PROGRAMME INSTITUTS ET INITIATIVES
Appel à projet – campagne 2021
Proposition de projet de recherche doctoral (PRD)
IMer - Institut de la Mer

Intitulé du projet de recherche doctoral (PRD): Biogeochemical proxies in bivalve shell mineral components: Are environmental fluctuations from marine settings faithfully recorded?

Directrice ou directeur de thèse porteuse ou porteur du projet (titulaire d'une HDR) :

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Unité de Recherche :
Intitulé : ISTeP - Institut des Sciences de la Terre de Paris
Code *(ex. UMR xxxx)* : UMR 7193

École Doctorale de rattachement de l'équipe (future école doctorale de la doctorante ou du doctorant) : ED398-Géosciences, Ressources Naturelles et Env.

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : 0

Co-encadrante ou co-encadrant :

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Unité de Recherche :
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Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : 0

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Unité de Recherche :
Intitulé : LABORATOIRE D'ECOGEOCHIMIE DES ENVIRONNEMENTS BENTHIQUES
Code *(ex. UMR xxxx)* : UMR 8222

École Doctorale de rattachement : Ou si ED non Alliance SU : **ED129-Sciences de l'Environnement d'Ile de France**

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) :
2 doctorants : V. Louis (2019 - , co-encadrement 50%) et M Chemel (2021 - , co-encadrement 50%)

Cotutelle internationale : ☐ Non Oui, précisez Pays et Université : **Université de Lausanne - Suisse**

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?
Non Oui, précisez ITE - Institut de la Transition Environnementale

SORBONNE UNIVERSITÉ

Description du projet de recherche doctoral *(en français ou en anglais) :*

1. Context and main goals

Geochemical proxies from biogenic carbonate (*e.g.*, bivalve shells) still present uncertainties that hamper their accurate use to estimate physicochemical parameters of the environment for past times. Bivalve shells are very promising in terms of temporal resolution for climate reconstruction because of their fast growth over several years. However, previous studies have indicated that their geochemical composition is different for unknown reasons from one site to another under the same temperature conditions. In addition, the accuracy of classical isotope proxies (*e.g.* $\delta^{18}O$) seems to differ depending on the season in estuarine environments due to salinity fluctuations. Based on studies showing that Mg incorporation in inorganic calcite was thermodependant, Mg/Ca in biominerals was substantially considered, as well as other elemental ratios (Sr/Ca, Mg/Li, Ba/Ca). More recently, the thermodependence of carbon and oxygen clumped isotopes (Δ47) have also been explored although still requiring accurate calibration. It has also been suggested that metabolim (such as gametogenesis and energy budget) may have an influence on the composition of the shell ('vital effects'), inducing bias in the use of such proxies. This assumption has never been properly studied, and important questions remain unanswered: which isotopic and elemental ratios are the best proxies to characterize the main parameters of the environment? Is there a taxonomic specificity of elemental incorporation in bivalve shells of a same site? What is the impact of the hydrological conditions, *i.e.* the influence of continental water input in the coastal environment, and the result of an open marine water on the shell record?

By comparing the various models of Mg/Ca as a palaeotemperature proxy in bivalve shells available in the literature, we can see that, for the same range of temperature values, Mg/Ca ratios show different values and amplitude depending on the study (**Fig. 1**). These differences can be explained by the fact that these models are built from different species, but more probably in different localities. Indeed, the models of Vander Putten et al. (2000) on the mussel *M. edulis* and those of Surge & Lohmann (2008) and of Tynan et al. (2017) on the oysters *C. virginica* and *S. glomerata* respectively are extremely similar and all three correspond to an estuarine environment. In general, open marine locations tend to have lower shell Mg/Ca values than localities from estuarine settings. The only exception is the Moreton Bay: although the salinity of this locality corresponds to a marine location, Moreton Bay is protected by sand reefs and an influence of the local rivers on the water chemistry cannot be excluded (**Fig. 2**). An empirical relationship between salinity regime (open marine *VS* estuarine settings) and the amplitude values of Mg/Ca in bivalve shells can therefore be proposed, but has never been properly investigated.

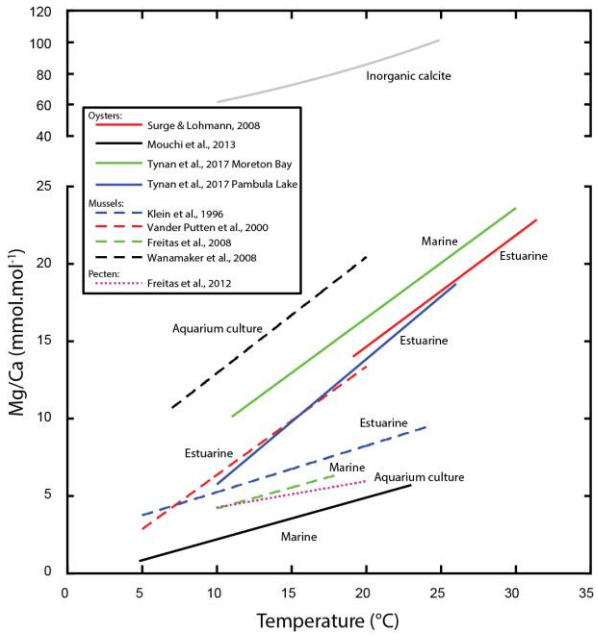

Figure 1 (left): *Bivalve shell Mg/Ca range values for common seawater temperature settings from various published studies. Each relationship has been established from a different locality. Solid lines correspond to relationships measured from oysters, dashed lines correspond to the Mytilus mussel genus and the dotted line corresponds to Pecten maximus. From Mouchi et al. (2018)*

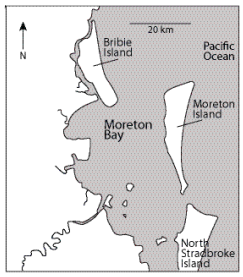

Figure 2 (above): *Moreton Bay location. From Tynan et al. (2017).*

As Mg concentration is higher in bivalve shells from estuarine environments (within which salinity is supposed to be lower if not equivalent), it appears that Mg concentration in seawater is not the main incorporation factor in bivalve shells. Other parameters must be explored to explain this relationship, such as pH and bioavailability of Mg in seawater/food source. This PhD project will assess the true potential of elemental ratios as environmental proxies, by investigating the Mg incorporation factors in oyster shells from various natural settings. The following questions will be addressed:

Q1: Is the empirical relationship between salinity regime and shell Mg concentration legitimate?

Q2: Is there a taxonomic specificity of Mg incorporation in bivalve shells from a same location?

Q3: Is Mg incorporation driven by endogenous (i.e., 'biological clock') or external (i.e., environmental) factors?

Q4: Which geochemical proxies (trace elements, stable isotopes) are the most accurate to reconstruct modern environmental settings from bivalve shells?

Q5: Are the studied geochemical proxies (trace elements, stable isotopes) adequate for palaeoenvironmental reconstruction?

2. Project description

Oysters (*Ostrea edulis* and *Magallana gigas*) will be implemented in three sites on the French coastline with different salinity regimes (Géfosse and Grandcamp, Baie des Veys, Normandy; Salses-Leucate lagoon, Occitany), with the collaboration of IFREMER. All sites have been selected due to their restricted access from the public and/or current farming facilities. This will extremely limit the risks of theft or violation. A potential risk of mortality of marine specimens due to diseases is present, as it has been the case for decades. The impact on the project is however reduced as we chose localities with low mortality rates. Specimens will be collected from pre-existing hatchery-cultured batches of 1-year-old specimens and will be identified by Hallprint shellfish tags. The specimens will be bred for two years. For each species at each site, 120 specimens will have to be implemented in order to proceed to the scheduled specimen collections throughout the project period.

As soon as the rearing will start, a first *in vivo* labelling will be performed on all specimens. On all sites, oysters will be labelled using manganese-enriched seawater according to the protocol described by Lartaud et al. (2010). Each labelling day (*i.e.*, every two months), 10 specimens from each species will be collected to measure the energy budget (proteins, lipids, carbohydrate). In addition, a water sample will be collected and immediately filtered and acidified to be analysed for trace elements, oxygen and carbon stable isotopes, and dissolved inorganic carbon (DIC). Elements of interest will be Ca, Mg, Sr, Mn, Al, K, Na, and Ba, to be compared with incorporated elements in bivalve shells. Time of immersion, temperature and salinity will be monitored on all sites. To this end, electronic probes will be purchased and placed on the rearing tables and cages in order to measure water physicochemical parameters every 15 minutes. As a last resource, if necessary, data will be recovered from the Sea Temperature website as the chosen research stations have been monitoring the shores for decades (https://www.seatemperature.org/europe/).

Thin sections from the shells will be used for microscope observations and *in situ* measurements. Cathodoluminescence will be performed to locate and identify each Mn label in oyster shells and to obtain the seasonal calibration of the shells from the naturally-occurring cathodoluminescence signal following Lartaud et al. (2010). *In situ* measurements on a selection of thin sections will be performed in two steps. First, LA-ICP-MS will be used at the Institute of Earth Sciences (UNIL) on specimens to measure Mg, Sr, Mn, Al, K, Na, Ba, Pb as well as Ca as the internal standard for data reduction. The proxy investigated for each element is reported in **Table 1**. For most specimens, the analyses will focus on the last few months of life, corresponding to the last label prior collection. This will help characterise, during the experiment, the impact of physiological state on shell composition. Specimens which would have been collected last will have their shells analysed for the whole experimental period (marked by labels).

Element	Justification
Ca	Internal standard for reduction
Mg	Mg/Ca: temperature and salinity proxy
Sr	Sr/Ca: temperature and salinity proxy
Mn	Locate Mn labels in oyster shells
Al, K	Al/Ca, K/Ca: rainfall proxy
Na	Na/Ca: salinity proxy
Ba	Ba/Ca: temperature or productivity proxy
Pb	Check for sample contamination and potential temperature proxy

Table 1: Proxies investigated for each analyte measured by LA-ICP-MS. Calcium is necessary for data reduction.

After elemental measurements are performed, small powder samples will be extracted from the thin section by a micromill (available at Sorbonne Université). Sample line positions will be optimised for spatial (and thus temporal) resolution in order to obtain the 40 µg required for the analysis. Expected spatial resolution is 100 µm. These samples will be analysed for $\delta^{13}C$ and $\delta^{18}O$ on a DELTA V IRMS spectrometer at Sorbonne Université (ISTeP). Clumped isotope measurements will also be performed on some shells. Measurements of $\Delta 47$ will be performed with the Nu Instrument IRMS Perspective at UNIL. These data will add to the calibration of this newly-investigated proxy and supplement the works currently being performed (F. Lartaud) within the AMOR ANR project.

All geochemical measurement time series will be compared to the entirety of monitored physicochemical parameters of the environment mentioned above. In addition, data on river rate of flow, local rainfall and marine tidal coefficients will be downloaded from meteorological websites from all locations, which publish monthly open reports. A first comparison procedure will involve a principal component analysis (PCA) to identify clear linear correlations in the multivariate space. Secondly, each time-series measurement will be independently converted to exponential and logarithmic values to investigate non-linear relationships, as suggested by Bauwens et al. (2011). Finally, all combinations of measured elemental variables will be investigated to build potential multi-proxy models for environmental reconstruction (such as MEM: Mixed-Effects Models).

The project will be concluded by a short fossil application of the environmental reconstruction models resulting

from this work. Using available oyster shells from the Medieval Warm Period (10^{th}-14^{th} century CE) and the Little Ice Age (14^{th}-19^{th} century CE), isotopic and elemental measurements will be performed to reconstruct temperature fluctuations over the last millennium.

This project will investigate in strongly monitored natural sites the effects of the environmental control on isotopic and elemental incorporation in bivalve shells as well as the potential differences occurring between estuarine and marine environments. This rearing experiment will be the first multi-species, and multi-proxy study on a variety of environmental settings to obtain the most accurate reconstruction models.

Since the beginning of palaeoenvironmental reconstruction from biogenic carbonates at high resolution in the 1950's, vital effects have been preventing the correct and unbiased interpretation from geochemical measurements. The search for accurate environmental proxies is still a hot topic, as exemplified by full-day sessions at the Goldschmidt's conferences. Incorporated in a transdisciplinary and international team of researchers, the project will provide opportunities to the Ph.D. student to gain experience in both cutting-edge geochemistry and environmental reconstructions. Results will bring substantial knowledge to the proxy development field, and will have applications to the seafood stock management in terms of age models of specimens from sclerochronology of the shells. If successful, the project will bring substantial information and report the use of techniques and protocols to reduce biases and uncertainties in temperature reconstruction models and improve the quality of the interpretations on past climates on Earth.

3. Relevance to the Institute of the Sea

This project lies within the first scientific axis of the Sorbonne University Institute of the Sea regarding the marine environment in the history of Earth, life and societies. The project is strongly transdisciplinary: data will comprise geochemical (shell analyses), biological (energy budget) and physicochemical (environmental monitoring) sources, and all will be compiled to study their interactions, in order to reconstruct historical climate evolution. Numerous timescales overlap in this project, from infra-seasonal to millennial fluctuations of environmental parameters.

4. Role of supervisors and collaborations

The PhD project involves academic partners from Sorbonne University (ISTeP, LECOB, METIS) and the University of Lausanne (IDYST), and industrial partner such as IFREMER.

PIs of this PhD project:

- Loïc Segalen (ISTeP): Elemental geochemistry and biogeochemical processes.
- Laurent Emmanuel (ISTeP): Isotope geochemistry and management of the PhD project
- Franck Lartaud (LECOB): Sclerochronology and energy budget measurements.

Academical and industrial partners:

- Maryse Castrec Rouelle (METIS): Water chemistry measurements
- Vincent Mouchi (AD2M): elemental geochemistry and data processing
- Eric Verrecchia (IDYST- Lausanne – Switzerland): Clumped isotopes and data processing
- Julien Normand (IFREMER): Rearing experimental support

5. PhD student profile

The PhD project will require both field (rearing and monitoring experiments) and laboratory work (physiological and geochemical analyses) within the different partner institutions.

The successful candidate will have to hold a MSc in Geosciences and Geochemistry with strong interest in Biological systems and Statistics. The candidate will have to be proficient in English for publications and scientific communications.

6. References

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Lartaud F., Le Callonnec L., De Rafelis M., Emmanuel L., Missang E., Castrec-Rouelle M., Mouchel J.M. & Segalen L. 2009. Laboratory and field-based calibration study for the use of freshwater bivalve shells as an archive of environmental and climatic conditions. ***Geophysical Research Abstracts***,Vol. 11, EGU2009-8045, 2009.