# Mineralogical, Elemental, Stable and Clumped Isotope composition of modern Bryozoan skeletons


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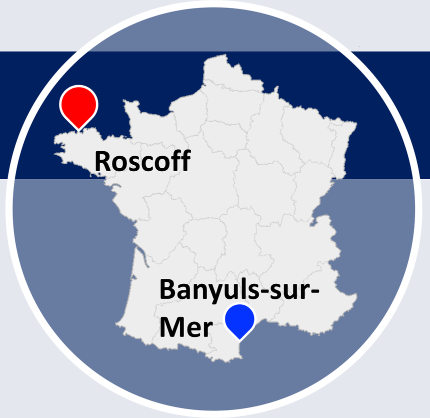
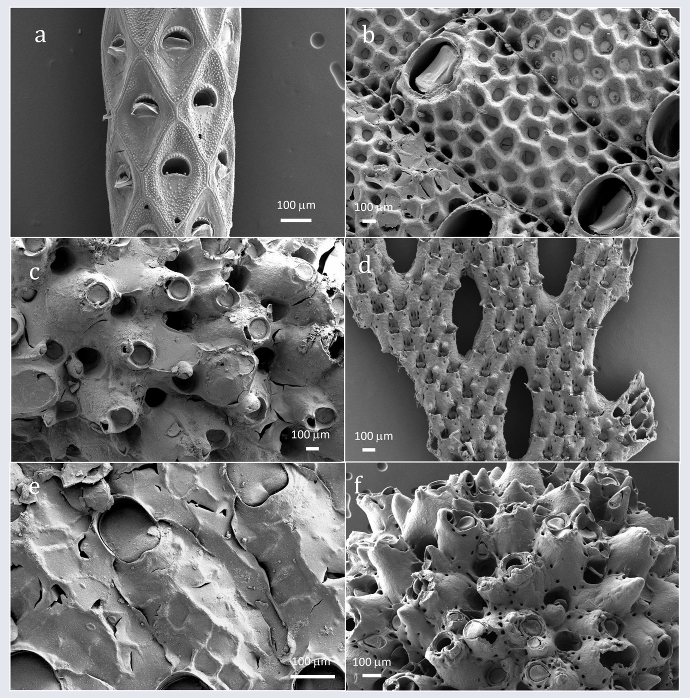
**Bryozoans** are one of the most invasive phyla on Earth. Since their appearance in the Upper Ordovician period, these colonial organisms have developed the ability to form a carbonate skeleton. Despite the fact that these reef builders can represent up to 80% of the carbonate production (Fortunato, 2015), bryozoans have been poorly studied compared to other bio-carbonate archives. The diversity of bryozoan morphology and bi-mineralogy behaviours is an impediment to their identification and their use for paleoenvironmental reconstruction. On the other hand, the assumption that bryozoan skeleton precipitates at oxygen isotopic equilibrium is still under debate. In order to retrieve useful paleoenvironmental information from this extensive record, we investigated the mineralogical and isotopic composition ($\delta^{18}O$ and $\Delta_{47}$) of different species of bryozoan living in the same environment. This approach has been coupled with to precisely map the element incorporation within bryozoan skeleton microstructures.

## Bryozoan samples




**Sample collection:** live bryozoan colonies (Cheilostomes) were collected in September 2019 from two sites where environmental parameters are continuously measured.

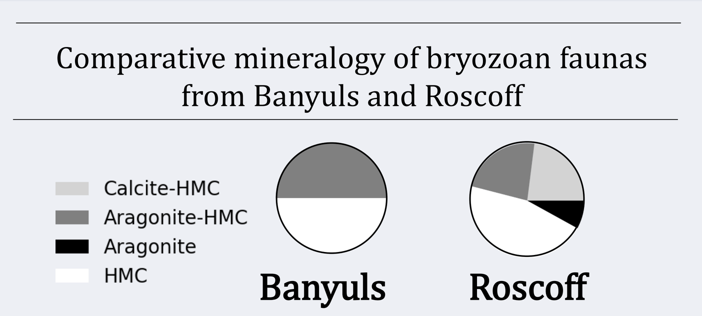
| | T°C | S (‰) | pH | $\delta^{18}O_w$ | $\delta^{13}C_{DIC}$ | Nb species |
|---|---|---|---|---|---|---|
| Roscoff | 13.0 ± 1.7 | 35.2 ± 0.1 | 7.84 ± 0.06 | 0.45 ± 0.02 | -1.8 ± 0.5 | 13 |
| Banyuls | 15.3 ± 2.6 | 38.1 ± 0.3 | 8.04 ± 0.58 | 1.2 ± 0.08 | 0.9 ± 0.5 | 3 |



SEM images of (a) *Cellaria fistulosa*, (b) *Schizoporella errata*, (c) *Tubicellepora avicularis*, (d) *Sertella beniana*, (e) *Pentapora foliacea* and (f) *Cellepora pumicosa*

**Sampling:** The most recent part of bryozoan skeleton was sampled. Last yearsof growth is marked by growth line or new branch bifurcation.

**Cleaning:** Rinse with distilled water (pH>8). Removal of organic matter with 10% $H_2O_2$ neutralize with NaOH during 30 min at 40°C. No significant cleaning treatment-related effect could be observed on the $\Delta_{47}$ values.




**Mineralogy:** XRD analyses were done on each bryozoan colony from the base to the top.

## Methods

**Clumped isotopes measurements:** They were performed using the Isoprime 100 dual-inlet mass spectrometer. Raw $\Delta_{47}$ values were converted to the I-CDES reference frame (Bernasconi et al., 2021) using a pooled regression approach (Daëron, 2021).

**Synchrotron XRF:** High resolution XRF mappings were performed at the Nanoscopium beamline (Synchrotron Soleil) to image at a nanometric scale the elemental repartition on a single bryozoan chamber (Zoecium).

## Bryozoan oxygen isotopic composition variability: Apparent disequilibrium

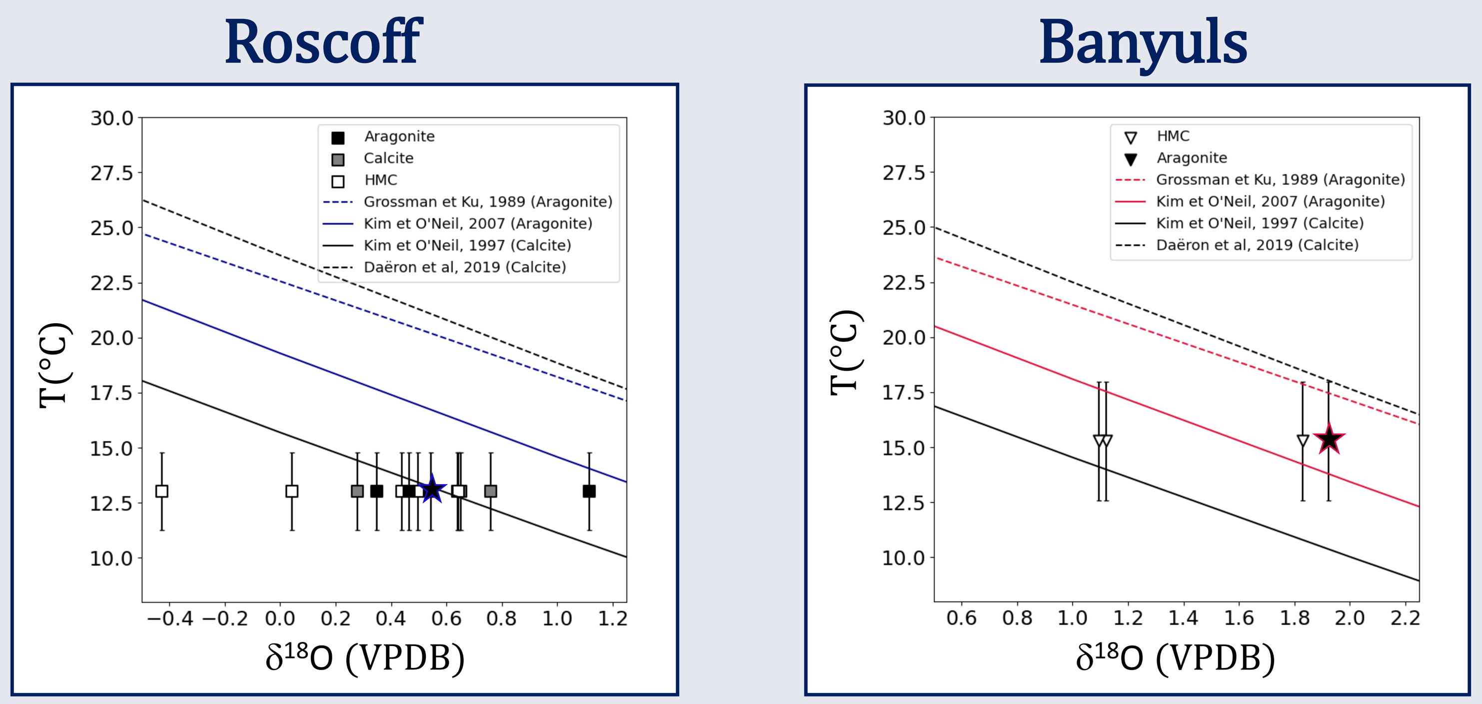



**Fig 1:** Mesured $\delta^{18}O_{bryozoan}$ versus in situ seawater temperature records, as a function of sample mineralogy.

## Bryozoan clumped isotopes derived temperatures

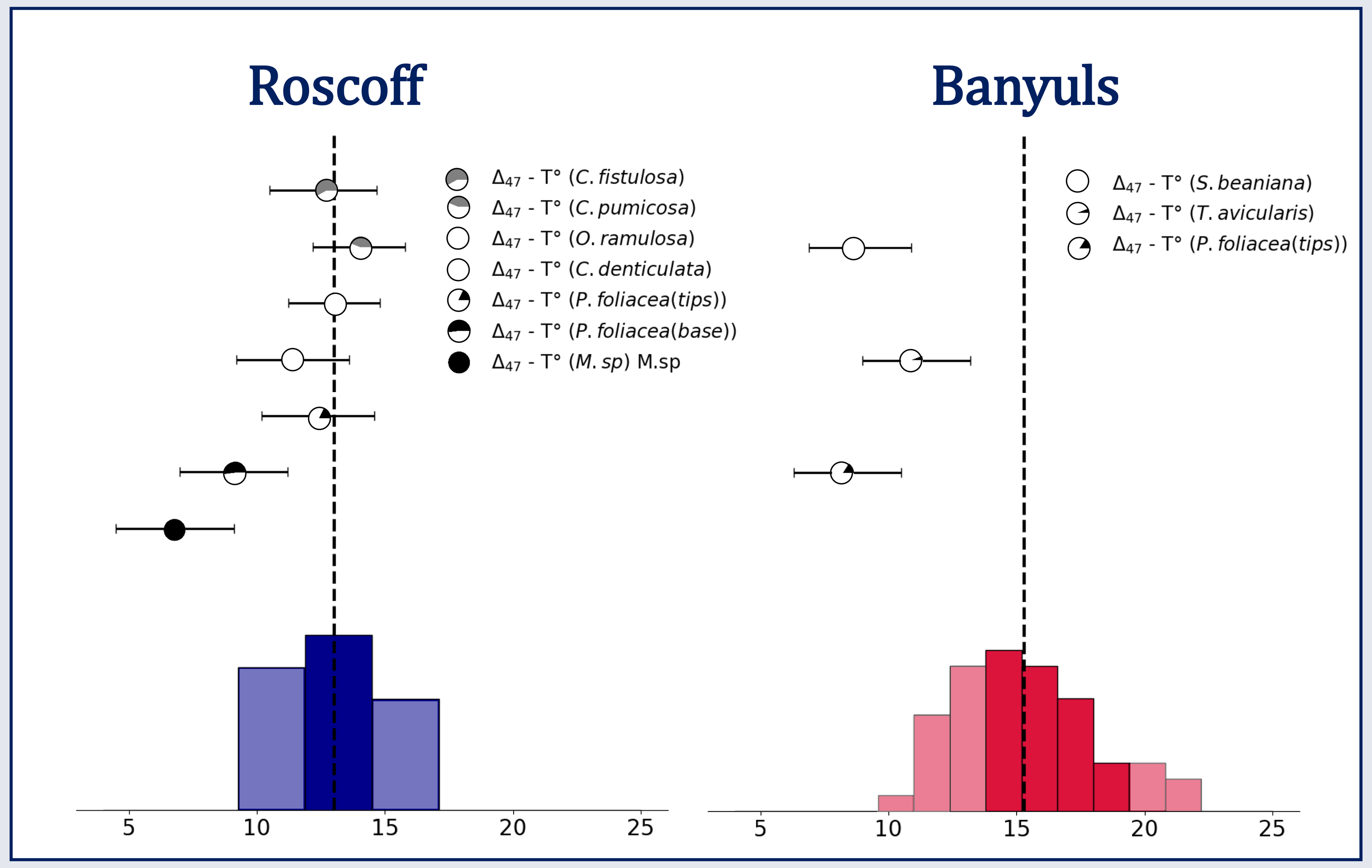
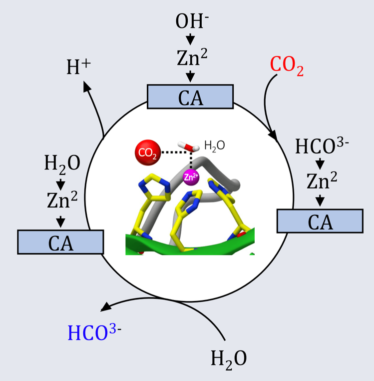



**Fig 2:** Comparison, for eight bryozoan species, of weekly in situ sea water temperature record (histogram) and apparent calcification temperature derived from $\Delta_{47}$ based on (Fiebig et al, 2021) calibration. Dashed line represents the annual average temperature measured in situ. Darkest bars correspond to the temperatures recorded in spring and early autumn (privileged periods of bryozoan growth).

## Potential role of salinity and Br- on CA activity



Modified from Fu et al, 2018

**Carbonic-Anhydrase (αCA)** is a Zn-metalloenzyme present in all metazoan catalysing the reversible reaction of $CO_2$ hydration (Roy et al, 2014). By increasing the rate constants of $CO_2$ (de)hydration reactions, CA activity reduces the magnitudes of the isotopic disequilibrium.

**CA activity,** can be affected by various environmental factors, such as temperature, pH, and particularly salinity increase that drastically decreases CA efficiency (Olsen et al, 2022, Henry et al, 2003). Some organic complex and inorganic anions such as $Br^-$, $F^-$, $SO_4^{2-}$ and $NO_3^-$ are also responsible of CA inhibition (De Simone et al, 2012)

**Synchrotron XRF** map reveals the presence of localized bromine structures within the skeleton of all bryozoan species analysed. In species that precipitated their skeleton close to clumped isotopic equilibrium, a high proportion of Zinc is observed.

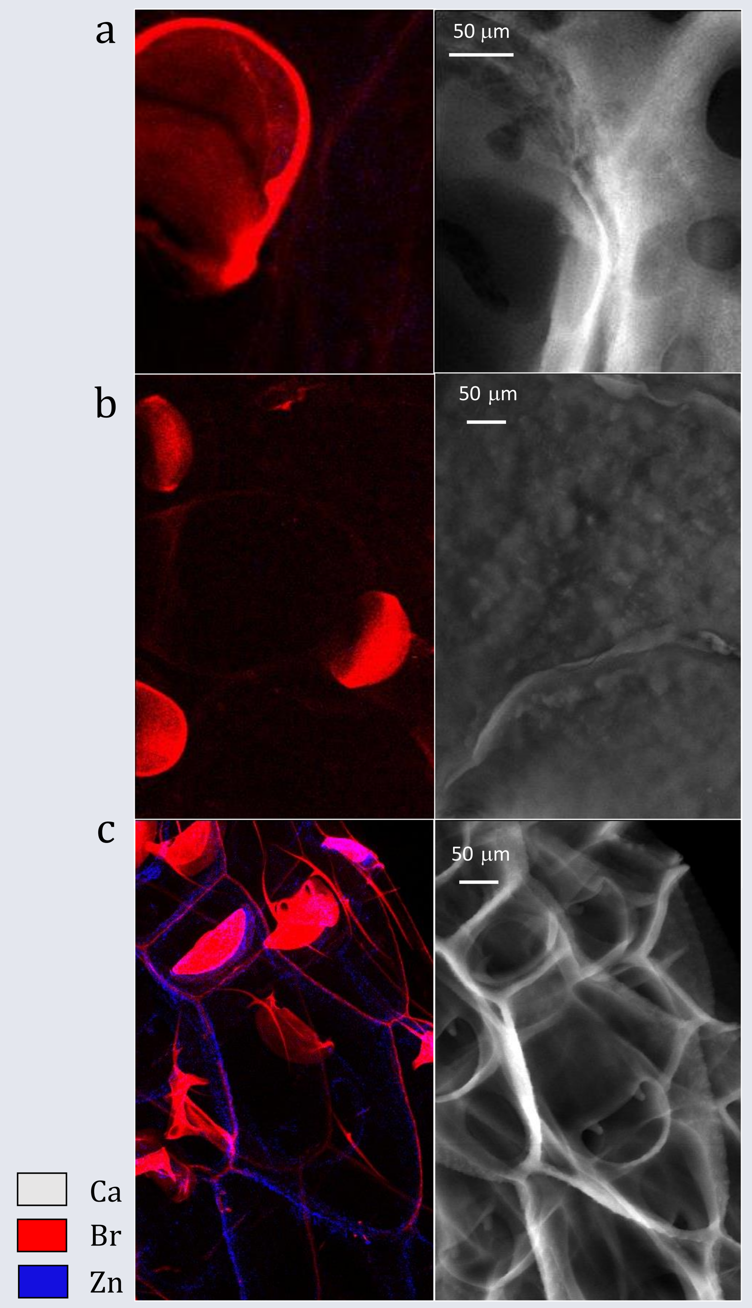



**Fig 3:** Synchrotron XRF map of calcium (right), bromine and zinc (left) distribution in (a) *P. foliacea*-base, (b) *S. beaniana*, (c) *C. fistulosa* carbonate skeleton. From $\Delta_{47}$ results (a) and (b) seems to precipitated their skeleton out of isotopic equilibrium unlike (c).

## Conclusion

- No clear relationship can be observed between bryozoan mineralogy and the magnitude of isotopic disequilibrium. However, we note that a larger isotopic disequilibrium is observed for aragonitic bryozoan.
- $\Delta_{47}$ apparent equilibrium/disequilibrium in bryozoan skeleton appears to be linked with growth environment conditions (i.e Salinity).
- Further research is needed to study the potential impact of salinity and bromine on CA efficiency in bryozoan leading to site-specific apparent isotopic disequilibrium.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