Boron and Strontium Isotopic Composition in the Aragonitic Shell Material of Cultured *Arctica islandica*

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Motivation

1. Ocean acidification has become an important issue because it impacts many calcifying marine organisms and therefore it is essential to expand our knowledge of how the seawater chemistry is impacted by rising atmospheric CO_2 levels.
2. The long-lived ocean quahog *Arctica islandica (A. islandica)* has a wide habitat range around much of the coastal ocean in the northern North Atlantic (Fig. 1), which is an ideal archive for addressing temporal and spatial changes in ocean chemistry during recent centuries.
3. Relatively less attention has been devoted to other "non-traditional" isotope systems within this proxy archive.

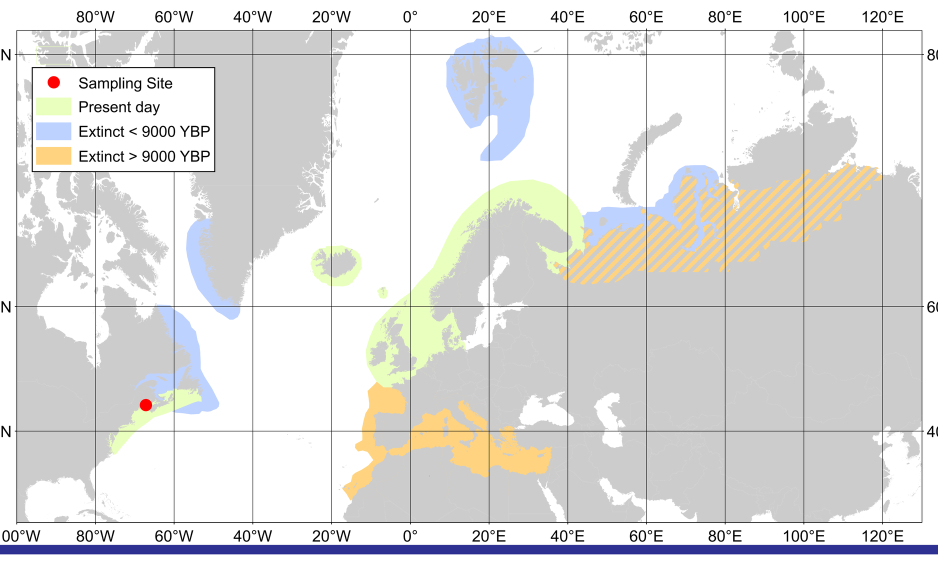
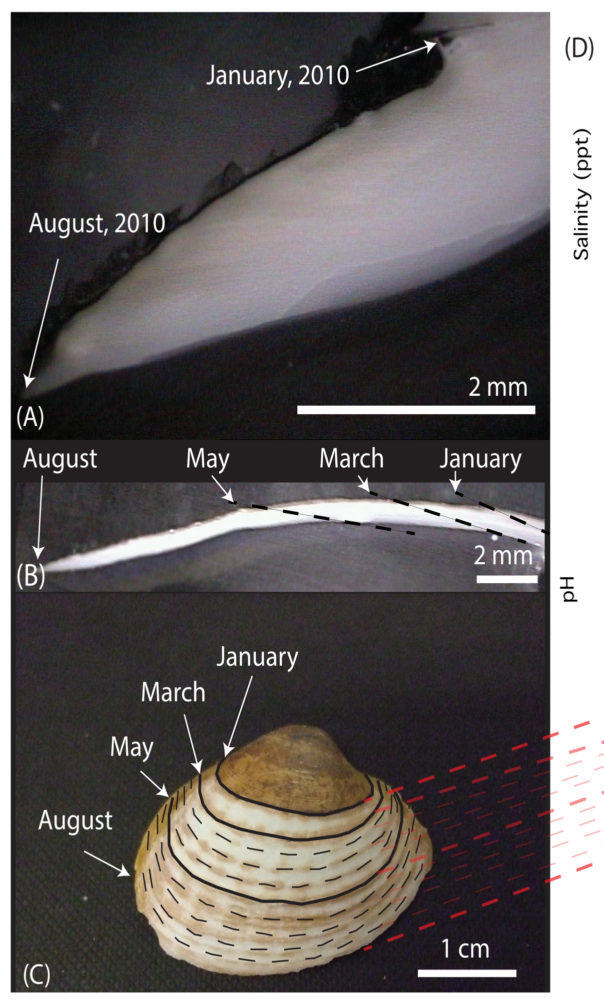


Fig. 1 The distribution map of living and fossil *A. islandica* shell and the location of sampling site for the culture experiment (Modified from Dahlgren et al. (2000)).

Samples and Methods

High-resolution boron and strontium records from an 8-month culture experiment under ambient conditions from the Gulf of Maine are compared with in-situ measurements of temperature, salinity, and pH to examine the relationships between the isotope systems and the environmental conditiions (Fig. 2).

An high-throughput microsublimation method with total evaporation method conducted on nagtive TIMS was applied in the study (Liu et al., 2013). The residual from the microsublimation was used for strontium isotope analysis. An 84-87 Sr double spike was applied to obtain the stable Sr isotopic composition and concentration of the shells.



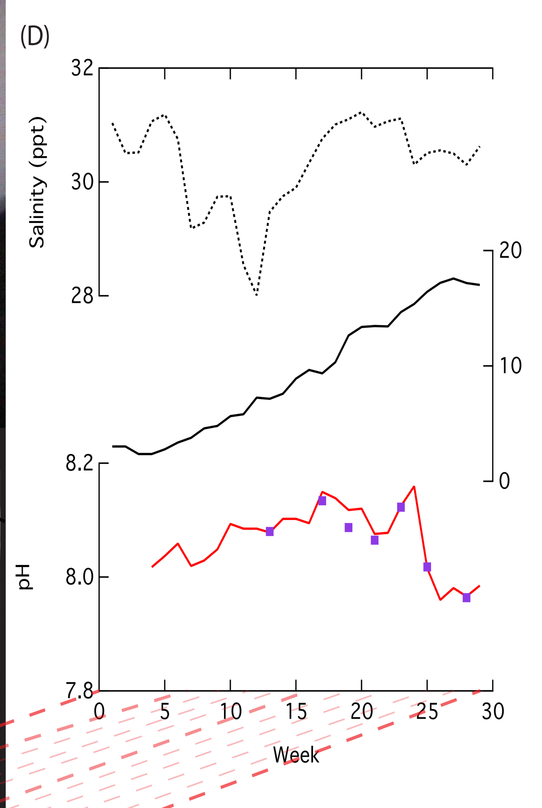


Fig. 2 Photos of (A) adult and (B) (C) juvenile *A. islandica* from the culture experiment. (D) shows the is-situ measurements of tankwater salinity, temperature and pH during the 31 weeks of culturing. In order to obtain high-resolution records and compare to the instrumental data, juvenile shells were used in this study, and were sampled in 10 intervals. Note that because of different growth rates during the season, each interval reperesents different time durations (C).

Results and Discussion

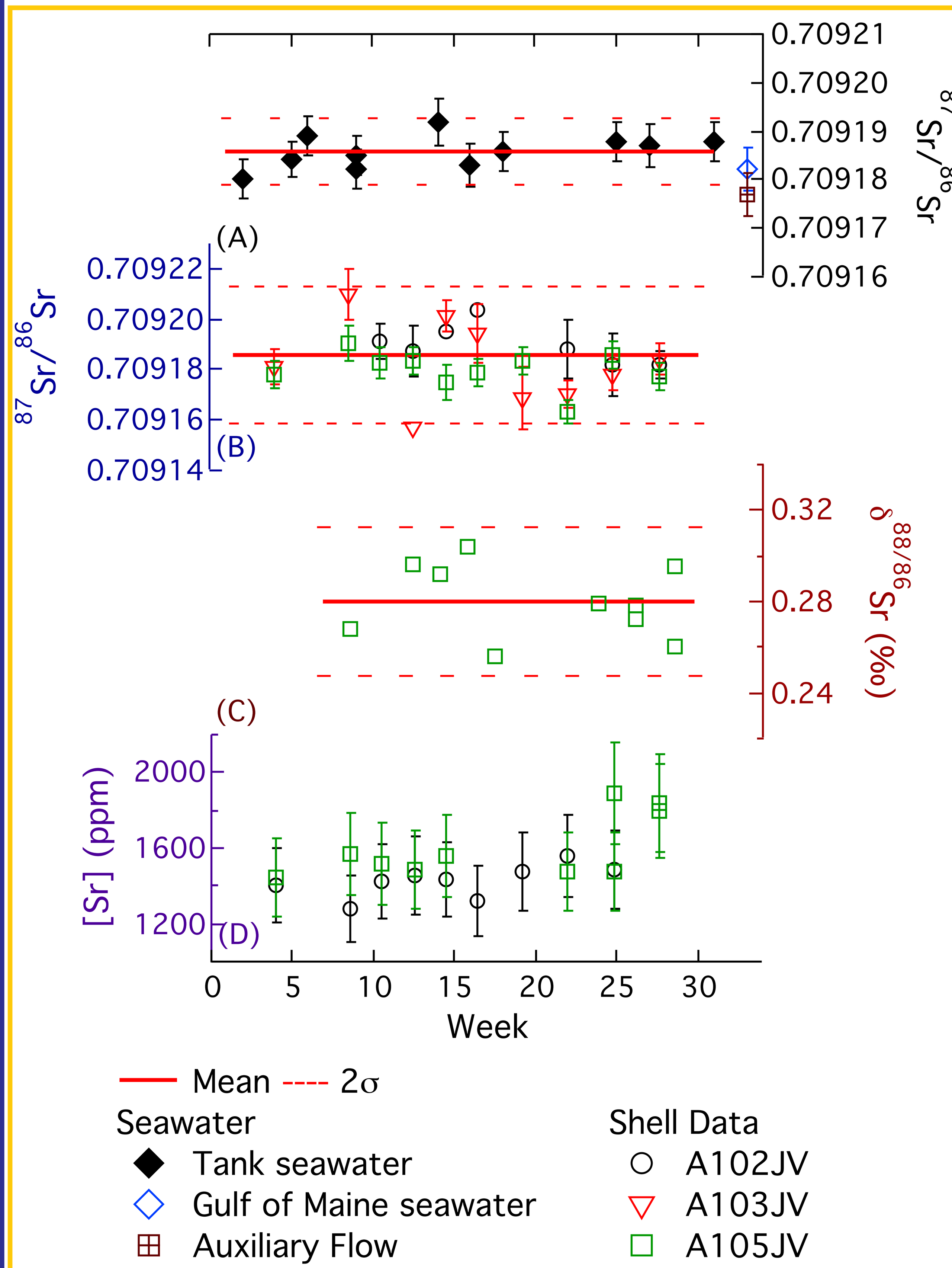


Fig. 3 Radiogenic Sr isotope data from (A) seawater and (B) 4 individual *A. islandica* juvenile shells. (C) and (D) show the stable Sr ($\delta^{88/86}Sr$) results and the range of shell Sr concentration that deconvolved with ^{84}Sr-^{87}Sr double spike technique. The longterm reproducibility Error bars in figure (A) and (B) show the 2 SE of the measurements and the error bars for [Sr] were estimated from the error of weighing spike materials.

1. The $^{87}Sr/^{86}Sr$ ratios from both tank water and shell samples (Fig. 3 (A) and (B)) show ratios nearly identical to the open ocean, which suggests that the shell material reflects ambient ocean chemistry without interferences from terrestial sources.
2. It has been suggested that stable Sr isotopic ratios ($\delta^{88/86}Sr$, $\delta^{88/86}Sr = \left[\frac{(^{88}Sr/^{86}Sr)_{sample}}{(^{88}Sr/^{86}Sr)_{SRM\ 987}} - 1\right] \times 1000$ (‰)) in biogenic carbonates are influenced by the temperature of the precipitating fluid, however, our $\delta^{88/86}Sr$ data show identical values throughout the experiment despite a temperature change of >15 °C.
3. No distinguishable [Sr] trend in the culture experiment.
4. Identical $\delta^{11}B$ results form the tank water, in which $\delta^{11}B = \left[\frac{(^{11}B/^{10}B)_{sample}}{(^{11}B/^{10}B)_{SRM\ 951a}} - 1\right] \times 1000$ (‰).
5. The $\delta^{11}B$ records from the experiment show at least a 5‰ of increase through the culture season (January – August, 2010), with low values for weeks 5-15 and higher values after week 19 (Fig. 4 (B)) in all shell records, which are opposite to the pH trend we expected (Fig. 2 (D)).
6. When a certain temperature threshold (>13 °C) has been reached, the fast shell growth may cause boron limitation in the calcifing fluid and cause the rise in $\delta^{11}B$ values instead of preferential uptake of ^{11}B enriched $B(OH)_4^-$. The regulation of pH in the extrapallial fluid may also cause the rise in $\delta^{11}B$ in the shell. However, the offset between ΔpH (pH_{shell}-pH_{sw}) to pH cannot fully explain the high $\delta^{11}B$ ratios.

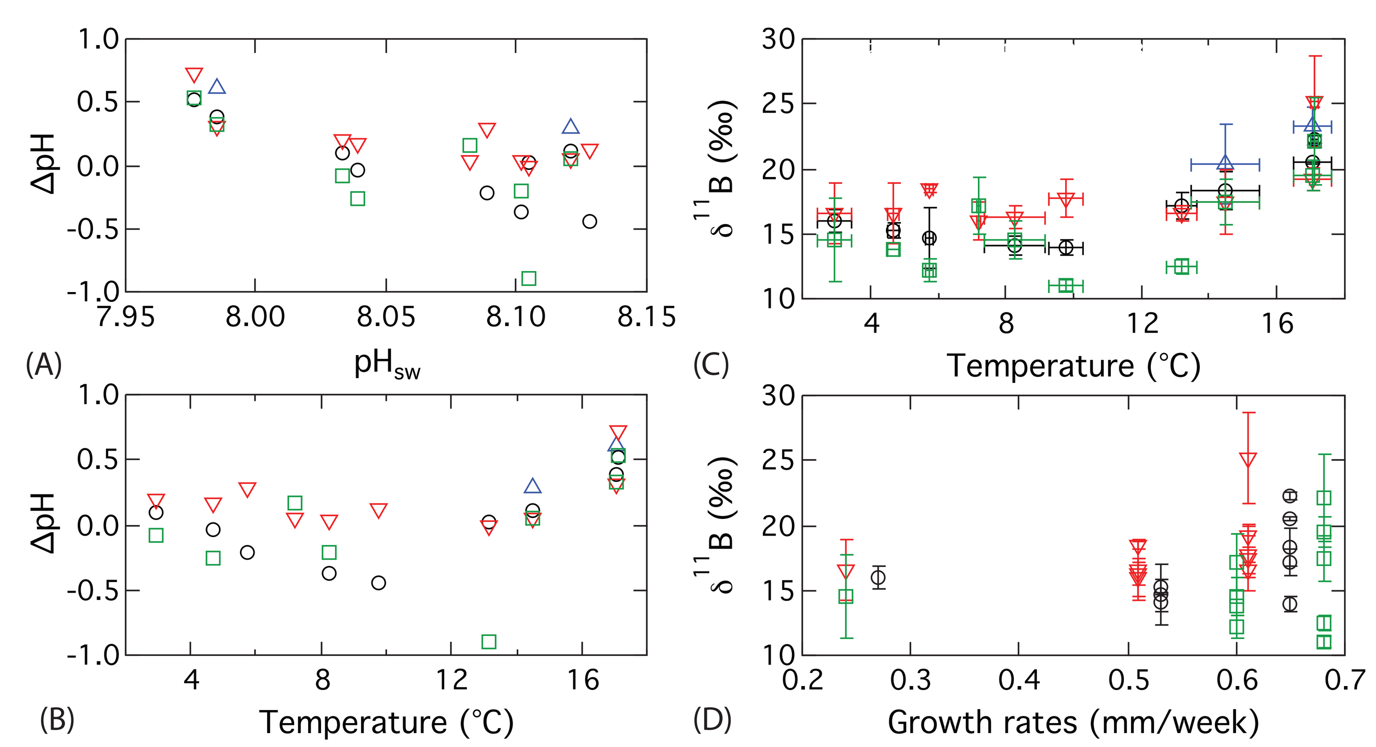


Fig. 5 The comparisons of (A) the differences between shell infered pH and seawater pH (ΔpH) and seawater pH (pH_{sw}) (B) ΔpH and temperature, (C) shell $\delta^{11}B$ and temperature and (D) shell $\delta^{11}B$ and growth rates . There is weak negative correlation between ΔpH and pH_{sw} but stronger correlation between ΔpH and temperature after temperature over about 13 °C. Althouth the growth rates increase throughout the season, no clear relationship can be found between $\delta^{11}B$ the growth rates. This suggests the effect from the temperature to the boron uptake might be stronger than the increasing shell growth throughout the season.

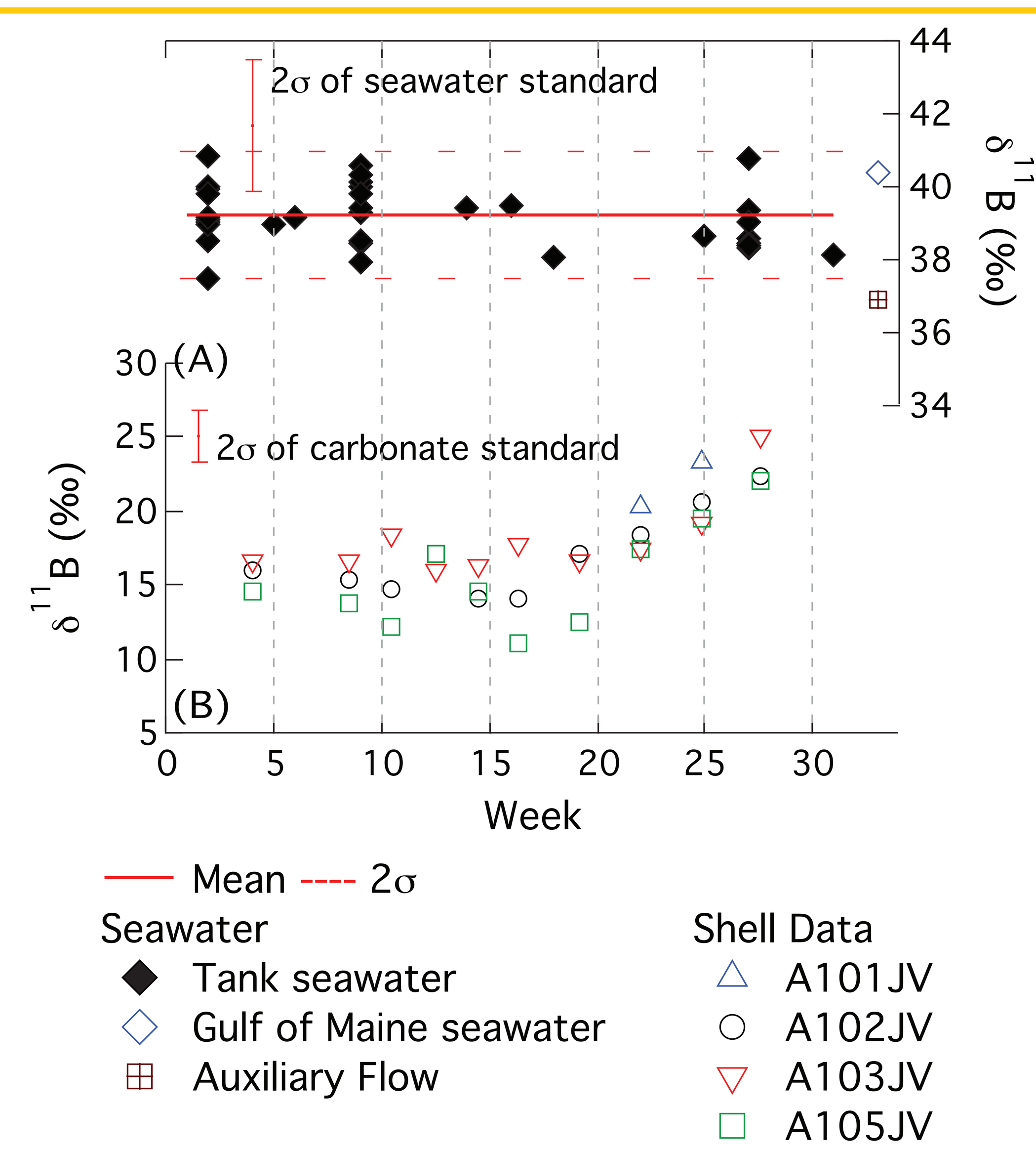


Fig. 4 The $\delta^{11}B$ results from (A) seawater and (B) 4 individual *A. islandica* juvenile shells. The longterm reproducibility of boron isotopic standard SRM 951a is 4.0332±0.0064 (2σ, n=97) before treated 30% H_2O_2, and is 4.0302±0.0084 (2σ, n=13) after the extra treatment. The precisions of $\delta^{11}B$ for seawater and biogenic carbonate standards without addition of peroxide are 40.46±1.29 (2σ, n=54) and 24.94±2.35 (2σ, n=39) for IAEA B-1 and JCp-1, respectivley; 41.70±1.13 (2 σ, n=8) and 24.93±1.83 (2 σ, n=18) for IAEA B-1 and JCp-1 with H_2O_2 treatment.

Conclusion

The larger $\delta^{11}B$ ranges from the shells than from the prediction based on the instruental measurements and a rising trend after temperature over 13 °C suggests that the shell $\delta^{11}B$ might not directly reflect the seawater pH in habitats with large temperature fluctuations. A better constraint of environmetnal factors is required for constructing a species-specific fractionation factor.

A pH control culture experiment has been conducted from February 2014 to August 2014, with nearly constant seawater temperature and salinity. This study may provide further information for the usage of $\delta^{11}B$ in *A. islandica* shell as a seawater pH proxy.

References and Acknowledgements

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