

## INTRODUCTION

- **Stable oxygen isotopes** ( $\delta^{18}\text{O}$ ) values from well-preserved *Arctica islandica* bivalve shells are frequently used as a proxy for **water temperature** (and salinity).
- We present the first stable isotope ( $\delta^{18}\text{O}$  &  $\delta^{13}\text{C}$ ) analysis on a fossil **semi-recrystallized** *A. islandica* shell (Figure 1) from the **Tjörnes Beds** of Iceland (**Pliocene**).
- We compare **paleo-water temperatures** inferred from stable oxygen isotope ( $\delta^{18}\text{O}$ ) ratios of both recrystallized and non-recrystallized portions of the shell to **highlight and discuss the impacts of taphonomic alterations on a micro-scale** and its implications for paleo-environmental reconstructions based on this versatile, high-resolution biogenic archive.

## MATERIAL & METHODS

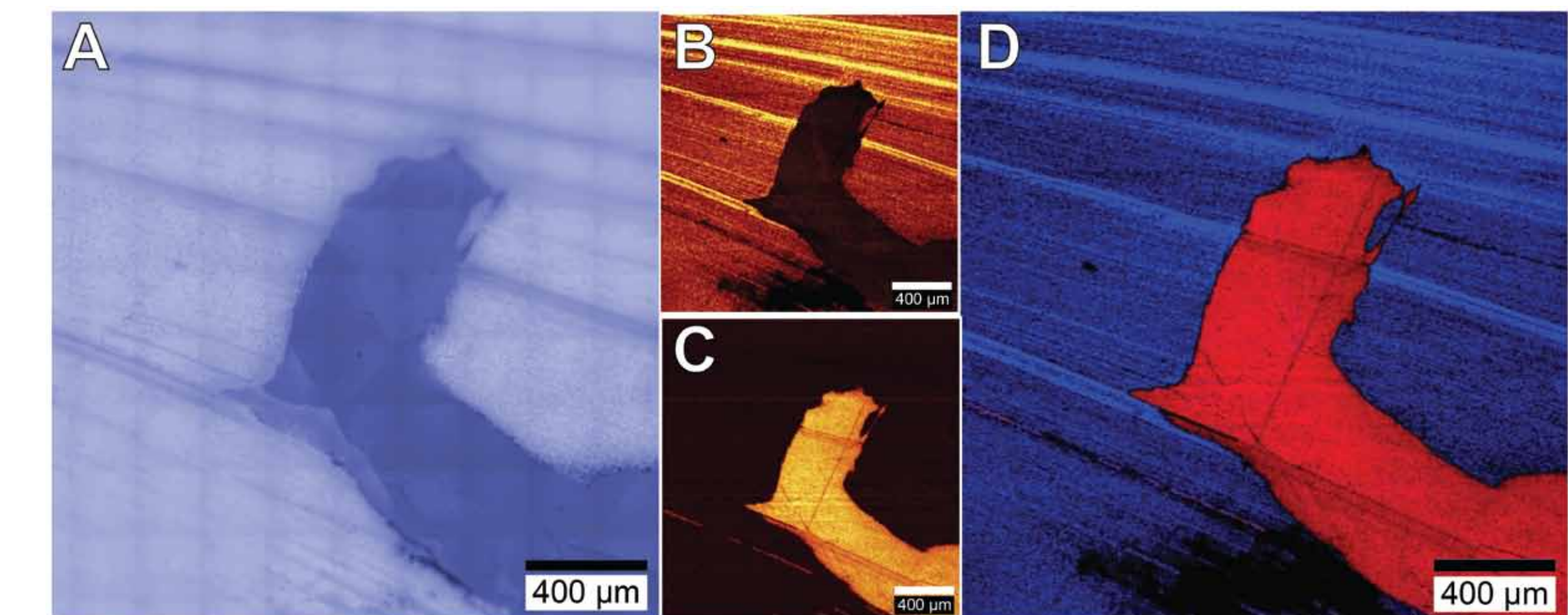
- **Biostratigraphy** dates Tjörnes Beds layers ~3.5 Ma.
- **Raman microscopy** is used to identify pristine aragonite and recrystallized calcite shell portions (see box on right), which were then sampled by **drilling** and high-resolution **micro-milling**.
- Note: **Oxygen isotopes** ( $^{16}\text{O}$ ,  $^{18}\text{O}$ ) are incorporated into the shell carbonate **in equilibrium** with the ambient water (Schöne, 2013).
- Carbonate samples were taken manually by **drilling** (red dots in Figure 1) to verify entire **range of isotopic variability** within the shell and infilled secondary calcite material.
- **Milling** samples were taken (along the transect in Figure 4a) to assess the impact of recrystallization through the **direct transition from calcite to aragonite**.
- $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  measurements were conducted on a Thermo Finnigan MAT 253 **isotope ratio mass spectrometer** at AWI Bremerhaven.



**Figure 1:** Thick-section of *A. islandica* specimen AI-TjBe-01 from the Tjörnes Beds, Iceland. Both shells are still articulated, while the internal cavity has been filled with sediment (grey in the lower cavity half) and secondary blocky crystals (amber coloured in the upper part), which have been identified as calcite based on CRM analysis. Shell mainly consists of amber coloured crystals (calcite) with white patches of aragonite. Red dots give locations for isotopes samples taken by drilling. Black square gives location for CRM map shown in Fig. 2. Adjacent area is used for isotope milling approach and shown with higher magnification in Fig. 4. Scale bar is 1 cm.

## RAMAN MICROSCOPY

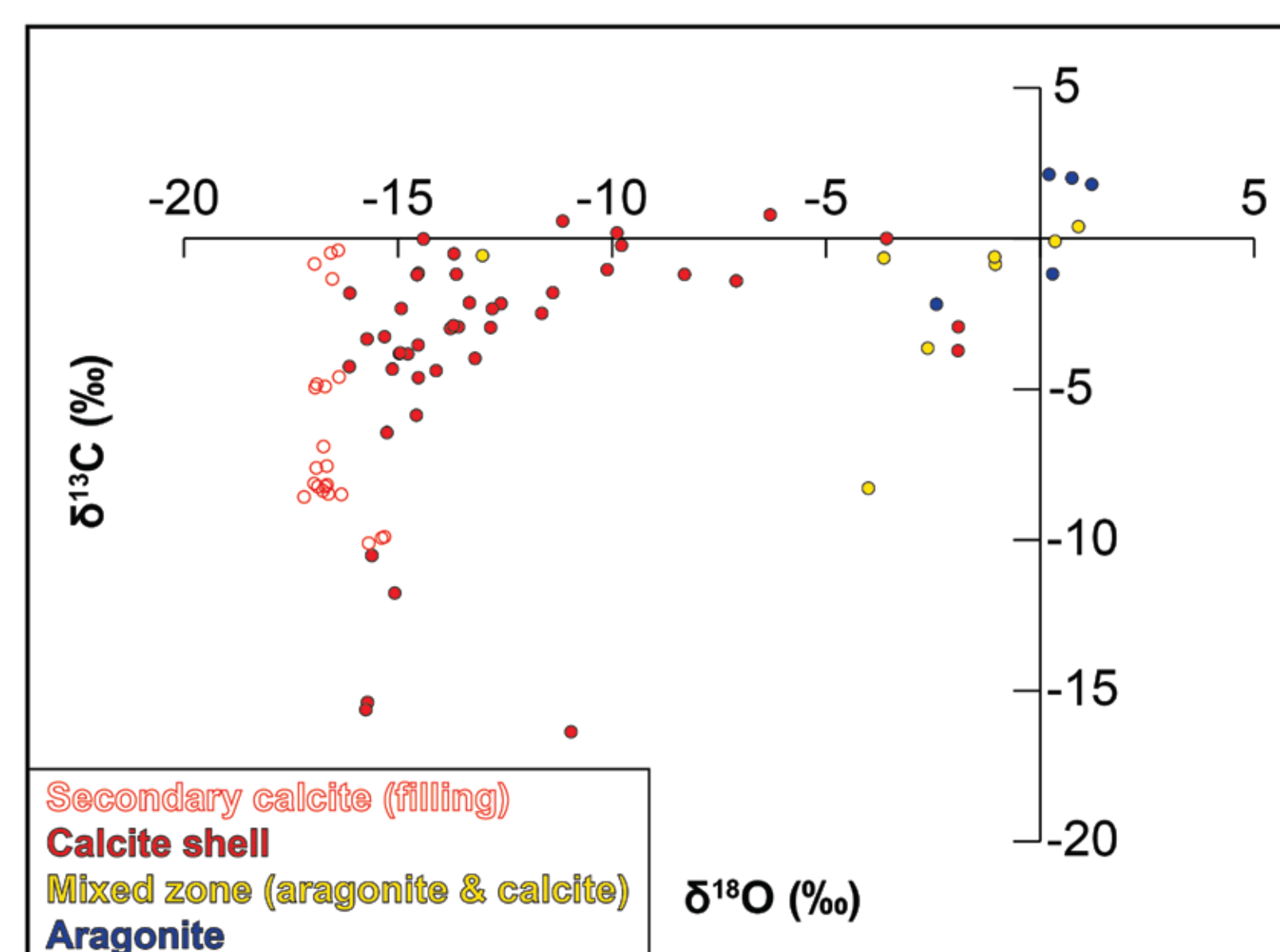
- Raman microscopy is used to identify areas of **pristine aragonite (Figure 2b)** and **recrystallized calcite (Figure 2c)** shell.
- We used a confocal Raman microscope (CRM) (WITec alpha 300 R), equipped with a diode laser (excitation wavelength 152 nm) and a 20x Zeiss objective housed at AWI Bremerhaven to examine the mineralogy of the shell. Instrumental procedure follows Nehrke et al. (2012).



**Figure 2:** Shell section as indicated by black square in Figure 1 shown by reflected-light microscopy (a) and means of CRM analysis (b-d). Raman map solely visualizing aragonite-derived information (b) and calcite-derived information (c) is used to create stacked information (d) showing entire spectral information with aragonite in blue and calcite in red. Note that (secondary, altered) calcite as well as original aragonite retain detailed growth increments.

## $\delta^{18}\text{O}$ & $\delta^{13}\text{C}$ DRILLING RESULTS

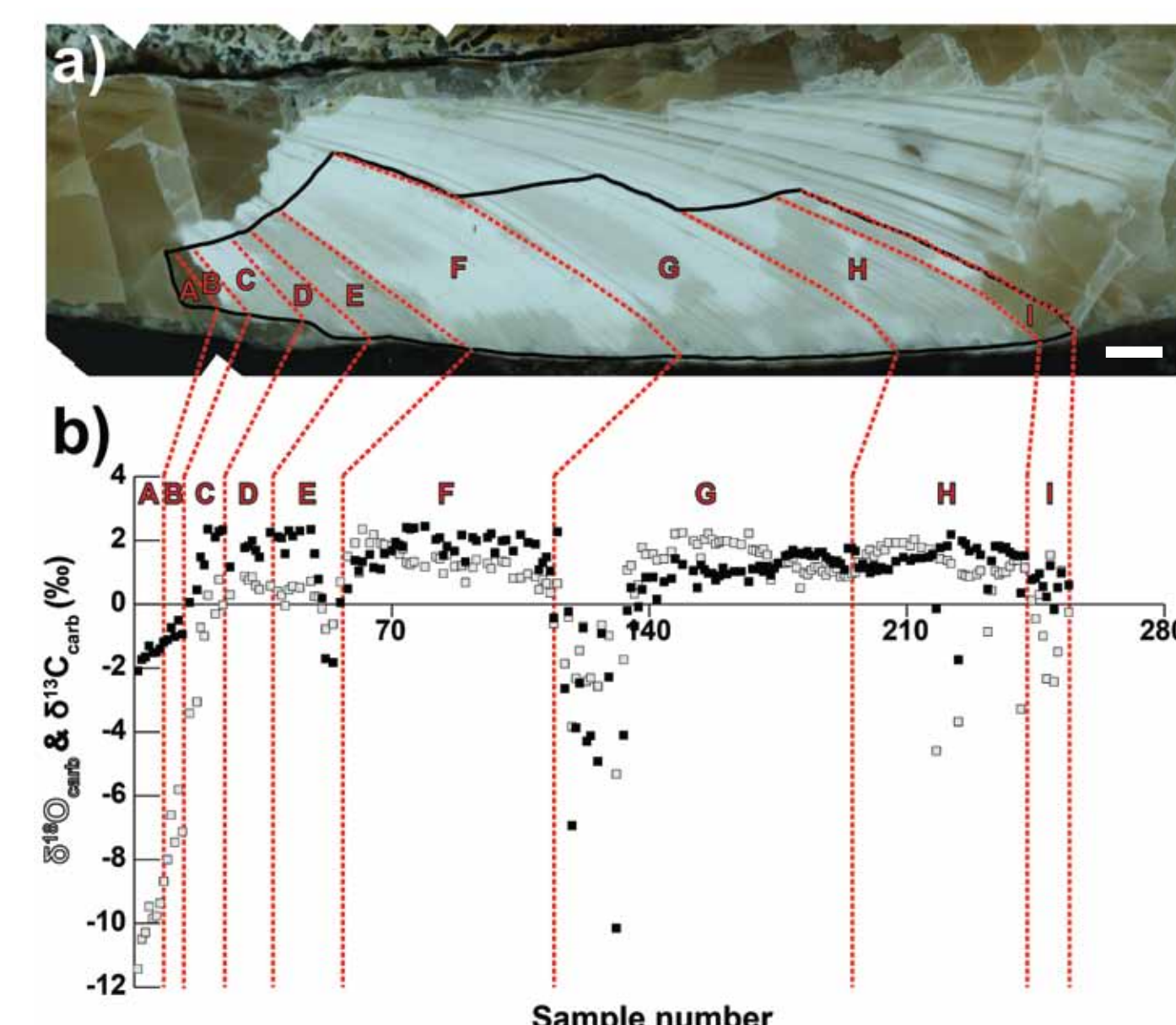
- For  $\delta^{13}\text{C}$ , a maximum value of 2.13‰ and a minimum value of -16.37‰ were measured.
- For  $\delta^{18}\text{O}$ , a maximum value of 1.21‰ and a minimum value of -17.20‰ were measured.
- The **most negative**  $\delta^{18}\text{O}$  values and negative  $\delta^{13}\text{C}$  values are found in the **secondary calcite filling** the internal cavity (Figure 3).



**Figure 3:** Stable isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) measurements at drilling spots indicated in Figure 1. Division into four categories based on naked eye observations and Raman microscopy analysis.

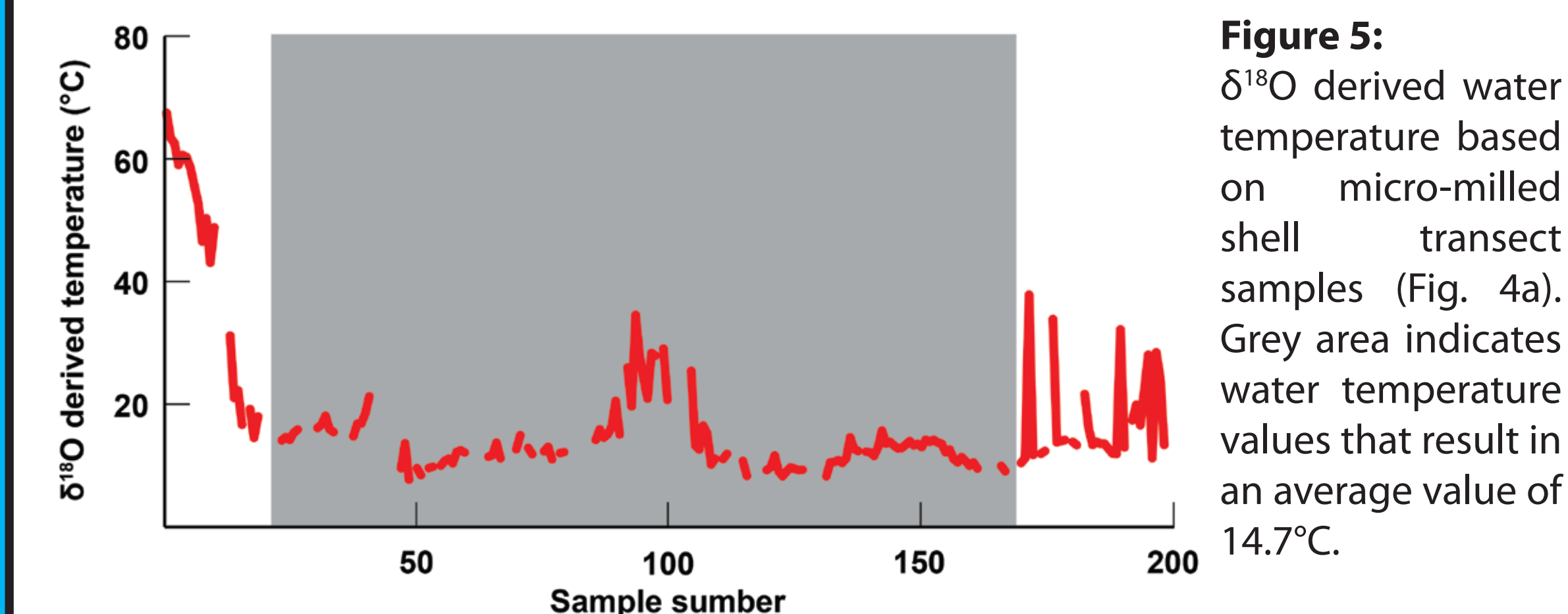
## $\delta^{18}\text{O}$ & $\delta^{13}\text{C}$ MILLING RESULTS

- Subsection A is entirely calcitic, subsections B, C and I are mixed aragonite and calcite, and subsections D to H are entirely aragonitic.
- For  $\delta^{13}\text{C}$ , a maximum value of 2.44‰ and a minimum value of -10.15‰ were measured.
- For  $\delta^{18}\text{O}$ , a maximum value of 2.35‰ and a minimum value of -11.42‰ were measured.



**Figure 4:** Transect for the micro-milling approach (a), which has been subdivided into subsections A to I, based on polymorph composition. Associated  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values for 194 single measurements (b) both showing variability of more than 13%.

## PALEO-TEMPERATURE RECONSTRUCTION



**Figure 5:**  $\delta^{18}\text{O}$  derived water temperature based on micro-milled shell transect samples (Fig. 4a). Grey area indicates water temperature values that result in an average value of 14.7°C.

- We applied a  $\delta^{18}\text{O}_{\text{seawater}}$  value range from **-0.2‰ to -0.5‰** following Buchardt and Simonarson (2003) in order to guarantee **comparability between our results and those previously published**, and to provide an error estimate.
- **Reconstructed water temperatures** for the entire sequence (Figure 5) vary from **68.1°C to 7.1°C**.
- Grey area indicated in Figure 5 includes paleo-temperatures of **up to 40°C** (for winter conditions), which clearly **indicates a diagenetic overprint** but results in an **average water temperature of 14.7°C**.
- **Significance:** In Buchardt and Simonarson (2003) **bulk carbonate samples** taken from fossil *A. islandica* shells (Tjörnes Beds) giving water temperatures of more than 16°C are **not rejected**, but are **interpreted as paleo-environmental signals**.

## CONCLUSIONS

- **Raman microscopy** can identify growth related structures in recrystallized shell calcite (**'ghost structures'**), which indicate a **slow recrystallization process**. These are suggested to be **associated with organic-depleted winter growth lines** that provide pathways through the shell material for diagenetic fluids.
- **Isotope values ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ )** argue for an **open system** recrystallization process with a **circulating reservoir of more negative values**. Meteoric water is the most likely source of strongly negative  $\delta^{18}\text{O}$  values in recrystallized calcite.
- **Pristine aragonite** appears to **preserve the original isotopic composition**, in contrast to recrystallized calcite, which reflects the isotopic composition of the substituting fluid.
- Our findings emphasize the need for **careful interpretation of carbonate-based water temperature reconstructions**, because **small-scale diagenesis** can significantly modify the original stable oxygen isotope signature and substantially distort the paleo-climatic or paleo-environmental signals inferred thereof.

## ACKNOWLEDGEMENTS & REFERENCES

LB is particularly grateful for the support by the Department of Earth Sciences at Syracuse University, the IMCONet Network, the AWI Functional Ecology section, as well as Hugh Ducklow (Lamont-Doherty Earth Observatory, Columbia University), which allowed for a 3-month research exchange in the US and the participation at GSA2015. Further, LB was financed by the "Earth System Science Research School (ESSReS)", an initiative of the Helmholtz Association of German Research Centres (HGF). Lisa Schönborn and Kerstin Beyer are thanked for their help with the isotope measurements. Michael Seebeck is thanked for helping with initial shell preparation. We thank Lovisa Ásbjörnsdóttir (Icelandic Institute of Natural History, Gardabaer, Iceland) for providing the shell material. References: Buchardt and Simonarson 2003, PalPalPal 189, 71-95; Nehrke et al. 2012, GGG 313, Q05014; Schöne 2013, Global Planet Change 111, 199-225.