

PhD PROPOSAL FOR THE DOCTORAL SCHOOL « Végétal, Animal, Aliment, Mer, Environnement »

GENERAL INFORMATION

Thesis title: Sulfur incorporation in foraminiferal shells to unlock past ocean carbonate chemistry
Acronym of the project: SHERLOCK
Disciplinary field 1: Marine geosciences, Paleoclimatology, Paleoenvironment Disciplinary field 2: Geochemistry and Biogeochemistry
Three keywords: Foraminifera, ocean acidification, carbonate chemistry
Registration establishment: Université d'Angers
Research unit: UMR 6112, LPG
Name of the thesis director: Emmanuelle Geslin Email address of the thesis director: emmanuelle.geslin@univ-angers.fr Name of the thesis co-supervisor 1: Inge van Dijk Email address of the thesis co-supervisor 1: inge.vandijk@univ-angers.fr Name of the thesis co-supervisor 2: Christine Barras Email address of the thesis co-supervisor 2: christine.barras@univ-angers.fr
Contact(s) (mailing address and E-mail): Faculté des Sciences, Université d'Angers 2 Bd Lavoisier 49 045 Angers cedex
<input checked="" type="checkbox"/> Doctoral school contest <input type="checkbox"/> Interview <input type="checkbox"/> Other (specify):

SCIENTIFIC DESCRIPTION OF THE PhD PROJECT

Socio-economic and scientific context: (10 lines)

The chemical signature of the foraminiferal shell reflects the composition of the seawater, which in turn is often linked to a relevant paleo-oceanographic parameter. The cosmopolitan distribution, great preservation potential and abundance in the oceanic record make foraminifera the ideal candidate for reconstructing past climate in deep times. Currently, the development and application of biogeochemical proxies aims to determine the evolution of the past carbon cycle, which is essential to understand the responsiveness of the climate in the past and in the future in view of atmospheric $p\text{CO}_2$ emissions. Reconstruction of the marine inorganic carbon system currently relies on proxies that target only part of the system. However, it is necessary to reconstruct a second parameter of the carbonate system to reconstruct the complete system and therefore the atmospheric $p\text{CO}_2$.

Assumptions and questions (8 lines)

To complement the existing pH proxies, another reliable and pH-independent proxy is needed to reconstruct the complete carbonate system. We propose to develop (calibrate, validate and apply) a proxy based on the incorporation of sulfur in foraminiferal shells, as a new indicator of the concentration of carbonate ions $[\text{CO}_3^{2-}]$. It is hypothesized that SO_4^{2-} in seawater is the only source of sulfur (S) in the biogenic carbonate and that the S/Ca values of foraminifera change with $[\text{CO}_3^{2-}]$ due to the substitution of SO_4^{2-} by CO_3^{2-} in the crystal lattice. The SO_4/CO_3 ratio in seawater can be reconstructed by the S/Ca ratio of foraminifera by ICP-MS measurements. Calibrations under controlled conditions are necessary on various species of foraminifera.

The main steps of the thesis and scientific procedure (10-12 lines)

To meet the challenges linked to the application of the S/Ca proxy as a $[\text{CO}_3^{2-}]$ tracer, three main approaches will be explored during the thesis:

A) Experiments under controlled laboratory conditions to study the incorporation of sulfur into the shell of foraminifera: «S/Ca proxy development»

A1: What is the effect of different environmental parameters (e.g. pH, $[\text{CO}_3^{2-}]$, $[\text{SO}_4^{2-}]$ in seawater) on the S/Ca ratio of the calcite of the foraminifera studied?

A2: How is sulfur incorporated into the foraminifera shell?

B) Validation of laboratory data on current field samples, «Field validation»

C) «Application» on long sediment cores to reconstruct the past carbonate system

Methodological and technical approaches considered (4-6 lines)

Part A1: Foraminiferal growth experiments under controlled conditions (e.g. pH or $[\text{CO}_3^{2-}]$) and analysis of the chemical composition of the shells with ICP-MS

In A2: Use of high-resolution techniques (e.g. microXRF, NanoSims, synchrotron) on foraminifera from these controlled growth experiments to study the sulfur incorporation pathway.

In B: Measurements of the S/Ca of recent shells (in situ) allowing us to validate our experimental results

In C: Application of this proxy on geological cores.

Scientific and technical skills required by the candidate

The candidate must have training in marine geosciences and/or biogeochemistry. The thesis includes physicochemical and geochemical analyzes of the culture medium and shells with various analytical techniques in which the candidate will have to train. Knowledge of the carbonate system will be a plus. The candidate will have to quickly adapt to laboratory techniques to develop systems under controlled conditions. Binocular sorting skills are necessary to select and identify foraminifera.

THESIS SUPERVISION

Unit name: UMR 6112 LPG Site angevin	Team name: LPG Site angevin Thème : Systèmes littoraux et marins
Unit director name: Benoit Langlais	Team director name: Edouard Metzger (Site representative), Aurelia Mouret (Thème representative)
Mailing address of the unit director: benoit.langlais@univ-nantes.fr	Mailing address of the team director: edouard.metzger@univ-angers.fr aurelia.mouret@univ-angers.fr
Thesis director Surname, first name: GESLIN, Emmanuelle Position: PR Obtained date of the HDR (Accreditation to supervise research): 011 Employer: University of Angers Doctoral school affiliation: VAAME Rate of thesis supervision in the present project (%): 40% Total rate of thesis supervision in ongoing theses (supervisions and co-supervisions) (%): 60% Number of current thesis supervisions/co-supervisions: 1	

Thesis co-supervisor 1

Surname, first name: VAN DIJK, Inge

Position: CPJ

Accreditation to supervise research yes no If yes, date diploma received:

Employer: University of Angers

Doctoral school affiliation: VAAME

Rate of thesis supervision in the present project (%): 30%

Total rate of thesis supervision in ongoing theses (supervisions and co-supervisions) (%): 0

Number of current thesis supervisions/co-supervisions: 0

Thesis co-supervisor 2

Surname, first name: Barras, Christine

Position: Research Engineer

Accreditation to supervise research yes no If yes, date diploma received:

Employer: University of Angers

Doctoral school affiliation: VAAME

Rate of thesis supervision in the present project (%): 30%

Total rate of thesis supervision in ongoing theses (supervisions and co-supervisions) (%): 20%

Number of current thesis supervisions/co-supervisions: !

Professional status of previous PhD students supervised by both director and co-supervisors (from 5 years)

Please provide the following information for each PhD students supervised

Surname, first name: Choquel, Constance

Date of PhD beginning and PhD defence: PhD defence July 2021 – Duration 42 months

Thesis supervision: E. Geslin

Professional status and location: ATER Univ. Marseille (2023-2024)

Contract profile (post-doc, fixed-term, permanent): Pos-doc Univ. Lund (2021-2023)

List of publications from the thesis work:

CHOQUEL C., E. **GESLIN**, E. METZGER, H. L. FILIPSSON, N. RISGAARD-PETERSEN, P. LAUNEAU, M. GIRAUD, T. JAUFFRAIS, B. JESUS, A. MOURET, 2021, Denitrification by benthic foraminifera and their contribution to N-loss from a fjord environment, Biogeosciences, 18, 327–341, doi.org/10.5194/bg-18-327-2021.

Surname, first name: de Chavalon Aubin, Thibault

Date of PhD beginning and PhD defence: PhD defence in 2016 – Duration 40 months

Thesis supervision: E. Geslin

Professional status and location: CR CNRS Univ Pau

Contract profile (post-doc, fixed-term, permanent): -

List of publications from the thesis work:

THIBAULT DE CHAVALON A., METZGER E., MOURET A., KNOERY J., **GESLIN E.**, MEYSMAN F.J.R., 2017 Two dimensional mapping of Fe release in marine sediments at submillimetre scale. *Marine Chemistry* 191,34-49.

THIBAULT DE CHAVALON A., MOURET A., KNOERY J., **GESLIN E.**, PERON O., METZGER E., 2016, Manganese, iron and phosphorus cycling in an estuarine mudflat, Loire, France, *Journal of Sea Research* 118: 92-102. doi:10.1016/j.seares.2016.10.004

THIBAULT DE CHAVALON A., METZGER E., MOURET A., CESBRON F., KNOERY J., ROZUEL E., LAUNEAU P., NARDELLI MP., JORISSEN F., **GESLIN E.**, 2015, Two-dimensional distribution of living benthic foraminifera in anoxic sediment layers of an estuarine mudflat (Loire estuary, France) *Biogeosciences*, 12, 6219–6234. doi:10.5194/bg-12-6219-2015.

Surname, first name: Brinkmann, Inda

Date of PhD beginning and PhD defence: 2018-2022, PHD defense Octobre 2022

Thesis supervision: Helena Filipsson, co-encadrante C. Barras

Professional status and location: Post-doc, Malmö en Suède

Contract profile (post-doc, fixed-term, permanent): -

List of publications from the thesis work:

BRINKMANN, I., **BARRAS, C.**, JILBERT, T., PAUL, K.M., SOMOGYI, A., NI, S., SCHWEIZER, M., BERNHARD, J.M., FILIPSSON, H.L., 2023. Benthic foraminiferal Mn/Ca as low-oxygen proxy in fjord sediments. *Global Biogeochemical Cycles*. 37, e2023GB007690. <https://doi.org/10.1029/2023GB007690>

BRINKMANN, I., SCHWEIZER, M., SINGER, D., QUINCHARD, S., **BARRAS, C.**, BERNHARD, J.M., FILIPSSON, H.L., 2023. Through the eDNA looking glass: Responses of fjord benthic foraminiferal communities to contrasting environmental conditions. *Journal of Eukaryotic Microbiology*, 00, e12975. <https://doi.org/10.1111/jeu.12975>

BRINKMANN, I., **BARRAS, C.**, JILBERT, T., NAERAA, T., PAUL, K.M., SCHWEIZER, M., FILIPSSON, H.L., 2022. Drought recorded by Ba/Ca in coastal benthic foraminifera. *Biogeosciences*, 19, 2523-2535. <https://doi.org/10.5194/bg-19-2523-2022>

BRINKMANN, I., NI, S., SCHWEIZER, M., OLDHAM, V.E., QUINTANA KRUPINSKI, N.B., MEDJOUBI, K., SOMOGYI, A., WHITEHOUSE, M.J., HANSEL, C.M., **BARRAS, C.**, BERNHARD, J.M., FILIPSSON, H.L., 2021. Foraminiferal Mn/Ca as Bottom-Water Hypoxia Proxy: An Assessment of *Nonionella stella* in the Santa Barbara Basin, USA. *Paleoceanogr. Paleoclimatology* 36. <https://doi.org/10.1029/2020PA004167>

Surname, first name: Depuydt Pauline

Date of PhD beginning and PhD defence: 2019-2023, PHD defense February 2023

Thesis supervision: Meryem Mojtahid, co-encadrante C. Barras

Professional status and location: Post-doc, LSCE Paris Saclay

Contract profile (post-doc, fixed-term, permanent): -

List of publications from the thesis work:

DEPUYDT, P., TOUCANNE, S., **BARRAS, C.**, LE HOUEDEC S., MOJTAHID, M., 2024. Last Glacial – Holocene variability of the European Slope Current, NE Atlantic. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 633, 111884. <https://doi.org/10.1016/j.palaeo.2023.111884>

DEPUYDT, P., **BARRAS, C.**, TOUCANNE, S., FOSSILE, E., MOJTAHID, M., 2023. Implication of size fraction on benthic foraminiferal-based paleo-reconstructions: a case study from the Bay of Biscay (NE Atlantic). *Marine Micropaleontology*, 181, 102242. <https://doi.org/10.1016/j.marmicro.2023.102242>

DEPUYDT, P., MOJTAHID, M., **BARRAS, C.**, BOUHDAYAD, F.Z., TOUCANNE, S., 2022. Intermediate ocean circulation and cryosphere dynamics in the northeast Atlantic during Heinrich Stadials: benthic foraminiferal assemblage response. *Journal of Quaternary Science*. 1-15. DOI: 10.1002/jqs.3444

Five main recent publications of the supervisors on thesis subject:

DAVIRAY M., **GESLIN E.**, RISGAARD-PETERSEN N., SCHOLZ V., FOUET M., METZGER E., 2024, Potential impacts of cable bacteria activity on hard shelled benthic foraminifera: a prelude to implications for their interpretation as bioindicators or paleoproxies. *Biogeosciences*, 21, 911–928. <https://doi.org/10.5194/bg-21-911-2024>

LEKIEFFRE C., JAUFFRAIS T., J. M. BERNHARD, H. L. FILIPSSON, H. ROBERGE, C. SCHMIDT, O. MAIRE, G. PANIERI, **E. GESLIN**, A. MEIBOM, 2022, Ammonium and sulfate assimilation is widespread in benthic foraminifera. *Frontiers in Marine Science*, 9:861945.doi: 10.3389/fmars.2022.861945

BOUCHET V., FRONTALINI F., FRANCESCANGELI F., SAURIAU P.G., **GESLIN E.** et al., 2021, Benthic foraminifera - Transitional environments - Environmental biomonitoring - Totalorganic carbon - Foraminifera

AMBI - English Channel - European Atlantic coasts -Mediterranean Sea. Marine Pollution Bulletin 16. <https://doi.org/10.1016/j.marpolbul.2021.112071>

CHOQUEL C., E. GESLIN, E. METZGER, H. L. FILIPSSON, N. RISGAARD-PETERSEN, P. LAUNEAU, M. GIRAUD, T. JAUFFRAIS, B. JESUS, A. MOURET, 2021, Denitrification by benthic foraminifera and their contribution to N-loss from a fjord environment, Biogeosciences, 18, 327–341, doi.org/10.5194/bg-18-327-2021.

I. VAN DIJK, L.J. DE NOOIJER, **C. BARRAS** AND G.-J. REICHART (2020), Mn Incorporation in Large Benthic Foraminifera: Differences Between Species and the Impact of pCO₂. Frontiers in Earth Science 8, 439, <https://doi.org/10.3389/feart.2020.567701>

I. VAN DIJK, A. MOURET, M. COTTE, S. LE HOUEDEC, G.-J. REICHART, J. REYES-HERRERA, H. FILIPSSON, AND **C. BARRAS** (2019). Chemical heterogeneity in benthic foraminiferal calcite: Mn versus Mg, Na, S and Sr, Frontiers in Earth Science, <https://doi.org/10.3389/feart.2019.00281>

I. VAN DIJK, **C. BARRAS**, L.J. DE NOOIJER, A. MOURET, S. ORON, E. GEERKEN, AND G.-J. REICHART (2019). Coupled Ca and inorganic carbon uptake suggested by magnesium and sulfur incorporation in foraminiferal calcite, Biogeosciences, 16, 2115-2130 <https://doi.org/10.5194/bg-16-2115-2019>

BRINKMANN, I., **BARRAS, C.**, JILBERT, T., PAUL, K.M., SOMOGYI, A., NI, S., SCHWEIZER, M., BERNHARD, J.M., FILIPSSON, H.L., 2023. Benthic foraminiferal Mn/Ca as low-oxygen proxy in fjord sediments. Global Biogeochemical Cycles. 37, e2023GB007690. <https://doi.org/10.1029/2023GB007690>

MOJTAHID, M., DEPUYDT, P., MOURET, A., LE HOUEDEC, S., FIORINI, S., CHOLLET, S., MASSOL, F., DOHOU, F., FILIPSSON, H.L., BOER, W., REICHART, G.-J., **BARRAS, C.**, 2023. Decoupling the impact of different carbonate system parameters on benthic foraminifera from controlled growth experiments. Chemical Geology, 663, 121396. <https://doi.org/10.1016/j.chemgeo.2023.121396>

BRINKMANN, I., NI, S., SCHWEIZER, M., OLDHAM, V.E., QUINTANA KRUPINSKI, N.B., MEDJOUBI, K., SOMOGYI, A., WHITEHOUSE, M.J., HANSEL, C.M., **BARRAS, C.**, BERNHARD, J.M., FILIPSSON, H.L., 2021. Foraminiferal Mn/Ca as Bottom-Water Hypoxia Proxy: An Assessment of Nonionella stella in the Santa Barbara Basin, USA. Paleoceanogr. Paleoclimatology 36. <https://doi.org/10.1029/2020PA004167>

THESIS FUNDING

Origin(s) of the thesis funding: CDE
Gross monthly salary: 2100€
Thesis funding state: Acquired
Funding beginning date/duration of the thesis funding: 01/10/2024 (3 years)

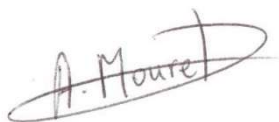
Date: 14/03/2024

Name, signature of unit director:

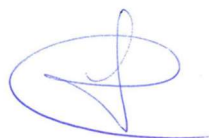
Directeur du LPG
Benoit LANGLAIS



Name, signature of team director:



Name, signature of project director:



E. Geslin