

Interactive comment on “Environmental controls on the boron and strontium isotopic composition of aragonite shell material of cultured *Arctica islandica*” by Y.-W. Liu et al.

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Response to the referees

Anonymous Referee #1

This article presents B and Sr isotope data in *Arctica islandica* to decipher any environmental parameter effects on these proxies. I found the data very interesting, but I think that the discussion should be pushed 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).

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We thank the anonymous referee for providing the helpful and thoughtful comments. For the Sr isotopes data, we think it is also closely related to the work to investigate the environmental controls to boron incorporation in *A. islandica* shell. Especially in the coastal region, fresh water input can potentially change the water isotopic composition in seawater. We do need constraints to the seawater isotopic composition. Although $^{87}\text{Sr}/^{86}\text{Sr}$ has been widely used to determine the water sources, it hasn't been evaluated if the proxy would work in *A. islandica*. As boron and strontium both have a 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 in future applications of boron isotopic composition in *A. islandica* in a region without knowing if there are any changes in water source when no water sample is available. In addition to radiogenic Sr isotopic ratios, it has also been suggested that $\delta^{88}/^{86}\text{Sr}$ may reflect growth effects in biogenic carbonate. There is no $\delta^{88}/^{86}\text{Sr}$ data reported in shell yet so that we also want to test if $\delta^{88}/^{86}\text{Sr}$ in *A. islandica* would show growth-related fractionation, which might help to differentiate the influences from vital effects or other environmental factors. We think it is important to understand how these 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 $\delta^{11}\text{B}$ to pH conversion and recalculated our results using the $\delta^{11}\text{B}_{\text{sw}}$ of our seawater results instead of the $\delta^{11}\text{B}_{\text{sw}}$ from Foster et al. (2010). No significant changes were made to the pH values, but the correlation $R^2 = 0.34$ is updated

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to $R2 = 0.35$. 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 $\delta^{11}\text{B}$ -pH proxy in a new species of marine carbonate later in the same paragraph.

P2983, L10: As it is an 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 $\delta^{11}\text{B}$ values are higher than the one determined by

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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).

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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 $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ -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 $\text{pH}(\text{shell})$ and the DpH . I think that 1 significant figure is sufficient.

We added in the table.

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C1524/2015/bgd-12-C1524-2015-supplement.pdf>

Interactive comment on Biogeosciences Discuss., 12, 2979, 2015.

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