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Feeding and ecological diversity of Tournaisian holocephalans: insights from dental microwear

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At the end of the Devonian, several profound extinctions affected a large number of marine groups. However, some of them, such as holocephalan chondrichtyans, showed a great diversification during the recovery of the ecosystems, during the Tournaisian. Despite the fact that a large taxic diversity has been documented for these holocephalans, their ecological diversity is however poorly known, because the shape of isolated teeth can be a poor predictor of the ecology of these animals. Microwear analysis has the potential to reveal distinct diets and actual use of teeth in these extinct animals during the Tournaisian. We analysed the microwear of Tournaisian holocephalans from the Tournai and Ourthe formations of Belgium. Dental microwears were observed qualitatively on 20 teeth with a scanning electron microscope and mapped and analysed in detail for 7 of them with ArcMap software. While pits are almost totally absent in our sample, our microwear dataset revealed two populations of scratches with distinct length distributions. We suggest that these populations were produced by two different mechanisms. The first population contains mainly long scratches (>0.2 mm, up to 2.0 mm) that are often oriented 40° to 70° compared to the anteroposterior axis of the tooth. We propose that these scratches would have been produced by trituration. The second population comprises almost exclusively of short scratches (<0.2 mm) especially abundant on the mesial face of the teeth and preferentially oriented subparallel to the anteroposterior axis. They would have been produced when the holocephalans dug into sea bottom sediments while searching for food. To identify materials that might have caused the observed microwear, we compared the hardness of the holocephalan orthodentine, making the bulk of the crown of holocephalan teeth, and materials present in their environment. The skeleton of a wide series of marine organisms (crinoids, brachiopods, molluscs) is composed of calcite or aragonite, which appears to be slightly harder than holocephalan orthodentine. These materials may thus scratch holocephalan teeth but are hardly able to produce pits because of the small difference in hardness. Tournaisian holocephalans were thus probably feeding on benthic faunae and they likely dug in the sediment at the search of food. If correct, this might rule out prey items located clearly above the sea floor, such as ammonioids or high-stalked crinoids. However, most of our specimens showed similar microwear features, which prevents us to highlight ecological differences between the taxa we sampled.

Analogue modelling of passive-margin tectonic inversion: example from the Ardennes Variscan foldand-thrust belt

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The Ardennes is a region of Northern Europe located across Belgium, Luxembourg, France and Germany. Geologically, the Ardennes represents the northern front of the Paleozoic era's great chain of mountains: the Hercynian orogeny (also called Variscan). These mountains erected mainly during the Upper Devonian – Carboniferous following the closure of various oceanic domains formed in the lower Silurian – Devonian. Later, they were dislocated and greatly eroded before being altered during the Alpine orogeny (Late Mesozoic). In the Ardennes, the northern Variscan front is described as an intertwining of structures whose envelope surface is called the "Faille du Midi". This allows the *Allochtone Ardennais*, located in the South, to ride over the *Parautochtone Brabançon*, located in the North, for about 70 km.

In this Master thesis, we attempted to understand better the potential influence of some parameters on the evolution and dynamic of the Ardennes notably in studying the tectonic dynamics of the northern Variscan front formation with an analogue modelling approach. This consists on a "physical mock-up" simulating, at a short space and time scale, with natural and synthetic material, the geological dynamic of the natural example.

The main interest of this method is that there is only very little amount of documentation published, related to the Ardennes. Therefore, this allowed us to test some suggested ideas on global sections drawn more than one century ago by various French or Belgian authors. We investigated the influence of the variation of some geodynamic parameters on the evolution and the inversion in compression of a passive margin, notably (1) the extension's rate affecting a margin before its tectonic uptake, (2) the surface processes (erosion, sedimentation) affecting the structural reliefs resulting from the shortening phase and (3) the nature of the filling during the process of rifting. Also, the study of the tectonic inversion of a passive margin is poorly documented in experimental modelling. Our work strives to propose protocols and methodological advances to explore this key stage of geodynamics. The analyses of the results involve the comparison of sections of models with geological sections of the Ardennes already carried out, animations realized with cameras placed above and on the side of the mock-up taking photographs at defined steps of time through the duration of the experiment.

The results we obtained with the extension tectonics depend on the slope of the mock-up and its stretching rate. Each experiment allows the improvement of the next one by adjusting some parameters, this in order to get stranded blocks – typical structure of a continental margin. As for the various experiments conducted in tectonic inversion, the results depend on the extension rate set up previously, the shortening rate and the presence of residual reliefs. Finally, experiments conducted to estimate the impact of synorogenic surface processes or rifting filling rheology attest that those parameters are important in the northern Variscan front

X-ray CT-technology revealing the effects of denitrifying bacteria on porous limestone

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Introduction

Bacteria can colonize rocks in natural outcrops and building stones. In the past, the negative effect (i.e. biodeterioration) of bacterial colonization have been studied, while more recent studies also focus on the beneficial effect of controlled or induced bacterial growth. The colonization potential (or bioreceptivity) is mainly related to the stone's chemical composition, texture and structure and the local environment. As bacteria colonize a stone, they can alter the stone's properties through their metabolism (e.g. microbial induced calcite precipitation (MICP) and gas production) as well as through the formation of biofilms. Mineral precipitation can improve the stone's mechanical properties, gas production and the presence and location of the biofilms can alter the fluid transport (e.g. bioclogging (Vandevivere & Baveye, 1992)) and therefore the stone's durability.

The relationship between bacteria and porous rocks is still poorly understood. Although MICP has been extensively studied in the past (De Muynck et al., 2010.), the role of the organisms itself, the mechanism and its link with the petrophysical properties remains however poorly understood (e.g. Umar et al., 2016). New techniques, such as high resolution X-ray μ CT are needed to reveal the interconnection between bacteria and porous rocks. It can visualize opaque materials in 3D non-destructively and can distinguish different phases down to a few micrometres (Cnudde & Boone, 2013), including MICP (e.g. Wang et al., 2014).

Materials and methods

Paracoccus denitrificans (LMG 4049) was the model species within this research. By denitrification it is capable to produce both MICP and nitrogen gas. Denitrification is an alternative less studied pathway to induce MICP that does not produce toxic by-products and lacks the need of oxygen (Erşan et al., 2015; Erşan, 2016). All the experiments have been executed on two rocks with a similar calcareous composition but a distinct pore structure: Savonnières (France) and Tabaire (Spain).

Three main experiments have been executed to reveal the geological-microbial relationship. 1) Flow experiments: Paracoccus denitrificans was flushed manually in a physiological solution through the stone samples (i.e. colloid transport, e.g. Molnar et al., 2015). Hereafter demineralized water flushed them directly out. Flow cytometry counted the amount of bacteria leaving the samples. 2) Growth experiments: Stone samples were primarily immersed under vacuum with bacteria in a nutrient rich water solution. The samples were stored at 35 °C for one week to let the bacteria grow. The samples were conditioned under different growth conditions: some started in a more or less neutral nutrient rich solution, others in more alkali conditions or within a more or less neutral depleted nutritious solution. HECTOR (Masschaele et al., 2013), an X-ray µCT scanner of UGCT at Ghent University imaged the samples within a predefined time interval for a total period of one week to visualize the MICP and biogenic nitrogen gas. The growth itself was also verified by the volatile fatty acid

(VFA) concentration and pH measurements. 3) Radiation experiments: A physiological bacterial solution was exposed to Xray radiation, produced by HECTOR with the similar scanning parameters as during the growth experiments including the same exposure time. Optical-density (OD) measurements and flow cytometry measured respectively their growth and the mortality. Blank samples allowed comparison with non-radiated bacteria.

Results and discussion

1) *Paracoccus denitrificans* saturated directly the stone samples during the flow experiments. The demineralized water flushed the bacteria out of the samples. The bacteria however still left the samples after flushing a relatively large volume of demineralized water exceeding the pore volume multiple times. This indicates that a significant amount of bacteria was initially retained within the rock samples.

2) Growth experiments: Paracoccus denitrificans grew well within the rock samples. VFA concentration, pH and produced gas indicated only a limited growth when less nutrients were available. It also showed the capability of the microorganisms to create other growth conditions, than anticipated. During extensive growth within a fully water (+ nutrients) saturated rock sample they produced a gas saturation of maximum 25%. However, this value fluctuated largely over the different samples, indicating the complexity between stone and biological activity. The gas bubble size distribution was linked to the pore space connectivity: Tabaire contained with its very well connected pore system, less but larger bubbles compared to Savonnières (Fig. 1). The differences between the gas phases of the two rocks decreased when only a limited amount of gas was present. MICP, the other anticipated reaction product, was only indicated by a very small weight increase. Its exact location within the stones remained difficult to detect both in 2D as in 3D.

3) During the growth experiments, an X-ray μ CT scan performed on HECTOR exposed the bacteria to a theoretical maximal dose of 117.40 Gy. Here, during the radiation experiments, the radiation was similar. Optical density measurements indicated no reduced growth rate compared to non-radiated samples while flow cytometry did not reveal a significant amount of dead cells.

Conclusions and future research

Several experiments were performed in order to reveal the geological-microbial relationship. Using X-ray µCT the bacterial activity in the form of biogenic gas could be visualized within rocks and the first experiments did not reveal a clear negative impact of the radiation on the bacterial growth. This study brought three different fields together: Geology, Bioscience Engineering and Physics. It introduced bacterial adhesion and growth in porous limestone and is the starting point of a larger research project as it illustrated the potential and challenges of this approach. Flow experiments with the easy adhesion of the bacteria proved its potential for further detailed experiments, such as bioclogging. Towards the future, the setup will be improved with a syringe pump to create a constant controlled flow. Contrast agents will be added to reveal the biofilms itself (Carrel et al., 2017). Working with bacteria in such a complex environment like rocks proved however to be difficult. This is indicated by the variable gas saturations, the lack of clear calcium carbonate precipitation and varying growth conditions. Therefore, in future research we will start from more simple experiments with bacteria and rocks separately. This will allow a clearer understanding of the behaviour of the bacteria, and the rocks pore structure.

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Figure 1. Vertical cross section of 3D µCT image through (left) Savonnières and (right) Tabaire revealing the 3D rendered volume of biogenic gas after one week of bacterial growth. Diameter of the samples is 6 mm.

Spatial variability in proglacial sediment composition along the Southern Patagonian Icefield (47–51°S)

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Fjord sediments are increasingly used as high-resolution archives of past climate and environmental change (e.g., Howe et al., 2010). An accurate interpretation of fjord sediments in terms of past changes in hydrology and glacier mass balance however requires a comprehensive understanding of the variables that affect sediment composition (Bertrand et al., 2012b; Munoz & Wellner, 2016). This is particularly important in Patagonia, where fjord sediments are known to contain high-resolution records of Holocene changes in precipitation (Bertrand et al., 2014; Lamy et al., 2010) and glacier mass balance (Bertrand et al., 2012a; Bertrand et al., 2017; Kilian & Lamy, 2012).

With this in mind, this study investigates spatial variations in sediment physical properties, composition, and bulk organic and inorganic geochemistry within the fjords located to the north and west of the Southern Patagonian Icefield (SPI). The studied surface sediment samples are located along transects from the fjord heads towards the open ocean. The main research objective is to identify suitable proxies for estimating past changes in terrestrial sediment input in these fjord systems.

This study makes use of two fjord systems: the Baker-Martinez Fjord Complex (BMFC), which is located to the north of the SPI and mostly composed of river-fed fjords, and the fjord system west of the SPI, including Canal Messier and Canal Wide, which is mainly influenced by calving glaciers. The main difference between these two fjord systems is the number of calving glaciers, and therefore the sediment delivery processes.

Throughout both fjord systems, carbon and nitrogen stable isotopic composition of fjord sediments are well suited to estimate past changes in terrestrial sediment input. More depleted $\delta^{13}C$ and δ^{15} N values are found near glacier fronts and river outlets, while less depleted δ^{13} C and δ^{15} N values represent more marine environments.

The spatial variations in inorganic elements (expressed as logratios) differ between the fjords. Mg/Al increases linearly with distance from the fjord heads throughout the Baker Channel, while an exponential increase is observed in the Martinez Channel. In the fjord system west of the SPI, Mg/Al has no significant correlation

with distance; however, an increase with distance can be observed in Canal Messier and Canal Wide. Ti/Al, on the other hand, increases linearly with distance throughout Baker Channel, while no significant correlations were found in the other channels. Therefore, given the large variability observed, we suggest that the application of bulk inorganic geochemical proxies to reconstruct terrestrial sediment input in the fjords along the SPI should be confined to a specific fjord solely, and not over an entire fjord system.

Within the BMFC, the elemental log-ratios Fe/Al, Zr/Al, Ti/Al, Mg/Al and litho-Si/Al show promising results to estimate past changes in terrestrial sediment input. Over the entire BMFC, Fe/Al increases exponentially and Zr/Al decreases logarithmically with increasing distance from the fjord heads. Litho-Si/Al decreases logarithmically with distance throughout the Martinez Channel, however no significant correlation is observed in the Baker Channel.

Due to a low sampling density, no significant correlations between elemental log-ratios and distance could be established within Canal Messier and Canal Wide, west of the SPI. As such, no inorganic geochemical proxies were identified within this western fjord system.

In addition, our results show that the mass-specific magnetic susceptibility signal of fjord sediments can be used to differentiate terrestrial sediments from the Northern and Southern Patagonian Icefields, due to the distinct lithologies on which these ice masses occur. The Patagonian Batholith (PB) below the Northern Patagonian Icefield (NPI) is rich in Fe- and Ti- bearing ferroand/or paramagnetic minerals. These minerals induce the high mass-specific magnetic susceptibility observed in the terrestrial sediments from the NPI. Contrary to PB, the Eastern Andes Metamorphic Complex below the SPI contains little Fe and Ti, resulting in low mass-specific magnetic susceptibility of the terrestrial sediments from the SPI.

The results of this study should contribute to the interpretation of fjord sediment records in terms of past changes in provenance, glacier variability and river discharge.

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