth, 1976]). [...] The  $\delta^{18}\text{O}_{\text{sw}}$  values were calculated from the coral Sr/Ca and the  $\delta^{18}\text{O}$  records using the equation established by Juillet-Leclerc and Schmidt, 2001 (Sr/Ca was converted into SST using the mean equation for *Porites* sp. Corrège, 2006)." *Extracts from Duprey et al. (2012)*.

*Main results and conclusion:*

All the studied samples were very well preserved except for one restricted area in one New Caledonian coral colony which was excluded from the interpretations (Chap. III, § 3.2., p. 47). The dating results and mean  $\delta^{18}\text{O}$  and Sr/Ca values are presented in **Table 6**.

The two early Mid-Holocene corals from Vanuatu have almost similar Sr/Ca and  $\delta^{18}\text{O}$  values. Compared to the modern Vanuatu coral, they have slightly higher Sr/Ca (i.e., slightly lower SST) values and more positive  $\delta^{18}\text{O}$  and  $\delta^{18}\text{O}_{\text{sw}}$  values (**Table 6**). Concerning the Mid-Holocene New Caledonian coral, its average Sr/Ca signature is similar to that of modern equivalents while the seasonal SST amplitude mean and variability are higher (**Fig. 34**). The Mid-Holocene  $\delta^{18}\text{O}_{\text{sw}}$  is on average enriched by +0.35 compared to modern value (**Table 6**).

**Table 6: Datation results and main geochemical characteristics of modern and early-Mid-Holocene corals from Vanuatu. All results are based on raw data. Modified from Duprey et al., 2012.**

Sample name	<i>Porites</i> sp.; Vanuatu			<i>Porites</i> sp.; New Caledonia	
	Epi-VA	Psp-06-08	Psp-07-08	Amédée	Naia
<b>Date <math>^{14}\text{C}</math> (yr. BP <math>\pm</math> uncert.)</b>	1999-2006	<b>6208 <math>\pm</math> 35</b>	<b>6220 <math>\pm</math> 32</b>	1974-1999	<b>5230 <math>\pm</math> 52</b>
<b>Date cal (yr. BP - <math>2\sigma</math> range)</b>	/	<b>6.7-6.5</b>	<b>6.7-6.5</b>	/	<b>5.5</b>
<b>Record length (yr.)</b>	7	<b>25</b>	<b>19</b>	25	<b>20</b>
<b>Sr/Ca (mmol.mol<math>^{-1}</math>)</b>	8.98 $\pm$ 0.10	<b>9.01 <math>\pm</math> 0.08</b>	<b>9.03 <math>\pm</math> 0.08</b>	9.18 $\pm$ 0.10	<b>9.17 <math>\pm</math> 0.15</b>
<b><math>\delta^{18}\text{O}</math> (VPDB‰)</b>	-4.66 $\pm$ 0.47	<b>-4.35 <math>\pm</math> 0.16</b>	<b>-4.34 <math>\pm</math> 0.43</b>	-4.36 $\pm$ 0.28	<b>-4.10 <math>\pm</math> 0.40</b>
<b><math>\delta^{18}\text{O}_{\text{sw}}</math> (VPDB ‰)</b>	+0.15 $\pm$ 0.67	<b>+0.25 <math>\pm</math> 0.47</b>	<b>+0.27 <math>\pm</math> 0.25</b>	-0.30 $\pm$ 0.12	<b>+0.05 <math>\pm</math> 0.37</b>
<b>Difference <math>\delta^{18}\text{O}_{\text{sw}}</math> 0 ka vs. Mid-Holocene</b>		~ + 0.10		+ 0.35	

"The early Mid-Holocene coral from Vanuatu recorded an ENSO variability that was in average 20–30% lower than the variability recorded by the modern coral for the period 1928–1992." *Extract from Duprey et al. (2012)*. The Mid-Holocene record from New Caledonia was too short to establish ENSO variability.

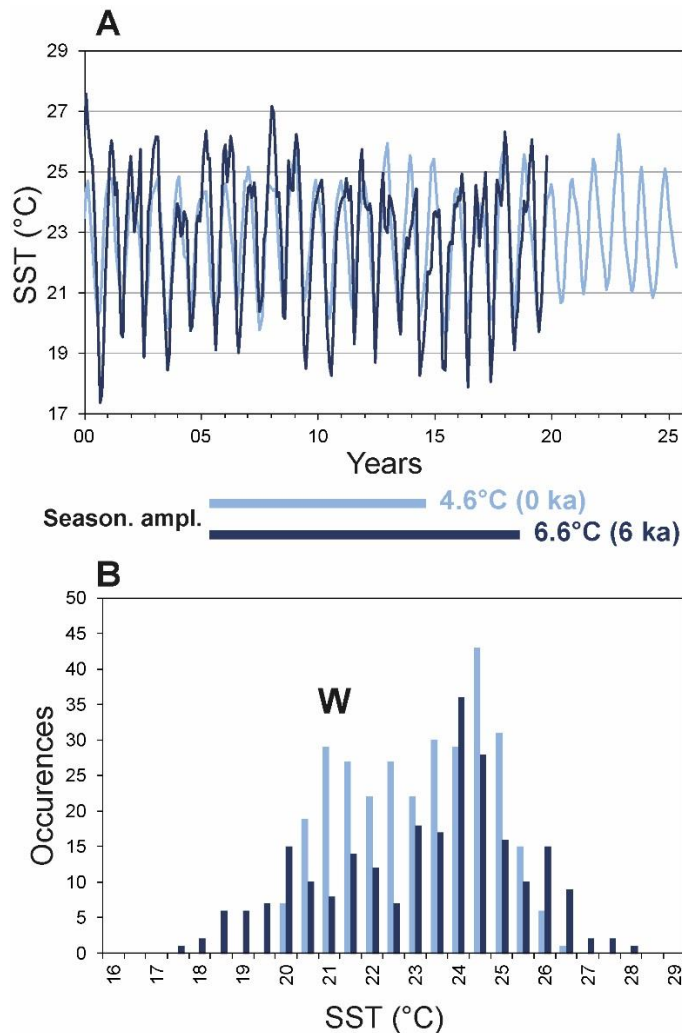


Fig. 34: Comparison of reconstructed sea surface temperature (SST; °C) characteristics in the New Caledonia region for the present (light colors) and the Mid-Holocene (dark colors) situations. A. Monthly coral time series, at present (light blue, Stephans et al., 2004, 2005) and from a coral fossil from the Mid-Holocene (5.5 ka BP, dark blue; Lazareth et al., 2013b). B. Monthly SST histograms and calculated seasonal amplitudes. In the 6 ka BP coral, colder temperatures prevail in the winter mode (W) and SST has a wider distribution compared to the 0 ka coral. Modified from Lazareth et al. (2013a).

What were the climatic characteristics at around 6 ka, in terms of SST, position and seasonal variability of the SPCZ, and ENSO variability? The similar Sr/Ca signature observed between our fossil and modern corals "indicates that the early Mid-Holocene mean SST was *almost* similar to its modern value. [...]. Our results show that the post-glacial SST rise was *almost* completed by the early Mid-Holocene in the SW Pacific. This observation is in agreement with the slightly warmer SST reported from other coral records from New Caledonia [Montaggioni et al., 2006] and in the Australian Great Barrier Reef [Gagan et al., 1998; Gagan et al., 2004]. All these coral records support the hypothesis of a moderate warming of the equatorial Western Pacific during the "Holocene Thermal Maximum" (ca. 8–7 ka BP), as it is also suggested by marine sediment records [Stott et al., 2004] and by global atmosphere-ocean-vegetation model simulations [Renssen et al., 2012]." *Slightly modified extract from Duprey et al. (2012)*. The same result obtained from the Mid-Holocene New Caledonian coral confirms that mean modern SST was reached in this part of the Southwest Pacific region at that time.

In addition, "the post-glacial stabilization of SST around its present value in the SW Pacific at 6.7–6.5 ka BP was accompanied by change of the surface-ocean water balance compared to modern conditions. The modern coral record from Vanuatu displays a low average  $\delta^{18}\text{O}_{\text{sw}}$  value (0.15‰VPDB) that reflects the strong influence of  $^{18}\text{O}$ -depleted waters brought by the SPCZ-related precipitation." Comparatively, the higher early-mid Holocene average  $\delta^{18}\text{O}_{\text{sw}}$  composition indicates a "reduction of SPCZ-related precipitation input implying that the SPCZ was most likely located northward from its present location and possibly merged with the ITCZ." *Slightly modified extract from Duprey et al. (2012)*. A similar conclusion was reached from the New Caledonian 5.5 ka BP coral results since higher seasonal SST amplitude mean and variability "could mean that the SPCZ was weaker or reached locations more northerly than at present, which could fit with northward shifts of the ITCZ during South Hemisphere winter." *Extract from Lazareth et al. (2013b)*.

From these two studies it appears that the SPCZ influence on the Southwest Pacific was most probably reduced from the early-mid- to the Mid-Holocene, either because it was weaker, or located more to the north, or even merged with the ITCZ. From the model simulations, "The changes in SPCZ position [...] are however very limited. The northward shift of the ITCZ position during the Mid-Holocene is more evident west of 130°E (Braconnot et al., 2007; Yokoyama et al., 2011), probably because it is linked to the Asian Monsoon. The main feature in the multi-model mean map is a marked reduction of SPCZ precipitation which indicates a less intense SPCZ. Therefore, from a "model point of view" the observed *change in SST seasonal amplitude* in the New Caledonia region (5.5 ka coral data) would be more probably due to a less intense SPCZ rather than to its northward shift." *Slightly modified extract from Lazareth et al. (2013b)*. However, recent model simulations argued that, at 6 ka, the SPCZ was shifted southward in relationship with an increase of the meridional SST gradient in connection with the change in insolation forcing at this period (Mantsis et al., 2013; Saint-Lu et al., 2015) not to mention the SPCZ strength. Discussions on SPCZ location variability during the Mid-Holocene are still on going, as its possible link with ENSO variability modifications (Chen et al., 2016; Emile-Geay et al., 2016; Saint-Lu et al., 2015).

The more positive  $\delta^{18}\text{O}_{\text{sw}}$  values in our Mid-Holocene New Caledonian coral implies less precipitation in accordance with our previous hypothesis of a less intense SPCZ. However here, evaporation was certainly higher too since the large difference observed can barely be only explained by a less intense SPCZ. Several works have previously shown this implication. "An average surface-ocean water balance shifted toward evaporation during the Mid-Holocene was shown *from south-west and western equatorial Pacific settings* (Gagan et al., 1998; Stott et al., 2004; Tudhope et al., 2001). Increased evaporation in the early Mid-Holocene is also supported by the similar or warmer conditions than today recorded by early Mid-Holocene fossil corals from PNG, GBR, and New Caledonia [Abram et al., 2009; Gagan et al., 1998; Gagan et al., 2004;



Montaggioni et al., 2006]. Moreover, general circulation model simulations indicate a strengthening, or an extension, of the Hadley cell as a response of a slight warming of the tropical zone [Lu et al., 2007; Rind, 2000]. Stronger, or extended, Hadley cell would enhance the poleward water vapor transport, and thus the poleward heat flux, increasing the evaporation in the tropics." *Slightly modified extract from Duprey et al. (2012)*. Such a situation is coherent with a "La Niña-like" state evidenced during the early- to Mid-Holocene period (Clement et al., 2000; Gagan and Thompson, 2004; Koutavas and Joanides, 2012; Koutavas et al., 2002; McGregor and Gagan, 2004). Indeed, during current La Niña episodes in the western Pacific, the convection is higher for the regional Hadley circulation in combination with a move of the regional Walker circulation over the western Pacific (Schwendike et al., 2014).

Regarding ENSO reconstructed variability, "a change in the ENSO teleconnections over the Pacific area during the early Mid-Holocene may result in a reduced ENSO signal in the SW Pacific fossil corals records. On the other hand, the decoupling between the precipitation and the SPCZ in the SW Pacific, evidenced from the early Mid-Holocene coral records, may also have contributed to a reduced ENSO signal in the  $\delta^{18}\text{O}$  coral record. Indeed, the strength of the ENSO signal in the coral  $\delta^{18}\text{O}$  record relies on the tight coupling between the SPCZ and the precipitation. The decoupling of the SPCZ and the precipitation regime observed during the early Mid-Holocene would have led to a disruption between the ENSO variability and coral  $\delta^{18}\text{O}$  variations, leading to a weaker ENSO signal in the  $\delta^{18}\text{O}$  record." *Extract from Duprey et al. (2012)*. Various works already concluded in a reduced ENSO variability during the early Mid-Holocene period (Haberle et al., 2001; Koutavas et al., 2006; Moy et al., 2002; Sandweiss et al., 2001; Tudhope et al., 2001; Vargas et al., 2006) that lead us to conclude that "the reduced amplitude of the ENSO signal in the early Mid-Holocene coral  $\delta^{18}\text{O}$  record reflect both 1) a global weaker ENSO variability and 2) the decoupling between the precipitation and the SPCZ." *Extract from Duprey et al. (2012)*.

A summary of the results and interpretations from the two studies described above is presented in [Fig. 35](#).

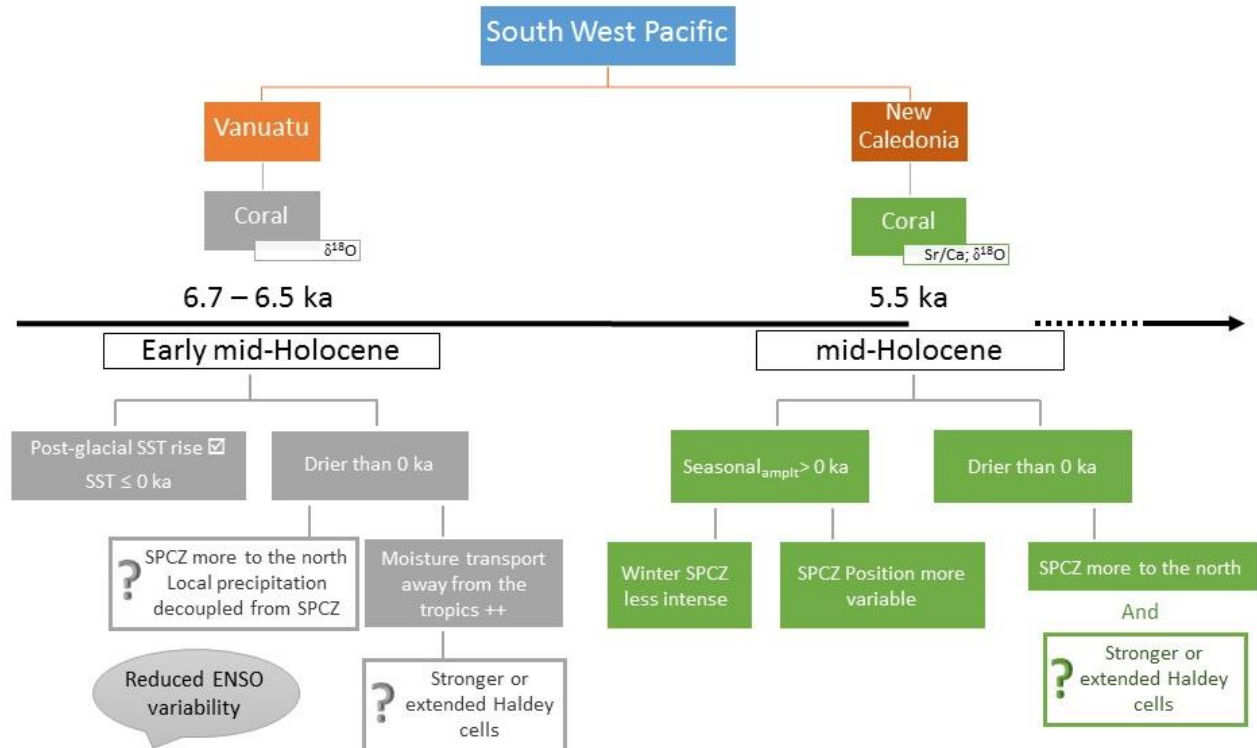


Fig. 35: Summary of South-west Pacific early- to Mid-Holocene climate as obtained from our coral studies. ++: more intense.

## 4.2 The Lapita colonization

At c. 3 ka BP, an intensification of ENSO activity was observed in Australia and Papua New Guinea (PNG) (Gagan et al., 2004). This period coincides with a new phase of the Pacific colonization (c. 3.5-3.25 ka BP) "with the emergence of the Lapita culture in the Bismarck Archipelago (Denham et al., 2012; Kirch, 1997). Within *less than 3* centuries, the Lapita people established permanent colonies over the previously unexplored Remote Oceania (Burley et al., 1999; Denham et al., 2012). The fascinating Lapita colonization raises many questions in particular regarding the natural factors that may have influenced this remarkable event." *Slightly modified extract from Duprey et al. (2014)*. To further investigate a possible link between climate variability and Lapita migration, we took advantage on the fact that giant clam shells are found in archeological Lapita-dated sites, because their flesh was eaten by the Lapita people. The stable isotopic composition of such well dated shells was investigated to know if the precipitation/evaporation balance was modified at that time in New Caledonia and Vanuatu.

### Main question:

- Was the Lapita colonization triggered by a change in climatic variability in the South-West Pacific region at around 3 ka BP?

#### Work done:

- Recovering of giant clam shells on Lapita-related archeological sites from New Caledonia and Vanuatu,
- Stable isotope analyses of shells and comparison with modern shell signatures,
- Interpretation in terms of climate variability.

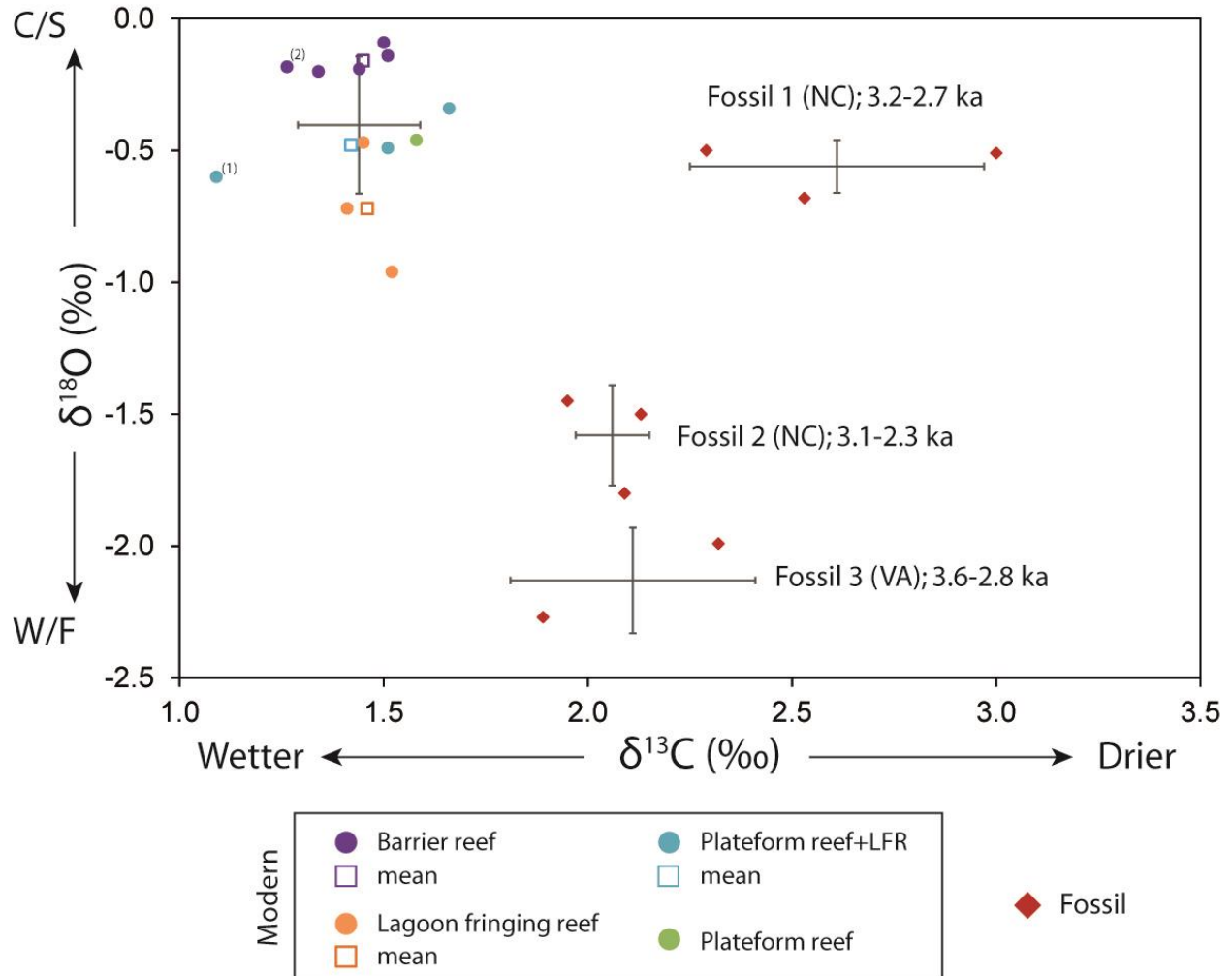
#### Methodology in brief:

Giant clam fossil shells, from different genus and species, were collected from several Lapita or Lapita-related archaeological sites, both in New Caledonia and Vanuatu, and dated ( $^{14}\text{C}$ ). When (and where) possible, modern equivalents were collected. Then, after verification of the preservation state of the fossil shells, isotopic ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) signatures on all samples were obtained, either by collecting powder corresponding to their whole life ("bulk composition"; Duprey et al., 2014) or collecting samples using a microdrilling device (Micromill Merchantek<sup>®</sup>) to obtain data at a monthly or infra-monthly resolution (Aubert, 2007 and Lazareth & Elliot, unpublished data). Note that for the interpretation below, data obtained at a high-temporal resolution were averaged to be comparable to "bulk composition". An estimation of the climatic variability was obtained by calculating the standard deviation of the 12  $\delta^{18}\text{O}_{\text{shell}}$  records.

#### Main results:

"The  $\delta^{18}\text{O}_{\text{shell}}$  records of modern giant clams do reflect the local reef environment (**Fig. 36**). [...] in agreement with the SST and SSS gradients observed in these reef environments. [...] Because the baseline integrates 12  $\delta^{18}\text{O}_{\text{shell}}$  records ranging from 1 to 7 yr. during the period 2002–2009, the variability of these records also reflects the  $\delta^{18}\text{O}_{\text{sw}}$  and SST variations due to the interannual climate variability dominated by ENSO." *Slightly modified Extract from Duprey et al. (2014)*. Three fossil groups are evidenced in **Fig. 36**, fossil 1 and 2 from New Caledonia and fossil 3 from Vanuatu.

With regard to the  $\delta^{13}\text{C}$  signature, "Bivalves synthesize their shell by precipitating calcium carbonate mainly from dissolved inorganic carbon. The  $\delta^{13}\text{C}_{\text{shell}}$  will reflect the isotopic signature of the main source of DIC used by the organism (McConnaughey and Gillikin, 2008). DIC originating from terrestrial sources has generally a lower  $\delta^{13}\text{C}$  than oceanic DIC. DIC originating from terrestrial runoff or a river may be detectable in the  $\delta^{13}\text{C}_{\text{shell}}$ , providing a proxy for freshwater input (runoff/river flow intensity) which in turn provides information on the precipitation regime (e.g., Mook and Vogel, 1968 Gillikin et al., 2006). [...] The  $\delta^{13}\text{C}_{\text{shell}}$  records of our *modern shells* suggest that, under present climate conditions, there is no detectable DIC gradient in these environments. By analogy with the modern records, fossil  $\delta^{13}\text{C}_{\text{shell}}$  records falling below (above) the modern baseline would indicate higher (lower) terrestrial DIC influence and, as such, more (less) rainfall.



**Fig. 36: Isotopic signature of modern and Lapita-related giant clams from the Southwest Pacific and environmental interpretation.** For the modern group, clams all lived in New Caledonia and are identified depending on their living environment. LFR: Lagoon fringing reef. Clams that lived part of their life in the aquarium are indicated as "lagoon fringing reef" since the seawater provided continuously to the aquarium came from such environment (details in Duprey et al., 2014). <sup>(1)</sup> indicates the *Hippopus hippopus* specimen studied by Aubert et al. (2009) and <sup>(2)</sup> the *Tridacna squamosa* studied by Lazareth & Elliot (unpublished data). For each group, the mean isotopic values ( $\pm 1$  standard deviation) is provided (error bars). C/S: colder/saltier; W/F: warmer/fresher. Modified from Duprey et al. (2014).

The constant depletion of the modern  $\delta^{13}\text{C}_{\text{shell}}$  records relative to the fossil records indicates that modern giant clams use a DIC source depleted in  $^{13}\text{C}$  compared to the fossil giant clams, independently of the climate context. The order of magnitude of the depletion observed is similar to the shift observed in the last 200 yr. in  $\delta^{13}\text{C}_{\text{shell}}$  records obtained from sclerosponges, scleractinian corals, and bivalves (e.g., Benavides and Druffel, 1986; Böhm et al., 1996; Butler et al., 2010; Swart et al., 2010). This shift is believed to reflect the release of enormous amounts of light carbon in the atmosphere due to the intense fossil fuel burning that started during the industrial revolution, referred to as the Suess effect (Revelle and Suess, 1957). [...] Consequently, the

differences between the modern  $\delta^{13}\text{C}_{\text{shell}}$  baseline and the fossil records cannot be interpreted in terms of past climate variability, however qualitative comparison between the fossil  $\delta^{13}\text{C}_{\text{shell}}$  records is still meaningful. [...]

The  $\delta^{13}\text{C}_{\text{shell}}$  records of group fossil 1 indicate a greater influence of oceanic DIC than the  $\delta^{13}\text{C}_{\text{shell}}$  records of groups fossil 2 and fossil 3 (Fig. 5). The magnitude of this difference is greater than the modern baseline range suggesting that this difference does not reflect different reef environments (fringing reef or outer barrier reef), but rather broad environmental changes in the precipitation regime. Groups fossil 2 and 3 show  $\delta^{18}\text{O}_{\text{shell}}$  values lower than the group modern, indicating that giant clams from fossil 2 and 3 experienced warmer conditions and/or  $^{18}\text{O}$ -depleted seawater (i.e., lower SSS) than the conditions found today in New Caledonia. Both the  $\delta^{13}\text{C}_{\text{shell}}$  and the  $\delta^{18}\text{O}_{\text{shell}}$  results indicates that group fossil 1 experienced lower precipitation than groups fossil 2 and fossil 3.

The standard deviation of the  $\delta^{18}\text{O}_{\text{shell}}$  modern records was 0.26‰ VPDB. The standard deviation of the archeological giant clam's  $\delta^{18}\text{O}_{\text{shell}}$  records is 0.57‰ VPDB. This value is 50% higher than the  $\delta^{18}\text{O}_{\text{shell}}$  standard deviation recorded by the modern specimens (Fig. 6; here [Fig. 37](#)).

**Was the Lapita colonization triggered by a change in climatic variability in the South-West Pacific region at around 3 ka BP?** The combined information of the oxygen and the carbon isotopic records identified the occurrence of two different climate states in New Caledonia within the period ca. 3.8–2.3 ka BP. State 1 is characterized by a climate similar to the modern climate and state 2 is characterized by warmer and wetter conditions than the modern climate [...]. Considering that the fossil giant clams lived within a 900 yr. period and that the length of the bulk records encompasses time periods inferior or equal to 10 yr., the giant clams may reflect an abrupt shift of the mean climate state from state 1 to state 2 (or vice versa) or a centennial, multi-decadal or inter-annual oscillation of the mean climate between the two states.

Based on sediment records including the same period studied here, it was shown that "The maximum SST ( $\delta^{18}\text{O}_{\text{sw}}$ ) variation during this period was 0.9°C (0.3‰ VPDB; Stott et al., 2004). This range, which can be considered as reflecting the centennial variability of the west Pacific climate, is lower than the difference observed between the four groups of giant clams identified. Consequently, the centennial climate or oceanic variability alone cannot account for the variations observed in the fossil giant clam isotopic composition. [...] The higher standard deviation of  $\delta^{18}\text{O}_{\text{shell}}$  records ca. 3 ka BP compared to 0 ka rather indicates strong climate variability during the main phase of the Lapita colonization, possibly due to changes in ENSO variability.

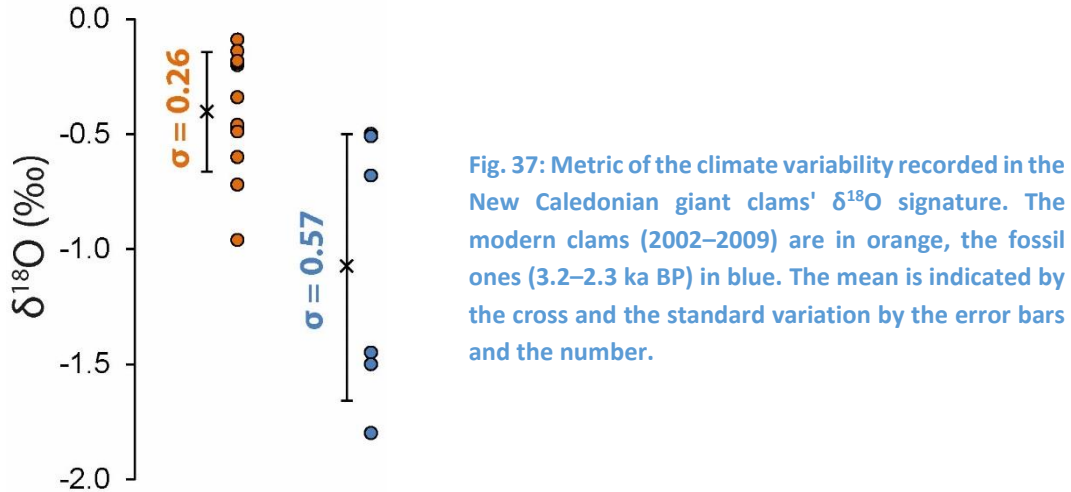


Fig. 37: Metric of the climate variability recorded in the New Caledonian giant clams'  $\delta^{18}\text{O}$  signature. The modern clams (2002–2009) are in orange, the fossil ones (3.2–2.3 ka BP) in blue. The mean is indicated by the cross and the standard variation by the error bars and the number.

A variable climate ca. 3.0 ka BP is consistent with previously published paleo-climate reconstructions from the Pacific, which report an increase in ENSO amplitude and frequency ca. 3.0 ka BP (Combettes et al., 2015; Haberle et al., 2001; Haug et al., 2001; Koutavas et al., 2006; Koutavas and Joanides, 2012; McGregor and Gagan, 2004; Moy et al., 2002; Rodbell et al., 1999; Sandweiss et al., 2001). In addition, continental records from Vanuatu and New Caledonia indicate drier conditions ca. 3.0 ka BP, suggesting that the SW Pacific experienced severe droughts that were most likely related to strong El Niño events (Wirrmann et al., 2011a; 2006; 2011b). Yet some recent studies have shown that ENSO variability was reduced ca. 4–3 ka BP in the central Pacific, highlighting the spatial heterogeneities of the ENSO regime (Cobb et al., 2013; McGregor et al., 2013). These discrepancies between the Western Pacific and the Central Pacific records emphasize the importance of producing climate reconstructions from local records when investigating punctual and rather localized events such as the Lapita colonization. The highly variable climate evidenced here support the hypothesis of an ENSO-forced Lapita colonization as suggested by Anderson et al., 2006" *Extract from Duprey et al. (2014).*

Here are some very concise elements of response to the main questions that were put p. 18, considering the work presented here.

- Can molluscan shells be good recorders of SST?

Only the Tridacnidae could be good recorders of SST changes; either using sclerochronology or  $\delta^{18}\text{O}_{\text{shell}}$ . In both cases, records should be interpreted keeping in mind that side effects, related to the physiology and/or to the environment (e.g., SSS variations) exists.

- Can we use bivalves to reconstruct climate variability in the East Pacific, including El Niño Southern Oscillation (ENSO)?

The South American studied species can hardly be used as recorder of ENSO variability. Only shell growth halts in *Protothaca thaca* might provide an indication of El Niño occurrences in the past.

- What are the effects of diagenesis on the geochemical signature of biocarbonates and can diagenesis processes be proposed?

Very early diagenesis in the South American bivalve *Protothaca thaca* might have increased the Mg/Ca ratio in the part of the layer close to the environment and this in the oldest part of the shell. The main diagenesis features observed in Tridacnidae shells were dissolution and calcite crystallization. Preliminary data showed the calcite  $\delta^{18}\text{O}$  signature is particularly depleted and even slight mix of aragonite and calcite can change the signal, and thus the reconstructed environmental parameter.

In corals, dissolution was shown to increase U/Ca and  $\delta^{18}\text{O}$  while the presence of intra-skeletal calcite impacted almost all the studied proxies.

In most cases, it was not possible to propose a conclusive process that led to the observed diagenesis without further studies. Only hypotheses can be sometimes proposed.

- What were the climatic characteristics in the South-west Pacific at around 6 ka BP?

Since the Mid-Holocene, the SST in the South-west Pacific was close to that of the present day. All our records show drier conditions at around the Mid-Holocene that is interpreted slightly differently depending on the exact period (early-Mid-Holocene vs. Mid-Holocene). It is a strong possibility that the SPCZ was more to the north, with a more variable position than currently. The existence of stronger or extended Hadley cells is suspected but needs confirmation. Lastly, ENSO variability was lower during the early-Mid-Holocene (c. 6.7-6.5 ka BP).

- What climate prevailed during the Lapita colonization?

Our study confirms that climate was highly variable at c. 3 ka BP with abrupt shifts between two states, one close to modern conditions, the other warmer and wetter. This alternation might be related to a change in ENSO variability and support a climate-related migration of the Lapita population.

## V / AND NOW...?

In the process of using biocarbonates as recorders of environmental variables, I identified, and developed above, three main subjects:

- validate the link between the chosen proxy and the considered environmental parameter (calibration),
- assess the preservation of the archive and of the geochemical signal (diagenesis),
- use the validated proxy in pristine archives for environmental reconstruction (application).

Since the 2000's, when I started working on biocarbonates, I focused on point 1, without occluding the other ones, which I worked equally on. Looking at the current literature, while papers on reconstructions are increasing, there is still a high need in understanding biomineralization processes. One of my future projects consists in trying to link the mantle ultrastructure and composition to the composition of the secreted shell. To do that I started working on the European abalone *Haliotis tuberculata*, in collaboration with Stéphanie Auzoux-Bordenave and Aïcha Badou (UMR 7208 - BOREA; § 5.1). In addition, while starting working on this model, I was intrigued by the presence of large calcite crystals inside the aragonitic nacreous layer. I would like thus to understand if such crystals are related to biomineralization or to diagenesis.

Another subject I would like to develop from now is in link with tropical ecosystems and their management. To set relevant sustainable actions for endangered ecosystems, some being essential for human population life or even survival, it is very important to assess human *vs.* climatic impacts, especially in the context of the current global change. Among those endangered systems, coral reefs and tropical ecosystem as a whole are threatened by multiple stressors. At the same time, those ecosystems are extremely valuable, for the biodiversity they host but also for the livelihood of millions of persons worldwide. Consequently, one of my objectives is to bring answers about the current and recent threats those ecosystems are submitted to by using the potentiality offered by various biocarbonates as environmental archives in combination with other disciplines (§ 5.2).

Because bivalves are present almost everywhere, they potentially represent very powerful tools in many studies. With the objective to validate such tools in another environment, freshwater ones, I recently started working on a very innovative project working on freshwater bivalves in the Amazon basin (§ 5.3). Preliminary results are very promising indicating these freshwater bivalves might be used as a bio-indicator of freshwater geochemical characteristics and of hydrological dynamics in this basin.



## 5.1 Project on biomineralization

A way to better understand and interpret the geochemical signal measured in mollusk shells is to better understand how the shell is produced and which are the processes of transfer and incorporation of the trace elements in the shell. As I observed in *Protothaca thaca* for example, at a given moment (along an isochronous layer) the element/Ca ratios in the shell are different depending on the location where the element is analyzed along the layer (Chap. II, § 2.2, p. 28). To understand what is occurring at the moment of shell deposition, it is essential to study the shell and its secreting tissue, i.e., the mantle. More precisely, both the outer epithelium of the mantle, responsible for shell layer secretion, and the shell must be studied together.

To try to understand the role of the outer epithelium of mollusks, many studies have already been done. A question that underlined these studies was: is there a link between outer epithelium cells or cell activity and the secretion of a given shell layer? Histological studies showed that the outer epithelium cells differ depending on their location relative to the shell edge (Bubel, 1973; Fang et al., 2008). This particularity is sometimes called the "mantle regionalization". Using various labeling techniques, some shell matrix proteins were shown to be expressed in localized part of the outer epithelium of the mantle of *Pinctada* sp. (Gardner et al., 2011; Marie et al., 2012; Sudo et al., 1997; Takeuchi and Endo, 2006). Because some of these proteins were found in a given shell microstructural layer (e.g., MSI60 in the nacreous layer); the part of the mantle where they are expressed was interpreted as representing mantle parts responsible for the secretion of the given microstructural shell layer. Some proteins are thus specific to a given layer and expressed in localized outer epithelium parts (e.g., MSI31; Sudo et al., 1997) and others are not layer-specific and are expressed all along the mantle (e.g., the nacrein; ex. Miyamoto et al., 2005), pointing to a more "global" role in shell biomineralization for these proteins. A review of the molluscan shell proteins already identified, and their relationships to a given shell microstructure and/or mantle area, can be found in Marin et al. (2012) and Zhang and Zhang (2006).

If the links between mantle and shell proteins start to be unraveled, the one between specific mantle cells and the shell layer's geochemistry remains a road to be paved. This is the purpose of studying the European abalone, *Haliotis tuberculata*. This gastropod was selected because i/ the *Haliotis* genus contains 70 species worldwide, including tropical settings, so such a work could then be used for future tropical species studies, ii/ it is found as fossil remnants (Geiger and Groves, 1999) so potential for paleo-reconstruction exists, as demonstrated on a fossil European abalone (Jolivet et al., 2015), iii/ its shell microstructure and development have already been studied (e.g., Auzoux-Bordenave et al., 2010; Dauphin et al., 1989; Gaume et al., 2011; Gilbert et al., 2008), and some mantle characterization has been done (Gaume et al., 2014; Le Roy et al., 2012; O'Neill et al., 2013).

In the framework of two projects, "ATM biomin 2015" and "Morphonacre" (Sorbonne-Universités - Emergence), headed by Stéphanie Auzoux-Bordenave (UMR 7208 - BOREA), we already did some work on the shell geochemistry itself. Using laser ablation ICP-MS, we evaluated the geochemical spatial homogeneity along single growth layers of cultured juveniles and adults *Haliotis tuberculata* gastropod shells. The trace element ratios (Mg/Ca, Sr/Ca,

Ba/Ca, Mn/Ca) along isochronously shell layers vary but all shells display similar trace element isochronous distributions (Lazareth et al., 2014b, 2015).

To understand these trace element distributions, reproducible between individuals and independent on the environment (layer secreted at a given moment, i.e., constant environment), already observed in another bivalve (Chap. II, p. 28), our next goal will be to try to link the chemistry of the shell chemistry and of the secreting outer epithelium of the mantle. Preliminary LA-ICP-MS tests in analyzing the trace element composition along the outer epithelium points to the difficulty of mantle preparation for such analyses. Future work will thus imply to identify both the most appropriate analytical technique and the best outer epithelium preparation. If geochemical heterogeneities occur in the outer epithelium, and if we can link this to specific mantle cells, this would provide new insight in shell biomineralization.

While starting this work, I observed that calcite was present in the aragonite *Haliotis tuberculata* shell, and of course that this impacts the geochemical signature. This presence was confirmed and specified in specimens issued from the same environments (Lebreton, 2015) and already noticed by Dauphin et al., 2014. Nevertheless, the origin of this calcite still need to be understood. Therefore, the next steps will be to:

- characterize the habitus(es) of this calcite through additional SEM analyses of reared and wild individuals and see if differences occur between the two populations,
- confirm (and understand) the higher proportion of calcite in wild animals compared to reared-ones,
- evaluate the animal's age at which calcite starts to be observed (up to now, no calcite was observed in juveniles) and tentatively relate this to environmental stress if reliable,
- determine if such calcite has or not of a biogenic origin,
- examine if any environmental parameter (micro-borer presence, disease, food, water pH decrease, SST, etc.) could explain the presence of calcite.

Another objective would be to determine if calcite-related proteins could be found in the mantle of specimens which shell contains such calcite. Various *in vitro* experiments could be settled to understand the potential link between the presence of calcite and the environment. Lastly, starting collaboration with mineralogists working on biominerals will also provide new perspectives in understanding biomineralization processes (collab. Thierry Azais and Nadine Nassif, UMR 7574 - LCMCP).

## 5.2 Tropical ecosystems under threat: how could biocarbonate archives help?

Coral reefs constitute extremely invaluable ecosystems, from the biodiversity point of view but also by the many ecosystem services they return to the populations like food, protection, tourism, etc. However, these ecosystems are now severely endangered (Burke et al., 2011; Carpenter et al., 2008; Pratchett et al., 2014; Riegl et al., 2009) because they are subjected to many pressures. These threats can be grouped in two categories; global change (ocean warming and acidification; e.g., Doney et al., 2009; Gattuso and Hansson, 2011; Hoegh-Guldberg et al.,

2007) and local threats (sediment runoff, over-fishing, pollutions, coastal anthropisation, etc.; see review in Saha et al., 2016). In the future, I would like to use the knowledge I acquired on environmental reconstruction using giant clams and coral skeletons to provide historical records of environmental changes in places where coral reefs ecosystems are at high risk. I would also like to combine geochemical-based reconstructions to ecosystem dynamics knowledge, satellite remote-sensing, and information provided by the populations relying on these coral reef resources. Such multidisciplinary research is indeed fundamental to improve our knowledge on tropical ecosystem and consequently on its management.

In this context, I started recently to work on mining impacts in New Caledonia (§ 5.2.1) and would like to develop coral reef studies such as previously described in the Western part of the Indian Ocean (§ 5.2.2).

### 5.2.1 The impact of mine exploitations in New Caledonia

In the South-west Pacific, New Caledonia is surrounded by the largest lagoon worldwide and more than 60% of its coral reefs belong to the UNESCO World heritage. However, this coral reef ecosystem is under important anthropic pressure such as urban development, agriculture, livestock, fishery and mining exploitation. Exploitation of Nickel-rich lateritic soils that exploded at around the 1970s is continuing with the very recent opening of new mines like the Koniambo Nickel SAS - KNS in the North Province and the Vale NC (Goro Nickel in the past) in the South Province. These open-pit mines imply deforestation and thus an increase in soil erosion and in fresh waters charged in sediments rich in metals towards the lagoon, with the risk to impact the functioning of the reefs and their biodiversity (Fernandez et al., 2006; Fichez et al., 2005). Since 2009, a new mining-code has been adopted in New Caledonia with an imperative for the mine operator to implement environmental surveys, on land and in the lagoon, and to set up replanting programs. Among those environmental surveys, concentration of metals in the waters is measured, but remains sporadic, i.e., quarterly and semi-annual, and studies on impacts of these metallic contributions on corals are scarce. In the current context where many other threats weigh on corals and coral reef ecosystems like acidification and warming of the oceans and insofar as many reefs are potentially impacted by metals (ex: Cuba, Costa Rica, Indonesia, New Caledonia), it is crucial to determine the impact of the terrigenous contributions enriched in metals on the principal coral genus composing the coral reefs such as *Porites* sp..

A first study was done on *Porites* sp. colonies from two bays in the New Caledonian South Province. Geochemical analyses of *Porites* sp. colonies were conducted to reconstruct variations in metal concentrations, e.g.; Ni/Ca, Co/Ca, over the last ~ 15 yrs. and connect, or not, these variations to mining activities and/or climatic variability (e.g., precipitations; Boudeau, 2016; Milleret, 2016). Average Ni and Co concentration increase after 2010 in the "Baie de Kué" where freshwater inputs come from the river Kué that crosses recently exploited lands. We suppose that the deforestation in this zone increases the leaching of the Ni-Co-rich soil. However, we observed that the Ni-Co concentration in the colonies of the two sites was not so different, most probably because in any cases the Ni-Co signature in water is high

because of geological context. This work already showed both the feasibility of using *Porites* sp. colonies to look at potentially mine-impacted site as done for example in Indonesia, Philippines, etc. (David, 2003; Edinger et al., 2008 and Saha et al., 2016 for a review) but also the necessity of having the best possible knowledge of the sites. To improve and specify the conclusions of this study, another coral colony of one of the sites studied will be analyzed and all results will be compared with data obtained on other places of New Caledonia, less impacted by Ni-Co. This work also paved the road for future similar studies in other coral reef zones impacted by mining.

### 5.2.2 Near future studies on coral reefs environments: Western Indian Ocean

The Indian Ocean contains 13% of the coral reefs of the world and 65% of these reefs are regarded as “at risk” and 1/3 as “top” and “very high” risk (Burke and al., 2011). This is the case of reefs located along the east side of Africa, in Kenya (particularly in the South) and in Tanzania, where the coastal populations, extremely poor, are heavily based on the resources brought by these coral reefs. Overfishing largely weakens these ecosystems but this is not the only threat. Indeed, increase in the sedimentary contributions; in link with land-use changes, development of agriculture and breeding (e.g. case of bay of Malindi in Kenya; Johnson, 2013; Fleitmann and al., 2007); and pollution related to urbanization and/or mining exploitation, also have negative effects on these reefs.

To better understand the potential impacts of the various threats which weigh on the coral reefs of the coasts of the South of Kenya, it is necessary to understand the recent evolutions (last tens of years at last century) of the environments of these ecosystems. I intend thus to start a project in the Kwale district of Kenya; e.g., around Gazi where coral reefs are at "very high" risk. To potentially improve sustainable management in this zone, it would be very interesting to gather information on the recent evolution of coral reef water quality, freshwater sources reaching those reefs, land management, and fishing resources. Slightly south of Gazi, the possible impact(s) of the development of the Kwale Titanium mining activity might also be investigated. To reach these goals, inter-disciplinary work is needed. The study of the geochemistry of coral skeleton (e.g., *Porites* sp.) will be used to obtain historical data on water properties (e.g., heavy metal loads, freshwater inputs, temperature), at the monthly resolution. Such records could then be linked with other approaches, for example, ecosystem dynamic studies linking fisheries, coral reefs, mangroves, seagrass meadows (collab. with Kenyan partners Daniel Olago - ICCA-University of Nairobi; Bernerd Fulanda - Pwani University; D. Obura - CORDIO NGO and Melckzedek K. Osore - Kenya Marine & Fisheries Research Institute), microbial community and microborers diversities (e.g., on two contrasting sites in terms of coral reef health; collab. Santie De Villier - Pwani University and Aline Tribollet - UMR LOCEAN).

### 5.3 Hydrochemical data in the Amazon basin: the potential of freshwater bivalves

The Amazon basin holds several world records; it is the largest basin in the world, it hosts the largest tropical river, the Amazon, the largest rain forest, and the largest freshwater fish species diversity. Among the multiple ecosystem goods and services provided to the human populations, food and incomes via fisheries are of crucial importance. However, such richness both in terms of biodiversity and resources is highly vulnerable. Indeed, overfishing, the degradation of habitat (e.g., deforestation, dam constructions), pollutions, etc. threaten this enormous freshwater ecosystems and its associated assets (Castello and Macedo, 2016). In the Amazon basin it was shown that the strontium isotope signature of the water defines specific areas, in link with the surrounding geology (Santos et al., 2014). This specificity was used to determine fish origin and movements using otolith  $^{87}\text{Sr}/^{86}\text{Sr}$  (Hegg et al., 2015; Pouilly et al., 2014). However, such data, useful to many studies, are scarce because measuring the strontium isotope signature of every Amazon basin river, together with its seasonal variations, is impossible. An innovative methodology to acquire  $^{87}\text{Sr}/^{86}\text{Sr}$  data in various settings and at a high temporal resolution would be to use the record capacities of bivalve's shells. Indeed, bivalve could be viewed here as a naturally-fixed sensor that would record the geochemical signature of the water and its changes overtime. A preliminary study of  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures of Amazonian Unionidae shells at a high temporal resolution (collab. Marc Pouilly and Marc Duponchelle - BOREA; Christophe Pecheyran - LCABIE-IPREM - UMR 5254, and Brazilian collaborators), coupled to monthly stable isotope profiles (collab. with Elise Dufour - MNHN), showed that these bivalves record  $^{87}\text{Sr}/^{86}\text{Sr}$  faithfully (i.e., no fractionation between water and shell) and that  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data can provide useful information on the river dynamics (Hugo Lestrelin internship, 2016). Future research on this subject will include field studies, notably to validate the shell growth rhythms, and additional analyses to confirm the reliability of using Unionidae as a sensor of Amazonian river chemistry. Because Unionidae can be found more or less everywhere in this basin, other future subjects could include for example evaluations of pollution or changes of river dynamics after dam construction.

#### 5.4 Concluding remarks

I started my IRD career trying to develop the use of high-resolution archives in the East Pacific to improve our knowledge on ENSO. Indeed, in Peru and Chile, ENSO consequences on the environment and on human populations are particularly severe. Because molluscan shells might provide such high-resolution records, on present day environment but also on past ones based on fossil remnants, I worked first on the sclerochronology and geochemistry of tow South-American mollusks. Both vital effects and diagenesis on the chosen proxies (and species) precluded the validation of those species as potential ENSO recorders. Because to study ENSO and past environmental variability in the Western Pacific is also essential to better understand this phenomenon, I turned to New Caledonia and Vanuatu where biocarbonate archives are also present, Tridacnidae and corals. When I started, *Tridacna gigas* was almost the only species from the Tridacnidae family that had been studied as a potential environmental recorder. Because this species is extinct in the West Pacific, I choose other ones currently living there and also present as fossil remnants in the region. *Tridacna maxima* and *Hippopus hippopus* meet these requirements. I thus develop the calibration and validation of proxies in these species

and obtained then paleo-environmental data, essentially for the Lapita period. Lastly, to obtain paleo-environmental data on the Mid-Holocene period, fossil corals from that period were studied. As stated above, I would like now to develop more applied studies based on the competencies I acquired on biocarbonate archives, in a closer relationship with partners from South countries.

I would like to end these final remarks by saying that I really had pleasure to work on the subjects developed above, with a particular attraction for the understanding of what is really recorded by these archives, current or fossil. To finish, most these made within the framework of the training of student, a part of my researcher work I appreciate enormously.

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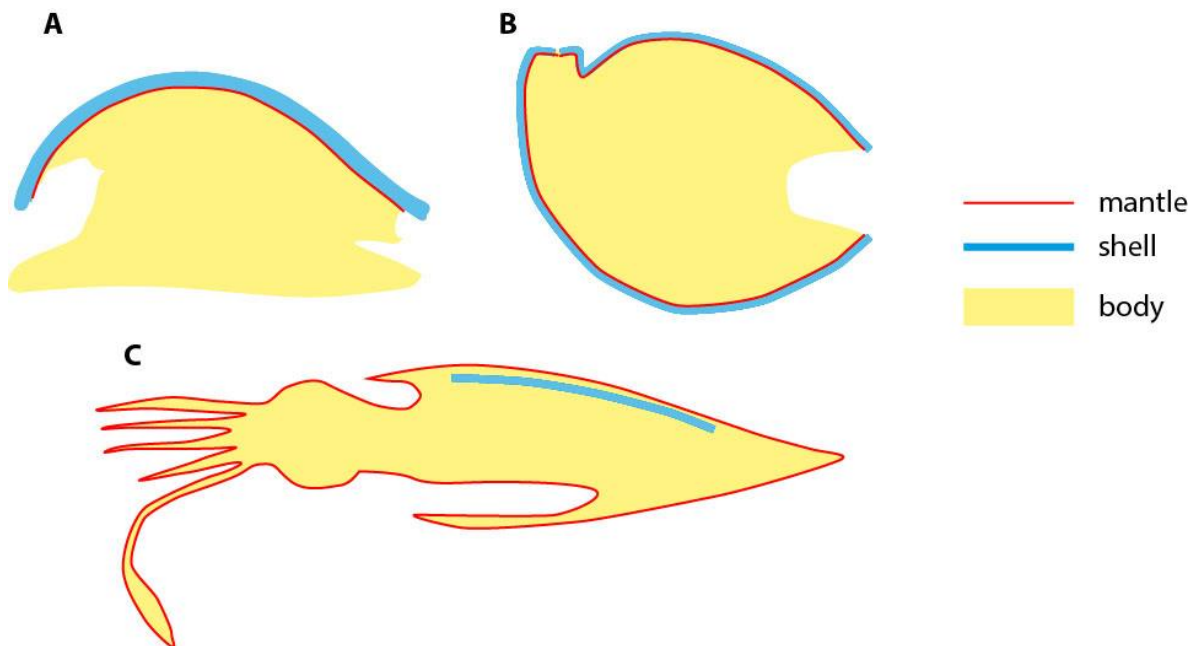
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## APPENDIX A - VERY BRIEF OVERVIEW ON MOLLUSKS AND THEIR SHELLS

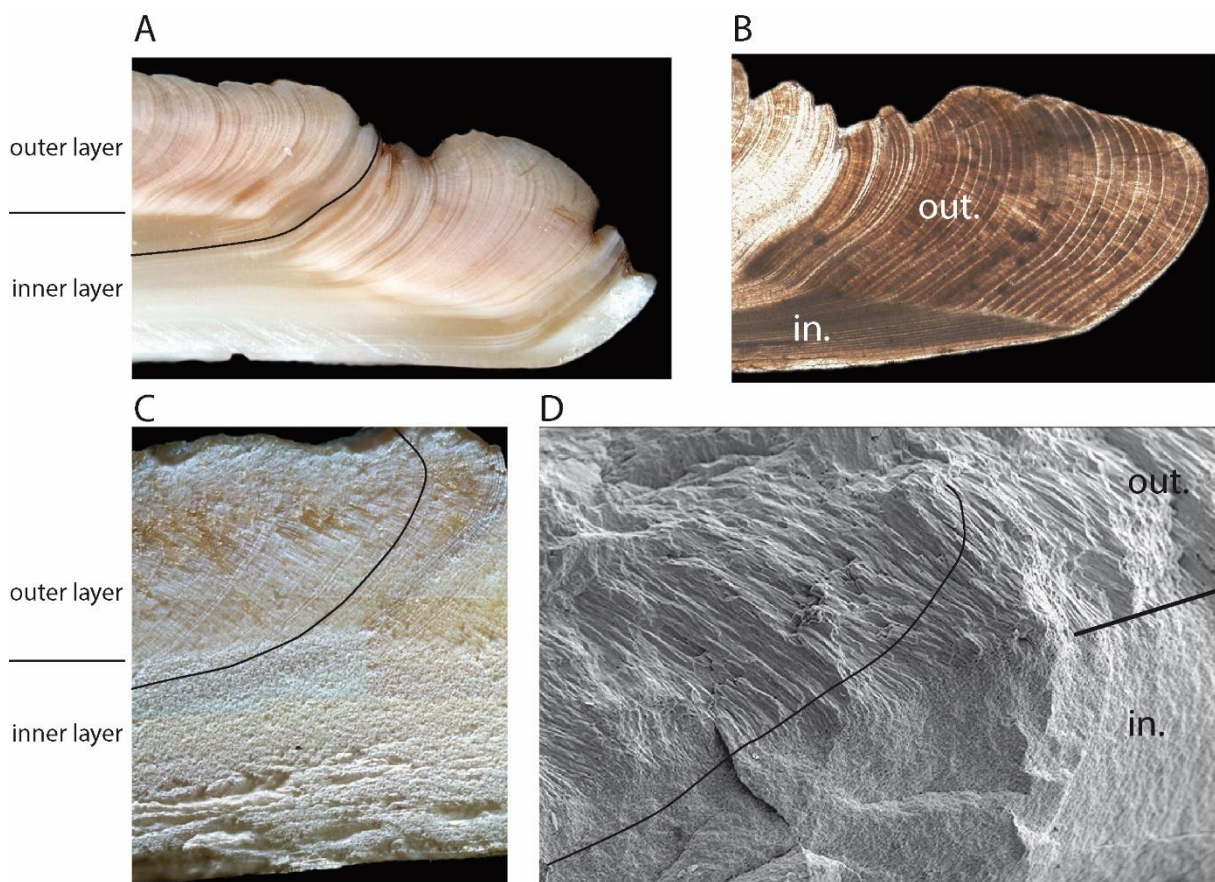
The molluscan phylum is divided in ten classes among which 3 genera were already used for environmental reconstructions based on their external (shell) or internal (e.g., cuttlebone) skeleton. These classes are the gastropods (e.g., ormers, snails), the bivalves (e.g., mussels, oysters), and the cephalopods (e.g., squids, nautilus). One common feature of all mollusks used as potential environmental recorder is the presence of a shell, in most cases external, but for sepiids, secreted by a tissue named mantle. In the case of gastropods, bivalves, and nautilids, this mantle is found between the animal body and the shell while in the case of sepiid this mantle is covering almost all the animal, except for its head, tentacles, and cuttlebone and has thus one of its surface in direct contact with the surrounding water (**Fig. A1**). The shell growth and geochemistry are linked to the mantle activity, which is linked to the organism physiology, itself partly linked to the environment. These intermingled processes make the use of molluscan shell as an environmental archive sometimes complicated like shown in this memory.



**Fig. A1: Schematic view of the relationship between the shell, the mantle, and the organism body for the molluscan genus already used for environmental reconstructions. A. Gastropod; B. Bivalve; C. Sepiid.**

The molluscan shell is a highly complex biomaterial composed of a carbonate ( $\text{CaCO}_3$ ) phase, aragonite or calcite, intermingled with an organic matrix (O.M.), itself complex. It is thus called a biocarbonate both because it is deposited by an animal and because it is not a "pure" carbonate phase (as opposed to geological carbonate for example). Many studies have been done to try to understand the way shells are secreted, i.e., the biomineralization process. If the process starts to be understood for some species, or sometimes for one layer of some species (e.g., the nacre of diverse mollusks), it remains globally a big black box. Here is a quick global description of the bivalve's shell itself, specifically the part where the shell secretion occurs, the shell edge.

The bivalve shell consists in at least two biocarbonate layers, an inner and an outer one<sup>5</sup>, generally covered by an organic layer called the periostracum. Each of these biocarbonate layers is characterized by specific features in terms of carbonate polymorph (calcite or aragonite), crystal size and arrangement (microstructure), and organic matrix composition. We will name these layers "microstructural layers". The microstructural layers are secreted together at a given time as evidenced by the increments and growth lines that cross those layers in continuity (Fig. A2). Note that crystals composing the microstructural layers have their main crystallographic direction close to perpendicular to the shell growth direction. This complexity; i.e., how a single tissue can be responsible for the secretion of diverse microstructural layers with crystals having crystallographic properties while being at the same time completely different than geological crystals; woke up the interest of the scientific community that tempted for long to understand the shell biomineralization processes (Schmidt, 1924Schmidt, 1924Schmidt, 1924).



**Fig. A2** Organization of the shell microstructural layers (example of the *Protothaca thaca* bivalve), with the growth lines crossing both microstructural layers evidenced (dark curve in A, C & D). All shells are oriented with the growth direction to the right. The external microstructural layer (outer layer and out.) has a prismatic microstructure (see C & D) and the inner one (inner layer and in.) a homogeneous microstructure (see C & D). A. Polished shell thick section viewed under an optical microscope. B. Thin section viewed under an optical microscope. The white lines here are the growth lines of the shell. C. Slightly etched thick section viewed under an optical microscope. D. Broken piece viewed under a scanning electron microscope. Growth lines are invisible with this preparation; the dark line is a virtual one.



As stated above, the mantle of mollusks is the tissue covering the animal body, and it is responsible for the shell production. This tissue consists in an inner and outer epithelium enclosing the mantle tissue itself. In bivalves, the distal part of the mantle; located at the shell margin where shell secretion occurs; is folded in three parts named outer, middle, and inner fold (Fig. A3). The groove between the outer and the mid-fold is named the periostracal groove because this is the place where the periostracum, a thick organic layer covering the outside of the shell for its protection and part of its formation in some cases is secreted. In gastropods, the mantle is folded only in two, with the periostracal groove between the outer and the inner fold. The organic and inorganic elements necessary for the shell formation are provided to the extrapalleal space; i.e., the space between the outer epithelium and the shell; through the mantle outer epithelium (OE). This place, where shell formation is achieved, is filled with the extrapalleal fluid (EPF). Note that, if it is commonly accepted that shell formation occur in the EPF, recent studies on *Pinctada fucata* suggest that mantle cells themselves are certainly involved in this process (Kong et al., 2015; Xiang et al., 2014Kong et al., 2015; Xiang et al., 2014Kong et al., 2015; Xiang et al., 2014).

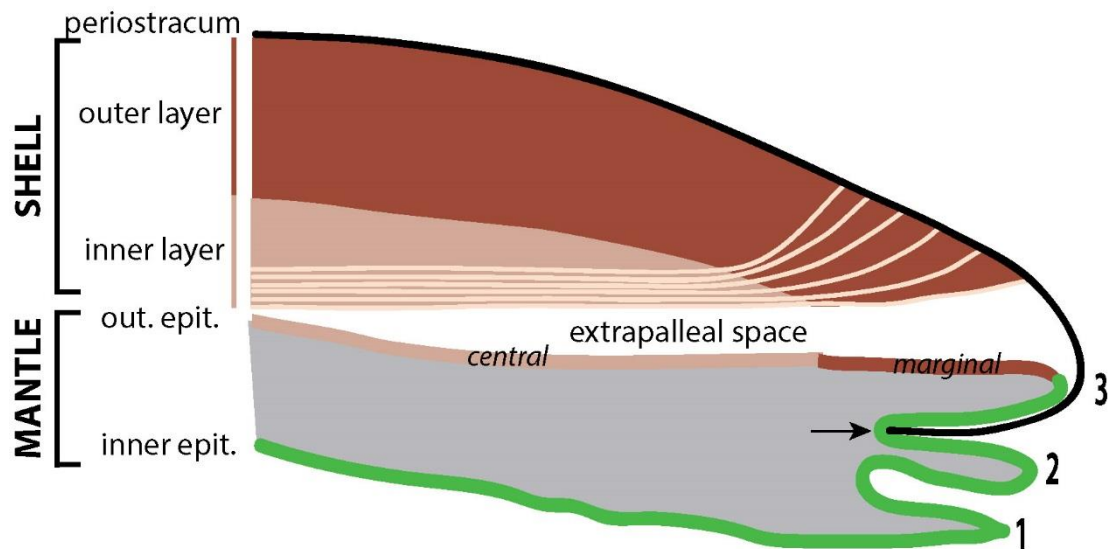


Fig. A3: Schematic cross section of the shell growing edge showing the relationships between the shell and the mantle. Growth lines are in rose with the growth direction to the right. 1 to 3: inner, mid and outer fold respectively. The arrow points the periostracal groove. Out.: outer; epit.: epithelium. The outer epithelium is represented with two colors, potentially presenting regionalization of this tissue in relation with the secretion of the outer and inner layer.



## APPENDIX B

### B.1 Curriculum vitae

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### Academic Qualification

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- March 1998**    **PhD in Earth Sciences**, University of La Rochelle (France).  
*"Ballast pebbles from the Poitou-Charentes sea-shore: granites and larvikites. Petrology, geochemistry, typology and geographic origin - Constraints on old commercial maritime sea-links"*, J.-C. C. Mercier as advisor.
- June 1994**    **French DEA** (Diplôme d'Etudes Approfondies) - **Earth option** - "Metamorphic and magmatic processes - Volcanology", Universities of Clermont-Ferrand and Saint-Etienne.
- June 1993**    **Master degree in Earth Sciences**. University Joseph Fourier (Grenoble I, France).

### Professional Experience

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- 2003**            **Researcher, IRD France-Nord (CR1 since 2008)**
- 2002**            **Associate researcher**  
*Department of geology, Vrije Universiteit Brussel, Belgium, collaboration E. Keppens.*
- 1998-2000**    **Post-doctoral position** at the Analytical Chemistry Department (ANCH) from the "Vrije Universiteit Brussel" (VUB, Belgium), "Training and Mobility of Researchers" (TMR) Marie-Curie Research Training Grant, contract n° ERBFMBICT 983440. *"LA-ICP-MS analysis of trace elements in biogenic minerals: time series recording of environmental changes"*.
- 1995-1996**    **Associate researcher**  
*University of La Rochelle, France*

### Teaching

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**1994-1995, 1998, 2001** **Temporary teacher**, University of Caen and La Rochelle (186 h in total).

### Publications and Communications

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- 20 Peer-reviewed publications (including 5 with supervised or co-supervised PhD students, 9 with Master 2 students)
- 46 communications in international meetings
- 20 communications in national meeting/workshops

## B.2 Research projects

- 2016** "BiBhy, Les bivalves comme bio-indicateurs des variations hydrochimiques dans les rivières amazoniennes", 2016, CNRS/PEPS. *P.I.: M. Pouilly (UMR BOREA).*
- 2015-16** "MORPHONACRE, Croissance de la nacre et impact des facteurs abiotiques sur la morphogénèse coquillière" IDEX Sorbonne Universités – Programme Emergence, *P.I.: S. Auzoux-Bordenave (UMR BOREA).*
- "DOC-SA, Studies on dissolved organic carbon dynamisa t basin level in support of better resilience of ecosystems to global changes and team building in Southern Africa" Hubert Curien PROTEA, *P.I.: V. Chaplot (LOCEAN).*
- 2015** "INTERFACE, Caractérisation de l'interface tissu-coquille chez l'ormeau *Haliotis tuberculata*: approches géochimique et ultrastructurale (MET-EDX)" ATM "Interactions Minéral-Vivant", *P.I.: S. Auzoux-Bordenave (UMR BOREA).*
- "La coquille de bénitier : un élément clé pour comprendre l'histoire de vie des individus, leur croissance et la structuration des mapiko ?" BQR – Université de Polynésie Française, *P.I.: C. Brahmi (UPF).*
- 2014** "CARBOMORPH, Phases précoces de la morphogénèse du squelette carbonaté: modèles Mollusques et Echinodermes" ATM "Interactions Minéral-Vivant", *P.I.: S. Auzoux-Bordenave (UMR BOREA).*
- "Inter-annual and interdecadal SST and pCO<sub>2</sub> variability in the South-west Pacific for the last millennium: insight from coral (*Diploastrea heliopora*) geochemistry and models" IPSL-soutien recherche, *P.I.: Claire E. Lazareth (LOCEAN).*
- 2013** "ACID-Antilles, Reconstruction annuelle des paléo-pHs sur 220 ans et quantification de l'ACIDification des eaux de surface de la Mer des Antilles: étude de son impact sur l'espèce coralliaire *Siderastrea siderea*", INSU/LEFE/CYBER. *P.I.: E. Douville (LSCE).*
- 2011-13** "AMICAL<sup>2</sup>, VARIabilité teMpoReLle des taux de DIssolution des carbonates dus à la microflore perforante dans le contexte du changement globAL (acidification des océans et élévation de la température)", GOPS. *P.I.: A. Tribollet (LOCEAN).*
- "SALOUM, Variabilité et saisonnalité de la mousson au Sénégal au dernier millénaire", INSU-LEFE-EVE, *P.I. M. Carré (ISEM).*
- 2010-14** "EL PASO, El-Niño: leçons du passé à partir de simulations et d'observations", ANR Programme Blanc, *P.I.: P. Braconnot (LSCE).*
- 2009-10** "HOLBECO, Variabilité climatique à l'HOLocène, à 6000 et 3000 ans BP, dans le Pacifique Sud-ouest déduite de l'étude conjointe des BENitiers et COraux", EC2CO – INSU, *P.I.: C. E. Lazareth (LOCEAN).*
- 2004-08** "SENSOR, Climate shift and El Niño Southern Oscillation: implications for natural Resources and management", Specific Targeted Research Project, INCO-2002-A2.2.
- 2005-09** "Estudios escleroclimatologicos en conchas de moluscos de la costa Peruana", PALEO-CONCHAS. *P.I.: F. Velazco (AGM-UIOQ), J. Argüelles (UIIM-DIRDL), D. Gutiérrez (ABM-UIOB), L. Ortlieb (UR055, PALEOTROPIQUE), C.E. Lazareth (UR055), N. Guzmán (IRD-CENSOR).*
- 2005-06** "Calibration de proxies dans la coquille de *Tridacna* sp.", PAI-Alliance – EGIDE. *P.I.: G. Cabioch (UR055, PALEOTROPIQUE), M. Elliot (Univ. Edinburgh).*
- 2002-05** "CONCHAS, Calibration du "proxy" coquilles de mollusques littoraux, pour la reconstruction de variations de température de la mer et de conditions El Niño dans l'Est du Pacifique tropical depuis la fin du Pléistocène.", PNEDC. *P.I.: L. Ortlieb (UR55, PALEOTROPIQUE).*

**1998-00** "LA-ICP-MS analysis of trace elements in biogenic minerals: time series recording of environmental changes". Département de chimie analytique et environnementale (ANCH), Vrije Universiteit Brussel (VUB), "Training and Mobility of Researchers" Marie-Curie Research Training Grant.

## B.3 Student training

### B.3.1 Post-Doctorate level

H. C. Wu, 2015-2016, founding L-IPSL, « *Towards improved proxies calibration for corals' Paleoclimatic reconstructions: Case study of the impact of seawater acidification on coral and boring microflora* ». Tutor: D. Dissard et A. Tribollet; co-tutors: **C.E. Lazareth**, F. Le Cornec, E. Douville (LSCE), D. Blamart (LSCE).

C. Brahmi, 2013-2014, bourse Ile-de-France, « *BIOREEF RESPONSE : Impact des micro-organismes perforants (cyanobactéries, micro-algues euendolithiques, champignons) sur la composition géochimique du squelette des coraux* ». Tutor: A. Tribollet; co-tutors: **C.E. Lazareth**, D. Dissard, F. Le Cornec.

### B.3.2 PhD

W. Ajili, 2015-: "*Croissance coquillière au cours du développement de l'ormeau européen Haliotis tuberculata/Impact du changement océanique sur la biominéralisation*". Supervisors: T. Azais (UMR 7574), S. Auzoux-Bordenave (UMR 7208 - BOREA); co-supervisors: **C.E. Lazareth**, N. Nassif (UMR 7574), A. Badou (MNHN, station de Concarneau), S. Huchette (SCEA France-Haliotis, Plouguerneau).

N. Duprey, 2009-2012, UPMC - Paris, ED 129: "*Variabilité climatique de deux périodes clés de l'Holocène, ca 6000 et 3000 ans BP, dans le Pacifique Sud-ouest à partir de l'analyse d'archives biocarbonatées*". Supervisor: G. Cabioch; co-supervisor: **C.E. Lazareth**.

D. Godiva Santana de Souza, 2007-2010, Univ Federal Fluminense (UFF), Niteroi, Brésil : « *Variations climatiques de l'Atlantique Sud et téléconnexions* ». Directeurs: A. Siffeddine, H. Evangelista, co-supervisors: **C.E. Lazareth**, F. Le Cornec.

M. Gosselin, 2005-2009, UPMC : « *Caractérisation microstructurale et géochimique des impacts du phénomène El Niño sur la croissance de coquilles de diverses espèces de mollusques littoraux du Pérou et du Chili, et calibration à haute-résolution d'enregistrements environnementaux*. » Supervisor: L. Ortlieb (LOCEAN); co-supervisor: **C.E. Lazareth**.

C. Liétard, 2004-2007, UPMC : « *Utilisation des mollusques bivalves comme enregistreurs des paramètres de l'environnement marin côtier et profond* » Supervisor: C. Pierre; co-supervisor: **C.E. Lazareth**.

### B.3.3 Internship

**2015** A. Gérard, Lithosphère Bassin Pétrole (LBP), UPMC, Paris VI « *Reconstruction de paramètres environnementaux du lagon de Tatakoto (Archipel des Tuamotus), de 2006 à 2012, pour comprendre l'origine d'une mortalité massive et de la diminution des stocks de bécotiers* » Supervisors: C. Brahmi et Nabila Gaertner-Mazouni (Univ. de Polynésie Française, UMR EIO), **C.E. Lazareth** et F. Le Cornec.

**2014** C. Assailly, Océanographie et environnement marin (OEM), UPMC, Paris VI « *Réponse des isotopes du bore ( $\delta^{11}B$ ) dans les carbonates biogéniques aux changements de pH: étude de coraux et bécotiers de Nouvelle-Calédonie* » Supervisors: **C.E. Lazareth**, E. Douville, D. Dissard et F. Le Cornec.

- 2012** C.-E. Deschamps, Environnement, océanographie littorale et hauturière (ENVOLH), Bordeaux I « *Dynamique du climat au Vanuatu (Pacifique Sud-ouest) à partir des archives coralliennes au cours de l'Holocène en lien avec la position de la Warm Pool et de la SPCZ* ». Supervisors: T. Corrège, F. Le Cornec et **C.E. Lazareth**.
- 2011** N. Pujol, Environnement, océanographie littorale et hauturière (ENVOLH), Bordeaux I « *Variabilité climatique du Pacifique Sud-ouest à l'Holocène (6200 BP) par l'étude des archives coralliennes* ». Supervisors: T. Corrège, F. Le Cornec et **C.E. Lazareth**.  
H. Younsi, Océanographie, Université de la Méditerranée, Aix-Marseille « *Analyses géochimiques de métaux dans un corail moderne de Nouvelle-Calédonie. Application aux études paléo-environnementales* » Supervisors: G. Cabioch, F. Le Cornec et **C.E. Lazareth**.
- 2010** N. Garnier, European Master of Marine Biodiversity and Conservation (Master Erasmus Mundus; UPMC – Paris VI) « *Reconstitutions of last interglacial stage (MIS 5<sup>e</sup>; ~125 000 years BP) paleo-SST from the study of giant clam of New Caledonia* ». Supervisors: **C.E. Lazareth**, F. Le Cornec et G. Cabioch.  
C. Soares-Pereira, Sciences de l'Univers, Environnement, Ecologie (SDUEE), UPMC: « *Caractérisation géochimique dans les coraux tropicaux, des événements climatiques et environnementaux récents dans le Sud-ouest Pacifique au Vanuatu* » Supervisors: G. Cabioch, F. Le Cornec et **C.E. Lazareth**.
- 2009** N. M.-G. Bustamante, Sciences de l'Univers, Environnement, Ecologie (SDUEE), UPMC, Paris « *Reconstitutions de paléo-températures à partir de l'étude de bénitiers et coraux Holocène de Nouvelle-Calédonie* » Supervisors: **C.E. Lazareth**, F. Le Cornec et G. Cabioch.  
C. Schwartzmann, Biodiversité, Ecosystèmes Continentaux et Marins, Université de la Côte d'Opale, Calais. « *Etude comparée de la croissance du bénitier géant Hippopus hippopus par sclérochronologie et analyse en ligne par électrodes électromagnétiques* » Supervisors: **C.E. Lazareth** et J.-C. Massabuau (EPOC, Université Bordeaux I).
- 2008** I. Valderrama, Sciences de l'Univers, Environnement, Ecologie; Spécialité 'Océanographie et Environnements marins' (SDUEE). UPMC, Paris VI « *Calibration de la relation température de l'eau - isotopes stables de l'oxygène et du carbone dans la coquille d'un gastéropode littoral (Concholepas concholepas) du Pérou-Chili*. » Supervisors: N. Guzman et **C.E. Lazareth**.  
P. Faylona, Evolution, Patrimoine Naturel et Sociétés, spécialité Quaternaire et Préhistoire ; MNHN – Paris: « *Etude de l'abri sous roche de Balobok; Ile de Sanga-Sanga; Tawi-Tawi, Philippines*. » Supervisors: **C.E. Lazareth** et A.-M. Semah.
- 2007** A. Aubert, ESA – Angers « *Calibration de marqueurs environnementaux au sein de la coquille d'un Hippopus hippopus (bivalve, Tridacnidae) moderne et application à un spécimen fossile*. » Supervisors: **C.E. Lazareth**.
- 2004** G. Lasne, Environnement, océanographie littorale et hauturière (ENVOLH), Bordeaux I « *Microstructure et croissance de coquilles de Protothaca thaca (Lamellibranche, vénéréidé) du Pérou et du Chili: enregistrement des variations saisonnières à interannuelles des conditions océanographiques littorales*. » Supervisors: **C. E. Lazareth** et L. Ortlieb.  
C. Liétard, Océanologie, Météorologie, Environnement, UPMC, Paris VI «  *$\delta^{18}O$  des coquilles de Protothaca thaca actuelles du Pérou : validation du protocole analytique pour la reconstruction des paramètres environnementaux*. » Supervisors: C. Pierre (LODYC) et **C. E. Lazareth**.

#### B.3.4 Other levels

- 2016** E. Milleret, M1, SDUEE UPMC, Université Paris VI « *Impact des activités minières sur le récif corallien de Nouvelle-Calédonie* », Supervisors: F. Le Cornec, **C.E. Lazareth**. 18/04 au 17/06.  
A. Boudeau, L3, Biologie Générale, Université de La Rochelle « *Impact des activités minières sur le récif corallien de Nouvelle-Calédonie* », Supervisors: F. Le Cornec, **C.E. Lazareth**.

- H. Lestrelin, L1, Physique Chimie Géoscience et Ingénierie option Géosciences, Université Paris VI « *Variations environnementales au sein de coquilles et d'otolithes d'Amazonie via la géochimie des isotopes stables* ». Supervisors: **C.E. Lazareth**, M. Pouilly (BOREA), E. Dufour (MNHN).
- 2012** R. Samyati Jatiningrum, M1, MNHN, Master Erasmus Mundus, « Evolution, patrimoine naturel, sociétés », spécialité « Quaternaire et Préhistoire », International Master ; QP11 : Quaternary and Prehistory of Southeast Asia ». « *Etude de l'état de conservation de coquilles de Tridacnidae fossiles* » Supervisors: **C.E. Lazareth**, A.-M. Semah.
- 2010** C. Soares-Pereira, M1, Master SDUEE; UPMC – Paris VI « *Caractérisation géochimique dans les coraux tropicaux, des événements climatiques et environnementaux récents dans le Sud-ouest Pacifique au Vanuatu* ». Supervisors: G. Cabioch, F. Le Cornec, **C.E. Lazareth**.
- 2008** E. Coutat, M1, Sciences et Technologies, Mention « Physique et applications », UPMC: « *Diagenèse, croissance et géochimie au sein d'une colonie de corail: évaluation de la variabilité intra-colonie.* » Supervisors: **C.E. Lazareth** et F. Le Cornec.
- 2007** K. Inamo, L3, Université de Cergy-Pontoise « *Mesure des épaisseurs des stries de croissance de coquilles actuelles, du mollusque bivalve Trachycardium procerum du Pérou et du Chili, et mise en évidence de la relation entre la croissance de la coquille et la température de l'eau dans laquelle vivait l'animal* » Supervisors: **C. E. Lazareth**, M. Gosselin.

## B.4 Research-related activities

### B.4.1 Scientific expertise

**PhD defense:** 4 (3 as an examiner, one invited)

**Internship defense:** 2

**PhD comity:** 3

**Scientific reviews:** Nature Communication, Scientific Report, PlosOne, Geosciences, Geochimica et Cosmochimica Acta, Palaeogeography Palaeoclimatology Palaeoecology, Chemical Geology, Biogeosciences, Geochemistry Geophysics Geosystems, Talanta, European Journal of Geomarine Letters, Marine Ecology Progress Series.

**Project reviews:** IPEV, INSU-LEFE, INSU-EC2CO, Paleo2, Polar Campaign, NSF, CONICYT, Thematic actions from the Museum (MNHN-Paris)

### B.4.2 Others

**2014-16** Steering committee of the "Thematic actions from the Museum", MNHN

**2011-15** Direction and management of the "west-Pacific" team of the BTP-team of the LOCEAN (5 researchers, 2 engineers).

**Between 2012 et 2014:** Training on "PhD training" from the "Institut de Formation Doctorale" - UPMC and IRD and 2 trainings as trainers.

## B.5 Publications & communications

Note: Students I supervised (or co-supervised) are in bold.

## B.5.1 Peer-reviewed journal articles

1. Carré, M., Azzoug, M., Zaharias, P., Camara, A., Chase, B., Cheddadi, R., Chevalier, M., Fiorillo, D., Gaye, A.T., Janicot, S., Khodri, M., Lazar, A., Lazareth, C.E., Mignot, J., Garcia, N.M., Patris, N., Perrot, O., Wade, M. Driest Sahel conditions in the last 1600 years linked to global warming. Submitted to Nature Geosciences.
2. Thil, F., Blamart, D., **Assailly, C.**, Lazareth, C.E., Leblanc, T., Butscher, J., Douville, E., 2016. Development of laser ablation multi-collector inductively coupled plasma mass spectrometry for boron isotopic measurement in marine biocarbonates: new improvements and application to a modern *Porites* coral. *Rapid Communications in Mass Spectrometry*. 30, 359–371.
3. Lazareth, C.E., **Soares-Pereira, C.**, Douville, E., Brahmi, C., Dissard, D., Le Cornec, F., Thil, F., Gonzalez-Roubaud, C., Caquineau, S., Cabioch, G., 2016. Intra-skeletal calcite in a live-collected *Porites* sp.: Impact on environmental proxies and potential formation process. *Geochimica et Cosmochimica Acta*. 176, 279-294.
4. Evangelista, H., Wainer, I., Sifeddine, A., Corrège, T., Cordeiro, R.C., Lamounier, S., **Godiva, D.**, Shen, C.C., Le Cornec, F., Turcq, B., Lazareth, C.E., Hu, C.Y., 2016. Ideas and perspectives: Southwestern tropical Atlantic coral growth response to atmospheric circulation changes induced by ozone depletion in Antarctica. *Biogeosciences*. 13, 2379-2386.
5. **Duprey, N.**, Lazareth, C.E., Dupouy, C., Butscher, J., Farman, R., Maes, C., Cabioch, G., 2015. Calibration of seawater temperature and  $\delta^{18}\text{O}_{\text{seawater}}$  signals in *Tridacna maxima*'s  $\delta^{18}\text{O}_{\text{shell}}$  record based on *in situ* data. *Coral Reefs*. 34, 437-450.
6. **Duprey, N.N.**, Galipaud, J.-C., Cabioch, G., Lazareth, C.E., 2014. Isotopic records from archaeological giant clams reveal a variable climate during the southwestern Pacific colonization ca. 3.0 ka BP. *Palaeogeography, Palaeoclimatology, Palaeoecology*. 404, 97-108<sup>6</sup>.
7. Lazareth, C.E., **Bustamante Rosell, M.G.**, **Duprey, N.**, Pujol, N., Cabioch, G., Caquineau, S., Corrège, T., Le Cornec, F., Maes, C., Mandeng-Yogo, M., Turcq, B., 2013. A controversial insight into South-west Pacific mid-Holocene seasonality: from corals to models. *PAGES NEWSLETTER*.
8. Lazareth, C.E., **Bustamante Rosell, M.G.**, Turcq, B., Le Cornec, F., Mandeng-Yogo, M., Caquineau, S., Cabioch, G., 2013. Mid-Holocene climate in New Caledonia (South-West Pacific): Coral and PMIP models monthly resolved results. *Quaternary Science Reviews*. 10.1016/j.quascirev.2013.02.024.
9. Lazareth, C.E., Le Cornec, F., Candaudap, F., Freydier, R., 2013. Trace element heterogeneity along isochronous growth layers in bivalve shell: consequences for environmental reconstruction. *Palaeogeography Palaeoclimatology Palaeoecology*. 10.1016/j.palaeo.2011. 1004.1024.
10. **Gosselin, M.**, Lazareth, C.E., Ortlieb, L., 2013. Sclerochronological studies in the Humboldt Current System, A highly variable ecosystem. *Journal of Shellfish Research*. 32, 867-882.
11. **Duprey, N.**, Lazareth, C.E., Cabioch, G., Corrège, T., Le Cornec, F., Pujol, N., Maes, C., Mandeng-Yogo, M., Caquineau, S., Soares Derome, C., 2012. Early mid-Holocene SST variability and surface-ocean water balance in the Southwest Pacific. *Paleoceanography*. 27, PA4207.

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<sup>6</sup> Included in a "Virtual issue of articles about palaeoclimatology";<http://www.journals.elsevier.com/palaeogeography-palaeoclimatology-palaeoecology/virtual-special-issues/virtual-issue-of-articles-about-palaeoclimatology/>



12. Azzoug, M., Carré, M., Chase, B.M., Deme, A., Lazar, A., Lazareth, C.E., Schauer, A.J., Mandeng-Yogo, M., Simier, M., Thierno-Gaye, A., Tito de Morais, L., 2012. Strengthened West African Monsoon from AD 460 to 1090 indicated by oxygen isotopes from mollusk shells in the Saloum Delta, Senegal. *Global and Planetary Change*. 98-99, 54-62.
13. **Faylona, M.G.P.**, Lazareth, C.E., Sémah, A.-M., Caquineau, S., Boucher, H., Ronquillo, W.P., 2011. A preliminary study of the preservation state of giant clam shells from Balobok Rockshelter, South Philippines. *Geoarchaeology*. 26, 888-901.
14. **Schwartzmann, C.**, Durrieu, G., Sow, M., Ciret, P., Lazareth, C.E., Massabuau, J.-C., 2011. *In situ* giant clam growth rate behavior in relation to temperature: A one year coupled study of high-frequency non-invasive valvometry and sclerochronology. *Limnology and Oceanography*. 56, 1940-1951.
15. **Aubert A.**, Lazareth C.E., Cabioch G., Boucher H., Yamada T., Iryu Y., Farman R., 2009. The tropical giant clam *Hippopus hippopus* shell, a new archive of environmental conditions as revealed by sclerochronological and  $\delta^{18}\text{O}$  profiles. *Coral Reefs*. 28:989-998
16. Lazareth C.E., Guzmán N., Poitrasson F., Candaudap F., and Ortlieb L., 2007. Nyctemeral variations of magnesium intake in the calcitic layer of a Chilean mollusc shell (*Concholepas concholepas*, Gastropoda) *Geochimica et Cosmochimica Acta*. 71, 5369-5383.
17. Lazareth C.E., **Lasne G.**, and Ortlieb L., 2006. Growth anomalies in *Protothaca thaca* (Mollusca, Veneridae) shells as markers of ENSO conditions. *Climate Research*. 30, 263-269.
18. Lazareth C.E., Vander Putten E., André L., and Dehairs F., 2003. High-resolution trace element profiles in shells of the mangrove bivalve *Isognomon ehippium*: a record of environmental spatio-temporal variations? *Estuarine, Coastal and Shelf Science*. 57, 1103-1114.
19. Lazareth C. E., Mercier J.-C. C., and Garnaud S., 2001. A geochemical study of larvikite from Brouage (France): evidence for European commercial sealinks in Early Modern times. *Comptes Rendus de l'Academie des Sciences - Series IIA - Earth and Planetary Science*. 332, 733-738.
20. Lazareth C.E., Willenz P., Navez J., Keppens E., Dehairs F., and André L. (2000b) Sclerosponges as a new potential recorder of environmental changes: Lead in *Ceratoporella nicholsoni*. *Geology*. 28, 515-518.
21. Lazareth C.E. and Mercier J.-C. C., 1999. Geochemistry of ballast granites from Brouage and La Rochelle, France: evidence for medieval to post-medieval trade with Falmouth, Cornwall, and Donegal, Ireland. In *Geoarchaeology: exploration, environments, resources*, Vol. 165 (ed. A. M. Pollard), pp. 123-137. Geological Society, Special Publications.

### B.5.2 Non-peer-reviewed articles

1. Lazareth, C.E., 2015. Le murmure des bénitiers. *Sciences au Sud - Le Journal de l'IRD*. 77 – décembre 14/janvier 15, p. 2.
2. Lazareth C. E., 2007. El Niño laisse ses empreintes sur les coquillages. *Sciences au Sud - Le journal de l'IRD*. 39 - mars/avril/mai, 3.
3. Que faire après une licence en Sciences de la Terre. Janvier 2006. *L'étudiant Magazine*, p. 46-47.
4. Levend fossiel gebruikt als klimaatmeter. (Un fossile vivant utilisé comme enregistreur du climat). Janvier 2001. *National Geographic*. Nederland-België.

5. L'éponge moucharde. 16 juin 2000. *Le Vif/L'express*. p. 18.

### B.5.3 Communications

#### Communications in international meetings

1. **Brahmi, C.**, Tribollet, A., Le Cornec, F., Lazareth, C.E., Dissard, D., 2014. Effects of pathology and micro-bioerosion on coral skeleton geochemical composition, Ocean Sciences Meeting, Hawaiï, 14948.
2. Corrège, T., Saint-Lu, M., Braconnot, P., Lazareth, C.E., Le Cornec, F., 2014. Interaction between ENSO and the SPCZ in different climate states: coral data and model results, Ocean Sciences Meeting, Hawaiï, 15904.
3. **Duprey, N.N.**, Galipaud, J.-C., Cabioch, G., Lazareth, C.E., 2014. The old man and the giant clam, Ocean Sciences Meeting, Hawaiï, 13883.
4. Azzoug M., Carré M., Chase B. M., Deme A., Lazar A., Lazareth C. E., et al., 2012, The West African monsoon duration and intensity from AD 450 - 1090 inferred from high resolution isotope sclerochronology of modern and fossil mollusk shells in the Saloum estuary (Senegal). 4<sup>th</sup> AMMA International Conference. Toulouse, France.
5. Braconnot, P., Zheng, W., Leloup, J., Guilyardi, É., Schneider, B., Luan, Y., Kageyama, M., Cobb, K., Lazareth, C. E., Corrège, T., Peterschmitt, J.-Y., Abdelaziz, G. and PMIP participating group, 2012, Attempt to evaluate simulated changes in monsoon and, ENSO from different time periods, WCRP Workshop on CMIP5 Model Analysis, University of Hawaii, Honolulu, HI, USA 5-9 March, and PAGES/CLIVAR Workshop: Using Paleo-Climate Model/Data Comparisons to Constrain Future Projections, Hawaii, USA, 1-3 March.
6. Corrège, T., Deschamps, C.E., **Duprey, N.**, Pujol, N., Braconnot, P., Charlier, K., Lazareth, C.E., Le Cornec, F., Malaizé, B., 2012. Change in seasonality in the southwest tropical Pacific during the Holocene: a data – model comparison (Invited), AGU Fall Meeting, San Francisco, California, pp. PP23E-01.
7. Lazareth, C.E., Turcq, B., **Bustamante Rosell, M.G.**, Le Cornec, F., Cabioch, G., Mandeng-Yogo, M., Caquineau, S., 2012. Mid-Holocene climate in New Caledonia (South West Pacific): Coral and PMIP models seasonal data, 2<sup>nd</sup> PMIP 3 Workshop, Crewe, UK.
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9. Lazareth, C.E., Cabioch, G., Turcq, B., Le Cornec, F., Caquineau, S., Mandeng-Yogo, M., **Duprey, N.**, **Bustamante, M.G.**, Maes, C., Galipaud, J.-C., Pujol, N., Corrège, T., 2011. Climatic variability in the South-west Pacific at ~ 6.6 and 5.5 ka: giant clam and coral data, PMIP III workshop on tropical climate variability with a focus on Last Millenium, Mid-Holocene and Last Glacial Maximum, Observatoire Océanologique de Villefranche sur Mer (France).
10. Lazareth, C.E., Williamson, D., Cabioch, G., Le Cornec, F., Caquineau, S., Mandeng-Yogo, M., Olago, D., 2011 (**Invited talk; Keynote speaker**). Reconstruction of coastal environments using corals and giant clams: a solution to better understand current and future climate changes, SUZA: First international symposium on impacts, vulnerability, and adaptation on to climatic change in small island developing states "Implications to poverty reduction", Zanzibar, p. 2.

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12. **Schwartzmann C.**, Durrieu G., Sow M., Ciret P., [Lazareth C. E.](#), and Massabuau J.-C. (2010) One year of giant clam growth: a combined HFNI valvometry and sclerochronology study. 2nd International Sclerochronology Conference. Mainz, Germany, 75.
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14. **Gosselin M.**, [Lazareth C. E.](#), Boucher H., and Ortlieb L. (2010) A Chilean bivalve as potential recorder of environmental changes: Sclerochronological and geochemical calibration of *Eurhomalea rufa*. 2nd International Sclerochronology Conference. Mainz, Germany, 177.
15. [Lazareth C. E.](#), Le Cornec F., Candaudap F., and Freydier R. (2010) Trace element high-resolution distribution in bivalve isochronous growth layers. 2nd International Sclerochronology Conference. Mainz, Germany, 56.
16. [Lazareth C. E.](#), Guzmán N., Le Cornec F., and Ortlieb L. (2009) The Mg – SST relationship in mollusc shells: is there a rule? Examples from three tropical species. *Geophysical Research Abstracts* **11**, EGU2009-0, 2009, [invited speaker](#).
17. [Lazareth C. E.](#), **Aubert A.**, Cabioch G., Galipaud J.-C., Guzmán N., Lasne G., Le Cornec F., Ortlieb L., and Valderrama I. (2009) Mollusc shells from the eastern and western tropical Pacific as recorders of environmental conditions. 11th Pacific Science Inter-congress, Tahiti, French Polynesia, PSI2009/351. ISBN N°978-2-11-098964-2.
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21. Ortlieb L., Guzman N., **Gosselin M.**, Fernandez E., [Lazareth C.](#), Le Cornec F., **Valderrama I.**, Velazco F., and Zevallos S. (2008) Progress in the sclerochronological approach on molluscan species from Peru and Chile for climate variability reconstruction. CENSOR Endterm Symposium, Lima, Peru, 21-22.
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26. Guzmán N., Ortlieb L., Cuif J., Dauphin Y., and Lazareth C. E. (2007) Subdaily and hourly growth patterns within the shell of the Chilean gastropod *Concholepas concholepas*: New perspectives for high-resolution sclerochronological studies. *1<sup>st</sup> International Sclerochronology Conference*, Saint Petersburg, Florida (USA), p. 60.
27. **Gosselin M.**, Fernandez E., Ortlieb L., Velasco F., and Lazareth C. E. (2007) Growth rate patterns in *Trachycardium procerum* (Mollusca) shells from coastal Peru and relationships with ENSO-related environmental parameters. *1<sup>st</sup> International Sclerochronology Conference*, St Petersburg, Florida (USA), p. 57.
28. **Gosselin M.**, Lazareth C. E., Dufour E., Guzman N., and Ortlieb L. (2007) Improvement of image analysis for sclerochronological and paleo-environmental studies on mollusc shells and fish otoliths. *1<sup>st</sup> International Sclerochronology Conference* St Petersburg, Florida (USA), p. 58.
29. **Gosselin M. J.**, Fernandez E., Guzmán N., Lazareth C. E., and Ortlieb L. (2006) Preliminary study of growth increments of the Peruvian mollusc shell *Trachycardium procerum* (Bivalvia, Sowerby 1833) throughout the last half-million years. *Bivalvia 2006*, Spain 40.
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33. Bashar B., De Ridder F., Keppens E., Lazareth C. E., Willenz P., Dehairs F., André L., and CALMAR group (2005) Stable isotopes and Mg/Ca, Sr/Ca ratios in a sclerosponge archive. EGU 05, Vienna (Austria), 24-29 April 2005. *Geophysical Research Abstracts* **7**, 08881.
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  38. Guzmán N., Lazareth C. E., Poitrasson F., Candaudap F., Cuif J.-P., and Ortlieb L. (2004) A high resolution temperature calibration study on the Chilean gastropod *Concholepas concholepas*. *Goldschmidt Geochemistry*, Copenhagen, 5 - 11 June.
  39. Guzmán N., Lazareth C. E., Poitrasson F., Cuif J.-P., and Ortlieb L. (2004) Mg and <sup>18</sup>O variations in the shell of the Chilean gastropod *Concholepas concholepas* reflect SST and Growth Rate variations. *Eos Trans. AGU* **85**, Fall Meet. Suppl., Abstract B21B-0877.
  40. Lazareth C. E., **Liétard C.**, **Lasne G.**, Pierre C., and Ortlieb L. (2004) Sclerochronological and geochemical study of *Protothaca thaca* (Veneridea, Bivalve) shells of the Peru-Chile region: environmental vs. physiological controls. *Eos Trans. AGU* **85**, Fall Meet. Suppl., Abstract B21B-0878.
  41. Lazareth C. E., Ortlieb L., **Lasne G.**, and Pierre C. (2004) Sclerochronological studies on the Chilean bivalve *Protothaca thaca* (Molina 1782) for paleoenvironmental reconstructions. EGU 04, Nice (France), 25-30 April. *Geophysical Research Abstracts* **6**, 05159.
  42. Lazareth C. E., Vander Putten E., André L., and Dehairs F. (2000) On the Potential of Bivalve Shells to Record Environmental Conditions: A LA-ICP-MS Study of Trace Element Distributions Along a Growth/Time Axis. *Goldschmidt 2000, September 3rd-8th, Oxford (UK), Journal of Conference Abstracts* **5**, 626.
  43. Lazareth, C. E., Navez, J., Willenz, Ph., Andre, L. and Dehairs, F. (2000) – Major and trace element profiles in carbonates (sclerosponges and bivalves): calibration strategies and drift corrections. 5th European Workshop on Laser Ablation-ICP-MS, ETH Zürich, 26-27 juin.
  44. Lazareth, C. E., Willenz, Ph., Dehairs, F. and André, L. (1999) - Calcification rate and high-resolution trace element distributions (ICP-MS and LA-ICP-MS) in the Caribbean coralline sponge *Ceratoporella nicholsoni*. EUG 10, 28 mars - 1 avril, Strasbourg (France), *J. Conf. Abs.*, 4, n°1, p. 212-213.
  45. Lazareth, C. E. and Mercier, J.-C. C. (1998) - Geochemistry of ballast granites and wine and salt trade between Brouage/La Rochelle and Cornwall. *Geoscience* 98, Université de Keele, 14-18 avril, p. 33.
  46. Lazareth, C. E. and Mercier, J.-C. C. (1997) - Characterisation of shoreline exotic granite boulders through phase-composition typology. EUG Strasbourg, Proc. 9th Europ. *Union Geosci.*, Terra Nova Abstr., 9, p. 679.

#### B.5.4 Public promotion

- COP 21 - talk "*Reconstruction of water temperature thanks to corals: a solution to better predict future climate*" and loan of objects in the area dedicated to "Notre Planète", Grand Palais, 09 Dec. 2015.
- Implementation and animation, in association with C. Hartmann (IEES, IRD) of the "kifékoa" on the IRD France-Nord; 10 min. of didactic presentation in user-friendliness, frequency: every 15 days (2013-2014)
- Creation of a notebook aimed at schoolchildrens: "Biocarbonates as recorders of the climate".
- Festival of Science: 2013, 2012, 2008 (Brest), 2007, 2006, 2005 (New Caledonia and metropole).
- Participation in the IRD exhibition "Oceans and climate", panel 8, "In search of past climates".
- Participation in the exhibition "New Caledonia: coral Earth" at the "Aquarium de la Porte Dorée", Paris, 2009 (slide show; loan of objects).
- Participation in the DVD "Climatology", for the teachers' resource center (CNDP), 2008.
- Shop window "Archive biocarbonatées of the climate" for the "European City of Sciences", Grand Palais,, Paris, from 14 to 16 Nov. 2008
- Participation in the exhibition "The coral reefs of France overseas" at the "Aquarium de la Porte Dorée", Paris, 2008 (slide show; loan of objects)
- Lazareth, C.E. (2007) "Studying climate through giant clams' shells" subject "Canal IRD". <http://www.ird.fr/la-mediatheque/videos-en-ligne-canal-ird/etude-du-climat-a-travers-les-coquilles-de-benitiers/etude-du-climat-a-travers-les-coquilles-de-benitiers>.
- Lazareth C. E. (2006) The shell of mollusks: memory of the environment. Futura Sciences. [Http: // www.futura-sciences.com/fr/comprendre/dossiers / doc / t /-zoologie-1/d/la-coquille-des-mollusques memoire-de-lenvironnement\\_662/c3/221/p 1/](http://www.futura-sciences.com/fr/comprendre/dossiers / doc / t /-zoologie-1/d/la-coquille-des-mollusques memoire-de-lenvironnement_662/c3/221/p 1/)
- E. Dufour, N. Guzman, M. Gosselin, Lazareth, C.E. (2006) - Marine biocarbonates as climate recorders. Festival of Science, IRD Ile-de-France, October 9-15<sup>th</sup>.

## APPENDIX C: REPRESENTATIVE PAPERS

Here are papers selected as representative of the studies I did since my post-doctoral position.

### Sclerochronology and calibration of proxies - bivalves (Chap. II)

Aubert, A., Lazareth, C.E., Cabioch, G., Boucher, H., Yamada, T., Iryu, Y., Farman, R. (2009) The tropical giant clam *Hippopus hippopus* shell, a new archive of environmental conditions as revealed by sclerochronological and  $\delta^{18}\text{O}$  profiles. *Coral Reefs* **28**, 989-998; 910.1007/s00338-00009-00538-00330.

Schwartzmann, C., Durrieu, G., Sow, M., Ciret, P., Lazareth, C.E., Massabuau, J.-C. (2011) In situ giant clam growth rate behavior in relation to temperature: A one year coupled study of high-frequency non-invasive valvometry and sclerochronology. *Limnol. Oceanogr.* **56**, 1940-1951.

### Diagenesis (Chap. III)

Lazareth, C.E., Soares-Pereira, C., Douville, E., Brahmi, C., Dissard, D., Le Cornec, F., Thil, F., Gonzalez-Roubaud, C., Caquineau, S., Cabioch, G. (2016) Intra-skeletal calcite in a live-collected *Porites* sp.: Impact on environmental proxies and potential formation process. *Geochim. Cosmochim. Acta* **176**, 279-294.

### Holocene paleo-reconstructions (Chap. IV)

Duprey, N., Lazareth, C.E., Cabioch, G., Corrège, T., Le Cornec, F., Pujol, N., Maes, C., Mandeng-Yogo, M., Caquineau, S., Soares Derome, C. (2012) Early mid-Holocene SST variability and surface-ocean water balance in the Southwest Pacific. *Paleoceanography* **27**, PA4207.

Lazareth, C.E., Bustamante Rosell, M.G., Turcq, B., Le Cornec, F., Mandeng-Yogo, M., Caquineau, S., Cabioch, G. (2013) Mid-Holocene climate in New Caledonia (southwest Pacific): coral and PMIP models monthly resolved results. *Quat. Sci. Rev.* **69**, 83-97.