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

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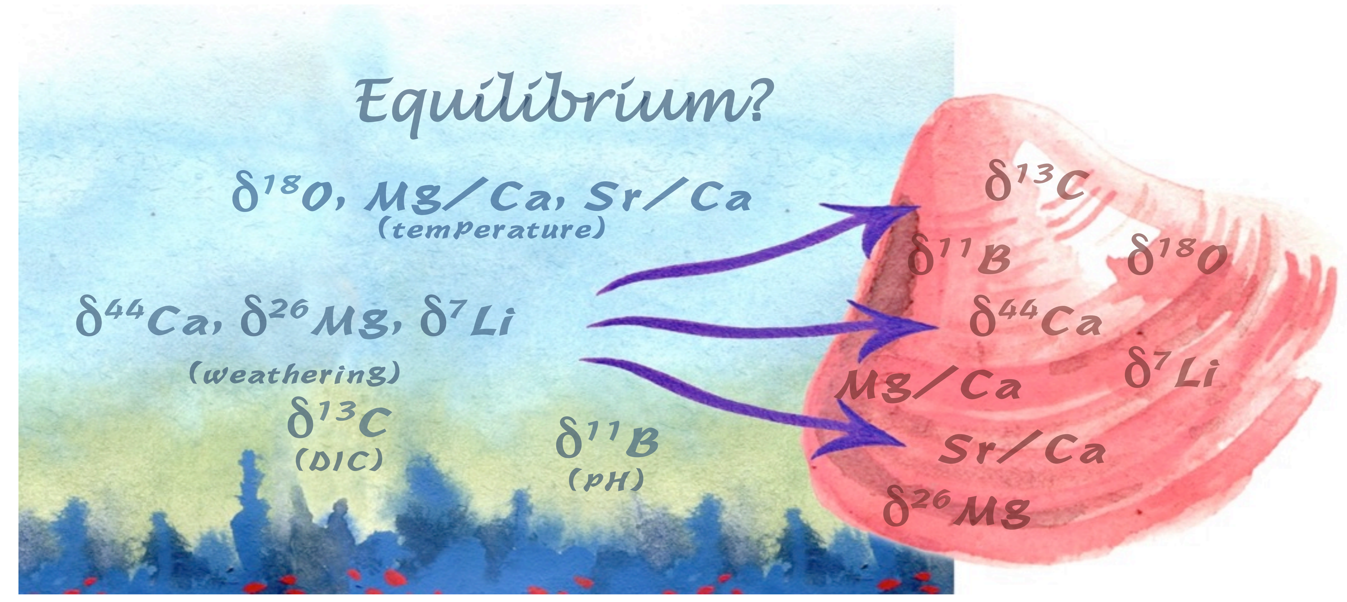
Brachiopod geochemistry as potential paleoenvironmental proxies

Fossil brachiopods have been extensively 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 reconstructing paleoenvironmental conditions.



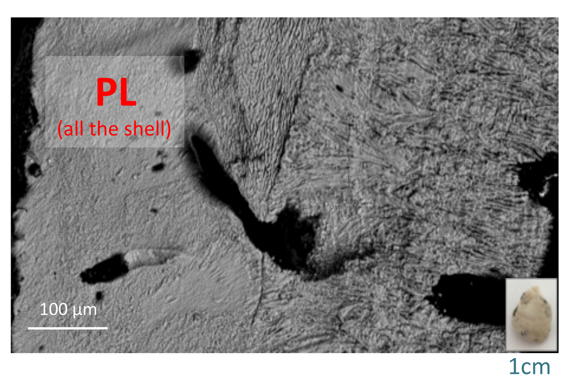
Material & Methods

Eight modern brachiopod species were selected. Using the scanning electron microscope, three main shell microstructures were identified: shells made of a) only primary layer (PL) (*Pajaudina atlantica*); b) primary and secondary fibrous layer (SL) (*Terebratalia transversa, Magasella sanguinea, Calloria inconspicua, Notosaria nigricans* and *Magellania venosa*) and c) 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 ICP-MS.

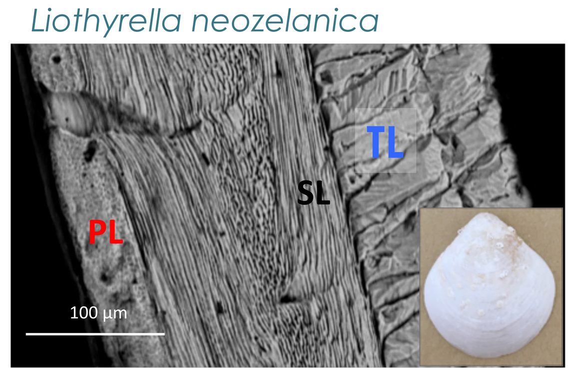
The shell microstructure

a. Shells with only PL
Pajaudina atlantica



b. Shells with PL and SL
Terebratalia transversa

c. Shells with PL, SL and TL
Liothyrella neozelanica



PL: Outer primary layer, made of acicular calcite.

SL: Inner secondary layer, made of calcite fibers.

TL: Tertiary layer, made of columnar calcite crystals.

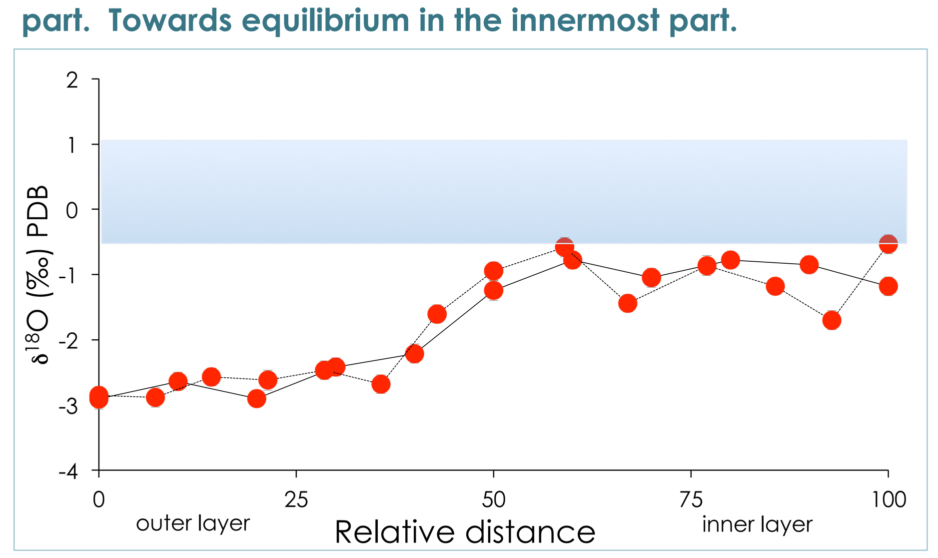
$\delta^{18}O$ values in modern brachiopod shells

There is a general trend **towards equilibrium values** from outer to inner part of the shell, as in Cusack et al., 2012.

This isotopic variations within the same shell microstructure is likely due to **kinetic effects**, with $\delta^{18}O$ equilibrium achieved as the shell becomes mature and precipitation rate slows.

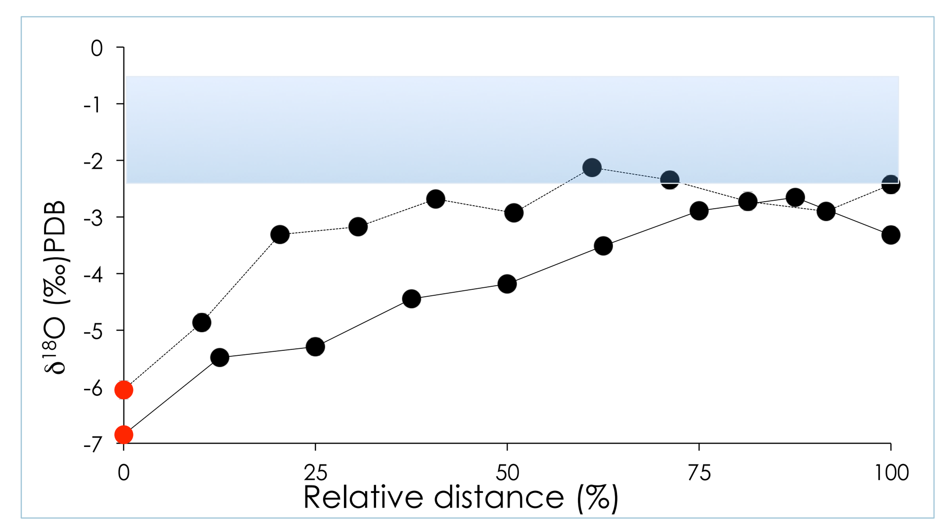
a) Pajaudina atlantica

PL: depleted in ^{18}O relative to equilibrium in the outermost part. Towards equilibrium in the innermost part.



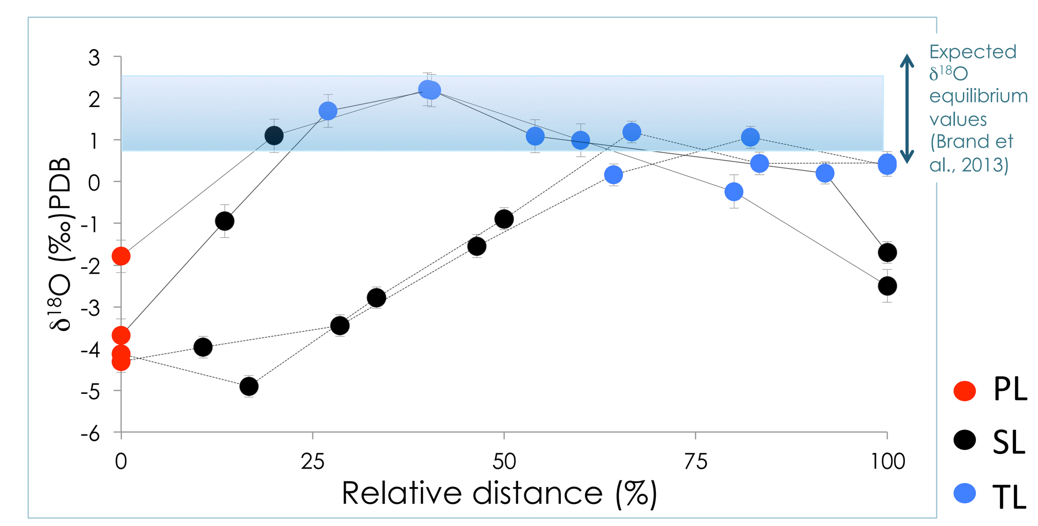
b) Terebratalia transversa

SL: Towards equilibrium $\delta^{18}O$ values.



c) Liothyrella neozelanica

TL: Closest to equilibrium $\delta^{18}O$ values.



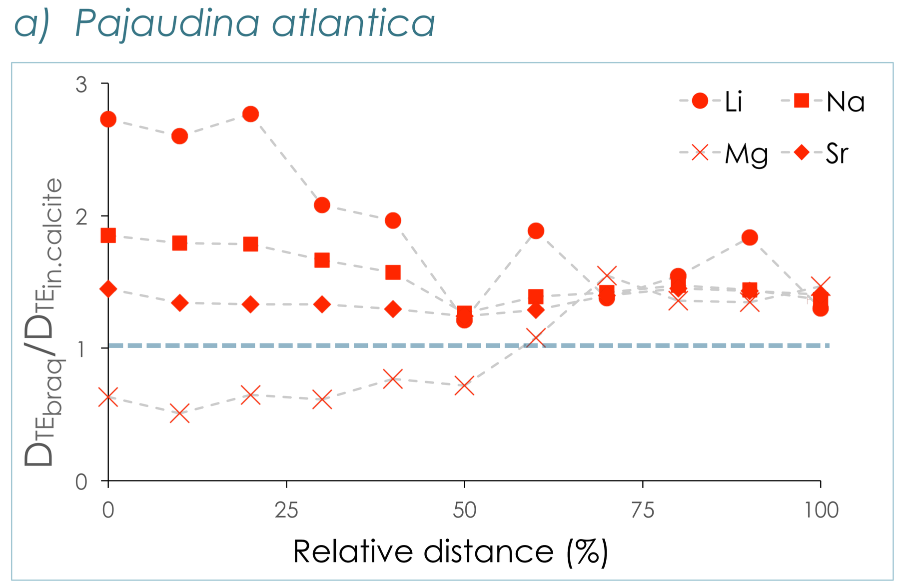
Trace Element ratios (TE) in modern brachiopod shells

a) Abrupt decrease from outer to inner "Steady state" zone in the innermost PL. Enriched in trace elements relative to equilibrium.

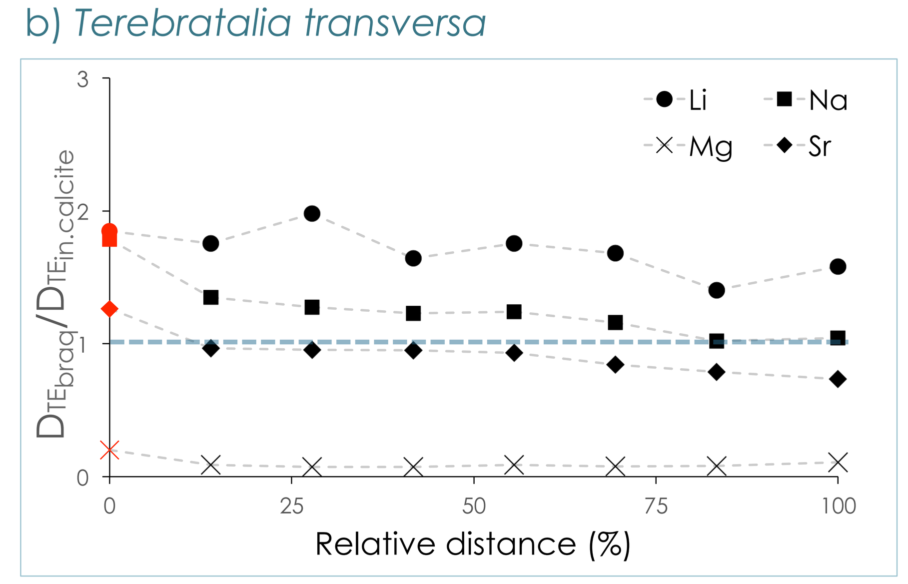
b) Decrease from outer to inner "Steady state" zone in the innermost SL.

c) Depleted in trace elements relative to equilibrium.

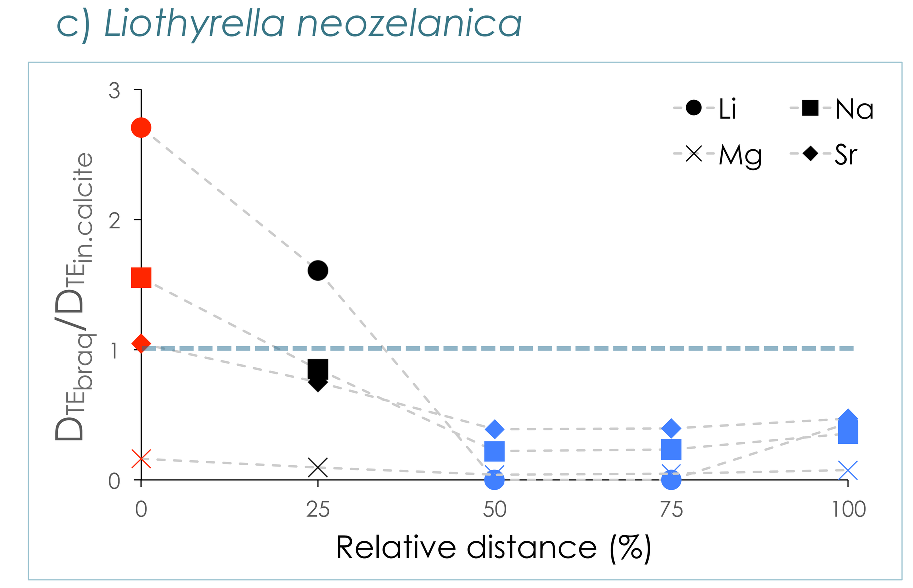
a) Pajaudina atlantica



b) Terebratalia transversa



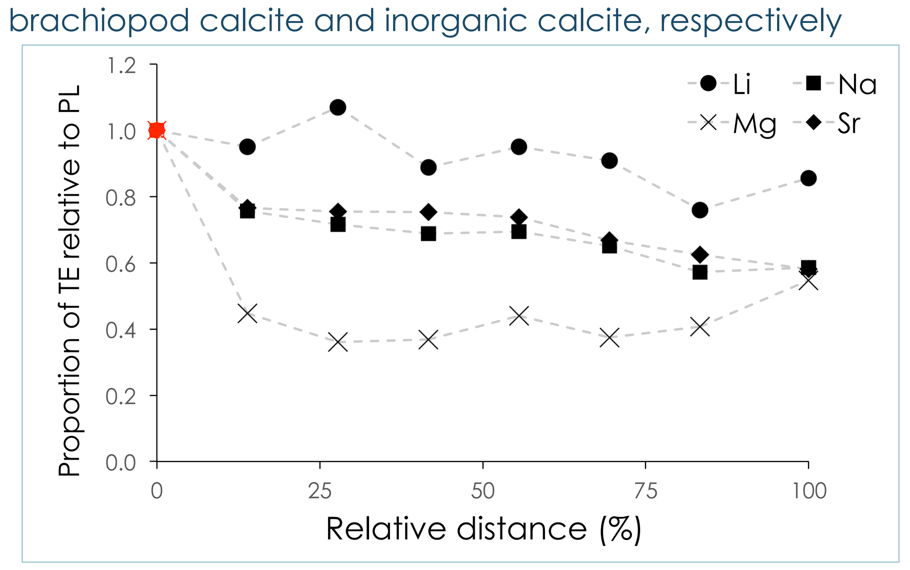
c) Liothyrella neozelanica

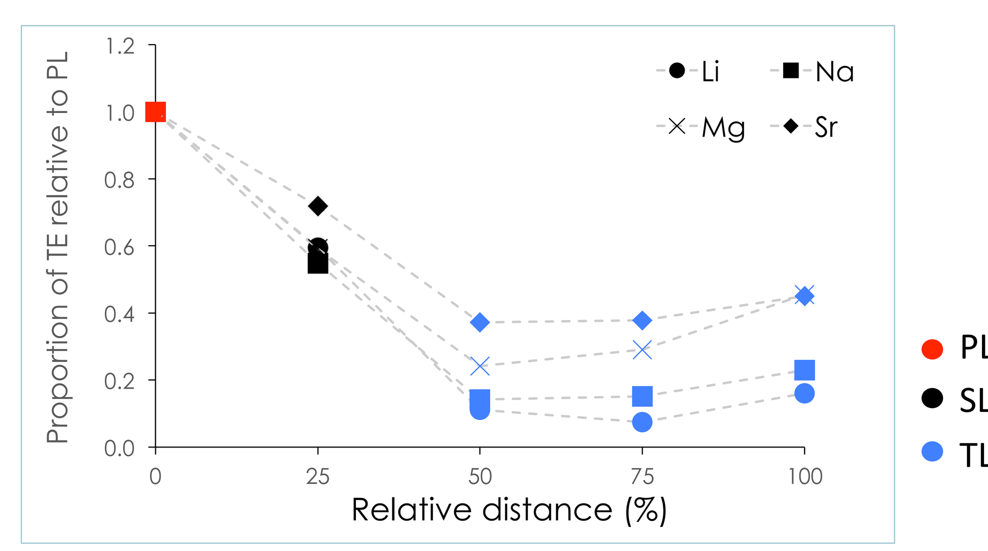


D_{TEbraq}, $D_{TEin.calcite}$: partition coefficient of trace elements in brachiopod calcite and inorganic calcite, respectively

In shells made of PL or PL and SL, there is always an **abrupt decrease from outer to inner** part, where a constant value is reached. This is likely due to kinetic effects within the shell microstructure.

The **PL, SL and TL have different trace element incorporation signatures**. This is likely due to **chemical modifications of the internal fluid** from which calcite precipitates the different shell microstructures (e.g. the biological discrimination against Mg and Na in the internal fluid, in which the SL precipitates).





Conclusions

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

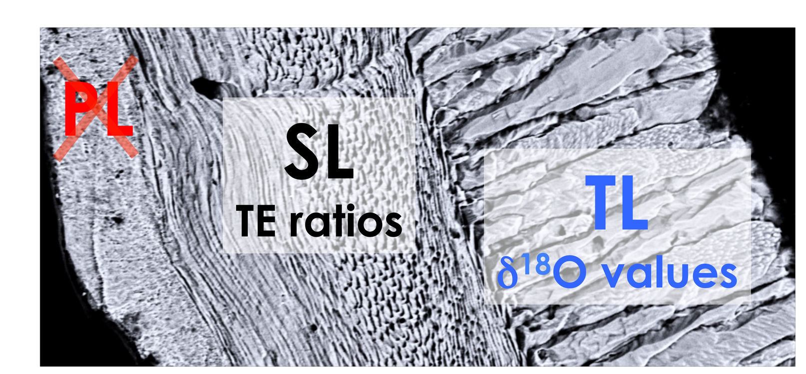
   The Tertiary layer is in $\delta^{18}O$ equilibrium with seawater. The innermost secondary layer is in or near equilibrium.

2. The best shell portion to use for **trace element** studies is the **innermost secondary layer**.

3. The **tertiary layer** is depleted in trace elements 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.

Best parts to use as proxies



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