Evaluating the biomineralization and chemical differentiation of modern brachiopod archives

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This PhD project focuses on the determination of biomineralization processes related to brachiopod shell formation and their impact on geochemical proxies, in order to evaluate the potential use of brachiopods as chemical proxies of paleo-seawater. We aim at deciphering the influence of the vital effects superimposing the original proxy record thereby improving proxy calibration and paleo-environmental reconstructions.

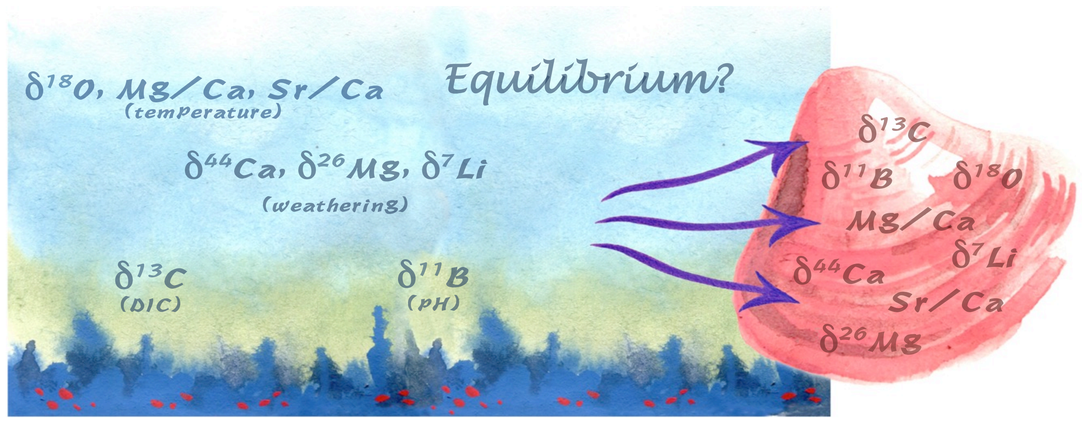
Brachiopods as potential paleoenvironmental proxies.

Fossil brachiopods have been extensively used to reconstruct physicochemical conditions and secular chemical variations of ancient oceans (Veizer et al., 1986), because their low-magnesium calcite shells is the diagenetically more stable polymorph of calcium carbonate and resistant to all except the most aggressive diagenetic processes. Most of the studies assume that brachiopods incorporate stable isotopes and trace elements into their calcitic into shell calcite into or near equilibrium. However, the use of brachiopod shells as paleoenvironmental archives is problematic due to the biological processes of the organism (the so called "vital effect"), which cause their chemical and isotopic compositions to be significantly different from inorganic calcite precipitated in isotopic equilibrium with ambient seawater .

Goal of the study

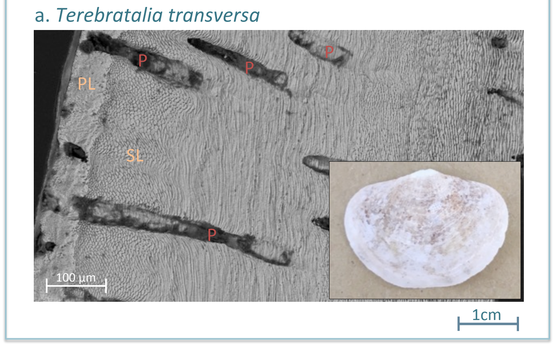
To unravel which brachiopod taxa and/or portions of the shells and brachiopod taxa are most reliable as paleoenvironmental proxies. We will determine the transport, the elemental discrimination and isotope fractioning processes of trace elements and their isotopes from seawater to the site of calcification.

We will measure in situ, at least, Oxygen, Carbon, Boron, Lithium, Magnesium and Calcium isotope compositions using the ion microprobe technique and trace element contents by LA-ICPMS of shells from modern environment and from culture specimens. Latter measurements will be combined with scanning electron microscopy to study the brachiopod shell structure.



Brachiopods. Shell structure.

a. *Terebratalia transversa*



b. *Notosaria nigricans*

c. *Liothyrella neozelanica*

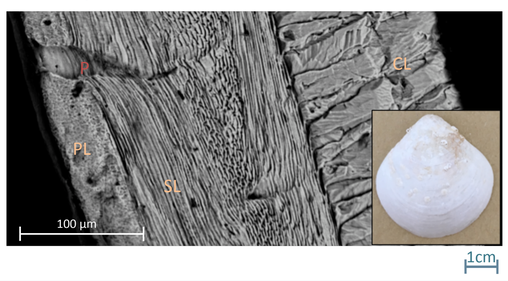


Figure 1. Brachiopod shell structure analyzed by SEM

PL: Outer primary layer, made of acicular calcite.
SL: Inner secondary layer, made of calcite fibers.
CL: Columnar layer, made of pillar-shaped calcite crystals.
P: Punctae. Characteristic perforations of brachiopod shells.

What do we know so far

$\delta^{11}B$ values in brachiopod shells.

Penman et al. (2013)

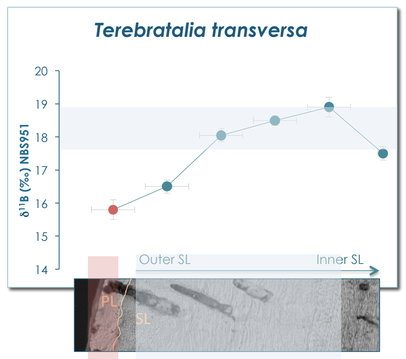


Figure 2. Depth transects of $\delta^{11}B$ through *T. transversa* by NTIMS analysis.

$\delta^{13}C$ and $\delta^{18}O$ values in brachiopod shells.

Fig. 3. Cusack et al. (2008d)

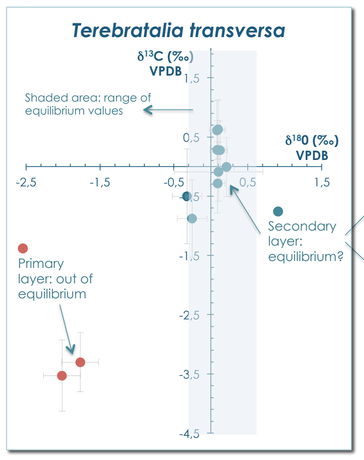


Fig. 4. Cusack et al. (2012)

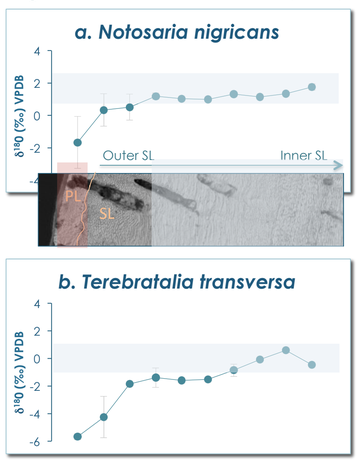
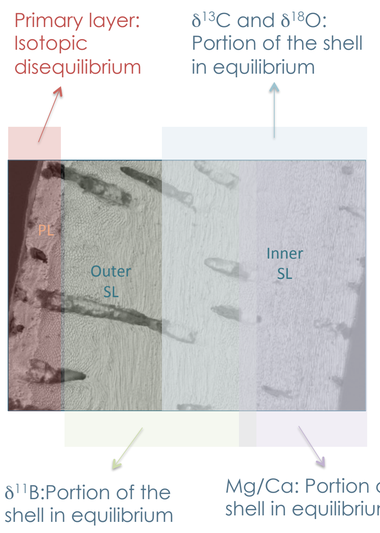


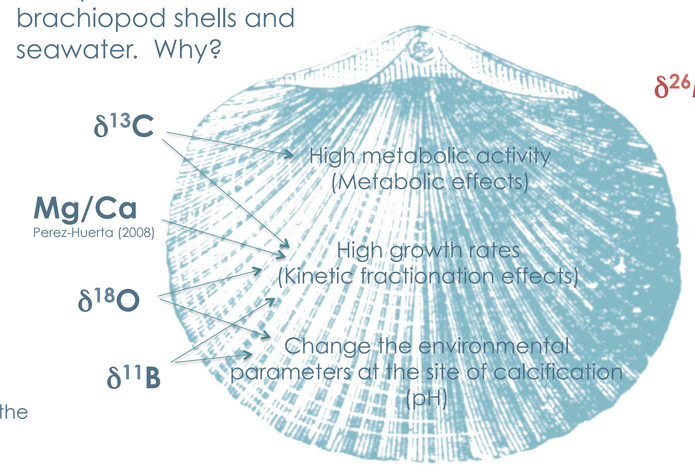
Figure 3. $\delta^{18}O$-$\delta^{13}C$ cross plot of *Terebratalia transversa*, determied by electron microprobe analyses.

Figure 4. $\delta^{18}O$ composition from outer to innermost secondary layer of *N. nigricans* and *T. transversa*, determined by SIMS.

Vital fractionation effects



Disequilibrium between brachiopod shells and seawater. Why?



$\delta^{26}Mg$?
$\delta^{7}Li$?
$\delta^{44}Ca$?
Li/Ca?
Sr/Ca?

Kinetic effect?

Kinetic effects have been observed for these elements in inorganic calcite experiments.

Still need to be tested the potential use of these isotopic and elemental ratios in brachiopods as **reliable paleoenvironmental proxies**

Bibliography

Auclair A., M.M. Joachimski, and C. Lécuyer. 2003. Deciphering kinetic, metabolic and environmental controls on stable isotope fractionations between seawater and the shell of Terebratalia transversa (Brachiopoda). Chem. Geol. 202: 59–78.

Brand U., A. Logan, N. Hiller, and J. Richardson. 2003. Geochemistry of modern brachiopods: applications and implications for oceanography and paleoceanography. Chem. Geol. 198: 305–334.

Cusack M., D. Parkinson, A. Perez-Huerta, J. England, G.B. Curry, and A.E. Fallick. 2008d. Relationship between d18O and minor element composition of Terebratalia transversa. Trans. R. Soc. Edinburgh. 98: 443-449.

Cusack M. and A.P. Huerta. 2012. Brachiopods recording seawater temperature—A matter of class or maturation?. Chem. Geol. 334: 139–143.

Penman, D.E., B. Hönisch, E.T. Rasbury, N.G. Hemming, and H.J. Spero. 2013. Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-shell variability, controls, and potential as a paleo-pH recorder. Chem. Geol. 340: 32-39.

Perez-Huerta, A., M. Cusack, T.E. Jeffries, C.T. Williams. 2008. High resolution distribution of magnesium and strontium and the evaluation of Mg/Ca thermometry in Recent brachiopod shells. Chem. Geol. 247 (1–2): 229–241.

Veizer, J., P. Fritz and B. Jones. 1986. Geochemistry of brachiopods: oxygen and carbon isotopic records of Paleozoic oceans. Geochim. Cosmochim. Acta. 50: 1679–1696.