Assessing the biomineralization processes in the shell microstructure of modern brachiopods: variations in the oxygen isotope composition and minor element ratios

Sara Milner[1]*, Claire Rollion-Bard[1], Pierre Burckel[1], Adam Tomašových[2], Lucia Angiolini[3], Hana Jurikova[4] and Daniela Henkel[4]

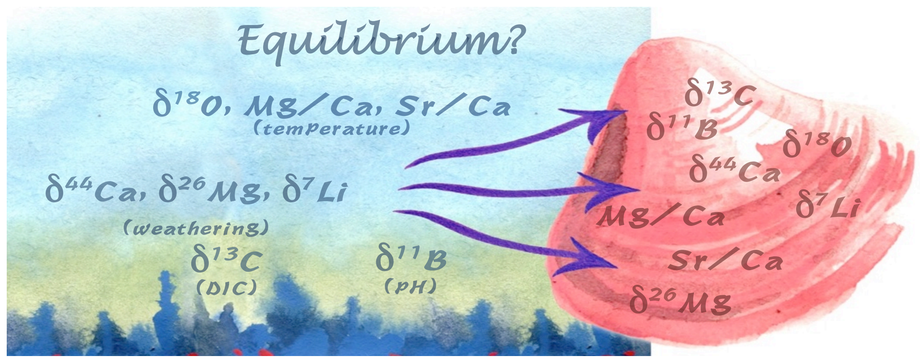
(1)Institut de Physique du Globe de Paris, France, (2) Slovak Academy of Sciences, Bratislava, Slovakia, (3) Università degli Studi di Milano, Italy, (4) GEOMAR, Kiel, Germany

*corresponding author: milner@ipgp.fr

Brachiopod geochemistry as potential paleoenvironmental proxies

Fossil brachiopods have been used to reconstruct physicochemical conditions of ancient oceans due to their extensive fossil record and shells made of stable low-Mg calcite. In this context, it is important to assess the impact of brachiopod shell biomineralization processes on geochemical proxies.

In this study, we analysed the variability of $\delta^{18}O$ values and trace element ratios in the shell microstructures of modern brachiopods, in order to assess which brachiopod shell portions or taxa are the most reliable for reconstruction of paleoenvironmental conditions.



Material & Methods

Seven modern brachiopod species were selected. Using the scanning electron microscopy, species were divided in two groups regarding their shell microstructure: a) shells of primary (PL) and secondary fibrous layer (SL) (*Terebratalia transversa, Magasella sanguinea, Calloria inconspicua, Notosaria nigricans* and *Magellania venosa*) and b) shells composed of primary, secondary and tertiary columnar layer (TL) (*Liothyrella neozelanica* and *Gryphus vitreus*).

Oxygen isotope compositions were measured in situ using the ion microprobe technique and trace element contents by Laser ablation coupled to an ICPMS.

The shell microstructure

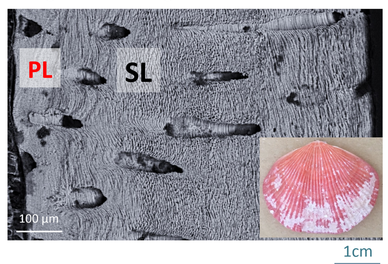
PL: Outer primary layer, made of acicular calcite.

SL: Secondary layer, made of calcite fibers.

TL: Tertiary layer, made of calcite columns.

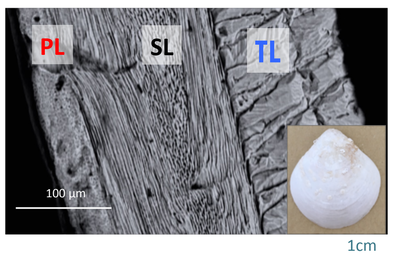
1. Shells with PL and SL

Magasella sanguinea



2. Shells with PL, SL and TL

Liothyrella neozelanica

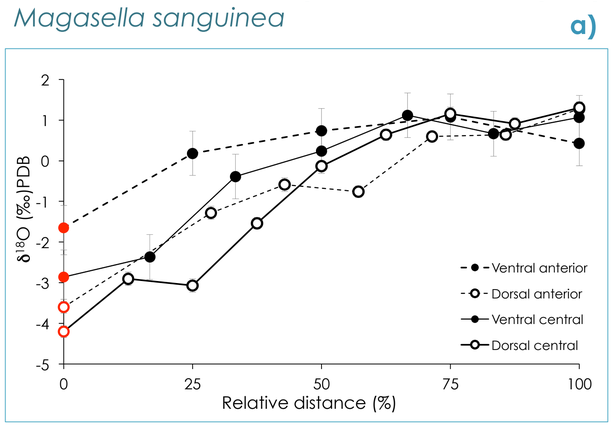


$\delta^{18}O$ values

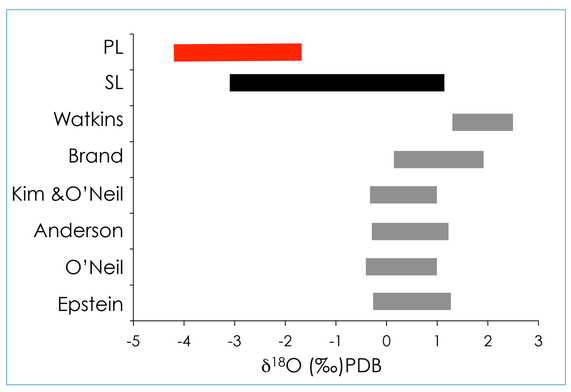
1. Shells with Primary and Secondary layers

Magasella sanguinea

a)



b)

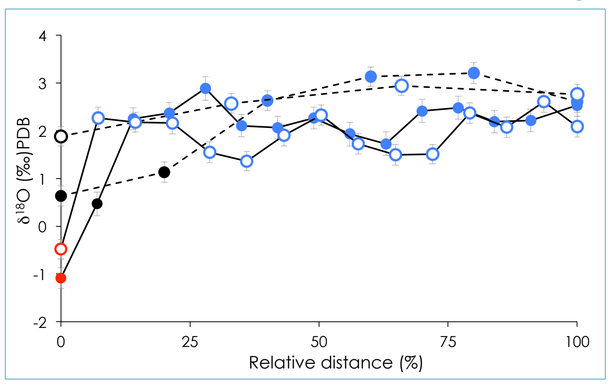


2. Shells with Primary, Secondary and tertiary layers

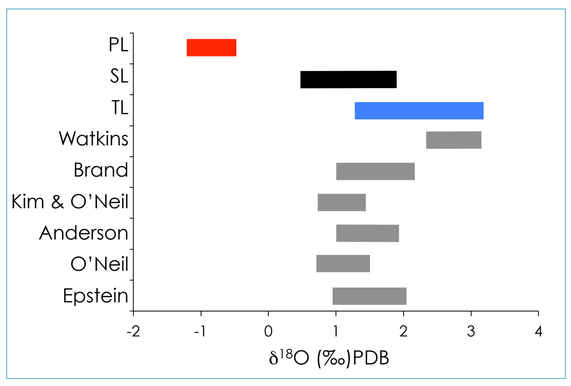
PL SL TL

Gryphus vitreus

a)



b)



a) Oxygen isotope composition of modern brachiopod shells from the outermost to the innermost shell thickness.
b) Measured $\delta^{18}O$ values in the modern brachiopod species and the calculated expected equilibrium values according to the paleotemperature equations of Watkins et al. (2013), Brand et al. (2013), Kim and O'Neil (1997), Anderson and Arthur (1983), O'Neil (1969) and Epstein et al. (1953).

PL: depleted in ^{18}O relative to equilibrium.

SL: towards equilibrium values from the outermost to innermost secondary layer, as in Cusack et al., 2012.

kinetic effects account for the $\delta^{18}O$ variability

TL: $\delta^{18}O$ equilibrium (Watkins et al., 2013 eq.)

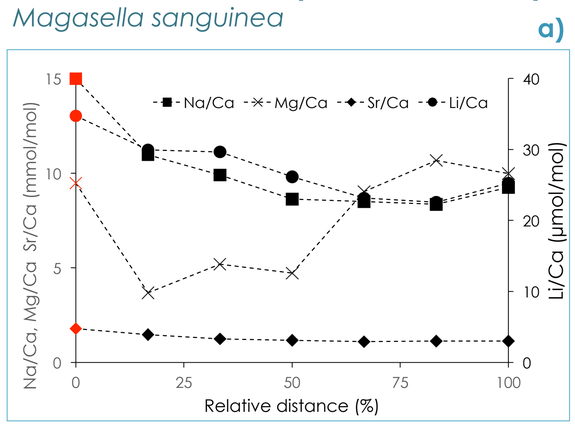
Different equations derived in different equilibrium fields → Careful when selecting the equation

Trace Element ratios (TE)

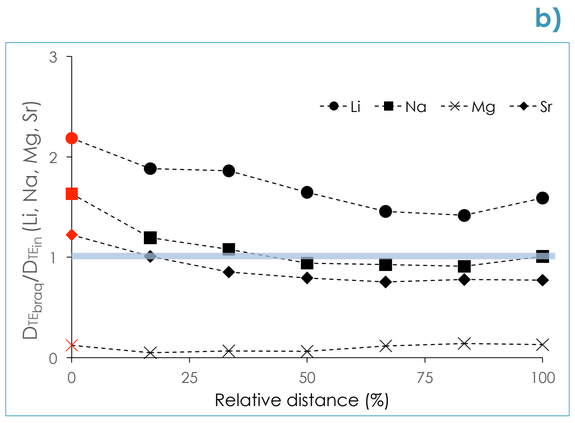
1. Shells with Primary and Secondary layers

Magasella sanguinea

a)



b)

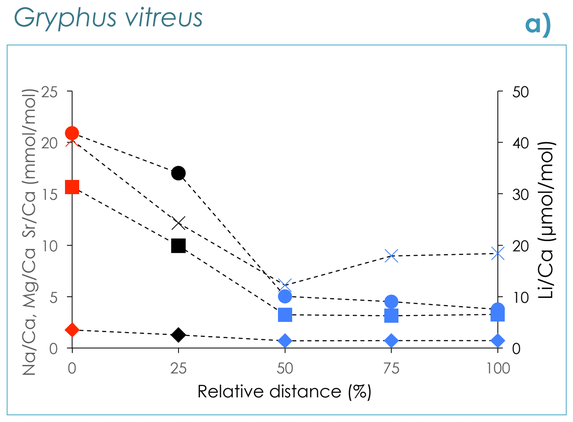


2. Shells with Primary, Secondary and tertiary layers

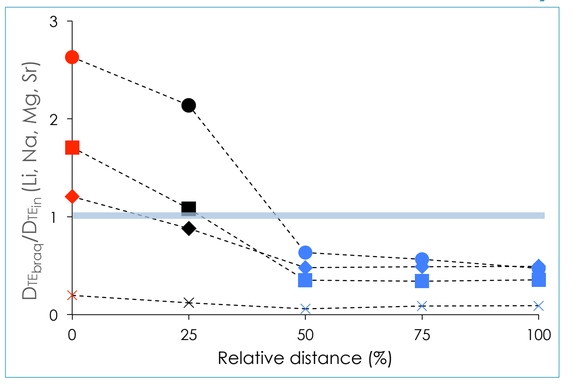
PL SL TL

Gryphus vitreus

a)

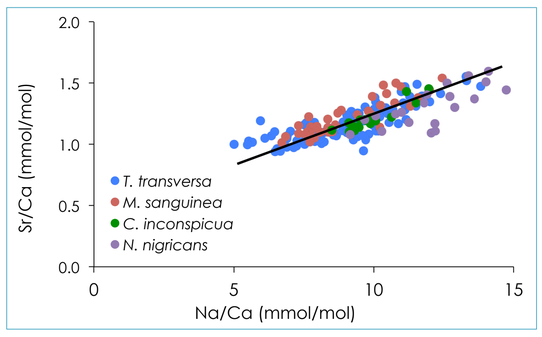


b)

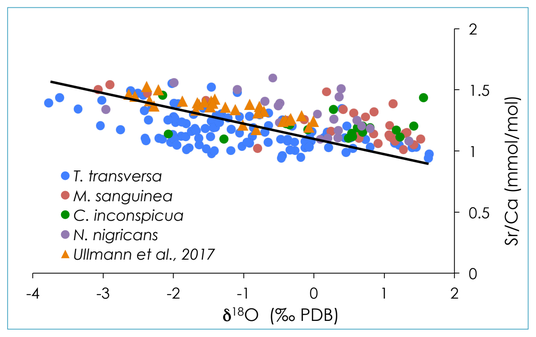


a) Trace element ratios from outermost to innermost shell thickness. External reproducibility (2σ RSD): 14% Li/Ca, 7% Na/Ca, 4% Mg/Ca and 2% Sr/Ca.
b) Ratio between the partition coefficient of braquiopod calcite and inorganic calcite in equilibrium. Partition coefficient of inorganic calcite from Marriot et al. (2004) for Li/Ca, Okumura and Kitano (1986) for Na/Ca, Oomori (1987) for Mg/Ca and Gabitov and Watson (2006) for Sr/Ca. Blue line indicates the value of equilibrium between brachiopod and inorganic calcite

Sr/Ca vs Na/Ca



Sr/Ca vs $\delta^{18}O$



*All data points are from the Secondary layer

Correlation of Trace elements and $\delta^{18}O$ in the SL due to Kinetic effects

PL: enriched in TE relative to the SL and TL (except Mg).

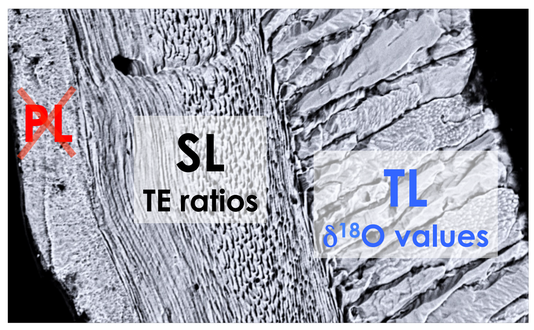
SL: **decrease from outer to inner** part until reaching a "steady state zone".

TL: depleted in all the trace elements measured relative to the PL and SL.

Different trace element incorporation. Likely due to **chemical modifications of the internal fluid** (e.g. the biological discrimination against Mg and Na in the internal fluid).

Best parts to use as proxies

1. The best shell portion to use for **$\delta^{18}O$ studies**, when present, is the **tertiary layer**. if not, the innermost secondary layer.
2. The best shell portion to use for **trace elements** studies is the **innermost secondary layer**.



3. The **tertiary layer** is depleted in trace element relative to equilibrium. This part is **not suitable for isotopic studies of trace elements (e.g. $\delta^{7}Li$, $\delta^{11}B$)** due to its very low content
4. The **primary layer has to be avoided** for both, $\delta^{18}O$ and trace element studies.

MARIE CURIE ACTIONS

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