A chemical investigation of microstructural changes in oyster (*Magallana gigas*) shells

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NOTE:

Throughout this presentation, axis tick labels have been hidden to prevent sharing of unpublished data

Introduction: The oyster enigma

- Many modern and fossil oyster species are characterized by thick shells composed of two types of microstructure:
  1. Porous, chalky calcite
  2. Dense, foliated calcite

- These two structures are textually distinct (see next slide) and seem to have a different chemical signature

- Why these microstructures are formed is unclear, and there are two ruling hypotheses:
  1. The microstructures are an adaptation that allows the oyster to grow faster and produce irregularly shaped shells (Morphological adaptation *Checa et al., 2018, SciRep 8:7507*)
  2. The porous microstructure is not actually precipitated by the oyster itself but by microorganisms (sulfur reducing bacteria) living in cavities in the shell (Microbial mineralization *Vermeij, 2014, BioOne 40(1):1-13*)

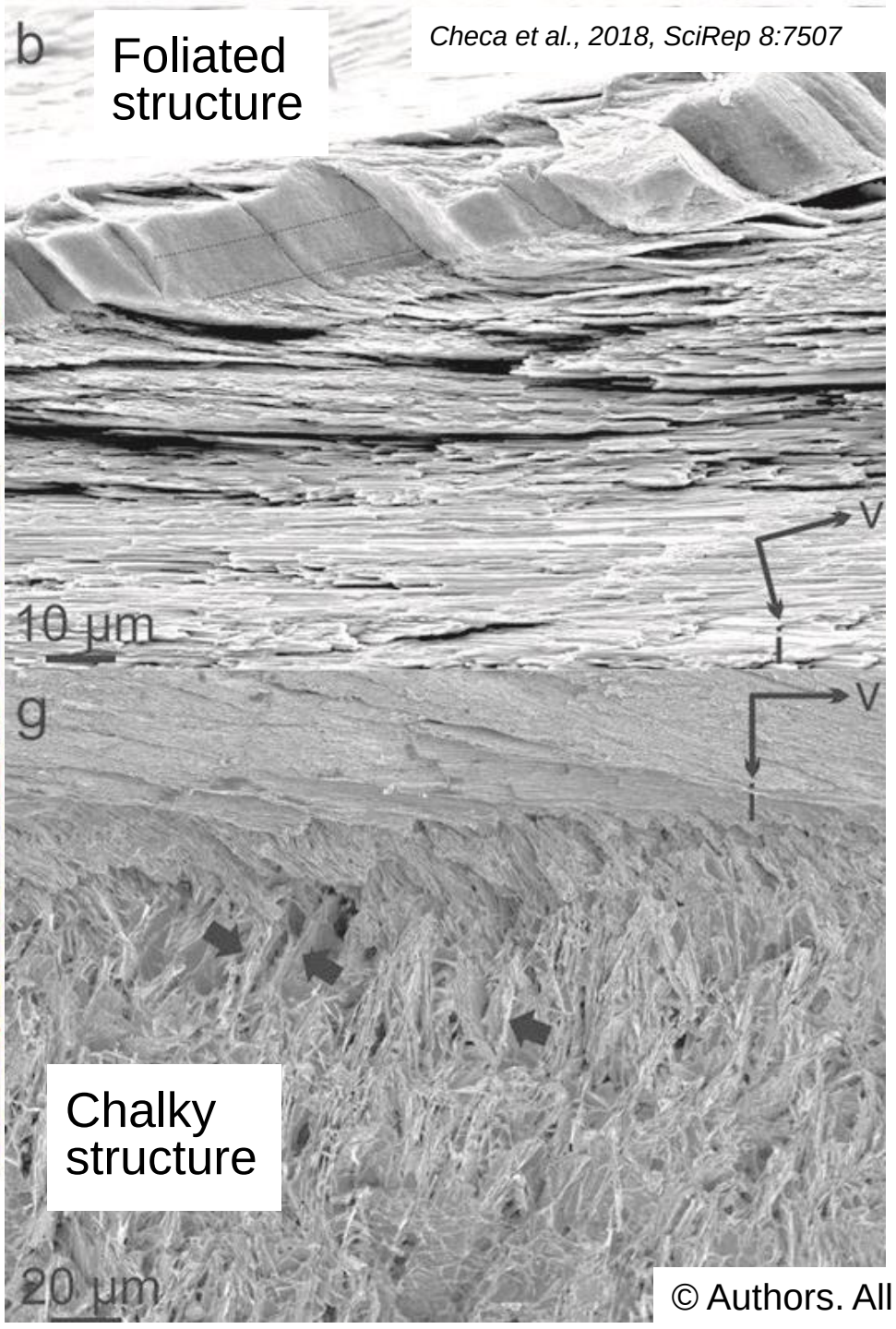
- There is some evidence for hypothesis 1 in the form of structural observations (SEM, EBSD, microCT)
- We add to this evidence by providing a comprehensive chemical and isotopic comparison between microstructures

- If hypothesis 2 is correct, fractionation of Bacterial Sulfur Reduction (BSR) should leave an isotopic and chemical signature *(Brunner et al., 2005, GCA 69:20, 4773-4785)*
- If hypothesis 1 is correct, microstructures should be more or less isotopically similar.

Microstructures

Foliated structure

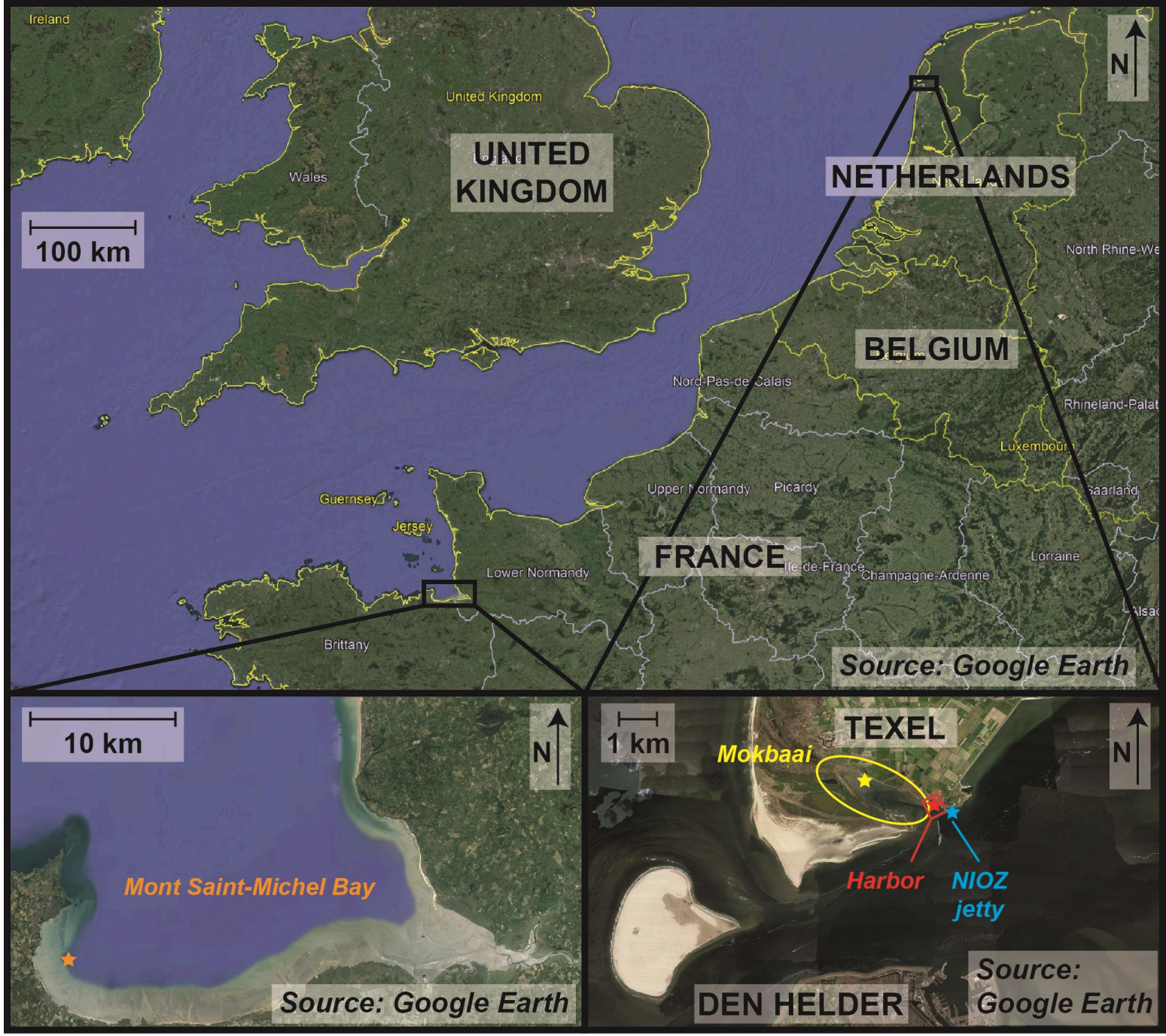
Chalky structure



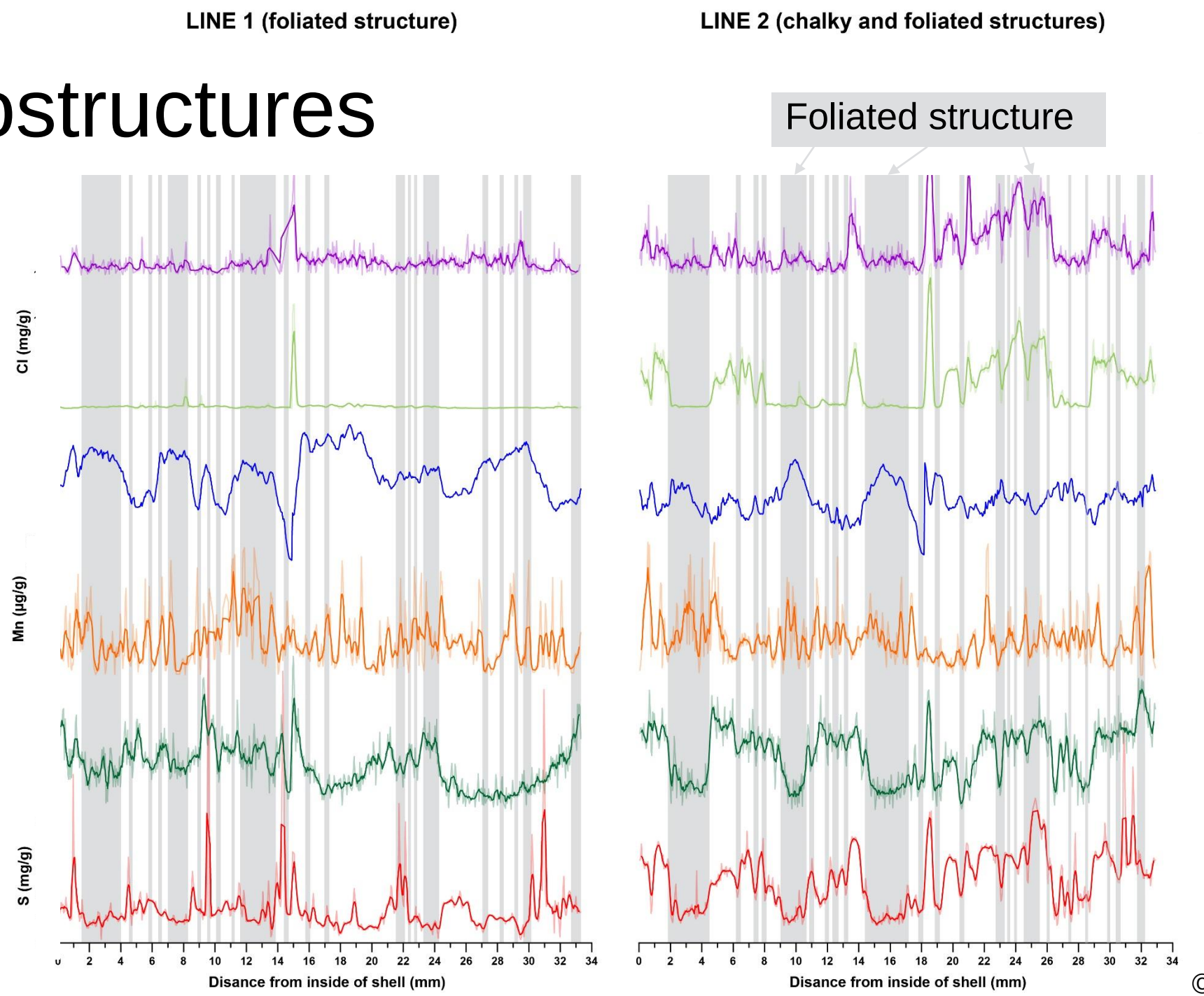
Sample locations

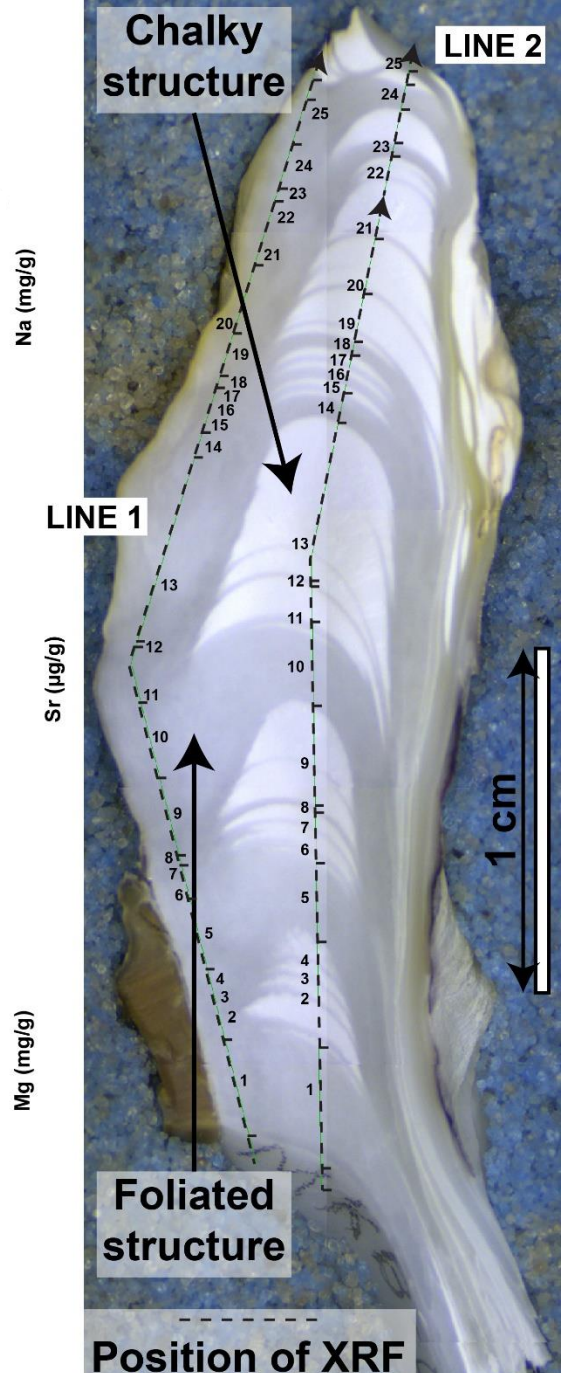
Oysters of the species *Magallana gigas* (formerly *Crassostrea gigas*) were sampled from three localities in the Netherlands and France:

1. Mokbaai (**MB**): a tidal estuary in National Park “Duinen van Texel”, NW Netherlands
2. TESO Harbor (**TH**): Harbor of the ferry connecting Texel island with mainland Netherlands
3. Brittany (**BR**): Commercial oyster aquaculture site in Mont Saint-Michel Bay



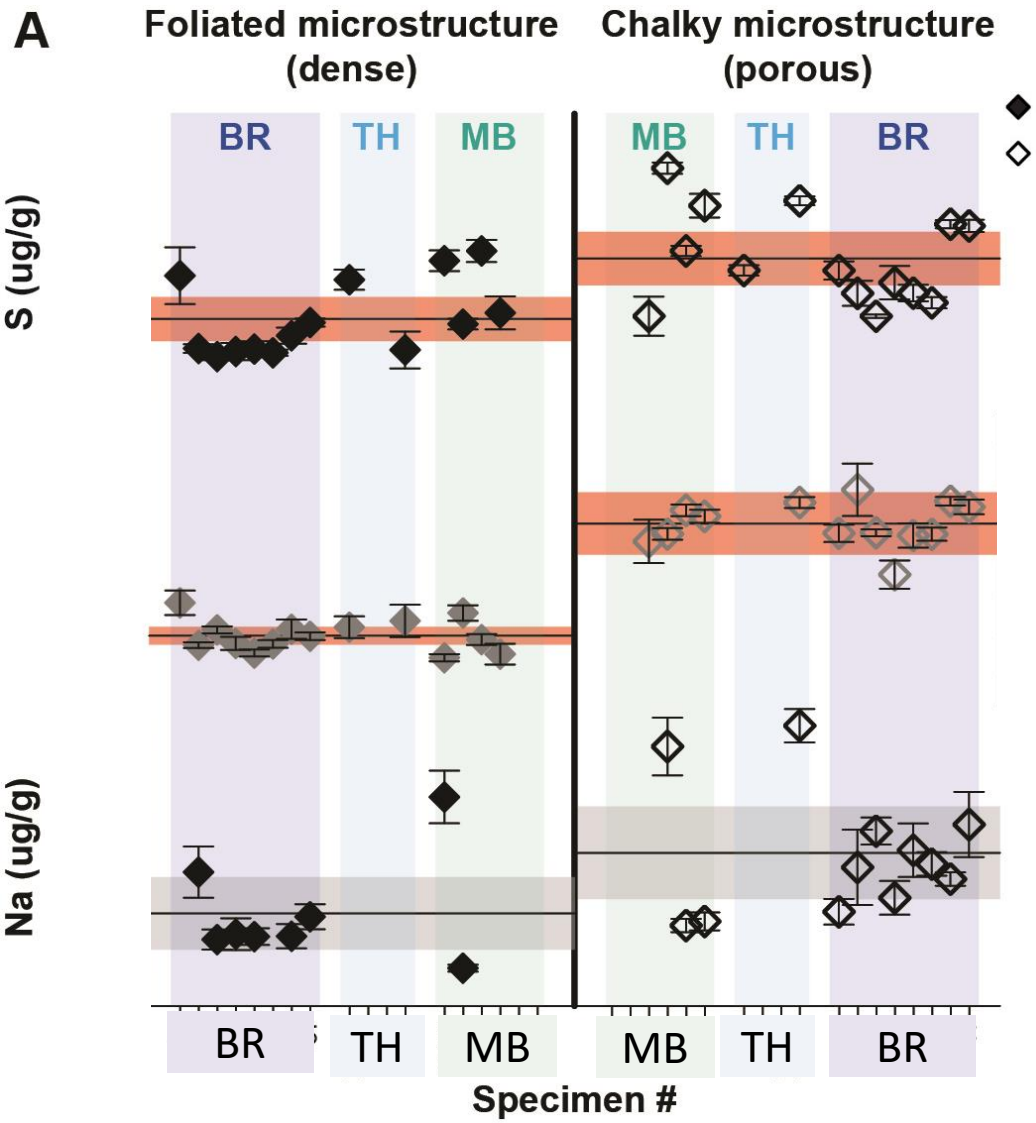
Microstructures





Trace element variability between microstructures

BR = Brittany
TH = TESO Harbor
MB = Mokbaai



Significant difference between microstructures

Significant difference between microstructures

No significant difference between microstructures

Trace element variability between microstructures

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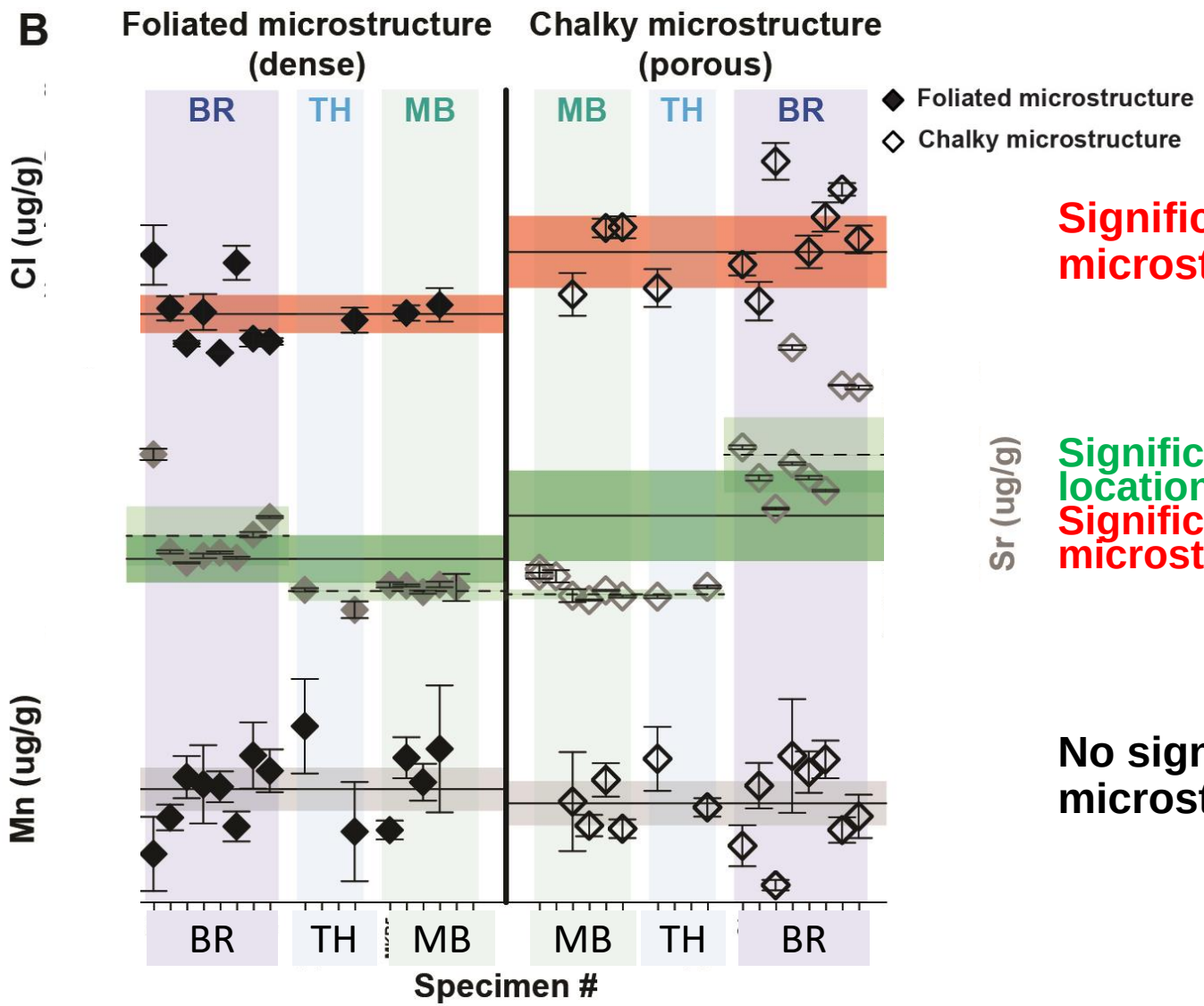


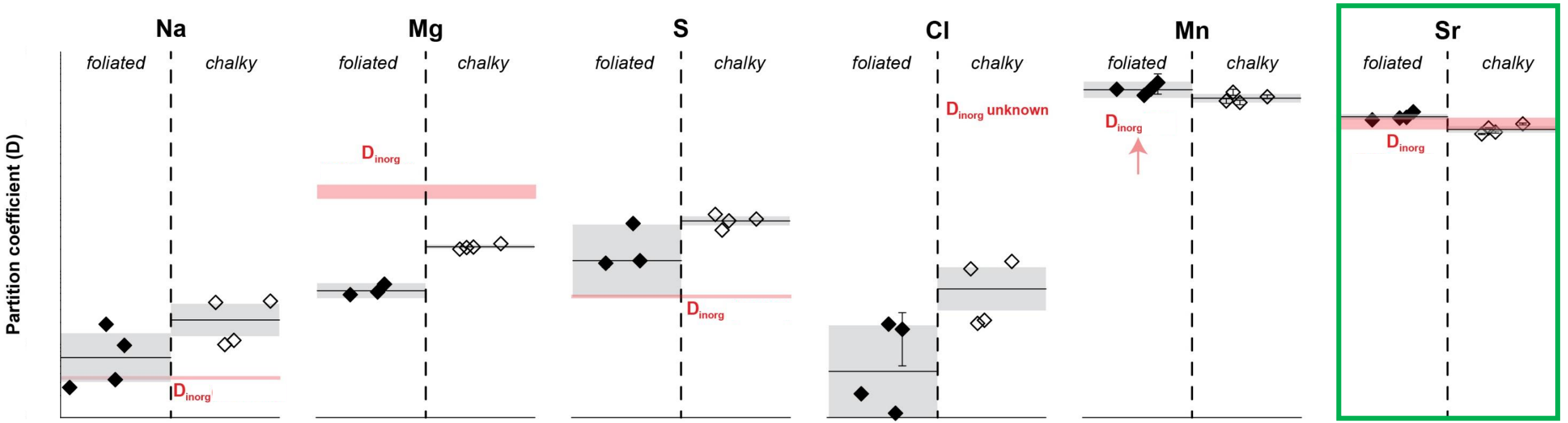
Significant difference between microstructures

Significant difference between locations
Significant difference between microstructures only in BR samples

No significant difference between microstructures

Trace element partition coefficients between microstructures

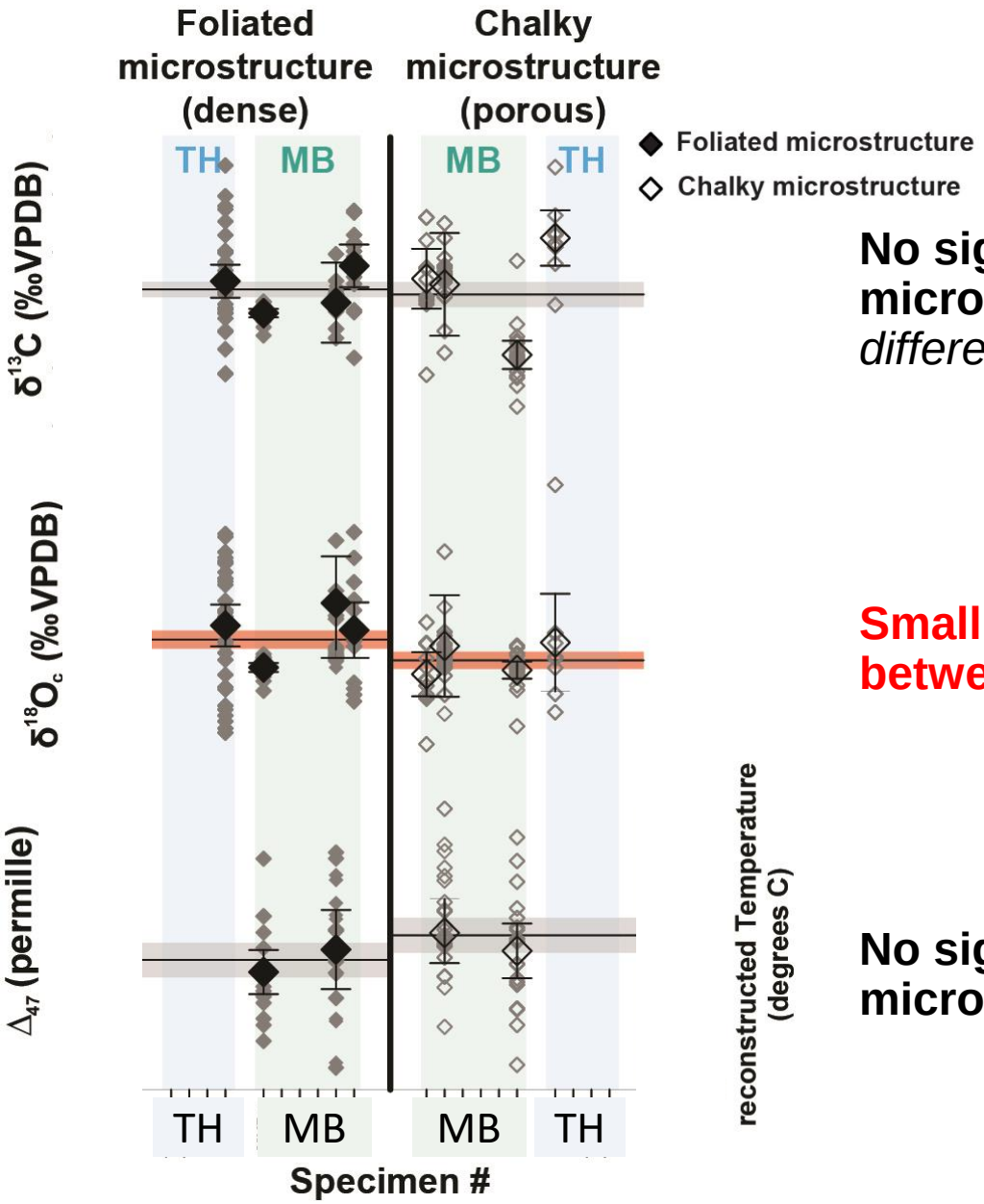
(only) Sr = close to trace element equilibrium



D_{inorg} = partition coefficient of inorganic calcite

Chalky structure has higher partition coefficients, especially in elements with high seawater concentrations (Na, Mg, S and Cl). No difference in Sr and Mn.

Isotopic variability between microstructures



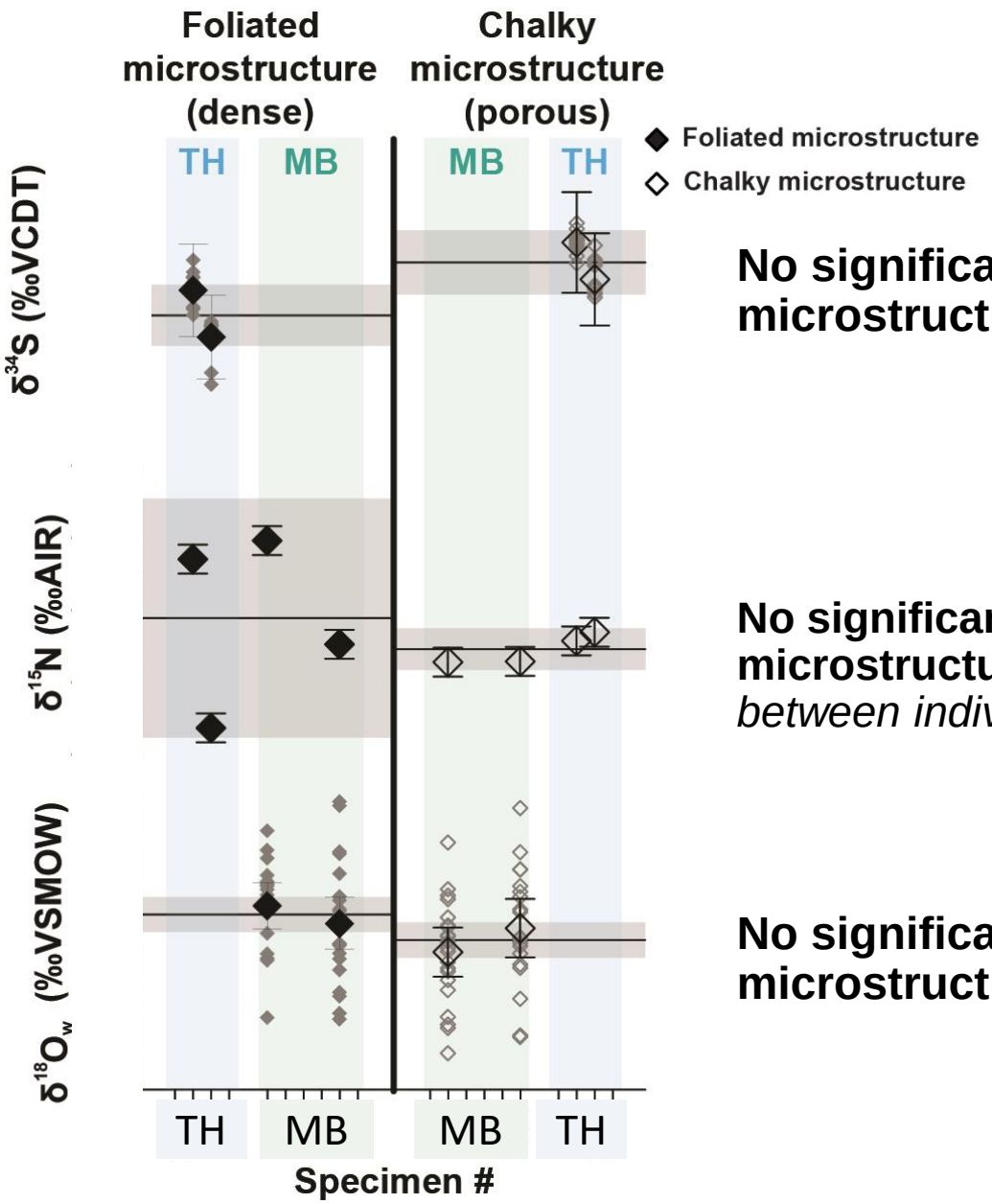
BR = Brittany
TH = TESO Harbor
MB = Mokbaai

No significant difference between microstructures *(but some difference between individuals)*

Small significant difference between microstructures

No significant difference between microstructures

Isotopic variability between microstructures



BR = Brittany
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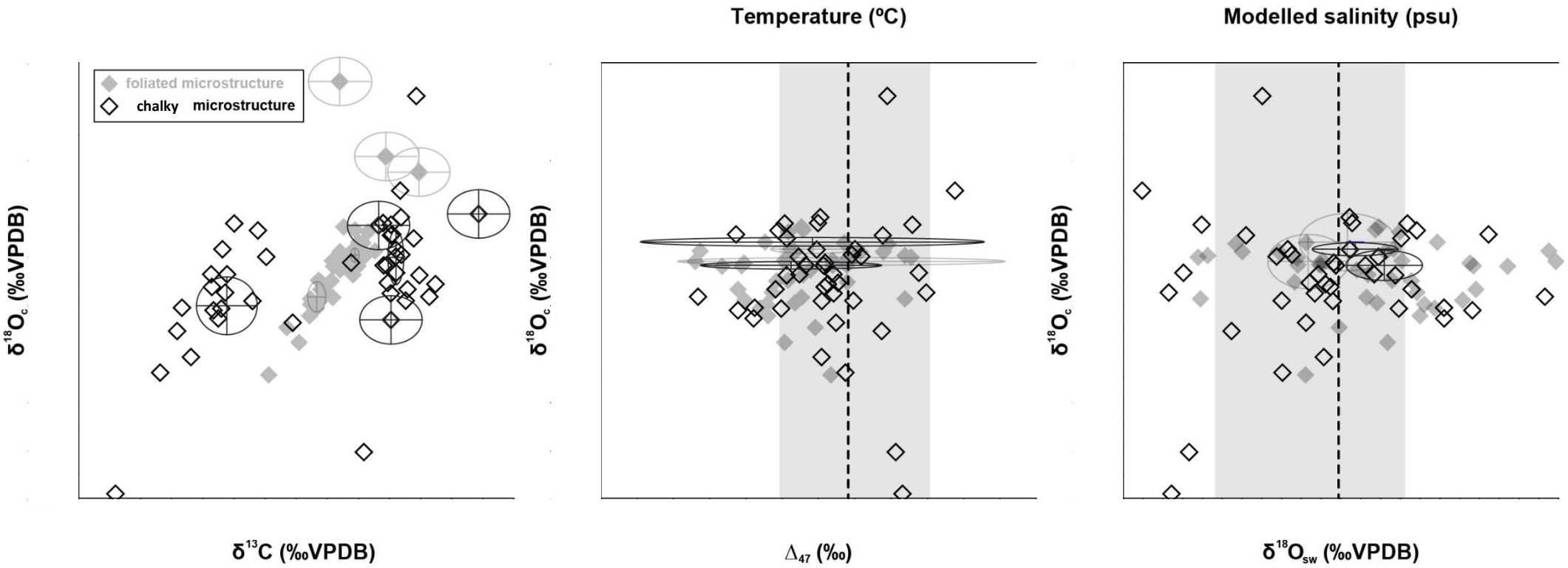
No significant difference between microstructures

No significant difference between microstructures *(but some difference between individuals in foliated)*

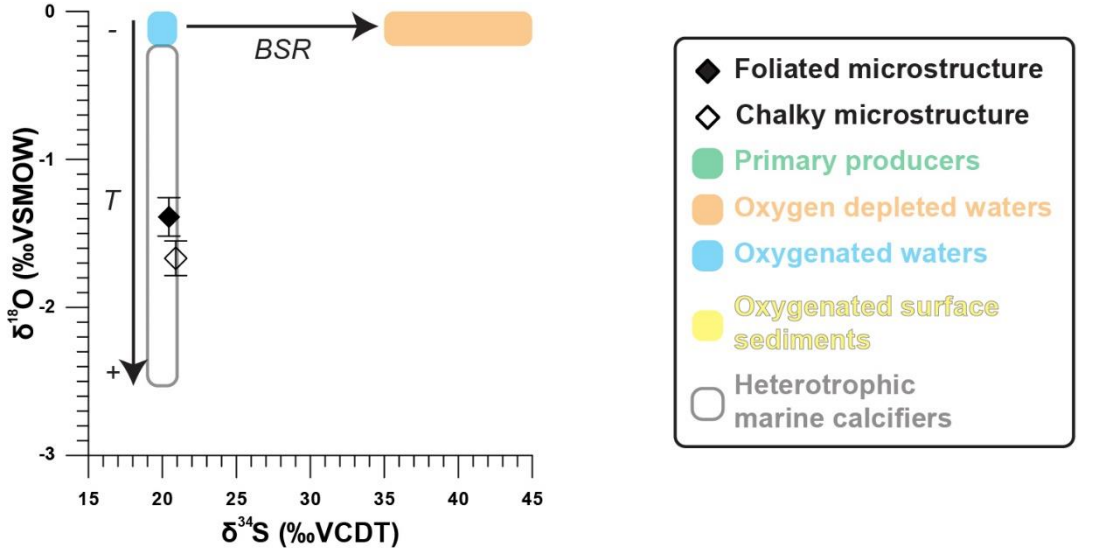
No significant difference between microstructures

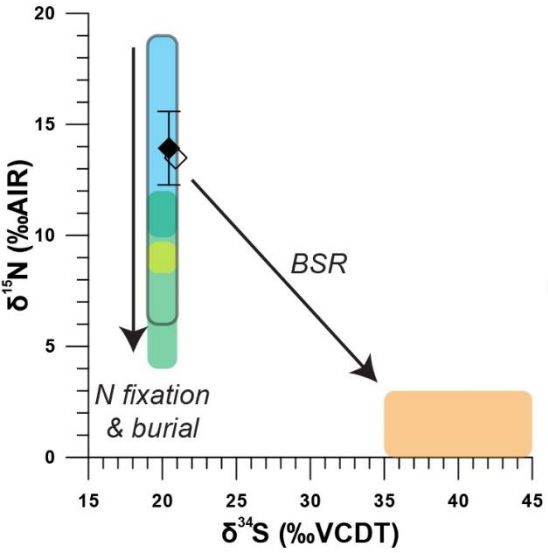
Isotopic variability between microstructures C, O and clumped isotope results

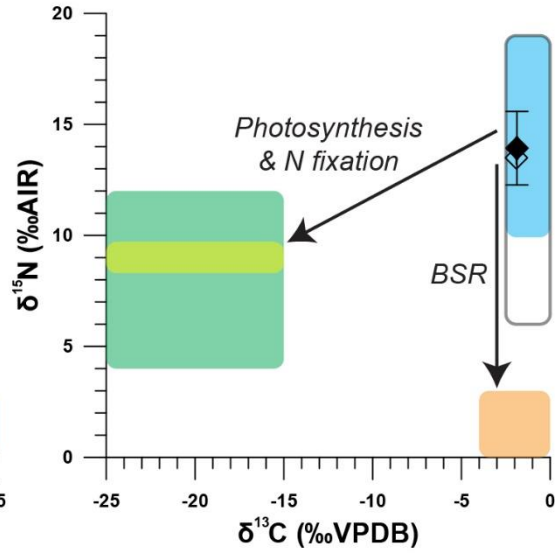


- **No significant difference between microstructures in clumped isotope results**
- **Both microstructures yield accurate SST and SSS reconstructions**
- **Small significant difference in d18O and d13C between microstructures, but largest differences are between individuals**

Isotopic variability between microstructures
C, N, S, O results







- **Isotopic composition of both microstructures strongly reflect isotopic compositions of seawater in North Sea**
- **No evidence of Bacterial Sulfate Reduction (BSR)**
- **No difference between microstructures**
- **Nitrogen and carbon isotopes show large link with DIC and DIN (nitrate) rather than with phytoplankton**

Conclusions

Trace elements

- Chalky structure has higher partition coefficients, especially in elements with high seawater concentrations (Na, Mg, S and Cl).
- The oyster grows faster during chalky calcite formation, and discriminates less against trace elements dissolved in the seawater.

Stable isotopes

- Isotopic composition of both microstructures strongly reflect isotopic compositions of seawater in North Sea
- No evidence of Bacterial Sulfate Reduction (BSR), so hypothesis 2 is not supported!

Implications for paleo studies

- No isotopic difference between microstructures, so both should be suitable for environmental reconstruction purposes

Implications for nitrogen isotope analyses in bivalve shells

- Nitrogen and carbon isotopes show link with DIC and DIN (nitrate) rather than with phytoplankton. Implications for paleodiet studies?