

## Interactive comment on "Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO<sub>2</sub> gradients" by Maxence Guillermic et al.

## Maxence Guillermic et al.

maxence.guillermic@gmail.com

Received and published: 23 October 2019

We wish to thank Michael Henehan for his helpful comments on the manuscript and previous help with the code. We believe that we addressed all of the major comments as indicated in the discussion below and the updated manuscript (see supplement).

Comment SC1 1: The authors on several occasions highlight the difference between their G. ruber data and the slope obtained by our culture experiments (Lines 385-387; 422-425; lines 525-526; 537-538; 563). In lines 422-425 the picture as presented is

C1

particularly confusing, since the authors first suggest "there is a difference in calibrations", then say "this is particularly notable for G. ruber", but then say "the sensitivity of the species analysed are not statistically different". In truth, only the final sentence is true (with the exception of the clause "and are close to unity". A slope of 1.12 \_ 1.67 is within uncertainty of our culture slope (0.6), and could technically allow a slope as low as -0.55: i.e. there is no significant difference between the slope they suggest and the slope that we observe in culture. Framing this as a difference seems even more odd given the authors do not draw any distinction between their T. sacculifer slope and that of previous calibrations, because their bounds of uncertainty do not allow it- so it seems logically inconsistent to draw distinctions for ruber where the statistical difference is equally unfounded. I would suggest the authors go through the manuscript and revise their phrasing to reflect this lack of statistically significant difference. Including "the sensitivity of d11B to pH is not statistically different from unity for G. ruber" as a main conclusion in line 563, for example, implies this study is in disagreement with cultures (which it isn't), and that we should consider a slope of 1 to be potentially suitable for this species. In reality, were we to calculate pCO2 with the slope and intercept that the authors suggest (m=1.12, c=-1.23), the fit of the downcore record of G. ruber from Chalk et al. 2017 with ice-core pCO2 would be considerably worse (see attached Fig. 1). The magnitude of pCO2 change between glacials and interglacials (i.e. the parameter that is driven by the slope of the calibration) is underestimated, with pCO2 too high in glacials by 50 ppm. The improved fit of the down-core record with pCO2 from ice-cores when our ruber calibration is used, however (see Chalk et al. 2017), offers support for the shallowerthan-unity slope we observed in this species. Incidentally, also, an R-squared of 0.98 for the ruber core-top data presented in this study seems anomalously high relative to the scatter/uncertainty bounds in the dataset- can the authors be clear how this Rsquared is computed? Is it the average R-squared of Monte Carlo regressions plotted through datapoints randomly subsampled from within the xand y-uncertainties? Or is this simply a least-squares linear regression through the central tendencies of the datapoints? The former might be more representative, but as

long as the authors are clear about what they are describing that is the main thing.

Response 1: We have mitigated our discussion, especially because our dataset is too limited and our trend driven by two datapoints (WP07-1 and FC01-a). The results presented for the sensitivity > 1 of  $\delta 11 B carbonate$  to  $\delta 11 B borate have been clearly written as speculative in the text; first of all because when doing the bootstrap on all compiled data the regression is similar to Raitzsch et al., (2018), sensitivity of 0.46 <math display="inline">\pm$  0.34 (updated table 3) compared to 0.45  $\pm$  0.16 for Raitzsch et al., (2018) and as highlighted the uncertainties based on 5 points is important and finally pCO2 reconstructions would not be consistent with the Vostok pCO2 record.

The  $R^2$  were calculated with R doing a linear regression not taking into account all simulated values of the Monte Carlo Simulation. Because we did not find a way to extract those data, we decided to not present the  $R^2$  and p-value.

Comment SC1 2: The authors report our generic culture intercept for ruber in their Table 3 (9.52), but erroneously list the size fraction as \_250 \_m. I would like to point them to Fig. 6 of this 2013 paper, where we give the average size fraction of our cultures to be \_380 \_m. A suggested size fraction correction on the intercept is given, such that for 300-355\_m it would be 8.87. On this same note, the authors also combine a wide size fraction (250-400\_m) for G. ruber, which given size-related offsets from the culture calibration (as shown in Fig. 6 of Henehan et al. 2013) has the potential over such a large range to skew the data, due to size-related changes in d11B. Can the authors give some estimate as to the distribution of test sizes within their broad sample range, so as to make them more easily comparable to published data?

Response 2: I changed the size fraction in Table 3, I missed this information in your paper. Most of the samples have been picked in the 250-300 size fraction (average weight/ shell of 11  $\pm$  4  $\mu$ g (n=4, SD) only when measurements were realized), we chose a restrained size fraction to avoid this size-related variability (at least in our calibration), we also chose this lower size fraction because some of the sites did not

C3

present shells in the higher size fractions and we wanted to stay consistent. Now, when compiling all the data this variability is not constrained. From your paper, our weight/shell variability could lead to an offset up to  $\sim$ 1% that we acknowledged can explain most of the variability for our G. ruber data. I have added line 582 "Henehan et al., (2013) reported a lighter  $\delta$ 11B with smaller test size, our sample add a weight/shell of 11  $\pm$  4  $\mu$ g (n=4, SD) which could also explain this variability."

Comment SC1 3: The authors screened for clay contamination using Ti/Ca ratios, as Al/Ca values were difficult to measure with their introduction system. However, they do not provide these data. Clay may carry isotopically-light sorbed d11B with it, and introduce bias towards lighter values. To allow maximum confidence in the data, and see which datapoints if any might have some influence of clay, can the authors please provide the Ti/Ca ratios in Table 2?

Response 3: We only had a contamination at one site which is not presented in the paper (site E035), with high Mn/Ca of  $79\mu$ mol/mol and high Fe/Ca of 3.0 mmol/mol. We have added the Mn/Ca and Fe/Ca in Table 2. We didn't add the Ti/Ca ratios as we monitored it with the raw ratios and do not have the absolute values. However, a minor correlation was found between Ti/Ca and B/Ca (R2=0.0887). Some of our samples have elevated Fe/Ca concentration but no high Mn/Ca, we don't suspect contamination from those samples since this high Fe can potentially come from MnCO3 overgrowth and this over growth will have negligible quantity of Mg and B unlike the Fe-Mn oxide and hydroxides.

Comment SC1 4: In Section 4.2.3 (note the paper skips 4.2.4 and goes straight on to 4.2.5?), the authors pool 'deeper-dwelling' foraminiferal species together, but this seems a bit unfounded since these foraminifera don't even have the same symbiont types (crysophyte vs. dinoflagellate), and have quite different ecologies. I'm not convinced there's enough of an a priori reason to even do this in the first place. However, I see that the authors do already concede this may be unfounded.

Response 4: We developed the discussion about the symbionts type/photosynthesis, lines 485-543. Even if the data are limited, we don't want to reject a chrysophytes/insolation limiting threshold resulting in a respiration-driven environment where this calibration can make sense. I have tried to reply to this comment for reviewer 2:

"I have tried to improve the discussion, focusing on the symbionts/photosynthesis, because the story is of course more complex. From what I see in the literature is that T. sacculifer, G. ruber, O. universa have mostly dinoflagellates symbionts (can have chrysophyte as well) where G. tumida, G. menardii, P. obliquiloculata and N. dutertrei will have chrysophyte algal symbionts. The photosynthesis is dependent of the nature of the host/symbionts interactions, symbionts type (pigment associated for light absorption efficiency), symbionts density. The recent study from Tagaki et al., (2019) is really helpful as he constrained the photosynthesis activity, light absorption efficiency and the symbiont density of those species.

Fv/Fm (photosyntethic activity) T. sacculifer>G. menardii > O. universa> G. ruber (white) > N. dutertrei > P. obliquiloculata  $\sigma$ psi (light absorption efficiency) N. dutertrei > P. obliquiloculata > G. menardii > G. ruber > T. sacculifer > O. universa Chla/biomass T. sacculifer>O.universa>G. ruber> N. dutertrei>G. menardii>P. obliquiloculata

What I assume is that T. sacculifer, O. universa and G. ruber photosynthesis are likely to be more affected by changes in insolation than other species due to their symbiont density, high photosynthetic capacity and their light absorption efficiency. Which is still in line with the argumentation we are giving. Also, the fact that the deeper dwellers have this low boron isotopic signature is likely due to a lower symbiont density, lower photosynthetic activity and a reduced insolated environment. P. obliquiloculata has the lowest density and photosynthetic activity, which would translate in a respiration driven environment the fact that most of the species are following this trend would go in the sense of a respiration driven environment. Also the fact that O. universa is following this trend would, I think, whether be due light limitation and/or a different symbiont due to its deeper depth."

C5

Comment SC1 5: In section 3.9, the authors make no mention of how they calculated pK\*B for each foraminifera. I take it they did indeed account for changes in pK\*B with temperature, salinity and pressure? It may sound blindingly obvious, but I'm constantly amazed at how many people make this error. On a similar theme Fig S3 the pH lines are no doubt helpful, but I'm not sure how the authors managed to calculate them, given the pK\*B is different for each foram. Is this calculated using the mean pK\*B of each of the forams plotted? This figure makes me worry that the authors just chose a single value of pK\*B for all forams in all calculations of the paper, which would be wrong.

Response 5: The pKB\* were calculated taking into account temperature, salinity and pressure in all calculations of the paper except in Fig S3 to draw the  $\Delta$ microenvironment pH line. We agree that individually, the parameters can significantly influence the calculations (figure below), especially temperature, then salinity and a minor effect for pressure. Maximum divergence was observed for site CD107-a due to colder temperature however for the other sites due to our uncertainties, the results were still consistent with our discussion. However, I have directly calculated the pH difference from the microenvironment for each of the species (every calculations taking into account, P, T and S). Results are shown in Figure 8 (or below).

Comment SC1 6: I think the decision to group 'shallow-dwelling' foraminifera (note it is not clearly defined what species this includes in any caption) in Fig. S4 (and in the text where this is referenced) is I think unfounded. It produces a correlation between B/Ca and Borate/DIC, sure, but it's entirely driven by the interspecies difference between ruber and sacculifer, and we know from Kat Allen's work for example that these species have fundamentally different B/Ca-Borate/DIC relationships.. hey shouldn't be lumped together in one group. As it is, it makes this look like a carbonate system relationship when on an intra-species level there is no significant correlation with the carbonate system (as we also observed elsewhere).

Response 6: We group G. ruber and T. sacculifer data in the "shallow-dwelling"

foraminifera. It is true that this calibration can be driven by interspecific differences. Then, I have added calibrations for T. sacculifer and G. ruber.

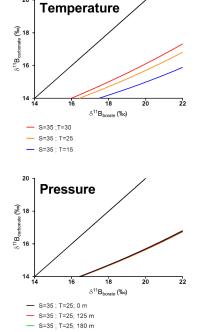
Line 429-432: "B/Ca ratios are presented in Table 2. Values are species specific consistent with previous work (e.g., compiled in Henehan et al., 2016) with ratios higher for G. ruber > T. sacculifer > T. sacculifer (w/o sacc) > P. obliquicloculata > O. universa > > G. menardii > N. dutertrei > G. tumida > G. inflata > N. pachyderma > G. bulloides (Fig. 7). This study supports interspecific B/Ca ratios (Allen and Hönisch, 2012; Henehan et al., 2016)."

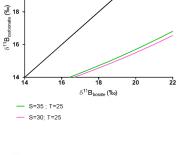
Line 565-568: "Those interspecific differences still remain to be explained, however, part of this variability is likely due to changes of the carbonate chemistry of the microenvironment resulting in changing competition between borate and bicarbonate ion, but we can't exclude specific biological processes, and for the mixed-dweller (e.g. non respiration-driven microenvironment) day/night calcification ratios."

Please also note the supplement to this comment: https://www.biogeosciences-discuss.net/bg-2019-266/bg-2019-266-AC2-supplement.pdf

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-266, 2019.

C7





Salinity

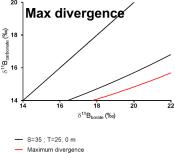


Fig. 1.

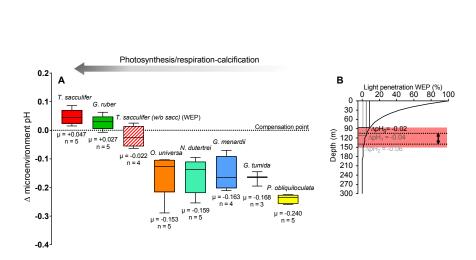


Fig. 2.