Dear Reviewers,

Thank you for your patience and your comments on the manuscript. We are grateful for your time and believe the feedback has improved the manuscript. We hope you find it suitable for publication.

This version has incorporated all of your comments. As suggested, we developed and re-formatted section 5.2 following the structure proposed by J. Farmer and we believe that it is written more clearly and will be easier for the reader to follow.

As suggested by M. Henehan, due to evidence of size-fraction effects on the $\delta^{11}B_{carbonate}$ for *G. ruber*, we made a linear regression based only on smaller size fractions. The resulting calibration did not show a significant change in the sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ compared to culture experiments (Henehan et al., 2013) but showed an offset of ~ -0.4‰.

The regression on smaller size fractions for *T. sacculifer* did not show a significant offset from the calibration from a culture study (Martinez-Boti et al., 2015b), which supports our discussion for *T. sacculifer* in the WEP.

The anonymous reviewer (AR) was concerned that although both *O. universa* and *T. sacculifer* have overlapping calcification depths at sites FC-02a and WP07-a, they record different $\delta^{11}B_{carbonate}$ signatures. We attribute the difference in $\delta^{11}B_{carbonate}$ to the different photosymbiosis characteristics of each species, and discuss this.

We also thank the AR for the note regarding gender assumptions during this process.

Best, Regards,

Report #1
Submitted on 02 Dec 2019
Referee #1: Jesse Farmer, jesse.farmer@princeton.edu

Revision review by Jesse Farmer

Guillermic et al. have made great progress in revising their manuscript. The introduction, background, materials and methods and results are publishable with very minor revisions. However, the manuscript loses focus and cohesiveness in the discussion, where the text becomes quite difficult to read and understand in its current iteration. I do note that, to my reading, this is an issue only with the writing presentation; the technical aspects of the discussion are sound and the figures are generally excellent and supportive of the text. Still, unfortunately I cannot yet recommend this for publication until the discussion text is improved. I encourage the coauthors to churn through a few rounds of revision to the discussion, with a particular focus on English grammar, and have provided detailed comments below that hopefully aid their work. I look forward to approving the revised manuscript for publication.

L84. Change to "samples from sites that are currently in quasi-equilibrium with the atmosphere" (less ambiguous)
Changed

L125-127. Suggest change to "Furthermore, d11B differences between foraminifera species inhabiting waters of the same pH makes the acquisition of more coretop and culture data essential for applications of the d11B-pH proxy."
Changed

L149. State here which fractionation value you use in this study, e.g., "We use the fractionation of 27.2 ‰ from Klochko et al. (2006) in this study."
Changed

L176-177. Be a little more specific here, e.g., "The extent to which these results apply to the planktonic foraminifera studied here are not known. Nonetheless, pH modulation of the calcifying fluid may influence the d11B of planktonic foraminifera."
Changed

Section 2.5. Please clarify- To what extent are these depth and habitat preferences global? Do foraminifera can show regional deviations in their depth & habitat preferences? Do we know? Many of the referenced studies of foraminifera habitats focus on the tropical/subtropical Atlantic.
"Although the studies listed above showed evidence for species-specific living depth-habitat affinities, recent direct observations showed that environmental conditions (e.g. temperature, light) was locally responsible for the variability in the living depth of certain foraminifera species in the eastern North Atlantic (Rebotim et al., 2017). The same study showed evidence for a correspondence between living depth habitat and indirectly-derived calcification depth, supporting the approach utilized in this study. "

L232. Change “drilled” to ”recovered” or “cored”. It is only appropriate to say “drilled” when a drilling system was used for core recovery (as is the case for ODP/IODP)
Changed for “cored”

L255. Good points on the response to my comment; please incorporate your response into a sentence in the manuscript here.
L256. “Hydrochloric acid was used to allow complete dissolution of the sample including Fe-Mn oxide and hydroxides if present. No matrix effect resulting from the mix HCl/HF was observed on the $\delta^{11}B$.

L266. Typo, should read “3.5”
Fixed

L269. Change to “70 uL of carbonate sample dissolved in 1N HCl was loaded...”. This gets around the ambiguity of acid used in my above comment on L256-257.
Changed

L289. Remove “internal”
Removed

L291. Change “boron isotopes liquid standard” to “boric acid standard”
Changed

L303. Again on the 1N HCl dissolution from L256-257. If I follow your protocol, you have a foram aliquot dissolved in 1N HCl, to which you have added HNO3 and HF for the ICP-MS measurement. Was HCl added to the standards to properly matrix-match? Or was the volume of HCl sufficiently small that you ignored it? Please specify.
The volume of HCl was sufficiently small (<1%) to be ignored.
Line 205 “any matrix effect (Misra et al., 2014b), the remaining HCl (<1%) was negligible.”

L339. Suggest “during their growth” in lieu of “along their ontogeny”
Removed instead following reviewer 2 comment. “We applied (based on uncertainties of our measurements) an uncertainty of ±10m for calcification depths > 70 m and an uncertainty of ± 20 m when calcification depths < 70 m.”

L339-341. Are these uncertainties truly representative of foram depth migration during their lifespan, or are they more indicative of uncertainty in different measurements of foram depth habitats? Please specify.
“Direct observations of living depths of foraminifera remain limited. However, the depth uncertainties reported here are in line with the uncertainties calculated based on direct observations in the eastern North Atlantic which give a standard error on average living depths ranging from 6-22 m for the same species (Rebotim et al., 2017).”

Section 4.1. This is a fair response to my comment; please incorporate this response into the text by adding a paragraph in Section 3.8. It is certainly fine to use a best guess and reasoned approach to derive CDs, as long as the reader is aware of your approach. (Note- it might also

help to mock up a figure showing the data in Tables S6 and S7).

"Because both methods have their uncertainties (in one case, use of taxon-specific calibrations, and in the other, analytical limitations), both estimates of calcification depth were compared to published values for the basin, and where available, for the same site (Table S6). To select which calcification depth to use for further calculations, we first looked at CD_1, CD_2 and CD_3. If, two CDs were similar we selected that one, if CD_1 and CD_2 were different we chose literature values (CD_3) when available. For some less studied species, like *G. tumida, G. menardii* or *P. obliquiloculata,* CD_3 was not always available but showed good correspondence with our CD_2, moreover due to availability of Mg/Ca-temperature taxon-specific calibrations we preferentially use CD_2 for those species."

Section 4.2
To what extent are your foraminifera samples and those from the literature in Fig. 5 from different size fractions? If so, given the noted d11B differences between size fractions, is it worth regressing against literature data from different size fractions? How much of the "large uncertainty given variability in the data" (L399) might reflect size class differences? Please address in the text.

We have added more informations to the section 4.2.1. for *G. ruber*. Results can be in line with a size fraction effect for *G. ruber*, but not for *T. sacculifer*. However, no significant differences are observed yet between the different calibrations due to the limited datasets.

Starting line 400: "Samples were picked from the 250-300 µm fraction, except for the WEP sites where they were picked from the 250-400 µm fraction. Weight per shell averaged 11 ± 4 µg (n=4, SD) although the weight was not measured on the same sub-sample analyzed for $\delta^{11}B$ and trace elements or at the WEP sites. In comparison to literature, the size fraction used for this study was smaller: Foster et al. (2008) used the 300-355µm fraction, Henehan et al. (2013) utilized multiple size fractions (250-300, 250-355, 300-355, 355-400 and 400-455 µm) and Raitzsch et al. (2018) used the 315-355 µm fraction.

Our results for *G. ruber* (Fig. 5) are in close agreement with published data from other core-tops, sediment traps, tows, and culture experiments for $\delta^{11}B_{borate}$>19 ‰ (Foster et al., 2008, Henehan et al., 2013, Raitzsch et al., 2018). However, the two datapoints from $\delta^{11}B_{borate}$<19 ‰ are lower compared to previous studies. Elevated $\delta^{11}B_{carbonate}$ values relative to $\delta^{11}B_{borate}$ has been explained by the high photosynthetic activity (Hönisch et al., 2003; Zeebe et al., 2003). Three calibrations have been derived (Table 3). Linear regression on our data alone yields a slope of 1.12 (±1.67). While this regression is not significantly different from a 1:1 line, the uncertainty term are significant given limited data in our study. Therefore, the sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ of our linear regression is not statistically different from 1, the uncertainty on this regression is important due to our small dataset, thus not inconsistent with the low sensitivity trend of the culture experiments from Sanyal et al., (2001) or Henehan et al., (2013). The second calibration made compiling all data from literature shows a sensitivity similar (e.g. 0.46 (±0.34) to the one recently published by Raitzsch et al., (2018) (e.g. 0.45 (±0.16), Table 3). The third linear regression made only on data from the 250-400 µm fraction from our study and from the 250-300 µm from Henehan et al. (2013) yields a slope of 0.58 (±0.91) similar to culture experiments from Henehan et al., (2013) (e.g. 0.6 (±0.16), Table 3). This third calibration is

offset by ~ -0.4 ‰ ($p>0.05$) compared to culture calibration from Henehan et al. (2013). The variability in our weight per shell based data from Henehan et al., (2013) can potentially imply a deviation down to 1‰ relative to its calibration line, which can be in line with the maximum deviation observed in our data (~1.2 ‰) and not inconsistent with a size effect explaining the offset in our calibration.

Line 431: "It is also noticeable that *T. sacculifer* (w/o sacc) samples from the WEP have a $\delta^{11}B_{carbonate}$ close to expected $\delta^{11}B_{borate}$ and are significantly lower compared to the combined *T. sacculifer* of other sites ($p=0.01$, unpaired t-test). When doing the regression using data from the 250-400 µm fraction, our results are not significantly different from the regression through data that combine all size fractions (Fig. 5).

Also, suggest changing " fall (above/below) the 1:1 line" to "exhibit (higher/lower) d11B compared to expected d11B_borate at their collection location" throughout the text. It is less confusing and more precise. (see L396, 400)

Changed throughout the text

Section 4.2.1 G. ruber. This section is confusing as currently written. Some rephrasing ideas:

• L383: Rephrase to "However, our two datapoints from d11B_borate < 19 ‰ are lower compared to previous studies." "Lighter d11B" is not correct; use either "lighter B isotopic composition" or "lower d11B".

Changed

• L383-384: Regarding the comment from M. Henehan and response, are your samples from different size fractions than

I think I have given more informations in this section.

• L384-385: "Whilst..." Delete this unnecessary sentence. Deleted

• L385-386: "The positive offset from the 1:1 curve..." change to say elevated d11B foram values relative to d11B_borate. Changed

• If you want to discuss the properties of the calibration curves, you should state the curves in the text for the reader. You should say something like you do for T. sacculifer on L396-397: "Linear regression on our data alone yields a regression of _____. While this regression is not significantly different from a 1:1 line, the uncertainty terms are significant given limited data in our study. Therefore, our data are not inconsistent with the low sensitivity trend.... (append the rest of the paragraph as written)".

Line 410: "Three calibrations have been derived (Table 3). Linear regression on our data alone yields a slope of 1.12 (±1.67). While this regression is not significantly different from a 1:1 line, the uncertainty term are significant given limited data in our study. Therefore, the sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ of our linear regression is not statistically different from 1, the uncertainty on this regression is important due to our small dataset, thus not inconsistent with the low sensitivity trend of the culture experiments from Sanyal et al., (2001) or Henehan et al., (2013). The second calibration made compiling all data from literature shows a sensitivity similar (e.g. 0.46 (±0.34) to the one recently published by Raitzsch et al., (2018) (e.g. 0.45 (±0.16), Table 3). The third linear regression made only on data from the 250-400 µm fraction from our study and from the 250-300 µm from Henehan et al. (2013) yields a slope of 0.58 (±0.91) similar to culture experiments from Henehan et al., (2013) (e.g. 0.6 (±0.16), Table 3)."

L400. Remove “below the 1:1 line” as no data are significantly below this line.
“close to” is fine. Can you indicate the WEP samples on this plot with a star or other indication?
Changed, I have highlighted the WEP samples in Fig. 5 for *T. sacculifer*.

L408-409. Rephrase to “, and is not significantly different from ($p > 0.05$) the O. universa calibration previously reported by Henehan et al. (2016) (0.95 ± 0.17).”
Changed

L413. “For O. universa and all deep-dwelling species,”
Changed

L417. Change “may remain” to “remains”
Changed

L430. Typo T. sacculifer (sacc)
Fixed

L432-433. What do you mean by interspecific B/Ca ratios? Please elaborate. I do not think it comes as any surprise that B/Ca ratios are different in different foraminifera species.
This has been changed to: “This study supports species-specific B/Ca ratios as previously published (Yu et al., 2007; Tripati et al., 2009, 2011; Allen and Hönisch, 2012; Henehan et al., 2016).”

L441-444. Confusing. Please split into two sentences, with one about core site depth and one about calcification depth. Also please note that you see a weak decrease in B/Ca with increasing calcification depth, although it is significant ($p<0.05$).
“When comparing data from all sites together, a weak decrease in B/Ca with increasing calcification depth is observed ($R^2=0.11$, $p<0.05$, Fig. S4). A correlation also exists between B/Ca and the water depths of the cores (not significant, Fig. S4).”

L454. Typo (w/o sacc)
Fixed

L487-488. Instead of saying seasonality is not important, rephrase to “seasonality is of relatively minor impact on the carbonate system parameters at the sites we examined.”
Changed

L499-503. Specify symbiont photosynthesis
Added

L502-503. lower/lowest
Changed: “Dinoflagellate-bearing foraminifera (*G. ruber, T. sacculifer* and *O. universa*) tend to have a higher symbiont density and photosynthesis activity while *P. obliquiloculata, G. menardii* and *N. dutertrei* have lower symbiont density and *P. obliquiloculata*, *N. dutertrei* lowest photosynthetic activity (Takagi et al., 2019).”

L508-549. This is difficult to understand as written and needs revising, otherwise these points will be completely lost by the reader.
L508-513. Present items in logical order: First what you observe (low d11B of deep-dwelling species relative to d11B borate), then context (lower symbiont density and photosynthetic activity in these forams), and combine this into an interpretation (lower symbiont activity leads to lower microenvironment pH and may explain the low d11B of these taxa).
We reformatted this section according to your suggestions.

L513. "and" instead of "et"
Changed

L514 and throughout. Do not use "they" or any pronouns, as it is not clear to what you are referring. Use the noun itself. Here, "they" = "symbionts"
Changed

L518. Be specific. "A deeper depth habitat will reduce the light intensity the symbionts receive, and as a consequence may lower symbiont photosynthetic activity, possibly reducing pH in the microenvironment surrounding the foraminifera".
Changed

L521. What does "basically support" mean? Either the trend supports the fact or it does not.
Fixed

L524. Start a new paragraph here. "To test if the d11B signature was inferred to a light driven"- what does this mean?
I changed this section according to your previous comment.

L524-525. change to "we have independently calculated foraminifera (calcification?) dpeth based on various light insolation culture experiments and the microenvironment ΔpH derived from our data".
Changed

L535. Change to Microenvironment ΔpH
Changed

L537-541. Please rephrase these sentences. I think this may be a key point, but I cannot follow it as currently written.
We have edited this paragraph.

L542. Change to "G. menardii and G. tumida are similar..."
Changed

L547-549. Need to add some commas here to make this understandable.
We changed for: "We can also note that *P. obliquiloculata,* which has the lowest symbiont density and photosynthetic activity (Takagi et al., 2019), has the lowest microenvironment pH

compared to other deeper-dweller species, supporting this respiration driven microenvironment”

L555-557. “more borate ion may be incorporated.... more boric acid may be incorporated.” This is just a hypothesis.
Changed

L560-572. Again, this is difficult to read as currently written. Please revise and particularly correct English grammar.
Edited

L582. Change to “which supports previous paleo-reconstructions using existing calibrations of d11B_carbonate to d11B_borate”.
Changed

L583. Which observations are these from Henehan et al. (2016)? Be specific.
Edited: “Our $\delta^{11}B_{carbonate}$ date and their sensitivity to $\delta^{11}B_{borate}$ for *O. universa* support previous data from Henehan et al., (2016).”

L590-592. Please rephrase and be much much more specific, I have no idea what you are trying to say here. What do you mean “add a weight/shell”? Is 11 µg per shell small or large? Context needed!
I removed this part, as I have developed it in the other sections 4.2.1 and section 5.4.

L594. What correction? What coretop study?
“Results for *G. ruber* are the most scattered, potentially due to difference in test sizes (Henehan et al., 2013), or depth habitat, althought we can not exclude undocumented diagenetic effects. Results reaffirm the importance of working with narrow size fractions (Henehan et al., 2013), the utilization of calibrations derived from the same size fraction or use of offsets to take into account this size fraction effect, and the importance of core-top studies before paleo-application.”

L597. Typo on species
“We also find that for two species, the boron proxy is a relatively straightforward recorder of ambient pH, with sensitivities close to unity for *O. universa and N. dutertrei*.”

References. Please double check these and their formatting. Some citations missing and formatting issues.
Checked

Figures.
Fig. 2. Change figure and caption to B(OH)3 and B(OH)4- to match main text. Note typo on Figure α, should be 1.0272.
Changed

Report #2
Submitted on 02 Dec 2019
Anonymous Referee #2

This is my second review of this MS. As it stands, the edits are generally ok, but in some cases the authors chose to only reply to edits in the response and not always insert their response into the MS. Sometimes this was ok, but if a reviewer requests an explanation, the response should generally be incorporated into the manuscript. Reviewer 1 should also review the edits as some of Dr. Farmer's suggestions were also not implemented into the revised MS. I have specific comments below. The new section on symbiosis and the findings of Tagaki was very poorly written and should be edited prior to final publication.

We have reviewed the edits and incorporated them, including the explanation for the depth habitat and the cleaning. We also have rewritten section 5.2.

As an aside: please do not assume that anonymous reviewers are CIS gendered males. The opening response to my review was "We wish to thank this reviewer for HIS thorough review of our manuscript and HIS helpful comments". Instead: We thank the reviewer for helpful comments and suggestions.

We thank the reviewer for pointing this out.

There is no evidence that foraminifers change their symbiont assemblages to ones more similar to what are found in deeper dwelling species. In addition, the paragraph beginning on line 195 where differences in the boron isotope data between T. sacculifer, G. ruber, and O. universa is explored states that O. universa exhibits lower d11B because it lives deeper in the water column, but the depth habitats chosen for these species IN THIS STUDY overlap or are at the same depth according to table S7.

Line 176: Change: "We acknowledge this is speculative as it is based upon benthic foraminifer experiments" to "We acknowledge this process may not be the same for planktic species as these findings were based upon benthic foraminifer experiments"

This has been changed from "The extent to which these results apply to the planktonic foraminifera studied here are not known. Nonetheless, pH modulation of the calcifying fluid may influence the $\delta^{11}B$ of planktonic foraminifera."

Section 3.3: the reviewers responded to my comment but did not add any additional text to the MS. The reason the full reductive cleaning protocol was used should be included in this paragraph so that other readers are aware of the study by Misra 2014 and the purpose of the full cleaning protocol.

This states: "Samples were then cleaned using full reductive and oxidative cleaning (Boyle and Keigwin, 1985; Barker et al., 2003). We utilized the reductive cleaning because some of the sites where not previously studied and previous comparison have shown no effect on B/Ca (Misra et al., 2014b), nevertheless, Fe-Mn oxide and hydroxides can result in non-negligible content of Mg and B contamination. Overall, the samples did not present high Mn concentration. Reductive cleaning leads to a decrease in Mg/Ca which would result in deeper CDs, which is not the case when comparing with CD1 and CD3, we then no longer assume this decrease problematic for the purpose of this study."

Line 339: I suggest removing the clause "As foraminifera can migrate in the water column along their ontogeny" because it is misleading. Foraminifers can occupy a deeper depth habitat at the end of their ontogeny, but as written it still seems to imply that foraminifers migrate up and down, which they likely do not. Removing this clause bears no impact on the rest of the sentence.
Removed

Line 456: Again: I think this should be more carefully written. The use of the word "migrate" with foraminifer depth habitats usually implies that they move up and down in the water column, which they do not. This should be reworded to state that at the end of their life cycle they often transition to deeper waters prior to gametogenesis.
Changed for: "We note that calculation of absolute calcification depths can be challenging in some cases as many species often transition to deeper waters at the end of their life cycle prior to gametogenesis"

Line 495: G. ruber, T. sacculifer and O. universa do not have chrysophyte algal symbionts, only dinoflagellates. There is no mention of chrysophytes in the Anderson and Be paper nor in Spero 1987. N. dutertrei has pelagophyte symbionts not chrysophytes, confirmed using genetics, see Bird et al., 2018.
Thank you for those inputs. We have added the pelagophyte symbionts for *N. dutertrei.*

Paragraph beginning line 500 is poorly worded.
The substance does not change, but we have edited it.

Line 509: have microenvironments with lower "pH" than ambient seawater (insert pH)
Changed
Line 513: 'et'?
Changed
Line 514: insert 'a' between also and function.
Added
Line 515: Should "for the purpose of this study" be a new sentence?
Split in two sentences
Line 537: Tagazaki should be Tagaki.
Changed
Line 540: specie is spelled incorrectly
Changed

Paragraph beginning on line 540: O. universa in this study occupy similar depths to the G. ruber and G. sacculifer. Thus, I do not agree with the discussion here.
That is actually where Tagaki's study is relevant, as it shows that each species has their own characteristics in terms of photosymbiosis. What we found interesting is that potentially, *T. sacculifer*, which seems to have a higher potential for photosynthesis, might also be more sensitive to changes of insolation depending of its habitat in the water column. Also, its photosynthetic activity might be more effective at depth due to its higher symbiont density, reflected in higher δ^{11}Bcarbonate than *O. universa* which has a lower potential for

photosynthesis **for the same depth.**

Line 560: "*T. sacculifer* has the potential to support more photosynthesis due to its higher symbiont density. Higher photosynthetic activity is observed compared to other species potentially supporting higher symbiont/host interactions (Tagaki et al., 2019). Those results could be in line with a greater sensitivity of *T. sacculifer's* photosynthetic activity with changes in insolation/water depth."
Line 577: "The low $\delta^{11}B_{carbonate}$ of *O. universa* compared to *T. sacculifer* for the similar calcification depth at few sites (e.g. FC-02a, WP07-a) might reflect difference in photosynthetic potential between the two species, Tagaki et al. (2019) showed a lower photosynthetic potential for *O. universa* compared to *T. sacculifer*."

Section 5.4 is very confusing. It seems haphazardly put together and some sentences are poorly structured. Paragraph 580 could be deleted.
We have edited this part following suggestions from Jesse Farmer

Report #3 Henehan

The manuscript is greatly improved from its previous incarnation. Although it is for the previous reviewers to judge whether their comments are adequately dealt with, my sense is that they seem to be largely adequately discussed.

I am personally still a bit unconvinced in the point of plotting a calibration line through data that come from different size fractions for G. ruber and T. sacculifer, when there is clearly a known size fraction effect which is muddling the pH (/borate) signal and potentially influencing the slope. I guess particularly also in this study using such wide size fractions (perhaps by necessity due to sample limitations) means that there is always the possibility that the size distribution could have varied within this range and introduced inter-site differences that change the slope. The authors now provide some shell weight data to inform a little as to the possibility of there being inter-site differences in the sampled shell size fraction – I presume because there are no photos of the samples to measure the actual size distribution. This is at least something, but just telling us that the average shell weight varied is only of limited use- why not give us this data in the tables, so we can see if those boron samples that diverge most strongly from the existing calibration line of ruber/sacculifer were indeed on average the smallest test sizes? It would be helpful.

Unfortunately, no weight per shell determinations was done on the WEP samples. Also, the weight per shell we discuss in the manuscript are from other sub-samples picked for oxygen and carbon isotopes only.
We have derived the calibrations from the smaller size fractions, results for *G. ruber* can be in line with a size effect on the δ^{11}Bcarbonate, same sensitivity to $\delta^{11}B_{borate}$ but offset of ~0.4‰ from your culture calibration.

There are also still quite a few oddities in sentence structure, word choice, spelling/typos which I will outline below.

Otherwise, with these edits/additions, I have no objections the paper being published. Congratulations to the authors on some nice work.

Line 94: Anagnostou et al. (2016) also did this for core-top and Eocene samples.
Added

Line 144: B(OH)3 and B(OH)4-, as used here, are the more common notations for these aqueous species.. I would favour using these. But then for whatever reason in Fig. 2 and its caption (but I think nowhere else?) you have called them H4B(OH)3 etc. I think you should be consistent so the unfamiliar reader can relate what you are talking about better. Why not stick to what you have here to be more consistent with the literature?
Changed

Line 157: as far as I am aware Noireaux et al 2015 did not look at taxonomic differences in

forams- rather inorganic carbonate polymorphs. Either rephrase the sentence or delete the reference.
We removed it, this is a typo from previous version.

Line 196: within the parentheses, insert comma after the subscript borate, followed by 'hereafter'
added

Line 204: Note that the culture slopes of T. sacculifer and O. universa are also within error of 1, when one propagates the error on each datapoint (which for universa in particular is rather large).
"More core-top and culture calibrations are needed to refine those slopes and fully understand why different slopesif significant differences are observed, which is part of the motivation for this study"

Line 273: I may be being ignorant, but I have never heard of H or X sample cones, only skimmer cones. Is this correct here?
Thank you for picking on that, you are right, skimmer are X or H but sample are normal or jet. We utilized "normal" sample cones.

Line 282: delete 'the' before 11B.
Removed

Lines 285, 293, possibly elsewhere: Inconsistent nomenclature of JCp-1 coral standard. How I just wrote it is the official notation.
Changed

Line 300: Subscript needed for 3 on nitric acid.
Changed

Line 329: 'prerequisite' would be a better word than 'postulate'.
Changed

Line 331: apostrophe after the 's' of species.
Added

Line 426: typo in obliquiloculata.
Changed

Line 427: What do the authors mean by 'This study supports interspecific B/Ca ratios'.. ? Rewrite.
" B/Ca data are species-specific and consistent with previous work (e.g., compiled in Henehan et al., 2016) with ratios higher for *G. ruber* > *T. sacculifer* (sacc) > *T. sacculifer* (w/o sacc) > *P. obliquiloculata* > *O. universa* > > *G. menardii* > *N. dutertrei* > *G. tumida* > *G. inflata* > *N. pachyderma* > *G. bulloides* (Fig. 7)."

Line 451: correct names are 'Kemle-von Mücke and Oberhänsli'
Changed

Line 486: Is this statement really true? See Shaked and de Vargas (2008), doi:10.3354/meps325059
I removed this statement and added the reference

Line 517-518: Sentence poorly written. Not exactly sure what it is the authors want to say.
We have reedited this part

Line 532: missing s on species.
Added

Line 537: 'deep-dwelling species' or 'deeper-dwelling species', not 'deep dweller species'
Changed thorough the text

Line 546: Joji Uchikawa, not Ushikawa.
Changed thorough the text

Lines 550-551: Not sure it's wise to pool all different size fractions like this- what does this truly tell you about pH?
We made regressions based on the different size fractions.

Line 552: missing 'and' before 'the observation'? Also 'is', not 'are'.
Changed

Line 567-568: "the main interest with utilizing boron-based proxies relates to the…" poorly written sentence. "The main aim of utilizing" or "The primary applications of boron-based proxies are"?
Changed for: "The main aim of utilizing boron-based proxies relates to the reconstruction of past oceanic conditions"

Line 567-575: Odd paragraph separation, and first line of second paragraph in line 572 isn't particularly self-contained. In line 574: 'which is also supporting of' should be 'which supports'.
Changed

Lines 576-578: I would suggest that Chalk et al. (2017)'s accurate downcore data would suggest there isn't necessarily need for a calibration from the same location or setting? Is it fair to make such a bold statement, and advocate for every downcore reconstruction from now on to have a calibration point from the same setting, based on your sacculifer data alone (that could in theory be different in some places just because the size distribution isn't exactly the same in all sample sites)?
Yes, only the WEP presents those low d11B in our data, I think it is still best explained by their calcification depths. At this stage, for reconstruction in the WEP, correction / calibration will have to be applied. Nevertheless, this is reassuring to observe that the sensitivity of the calibrations for G. ruber is the not significantly different between size fractions, which would make the use of an offset ok for the reconstruction.

Lines 579-580: What correction do you mean? And why? Correction relative to what, the culture calibration?
"Results for *G. ruber* are the most scattered, potentially due to difference in test sizes (Henehan et al., 2013), or depth habitat, althought we can not exclude undocumented diagenetic effects. Results reaffirm the importance of working with narrow size fractions (Henehan et al., 2013), the utilization of calibrations derived from the same size fraction or use of offsets to take into account this size fraction effect, and the importance of core-top studies before paleo-application."

Line 583: what is meant by 'our sample add a weight/shell'?
Edited

Line 584: Suggest "Greater divergence" rather than "The higher divergence"
Changed

Line 588: insert 'isotope-pH' after boron.
Added

Line 592 (and elsewhere): in situ is not hyphenated.
Addressed

Lines 592-594: This sentence could be rewritten to explain a bit more clearly what you did.
This section has been reedited

Line 600: 'Sparsest' seems an odd choice of word- implies not only that there is more scatter, but there is also not as much data. 'most scattered' might be better?
Changed

Line 606: 'can impact' rather than 'impacts', as for example your deep dwellers are not very affected.
Changed

Line 614: insert 'similarly' before respiration
Added

Line 617: "those calibrations" – which calibrations are you referring to?
"the calibrations published to date"

Line 618: 'taxon-specific', not 'taxa-specific', I would think here?
Changed

Figure 5: Include the size fraction in each ruber and sacculifer dataset's legend entry, not just one.. and why are the ruber culture data not plotted?
Added and plotted the culture data

Figure captions: In general the figure and table captions are a little spartan, and could be a bit

more in-depth and informative. Examples, for instance:

Fig. 4 caption, 'Pre-industrial data' is vague.. hydrographic data (also 'for the sites', rather than 'of the sites')? Are these actual measurements or interpolations? What are the dotted lines? Why are the temperatures seasonally defined but nothing else?
We utilized the GLODAP database that does not resolve seasonal variations. We have added "Dotted lines are the calculated uncertainties based errors on TA and DIC from the GLODAP database."

Fig.5 caption: d11Bborate was, not were. Are the measurements from core-tops, tows, cultures, etc? Are these just the MC-ICPMS data, if so state, so it's clear why there's no NTIMS measurements in here? How are the error bars defined, are they one sigma or two?
" Boron isotopic measurements of mixed-layer foraminifera plotted against the δ11Bborate. δ11Bborate was characterized by determination of the calcification depth of the foraminifera utilizing data presented in Fig. 4, A) G. ruber, B) T. sacculifer, C) O. universa. Mono-specific calibrations (Table 3) and error bars on δ11Bborate were derived utilizing the wild bootstrap code from Henehan et al. (2016), errors on the δ11Bcarbonate for this study are reported as 2σ of measured AE121 standards during the session of the sample. Calibrations were also derived on the 250-400 size fraction for G. ruber and T. sacculifer (black dashed lines). Data reported on those graphs have been measured with an MC-ICP-MS."

Fig. 6: 'plotted', not 'plot'.
Changed

Fig. 8: watch your superscripts. Does the light attenuation coefficient have a unit? State how the calcification depth marked by the grey band was derived.
So, no units were reported in Rink et al., 1998, but we believe it may be m^{-1}

Fig. 10: say a little bit more about what the 'reconstructed' values come from and how they were calculated.
" **Figure 9:** Water depth pH profiles reconstructed at every site applying the mono-specific calibrations derived from our results (Table 3). Figure is showing measured $\delta^{11}B_{calcite}$, $\delta^{11}B_{borate}$ calculated according to different calibrations (see Table 3 and text), calculated pH based on $\delta^{11}B$ ($pH_{\delta 11B}$) and pCO_2 calculated from $pH_{\delta 11B}$ and alkalinity.
Figure 10: Evaluation of the reconstructed parameters, $\delta^{11}B_{borate}$, pH and pCO_2 versus *in situ* parameter calculated in Fig. 9 (based on $\delta^{11}B$ and alkalinity). The recalculated parameters are consistent with *in situ* data, except for *G. ruber*, this variability might be explained by the different test sizes within our size fractions."

Table 2: Is it necessary to have a column for the cleaning method when it's the same for every sample?
We have removed this column.

Quick question- Site A14 (to a lesser extent also FC-02a) has a really weird vertical pH gradient.. any idea what causes this?
We are not sure how to explain the A14 profile.

Résultats de la comparaison

Ancien fichier :

Maxence Guillermic coretop manuscript - 03092020.pdf

31 pages (736 KB)
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Total des modifications

1187

Comparaison du texte seulement

Contenu

795 remplacements
187 insertions
205 suppressions

Styles et annotations

0 style
0 annotations

Consulter la 1re modification (page 1)

Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO_2 gradients

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ABSTRACT

Boron isotope systematics of planktonic foraminifera from core-top sediments and culture experiments have been studied to investigate the sensitivity of $\delta^{11}B$ of their calcite tests to seawater pH. However, our knowledge of the relationship between $\delta^{11}B$ and pH remains incomplete for many taxa. Thus, to expand the potential scope of application of this proxy, we report $\delta^{11}B$ data for 7 different species of planktonic foraminifera from sediment core-tops. We utilize a method for the measurement of small samples of foraminifera and calculate the $\delta^{11}B$-calcite sensitivity to pH for *Globigerinoides ruber*, *Trilobus sacculifer* (sacc or w/o sacc), *Orbulina universa*, *Pulleniatina obliquiloculata*, *Neogloboquadrina dutertrei*, *Globorotalia menardii* and *Globorotalia tumida*, including for unstudied core-tops and species. The sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ (eg. $\Delta\delta^{11}B_{carbonate}/\Delta\delta^{11}B_{borate}$) in core-tops is consistent with previous studies for *T. sacculifer* and *G. ruber* and close to unity for *N. dutertrei*, *O. universa* and combined deep-dwelling species. Deep-dwelling species closely follow the core-top calibration for *O. universa*, which is attributed to respiration-driven microenvironments, likely caused by light limitation and/or symbiont/host interactions. These taxa have diverse ecological preferences and are from sites that span a range of oceanographic regimes, including some that are in regions of air-sea equilibrium and others that are out of equilibrium with the atmosphere. Our data support the premise that utilizing boron isotope measurements of multiple species within a sediment core can be utilized to constrain vertical profiles of pH and pCO_2 at sites spanning different oceanic regimes, thereby constraining changes in vertical pH gradients and yielding insights into the past behavior of the oceanic carbon pumps.

1. Introduction

The oceans are absorbing a substantial fraction of anthropogenic carbon emissions resulting in declining surface ocean pH (Fig. 1; IPCC, 2014). Yet there is a considerable uncertainty over the magnitude of future pH change in different parts of the ocean and the response of marine biogeochemical cycles to physio-chemical parameters (T, pH) caused by climate change (Bijma et al., 2002; Ries et al., 2009). Therefore, there is an increased interest in reconstructing past seawater pH (Hönisch and Hemming, 2005; Liu et al., 2009; Wei et al., 2009; Douville et al., 2010), in understanding spatial variability in aqueous pH and carbon dioxide (pCO_2) (Foster et al., 2008; Martinez-Boti et al., 2015b; Raitzsch et al., 2018), and in studying the response of the biological carbon pump utilizing geochemical proxies (Yu et al., 2007, 2010, 2016).

Although proxies for carbon cycle reconstruction are complex in nature (Pagani et al., 2005; Tripati et al., 2009, 2011; Allen and Hönisch, 2012), the boron isotope composition of foraminiferal tests is emerging as one of the more robust candidates (Hönisch et al., 2005, 2009; Ni et al., 2007; Foster et al., 2008, 2012; Bartoli et al., 2011; Henehan et al., 2013; Martinez-Boti et al., 2015b; Chalk et al., 2017). The study of laboratory cultured foraminifera has demonstrated a systematic dependence of the boron isotope composition of tests on ambient pH (Sanyal et al., 1996, 2001; Henehan et al., 2013, 2016). Core-top measurements on globally distributed samples also show a $\delta^{11}B$ sensitivity to pH with taxa-specific offsets from the theoretical fractionation line of borate ion (Rae et al., 2011; Henehan et al., 2016; Raitzsch et al., 2018).

Knowledge of seawater pH, in conjunction with constraints on one other carbonate system parameter (Total Alkalinity (TA), DIC (dissolved inorganic carbon), $[HCO_3^-]$, $[CO_3^{2-}]$), can be utilized to constrain aqueous pCO_2. Application of empirical calibrations for boron isotopes, determined for select species of foraminifera from core-tops and laboratory cultures, has resulted in accurate reconstructions of pCO_2 utilizing downcore samples from sites that are in quasi-equilibrium with the atmosphere at present. $\delta^{11}B_{carbonate}$ based reconstructed values of pCO_2 are analytically indistinguishable from ice core CO_2 records (Hönisch et al., 2005, 2009; Foster et al., 2008; Henehan et al., 2013; Chalk et al., 2017).

Therefore, the last decade has produced several studies aiming at reconstructing past seawater pH using boron isotopes to constrain atmospheric pCO_2 in order understand the changes in the global carbon cycle (Hönisch et al., 2005, 2009; Foster et al., 2008, 2012, 2014; Seki et al., 2010; Bartoli et al., 2011; Henehan et al., 2013; Martinez-Boti et al., 2015a, 2015b; Chalk et al., 2017). In addition to reconstructing atmospheric pCO_2, in a few studies, the $\delta^{11}B$ proxy has been applied to mixed-layer planktonic foraminifera at sites out of equilibrium with the atmosphere to constrain past air-sea fluxes (Foster et al., 2014; Martinez-Boti et al., 2015b). A small body of work has examined whether data for multiple species in core-top (Foster et al., 2008) and down-core samples could be used to constrain vertical profiles of pH through time (Palmer et al., 1998; Pearson and Palmer, 1999).

In this study, we make critical additions to the emerging pool of boron isotope data of core-top planktonic foraminifera from different oceanographic regimes, including data for species that have not previously been examined. We utilize a low-blank (15 pg B to 65 pg B), high precision (2sd on the international standard JCP-1 is 0.20 ‰, n=6) $\delta^{11}B_{carbonate}$ analysis method (down to ~250 µg $CaCO_3$), modified after Misra et al. (2014), to study multiple species of planktonic foraminifera from sediment core-tops that span a range of oceanographic regimes, including open-ocean oligotrophic settings and marginal seas. We constrain calibrations for different species, and compare results to published work (Foster et al., 2008; Henehan et al., 2013; Henehan et al., 2016; Martinez-Boti et al., 2015b; Raitzsch et al., 2018). We also test whether these data support the application of boron isotope

measurements of multiple species within a sediment core as a proxy for constraining vertical profiles of pH and pCO_2.

2. Background

2.1 Planktonic foraminifera as archives of seawater pH

Planktonic foraminifera are used as archives of past environmental conditions within the mixed layer and thermocline, as their chemical composition is correlated with the physio-chemical parameters of their calcification environment (Ravelo and Fairbanks, 1992; Elderfield and Ganssen, 2000; Dekens et al., 2002; Anand et al., 2003; Sanyal et al., 2001; Ni et al., 2007; Henehan et al., 2013, 2015, 2016; Howes et al., 2017; Raitzch et al., 2018). The utilization of geochemical data for multiple planktonic foraminifera species with different ecological preferences to constrain vertical gradients has been explored in several studies. The framework for such an approach was first developed using modern samples of planktonic foraminifera for oxygen isotopes, where it was proposed as a tool to constrain vertical temperature gradients and study physical oceanographic conditions during periods of calcification (Ravelo and Fairbanks, 1992).

Because planktonic foraminifera species complete their lifecycle in a particular depth habitat due to their ecological preference (Ravelo and Fairbanks, 1992; Farmer et al., 2007), it is theoretically possible to reconstruct water column profiles of pH using data from multiple taxa (Palmer and Pearson, 1998; Anagnostou et al., 2016). The potential use of an analogous approach to reconstruct past profiles of seawater pH was first highlighted by Palmer and Pearson (1998) on Eocene samples to constrain pH-depth gradients. However, in these boron isotope-based studies, it was assumed that boron isotope offset from seawater and foraminiferal carbonate were constant, which is an assumption not supported by subsequent studies (e.g., Hönisch et al., 2003; Foster et al., 2008; Henehan et al., 2013, 2016; Raitszch et al., 2018; Rae, 2018). Furthermore, $\delta^{11}B$ differences between foraminifera species that inhabit waters that are the same pH makes the acquisition of more core-top and culture data essential for applications of the proxy.

2.2 Boron systematics in seawater

Boron is a conservative element in seawater with a long residence time (τ_B ~ 14 Myr) (Lemarchand et al., 2002a). In seawater, boron exists as trigonal boric acid $B(OH)_3$ and tetrahedral borate ion $B(OH)_4^-$ (borate). The relative abundance of boric acid and borate ion is a function of the ambient seawater pH. At standard open ocean conditions (T = 25 °C and S = 35), the dissociation constant of boric acid is 8.60 (Dickson, 1990), implying that boron mainly exists in the form of boric acid in seawater. Since the pK_B and seawater pH (e.g., ~8.1, NBS) values are similar, it implies that small changes in seawater pH will induce strong variations in the abundance of the two boron species (Fig. 2).

Boron has two stable isotopes, ^{10}B and ^{11}B, with average relative abundances of 19.9 and 80.1 %, respectively. Variations in B isotope ratio are expressed in conventional delta (δ) notation:

$$\delta^{11}B\ (‰) = 1000 \times \left(\frac{^{11}B/^{10}B_{Sample}}{^{11}B/^{10}B_{NIST\ 951\text{-}a}} - 1 \right) \quad (1)$$

where positive values represent enrichment in the heavy isotope ^{11}B, and negative values enrichment in the light isotope ^{10}B, relative to the standard reference material. Boron isotope values are reported versus the NIST SRM 951 (Cantazaro et al., 1970).

$B(OH)_3$ is enriched in ^{11}B compared to $B(OH)_4^-$ with a constant offset between the two chemical species, within the range of physio-chemical variation observed in seawater, given by the fraction factor (α). The fractionation (ε) between $B(OH)_3$ and $B(OH)_4^-$ of 27.2 ± 0.6 ‰ has been empirically determined by Klochko et al., (2006) in seawater. Note, Nir et al., (2015) calculate this fractionation, using an independent method, to be 26 ± 1 ‰, which is within the analytical uncertainty of the Klochko et al., (2006) value.

2.3 Boron isotopes in planktonic foraminifera calcite

Many biogenic carbonate-based geochemical proxies are affected by "vital effects" or biological fractionations (Urey et al., 1951). The $\delta^{11}B_{carbonate}$ in foraminifera exhibits species-specific offsets (see Rae et al., 2018 for review) compared to theoretical predictions for the boron isotopic composition of $B(OH)_4^-$ (α=1.0272, Klochko et al., 2006). As the analytical and technical aspects of boron isotope measurements have improved (Foster et al., 2008; Rae et al., 2011; Misra et al., 2014; Lloyd et al., 2018), evidence for taxonomic differences have not been eliminated, but have become increasingly apparent (Foster et al., 2008, 2018; Henehan et al 2013, 2016; Noireaux et al., 2015; Foster et al., 2016; Rae et al., 2018; Raitzsch et al., 2018).

At present, culture and core-top calibrations have been published for several planktonic species including *Trilobatus sacculifer*, *Globigerinoides ruber*, *Globigerina bulloides*, *Neogloboquadrina pachyderma*, *Orbulina universa* (Foster et al., 2008; Henehan et al., 2013; Henehan et al., 2015; Sanyal et al., 1996; Sanyal et al., 2001). Although the boron isotopic composition of several species of foraminifera are now commonly used tools for reconstructing surface seawater pH, for other species, there is a lack of data constraining boron isotope sensitivity between foraminiferal carbonate and borate ion in seawater.

2.4 Origin of biological fractionations in foraminifera

Perforate foraminifera are calcifying organisms that maintain a large degree of biological control over their calcification space, and thus, mechanisms of biomineralization may be of significant importance in controlling the $\delta^{11}B$ of the biogenic calcite. The biomineralization of foraminifera is based on seawater vacuolization (Erez, 2003; de Nooijer et al., 2014) with parcels of seawater being isolated by an organic matrix thereby creating a vacuole filled with seawater. Recent work has also demonstrated that even if the chemical composition of the reservoirs is modified by the organism, seawater is directly involved in the calcification process with vacuoles formed at the periphery of the shell (de Nooijer et al., 2014). Culture experiments by Rollion-Bard and Erez., (2010) have proposed that the pH at the site of biomineralization is elevated to an upper pH limit of ~9 for the shallow-water, symbiont-bearing benthic foraminifera *Amphistegina lobifera*, which would support a pH modulation of a calcifying fluid in foraminifera. We acknowledge this is speculative as it is based upon benthic foraminifer experiments.

For taxa with symbionts, the microenvironment surrounding the foraminifera is chemically different from seawater due to photosynthetic activity (Jorgensen et al., 1985; Rink et al., 1998; Köhler-Rink and Kühl, 2000). Photosynthesis by the symbionts elevates the pH of the microenvironment (Jorgensen et al., 1985; Rink et al.,

1998; Wolf-Gladrow et al., 1999; Köhler-Rink and Kühl, 2000), while calcification and respiration decrease it (Equation 2 and 3).

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2 \text{ or } Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad \text{[calcification]} \quad (2)$$

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \quad \text{[respiration/photosynthesis]} \quad (3)$$

$\delta^{11}B$ in foraminifera is primary controlled by seawater pH, but is also dependent of the pH alteration of microenvironments due to calcification, respiration and symbiont photosynthesis. $\delta^{11}B$ should therefore reflect the relative dominance of these processes and may account for species-specific $\delta^{11}B$ offsets. Theoretical predictions from Zeebe et al. (2003) and foraminiferal data from Hönisch et al., (2003) highlighted the dominance of microenvironment pH in $\delta^{11}B$ signature of foraminifera. Their work also suggested that for a given species, there should be a constant offset observed between the boron isotope composition of foraminifera and borate ion over a large range of pH, imparting confidence in utilizing species-specific boron isotope data as a proxy for seawater pH.

Comparison of boron isotope data for multiple planktonic foraminiferal species indicate that taxa with high levels of symbiont activity such as *T. sacculifer* and *G. ruber* show higher $\delta^{11}B$ values than the $\delta^{11}B$ of ambient borate (Foster et al., 2008, Henehan et al., 2013, Raitzsch et al., 2018). The sensitivities ($\Delta\delta^{11}B_{carbonate}/\Delta\delta^{11}B_{borate}$ referred to as the slope) of existing calibrations suggest a different species-specific sensitivity for these species compared to other taxa (Sanyal et al., 2001; Henehan et al., 2013; Henehan et al.,2015; Raitzsch et al., 2018). For example, *Orbulina universa* exhibits a lower $\delta^{11}B$ than *in situ* $\delta^{11}B$ values of borate ion (Henehan et al., 2016), consistent with the species living deeper in the water column characterized by reduced photosynthetic activity.

It is possible that photosynthetic activity by symbionts might not be able to compensate for changes in calcification and/or respiration, leading to an acidification of the microenvironment. It is interesting to note that for *O. universa* the slope determined for the field-collected samples is not statistically different from unity (0.95 ± 0.17) (Henehan et al. 2016), while culture experiments report slopes of ≤ 1 for multiple species including *G. ruber* (Henehan et al., 2013), *T. sacculifer* (Sanyal et al., 2001), and *O. universa* (Sanyal et al., 1999). More core-top and culture calibrations are needed to fully understand why different slopes are observed, which is part of the motivation for this study.

2.5 Planktic foraminifera depth and habitat preferences

The preferred depth habitat of different species of planktonic foraminifera depends on their ecology, which in turn relies on the hydrographic conditions. For example, *G. ruber is* commonly found in the mixed layer (Fairbanks and Wiebe, 1980; Dekens et al., 2002; Farmer et al., 2007) during the summer (Deuser et al., 1981) whereas *T. sacculifer* is present in the mixed layer until mid-thermocline depths (Farmer et al., 2007) during spring and summer (Deuser et al., 1981, 1989). Specimens of *P. obliquiloculata* and *N. dutertrei* are abundant during winter months (Deuser et al., 1989), with an acme in the mixed layer (~60m) for *P. obliquiloculata*, and at mid-thermocline depths for *N. dutertrei* (Farmer et al., 2007). In contrast, *O. universa* tends to record annual average conditions within the mixed layer. Specimens of *G. menardii* calcify within the seasonal thermocline (Fairbanks et al., 1982, Farmer et al., 2007, Regenberg et al., 2009), and in some regions in the upper thermocline (Farmer et

al., 2007), and records annual temperatures. *G. tumida* is found at the lower thermocline or below the thermocline and records annual average conditions (Fairbanks and Wiebe, 1980; Farmer et al., 2007, Birch et al., 2013).

3. Materials and Methods

3.1 Localities studied

Core-top locations were selected to span a broad range of seawater pH, carbonate system parameters, and oceanic regimes. Samples from Atlantic Ocean (CD107-A), Indian Ocean (FC-01a and FC-02a), Arabian Sea (FC-13a and FC-12b) and Pacific Ocean (WP07-01, A14, and Ocean Drilling Program 806A and 807A) were analyzed; characteristics of the sites are summarized in Table 1 and S7, Fig. 3, and Fig. 4.

Atlantic site CD107-a (CD107 site A) was drilled in 1997 by the Benthic Boundary Layer program (BENBO) (K.S. Black et al., 1997 - cruise report RRS Charles Darwin Cruise 107). Arabian Sea sites FC-12b (CD145 A150) and FC-13a (CD145 A3200) were retrieved by the *Charles Darwin* in the Pakistan Margin in 2004 (B.J. Bett et al., 2003 - cruise report n°50 RRS Charles Darwin Cruise 145). A14 was recovered by box corer in the southern area of the South China Sea in 2012. Core WP07-01 was obtained from the Ontong Java Plateau using a giant piston corer during the Warm Pool Subject Cruise in 1993. Holes 806A and 807A were retrieved on Leg 130 by the Ocean Drilling Program (ODP). The top 10 cm of sediment from CD107-A have been radiocarbon dated to be Holocene <3 ky (Thomson et al., 2000). Samples from multiple box cores from Indian Ocean sites were radiocarbon dated as Holocene <7.3 ky (Wilson et al., 2012). Samples from western equatorial Pacific Site 806B, close to site WP07-01, are dated to between 7.3-8.6 ky (Lea et al., 2000). Arabian Sea and Pacific core-top samples were not radiocarbon dated but are assumed to be Holocene.

3.2 Species

Around 50-100 foraminifera shells were picked from the 400-500 µm fraction size for *Globorotalia menardii* and *Globorotalia tumida*, >500 µm for *Orbulina universa*, from the 250-400 µm fraction size for *Trilobatus sacculifer* (w/o sacc, without sacc-like final chamber), *Trilobatus sacculifer* (sacc, sacc-like final chamber), *Globigerinoides ruber (*white, sensu stricto), *Neogloboquadrina dutertrei*, *Pulleniatina obliquiloculata*. The samples picked for analyses were visually well preserved.

3.3 Sample cleaning

Briefly, picked foraminifera were gently cracked open, clay removed and checked for coarse-grained silicates. The next stages of sample processing and chemical separation were performed in a class 1000 clean lab equipped with boron-free HEPA filters. Samples were then cleaned using full reductive and oxidative cleaning (Boyle and Keigwin, 1985; Barker et al., 2003). A final leaching step with 0.001N HCl was done before dissolution in 1N HCl. Each sample was divided into two aliquots: an aliquot for boron purification and one aliquot for trace element analysis.

3.4 Reagents

Double-distilled HNO_3 and HCl acids (from Merck® grade) and a commercial bottle of HF Ultrapure grade were used at Brest. Double-distilled acids were used at Cambridge. All acids and further dilutions were prepared using double-distilled 18.2 MΩ.cm-1 MQ water. Working standards for isotope ratio and trace element

measurements were freshly diluted on a daily basis with the same acids used for sample preparation to avoid any matrix effect.

32.5 Boron isotopes

Boron purification for isotopic measurement was done utilizing microdistillation method developed by Gaillardet et al., (2001), for Ca-rich matrices by Wang et al., (2010) and adapted at Cambridge by Misra et al., (2014a). 70 µL of dissolved carbonate sample was loaded on a cap of a clean fin legged 5 mL conical beaker upside down. The tightly closed beaker was put on a hotplate at 95°C for 15 hours. The beakers were taken off the hotplate and were allowed to cool for 15 min. The cap where the residue formed was replaced by a clean one. Then, 100 µL of 0.5% HF were added to the distillate.

Boron isotopic measurements were carried out on a Thermo Scientific ®Neptune+ MC-ICP-MS at the University of Cambridge. Neptune+ was equipped with Jet interface and two 10^{13} Ω resistors. The instrumental setup included Savillex® 50µl/min C-flow self-aspirating nebulizer, single pass Teflon® Scott-type spray chamber constructed utilizing Savillex® column components, 2.0 mm Pt injector from ESI®, Thermo® Ni 'H' type sample cone and 'X' type skimmer cones. Both isotopes of boron were determined utilizing 10^{13} Ω resistors (Misra et al., 2014a; Lloyd et al., 2018).

The sample size for boron isotope analyses typically ranged from 10 ppb B (~5 ng B) to 20 ppb B samples (~10 ng B). Instrumental sensitivity for ^{11}B was 17 mV/ppb B (eg. 170 mV for 10ppb B) in wet plasma at 50µl/min sample aspiration rate. Intensity of ^{11}B for a sample at 10ppb B was typically 165mV ± 5mV closely matched the 170mV ± 5mV of the standard. Due to the low boron content of the samples extreme care was taken to avoid boron contamination during sample preparation and reduce memory effect during analysis. Procedural boron blanks ranged from 15pg B to 65 pg B (contributed to less than <1% of the sample signal). The acid blank during analyses was measured at ≤ 1mV on the ^{11}B, meaning a contribution < 1% of the sample intensity, no memory effect was observed within and across sessions.

Analyses of external standards were done to ensure data quality. For $\delta^{11}B$ measurements two carbonate standards were utilized: the JCP-1 (Geological Survey of Japan, Tsukuba, Japan) international standard (Gutjahr et al., 2014) and the NEP internal coral (Porites sp., $\delta^{11}B$ = 26.12 ± 0.92 ‰, 2SD, n=33 Holcomb et al., 2015 and Sutton et al., 2018, Table S2) from University of Western Australia/Australian National University. Certified boron isotopes liquid standard, the ERM© AE121 ($\delta^{11}B$ = 19.9 ± 0.6 ‰, SD, certified) was used to monitor reproducibility and drift during each session (Vogl and Rosner, 2011; Foster et al., 2013; Misra et al., 2014). Results for the isotopic composition of the NEP standard are shown in Table S2, average values are $\delta^{11}B_{NEP}$ = 25.70 ± 0.93 ‰ (2SD, n=22) over different 7 analytical sessions with each number representing an ab-initio processed sample - this study). Our results are within error of published values of 26.20 ± 0.88 ‰ (2SD, n = 27) and 25.80 ± 0.89 ‰ (2SD, n = 6) by Holcomb et al. (2015) and Sutton et al. (2018) respectively. Chemically cleaned JCP_1 samples were measured at 24.06 ± 0.20 (2SD, n=6) and is within error of published values of 24.37 ± 0.32 ‰ and 24.42 ± 0.28 ‰ by Holcomb et al. (2015) and Sutton et al. (2018) respectively.

3.6 Trace elements

The calcium concentration of each sample was measured on an ICP-AES ® Ultima 2 HORIBA at the Pôle spectrometrie Océan (PSO), UMR6538 (Plouzané, France). Samples were then diluted to fixed calcium

concentrations (typically 10 ppm or 30 ppm Ca) using 0.1 M HNO3 & 0.3 M HF matching multi-element standards Ca concentration to avoid any matrix effect (Misra et al., 2014b). Trace elements (e.g. X/Ca ratios) were analyzed on a Thermo Scientific ® Element XR HR-ICP-MS at the PSO, Ifremer (Plouzané, France).

Trace element analyses were done at a Ca concentration of 10 or 30 ppm. The typical blanks for a 30 ppm Ca session were: ^{7}Li < 2%, ^{11}B < 7%, ^{25}Mg < 0.2% and ^{43}Ca < 0.02%. Additionally, blanks for a 10 ppm Ca session were: ^{7}Li < 2.5%, ^{11}B < 10%, ^{25}Mg < 0.4% and ^{43}Ca < 0.05%. Due to strong memory effect for boron and instrumental drift on the Element XR, long sessions of conditioning were done prior analyses. Boron blanks were driven below 5% of signal intensity usually after 4 to 5 days of continuous analyses of carbonate samples. External reproducibility was determined on the consistency standard Cam-Wuellestorfi (courtesy of the University of Cambridge) (Misra et al., 2014b), Table S3. Our X/Ca ratio measurements on the external standard Cam-Wuellestorfi were all the time within error of the published value (Table S3) validating the robustness of our trace elements data. Analytical uncertainty of a single measurement was calculated from the reproducibility of the Cam-Wuellestorfi, measured during a particular mass spectrometry session. The analytical uncertainties on the X/Ca ratios are: 0.4 µmol/mol for Li/Ca, 7 µmol/mol for B/Ca and 0.01 mmol/mol for Mg/Ca (2SD, n=31) respectively.

3.7 Oxygen isotopes

Carbonate δ^{13}C and δ^{18}O were measured on a Gas Bench II coupled to a Delta V mass spectrometer at the stable isotope facility of Pôle spectrometrie Océan (PSO), Plouzané. Around 20 shells were weighed, crushed and clay removed. The recovered foraminifera were weighed in tubes and flushed with He gas. Samples were then digested in phosphoric acid and analyzed. Results were calibrated to the VPDB scale by international standard NBS19 and analytical precision on the in-house standard Ca21 was better than 0.11‰ for δ^{18}O (1SD, n=5) and 0.03‰ for δ^{13}C (1SD, n=5).

3.8 Calcification depth determination

We utilized two different chemo-stratigraphic methods to estimate the calcification depth in this study (Table S6 and S7). The first method, commonly used in paleoceanography, utilizes δ^{18}O measurements of the carbonate ($\delta^{18}O_c$) to estimate calcification depths (referred to as δ^{18}O-based calcification depths) (Schmidt et al., 2002; Mortyn et al., 2003; Sime et al., 2005; Farmer et al., 2007; Birsh et al., 2013). The second method utilizes Mg/Ca-based temperature estimates ($T_{Mg/Ca}$) to constrain calcification depths (Quintana Krupinski et al., 2017). In both cases, the postulate was that vertical profiles of seawater temperature are available for different seasons in ocean atlases and cruise reports, and that hydrographic data and geochemical proxy signatures can be compared to assess the depth in the water column that represents the species maximum abundance.

The two different methods to estimate calcification depth were then compared to published depth estimates for the basin, and where available, for the same site (Table S6). We chose literature values for calcification depths when available, or depths that were closest to what is known for the region or basin. As foraminifera can migrate in the water column along their ontogeny, we applied (based on uncertainties of our measurements) an uncertainty of ±10m for calcification depths > 70 m and an uncertainty of ±20 m when calcification depths <70 m. The depth habitats utilized to derive *in situ* parameters are summarized in Table S7.

3.9 $\delta^{11}B_{borate}$

Two carbonate system parameters are needed to fully constrain the carbonate system. Following the approach of Foster et al., (2008) we used the GLODAP database (Key et al., 2004) corrected for anthropogenic inputs in order to estimate pre-industrial carbonate system parameters at each site. Temperature, salinity and pressure for each site are from the World ocean database 2013 (Boyer et al., 2013). We utilized the R© code in Henehan et al, (2016) (courtesy of Michael Henehan) to calculate the $\delta^{11}B_{borate}$ and derive our calibrations. Uncertainty for $\delta^{11}B_{borate}$ utilizing the code was similar to the one calculated by applying 2 standard deviations of the calculated $\delta^{11}B_{borate}$ within the limits imposed by the calcification depth.

The Matlab© template provided by Zeebe and Wolf-Gladow, (2001) was used to calculate pCO_2 from TA; temperature, salinity and pressure were included into the calculations. Total boron was calculated from Lee et al., (2010), K_1 and K_2 were calculated from Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

Statistical tests were made utilizing GraphPad© software, linear regressions for calibration where derived utilizing R© code in Henehan et al, (2016) (courtesy of Michael Henehan) with a k=500.

4. Results

4.1 Depth habitat

The calcification depths utilized in this paper are summarized in Tables S6 and S7, including a comparison of calcification depth determination methods. The calculated calcification depths are consistent with the ecology of each species and the hydrography of the sites. Specimens of *G. ruber* and *T. sacculifer* appear to be living in the shallow mixed layer (0-100 m), with *T. sacculifer* living or migrating deeper than *G. ruber* (down to 125 m). Specimens of *O. universa* and *P. obliquiloculata* are living in the upper thermocline; *G. menardii* is found in the upper thermocline until the thermocline depth specific to the location; *N. dutertrei* is living around the thermocline depth and specimens of *G. tumida* are found in the lower thermocline.

Data from both approaches implies that some species inhabit deeper environments in the Western Equatorial Pacific (WEP) relative to the Arabian Sea, which in turn are deeper dwelling than in the Indian Ocean. In some cases, we find evidence for differences in habitat depth of up to ~100m between the WEP and the Arabian Sea. This trend is observed for *G. ruber* and *T. sacculifer*, but not for *O. universa*.

Some differences in calcification depth are observed between the two calcification depth determination methods. These differences might be due to the choice of calibrations. Alternatively, our uncertainties for $\delta^{18}O$ implies larger uncertainties on the calcification depth determination using this approach, compared to Mg/Ca measurements.

4.2 Empirical calibrations of foraminiferal $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$

Results for the different species analyzed in this study are presented in Fig. 5, Fig. 6 and summarized in Table 2; additionally, published calibrations for comparison are summarized in Table 3.

4.2.1 *G. ruber*

Our results for *G. ruber* (Fig. 5) are in good agreement with published data from other core-tops, sediment traps, tows, and culture experiments for $\delta^{11}B_{borate}$>19 ‰ (Foster et al., 2008, Henehan et al., 2013, Raitzsch et al., 2018). However, for $\delta^{11}B_{borate}$<19 ‰ our results show lighter $\delta^{11}B_{carbonate}$ compared to published values. Whilst this

species has been widely studied previously, the sites selected in this study allow us to extend the calibration. The positive offset from the 1:1 curve has been explained by the high photosynthetic activity (Hönisch et al., 2003; Zeebe et al., 2003). Two calibrations have been derived. Utilizing only our data, the sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ of our linear regression is not statistically different from 1, the uncertainty on this regression is important due to our small dataset and not inconsistent with the low sensitivity trend of the culture experiments from Sanyal et al., (2001) or Henehan et al., (2013). The second calibration made compiling all data from literature shows a sensitivity similar (e.g. 0.46 (±0.34) to the one recently published by Raitzsch et al., (2018) (e.g. 0.45 (±0.16), Table 3).

4.2.2 *T. sacculifer*

$\delta^{11}B_{carbonate}$ results for *T. sacculifer* (sacc and w/o sacc) (Fig. 5) are compared to published data (Foster et al., 2008; Martinez-Boti et al., 2015b, Raitzsch et al., 2018). Results for *T. sacculifer* are in good agreement with the literature and fall above the 1:1 line. Linear regression on our data yields a slope of 1.3 ± 0.2 but is not statistically different to the results from Martinez-Boti et al., (2015b) (Table 3), ($p>0.05$). However, when compiled with published data using the bootstrap method a slope of 0.83 ± 0.48 is calculated, with a large uncertainty given the variability in the data. It is also noticeable that *T. sacculifer* (w/o sacc) samples from the WEP have a $\delta^{11}B_{carbonate}$ close or below the 1:1 line and are significantly lower compared to the combined *T. sacculifer* of other sites ($p=0.01$, unpaired t-test).

4.2.3 *O. universa* and deeper dwelling species: *N. dutertrei, P. obliquiloculata, G. menardii* and *G. tumida*

Our results for *O. universa* (Fig. 5), *N. dutertrei, P. obliquiloculata, G. menardii* and *G. tumida* (Fig. 6) fall below the 1:1 line. These data for *O. universa* are not statistically different from the Henehan et al. (2016) calibration ($p>0.05$). Our results for *N. dutertrei* expand upon the initial measurements presented in Foster et al., (2008). The different environments experienced by *N. dutertrei* in our study permit us to extend the range and derive a calibration for this species; the slope is close to unity (0.93 ± 0.55), and is similar to the (0.95 ± 0.17) previously reported by Henehan et al., (2016) for *O. universa* and not statistically different ($p>0.05$). The data for *P. obliquiloculata* exhibits the largest offset from the theoretical line. The range of $\delta^{11}B_{borate}$ from the samples we have of *G. menardii* and *G. tumida* is not sufficient to derive calibrations, but the points are in good agreement with the *N. dutertrei* calibration and Henehan et al. (2016) calibration for *O. universa*.

For all species, the slopes are not statistically different from Henehan et al. (2016) ($p>0.05$) and are close to unity. If data for deep-dwelling foraminiferal species are pooled together with each other and with data from Henehan et al., (2016) and Raitzch et al., (2018), we calculate a slope of 0.95 (± 0.13) ($R^2=0.7987$, $p<0.0001$); if only our data are used, we calculate a slope that is not significantly different (0.82 ± 0.27; $p<0.05$). However, it may remain premature to assume that a unique calibration with a slope of ~0.9 can be used for all deeper-dwelling species; more data is needed for *P. obliquiloculata, G. menardii* and *G. tumida* to robustly test this assertion.

4.2.4 Comparison of core-top and culture data

The data for *G. ruber* and *T. sacculifer* from the core-tops we measured are broadly consistent with previous published results. The calibrations between these core-top derived estimates and culture experiments are not statistically different due to small datasets and uncertainties on the linear regressions (Henehan et al., 2013;

Marinez-Boti et al., 2015; Raitzsch et al., 2018; Table 3). The sensitivities of the species analyzed are not statistically different and are close to unity.

4.3 B/Ca ratios

B/Ca ratios are presented in Table 2 and Fig. 7. Values are species-specific consistent with previous work (e.g., compiled in Henehan et al., 2016) with ratios higher for *G. ruber* > *T. sacculifer* *T. sacculifer* (w/o sacc) > *P. obliquicloculata* > *O. universa* > > *G. menardii* > *N. dutertrei* > *G. tumida* > *G. inflata* > *N. pachyderma* > *G. bulloides* (Fig. 7). This study supports interspecific B/Ca ratios (Yu et al., 2007; Tripati et al., 2009, 2011; Allen and Hönisch, 2012; Henehan et al., 2016). Differences between surface- and deep-dwelling foraminifera are observed, with lower values and a smaller range for the deeper dwelling taxa (58-126 µmol/mol vs 83-190 µmol/mol for shallow dwellers), however, the trend for the surface-dwellers can also be driven by interspecies B/Ca variability. The B/Ca data for deep-dwelling taxa exhibits a significant correlation with $[B(OH)_4^-]/[HCO_3^-]$ ($p<0.05$), but no correlation with $\delta^{11}B_{carbonate}$ and temperature (Fig. S3). Surface-dwelling species have B/Ca ratios that exhibit significant correlations with $[B(OH)_4^-]/[HCO_3^-]$, $\delta^{11}B_{carbonate}$ and temperature. The sensitivity of B/Ca to $[B(OH)_4^-]/[HCO_3^-]$ is lower for deep-dwelling species compared to surface dwelling species. When all the B/Ca data are compiled, significant trends are observed with $[B(OH)_4^-]/[HCO_3^-]$, $\delta^{11}B_{carbonate}$ and temperature (Fig. S3). We also observe that if we compare data from all sites together, correlations exist between B/Ca and the water depths of the cores (not significant, Fig. S4) but these correlations may also be related to the different the depth habitats of different taxa in each region, a significant trend is observed when all the data are plotted ($R^2=0.11$, $p<0.05$, Fig. S4).

5. Discussion

5.1 Sources of uncertainty relating to depth habitat and seasonality at studied sites

5.1.1 Depth habitats and $\delta^{11}B_{borate}$

Because foraminifera will record ambient environmental conditions during calcification, the accurate characterization of *in-situ* data is needed not only for calibrations, but also to understand the reconstructed record of pH or pCO_2. The species we examined are ordered here from shallower to deeper depth habitats: *G. ruber* >*T. sacculifer* (sacc) > *T. sacculifer* (w/o sac) > *O. universa* > *P. obliquiloculata* > *G. menardii* > *N. dutertrei* > *G. tumida* (this study; Birch et al., 2013; Farmer et al., 2007), although the specific water depth will vary depending on the hydrology of the site (Kemle-von and Oberhänhsli, 1999). We note that calculation of absolute calcification depths can be challenging in some cases as many species migrate during their ontogeny (Steinhardt et al., 2015).

We find that assumptions about the specific depth habitat a species of foraminifera is calcifying over, in a given region, can lead to differences of a few per mil in calculated isotopic compositions of borate (Fig. 4). Hence this can cause a bias in calibrations if calcification depths are assumed instead of being calculated (i.e., with $\delta^{18}O$ and/or Mg/Ca). Factors including variations in thermocline depth can impact depth habitats for some taxa. At the sites we examined, most of the sampled species live in deeper depth habitats in the WEP relative to the Indian Ocean, which in turn is characterized by deeper depth habitats than in the Arabian Sea. In the tropical Pacific, *T. sacculifer* is usually found deeper than *G. ruber* except at sites characterized by a shallow thermocline,

in which case they tend to overlap their habitat (e.g., ODP Site 806 in the WEP which has a deeper thermocline than at ODP Site 847 in the Eastern Equatorial Pacific; EEP) (Rickaby et al., 2005). The difference in depth habitats for *T. sacculifer* and *N. dutertrei* between the WEP and EEP can be as much as almost 100 m (Rickaby et al., 2005).

5.1.2 Seasonality and *in-situ* $\delta^{11}B_{borate}$

As discussed by Raitzsch et al., (2018), depending of the study area, foraminiferal fluxes can change throughout the year, so seasonality can have a major impact on hydrographic carbonate parameters calculations for any given water depth. We therefore recalculated the theoretical $\delta^{11}B_{borate}$ using seasonal data for temperature and salinity and annual values for TA and DIC for each depth at each site. The GLODAP (2013) database does not provide seasonal TA or DIC values.

The low sensitivity of $\delta^{11}B_{borate}$ to temperature and salinity means that calculated $\delta^{11}B_{borate}$ for each water depth at our sites were not strongly impacted (Fig. S1). Thus, these findings support Raitzsch et al. (2018), who concluded that calculated $\delta^{11}B_{borate}$ values corrected for seasonality was within error of non-corrected values for each water depth. As Raitzsch et al, (2018) highlight, seasonality might be more important at high latitude sites where seasonality is more marked, however, the seasonality of primary production will also be more tightly constrained due to the seasonal progression of winter light limitation and intense vertical mixing and summer nutrient limitation.

Data for our sites suggests that most $\delta^{11}B_{borate}$ variability we observe does not come from seasonality but from the assumed water depths for calcification. With the exception of a few specific areas such as the Red Sea (Henehan et al., 2016, Raitzsch et al., 2018), at most sites examined, seasonal $\delta^{11}B_{borate}$ at a fixed depth does not vary by more than ~0.2‰. We conclude that seasonality is not an important factor impacting carbonate system parameters at the sites we examined.

5.2 $\delta^{11}B$, microenvironment pH and depth habitats

In planktonic foraminifera, algal symbiosis is the more common symbiotic relationship. For most of planktonic foraminifera, the host presents only one species of symbionts (Gast and Caron, 2001). The family Globigerinidae, including *G. ruber*, *T. sacculifer* and *O. universa*, commonly have dinoflagellates or chrysophyte algal symbionts (Anderson and Be, 1976; Spero, 1987). The families Pulleniatinidae, Globorotaliidae, including *N. dutertrei*, *P. obliquiloculata*, *G. menardii* and *G. tumida*, have chrysophyte algal symbionts (Gastrich, 1988).

The relationship between the symbionts and the host is complex by nature. Nevertheless, this symbiotic relationship provides energy (Hallock, 1981b) and promotes calcification of the foraminifera (Duguay, 1983; Erez et al., 1983) by providing the inorganic carbon to the host (Jorgensen et al., 1985). Also, for *T. sacculifer* and *O. universa* photosynthesis increases with higher insolation (Jorgensen et al., 1985; Rink et al., 1998).

Dinoflagellate-bearing foraminifera (*G. ruber*, *T. sacculifer* and *O. universa*) tend to have a higher symbiont density and photosynthesis activity while *P. obliquiloculata*, *G. menardii* and *N. dutertrei* have lowered symbiont density and *P. obliquiloculata*, *N. dutertrei* lower photosynthetic activity (Takagi et al., 2019). *P. obliquiloculata* showed the minimum symbiont density and photosynthetic activity (Takagi et al., 2019).

It is now accepted that the foraminifera $\delta^{11}B$ signature comes from the microenvironment pH (Jorgensen et al., 1985; Rink et al., 1998; Köhler-Rink and Kühl, 2000, Hönisch et al., 2003; Zeebe et el., 2003). Foraminifera

with high photosynthetic activity and symbiont density like *G. ruber* and *T. sacculifer* present a pH of microenvironment higher than ambient seawater, $\delta^{11}B$ higher than 1:1 line (Foster et al., 2008, Henehan et al., 2013, Raitzsch et al., 2018). The opposite can also be true, from our study, species with lower photosynthetic activity and lower symbiont density present microenvironments lower than ambient seawater, $\delta^{11}B$ lower than 1:1 line (Martinez-Boti et al., 2015b; Henehan et al., 2016), this is the case in our data for *N. dutertrei*, *G. menardii* and *P. obliquiloculata* and likely *G. tumida*. Nevertheless, the low $\delta^{11}B$ of *O. universa* and *T. sacculifer (w/o sacc)* from the WEP are difficult to reconcile with a high photosynthetic activity compared to *T. sacculifer* et *G. ruber.*

The photosynthetic activity is also function of the light level they received which is, in the natural system, dependent of their depth in the water column, for the purpose of this study we will not consider turbidity which also influences the light penetration in the water column. In this case, the photosynthetically active foraminifera living close to the surface should see their microenvironment pH (thus $\delta^{11}B$) more sensitive to water depth changes. A deeper depth habitat will change the light intensity they received and as a consequence may lower their photosynthetic activity reducing their microenvironment pH. This thought is supported by the significant trend observed between our $\Delta^{11}B$ and the calcification depth for *G. ruber* and *T. sacculifer* of our sites (Fig. S2). This trend basically supports the fact that the microenvironment pH decrease with calcification depth. We observe a decrease of $\delta^{11}B$ in the WEP for *T. sacculifer (w/o sacc)*, significantly different from the other sites ($p<0.05$). The $\Delta^{11}B$ of *G. ruber*, *T. sacculifer* (w/o sacc and sacc) is also significantly lower in the WEP compared to the other sites ($p<0.05$). To test if the $\delta^{11}B$ signature was inferred to a light driven, we have been able to independently calculate the depth of the foraminifera based on various light insolation culture experiments (Jorgensen et al., 1985) and the Δmicroenvironment pH derived from our data (Fig. 8A and B). This exercise verified that this low $\delta^{11}B$ can be explained by the reduced light environment due to a deeper depth habitat in the WEP (Fig. 8B). Also, *T. sacculifer* has the potential to support more photosynthesis due to its higher symbiont density. Higher photosynthetic activity is observed compared to other species potentially supporting higher symbiont/host interactions. Those results could be in line with a greater sensitivity of *T. sacculifer* photosynthetic activity with changes in insolation/water depth. It can also be noted that this species presents the largest variations in symbiont density versus its test size. When applied to the other species *O. universa* data suggest a microenvironment pH 0.10 to 0.20 lower than ambient seawater pH which would be in line with species living deeper than 50m (light compensation point (Ec), Rink et al., 1998) also consistent with our calcification depth reconstructions. Δmicroenvironment pH is higher in *T. sacculifer* > *G. ruber* > *T. sacculifer* (w/o sacc - WEP) > *O. universa*, *N. dutertrei*, *G. menardii*, *G. tumida* > *P. obliquiloculata* in line with photosymbiosis findings from Tagazaki et al., (2019). Also, the higher $\delta^{11}B$ data from the African upwelling published by Raitzsch et al., (2018) for *G. ruber* and *O. universa* might reflect the higher microenvironment pH due to a shallower depth habitat. This could highlight a potential issue with calibration when applied to sites with different oceanic regimes as the $\delta^{11}B$ specie-specific calibrations could be also location-specific for the mixed dweller species.

Microenvironment pH results for *N. dutertrei*, *G. menardii*, *G. tumida*, are similar to *O. universa* and suggest a threshold for respiration driven $\delta^{11}B$ signature. This threshold can be driven by a change of photosynthetic activity due to lower light intensity at deeper depth and/or a change in the symbiont assemblage with non-dinoflagellate symbionts at deeper depth. We can explain this threshold because deep dweller species do not experience important changes of insolation at those depths so their microenvironments should be respiration driven and relatively stable. We can also note that *P. obliquiloculata* which has the lowest symbiont density and

photosynthetic activity has the lowest microenvironment pH compared to other deeper dweller species supporting this respiration driven microenvironment.

5.3 $\delta^{11}B$ sensitivity to $\delta^{11}B_{borate}$ and relationship with B/Ca signatures

$\delta^{11}B_{carbonate}$ and B/Ca data have shown to be sensitive to precipitation rate with at higher precipitation rate increasing $\delta^{11}B_{carbonate}$ (Farmer et al., 2019) and B/Ca (Farmer et al., 2019; Gabitov et al., 2014; Kaczmarek et al., 2016; Mavromatis et al., 2015; Ushikawa et al., 2015). A recent study from Farmer et al, (2019) has proposed that in foraminifera at higher precipitation rates, more borate ion is incorporated into the carbonate mineral, while at lower precipitation rates, more boric acid is incorporated. They also suggest this may explain low sensitivities of culture experiments.

When combining all literature data, *T. sacculifer* and *G. ruber* have sensitivities of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ of 0.83 ± 0.48 and 0.46 ± 0.34 respectively in line with previous literature and paleo-CO_2 reconstructions. Also, if we only take into account our data, the observation that the sensitivity of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ are not statistically different from unity for most of the species investigated we can speculate that for these taxa, changes in precipitation rate and contributions of boric acid are not likely to be important. If considering only the data from this study, *G. ruber* (1.12 ± 1.67) and *T. sacculifer* (1.38± 1.35) present higher sensitivities of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$. We can then again speculate that the observed high values for $\delta^{11}B_{carbonate}$ at high seawater pH can be due to higher precipitation rates. We note this could also be consistent with the higher sensitivity of B/Ca signatures in these two surface dwelling species to ambient $[B(OH)_4^-]/[HCO_3^-]$ relative to deeper dwelling species. Those interspecific differences still remain to be explained, however, part of this variability is likely due to changes in the carbonate chemistry of the microenvironment resulting in changing competition between borate and bicarbonate. A caveat is that we can not exclude specific biological processes, and that in taxa with a non respiration-driven microenvironment, changes in day/night calcification ratios also impacting observed values. As indicated by Farmer et al., (2019), studies of calcite precipitation rates in foraminifera may help to improve our understanding of the fundamental basis of boron-based proxies.

5.4 Evaluation of species for pH reconstructions and water depth pH reconstructions

This data set allows us to reassess the utility of boron-based proxies for the carbonate system. The main interest with utilizing boron-based proxies relates to the reconstruction of past oceanic conditions - specifically pH and pCO_2. Mixed-layer species (eg. *G. ruber* and *T. sacculifer)* are potential archives for atmospheric CO_2 reconstructions. Other species can shed light on other aspects of the carbon cycle including the physical and biological carbon pumps.

There are a few main inferences we can make. When compiled with data from the literature, sensitivities of $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ for *G. ruber* and *T. sacculifer* are similar to previous studies (Martinez-Boti et al., 2015b; Raitzsch et al., 2018) which is also supporting of previous paleo-reconstructions. Our data also support the observations of Henehan et al., (2016) for *O. universa*.

In order to derive accurate reconstructions of past ambient pH and pCO_2, accurate species-specific calibrations need to be used that are constrained by core-tops or samples from similar types of settings (Fig. 9, 10, S6). Lighter $\delta^{11}B$ signatures in *T. sacculifer* (w/o sacc) are observed in the WEP, which may be explained by the deeper depth habitat for these taxa, where lower light levels might reduce symbiont photosynthetic activity. Also,

correction will be needed for *T. sacculifer* (w/o sacc) in the WEP. When applying the calibrations n°2 and 4 to *T. sacculifer* and *G. ruber* (compilation of all data, Table 3) our data show more variability, especially for *G. ruber* which lead to the larger mismatch compared to *in-situ* parameters. Henehan et al., (2013) reported a lighter $\delta^{11}B$ with smaller test size, our sample add a weight/shell of 11 ± 4 µg (n=4, SD) which, despite a narrow range, could still explain this variability. The higher divergence of reconstructed values from *in-situ* measurements are observed at site WPO7-01 for both *T. sacculifer* (w/o sacc) and *G. ruber*. More data would be needed to determine a proper correction for both species, coretop study will be determinant for future downcore reconstructions, especially in the WEP.

We also find that for two species, the boron proxy is a relatively straightforward recorder of ambient pH, with sensitivities close to unity for and *O. universa, and N. dutertrei*. There is also promise in using multiple species in a sample from different hydrographic regimes to reconstruct vertical profiles of pH and pCO_2. We are able to reproduce pH and pCO_2 profiles from multiple sites with different water column structures (Fig. 9) with those reconstructions within error of the *in-situ* values, for most sites. In order to avoid circularity, to validate these calibrations, we recalculated ambient pH and pCO_2 by first excluding site-specific data and then recalculating species-specific calibrations, followed by application to each specific site. The comparison of the two methods does not show significant differences and validates the robustness of the calibrations (Fig. S5). We utilized the calibrations derived from our data for *G. ruber* (calibration n°1 and 2, Table 3), *T. sacculifer* (calibration n°3 and 4, Table 3), *O. universa* (calibration n°8, Table 3), for *P. obliquiloculata* (calibration n°11, Table 3), and for *N. dutertrei*, *G. tumida* and *G. menardii* the calibration made on the compilation of the deep-dweller (calibration n°13, Table 3). Results are shown in Fig. 9 and evaluated in Fig. 10. For *G. menardii*, more data would be helpful to provide additional constraints. Results for *G. ruber* are the sparsest, potentially due to difference in test sizes (Henehan et al., 2013) or undocumented diagenetic effects. Results reaffirm the importance of working with narrow size fractions (Henehan et al., 2013) and the importance of core-top study to determine corrections.

6. Conclusions and future implications

Our study has extended the boron isotope proxy with data for new species and sites. The work supports previous work showing that depth habitats of foraminifera vary depending on the oceanic regime, and this impacts boron isotope signatures. Low $\delta^{11}B$ values in the WEP compared to other regions for *T. sacculifer* (w/o sacc) may be explained by a reduction in microenvironment pH due to a deeper depth habitat associated with reduced irradiance and thus photosynthetic activity. Those results might also highlight a potential need for studying core-tops in order to establish what factors are important to accurately develop reconstructions in different areas.

The sensitivity of $\delta^{11}B$ to pH is in line with previously published data for *T. sacculifer*, *G. ruber*. The sensitivity of $\delta^{11}B$ to pH of *O. universa* (mixed-dweller), *N. dutertrei*. *G. menardii* and *G. tumida* (deep-dwellers) are similar but more data are needed to fully determine those sensitivities. The similarity of boron isotope calibrations for deep-dwelling taxa might be related to respiration-driven microenvironments.

Reconstruction of seawater pH and carbonate system parameters is achievable using foraminiferal $\delta^{11}B$ but additional core-top and down-core studies reconstructing depth profiles will be needed in order to further verify those calibrations. Past pH and pCO_2 water depth profiles can potentially be created by utilizing multiple foraminiferal species in concert with taxa-specific calibrations for similar settings. This approach has much

potential for enhancing our understanding of the past workings of the oceanic carbon cycle, and the biological pump.

Author contribution

R.E and A.T. wrote the proposals that funded the work. A.T. and F.C. provided the samples. M.G., S.M. and A.T. contributed to the experimental design. A.V. helped for sample preparation. M.G. and S.M contributed to developing the method of boron isotope analysis. M.G. performed the measurements with assistance from S.M. M.G conducted the data analysis. M.G. drafted the paper, which was edited by all authors. Interpretation was led by M.G., A.T., S.M. with input from R.E., A.V. and F.C.

Competing interests

The authors declare that they have no conflict of interest.

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Figure caption

Figure 1: Reactions governing dissolved inorganic carbon equilibria**.**

Figure 2: (A) Speciation of H_3BO_3 and $H_4BO_4^-$ as function of seawater pH (total scale), (B) $\delta^{11}B$ of dissolved inorganic boron species as a function of seawater pH, (C) sensitivity of $\delta^{11}B$ of $H_4BO_4^-$ for a pH ranging from 7.6 to 8.4. T=25°C, S=35, $\delta^{11}B$=39.61 ‰ (Foster et al., 2010), dissociation constant α = 1.0272 (Klochko et al., 2006).

Figure 3: Map showing locations of the core-tops used in this study (white diamonds). Red open circles represent the sites used for *in-situ* carbonate parameters from GLODAP database (Key et al., 2004).

Figure 4: Pre-industrial data versus depth of the sites used in this study. The figure shows seasonal temperatures (extracted from World Ocean Database 2013), density anomaly (kg/m^3), pre-industrial pH and pre-industrial $\delta^{11}B$ of $H_4BO_4^-$ (calculated from the GLODAP database and corrected for anthropogenic inputs).

Figure 5: Boron isotopic measurements of mixed-layer foraminifera plotted against the $\delta^{11}B_{borate}$. $\delta^{11}B_{borate}$ were characterized by determination of the calcification depth of the foraminifera, A) *G. ruber*, B) *T. sacculifer*, C) *O. universa*. Mono-specific calibrations are summarized in Table 3.

Figure 6: Boron isotopic measurements of deep-dwelling foraminifera ($\delta^{11}B_{carbonate}$) plot against $\delta^{11}B_{borate}$. $\delta^{11}B_{borate}$ were characterized by determining the calcification depth of foraminifera, A) *P. obliquiloculata*, B) *G. menardii*, C) *N. dutertrei*, D) *G. tumida* and E) Compilation of deep dweller species. Mono-specific calibrations are summarized in Table 3.

Figure 7: Boxplots of B/Ca ratios for multiple species, *T. sacculifer* (this study; Foster et al., 2008; Ni et al; 2007; Seki et al., 2010), *G. ruber* (this study; Babila et al., 2014; Foster et al., 2008; Ni et al., 2007), *G. inflata*, *G. bulloides* (Yu et al., 2007), *N. pachyderma* (Hendry et al., 2009; Yu et al., 2013), *N. dutertrei* (this study; Foster et al., 2008), *O. universa*, *P.obliquiloculata*, *G. menardii*, *G. tumida* (this study).

Figure 8: A) Boxplot showing the calculated microenvironment pH difference (Δmicroenvironment pH) between microenvironment and external pH based on the $\delta^{11}B$ data. B) This figure shows that a decrease in insolation can explain the low $\delta^{11}B$ from the WEP. Light penetration profile in the Western Pacific, with E_0 in the WEP of 220 J.s-1.m-2 (Weare et al., 1981) and a light attenuation coefficient of 0.028 (Wang et al., 2008). Theoretical depths were calculated for a decrease in microenvironment pH of ΔpH_1= -0.02 (e.g. WP07-a); ΔpH_1= -0.04 (e.g. A14), ΔpH_2= -0.06 (e.g. 806A). Light penetration corresponding to Ec is ~12%, ΔpH_0~7%, ΔpH_1 ~5%, ΔpH_2 ~1% respective depth are 75m, 90m, 110m and 150m. Grey band is the calcification depth of *T. sacculifer* (w/o sacc) utilized in this study.

Figure 9: Water depth pH profiles reconstructed at every site applying the mono-specific calibrations derived from our results (Table 3). Figure is showing measured $\delta^{11}B_{calcite}$, $\delta^{11}B_{borate}$ calculated according to different calibrations (see Table 3 and text), calculated pH based on $\delta^{11}B$ ($pH_{\delta 11B}$) and pCO_2 calculated from $pH_{\delta 11B}$ and alkalinity.

Figure 10: Evaluation of the reconstructed parameters, $\delta^{11}B_{borate}$, pH and pCO_2 versus *in-situ* parameter. The recalculated parameters are consistent with *in-situ* data, except for *G. ruber*. This variability might be explained by the different test sizes.

Table caption

Table 1: Box-core information

Table 2: Analytical results of $\delta^{13}C$, $\delta^{18}O$, $\delta^{11}B$ and elemental ratios Li/Ca, B/Ca and Mg/Ca

Table 3: Species-specific $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ calibrations from literature and from our data