Author's Response to Research Article "Environmental Controls on the Boron and Strontium Isotopic Composition of Aragonite Shell Material of Cultured *Arctica islandica*" in Biogeosciences Discussion

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Dear Dr. Gillikin:

Here we attach our responses to comments by reviewers and address the changes done to the revised version of the manuscript.

Response to the referees

Anonymous Referee #1

This article presents B and Sr isotope data in *Antarctica islandica* to decipher any environmental parameter effects on these proxies. I found the data very interesting, but I think that the discussion should be push forward. I am not sure if the Sr isotopes should be mentioned in the title as nothing was done with these data due to the homogeneity of the samples (or data within errors).

We thank the anonymous referee for providing the helpful and thoughtful comments.

For the Sr isotopes data, we think it is also close related to the work to investigate the

environmental controls to boron incorporation in *A. islandica* shell. Especially in coastal region, fresh water input can potentially change the water isotopic composition in seawater. We do need constraints to the seawater isotopic composition. Although $^{87}Sr/^{86}Sr$ has been widely used to determine the water sources, it hasn't been evaluate if the proxy would work in *A. islandica*. As boron and strontium both have relative long residence time in seawater, we think the nearly equilibrium radiogenic Sr composition can indicate if there is any water source change in an area. Therefore we can better interpret boron isotopic data as an environmental proxy. This can help us future applications of boron isotopic composition in *A. islandica* in a region without knowing if there is any changes in water source when no water sample is available. In additional to radiogenic Sr isotopic ratios, it has also been suggested that $\delta^{88/86}Sr$ may reflect growth effect in biogenic carbonate. There is no $\delta^{88/86}Sr$ data reported in shell yet so that we also want to test if $\delta^{88/86}Sr$ in A. islandica would show growth related fractionation, which might help to differentiate the influences from vital effect or other environmental factors. We think it is important to understand how those useful isotopic compositions recorded in the shell for future applications with this geological archive and we would like to incorporate the Sr data along with our boron samples.

Abstract: I don't consider that $R^2 = 0.34$ is "relatively strong". I would only note that there is a correlation.

We remove the words "relatively strong" with significant in the text. In many biogeochemical studies, a correlation with R = 0.5 – 0.8 was interpreted as strong correlation as in nature, biological responses are seldom being perfectly correlated (e.g. R = 1). We also note the low p value that reinforces the significance of the correlation. Here we also re-examined our $\delta^{11}B$ to pH conversion and recalculated our results using the $\delta^{11}B_{sw}$ of our seawater results instead of the $\delta^{11}B_{sw}$ from Foster et al. (2010). No significant changes are made to the pH values, but the correlation $R^2 = 0.34$ is updated to $R^2 = 0.35$. The results are updated in Table 1 and Table 3.

P2932: There is no more ancient reference for the proportions of boron isotopes?

Here we used the updated values from the latest IUPAC Technical Report for the most

precise statement. The numbers we originally listed are the best measurement assessed by CIAAW. We also made a correction to the abundances with the representative values suggested in the report (19.9(7) and 80.1(7)).

P2983, L8: 'It is assumed that marine carbonates...'. It is an assumption that is highly debated and, to my knowledge, there is no definite proof of this.

We added, "It is assumed that…" in to the sentence as suggested. We also addressed the need to do species-specific calibration before applying the δ^{11}B-pH proxy in a new species of marine carbonate later in the same paragraph.

P2983, L10: As it is a acid-base reaction, it is normal that pH of the solution dictates the amount of each species. There is no need of reference, here.

We deleted the reference as suggested.

P2983, L22: please add 'e.g.' before the references listed here. Many other studies used this fractionation factor. You should also remove in the list Kakihana et al (1977) as it was already stated before (L21).

We revised as suggested.

P2983, L25: that is strange, here, to have a reference prior to the study of Klochko. Again you could here remove the reference to Klochko et al (2006). You could add here the reference to Rollion-Bard and Erez (2010) as they compared the signification of the two fractionation factors.

We revised as suggested.

P2993, L17: Why the seawater d11B values are higher than the one determined by Foster et al (2010)? Could you please here add the literature values for the different standards?

We do not really know the reason to have slightly higher boron isotopic composition in IAEA B-1 seawater standard. To be cautious in the study, we therefore also measured the water samples in the culture medium and in the offshore water, which suggests the tank water isotopic composition is consistent to open ocean. In Figure 4 we listed boron references measured only by NTIMS method for different inter-laboratory boron isotopic

standards and our isotopic data is within error to the references, although we have slightly larger error so far due to small boron sample size. We will keep tracking our standards to evaluate our boron measurements.

P2998, L10: You could also add the reference to Purton et al (1999) who studied the influence of metabolism on Sr/Ca ratios.

We added the reference from Purton et al. (1999) as suggested.

P2998, section4.3: were the prediction lines calculated using the T and S variations (for the pKB values)? It is not clear for me. The line with alpha of Kakihana et al (1977) must be removed as it was shown that this factor doesn't reflect the theoretical fractionation between boron species. However, you could add the line with the fractionation factor determined by Nir et al (2015). It would be very useful to add the pKB values used to draw the line in Table 1. Idem line 26, this alpha is not used anymore.

We calculated the prediction lines based on our instrumental temperature, salinity and pH data, which was defined on P2995, L17-19. We also removed the higher prediction line base on the alpha derived from Kakihana et al (1977) and listed reference line determined based on Nir et al. (2015) (P2995 line 26 and Fig 6 (b)). We also added the equation we used to determine the pKb values for drawing the prediction lines.

P2999, L3: You should inverse corals and foraminifera (it would be better relied to the studies cited here).

We revised as suggested.

P2999, L17: Please precise here the measured pH

We modified as suggested.

P2999, L17: I suppose that 'be' is missing in the sentence 'She concluded....' Why some d11B values are below the predicted line? How it could be explained? You calculated some DpH down to -1.013. It is surprising for a organism precipitating carbonates. Moreover, it seems to not be in agreement with the measured pH. This section really needs more discussion. Why the DpH vs pHsw figure is not in the paper? It really needs to be added. I don't really understand why the pH increase measured by Stemmer

(2013) is not recorded in the d11B values. Is there any fractionation during the boron incorporation that could be envisioned?

1) We updated the DpH-pHsw figure in the revision.
2) The negative DpH values can be attributed to a species-specific offsets from the theoretical fractionation line. We addressed the detail in the revised text: Previous studies suggested a range of fractionation factors might be applied, and an additional constant offset might better describe the empirical $\delta^{11}B$-pH relationship (Anagnostou et al., 2012; Hönisch et al., 2004; Rae et al., 2011). Therefore a species-specific offset many accounts for the smaller variations before week 19, where many of the results lie under the prediction lines and the negative ΔpH here. In this study, because the temperature and salinity are not close to constant, we can hardly determine precise transfer function for *A. islandica*. However, the total variation throughout the experiment is about 10 ‰, and has an obvious trend after week 19, there must be some other controls to boron incorporation in the shell.

Table 3: Please add the errors on the calculated pH(shell) and the DpH. I think that 1 significant figure is sufficient.

We added in the table.

Referee #2: R. Gabitov

The manuscript submitted to Biogeosciences entitled: “Environmental controls on the boron and strontium isotopic composition of aragonite shell material of cultured Arctica islandica” by Liu et al. is focused on evaluating of geochemical response of bivalve aragonitic shells on change in marine environmental conditions, and therefore, this work is within the scope of Biogeosciences journal. Abstract and title reflect the content of the paper. I think the paper is generally well written. Please see my comments and concerns below.

We thank R.I. Gabitov for his helpful and constructive comments to improve the manuscript. All the comments from the referee have been addressed. Our response to specific comments is listed below each comment from the referee.

Page 2980, Line 19: Please define pH(shell)

We added the definition of pH_{shell} in the abstract.

Page 2981, Lines 16-19: I suggest splitting this sentence into two.

We revised as suggested.

Page 2982, Line 4: Additional explanation why Sr isotopes were chosen to evaluate growth rate effect will be helpful. Sr is heavy and relative mass difference between 86 and 88 is small. Why effect of growth rate is expected?

Temperature range in the experiment is over 15 °C and the growth rate at least double during the experiment, in which may result in over 1.5 ‰ change in $\delta^{88/86}Sr$ (Stevenson et al., 2014). Because we would like to use radiogenic Sr to determine the seawater source, we incorporate the stable Sr isotopic ratios, which can be analyzed at the same run of sample, to assess the potential kinetic effect. We added explanation to the expectation of the potential $\delta^{88/86}Sr$ changes with respect to the temperature or growth change during the experiments in our discussion.

Page 2983, Line 6: Please explain what "equilibrium pH" means or rewrite the sentence. For example: " Equilibrium 11B fractionation factor between B(OH)3 and B(OH)4- does not depend on pH (REF) "

We deleted “equilibrium” in the text. Here we simply want to express the off set is constant at a certain pH condition.

Page 2983, Lines 8-9: There are a number of works suggesting strong effect of B(OH)3 especially for calcite. Please mention it here.

We added in the text.

Page 2984, Line 7: Are there references about those few measurements? Please specify.

We revised the sentence and added references from Heinemann et al. (2012) and Penman et al. (2012).

Page 2989, Line 2: Please specify the relative masses of sample and H2O2 solution.

Was the sample ultrasonicated, centrifuged, or kept stagnant?

To further improve the reproducibility for carbonate samples, an extra 2 µL of 30 % H_2O_2 was added to the purified solution (~ 90 % of the volume before sublimation) for all the runs after 23 April 2014. Sample solution was then set stagnant in the vial, and the cap of the conic vial was then loosened for two hours to reduce the organic levels and liberate the product oxygen gas.

Page 2990, Lines 15-16: Please expand this sentence. In the present form it is confusing for people who do not use TIMS routinely.

We expanded the sentence to better show the settings.

Page 2996, Lines 1-2: Based on Figure 6b significant number of shell d11B data lie below the curve where alpha=1.0272. I think it should be addressed here.

We mention the lower boron in the result section as suggested and address more in the discussion section to explain the data.

Page 2996, Lines 25-26: I think the term equilibrium is vague here because variation between individual samples was observed. The previous sentence already addressed the observations on Sr isotopic consistency between shell and seawater. I suggest to remove the sentence “Therefore, incorporation of radiogenic Sr ratios into the shells are in equilibrium with ambient seawater.” or say that fractionation of radiogenic Sr isotopes is close to equilibrium.

We re-worded the sentence as suggested.

Page 2997, Line 18: Do you mean d88/86Sr? If yes then please continue to use delta notation further in the text.

We replaced “stable Sr” with “$\delta^{88/86}Sr$” in the text

Page 2997, Line 20: Please identify the studied temperature and growth rate ranges.

We added the temperature and growth range and the expected change in stable Sr isotopic composition in the text (P2997 line 18).

Page 2997, Line 26: The suggested physiological control is questioning an achievement

of thermodynamic equilibrium stated in the sentence at the end of the page 2996 (Lines 25-26).

We revised as “Therefore, incorporation of radiogenic Sr ratios into the shells occurs without measurable fractionation and reflects the composition of ambient seawater” in the text on page 2996 line 25 to differentiate the physiological control to Sr/Ca uptake from isotope incorporation here.

Page 2998, Line 3: You may add Gaetani and Cohen (2006) here.

Reference added as suggested.

Page 2998, Line 22: Fig.6b shows that some data deviate from the range between prediction lines. Based on Figure 6b significant number of shell d11B data lie below the curve where alpha=1.0272. Please address it in the text.

Previous studies suggested a range of fractionation factors might be applied, and an additional constant offset might better describe the empirical δ^{11}B-pH relationship (Anagnostou et al., 2012; Hönisch et al., 2004; Rae et al., 2011). Therefore a species-specific offset many accounts for the smaller variations before week 19, where many of the results lie under the prediction lines and the negative ΔpH here. In this study, because the temperature and salinity are not close to constant, we can hardly determine precise transfer function for *A. islandica*. However, the total variation throughout the experiment is about 10 ‰, and has an obvious trend after week 19, there must be some other controls to boron incorporation in the shell. We addressed the interpretation above in our text to explanation the boron data lie below the curve and try to differentiate the potential cause to positive deviation trend later in the season.

Page 3000, Line 3: It is possible to relate spring bloom to the data on Figure 7b? Otherwise this sentence could confuse the reader.

The rapid growth rate change is related to spring bloom. Our data shows no correlation between boron isotopic compositions in the shell and the shell growth so we do not think growth or spring bloom is the primary control to the boron deviation in the culture

experiment. We also reword the sentence to clarify our interpretation.

Page 3014, Table 1: Please define the alpha below in the table.

We added as suggested.

Page 3016, Table 3: Please add below: deltapH=(pHshell - pHsw).

We added as suggested.

Page 3016, Fig 1: I like illustration of c and d. However, more details are needed for description of Figures a-c. It will help reader to identify differences between those images. Figure captions do not address why figures a and b are shown here. I was not able to find it in the text too.

Fig 1 (a) to (c) show that one can see nature marking on the external shell, or calcein mark in the cross-section under microscope to constrain the shell growth.

Page 3022, Fig 6: Please define fractionation factors presented here , i.e. alpha =

1.0272 (Klochko et al., 2006) and alpha = 1.0194 (Kakihana et al., 1977). Specify between what phases or species fractionation occur.

We modified as suggested and also added the definition of fractionation factor alpha is the text.

Page 3023, Fig 7b: Please identify the colors of the symbols in (b)

Colors shown in (b) represent the temperature corresponded to each data point, with low temperature in blue to high temperature in red.

Anagnostou, E., Huang, K. F., You, C. F., Sikes, E. L., and Sherrel, R. M., 2012, Evaluation of boron isotope ratio as a pH proxy in the deep sea coral Desmophyllum dianthus: Evidence of physiological pH adjustment: Earth and Planetary Science Letters, v. 349, p. 251-260.

Foster, G. L., Pogge von Strandmann, P. A. E., and Rae, J. W. B., 2010, Boron and magnesium isotopic composition of seawater: Geochemistry, Geophysics, Geosystems, v. **11**, no. **8**, p. Q08015.

Heinemann, A., Fietzke, J., Melzner, F., Böhm, F., Thomsen, J., Garbe-Schönberg, D., and Eisenhauer, A., 2012, Conditions of *Mytilus edulis* extracellular body fluids and shell

composition in a pH-treatment experiment: Acid-base status, trace elements and $\delta^{11}B$: Geochemistry, Geophysics, Geosystems, v. 13, no. 1.
Hönisch, B., Hemming, N. G., Grottoli, A. G., Amat, A., Hanson, G. N., and Bijma, J., 2004, Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects: Geochimica et Cosmochimica Acta, v. 68, no. 18, p. 3675-3685.
Nir, O., Vengosh, A., Harkness, J. S., Dwyer, G. S., and Lahav, O., 2015, Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH: Earth and Planetary Science Letters, v. 414, no. 0, p. 1-5.
Penman, D. E., Hönisch, B., Rasbury, E. T., Hemming, N. G., and Spero, H. J., 2012, Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-shell variability, controls, and potential as a paleo-pH recorder: Chemical Geology.
Purton, L. M. A., Shields, G. A., Brasier, M. D., and Grime, G. W., 1999, Metabolism controls Sr/Ca ratios in fossil aragonitic mollusks: Geology, v. 27, no. 12, p. 1083-1086.
Rae, J. W. B., Foster, G. L., Schmidt, D. N., and Elliott, T., 2011, Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system: Earth and Planetary Science Letters, v. 302, no. 3-4, p. 403-413.
Stevenson, E. I., Hermoso, M., Rickaby, R. E. M., Tyler, J. J., Minoletti, F., Parkinson, I. J., Mokadem, F., and Burton, K. W., 2014, Controls on stable strontium isotope fractionation in coccolithophores with implications for the marine Sr cycle: Geochimica et Cosmochimica Acta, v. 128, no. 0, p. 225-235.

Environmental Controls on the Boron and Strontium Isotopic Composition of Aragonite Shell Material of Cultured *Arctica islandica*

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Abstract

Ocean acidification, the decrease in ocean pH associated with increasing atmospheric CO_2, is likely to impact marine organisms, particularly those that produce carbonate skeletons or shells. Therefore it is important to investigate how environmental factors (seawater pH, temperature and salinity) influence the chemical compositions in biogenic carbonates. In this study we report the first high-resolution strontium ($^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$) and boron ($\delta^{11}B$) isotopic values in the aragonite shell of cultured *Arctica islandca* (*A. islandica*). The $^{87}Sr/^{86}Sr$ ratios from both tank water and shell samples show ratios nearly identical to the open ocean, which suggests that the shell material reflects ambient ocean chemistry without terrestrial influence. The ^{84}Sr-^{87}Sr double spike resolved shell $\delta^{88/86}Sr$ and Sr concentration data show no resolvable change throughout the culture period and reflect no theoretical kinetic mass fractionation throughout the experiment despite a temperature change of more than 15 °C. The $\delta^{11}B$ records from the experiment show at least a 5 ‰ increase through the 29-week the culture season (January, 2010 – August, 2010), with low values from the beginning to week 19 and higher values hereafter. The larger range in $\delta^{11}B$ in this experiment compared to predictions based on other carbonate organisms (2 to 3 ‰) suggests that a species-specific fractionation factor may be required. A significant correlation between the ΔpH (pH_{shell}-pH_{sw}) and seawater pH (pH_{sw}) was observed (R^2 = 0.35), where the pH_{shell} is the calcification pH of

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the shell calculated from boron isotopic composition. This negative correlation suggests that *A. islandica* partly regulates the pH of the extrapallial fluid. However, this proposed mechanism only explains approximately 35 % of the variance in the $\delta^{11}B$ data. Instead, a rapid rise in $\delta^{11}B$ after week 19 suggests that the boron uptake of the shell changes when a temperature threshold of 13 °C is reached.

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1 Introduction

Since the onset of the Industrial Revolution (ca. 1750 AD) the global ocean has absorbed approximately 30 % of the emitted anthropogenic carbon dioxide (CO_2) causing ocean acidification (IPCC, 2013). The ecological effects from lowering the pH of the surface ocean on marine organisms, especially those which calcify, will likely be substantial (Doney et al., 2009; Hofmann et al., 2010; Orr et al., 2005), highly variable among taxa (Kroeker et al., 2010; Riebesell et al., 2013), and extend throughout the global ocean (Feely et al., 2004; Orr et al., 2005). Furthermore, anthropogenic CO_2 is not evenly distributed among the ocean basins. In particular, the North Atlantic Ocean stores about 23 % of anthropogenic CO_2 despite representing only 15 % of the global ocean area (Sabine et al., 2004). Consequently, the North Atlantic Basin, compared to other regions, might be more susceptible to ocean acidification. In situ measurements of surface ocean pH are rare prior to about 1990 (Byrne et al., 2010; Dore et al., 2009), however, instrumental data show that the surface global ocean pH has decreased by approximately 0.05 pH units in the last 20 to 25 years (IPCC, 2013). Time-series data from the North Pacific and North Atlantic Oceans indicate that the surface ocean pH has been changing between -0.0015 to -0.0024 pH units per year (IPCC, 2013; Vázquez-Rodrıguez et al., 2012).

This global rise in atmospheric CO_2 has resulted in changes in surface ocean pH and shows a projected persistence in the near future. Therefore, proxy records from the geologic record sensitive to oceanic carbon dynamics are highly desired to place modern pH trends into context (e.g., Hönisch et al., 2012). Biogenic proxy archives calcifying within the surface waters of the global oceans have the unique potential to reveal spatial and temporal patterns and trends in pH using boron isotopes (e.g., Anagnostou et al., 2012; Shinjo et al., 2013). However, in the dynamic coastal regions of the global ocean, local and regional processes have the potential to complicate the boron-pH proxy (described in detail below). Freshwater mixing has the potential to change (1) temperature, salinity, and pH, (2) nutrient availability

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and productivity leading to changes in pH, and (3) local seawater boron isotopic composition. Additionally, potential species-specific biological effects that occur during calcification need to be evaluated. Here we apply multiple isotope systems to evaluate the boron-pH proxy in the northern North Atlantic coastal and shelf-dwelling marine bivalve *Arctica islandica* (*A. islandica*) exposed to ambient conditions. We use radiogenic strontium isotopes to assess terrestrial river water influence on seawater and shell geochemistry for elements with long residence times in coastal water, such as boron. We utilize stable strontium isotopes from shell material to evaluate the potential impacts of growth rates during biomineralization.

1.1 Boron isotopes as pH indicators in biogenic carbonates

Boron has two natural stable isotopes, ^{10}B and ^{11}B, which comprise 19.9(7) % and 80.1(7) % of total boron, respectively (Berglund and Wieser, 2011). The dominant aqueous species of boron in seawater are $B(OH)_3$ and $B(OH)_4^-$. The relative proportion of these two species in an aqueous environment is a function of pH with the following relationship:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad (1)$$

At low pH, boron exists as $B(OH)_3$ in solution, conversely at high pH, boron exists as $B(OH)_4^-$. The governing reaction for isotope exchange between these two species is:

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightleftharpoons {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \quad (2)$$

The stable isotope ^{11}B is enriched in $B(OH)_3$ compared to $B(OH)_4^-$, and the combination of Eq. (1) and (2) can be used to determine the distribution of the two boron species and the isotopic composition of each for a given pH. The isotopic composition of boron is generally reported as:

$$\delta^{11}B = \left[\frac{(^{11}B/^{10}B)_{sample}}{(^{11}B/^{10}B)_{SRM\ 951a}} - 1\right] \times 1000\ (‰) \quad (3)$$

where SRM 951 is the internationally recognized boron isotope standard. Because the residence time of seawater boron is approximately 14 million years (Lemarchand et al., 2000), boron isotopic composition in the open ocean is considered constant over this time period, with an average seawater $\delta^{11}B$ value of 39.61 ‰ (Foster et al., 2010). Therefore, $\delta^{11}B$ has the following relationship: at low pH, the isotopic composition of $B(OH)_3$ is equal to the isotopic composition of the total dissolved boron (39.61 ‰). In contrast, at high pH, the isotopic composition of $B(OH)_4^-$ is equal to the isotopic composition of the total dissolved boron.

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Therefore the $\delta^{11}B$ is enriched in $B(OH)_3$ by about 20 ‰ with respect to $B(OH)_4^-$ at any equilibrium pH based on a constant fractionation factor.

During growth, it is assumed that marine carbonates primarily incorporate $B(OH)_4^-$ into the carbonate structure. Building on these relationships, seawater pH dictates the amount of $B(OH)_4^-$ in seawater and thus the isotopic composition of boron in marine carbonates. The possibility of trigonal $B(OH)_3$ incorporation in carbonates, especially in calcite, is still under debate (Klochko et al., 2009; Rollion-Bard et al., 2011a); but after thorough calibration in targeted marine carbonate species, the $\delta^{11}B$ to pH transfer function can be applied. Changes in the $\delta^{11}B$ composition of shell carbonates are based on the equation:

$$pH = pK_b - \log\left(\frac{\delta^{11}B_{sw} - \delta^{11}B_{carbonate}}{\alpha\delta^{11}B_{carbonate} - \delta^{11}B_{sw} + 1000(\alpha - 1)}\right) \quad (4)$$

where pK_b is the pK value for boric acid at a given temperature and salinity, and is 8.5975 at 25 °C and 35 PSU salinity (DOE, 1994), $\delta^{11}B_{sw}$ is the isotopic composition of seawater, and α is the equilibrium isotopic fractionation factor between boric acid and borate ion $\left(\alpha \equiv \frac{\left(^{11}B/^{10}B\right)_{B(OH)_3}}{\left(^{11}B/^{10}B\right)_{B(OH)_4^-}}\right)$. Of these variables, only the seawater composition can be considered known and constant for all geographic locations and carbonate-precipitating species. Temperature, salinity and the fractionation factor must be estimated. Two empirical and analytical values of α are suggested for seawater: (1) α = 1.0194, a theoretical result of Kakihana et al. (1977), which has been applied widely on paleo-reconstructions (Hönisch et al., 2004; Sanyal et al., 1995); and (2) α = 1.0272, which was empirically obtained from Klochko et al. (2006) and is considered to better describe the distribution of the two boron species in nature today (Foster, 2008; Rollion-Bard et al., 2011b; Rollion-Bard and Erez, 2010). Recent work of Nir et al. (2015), using reverse osmosis membrane under controlled pH, also suggests a higher fractionation factor than the theoretical result from Kakihana et al. (1977). However, due to the ability of calcifying organisms to buffer their own local environments, species specific fractionation factors and transfer functions are likely more appropriate than theoretical α values (Anagnostou et al., 2012; Hönisch et al., 2004; Krief et al., 2010; Rae et al., 2011; Reynaud et al., 2004; Reynaud et al., 2008; Trotter et al., 2011). Thus far, the pH-$\delta^{11}B$ relationship has been tested extensively on some biogenic marine carbonates (foraminifera and coral) with broad success (Anagnostou et al., 2012; Henehan et al., 2013; Hönisch et al., 2004; Ni et al., 2007; Rae et al., 2011; Reynaud et al., 2004), a few measurements have been

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made on calcite shells (Heinemann et al., 2012; Penman et al., 2012), but no published data exists for aragonite bivalves.

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As indicated earlier, one of the primary assumptions in applying the boron isotope/pH proxy technique is that the boron isotopic composition of the seawater from which the biogenic carbonates form remains constant. Therefore, in order to use such a proxy to understand pH changes through the geological past, a technique is required to evaluate variability in local seawater geochemistry.

1.2 Radiogenic strontium isotopes as a water mass tracer

To evaluate the potential impacts of freshwater on local or regional ocean chemistry, it is necessary to differentiate sources that influence the chemical composition of the target water mass. This is especially important in coastal regions where fresh water input from river, surface runoff and/or groundwater mix with seawater often modifying both physical (e.g. temperature, salinity or turbidity) and chemical (e.g. nutrients, trace metal and/or isotopic compositions) conditions. Even for isotopic systems with long residence times in seawater (including boron), observations indicate that large fluxes of freshwater can cause substantial variations in coastal environments where conservative mixing behavior is generally assumed but not always achieved (Chung et al., 2009; D'Olivo et al., 2014; Huang and You, 2007; Huang et al., 2011; Widerlund and Andersson, 2006).

Radiogenic strontium has successfully been used to trace unique water masses. There are four naturally occurring isotopes of strontium: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, with the only radiogenic isotope being ^{87}Sr, which decays from ^{87}Rb. Therefore, the $^{87}Sr/^{86}Sr$ ratio is widely used to trace provenance in geological studies (Aarons et al., 2013; Bataille and Bowen, 2012; Huang and You, 2007; Jahn et al., 2001). Because the residence time of Sr in seawater is more than 4 My, similar to the residence time of boron (Broecker, 1963; Goldberg, 1963), $^{87}Sr/^{86}Sr$ is considered spatially homogeneous in seawater at any instant of geological time. However, in coastal areas, radiogenic Sr isotopes vary as inputs from continental sources are released from terrestrial sediments to fresh water and then exported to the open ocean (Huang et al., 2011). The variability in $^{87}Sr/^{86}Sr$ ratios in natural archives on seasonal and annual timescales has been used as a proxy for quantitatively evaluating proportions of different water mass sources in coastal regions (Huang et al., 2011). The similarity of residence times of Sr and B in the ocean, and potential large differences between ocean and terrestrial isotopic compositions,

suggests that the radiogenic strontium composition of shell material can be used to determine if there is a potential offset between local seawater and open-ocean B isotopic composition.

Prior studies have shown that bivalve shells record both ambient seawater composition and mixing of water sources in the ambient seawater. Widerlund and Anderson (Widerlund and Andersson, 2006) developed a two-endmember mixing model of terrestrial fluvial water and seawater radiogenic Sr in the Baltic Sea and compared the modern bivalve $^{87}Sr/^{86}Sr$ inferred salinity across the Baltic Sea from inland to the Atlantic coast to the *in-situ* measurements of water salinity. Their results indicate conservative characteristics of $^{87}Sr/^{86}Sr$ vs. salinity in the Baltic Sea. Maurer et al. (2012) also measured $^{87}Sr/^{86}Sr$ ratio in a freshwater bivalve species: the Sr isotopic ratios recorded in the shells, in both early and late ontogeny ages, agreed with local water samples, indicating their usefulness in investigating the effects of anthropogenic contamination in rivers.

1.3 Stable strontium isotopes in biogenic carbonates

In addition to $^{87}Sr/^{86}Sr$, the stable isotopes of Sr ($\delta^{88/86}Sr$, the deviation in $^{88}Sr/^{86}Sr$ of a sample relative to a standard given in parts per mil) in natural archives are potential indicators of environmental controls on vital effects, although the applicability is less well established and still controversial. Previously reported $\delta^{88/86}Sr$ values of coral, foraminifera and coccolithophores from the literature show ^{88}Sr depleted results compared to the $\delta^{88/86}Sr$ value in seawater, which suggest the lighter ^{86}Sr is preferentially incorporated into biogenic carbonates (Böhm et al., 2012; Fietzke and Eisenhauer, 2006; Krabbenhöft et al., 2010; Rüggeberg et al., 2008; Stevenson et al., 2014). If the fractionation of stable Sr isotopes in precipitated biogenic carbonates is dominated by kinetic isotope effects and not under equilibrium conditions, the $\delta^{88/86}Sr$ ratio would likely have a strong correlation with precipitation temperature and/or precipitation rate. As an environmental proxy, $^{88}Sr/^{86}Sr$ in both deep sea and tropical corals has been reported as a temperature proxy (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008). However, more recent, higher precision work, has indicated either a null relationship (foraminifera) or negative relationship (coccolithophores) between $\delta^{88/86}Sr$ and ambient seawater temperature, suggesting growth rate controls the uptake of Sr isotopes into biogenic carbonates (Böhm et al., 2012; Stevenson et al., 2014). Although stable strontium applications are in their infancy, the potential for vital effects (growth rate) fractionating $\delta^{88/86}Sr$ indicates it could be useful for assessing vital effects during calcification in bivalve archives.

1.4 The Biogenic Archive *Arctica islandica*

The long-lived bivalve mollusk *A. islandica*, common in the shelf seas of the temperate to sub-polar North Atlantic Ocean, is an excellent high-resolution marine archive with a huge potential for monitoring pH as well as other seawater properties (for a recent review, see Schöne, 2013). This stationary benthic clam lives in water depths ranging from ~10 m to as deep as 500 m and thrives in full marine conditions, yet can also tolerate salinities as low as 28 PSU for short time intervals (Merrill and Ropes, 1968; Nicol, 1951). *Arctica islandica* lives within the sediment and extends its relatively short siphons into the main water column, exchanging water to feed and remove waste. Weidman (1995) demonstrated that the geochemical signature in the shell material reflects that of the ambient water conditions and not pore water. *Arctica islandica* is highly suitable for environmental and ocean studies because: (1) *A. islandica* is extremely long-lived - up to 5 centuries (Butler et al., 2013; Schöne et al., 2005; Wanamaker Jr. et al., 2008a), (2) it produces annual growth increments in its shell (Jones, 1980), (3) regional increment series can be crossdated, demonstrating a common response to environmental forcing(s) (Schöne et al., 2003), (4) fossil shells can be crossdated and floating shell chronologies can be constructed after radiocarbon dating (Scourse et al., 2006), (5) live-caught shells can be crossdated with fossil shells to assemble very long, absolutely dated growth records (Butler et al., 2009; Butler et al., 2011; Marchitto et al., 2000), (6) master shell chronologies can be created that are as statistically robust as tree ring chronologies (Butler et al., 2010), (7) it precipitates its aragonitic shell in oxygen isotope equilibrium with ambient seawater (Weidman et al., 1994), and (8) the geochemical signature (e.g., ^{14}C, $\delta^{18}O$, $\delta^{13}C$) from shell material has been used to reconstruct ocean circulation, hydrographic changes, seasonal changes in ocean conditions, and ecosystem dynamics (Butler et al., 2009; Schöne et al., 2005; Schöne et al., 2011a; Scourse et al., 2012; Wanamaker Jr. et al., 2012; Wanamaker Jr. et al., 2008a; Wanamaker Jr. et al., 2011; Wanamaker Jr. et al., 2009; Wanamaker Jr. et al., 2008b; Weidman and Jones, 1993; Weidman et al., 1994; Witbaard and Bergman, 2003). Despite their effectiveness as environmental proxies, applications of non-traditional isotopic systems ($\delta^{11}B$ and $\delta^{88/86}Sr$) that have the potential to reveal additional environmental factors have not been explored.

2 Methods

2.1 Sample preparation

Living shells from the Gulf of Maine were collected from Jonesport, Maine, USA on 21 November 2009 with a commercial quahog-fishing vessel, F. V. Three of A Kind. The live-caught animals were then transported to the Darling Marine Center (University of Maine) in Walpole, Maine, USA for the culture experiment. Seawater was pumped from the Damariscotta River estuary from ~10 m and delivered to the flowing seawater laboratories. The shells were reared in flow-through seawater tanks without filtration, in which the temperature, salinity and seawater pH were monitored *in-situ* concurrently and continuously (Fig. 1 (d)). The pH of the culture seawater was also measured a total of seven times with a highly accurate Metrohm handheld pH meter (± 0.003 units). Additional details of the culture conditions are given in Beirne et al. (2012). Tank seawater was sampled biweekly throughout the culture period and filtered through a 0.45 µm filter. Two additional samples, one from the Gulf of Maine surface seawater and one from auxiliary water flow pumped into the culture tanks, were also sampled to evaluate if the culture experiment was representative of the natural marine environment. Boron isotopic data from seawater samples during the experiment were previously measured and published by Liu et al. (2013).

Shell subsamples were collected at Iowa State University via a Dremel hand drill, with 10 intervals throughout the 8-month culturing (Fig. 1 (c)). Based on the calcein staining (see Beirne et al., 2012 for details) and natural marking on the external shell, the timing of the winter (January to March), spring (March to May), and summer (May to August) growing seasons were evident (Fig. 1 (a) – (c)). These markings were used to establish growth rates during each season as well as to provide temporal controls on the sampled shell material. The instrumental data and shell growth-rates have been published by Beirne et al. (2012) and the average seawater salinity, temperature, and pH for shell record comparison are summarized in Table 1.

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The boron and strontium concentrations in *A. islandica* shells are about 10 ppm and 1000 ppm, respectively (Zhang, 2009); 1 mg of shell material, after cleaning (details noted below), is required for B (Liu et al., 2013) and Sr (Stevenson et al., 2014) isotopic measurements. Because shell growth rates differ throughout the year, and throughout ontogeny (Beirne et al.,

2012), we have one subsample from January to March, but we have four subsamples from March to May and five subsamples from May to August.

The subsample cleaning procedure was modified from Barker et al. (2003). In summary: coral and shell powders were first cleaned with Super-Q (SQ) water (Millipore, > 18.2 MΩ) in an ultrasonic bath three times and the suspension solution was extracted after centrifuging. Samples were then treated with 10 % H_2O_2 at room temperature overnight to remove organic particles embedded in skeletons. The samples were rinsed with SQ water, 0.001 N HNO_3 and SQ water again. After drying at 60 °C, samples were weighed and then dissolved in ~1.7 N HCl with a boron concentration equal to about 750 ppb.

Seawater samples were diluted to [B] = ~750 ppb in 1.7 N HCl for boron measurements. Because the strontium concentration in seawater is about 9 ppm, the residual after sublimation (see below) is not enough for strontium isotopes measurements. Therefore for strontium isotope analysis of seawater, an additional 100 µL of seawater sample was dried and redissolved in concentrated HNO_3 three times and brought into solution in 7 N HNO_3 for column chemistry. Spiked samples were mixed to have a sample to spike ratio of 1:1, with at least 600 ng of sample Sr in solution prior to preconditioning steps.

Separation of the boron and strontium elemental fractions was achieved using a combination of micro-sublimation (Liu et al., 2013) and elemental specific ion exchange resin. Briefly, < 50 µL of sample solution was loaded in the cap of a conic-bottom vials in an up-side-down position and put into the high-throughput system. After 12 hours of sublimation at 70-74 °C, the purified boron sample solution is condensed and collected on the conic tip. To further improve the reproducibility for carbonate samples, an extra 2 µL of 30 % H_2O_2 was added to the purified solutions (~ 90 % of the volume before sublimation) for all the runs after 23 April 2014. Sample solutions were then set stagnant in the vial, and the cap of the conic vial was then loosened for two hours to reduce the organic levels and liberate the product oxygen gas. The micro-sublimation method only extracts boron from the sample solution, therefore the residual on the cap of the vials is reserved for Sr separation and analysis.

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All measurements were conducted on a Thermo Fisher Triton PLUS multicollector thermal ionization mass spectrometer operating in positive ion mode for strontium isotope analysis and negative ion mode for boron isotope analysis at the Glaciochemistry and Isotope Geochemistry Lab (GIGL) at the Department of Earth and Environmental Sciences, University of Michigan.

2.2 Radiogenic and Stable Strontium Isotope analysis

2.2.1 General

The residuals of carbonate samples after sublimation were redissolved in concentrated HNO_3 to [Sr] = ~10 ppm, which is approximately the same Sr concentration in seawater. A small aliquot of sample was spiked with our ^{84}Sr-^{87}Sr double spike solution. Both unspiked normal sample and spiked mixture sample solutions were then dried down three times, then dissolved in 7 N HNO_3 for Sr column chemistry. In order to separate strontium element from matrix, samples were passed through a 50-100 μm Sr-spec resin (Eichrom), and 0.035 N HNO_3 was used to elute Sr after using 7 N HNO_3 to elute the others. The eluted Sr aliquots were refluxed with 30 % H_2O_2 overnight, dried, and finally dissolved in concentrated HNO_3 for loading (Liu, 2010).

For radiogenic isotopic measurements, 100-200 ng of Sr sample was loaded onto outgassed Re filaments with TaF_5 activator solution. Each sample was heated to an intensity of ~8 V ^{88}Sr. Four hundred cycles of data were collected for each measurement to determine the Sr isotopic ratios with within run precision better than 10 ppm (2 SE). Mass 84 to 86 were detected with five Faraday cups position from L1 to H3, respectively, with ^{85}Rb measured in the center cup. The long-term reproducibility of $^{87}Sr/^{86}Sr$ for SRM987 Sr standard was 0.710268 ± 21 (2σ, n = 140) from the time of Triton installation in January 2012 to April 2014. In May 2014, problems associated with the H3 Faraday cup resulted in change to a ^{86}Sr-centered cup configuration (June to October 2014). After H3 cup replacement, the ^{85}Rb-centered cup configuration was established again. The new SRM987 $^{87}Sr/^{86}Sr$ average value is 0.719246 ± 13 (2σ, n = 42) for data collected after June 2014 (for both cup configurations) and sample data were normalized based on this new SRM987 standard ratio. The reported $^{87}Sr/^{86}Sr$ data in this study were all normalized to SRM987 = 0.710250 for inter-laboratory comparisons.

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2.2.2 Double spike (84-87) Sr

High precision $^{88}Sr/^{86}Sr$ isotopic compositions are measured by double spike (DS); measurements by DS removes instrumental mass bias associated with thermal ionization during sample runs. The double spike method was first developed in the 1960s: Dodson (1963) outlined a methodology for determining the unknown mass discrimination factor directly if the sample is mixed with a double spike, consisting of an enriched mixture of two

stable isotopes. Later, Krogh (1964) worked out a graphical method for a spike enriched in both ^{84}Sr and ^{86}Sr. Finally, Long (1966) showed that the correction factor for mass discrimination can be calculated by using three elements, and it depends on the fractional abundances in the normal and spike elements. A simpler expression was then published by Boelrijk (1968). These pioneering studies founded the basis of the Sr double spike method, and Sr double spikes have already been successfully used to determine the Sr isotopic composition of the early solar system (Patchett, 1980b; 1980a). Optimal spike compositions are determined using a 3D data reduction method (Galer, 1999). The choice of isotope ratios used in the equations, the mathematical formulation to solve for the mass discrimination factor ε and the influence of the spike-to-sample ratio in the mixture should be taken into consideration. With the addition of "tuning" with IAPSO seawater standards (Krabbenhöft et al., 2009), this double spike method could produce more precise true isotopic compositions in an unknown sample solution.

A ^{84}Sr-^{87}Sr double spike solution was prepared at GIGL at the University of Michigan followed the method from Liu (2010). The optimal value of the spike depends on the angle of two planes, defined by normal sample (N) fractionation line and spike point and mixture (M) fractionation line and spike point, respectively (Fig. 2), expressed as θ here. Because all the measured points have their own errors, when the angle between these two planes approximate a right angle, the intersected area reaches a minimum and thus that the N-M-S line will be defined precisely (Fig. 2 (b)). Therefore, by checking different portions of spike mixing with normal (Qs) mathematically, the distribution of θ to spike composition can be derived (Fig. 2 (c)). For our ^{84}Sr-^{87}Sr double spike with an $^{84}Sr/^{87}Sr$ ratio of 0.8679, the optimal Qs is about 0.5, which makes the two planes perpendicular to each other. Within a range of Qs = 0.45-0.55, the θ is still in a range of ±2 degree, which supports a tolerance of spiking samples with a slight deviation from a 1:1 sample to spike ratio. The stable Sr data were reported as $\delta^{88/86}Sr$, which was defined as:

$$\delta^{88/86}Sr = \left[\frac{\left(^{88}Sr/^{86}Sr\right)_{sample}}{\left(^{88}Sr/^{86}Sr\right)_{SRM\ 987}} - 1\right] \times 1000\ (‰) \qquad (5)$$

In this study, a Python script was applied to evaluate true normal values of the shells. We assumed the measured isotopic ratios of normal sample and spiked mixture would follow exponential law, and the equations of each ^{87}Sr-based isotopic ratio for both normal and

mixture sample could be stated. After inputting the known isotopic composition of the spike, the true value of each isotope concentration can be solved using a least squares minimization of the residual of the non-linear equations.

For the spiked sample solution, 200-250 ng of Sr samples was loaded onto outgassed Re filaments with TaF activator solution and run the same as the unspiked samples described in the previous section. The deconvolved $\delta^{88/86}$Sr values for seawater standard IAPSO 141 and an inter-laboratory coral standard JCp-1 are 0.390 ± 16 ‰ (2σ, n = 4) and 0.144 ± 26 ‰ (2σ, n = 3), respectively. According to Krabbenhöft et al. (2009), using the IAPSO seawater standard to fine-tune the Sr double spike composition provides an optimal $\delta^{88/86}$Sr result. Here we used the same technique and obtained a compatible $\delta^{88/86}$Sr value for the IAPSO seawater standard to the reported values from Krabbenhöft et al. (2009). However, due to the H3 cup deficiency, the deconvolved $\delta^{88/86}$Sr value of inter-laboratory carbonate standard JCp-1 is about 0.05 ‰ lighter than the reported values between April 2014 and June 2014. This offset was fixed, with the alternate cup configuration and replacement of H3 cup, after June 2014 and new values of IAPSO = 0.365 ± 73 ‰ (2σ, n = 4) and JCp-1 = 0.195 ± 21 ‰ (2σ, n = 4) (Fig. 3) were obtained.

2.3 Boron Isotope Analysis

The procedure used for obtaining B isotopic compositions by total evaporation (TE) is described in Liu et al. (2013). In summary: one μL of boron free synthetic seawater matrix was loaded onto outgassed single Re filament at 0.8 A current, followed by 1 μL of sample solution with 30 seconds of waiting between the two steps. Samples were then dried down at 2 A current for 10 seconds and then the filaments were flashed to a dull red color in the center of the filament (about 2.5 A) and ready for analysis. Data collection was initiated when the intensity of mass 42 reached 20 mV, and terminated after the signal dropped lower than the initial 20 mV.

The long-term reproducibility (18 months) of $^{11}B/^{10}B$ for boric acid standard SRM 951a is 4.0332 ± 0.0064 (2σ, n = 97) before treated with 30 % H_2O_2 and is 4.0316 ± 0.0084 (2σ, n = 19) 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, respectively; 41.70 ± 1.13 ‰ (2σ, n = 8) and 24.93 ± 1.83 ‰ (2σ, n = 18) for IAEA B-1 and JCp-1, respectively, with H_2O_2 treatment (Fig. 4).

3 Results

The *in-situ* seawater salinity, temperature and pH results are summarized in Table 1. To compare the instrumental data to the shell records, the instrumental results were averaged with respect to the subsampling intervals. The seawater and shell results are summarized in Table 2 and Table 3, respectively

3.1 $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$

3.1.1 $^{87}Sr/^{86}Sr$

The $^{87}Sr/^{86}Sr$ ratios of seawater range from 0.709177 to 0.709192, with an average of 0.709185 ± 8 (2σ, n = 13). There is no distinguishable difference between samples from offshore Gulf of Maine seawater, auxiliary flow and tank waters (Fig. 5 (a)). For shell carbonate, the $^{87}Sr/^{86}Sr$ ratios range from 0.709163 to 0.709210, with an average of 0.709183 ± 23 (2σ, n = 27). Both of the seawater and shell $^{87}Sr/^{86}Sr$ are identical to the mean seawater values (Fig. 5 (a) and (b)). Because all the radiogenic Sr results are identical within error, there is no relationship with either seawater salinity, temperature or pH.

3.1.2 $\delta^{88/86}Sr$

Two sets of shell samples, A103JV and A105JV, were spiked for stable Sr measurements. However, due to the defect of H3 cup, the A103JV double spike results are underestimated and are not listed. The deconvolved $\delta^{88/86}Sr$ for A105JV and Sr concentrations values for both of A103JV and A105JV from high-resolution shell records are shown in Fig. 5 (c) and (d), respectively. The $\delta^{88/86}Sr$ values ranges from 0.215 to 0.296 ‰ with an average of 0.248 ± 48 ‰ (2σ, n = 10) and the concentration ranges from 1200-1800 ppm. Considering analytical uncertainty, no distinctive differences or trend for either Sr concentration or stable Sr isotopic compositions in the shells are observed throughout the culture season. Similarly, no correlation can be found between stable Sr or Sr concentration to any measured ambient seawater conditions.

3.2 Boron isotopic composition ($\delta^{11}B$) in ambient seawater the shell and aragonite shell

Boron isotopic compositions of 11 tank water samples are from 37.51 ‰ to 47.83 ‰, and the average for 36 sample runs is 39.20 ± 1.73 ‰. The $\delta^{11}B$ values for additional seawater samples from the offshore Gulf of Maine and the auxiliary flow to the culture tanks are 36.93 ‰ and 40.38 ‰, respectively (Fig. 6 (a)) (Liu et al., 2013). Similar to what has been observed from radiogenic Sr data in seawater, the boron isotopic composition of our culture seawater is invariant and identical to the open ocean composition reported by Foster et al. (2010).

High-resolution boron isotopic composition records from 4 juvenile shells (A101JV, A102JV, A103JV and A105JV) show nearly identical patterns and trends throughout the experiment. The shell $\delta^{11}B$ values range from 11.09 to 18.81 ‰ before week 19 and from 17.41 to 25.12 ‰ after week 19 (Fig. 6 (b)). Compared to seawater temperature and average shell growth rates in three growth seasons, we found a distinct rise in $\delta^{11}B$ for temperatures over ~13 °C. However, this rapid change in $\delta^{11}B$ did not correlate to the rapid change in shell growth during the culture period.

In order to evaluate the pH dependency of the $\delta^{11}B$, Eq. (4) is used. Based on *in-situ* temperature, salinity and pH measurements throughout the culture experiment, we calculated the predicted range in $\delta^{11}B$ of the *A. islandica* shell with α = 1.0272, which was empirically obtained from Klochko et al. (2006) and is considered to better describe the distribution of the two boron species in natural system (Foster, 2008; Rollion-Bard et al., 2011b; Rollion-Bard and Erez, 2010) (Fig. 6 (b)). Another prediction line calculated based on independently derived fractionation factor from (Nir et al., 2015) is also shown for reference (Fig. 6 (b)). The predictions suggest a slight increase in $\delta^{11}B$ throughout the culture season, primarily due to more than a 15 °C temperature increase. A 0.2 pH unit drop, observed between week 24 and 26, should have decreased the $\delta^{11}B$ value by about 2 ‰ even with the large temperature change. Most of the shell boron isotopic composition data followed the two prediction lines, before week 19, with some of the data points lower than the predictions. After week 19, the $\delta^{11}B$ deviate significantly and trend toward higher and higher $\delta^{11}B$ compositions. Duplications on different individual shells all suggest the same trend.

We also calculated shell pH (pH_{shell}) with α = 1.0272 based on average tank water $\delta^{11}B$, shell $\delta^{11}B$ and the corresponding average seawater temperature and salinity values. The results

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show a significant negative relationship between ΔpH and pH_{sw} (R^2 = 0.35; p-value ≤ 0.001) (Fig. 7).

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4 Discussion

4.1 Radiogenic Sr isotope incorporation into *A. islandica*

In this study, we measured the radiogenic Sr isotope ratios in seawater to estimate the source water contributions to the culture site, which is situated within the Damariscotta River estuary. The $^{87}Sr/^{86}Sr$ ratios in cultured seawater showed identical values to the open surface seawater ratio. Bedrock types in the Gulf of Maine coastal region are dominated by late Proterozoic and lower Paleozoic sedimentary rocks (Osberg et al., 1985), which would provide a terrestrial source with high $^{87}Sr/^{86}Sr$ values. Considering rock type, age and freshwater flux, a recent model of $^{87}Sr/^{86}Sr$ for flux-weighted catchment water suggests the $^{87}Sr/^{86}Sr$ value to be in a range of 0.7099 to 0.7145 (Bataille and Bowen, 2012). If river fluxes influence the Sr isotopic composition of coastal seawater, the value should be enriched in ^{87}Sr, driving the $^{87}Sr/^{86}Sr$ higher than the current seawater ratio. Therefore the Sr isotopic results suggest a negligible amount of fresh water input into the culture water at the Darling Marine Center.

The mean $^{87}Sr/^{86}Sr$ ratio in the shell is consistent with the isotopic composition in the culture seawater, but with a relatively larger variation between individual shell samples. Therefore, incorporation of radiogenic Sr ratios into the shells occurs without measurable fractionation and reflects the composition of ambient seawater. Although the shell $^{87}Sr/^{86}Sr$ values have a larger standard deviation compared to the seawater values, they are within the range of the long-term precision of Triton plus at the Department of Earth and Environmental Sciences, University of Michigan (see Sect. 2.2.1). The high content of calcium in carbonate samples, which cannot be fully separated using Sr-specific ion exchange column chemistry, may contribute to the larger variation of shell $^{87}Sr/^{86}Sr$ compared to seawater.

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4.2 Stable Sr isotope incorporation into *A. islandica*, and Sr concentrations

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In this study we observed no statistically significant correlation of $\delta^{88/86}Sr$ or Sr concentrations with respect to seawater temperature. The stable Sr isotopic composition of

some biogenic carbonates has been suggested to reflect ambient seawater temperature due to mass dependent kinetic fractionation, in which the relative mass difference of the isotopes involved accounts for the inverse correlation to the ion mass in a kinetic fractionation process (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008). However, more recent work has shown no relationship between seawater temperature and $\delta^{88/86}$Sr values from various biogenic archives (Böhm et al., 2012; Raddatz et al., 2013; Stevenson et al., 2014; Vollstaedt et al., 2014). Our results support the argument that a simple temperature dependent kinetic effect is not the primary control on $\delta^{88/86}$Sr in the aragonitic shell of *A. islandica*. The temperature range in the experiment is over 15 °C (2.4 – 17.6 °C) and growth rate more than doubles (0.24 – 0.68 mm/week) during the experiment, which could result in over 1.5 ‰ change in $\delta^{88/86}$Sr if *A. islandica* behaved similarly to coccolithophores (Stevenson et al., 2014). The lack of a consistent relationship between $\delta^{88/86}$Sr with temperature or shell growth rate during the experiment indicates that $\delta^{88/86}$Sr is not controlled by temperature or growth rates. Thus it is likely that $\delta^{88/86}$Sr records derived from *A. islandica* shells reflect ambient seawater conditions, and could be a potential archive for studying the global Sr cycle in the context of chemical weathering (Krabbenhöft et al., 2010; Raddatz et al., 2013; Vollstaedt et al., 2014). More work is needed to fully evaluate this potential proxy.

Our deconvolved shell Sr concentrations show no resolvable relationship with the seawater temperature, despite a possible physiological control on Sr uptake into bivalve shell material. In general, co-precipitation of Sr to Ca in aragonite decreases with temperature increases due to a declining distribution coefficient, which has been both measured and derived theoretically (Dietzel et al., 2004). The negative correlation between skeletal Sr/Ca ratios observed in some massive corals with ambient seawater temperature has been widely established and applied to reconstruct paleo seawater temperature (Beck et al., 1992; Corrège, 2006; de Villiers, 1999; McCulloch et al., 1994; McCulloch et al., 1996; Shen et al., 1996; Weber, 1973; Yan et al., 2013; Yu et al., 2005). However, these relationships may be biased by the influence from symbionts causing a vital effect (Böhm et al., 2012; Cohen et al., 2006; Cohen et al., 2002; Purton et al., 1999; Stevenson et al., 2014). Schöne et al. (2011b) observed a strong physiological regulation to Sr/Ca and Mg/Ca on ontogenically old adult *A. islandica* records. The metal to calcium ratio (Me/Ca) increased with shell age when the annual increment widths were below 30 to 200 µm. However, Schöne et al. (2013) concluded that the faster-growing juvenile portion of the shells showed a weak relationship between Me/Ca and ambient temperature and results from different specimens were variable. Schöne et al. (2013)

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Deleted: of stable Sr in the aragonitic shell of *A. islandica*. The lack of a consistent relationship between stable Sr with temperature or shell growth rate during the experiment indicates that stable Sr is not controlled by temperature or growth rates. Thus it may be possible stable Sr records derived from *A. islandica* shells may reflect ambient seawater conditions, and could therefore

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proposed that pronounced vital effects may control the trace metal uptake in juvenile shells. Our results are also consistent with the study of Schöne et al. (2011b), where the juvenile portion of the two *A. islandica* shells with annual growth increments larger than 750 μm, showed no clear relationship between Me/Ca ratios and growth rates.

4.3 Controls on $\delta^{11}B$ in *A. islandica* and an evaluation of the proxy archive as a seawater pH indicator

The range in measured shell $\delta^{11}B$ values lies between the prediction lines (Fig. 6 (b)), which suggest that the shell boron content generally reflects the ambient seawater conditions. However, our data do not consistently follow either prediction line. Previous studies on foraminifera have shown offsets between different genera and the empirical $\delta^{11}B$-pH relationship of α = 1.0194 (Hönisch and Hemming, 2004). The inconsistency between shell $\delta^{11}B$ and either prediction is therefore strong evidence that a species-specific fractionation factor is required for bivalves.

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The offsets between our shell data with the predicted trends (Fig. 6 (b)) are likely from vital effects during biomineralization. Previous studies suggested a range of fractionation factors might be applied, and an additional constant offset might better describe the empirical $\delta^{11}B$-pH relationship (Anagnostou et al., 2012; Hönisch et al., 2004; Rae et al., 2011). Therefore a species-specific offset may account for the smaller variations before week 19, where many of the results lie under the prediction lines and the negative ΔpH. In this study, because the temperature and salinity are variable, we cannot determine a precise transfer function for *A. islandica*. However, the total variation throughout the experiment is about 10 ‰, and has an obvious trend after week 19, suggesting other controls on boron incorporation in the shell.

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Rollion-Bard and Erez (2010) and Trotter et al. (2011) evaluated vital effects in corals and foraminifera, and the potential use of the $\delta^{11}B$-pH relationship in such biogenic carbonates. They observed a pH offset between calcifying fluid and ambient seawater, and this pH discrepancy (ΔpH) increases with decreasing ambient seawater pH (pH_{sw}). As the environment becomes more acidic, marine calcifiers likely adjust their internal microenvironment during calcification, resulting in larger ΔpH values than expected. Under careful culture conditions, species-specific ΔpH-pH_{sw} relationships can be developed, and after calibration, the corresponding ambient seawater pH can be determined.

It has been argued that bivalves have the ability to regulate their inner shell fluid chemistry, more specifically the extrapallial fluid (EPF), to achieve a carbonate saturation state in order to facilitate biomineralization (Crenshaw, 1980). Stemmer (2013) observed pH gradients between inner shell surface and outer mantle epithelium (OME) of *A. islandica* via *in-situ* pH microscopy method. During a short-term monitoring, Stemmer (2013) also observed the measured pH rose rapidly as the probe approached the OME. They concluded this elevation was due to active proton uptake by the epithelium. This result suggests a pH self-regulation occurs for *A. islandica* shell precipitation, and the shell will record the regulated calcification pH in the carbonate shell.

The calculated ΔpH shows a statistically significant negative relationship to pH_{sw} ($R^2 = 0.35$; p-value ≤ 0.001) (Fig. 7). The negative correlation supports the argument that *A. islandica* regulate their EPF pH for calcification. However, only 35 % of the variability can be explained by ΔpH, which indicates that the pH regulation in the EPF is likely not the prevailing factor. Instead, we found a rapid increase of the shell $\delta^{11}B$ when temperature increased over 13 °C (Fig. 8 (a)). This rapid change in boron isotopic composition can be explained with respect to two factors: (1) a growth rate controlled vital effect, or (2) a temperature controlled vital effect.

Herfort et al. (2008) suggested that carbonate species are the limiting factor in coral calcium precipitation rather than calcium: when ambient seawater temperature increases, $[CO_2]_{aq}$ decreases, and leads to rising $[CO_3^{-2}]$ as well as calcification rate. The rapid growth rate change is likely related to spring bloom. Our data shows no correlation between boron isotopic composition in the shell and the shell growth, indicating shell growth is not the primary control to the boron deviation in the culture experiment (Fig. 8b). Therefore, combined correlation with temperature and lack of correlation with growth to the shell $\delta^{11}B$ cannot be explained by a temperature controlled growth/precipitation effect.

Alternatively, a proton removal mechanism via Ca^{+2}-ATpase from the site of calcification has been proposed. This mechanism raises the pH of the calcification solution (Dissard et al., 2012; Rollion-Bard et al., 2011b). In this scenario, the activity of the enzyme is enhanced when a certain temperature has been reached, accelerating the proton removal process and resulting in a higher boron isotopic composition in the calcification solution with respect to the elevated pH. We suggest that there may be a temperature threshold of the boron incorporation into the aragonite *A. islandica.* This proposed threshold may be related to the

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upper-end thermal tolerance of *A. islandica*. For example, below 13 °C, the $\delta^{11}B$ values closely matched the predicted model of Klochko et al. (2006), supporting the assumption that borate is the dominate species incorporated into the shell and so can reflect the ambient seawater pH. At temperatures above 13 °C the utility of the $\delta^{11}B$ values as a pH indicator is questionable and likely unreliable. We suggest that the thermal tolerance of *A. islandica* was exceeded in the summer growing season in the culture conditions, causing biological stress on the animals.

5 Conclusion

Here we examined boron and strontium isotopic compositions recorded in the shell material of cultured aragonitic *A. islandica* with *in-situ* seawater temperature, salinity and pH measurements. Both seawater and shell $^{87}Sr/^{86}Sr$ show identical values to the mean global seawater composition, suggesting there is trivial influence from local continental runoff. Shell $\delta^{88/86}Sr$ and Sr concentration values during the culture season were not influenced by seawater temperature or calcification rates. These results suggest that well-preserved sub-fossil specimens may be use to determine the past isotopic composition ($^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$) of seawater.

The boron isotope results from the cultured aragonite *A. islandica* shells generally are within the range of two prediction lines utilizing previously published fractionation factors. Although to first order, these results indicate that the shell $\delta^{11}B$ values reflect ambient conditions, substantial variability not related to pH changes was noted. The 5 to 8 ‰ increase in shell $\delta^{11}B$ values is larger than theoretical predictions based on *in-situ* seawater temperature, salinity, pH and conventional boron fractionation factors for corals and foraminifera. A species-specific $\delta^{11}B$-pH transfer function is recommended for bivalve species because of their inherent ability to self regulate calcifying fluids. The fairly strong relationship ($r^2 = 0.35$) between ΔpH and pH_{sw} indicates that *A. islandica* does regulate the EPF pH during calcification, but self-regulation is not the primary control on shell $\delta^{11}B$. The largest increase in shell $\delta^{11}B$ values was observed after crossing an apparent temperature threshold at 13 °C, suggesting a possible influence from biological processes. To better evaluate the potential of $\delta^{11}B$ as a seawater pH indicator, a pH controlled culture experiment with limited seawater temperature and salinity variation is needed.

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Table 1. Summary of *in-situ* instrumental data of tank seawater salinity, temperature, pH during culture season

Week number (dates)	Salinity (PSU)[1]	Average to subsampling interval[3]	Temperature (°C)[1]	Average to subsampling interval[3]	pH[1]	Average to subsampling interval[3]	Predicted $\delta^{11}B$ with α = 1.0260[2]	Predicted $\delta^{11}B$ with α = 1.0272[2]
1 (1/17 - 1/23)	31.036		3.029		--		-	-
2 (1/24 - 1/30)	30.508		3.030		--		-	-
3 (1/31 - 2/6)	30.520		2.375		--		-	-
4 (2/7 - 2/13)	31.066	30.608 ± 0.683	2.369	2.960 ± 0.511	8.018	8.033 ±0.019	15.84	14.79
5 (2/14 - 2/20)	31.186		2.776		8.037		16.00	14.95
6 (2/21 - 2/27)	30.755		3.367		8.059		16.18	15.14
7 (2/28 - 3/6)	29.183		3.774		8.019		15.90	14.85
8 (3/7 - 3/13)	29.288	29.516 ± 0.322	4.596	4.698 ± 0.145	8.029	8.039 ± 0.014	16.03	14.99
9 (3/14 - 3/19 (3/20))	29.743		4.800		8.049		16.20	15.16
10 (3/21 - 3/27)	29.751	29.149 ± 0.851	5.646	5.735 ± 0.127	8.094	8.089 ± 0.006	16.59	15.57
11 (3/28 - 4/3)	28.547		5.825		8.085		16.49	15.47
12 (4/4 - 4/10)	28.011	28.745 ± 1.037	7.252	7.205 ± 0.066	8.085	8.082 ± 0.005	16.60	15.58
13 (4/11 (4/14) - 4/17)	29.478		7.158		8.078		16.61	15.59
14 (4/18 - 4/24)	29.751	29.827 ± 0.107	7.594	8.246 ±0.922	8.102	8.102 ± 0.000	16.85	15.84

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15 (4/25 - 5/1)	29.902		8.898		8.102		↓6.99	↓5.99
16 (5/2 - 5/8)	30.335		9.662		8.095		↓7.03	↓6.03
17 (5/9 - 5/15)	30.762	30.702 ± 0.341	9.364	9.784 ± 0.494	8.150	8.128 ± 0.029	↓7.48	↓6.50
18 (5/16 - 5/22)	31.008		10.328		8.139		↓7.51	↓6.53
19 (5/23-5/29)	31.102		12.653		8.118		↓7.59	↓6.61
20 (5/30-6/5)	31.227	31.099 ± 0.129	13.385	13.170 ± 0.450	8.120	8.105 ± 0.025	↓7.69	↓6.72
21 (6/6-6/12)	30.969		13.472		8.076		↓7.30	↓6.31
22 (6/13-6/19)	31.067		13.427		8.078		↓7.32	↓6.33
23 (6/20-6/26)	31.115	30.829 ± 0.454	14.676	14.494 ± 0.989	8.125	8.121 ± 0.041	↓7.88	↓6.91
24 (6/27-7/3)	30.306		15.380		8.159		↓8.24	↓7.30
25 (7/4-7/10)	30.508		16.445		8.015		↓7.07	↓6.08
26 (7/11-7/17)	30.555	30.521 ± 0.030	17.209	17.076 ± 0.577	7.960	7.985 ± 0.028	↓6.71	↓5.70
27 (7/18-7/24)	30.500		17.576		7.981		↓6.91	↓5.90
28 (7/25-7/31)	30.305	30.466 ± 0.227	17.188	17.107 ± 0.115	7.966	7.976 ± 0.013	↓6.75	↓5.73
29 (8/1-8/5)	30.626		17.026		7.985		↓6.89	↓5.89

1 [1.] Data from Beirne et al. (2012)

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[2] Calculation based on Eq. (4), where $\alpha \equiv \frac{\left({}^{11}B/{}^{10}B\right)_{B(OH)_3}}{\left({}^{11}B/{}^{10}B\right)_{B(OH)_4^-}}$ and

$$pK_b = -log\left(exp\left(\frac{-8966.90-2890.53S^{\frac{1}{2}}-77.942S+1.728S^{\frac{3}{2}}-0.0996S^2}{T} + 148.0248 + 137.1942S^{\frac{1}{2}} + 1.62142S - \left(24.4344 + 25.085S^{\frac{1}{2}} + 0.2474S\right)\ln T + 0.053105S^{\frac{1}{2}}T\right)\right)$$ (DOE, 1994).

[3] Standard deviation of the data

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1 Table 2. Summary of seawater data

Sample ID	Week	$^{87}Sr/^{86}Sr$ (2 SE)	$\delta^{11}B$ (‰)
Tank A 031710	9	0.709182(4)	38.48
Tank A 041810	14	0.709192(5)	39.41
Tank A 050810	16	0.709183(4)	39.47
Tank A 052210	18	0.709186(4)	38.04
Tank A 081610	31	0.709188(4)	38.10
Tank B 031910	9	0.709185(4)	39.31
			39.97
			38.50
			40.59
			38.51
			40.10
			39.45
			40.33
			39.81
			37.91
Flow A 021410	5	0.709184(4)	39.00
Flow A 070510	25	0.709188(4)	38.65
Flow A 072210	27	0.709187(4)	38.33
			39.36
			38.57
			38.48
			38.40
			39.02

			40.77
			40.78
Flow #2 013010	2	0.709180(4)	37.51
			38.53
			39.01
			39.91
			40.83
			40.01
			39.08
			38.98
			39.78
			39.14
Flow #2 022710	6	0.709189(4)	39.16
Aux.	33	0.709182(5)	36.93
GoM 112309	33	0.709177(4)	40.38

Table 3. Summary of shell data

Sample ID	Week number	$^{87}Sr/^{86}Sr$ (2 SE)	$\delta^{88/86}Sr$ (‰)	[Sr] (ppm)	$\delta^{11}B$ (‰)	Average growth rate (mm/week)[1]	pH_{shell}[2]	ΔpH[3]	2 STD for calculated pH[4]
A101JV-8	22	--	--	--	20.32	--	8.419	0.298	0.22
A101JV-9	24.8	--	--	--	23.34	--	8.595	0.610	0.10
A102JV-1	4	0.709181 (7)	0.132	1403	15.68	0.27	8.139	0.105	0.11
A102JV-2	8.5	0.709210 (10)	0.151	1282	14.94	0.53	8.020	-0.019	0.08
A102JV-3	10.5	0.709181 (10)	0.158	1422	14.28		7.898	-0.191	0.42
A102JV-4	12.5	0.709157 (15)	0.112	1452	--				
A102JV-5	14.5	0.709201 (7)	0.118	1435	13.77		7.756	-0.346	0.15
A102JV-6	16.4	0.709194 (12)	0.124	1319	13.65	0.65	7.705	-0.423	0.14
A102JV-7	19.2	0.709169 (13)	0.154	1474	16.80		8.132	0.028	0.10
A102JV-8	22	0.709170 (5)	0.099	1558	18.04		8.236	0.115	0.13
A102JV-9	24.8	0.709178 (6)	0.112	1491	20.23		8.382	0.397	0.02
A102JV-10	27.6	0.709184 (6)	0.097	--	21.93		8.502	0.527	0.02
A103JV-1	4	--	--	--	16.57	0.24	8.242	0.209	0.25
A103JV-2	8.5	--	--	--	16.57	0.51	8.225	0.186	0.25
A103JV-3	10.5	0.709191 (7)	--	--	18.41		8.389	0.300	0.03
A103JV-	12.5	0.709187	--	--	16.00		8.138	0.056	0.17

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-4		(5)			4				
A103JV	14.5	0.709195	--	--	16.2				0.11
-5		(9)			8		8.145	0.043	
A103JV	16.4	0.709204	--	--	17.7	0.61			0.13
-6		(15)			1		8.265	0.138	
A103JV	19.2	--	--	--	16.5				0.06
-7					7		8.108	0.003	
A103JV	22	0.709188	--	--	17.4				0.24
-8		(6)			5		8.182	0.061	
A103JV	24.8	0.709182(5	--	--	19.2				0.07
-9		)			1		8.305	0.319	
A103JV	27.6	0.709182	--	--	25.1				0.22
-10		(5)			2		8.708	0.733	
A105JV	4	0.709178	0.227	1414	14.5	0.24			0.53
-1		(6)			3		7.970	-0.064	
A105JV	8.5	0.709191	0.255	1534	13.7	0.60			0.39
-2		(7)			5		7.802	-0.237	
A105JV	10.5	0.709183	0.251	1482	12.2				0.76
-3		(6)			2		7.175	-0.914	
A105JV	12.5	0.709184	0.263	1453	17.1				0.21
-4		(5)			5		8.257	0.176	
A105JV	14.5	0.709175	0.216	1521	14.5				0.25
-5		(7)			9		7.916	-0.186	
A105JV	16.4	0.709179	0.273	2559	11.0	0.68			0.30
-6		(6)			9		--	--	
A105JV	19.2	0.709183	0.296	2048	12.5				0.33
-7		(5)			2		7.272	-0.833	
A105JV	22	0.709163	0.230	2204	17.4				0.17
-8		(5)			1		8.178	0.057	
A105JV	24.8	0.709186	0.234	1850	19.4				0.09
-9		(6)			3		8.322	0.337	
A105JV	27.6	0.709177	0.238	1795	22.1				0.23
-10		(6)			1		8.514	0.539	

1. Data from Beirne (2011)
2. pH_{shell} was calculated with Eq. 4, in-situ temperature and salinity data was used to determine pK_b and $\alpha = 1.0272$ was used.

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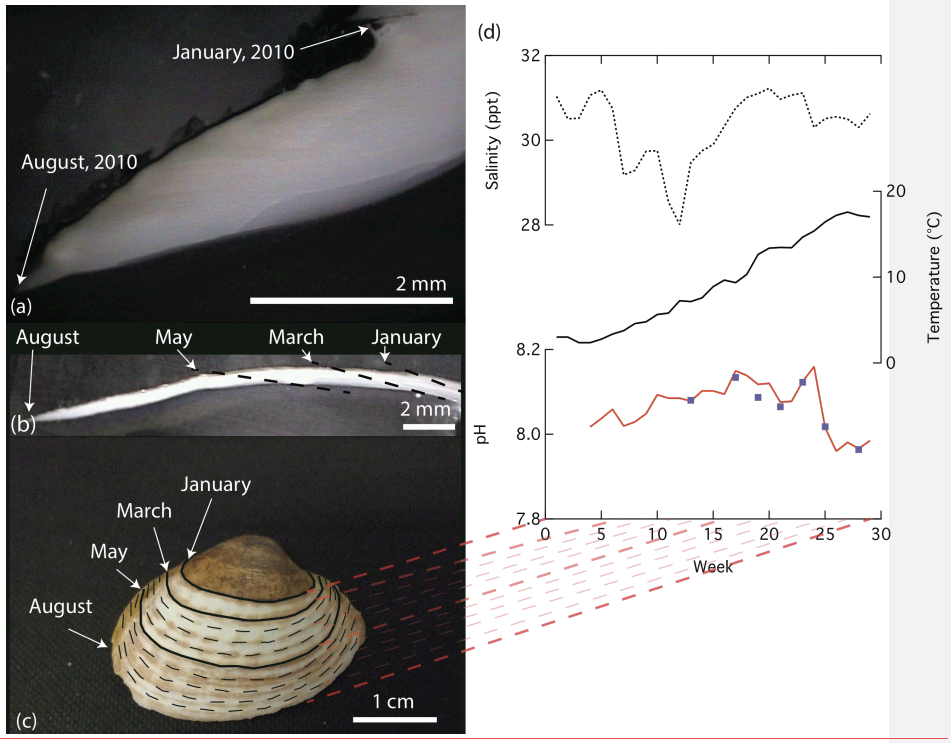
3. ΔpH (pH_{shell}-pH_{sw})
4. Propagation error determined from within run standard deviation of shell $\delta^{11}B$ (duplication or triplication of the same sample solution).



5.

Figure 1. Photos of (a) adult and (b) (c) juvenile *A. islandica* from the culture experiment. One can see nature marking on the external shell, or calcein mark in the cross-section under microscope to constrain the shell growth. (d) shows the corresponding *in-situ* measurements of tank water salinity, temperature and pH during the 31-week culture experiment. The juvenile shells were sampled in 10 intervals for this study (c). Note that because the growth rates differ during the season, each internal represents different durations (c) and (d).

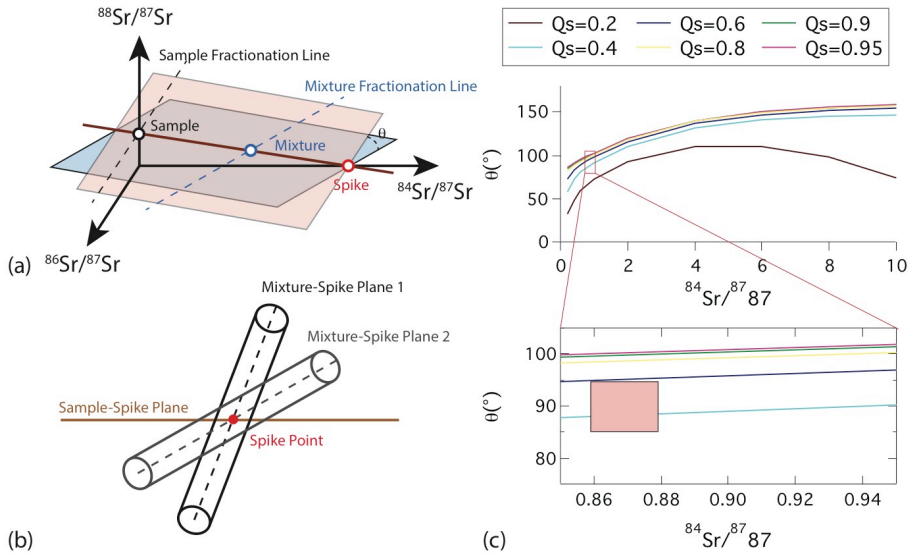


Figure 2. The illustrations of (a) the 84-87 Sr double spike method, (b) how the angle between Mixture-Spike plane and Sample-Spike plane can influence the precision of the deconvolved result, and (c) the optimal sample-spike ratio in our study.

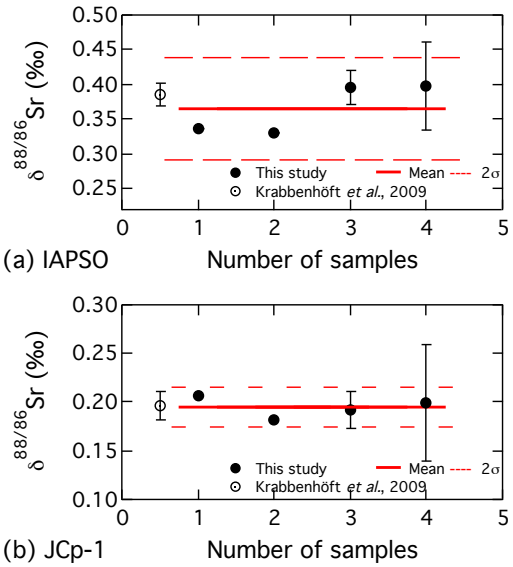
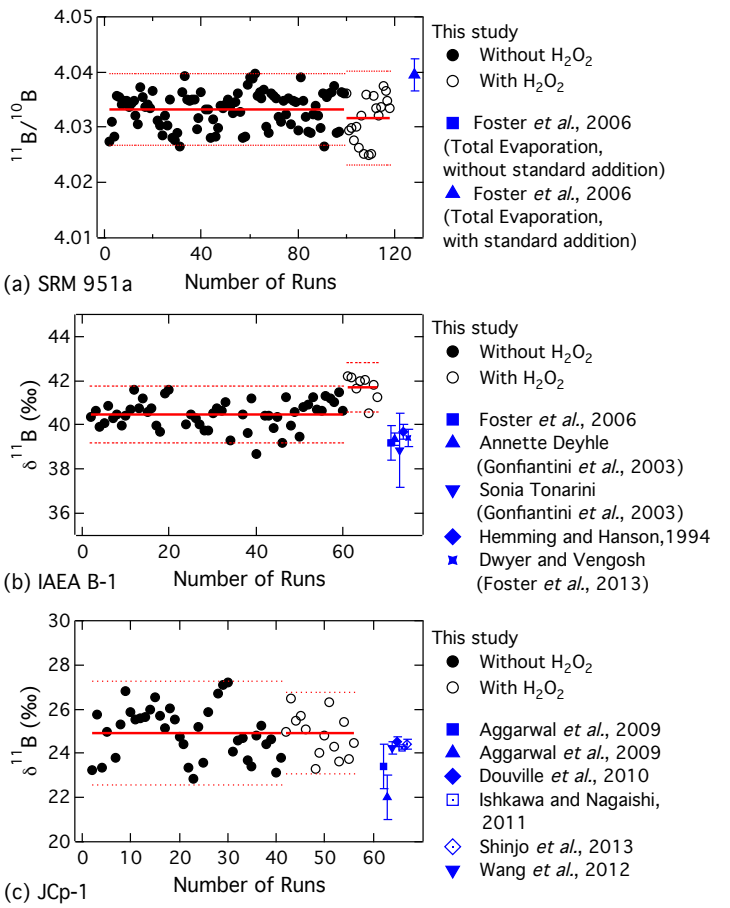


Figure 3. Stable Sr results for (a) seawater standard IAPSO and (b) inter-laboratory biogenic carbonate standards JCp-1.



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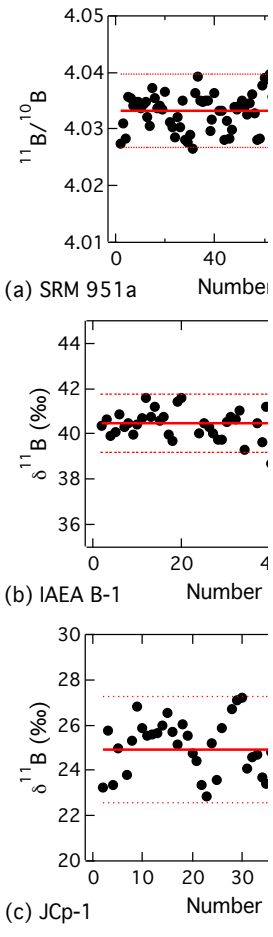

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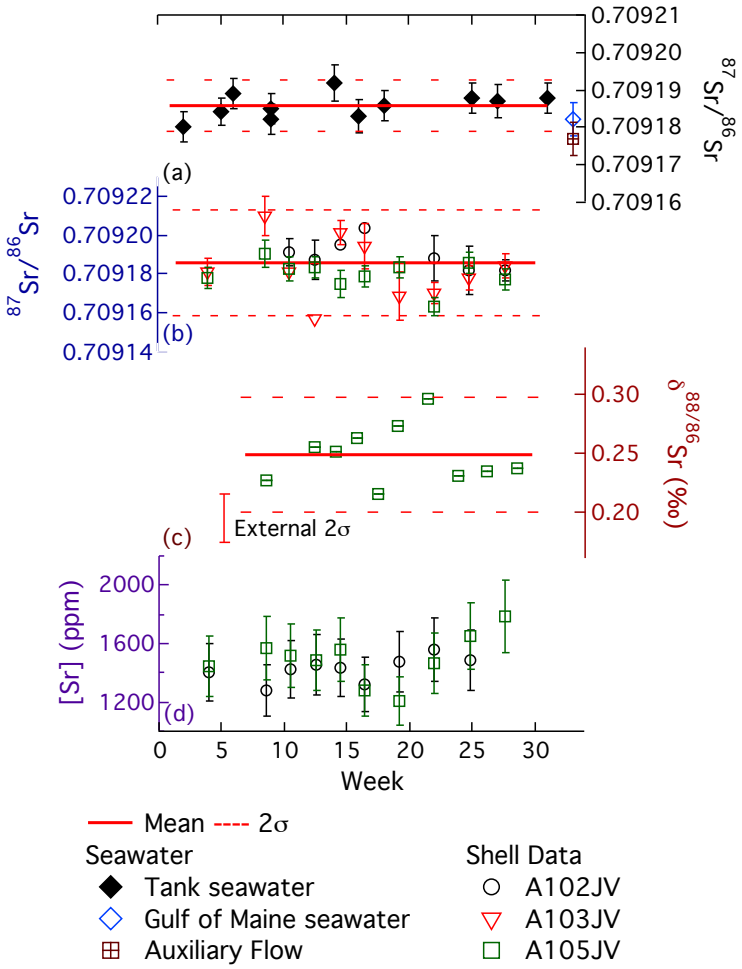
Figure 4. Long-term precision of (A) boric acid standard SRM 951a, (B) seawater standard IAEA B-1, and (C) inter-laboratory carbonate standard JCp-1.



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3 Figure 5. GoM $^{87}Sr/^{86}Sr$ data for (a) seawater samples and (b) shell samples and the double
4 spike deconvolved (c) $\delta^{88/86}Sr$ values and (d) Sr concentrations for the juvenile shell.

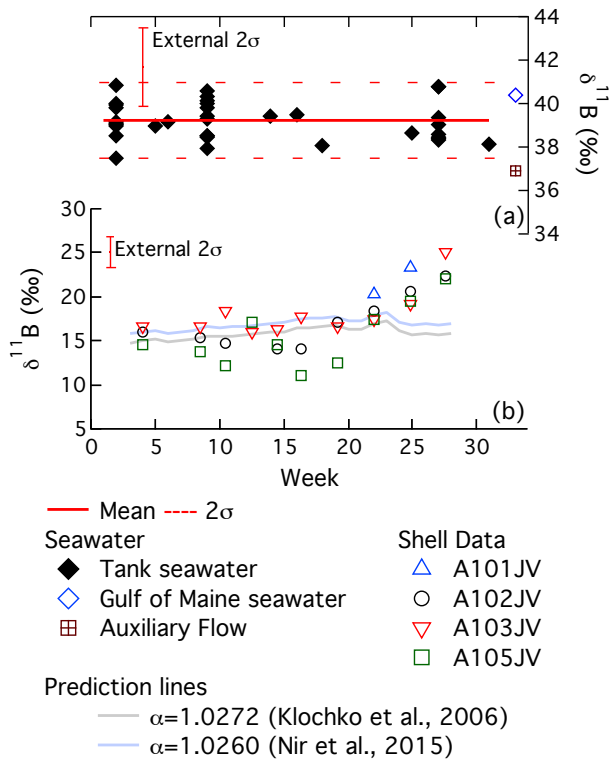

Figure 6. GoM boron data for (a) seawater samples and (b) shell samples. Two prediction lines listed were calculated based on our instrumental culture seawater pH, temperature, and salinity data, and two boron fractionation factors: α = 1.0272 (Klochko et al., 2006), and α = 1.0260 (Nir et al., 2015), where $\alpha \equiv \frac{(^{11}B/^{10}B)_{Boric\ aicd}}{(^{11}B/^{10}B)_{Borate}}$. Equation 4 was used fort he calculation.

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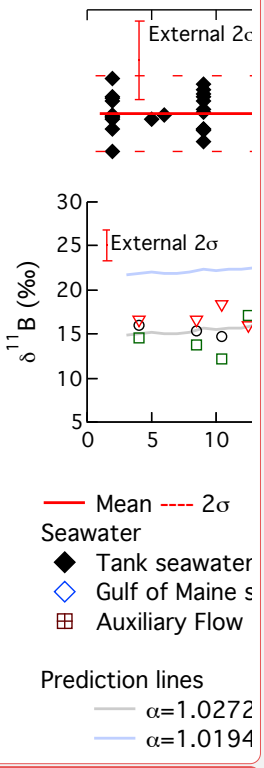

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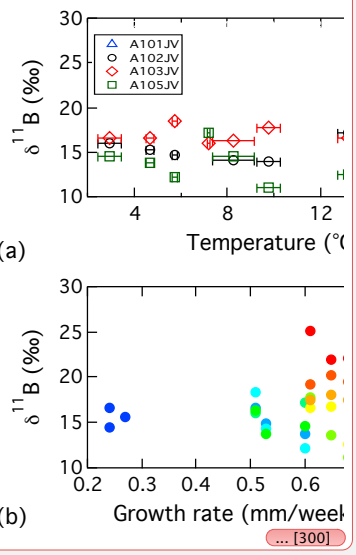

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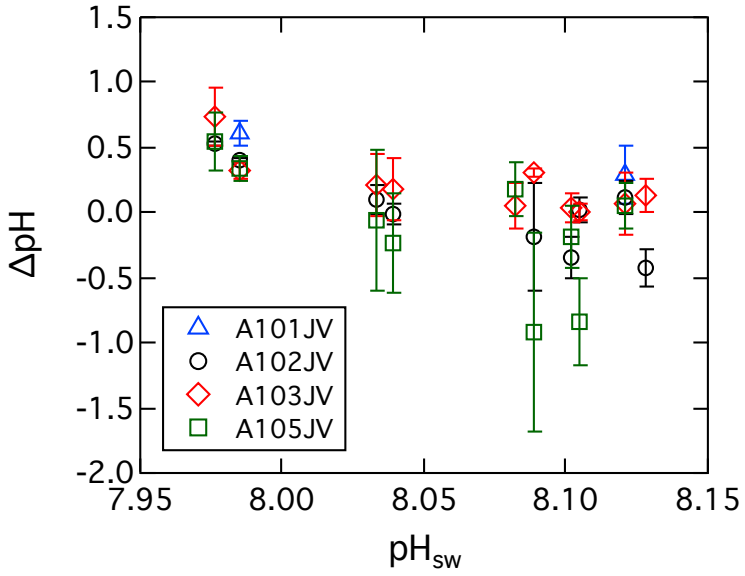

Figure 7 The calculated pH discrepancy ($\Delta pH = pH_{shell} - pH_{sw}$) shows a statistically significant negative relationship to pH_{sw} ($R^2 = 0.35$; p-value ≤ 0.001). The negative correlation supports the argument that *A. islandica* regulate their EPF pH for calcification. The shell calcification pH (pH_{shell}) were calculated based on in-situ water temperature $\alpha = 1.0272$ (Klochko et al., 2006).

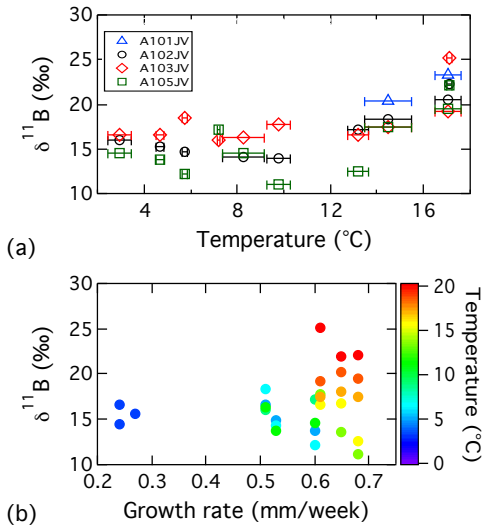

Figure 8 The comparisons between the shell $\delta^{11}B$ to (a) the corresponding culture water temperature and (b) the growth rates for individual shells. Colors shown in (b) represent the temperature corresponded to each data point, with low temperature in blue to high temperature in red.

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