Response to RC1 – Jesse Farmer

We wish to thank Dr. Jesse Farmer for his thorough review of our manuscript and his helpful comments. We believe that we addressed all of the major comments indicated by Dr. Farmer as indicated in the discussion below and the updated document.

The updated manuscript and figures can be found at the end after this response.

Comment 1: Foraminifera depth habitats and thermocline depth. To what extent are differences in foraminifera depth habitats between the different studied oceanographic regions simply a function of variations in thermocline depth? This point could be clarified throughout the manuscript. If true, it seems a particularly important outcome of this study is a need to combine planktonic foraminifera _11B with thermocline depth reconstructions.

Response 1: We have added a statement to line 460 acknowledging that "Factors including variations in thermocline depth can impact depth habitats for some taxa." Variations in thermocline depth are certainly one of several factors that impact the differences in foraminiferal depth habitats, but not the only factor, both in the present and in the past. Only some species follow the thermocline depth (like G. tumida), while others (such as N. dutertrei) are not and are usually found around the same water depth. So it will be dependent on the studied species.

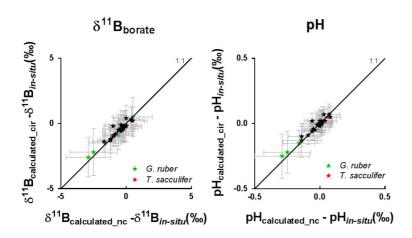
Comment 2: In section 5.2 (L482-514), the authors posit a primary control of light availability on foraminiferal _11B deviations from _11Bborate. While an interesting idea, unfortunately I think the weight of this section is not supported by the authors' data. This whole discussion is essentially predicated on a single T. sacculifer _11B measurement from the western Equatorial Pacific, which has anomalously low _11Bforam value (relative to _11Bborate) compared to previous studies. The authors use this single observation to make a complex argument about how foraminifera calcification depth impacts light availability, which impacts symbiont photosynthesis, which affects microenvironment pH and hence foram _11B. Not only does this strike me as insufficient evidence to justify a discussion of this length, there are numerous assumptions and issues within the discussion that require referencing and clarification (see detailed comments below).

Response 2: We understand this point. Further support for this comes from data for ODP Sites 806A and 807A which we have added to this study. The Holocene data for Sites 806A and record similar low values to what we reported for site WPO7. This strengthens and justifies the length of the discussion.

Comment 3: Section 5.4 gives a rather hasty overview of how measuring _11B in different foraminifera species can reconstruct the upper water column pH and pCO2 gradients. I believe this is one of the big strengths of this paper and would like to see an expanded discussion of the depth profiles. One concern is that there may be some circularity here. If the authors have calibrated _11Bforam to modern profiles of _11Bborate, then by default they would correctly reconstruct the pH and pCO2 profile of the water column with the calibration dataset. There are no free parameters.

Response 3: In order to avoid this circularity, we recalculated one calibration for each species excluding the site of interest. Meaning that the recalculated site is not into the calibration. We also use this subset of calibration data to reconstruct vertical profiles in figure 9 which validates the work. When we compare both differences between calibration with or avoiding circularity (figure below or S6), the difference of $\delta 11B$ is on average (0.8% on $\delta^{11}B_{borate}$, 0.2% on pH and 5% on pCO₂). The results are similar to the whole

calibration dataset, subset of the data for calibration purposes which validates this work. Maximum divergence can be observed for G. ruber and T. sacculifer when utilizing the calibration [2] and [4].



We also have added a statement to Line 618-620 stating "Reconstruction of seawater pH and carbonate system parameters is achievable using foraminiferal δ 11B but additional coretop and down-core studies reconstructing depth profiles will be needed in order to further verify those calibrations."

Detailed review

RC1: L148-153. The terminology for isotopic fractionation factors and fractionations is incorrect. For Klochko et al. (2006), the fractionation factor, _B, is 1.0272, and the fractionation, "B, is the per mil value of 27.2_0.6%S' ee, e.g., Table 1 in Farmer et al. (2019) GCA. Please change to correct terminology throughout this paragraph.

Response: Corrected

Line 146 "given by the fraction factor (α). The fractionation (ϵ) between B(OH)₃ and B(OH)₄ of 27.2 \pm 0.6 % has been empirically determined by Klochko et al., (2006) in seawater."

RC1: L166-167. Benthic foraminifera _ 11B are only tangentially relevant to the results of this manuscript, so I recommend deleting this clause and associated references. Unless the benthic _ 11B results directly shed light on your interpretation (as is the case for Amphestegina, below).

Response: *I removed the benthic species.*

Line 160-163: "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)."

RC1: L212-224. It may be worth noting here (or perhaps earlier) that this manuscript largely focuses on tropical/subtropical foraminifera.

Response: We have added this information in the abstract (line 50).

RC1: L255. Were the samples dissolved in 1N HCl or HNO3? And why the two different acid matrices? HCl causes interference issues with ICP-MS measurements. Maybe this does not matter with the microdistillation step, but I'd like to see some explanation (see L260).

Response: The samples were dissolved in 1N HCl, results from the microdistillation in order to get the entire dissolution of the sample, including Fe-Mn oxide and hydroxides (reductive acid). Different dissolution after microdistillation resulting in mix HCl/HNO₃ matrices were tested resulting in no significant $\delta^{11}B$ differences on standards, however, working with really low concentration samples resulting in running samples in HCl matrix might be an issue at some point.

RC1: L283-286. Recommend splitting this into two sentences, one on the procedural blanks and one on the acid backgrounds/memory effect.

Response: Lines 279-286: "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 11B was 17 mV/ppb B (eg. 170 mV for 10ppb B) in wet plasma at 50μ l/min sample aspiration rate. Intensity of 11B for a sample at 10ppb B was typically $165mV \pm 5mV$ closely matched the $170mV \pm 5mV$ 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 $\leq 1mV$ on the 11B, meaning a contribution $\leq 1\%$ of the sample intensity, no memory effect was observed within and across sessions."

RC1: L288. As a field, we need to stop considering NEP as a "standard". It is not sufficiently homogenous to be useful for _11B analyses in foraminifera, where precisions of «1‰ are absolutely necessary for the vast majority of paleoceanographic purposes.

Response: We agree but due to the specifics of these analytical runs, unfortunately the NEP was the only "relevant" carbonate standard we had. We also ran seawaters as well along with carbonate standards though they did not have the same matrix.

RC1: L349-350 and Figure 4. Please plot the 11Bborate uncertainties on Figure 4. If they are too small to be observed, please note that in the figure caption.

Response: We recalculated the uncertainties based on the errors of Alkalinity and DIC from the Glodap database. Temperature, salinity and pressure were taking into account for all calculations.

RC1: L308-310. I'm surprised that the HF matrix prevents a B memory effect on the Neptune+, but not on the Element XR. To my knowledge, both instruments have effectively the same frontend plasma setup. Can you comment more on this? Does this high B background result from other measurements on the XR, e.g., rock digestions with really high B content? Did you swap out cones, etc? (This comment does not necessarily need to be addressed within the manuscript, I'm just curious).

Response: HF matrix does prevent memory effects, but with the Element XR we are measuring X/Ca ratios, so working only in HF matrix will directly precipitate CaF₂, a mix of HF and HNO₃ prevents precipitation. The boron background comes from other measurements. The shared instrument is used to run a lot of seawater samples, rocks etc... However, the cones were properly cleaned. We suspect the extraction lengt was the issue. You can still try to decontaminate with HF solution before conditioning the cones but results are not sufficient; One way to decrease the boron background is to condition the cones with the [Ca] standards (HNO3 and HF) for few hours, and switching the boron concentration of the standards.

RC1: L380-382. Except your G. ruber results are not consistent at the low 11Bborate end; they are 1‰ lighter than Henehan et al. (2013) found in sediment traps. It is very important that you state this observation because this is the principal reason for your elevated 11Bforam to 11Bborate slope relative to Henehan and Sanyal.

Response:

Lines 381-391 "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 $\delta 11Bborate > 19$ ‰ (Foster et al., 2008, Henehan et al., 2013, Raitzsch et al., 2018). However, for $\delta 11Bborate < 19$ ‰ our results show lighter $\delta 11Bcarbonate$ 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 $\delta 11Bcarbonate$ to $\delta 11Bborate$ of our linear regression is not statistically different from 1 and do not follow the low sensitivity trend of the culture experiments from Sanyal et al., (2001) or Henehan et al., (2013), (p<0.05). The uncertainty on this regression is important due to our small dataset and not inconsistent with the second calibration made compiling all data from literature. The sensitivity of this regression is 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)."

It was also highlighted by Michael Henehan (SC1), he was especially asking about the size fraction of our samples, I replied:

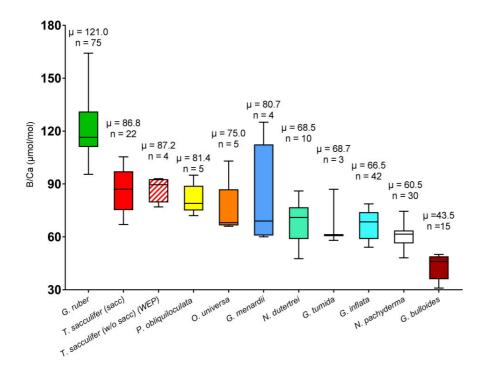
"Most of the samples have been picked in the 250-300 size fraction (average weight/shell of $11 \pm 4 \mu g$ (n=4, SD) only when measurements were realized), we chose a restrained size fraction to avoid this size-related variability (at least in our calibration), we also chose this lower size fraction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

RC1: L427-439. It could be worth making an updated version of Henehan et al. EPSL 2016's Figure 7 and including this in the main text.

We updated made this figure (below) and added it to the main text.



RC1: L438-439. One option- you could test the influence of sediment core water depth and foraminifer water depth with a multiple linear regression and see if either influence dominates B/Ca.

Response: At the end, linear regression was only significant when plotting B/Ca and the calcification depth not significant with water depth. From those results, the calcification depth is the parameter influencing B/Ca.

RC1: L457-459 and again L462-463. This is just another way of saying that the depth of the thermocline differs at each location, correct? If so, really what we need are proxies for thermocline depth.

Response: Please see our response to Comment 1.

RC1: L474-475. Yes, but this might not matter as much for foraminifera _11B. At higher latitudes, the seasonality of primary production (& hence foraminifera growing seasons) will be more tightly onstrained due to the seasonal progression of winter light limitation and intense vertical mixing and summer nutrient limitation.

Response: Yes, I agree, I changed for:

Line 478-481: "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."

RC1:1) You have not yet discussed symbionts in these different foraminifera species until near the end of the section (L509-512). Be explicit about what is known about symbionts in all studies species with an

introductory paragraph at the beginning of this section. How biologically similar are the symbiont assemblages in different foraminifera species? Is their concentration, photosynthetic activity, etc. similar? Do they show the same dependence on light intensity to maintain photosynthetic activity?

- 2) Following on the above, it is not clear to the reader whether "weaker photosynthetic activity" (L487) corresponds to an absence of symbionts, less active symbionts, lower symbiont density, lower light levels, etc. Please clarify.
- 3) L490. Is symbiont photosynthetic activity a function of light level alone? What about symbiont composition? This comes across as highly speculative without references; please either include references or phrase as a speculation. (In general, it is fine to speculate a little, as long as the reader is aware that you are speculating).

Response: We have expanded the discussion around the types of symbionts/photosynthetic activity/symbiont density. Although there is not a lot of data in the literature, there is a recent study from Takagi et al., (2019) – published this September – that was helpful in strengthening the discussion.

Note it seems that the nutrient concentrations were not impacting the photosynthesis activity for T. sacculifer, and that is why we did not mention it.

The following text was added,

Lines 489-501: "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)."

Lines 526-530: "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 most important variations in symbiont density versus its test size.

Microenvironment pH results for N. dutertrei, G. menardii, G. tumida, are similar to O. universa and suggest a threshold for respiration driven δIIB 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 lowered microenvironment pH compared to other deeper dweller species supporting this respiration driven microenvironment."

RC1: 4) Light intensity in the ocean is not a function of water depth alone; turbidity matters quite a lot. Is it reasonable to compare the light intensity in different oceanographic regions as a function of water depth alone?

Response: This is true, but we think it is still reasonable for the calculations because we used a light attenuation coefficient from Wang et al., (2008) which should take most of the parameters into account even if no variability is constrained.

RC1: 4) L492. The negative relationship between _11B and water depth in Figure S2 is driven only by the low _11B measured in western equatorial Pacific T. sacculifer. Have you propagated your uncertainty in depth habitat to _11Bborate in your calculation of _11B as plotted in Figure S2? Looking at the western equatorial Pacific (WP7-01), the 80_20m depth range from CD2 corresponds to a _1‰ _11Bborate range (Fig. 4). (If you include the CD3 estimate of 125_15 m, the total possible _11Bborate increases to _1.5‰. Add on the _11Bforam measurement uncertainty of _0.22‰ and I cannot see how you get a total _11B uncertainty of <1‰.

Response: The uncertainties on the $\delta 11B$ borate are calculated using Michael Henehan's code which takes into account the uncertainties on pH, temperature, salinity and $\delta 11B$ seawater. Uncertainties of pH, temperature and salinity were calculated integrating the parameters between uncertainties of the calcification depth. This is the same approach that was used in Raitzsch et al. (2018). Then the uncertainty on $\Delta 11B$ was measured by the square root of the sum of the square uncertainties on $\delta 11B$ borate and $\delta 11B$ carbonate.

RC1: 5) I do not think linear regression is the appropriate test statistical test for the significance of the _11B-water depth relationship, because depending on how you performed the regression, it may not account for the uncertainty on each datapoint. A t-test for mean difference between Arabian Sea, Indian Ocean, and western equatorial Pacific T. sacculifer _11B would be more robust. I would bet that such a test will indicate no significant _11B difference between the different regions given the small sample sizes. If true, this detailed line of discussion is unnecessary; instead, you can present this as an observation that requires future study to confirm or deny.

Response: We have added two data points from sites 806A and 807A which makes the t-test more robust.

For $\delta 11B$.

Unpaired t-test between the WEP and the rest of the samples for T. sacculifer (w/o sacc) is significantly different (p=0.01).

For ∆11B.

Unpaired t-test between the WEP and the rest of the samples for T. sacculifer (w/o sacc) is not significantly different (p=0.067). If now we look at both G. ruber and T. sacculifer (w/o sacc) which are presented in the plot, difference between Arabian Sea+Indian Ocean and WEP is significantly different (p=0.0075). If we also look at T. sacculifer (w/o sacc and sacc) + G.ruber between Arabian Sea+Indian Ocean and WEP the difference is significantly different (p=0.0427).

Lines 520-522: "Especially, we observe an important decrease of $\delta^{II}B$ in the WEP for T. sacculifer (w/o sacc), significantly different from the other sites (p<0.05) and a calculated $\Delta^{II}B$ of G. ruber, T. sacculifer (w/o sacc and sacc) significantly lower in the WEP compared to the other sites (p<0.05)."

RC1: Any precipitation rate implications need to be very carefully phrased. The higher "values" for G. ruber and T. sacculifer have large uncertainties, so they are probably not robustly higher than other species (unless a statistical test confirms this to be true). Moreover, it is unclear the extent to which the growth

rates of different foraminifera species differ from one another. Nevertheless, your point on higher B/Ca sensitivity to borate/bicarbonate in the shallower species is very interesting.

Response: We mitigated this paragraph.

Lines 556-567: "When combining all literature data, T. sacculifer and G. ruber have sensitivities of $\delta 11B$ carbonate to $\delta 11B$ borate of 0.83 ± 0.48 and 0.46 ± 0.34 respectively in line with previous literature and paleo-CO2 reconstructions. Also, if we only take into account our data, the observation that the sensitivity of $\delta 11B$ carbonate to $\delta 11B$ 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 $\delta 11B$ carbonate to $\delta 11B$ borate. We can then again speculate that the observed high values for $\delta 11B$ 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-]/[HCO3-] relative to deeper dwelling species. As indicated by Farmer et al., (2019), studies of calcite precipitation rates in foraminifera could help to test this hypothesis and improve our understanding of the fundamental basis of boron-based proxies."

RC1: L525-527. What do you mean by "higher values "here? Slopes of δ 11Bforam to δ 11Bborate regressions, or Δ 11B, or something else?

Response: Lines 561-562:" G. ruber (1.12 \pm 1.67) and T. sacculifer (1.38 \pm 1.35) present higher sensitivities of δ 11Bcarbonate to δ 11Bborate."

RC1: L541-542. Given the speculative nature of the depth/light effect on symbiont photosynthesis, foraminifer microenvironment pH and thus foraminifera _11B, change to "which may be explained by the deeper depth habitat for these taxa in the WEP, where lower light levels might reduce symbiont photosynthetic activity". Or remove.

Response: Changed.

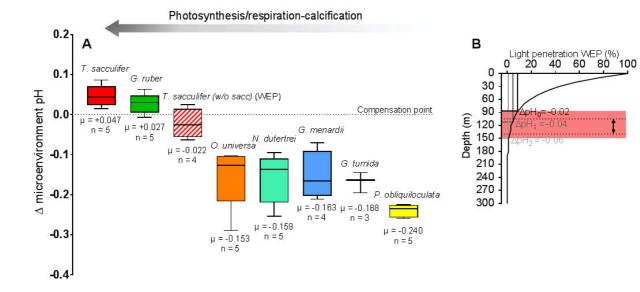
RC1: Fig.2/Fig.4

Response: Front made bigger

RC1: Figure 7. I really cannot follow this figure at all. Should there be a pH axis?

Response: For more clarity, we combined in Figure 8 (or below) the Δ microenvironment pH and this depth profile. This depth profile only aims to explain the low $\delta^{ll}B$ in the WEP.

This is based on the calculation of insolation needed to explain the decrease in $\Delta pH0$, $\Delta pH1$ and $\Delta pH2$ observed from the $\delta^{11}B$. This is an independent way to calculate the depth habitat explaining the $\delta^{11}B$. The insolation is calculated based on Jorgensen et al., (1985). I found the insolation needed to decrease of $\Delta pH0$, $\Delta pH1$ and $\Delta pH2$ and converted in % insolation in the water column. What is interesting is that the decrease of insolation around 125m can explain the low $\delta^{11}B$ values.



Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO₂ gradients Maxence Guillermic^{1,2}, Sambuddha Misra^{3,4}, Robert Eagle^{1,2}, Alexandra Villa^{2,5}, Fengming Chang⁶, Aradhna Tripati 1,2 ¹ Department of Earth, Planetary, and Space Sciences, Department of Atmospheric and Oceanic Sciences, Institute of the Environment and Sustainability, UCLA, University of California – Los Angeles, Los Angeles, CA 90095 USA ² Laboratoire Géosciences Océan UMR6538, UBO, Institut Universitaire Européen de la Mer, Rue Dumont d'Urville, 29280, Plouzané, France ³ Indian Institute of Science, Centre for Earth Sciences, Bengaluru, Karnataka 560012, India ⁴ The Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, UK ⁵ Department of Geology, University of Wisconsin-Madison, Madison, WI 53706 USA ⁶ Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China Submitted to Biogeosciences *Corresponding author: E-mail address: maxence.guillermic@gmail.com

ABSTRACT

45 46

47 48

49 50

51

52

53

54 55

56

57

58

59

60

61

62

44

Boron isotope systematics of planktonic foraminifera from core-top sediments and culture experiments have been studied to investigate the sensitivity of δ^{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 pCO₂ 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 δ^{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), [HCO₃-], [CO₃²-]), can be utilized to constrain aqueous pCO₂. 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 pCO₂ utilizing downcore samples from sites that are in quasi-equilibrium with the atmosphere at present. δ^{11} B_{carbonate} based reconstructed values of pCO₂ are analytically indistinguishable from ice core CO₂ 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 μ g CaCO₃), 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 pCO₂.

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, δ^{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 ($\tau_B \sim 14$ 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:

140
$$\delta^{11} B (\%_0) = 1000 x \left(\frac{{}^{11} B / {}^{10} B_{Sample}}{{}^{11} B / {}^{10} B_{NIST 951-a}} - 1 \right)$$
 (1)

where positive values represent enrichment in the heavy isotope ¹¹B, and negative values enrichment in the light isotope ¹⁰B, 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 ¹¹B 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 \sim 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).

184
$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2 \text{ or } Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$
 [calcification] (2)
185 $CaCO_3 + CH_2O + O_2 \leftrightarrow CO_2 + H_2O$ [respiration/photosynthesis] (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 \pm 0.17) (Henehan et al. 2016), while culture experiments report slopes of \leq 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 HNO₃ 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 M Ω .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 μ L 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 μ L 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® 50μ l/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 (\sim 5 ng B) to 20 ppb B samples (\sim 10 ng B). Instrumental sensitivity for 11 B was 17 mV/ppb B (eg. 170 mV for 10ppb B) in wet plasma at 50μ l/min sample aspiration rate. Intensity of 11 B for a sample at 10ppb B was typically $165\text{mV} \pm 5\text{mV}$ closely matched the $170\text{mV} \pm 5\text{mV}$ 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 $\leq 1\text{mV}$ 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., $\delta^{11}B = 26.12 \pm 0.92$ ‰, 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 ($\delta^{11}B = 19.9 \pm 0.6$ ‰, 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 $\delta^{11}B_{NEP} = 25.70 \pm 0.93$ ‰ (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 JCP₁ 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: $^7\text{Li} < 2\%$, $^{11}\text{B} < 7\%$, $^{25}\text{Mg} < 0.2\%$ and $^{43}\text{Ca} < 0.02\%$. Additionally, blanks for a 10 ppm Ca session were: $^7\text{Li} < 2.5\%$, $^{11}\text{B} < 10\%$, $^{25}\text{Mg} < 0.4\%$ and $^{43}\text{Ca} < 0.05\%$. 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 $\delta^{18}O$ measurements of the carbonate ($\delta^{18}O_c$) to estimate calcification depths (referred to as $\delta^{18}O$ -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 ± 10 m 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 δ¹¹B_{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^{\odot} 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 pCO₂ 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 \sim 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 δ^{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 and do not follow the low sensitivity trend of the culture experiments from Sanyal et al., (2001) or Henehan et al., (2013), (p<0.05). The uncertainty on this regression is important due to our small dataset and not inconsistent with the second calibration made compiling all data from literature. The sensitivity of this regression is 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 (\pm 0.13) (R²=0.7987, p<0.0001); if only our data are used, we calculate a slope that is not significantly different (0.82 \pm 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. 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). The B/Ca data for deep-dwelling taxa exhibits a significant correlation with [B(OH)₄-]/[HCO₃-] (p<0.05), but no correlation with δ^{11} B_{carbonate} and temperature (Fig. S3). Surface-dwelling species have B/Ca ratios that exhibit significant correlations with [B(OH)₄-]/[HCO₃-], δ^{11} B_{carbonate} and temperature. The sensitivity of B/Ca to [B(OH)₄-]/[HCO₃-] 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-]/[HCO₃-], δ^{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 (R²=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 δ¹¹B_{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 pCO₂. 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 δ^{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 δ¹¹B_{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 $\delta^{11}B_{\text{borate}}$ 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 δ¹¹B, 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).

499

500

501

502

503

504

505

506

507

508

509

510

511

512

513

514

515

516

517

518

519

520

521

522

523

524

525

526

527

528

529

530

531

532

533

534

535

536537

538

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 for aminiferal iving close to the surface should see their microenvironment pH (thus δ^{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 Δ^{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 δ^{11} B in the WEP for T. sacculifer (w/o sacc), significantly different from the other sites (p<0.05). The Δ^{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 δ^{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 δ^{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. Amicroenvironment 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 δ^{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 δ^{11} B sensitivity to δ^{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-CO₂ 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 pCO₂. Mixed-layer species (eg. *G. ruber* and *T. sacculifer*) are potential archives for atmospheric CO₂ 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 pCO₂, 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 δ^{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 δ^{11} B with smaller test size, our sample add a weight/shell of $11 \pm 4 \mu g$ (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 pCO₂. We are able to reproduce pH and pCO₂ 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 pCO₂ 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 deepdweller (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* (deepdwellers) 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 pCO₂ 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.

637638

631

Competing interests

The authors declare that they have no conflict of interest.

639640641

642

643

644

645

646

647

648

649

Acknowledgments:

The authors wish to thank Jesse Farmer for his valuable and detailed comments on the actual and a previous version of the manuscript. We wish to thank Michael Henehan for helpful discussion, comments on the manuscript and help with the code. We also want to thank the anonymous reviewer for helpful comments. Lea Bonnin for assistance with picking samples, the IODP repository for provision of samples, the Tripati Laboratory (UCLA) for their technical support, Mervyn Greaves, Madeleine Bohlin (University of Cambridge) for technical support and use of laboratory space, Yoan Germain, Emmanuel Ponzevera and Oanez Lebeau for technical support and use of laboratory space in Brest, Jill Sutton for helpful conversation on the manuscript. Research is supported by DOE BES grant DE-FG02-13ER16402, by the International Research Chair Program that is funded by the French government (LabexMer ANR-10-LABX-19-01), and IAGC student research grant 2017.

650 651

652 References

- Allen, K. A. and Hönisch, B.: The planktic foraminiferal B/Ca proxy for seawater carbonate chemistry: A critical evaluation, Earth Planet. Sci. Lett, 345–348, 203–211, 2012.
- Anand, P., Elderfield, H. and Conte, M. H.: Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. Paleoceanography 18, 2003.
- Anderson, O. R. and Bé, A.W. H.: The ultrastructure of a planktonic foraminifer, Globigerinoides sacculifer (Brady), and its symbiotic dinoflagellates, J. Foramin. Res., 6, 1–21, 1976.
- Arbuszewski, J., DeMenocal, P., Kaplan, A. and Farmer, E. C.: On the fidelity of shell-derived δ18Oseawater estimates, Earth Planet. Sci. Lett., 300, 185–196, 2010.
- Axelsson, M. D., Rodushkin, I., Ingri, J. and Öhlander, B.: Multielemental analysis of Mn–Fe nodules by ICP– MS: optimisation of analytical method, Analyst, 127, 76–82, 2002.
- Babila, T.L., Rosenthal, Y., Conte, M.H.: Evaluation of the biogeochemical controls on B/Ca of Globigerinoides ruber white from the Oceanic Flux Pro-gram, Bermuda. Earth Planet. Sci. Lett.404, 67–76, 2014.
- Barker S., Greaves M. and Elderfield H.: A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochemistry, Geophys. Geosystems 4, 1–20, 2003.
- Bartoli, G., Hönisch, B. and Zeebe, R. E.: Atmospheric CO2 decline during the Pliocene intensification of Northern Hemisphere glaciations. Paleoceanography 26, 1–14, 2011.
- Bemis, B. E., Spero, H. J., Bijma, J. and Lea, D. W.: Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. Paleoceanography 13, 150–160, 1998.
- Bemis, B. E., Spero, H. J. and Thunell, R. C.: Using species-specific paleotemperature equations with foraminifera: a case study in the Southern California Bight, Mar. Micropaleontol, 46, 405–430, 2002.
- Bijma, J., Faber Jr., W.W., Hemleben, C.: Temperature and salinity limits for growth and survival of some planktonic foraminifers in laboratory cultures, J. Foraminiferal Res. 20 (2), 95–116, 1990.
- Bijma, J., Hönisch, B. and Zeebe, R. E.: Impact of the ocean carbonate chemistry on living foraminiferal shell
 weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W.
 Broecker and E. Clark, Geochemistry, Geophys. Geosystems, 3, 1–7, 2002.
- Birch, H., Coxall, H. K., Pearson, P. N., Kroon, D. and O'Regan, M.: Planktonic foraminifera stable isotopes and water column structure: Disentangling ecological signals, Mar. Micropaleontol., 101, 127–145, 2013.
- Boyer, T.P., Antonov, J. I., Baranova, O. K., Coleman, C., Garcia, H. E., Grodsky, A., Johnson, D. R., Locarnini,
 R. A., Mishonov, A. V., O'Brien, T.D., Paver, C.R., Reagan, J.R., Seidov, D., Smolyar, I. V., and Zweng,
 M. M.: World Ocean Database, NOAA Atlas NESDIS 72, S. Levitus, Ed., A. Mishonov, Technical Ed.,
 Silver Spring, MD, 209, 2013.
- Boyle, E. A.: Manganese carbonate overgrowths on foraminifera tests, Geochim. Cosmochim. Acta., 47, 1815–1819, 1983.
- Branson, O., Kaczmarek, K., Redfern, S. A. T., Misra, S., Langer, G., Tyliszczak, T., Bijma, J. and Elderfield,
 H.: The coordination and distribution of B in foraminiferal calcite, Earth Planet. Sci. Lett., 416, 67–72,
 2015.

- 690 Catanzaro, E.J., Champion, C.E., Garner, A.L., Marinenko, G., Sappenfield, K.M. and Shields, W.R.: Boric
- Acid; Isotopic and Assay Standard Reference Materials. U.S. Natl. Bur. Stand. Spec., Publ. 260-17, 70p,
- **692** 1970.
- 693 Chalk, T. B., Hain, M. P., Foster, G. L., Rohling, E. J., Sexton, P. F., Badger, M. P. S., Cherry, S. G., Hasenfratz,
- A. P., Haug, G. H., Jaccard, S. L., Martínez-García, A., Pälike, H., Pancost, R. D. and Wilson, P. A.:
- 695 Causes of ice age intensification across the Mid-Pleistocene Transition, Proc. Natl. Acad. Sci., 114,
- 696 13114–13119, 2017.
- 697 Coadic, R., Bassinot, F., Dissard, D., Douville, E., Greaves, M. and Michel, E.: A core-top study of dissolution
- effect on B/Ca in Globigerinoides sacculifer from the tropical Atlantic: Potential bias for paleo-
- reconstruction of seawater carbonate chemistry, Geochemistry, Geophys. Geosystems 14, 1053–1068,
- 700 2013.
- de Nooijer, L. J., Spero, H. J., Erez, J., Bijma, J. and Reichart, G. J.: Biomineralization in perforate foraminifera.
- 702 Earth-Science Rev., 135, 48–58, 2014.
- Dekens, P. S., Lea, D. W., Pak, D. K. and Spero, H. J.: Core top calibration of Mg/Ca in tropical foraminifera:
- Refining paleotemperature estimation, Geochemistry, Geophys. Geosystems 3, 1–29, 2002.
- Deuser, W.G., Ross, E.H., Hemleben, Ch., Spindler, M.: Seasonal changes in species composition, numbers,
- mass, size, and isotopic composition of planktonic foraminifera settling into the deep Sargasso Sea,
- Palaeogeogr., Palaeoclimat., Palaeoecol., 33:103-127, 1981.
- 708 Deuser, W. G. and Ross, E. H.: Seasonally abundant planktonic foraminifera of the Sargasso Sea; succession,
- deep-water fluxes, isotopic compositions, and paleoceanographic implications, J. Foraminifer, Res. 19,
- 710 268–293, 1989.
- 711 Dickson, A. G.: Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15
- 712 K., Deep Sea Res., Part A, Oceanogr. Res. Pap. 37, 755–766, 1990.
- 713 Dickson, A.G., Millero, F.J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in
- 714 seawater media, Deep-Sea Res., 34, 1733–1743, 1987.
- 715 Douville, E., Paterne, M., Cabioch, G., Louvat, P., Gaillardet, J., Juillet-Leclerc, A. and Ayliffe, L.: Abrupt sea
- surface pH change at the end of the Younger Dryas in the central sub-equatorial Pacific inferred from
- boron isotope abundance in corals (Porites), Biogeosciences 7, 2445–2459, 2010.
- 718 Duguay, L.E.: Comparative laboratory and field studies on calcification and carbon fixation in foraminiferal-
- 719 algal associations, Journal of Foraminiferal Research 13, 252-261, 1983.
- 720 Duplessy, J., Labeyrie, L., Juilletleclerc, A., Maitre, F., Duprat, J. and Sarnthein, M.: Surface salinity
- 721 reconstruction of the north-atlantic ocean during the last glacial maximum, Oceanol. Acta, 14, 311–324,
- **722** 1991.
- 723 Elderfield, H., Yu, J., Anand, P., Kiefer, T. and Nyland, B.: Calibrations for benthic foraminiferal Mg/Ca
- paleothermometry and the carbonate ion hypothesis, Earth Planet. Sci. Lett., 250, 633–649., 2006.
- 725 Elderfield, H. and Granssen, G.: Past temperatures and O18 of surface ocean waters inferred from foraminiferal
- 726 Mg/Ca ratios, Nature 405, 442–445, 2000.
- 727 Erez J.: Calcification Rates, Photosynthesis and Light in Planktonic Foraminifera. In: Westbroek P., de Jong
- 728 E.W. (eds) Biomineralization and Biological Metal Accumulation. Springer, Dordrecht, 1983.
- 729 Erez, J.: The Source of Ions for Biomineralization in Foraminifera and Their Implications for Paleoceanographic
- 730 Proxies, Rev. Mineral. Geochemistry, 54, 115–149, 2003.

- Fairbanks, R. G. and Wiebe, P. H.: Foraminifera and Chlorophyll Maximum: Vertical Distribution, Seasonal Succession, and Paleoceanographic Significance, Science, 209, 1524–1526, 1980.
- Fairbanks, R. G., Sverdlove, M., Free, R., Wiebe, P. H. and Bé, A. W. H.: Vertical distribution and isotopic fractionation of living planktonic foraminifera from the Panama Basin, Nature, 298, 841–844, 1982.
- Farmer, E. C., Kaplan, A., de Menocal, P. B. and Lynch-Stieglitz, J.: Corroborating ecological depth preferences of planktonic foraminifera in the tropical Atlantic with the stable oxygen isotope ratios of core top specimens, Paleoceanography, 22, 1–14, 2007.
- Feely, R.: Impact of Anthropogenic CO2 on the CaCO3 System in the Oceans, Science, 305, 362–366, 2004.
- Ferguson, J. E., Henderson, G. M., Kucera, M. and Rickaby, R. E. M.: Systematic change of foraminiferal Mg/Ca ratios across a strong salinity gradient, Earth Planet. Sci. Lett., 265, 153–166, 2008.
- Foster, G. L.: Seawater pH, pCO2 and [CO32–] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera, Earth Planet. Sci. Lett., 271, 254–266, 2008.
- Foster, G. L. and Sexton, P. F.: Enhanced carbon dioxide outgassing from the eastern equatorial Atlantic during the last glacial, Geology, 42, 1003–1006, 2014.
- Foster, G. L., Lear, C. H. and Rae, J. W. B.: The evolution of pCO2, ice volume and climate during the middle Miocene, Earth Planet. Sci. Lett., 341–344, 243–254, 2012.
- Foster, G. L. and Rae, J. W. B.: Reconstructing Ocean pH with Boron Isotopes in Foraminifera, Annu. Rev.
 Earth Planet. Sci., 44, 207–237, 2016.
- Gabitov, R. I., Rollion-bard, C., Tripati, A. and Sadekov, A.: In situ study of boron partitioning between calcite and fluid at different crystal growth rates, Geochim. Cosmochim. Acta, 137, 81–92, 2014.
- Gaillardet, J., Lemarchand, D., Göpel, C. and Manhès, G.: Evaporation and Sublimation of Boric Acid:
 Application for Boron Purification from Organic Rich Solutions, Geostand. Newsl., 25, 67–75, 2001.
- 753 Gast R. J. and Caron D. A.: Photosymbiotic associations in planktonic foraminifera and radiolaria, 1–7, 2001.
- Gastrich, M.D.: Ultrastructure of a new intracellular symbiotic alga found within planktonic foraminifera, Journal of Phycology 23, 623-632, 1988.
- 756 Gattuso, J.P. and Hansson, L.: Ocean acidification, Oxford University Press, 2011.
- 757 Hallock P.: Algal Symbiosis: A Mathematical Analysis Marine Biology 62, 249-255, 1981b.
- Hemming, N. G. and Hanson, G. N. Boron isotopic composition and concentration in modern marine carbonates, Geochim. Cosmochim. Acta, 56, 537–543, 1992.
- Hendry, K.R., Rickaby, R.E.M., Meredith, M.P., Elderfield, H.: Controls on sta-ble isotope and trace metal
 uptake in Neogloboquadrina pachyderma (sinis-tral) from an Antarctic sea-ice environment. Earth Planet.
 Sci. Lett.278, 67–77, 2009.
- Henehan, M. J., Foster, G. L., Bostock, H. C., Greenop, R., Marshall, B. J. and Wilson, P. A.: A new boron
 isotope-pH calibration for Orbulina universa, with implications for understanding and accounting for 'vital effects', Earth Planet. Sci. Lett., 454, 282–292, 2016.
- Henehan, M. J., Foster, G. L., Rae, J. W. B., Prentice, K. C., Erez, J., Bostock, H. C., Marshall, B. J. and Wilson,
 P. A.: Evaluating the utility of B/Ca ratios in planktic foraminifera as a proxy for the carbonate system: A case study of Globigerinoides ruber, Geochemistry, Geophys. Geosystems 16, 1052–1069, 2015.

- Henehan, M. J., Rae, J. W. B., Foster, G. L., Erez, J., Prentice, K. C., Kucera, M., Bostock, H. C., Martínez-Botí,
- M. A., Milton, J. A., Wilson, P. A., Marshall, B. J. and Elliott, T.: Calibration of the boron isotope proxy in
- the planktonic foraminifera Globigerinoides ruber for use in palaeo-CO2reconstruction, Earth Planet. Sci.
- 772 Lett. 364, 111–122, 2013.
- Holcomb, M., Decarlo, T. M., Schoepf, V., Dissard, D., Tanaka, K. and McCulloch, M.: Cleaning and pre-
- treatment procedures for biogenic and synthetic calcium carbonate powders for determination of elemental
- and boron isotopic compositions, Chem. Geol., 398, 11–21, 2015.
- Hönisch, B., Hemming, N. G., Archer, D., Siddall, M. and McManus, J. F.: Atmospheric Carbon Dioxide
 Concentration Across the Mid-Pleistocene Transition, Science, 324, 1551–1554, 2009.
- Hönisch, B., Bijma, J., Russell, A. D., Spero, H. J., Palmer, M. R., Zeebe, R. E. and Eisenhauer, A.: The
- influence of symbiont photosynthesis on the boron isotopic composition of foraminifera shells, Mar.
- 780 Micropaleontol., 49, 87–96, 2003.
- Hönisch, B. and Hemming, N. G.: Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: Partial dissolution and shell size effects, Paleoceanography 19, 1–13, 2004.
- Hönisch, B., Bickert, T. and Hemming, N. G.: Modern and Pleistocene boron isotope composition of the benthic foraminifer Cibicidoides wuellerstorfi, Earth Planet. Sci. Lett., 272, 309–318, 2008.
- Howes, E. L., Kaczmarek, K., Raitzsch, M., Mewes, A., Bijma, N., Horn, I., Misra, S., Gattuso, J. P. and Bijma,
- 786 J.: Decoupled carbonate chemistry controls on the incorporation of boron into Orbulina universa,
- 787 Biogeosciences, 14, 415–430, 2017.
- 788 IPCC: Climate Change 2014 The Physical Science Basis, edited by Intergovernmental Panel on Climate
 789 Change, Cambridge University Press, Cambridge., 2014.
- Jørgensen, B. B., Erez, J., Revsbech, P. and Cohen, Y.: Symbiotic photosynthesis in a planktonic foraminifera,
- 791 Globigerinoides sacculifer (Brady), studied with microelectrodes, Limnol. Oceanogr., 30, 1253–1267
- **792** 1985.
- Kaczmarek, K., Nehrke, G., Misra, S., Bijma, J. and Elderfield, H.: Investigating the effects of growth rate and
- temperature on the B/Ca ratio and δ11B during inorganic calcite formation, Chem. Geol., 421, 81–92,
- 795 2016.
- Kemle-von Mücke S. and Oberhänsli H.: The Distribution of Living Planktic Foraminifera in Relation to Southeast Atlantic Oceanography, Use Proxies Paleoceanogr., 91–115, 1999.
- Key, R.M.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18, GB4031, 2004.
- Kim, S.-T. and O'Neil, J. R.: Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, Geochim. Cosmochim. Acta, 61, 3461–3475, 1997.
- Klochko, K., Cody, G. D., Tossell, J. A., Dera, P. and Kaufman, A. J.: Re-evaluating boron speciation in biogenic calcite and aragonite using 11B MAS NMR, Geochim. Cosmochim. Acta, 73, 1890–1900, 2009.
- Klochko, K., Kaufman, A. J., Yao, W., Byrne, R. H. and Tossell, J. A.: Experimental measurement of boron isotope fractionation in seawater, Earth Planet. Sci. Lett., 248, 276–285, 2006.
- Köhler-Rink, S. and Kühl, M.: Microsensor studies of photosynthesis and respiration in larger symbiotic
- 807 foraminifera. I. The physico-chemical microenvironment of Marginopora vertebralis, Amphistegina
- lobifera and Amphisorus hemrichii, Mar. Biol., 137, 473–486, 2000.

- Köhler-Rink, S. and Kühl, M., Microsensor studies of photosynthesis and respiration in the larger symbiont 809 810 bearing foraminifera Amphistegina lobifera, and Amphisorus hemprichii, Ophelia, 55, 111-122, 2001.
- 811 Lea, D. W., Pak, D. K. and Spero, H. J.: Climate impact of late quaternary equatorial Pacific sea surface 812 temperature variations, Science, 289, 1719-1724, 2000.
- Lemarchand, D., Gaillardet, J., Lewin, A. and Allègre, C. J.: Boron isotope systematics in large rivers: 813
- 814 Implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic, Chem. Geol.,
- 815 190, 123-14, 2002.
- 816 Liu, Y., Liu, W., Peng, Z., Xiao, Y., Wei, G., Sun, W., He, J., Liu, G. and Chou, C.-L.: Instability of seawater
- 817 pH in the South China Sea during the mid-late Holocene: Evidence from boron isotopic composition of
- 818 corals, Geochim. Cosmochim. Acta, 73, 1264–1272, 2009.
- 819 Lloyd, N. S., Sadekoy, A. Y. and Misra, S.: Application of 1013ohm Faraday cup current amplifiers for boron
- 820 isotopic analyses by solution mode and laser ablation multicollector inductively coupled plasma mass
- 821 spectrometry, Rapid Commun. Mass Spectrom., 32, 9-18, 2018.
- 822 Martínez-Botí, M. A., Foster, G. L., Chalk, T. B., Rohling, E. J., Sexton, P. F., Lunt, D. J., Pancost, R. D.,
- 823 Badger, M. P. S. and Schmidt, D. N.: Plio-Pleistocene climate sensitivity evaluated using high-resolution
- 824 CO2 records, Nature, 518, 49-54, 2015a.
- 825 Martínez-Botí M. A., Marino G., Foster G. L., Ziveri P., Henehan M. J., Rae J. W. B., Mortyn P. G. and Vance
- 826 D.: Boron isotope evidence for oceanic carbon dioxide leakage during the last deglaciation. Nature, 518,
- 827 219-222, 2015b.
- 828 Martínez-Botí, M. A., Mortyn, P. G., Schmidt, D. N., Vance, D. and Field, D. B.: Mg/Ca in foraminifera from
- 829 plankton tows: Evaluation of proxy controls and comparison with core tops, Earth Planet. Sci. Lett., 307,
- 830 113-125, 2011.
- 831 Mavromatis, V., Montouillout, V., Noireaux, J., Gaillardet, J. and Schott, J.: Characterization of boron
- 832 incorporation and speciation in calcite and aragonite from co-precipitation experiments under controlled
- 833 pH, temperature and precipitation rate, Geochim. Cosmochim. Acta, 150, 299-313, 2015.
- 834 McCulloch, M. T., D'Olivo, J. P., Falter, J. L., Georgiou, L., Holcomb, M., Montagna, P. and Trotter, J. A.
- 835 Boron Isotopic Systematics in Scleractinian Corals and the Role of pH Up-regulation, Boron Isot. Adv.
- 836 Isot. Geochemistry, 2018.
- 837 Millero, F.: Speciation of metals in natural waters, Geochem. Trans., 2, 57, 2001.
- 838 Millero, F., Woosley, R., DiTrolio, B. and Waters, J.: Effect of Ocean Acidification on the Speciation of Metals
- 839 in Seawater, Oceanography 22, 72-85, 2009.
- 840 Misra, S., Greaves, M., Owen, R., Kerr, J., Elmore, A. C. and Elderfield, H.: Determination of B/Ca of natural
- 841 carbonates by HR-ICP-MS, Geochemistry, Geophys. Geosystems, 15, 1617–1628, 2014a.
- 842 Misra, S., Owen, R., Kerr, J., Greaves, M. and Elderfield, H.: Determination of δ11B by HR-ICP-MS from mass
- 843 limited samples: Application to natural carbonates and water samples, Geochim. Cosmochim. Acta, 140,
- 531-552, 2014b. 844
- 845 Mortyn, P. G. and Charles, C. D.: Planktonic foraminiferal depth habitat and δ 18 O calibrations: Plankton tow
- 846 results from the Atlantic sector of the Southern Ocean, Paleoceanography, 18, 2003.
- 847 Mulitza, S., Boltovskoy, D., Donner, B., Meggers, H., Paul, A. and Wefer, G.: Temperature:δ18O relationships
- 848 of planktonic foraminifera collected from surface waters, Palaeogeogr. Palaeoclimatol. Palaeoecol., 202,
- 849 143-152, 2003.

- Ni, Y., Foster, G. L., Bailey, T., Elliott, T., Schmidt, D. N., Pearson, P., Haley, B. and Coath, C.: A core top assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers, Paleoceanography 22, 2007.
- Nir, O., Vengosh, A., Harkness, J. S., Dwyer, G. S. and Lahav, O.: Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH, Earth Planet. Sci. Lett., 414, 1–5, 2015.
- Noireaux, J., Mavromatis, V., Gaillardet, J., Schott, J., Montouillout, V., Louvat, P., Rollion-Bard, C. and Neuville, D. R.: Crystallographic control on the boron isotope paleo-pH proxy, Earth Planet. Sci. Lett., 430, 398–407, 2015.
- Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida,
 A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.
 G., Plattner, G. K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I.
 J., Weirig, M. F., Yamanaka, Y. and Yool, A.: Anthropogenic ocean acidification over the twenty-first
 century and its impact on calcifying organisms, Nature, 437, 681–686, 2005.
- Pagani. M.: Marked Decline in Atmospheric Carbon Dioxide Concentrations During the Paleogene, Science, 309, 600–603, 2005.
- Palmer, M. R., Pearson, P. N. and Cobb, S. J., Reconstructing Past Ocean pH-Depth Profiles, Science, 282, 1468–1471, 1998.
- Pearson, P. N. and Palmer, M. R.: Middle Eocene seawater pH and atmospheric carbon dioxide concentrations, Science, 284, 1824–1826, 1999.
- Peeters, F. J. C. and Brummer, G.-J. a.: The seasonal and vertical distribution of living planktic foraminifera in the NW Arabian Sea, Geol. Soc. London, Spec. Publ., 195, 463–497, 2002.
- Quintana Krupinski, N. B., Russell, A. D., Pak, D. K. and Paytan, A.: Core-top calibration of B/Ca in Pacific
 Ocean Neogloboquadrina incompta and Globigerina bulloides as a surface water carbonate system proxy,
 Earth Planet. Sci. Lett., 466, 139–151, 2017.
- Rae, J.W.B.: Boron Isotopes in Foraminifera: Systematics, Biomineralisation, and CO₂ Reconstruction. In:
 Marschall, H., Foster, G. (eds), Boron Isotopes. Advances in Isotope Geochemistry. Springer, Cham, 2018.
- Rae, J. W. B., Foster, G. L., Schmidt, D. N. and Elliott, T.: Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system, Earth Planet. Sci. Lett., 302, 403–413, 2011.
- Raitzsch, M., Bijma, J., Benthien, A., Richter, K.-U., Steinhoefel, G. and Kučera, M.: Boron isotope-based
 seasonal paleo-pH reconstruction for the Southeast Atlantic A multispecies approach using habitat
 preference of planktonic foraminifera, Earth Planet. Sci. Lett., 487, 138–150, 2018.
- Ravelo, A. C. and Fairbanks, R. G.: Oxygen isotopic composition of multiple species of planktonic foraminifera:
 recorder of the modern photic zone temperature gradient, Palaeogeogr. Palaeoclimatol. Palaeoecol., 7,
 815–831, 1992.
- Regenberg, M., Nürnberg, D., Steph, S., Groeneveld, J., Garbe-Schönberg, D., Tiedemann, R. and Dullo, W.-C.:
 Assessing the effect of dissolution on planktonic foraminiferal Mg/Ca ratios: Evidence from Caribbean core tops, Geochemistry, Geophys. Geosystems, 7, 2006.
- Regenberg, M., Steph, S., Nürnberg, D., Tiedemann, R. and Garbe-Schönberg, D.: Calibrating Mg/Ca ratios of multiple planktonic foraminiferal species with δ18O-calcification temperatures: Paleothermometry for the upper water column, Earth Planet. Sci. Lett., 278, 324–336, 2009.

- Rickaby, R. E. M. and Halloran, P.: Cool La Nina During the Warmth of the Pliocene?, Science, 307, 1948–1952, 2005.
- Ries, J. B., Cohen, A. L. and McCorkle, D. C.: Marine calcifiers exhibit mixed responses to CO2-induced ocean acidification, Geology, 37, 1131–1134, 2009.
- Rink, S., Kühl, M., Bijma, J. and Spero, H. J.: Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer Orbulina universa, Mar. Biol., 131, 583–595, 1998.
- Rollion-Bard, C. and Erez, J.: Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminiferan
 Amphistegina lobifera: Implications for δ11B vital effects and paleo-pH reconstructions, Geochim.
 Cosmochim. Acta, 74, 1530–1536, 2010.
- Rostek, F., Ruhland, G., Bassinot, F. C., Muller, P. J., Labeyrie, L. D., Lancelot, Y. and Bard, E.: Reconstructing
 Sea-Surface Temperature and Salinity Using δ18O and Alkenone Records, Nature, 364, 319–321, 1993.
- Russell, A. D., Hönisch, B., Spero, H. J. and Lea, D. W.: Effects of seawater carbonate ion concentration and
 temperature on shell U, Mg, and Sr in cultured planktonic foraminifera, Geochim. Cosmochim. Acta, 68,
 4347–4361, 2004.
- Sanyal, A., Bijma, J., Spero, H. J. and Lea, D. W.: Empirical relationship between pH and the boron isotopic composition of Globigerinoides sacculifer: Implications for the boron isotopes paleo-pH proxy,
 Paleoceanography, 16, 515–519, 2001.
- Sanyal, A., Hemming, N. G., Broecker, W. S., Lea, D. W., Spero, H. J., & Hanson, G. N. Oceanic pH control on
 the boron isotopic composition of foraminifera: evidence from culture experiments, Paleoceanography,
 11(5), 513-517, 1996.
- 911 Schmidt, G. A. and Mulitza, S.: Global calibration of ecological models for planktic foraminifera from core-top carbonate oxygen-18, Mar. Micropaleontol., 44, 125–140, 2002.
- 913 Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K. and Pancost, R. D.: Alkenone and boron-914 based Pliocene pCO2records, Earth Planet. Sci. Lett., 292, 201–211, 2010.
- 915 Shirayama, Y.: Effect of increased atmospheric CO2 on shallow water marine benthos, J. Geophys. Res., 110, C09S08, 2005.
- 917 Sime, N. G., De La Rocha, C. L. and Galy, A.: Negligible temperature dependence of calcium isotope 918 fractionation in 12 species of planktonic foraminifera, Earth Planet. Sci. Lett., 232, 51–66, 2005.
- Spero H. J.: Symbiosis in the planktonic foraminifer, orbulina universa, and the isolation of its symbiotic
 dinoflagellate, gymnodinium beii sp.nov, J. Phycol 23, 307-317, 1987.
- Sutton, J. N., Liu, Y. W., Ries, J. B., Guillermic, M., Ponzevera, E. and Eagle, R. A.: δ11B as monitor of
 calcification site pH in divergent marine calcifying organisms, Biogeosciences, 15, 1447–1467, 2018.
- Takagi H., Kimoto K., Fujiki T., Saito H., Schmidt C. and Kucera M.: Characterizing photosymbiosis in modern
 planktonic foraminifera, biogeosciences, 3377–3396, 2019.
- Thomson, J., Brown, L., Nixon, S., Cook, G. T. and MacKenzie, A. B.: Bioturbation and Holocene sediment
 accumulation fluxes in the north-east Atlantic Ocean (Benthic Boundary Layer experiment sites), Mar.
 Geol., 169, 21–39, 2000.
- Tripati, A.: Deep-Sea Temperature and Circulation Changes at the Paleocene-Eocene Thermal Maximum.
 Science, 308, 1894–1898, 2005.

- 930 Tripati, A. K., Roberts, C. D. and Eagle, R. A.: Coupling of CO2 and Ice Sheet Stability Over Major Climate 931 Transitions of the Last 20 Million Years, Science, 326, 1394–1397, 2009.
- 932 Tripati, A. K., Roberts, C. D., Eagle, R. A. and Li, G.: A 20 million year record of planktic foraminiferal B/Ca
- 933 ratios: Systematics and uncertainties in pCO2reconstructions, Geochim. Cosmochim. Acta, 75, 2582–
- 934 2610, 2011.
- Uchikawa, J., Penman, D. E., Zachos, J. C. and Zeebe, R. E.: Experimental evidence for kinetic effects on B/Ca
- 936 in synthetic calcite: Implications for potential B(OH)4– and B(OH)3 incorporation, Geochim. Cosmochim.
- 937 Acta, 150, 171–191, 2015.
- 938 Urey, H.C., Lowenstam, H.A., Epstein, S. & McKinney, C.R.: Measurement of paleo-temperature and
- temperatures of the upper cretaceous of England, Denmark, and the southeastern United-States. Geol. Soc.
- 940 Am. Bull., 62, 399-416, 1951.
- Wang, B.-S., You, C.-F., Huang, K.-F., Wu, S.-F., Aggarwal, S. K., Chung, C.-H. and Lin, P.-Y.: Direct
- 942 separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-
- 943 ICP-MS, Talanta, 82, 1378–1384, 2010.
- $\label{eq:wang} Wang,\,G.,\,Cao,\,W.,\,Yang,\,D.\,\,and\,\,Xu,\,D.:\,Variation\,\,in\,\,downwelling\,\,diffuse\,\,attenuation\,\,coefficient\,\,in\,\,the$
- northern South China Sea, Chinese J. Oceanol. Limnol., 26, 323–333, 2008.
- Weare, B. C., Strub, P. T. and Samuel, M. D. Annual Mean Surface Heat Fluxes in the Tropical Pacific Ocean, J.
- 947 Phys. Oceanogr., 11, 705–717, 1981.
- Wei, G., McCulloch, M. T., Mortimer, G., Deng, W. and Xie, L.: Evidence for ocean acidification in the Great
- Barrier Reef of Australia, Geochim. Cosmochim. Acta, 73, 2332–2346, 2009.
- 950 Wilson, D. J., Piotrowski, A. M., Galy, A. and McCave, I. N.: A boundary exchange influence on deglacial
- neodymium isotope records from the deep western Indian Ocean, Earth Planet. Sci. Lett., 341–344, 35–47,
- 952 2012.
- Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S. and Buma, J.: Direct effects of CO2 concentration on growth
- and isotopic composition of marine plankton, Tellus B Chem. Phys. Meteorol., 51, 461–476, 1999.
- 955 Yu, J., Menviel, L., Jin, Z. D., Thornalley, D. J. R., Barker, S., Marino, G., Rohling, E. J., Cai, Y., Zhang, F.,
- Wang, X., Dai, Y., Chen, P. and Broecker, W. S.: Sequestration of carbon in the deep Atlantic during the
- 957 last glaciation, Nat. Geosci., 9, 319–324, 2016.
- 958 Yu, J., Thornalley, D. J. R., Rae, J. W. B. and McCave, N. I.: Calibration and application of B/Ca, Cd/Ca, and δ
- 959 11 B in Neogloboquadrina pachyderma (sinistral) to constrain CO 2 uptake in the subpolar North Atlantic
- during the last deglaciation, Paleoceanography, 28, 237–252, 2013.
- Yu, J., Foster, G. L., Elderfield, H., Broecker, W. S. and Clark, E.: An evaluation of benthic foraminiferal B/Ca
- 962 and δ11B for deep ocean carbonate ion and pH reconstructions, Earth Planet. Sci. Lett., 293, 114–120, 20,
- 963 2010.
- 964 Yu, J., Elderfield, H., Hönisch, B.: B/Ca in planktonic foraminifera as a proxy for surface seawater pH.
- Paleoceanography22, PA2202, 2007.
- 966 Yu, J., Day, J., Greaves, M. and Elderfield, H., Determination of multiple element/calcium ratios in foraminiferal
- calcite by quadrupole ICP-MS, Geochemistry, Geophys. Geosystems 6, 2005.
- 968 Zeebe, R. E. and Wolf-Gladrow, D., CO2 in Seawater: Equilibrium, Kinetics, Isotopes Elsevier Oceanography
- 969 Series 65, Amsterdam, 2001.

Zeebe, R. E., Wolf-Gladrow, D. A., Bijma, J. and Hönisch, B., Vital effects in foraminifera do not compromise the use of δ 11 B as a paleo- pH indicator: Evidence from modeling, Paleoceanography, 18, 2003.

 972 Figure caption

973

974 Figure 1: Reactions governing dissolved inorganic carbon equilibria.

975

- 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.,
- 979 2006).

980

981 **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).

983

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/m³), pre-industrial pH and pre-industrial
 δ¹¹B of H₄BO₄⁻ (calculated from the GLODAP database and corrected for anthropogenic inputs).

987

Figure 5: Boron isotopic measurements of mixed-layer foraminifera plotted against the δ¹¹B_{borate}. δ¹¹B_{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.

991

Figure 6: Boron isotopic measurements of deep-dwelling foraminifera (δ¹¹B_{carbonate}) plot against δ¹¹B_{borate}.
 δ¹¹B_{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.

996

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).

1001

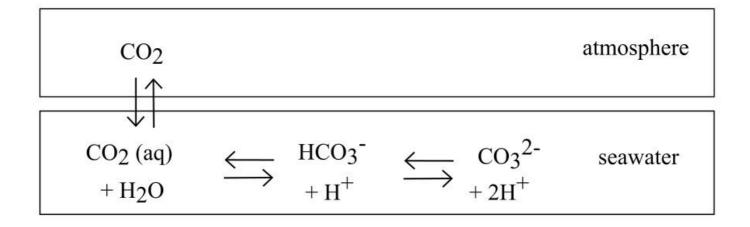
1002 Figure 8: A) Boxplot showing the calculated microenvironment pH difference (Δmicroenvironment pH) 1003 between microenvironment and external pH based on the $\delta^{11}B$ data. B) This figure shows that a decrease in 1004 insolation can explain the low δ^{11} B from the WEP. Light penetration profile in the Western Pacific, with E₀ in 1005 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). 1006 Theoretical depths were calculated for a decrease in microenvironment pH of $\Delta pH_1 = -0.02$ (e.g. WP07-a); 1007 $\Delta pH_1 = -0.04$ (e.g. A14), $\Delta pH_2 = -0.06$ (e.g. 806A). Light penetration corresponding to Ec is ~12%, $\Delta pH_0 \sim 7\%$, 1008 ΔpH₁~5%, ΔpH₂~1% respective depth are 75m, 90m, 110m and 150m. Grey band is the calcification depth of 1009 T. sacculifer (w/o sacc) utilized in this study.

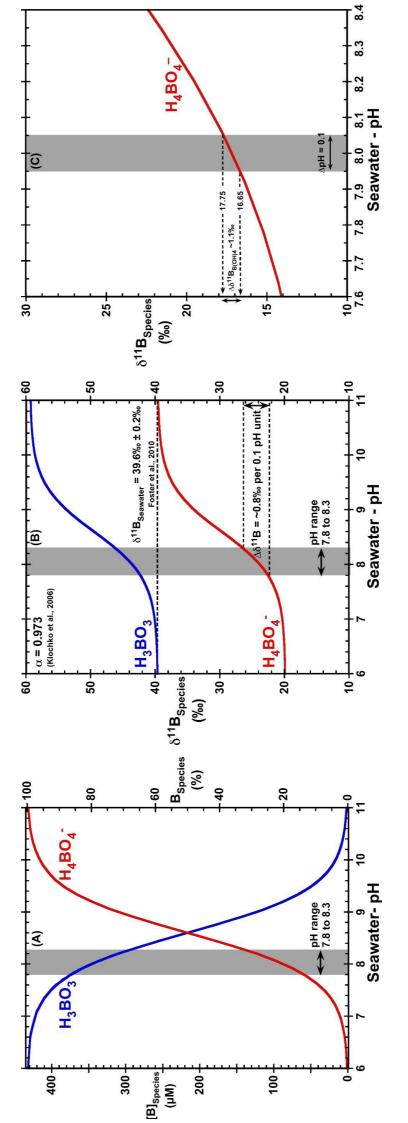
1010

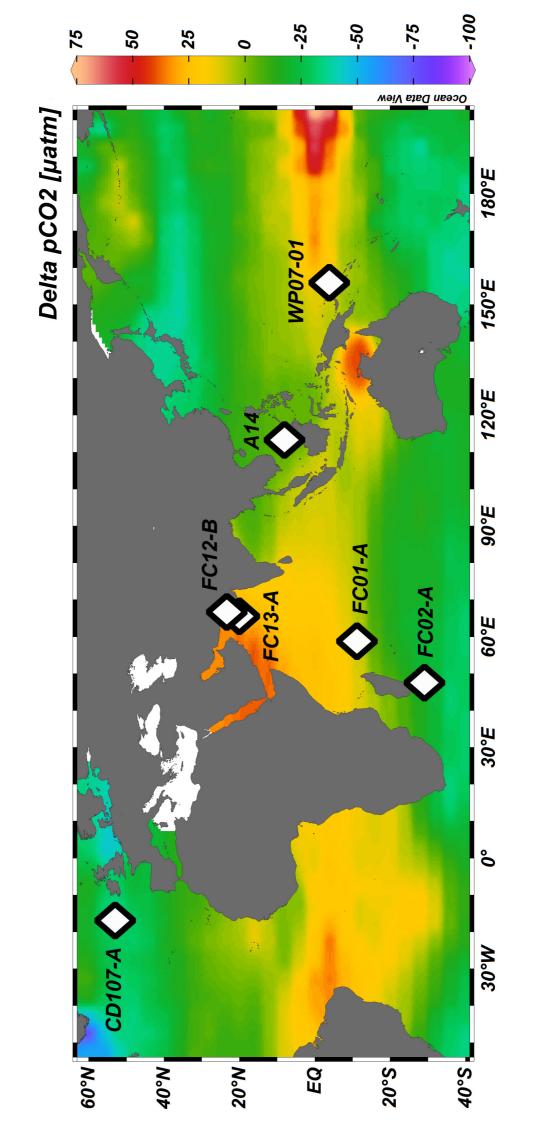
Figure 9: Water depth pH profiles reconstructed at every site applying the mono-specific calibrations derived from our results (Table 3). Figure is showing measured $\delta^{11}B_{calcite}$, $\delta^{11}B_{borate}$ calculated according to different calibrations (see Table 3 and text), calculated pH based on $\delta^{11}B$ (pH $_{\delta11B}$) and pCO $_2$ calculated from pH $_{\delta11B}$ and alkalinity.

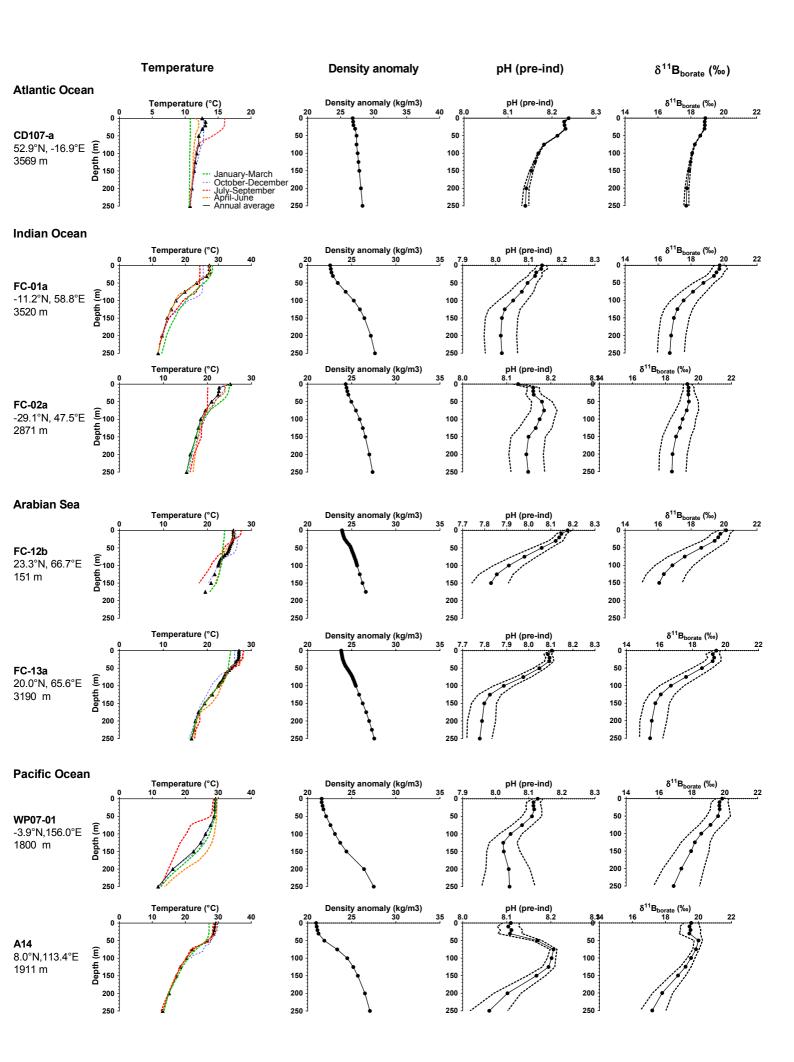
Figure 10: Evaluation of the reconstructed parameters, $\delta^{11}B_{borate}$, pH and pCO₂ versus *in-situ* parameter. The recalculated parameters are consistent with *in-situ* data, except for *G. ruber*. This variability might be explained by the different test sizes.

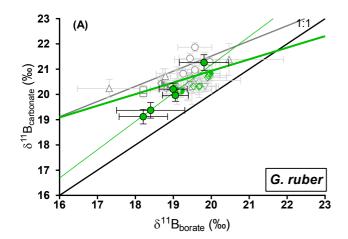
1019	Table caption
1020	
1021	Table 1: Box-core information
1022	
1023	Table 2: Analytical results of δ^{13} C, δ^{18} O, δ^{11} B and elemental ratios Li/Ca, B/Ca and Mg/Ca
1024	
1025	Table 3: Species-specific $\delta^{11}B_{carbonate}$ to $\delta^{11}B_{borate}$ calibrations from literature and from our data

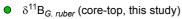




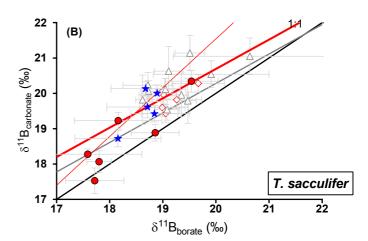




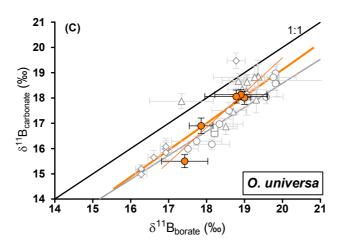




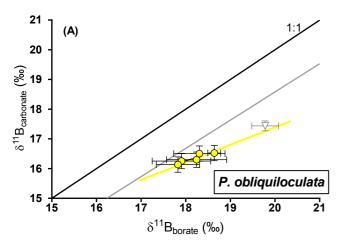
- \diamond $\delta^{11}B_{G. ruber}$ (core-top, Foster et al., 2008)
- $\delta^{11}B_{\text{G. ruber}}$ (core-top, 250-300µm, Henehan et al., 2013)
- \circ $\delta^{11}B_{G. ruber}$ (core-top, Henehan et al., 2013)
- \Box $\delta^{11}B_{G. ruber}$ (sediment trap, Henehan et al., 2013)
- $\delta^{11}B_{G, ruber}$ (tow, Henehan et al., 2013)
- ∇ $\delta^{11}B_{G, ruber}$ (grab sample, Henehan et al., 2013)
- \triangle $\delta^{11}B_{G. ruber}$ (Raizsch et al., 2018)
- G. ruber calibration line (All data, this study)
- G. ruber calibration line (Core-top, this study)
- G. ruber calibration line (Culture, Henehan et al., 2013)

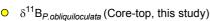


- δ¹¹B_{T.sacculifer (w/o sacc)} (core-top, this study)
- Δ $\delta^{11}B_{T. sacculifer (w/o sacc)}$ (core-top, Raitzsch et al., 2018)
- ★ δ^{11} B_{T.sacculifer (sacc)} (core-top, this study)
- $\delta^{11}B_{T. sacculifer (sacc)}$ (core-top, Foster et al., 2008)
- T. sacculifer (w/o sacc and sacc) calibration line (All data, this study)
- T. sacculifer (w/o sacc and sacc) calibration line (Core-top, this study)
- T. sacculifer (s) calibration line (Martinez-Boti et al., 2015)

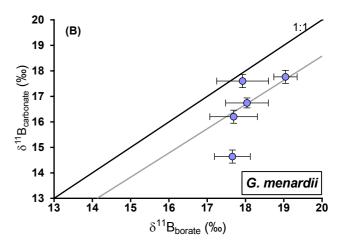


- $\delta^{11}B_{O.\ universa}$ (core-top, this study)
- \circ $\delta^{11}B_{O. universa}$ (core-top, Henehan et al., 2016)
- \Box $\delta^{11}B_{O. universa}$ (sediment trap, Henehan et al., 2016)
- \diamond $\delta^{11}B_{O. universa}$ (tow, Henehan et al., 2016)
- Δ $\delta^{11}B_{O. universa}$ (core-top, Raitzsch et al., 2018)
- O. universa calibration line (core-top, this study)
- O. universa calibration line (this study, Henehan et al., 2016, Raitzsch et al., 2018)
- O. universa calibration line (wild, Henehan et al., 2016)

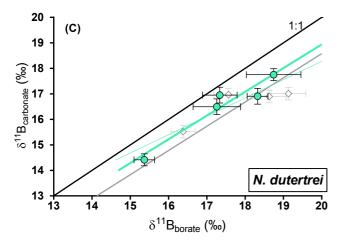




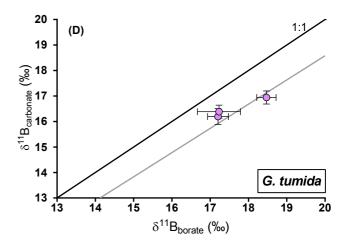
- ∇ δ^{11} B_{P.obliquiloculata}(Henehan et al., 2016)
- P. obliquiloculata calibration line (this study, Henehan et al., 2016)
- O. universa calibration curve (Henehan et al., 2016)



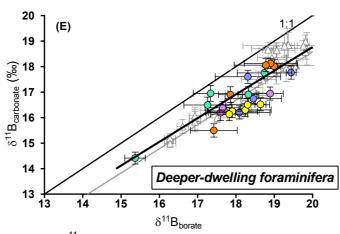
- \circ $\delta^{11}B_{G. menardii}$ (this study)
- O. universa calibration curve (Henehan et al., 2016)



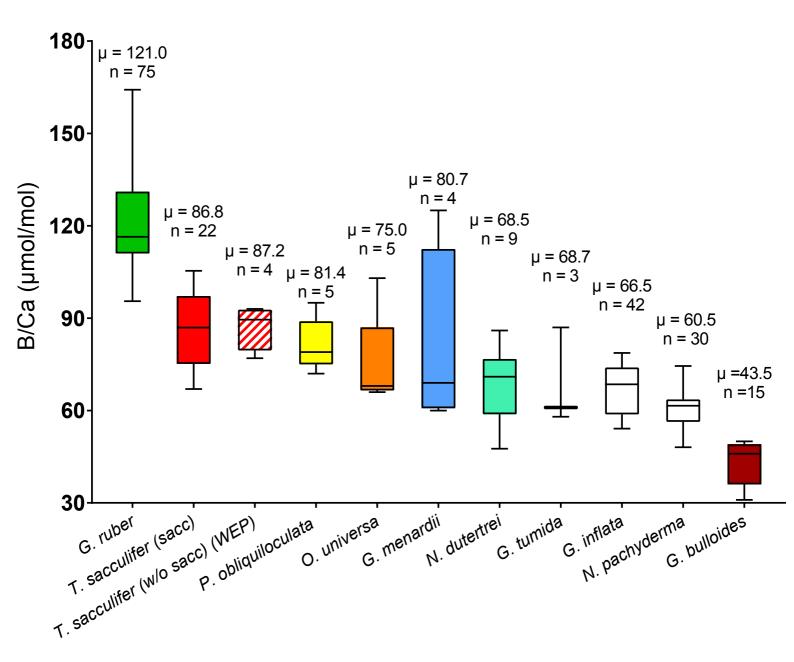
- $\qquad \delta^{11} B_{\textit{N. dutertrei}} (\text{Core-top, this study})$
- \diamond $\delta^{11}B_{N, dutertrei}$ (Core-top, Foster et al., 2008)
- O. universa calibration line (This study)
- O. universa calibration line (This study, Foster et al., 2008)
- O. universa calibration line (Henehan et al., 2016)

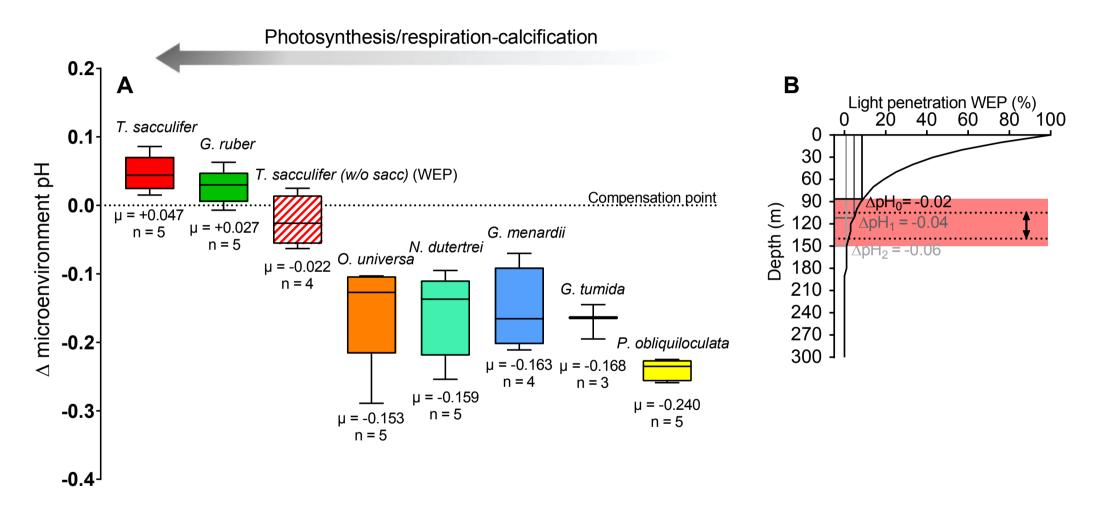


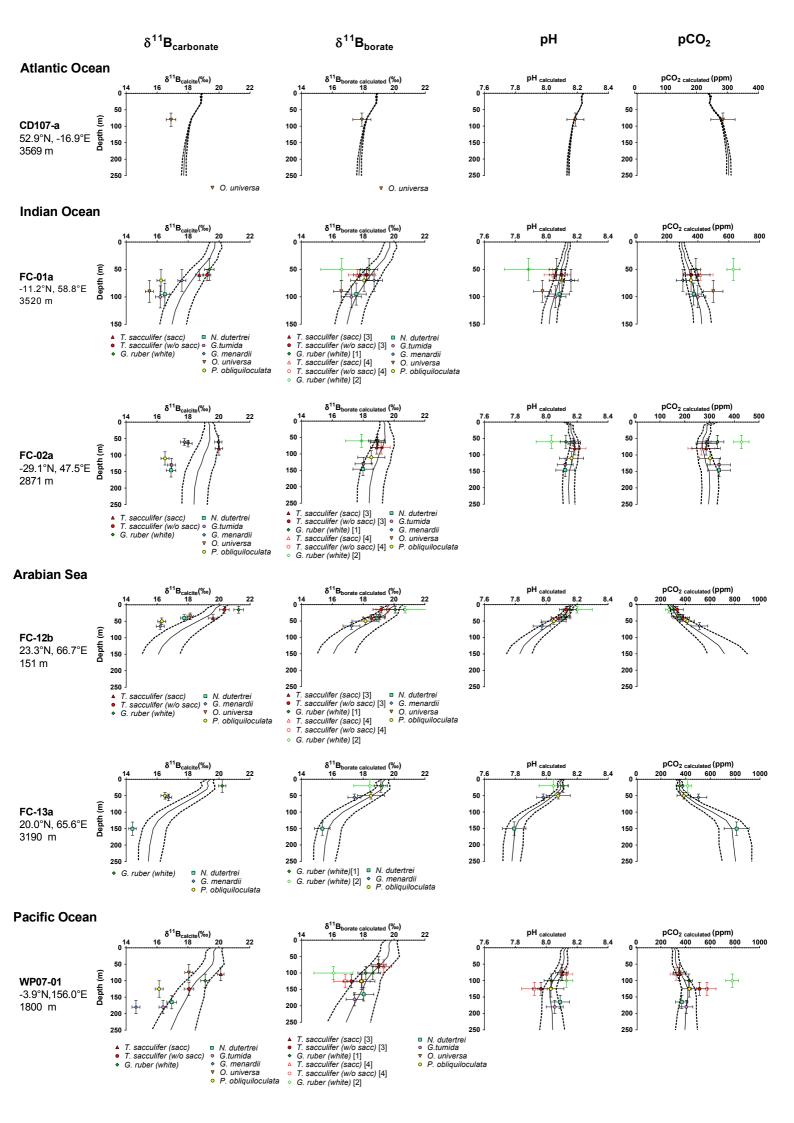
- $\delta^{11}B_{G. tumida}$ (this study)
- O. universa calibration curve (Henehan et al., 2016)



- δ¹¹B_{O.universa}
- $\bigcirc \quad \delta^{11} B_{\textit{P.obliquiloculata}}$
- δ¹¹B_{N. dutertrei}
- O δ¹¹B_{G. menardii}
- \circ $\delta^{11}B_{G. tumida}$
- δ^{11} B_{deep-dweller} from literature
- Deep-dweller calibration line
- O. universa calibration line (Henehan et al., 2016)







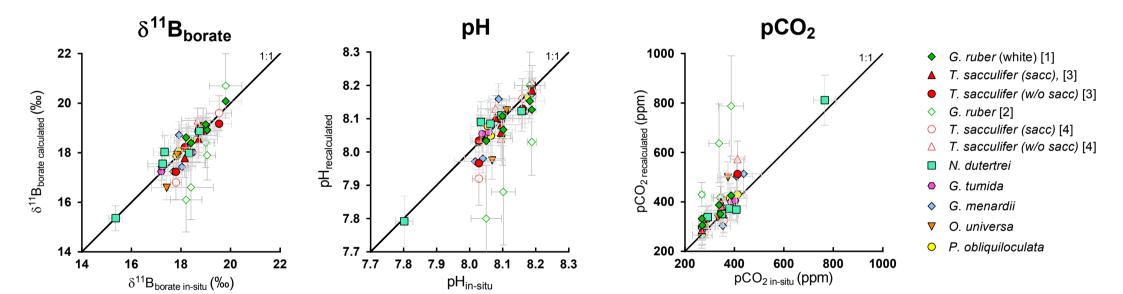


Table 1

Label	Box-Core	Site	Latitude (N)	Longitude (E)	Depth (mbsl)	Oceanic Regime	Δ^{14} C age (year)
Atlantic Oc	cean						
CD107-a	CD107	A	52.92	-16.92	3569	non-upwelling	<3000 ^a
Indian Oce	ean						
FC-01a	WIND-33B	I	-11.21	58.77	3520	non-upwelling	
FC-02a	WIND-10B	K	-29.12	47.55	2871	non-upwelling	7252 ± 27^{b}
Arabian Se	ea						
FC-12b	CD145	A150	23.30	66.70	151	seasonal upwelling	
FC-13a	CD145	A3200	20.00	65.58	3190	seasonal upwelling	
Pacific Occ	ean						
WP07-01			-3.93	156.00	1800	non-upwelling	$7.3-8.6^{c}$
A14			8.02	113.39	1911	non-upwelling	7.3-8.6 ^c
806		A	0.32	159.36	2521	equatorial divergence	7.3-8.6 ^c
807		A	3.61	156.62	2804	equatorial divergence	7.3-8.6°

^a Thomson et al., 2000

^b Wilson et al., 2012

^c Age for core-top of site 806B from Lea et al., 2000

Table 2

Core	Species	Fraction size (µm)	Cleaning	$\delta^{13}C^{\ast}$	$\delta^{18}O^{*}$	$\delta^{11}Bc_1$	$\delta^{11}Bc_2$	$\delta^{11}B_{average}{}^{**}$	Li/Ca***	B/Ca***	Mg/Ca***	Mn/Ca***	Fe/Ca***
				(‰)	(‰)	(‰)	(‰)	(‰)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(mmol/mol)
Atlantic Ocean CD107a	O. universa	>500	Ox-Red	1.99 ± 0.03	1.25 ± 0.11	16.85 ± 0.31 (2SD, nAE121=11)	16.95 ± 0.31 (2SD, nAE121=11)	16.90 ± 0.22	13.9 ± 0.4	68 ± 7	3.60 ± 0.01	13 ± 7	0.16 ± 0.01
Indian Ocean													
FC-01a	G. ruber (white ss)	250-300	Ox-Red	1.37 ± 0.03	-1.32 ± 0.11	19.33 ± 0.31 (2SD, nAE121=11)	19.41 ± 0.31 (2SD, nAE121=11)	19.37 ± 0.22	15.4 ± 0.4	109 ± 7	3.98 ± 0.01	10 ± 7	0.07 ± 0.01
FC-01a	T. sacculifer (sacc)	300-400	Ox-Red	1.88 ± 0.03	-2.20 ± 0.11	18.71 ± 0.24 (2SD, nAE121=10)	18.73 ± 0.24 (2SD, nAE121=10)	18.72 ± 0.17	12.1 ± 0.4	87 ± 7	3.45 ± 0.01	9 ± 7	0.03 ± 0.01
FC-01a	T. sacculifer (w/o sacc)	300-400	Ox-Red	2.02 ± 0.03	-1.05 ± 0.11	19.13 ± 0.24 (2SD, nAE121=10)	19.32 ± 0.24 (2SD, nAE121=10)	19.23 ± 0.17	12.1 ± 0.4	82 ± 7	3.42 ± 0.01	14 ± 7	0.03 ± 0.01
FC-01a	O. universa	>500	Ox-Red			15.50 ± 0.26 (2SD, nAE121=14)		15.50 ± 0.26					
FC-01a	P. obliquiloculata	300-400	Ox-Red		-0.55 ± 0.11		16.10 ± 0.26 (2SD, nAE121=14)		15.4 ± 0.4	78 ± 7	2.06 ± 0.01	14 ± 7	0.05 ± 0.01
FC-01a	G. menardii	300-400	Ox-Red	1.64 ± 0.03			17.69 ± 0.26 (2SD, nAE121=14)		12.7 ± 0.4	63 ± 7	2.26 ± 0.01	8 ± 7	0.07 ± 0.01
FC-01a	N. dutertrei	300-400	Ox-Red		-0.43 ± 0.11		16.59 ± 0.31 (2SD, nAE121=11)		18.6 ± 0.4	73 ± 7	1.81 ± 0.01	11 ± 7	0.03 ± 0.01
FC-01a	G. tumida	300-400	Ox-Red	1.29 ± 0.03	-0.53 ± 0.11	16.21 ± 0.31 (2SD, nAE121=11)	16.18 ± 0.31 (2SD, nAE121=11)	16.20 ± 0.22	10.0 ± 0.4	61 ± 7	1.79 ± 0.01	11 ± 7	0.02 ± 0.01
FC-02a	G. ruber (white ss)	250-300	Ox-Red		-1.40 ± 0.11		19.90 ± 0.24 (2SD, nAE121=10)		18.2 ± 0.4		3.47 ± 0.01	10 ± 7	0.07 ± 0.01
FC-02a	T. sacculifer (sacc)	300-400	Ox-Red	1.43 ± 0.03	-1.60 ± 0.11	20.07 ± 0.24 (2SD, nAE121=10)	19.93 ± 0.24 (2SD, nAE121=10)	20.00 ± 0.17	14.2 ± 0.4	106 ± 7	3.30 ± 0.01	10 ± 7	0.03 ± 0.01
FC-02a	T. sacculifer (w/o sacc)	300-400	Ox-Red		-1.40 ± 0.11		23.22 ± 0.24 (2SD, nAE121=10)		13.7 ± 0.4		3.34 ± 0.01	10 ± 7	0.04 ± 0.01
FC-02a	O. universa	>500	Ox-Red	1.79 ± 0.03			17.97 ± 0.26 (2SD, nAE121=14)		14.8 ± 0.4	67 ± 7	4.40 ± 0.01	11 ± 7	0.05 ± 0.01
FC-02a	P. obliquiloculata	300-400	Ox-Red	0.34 ± 0.03			16.69 ± 0.26 (2SD, nAE121=14)		16.6 ± 0.4	83 ± 7	2.33 ± 0.01	7 ± 7	0.03 ± 0.01
FC-02a	G. menardii	300-400	Ox-Red		-0.51 ± 0.11	17.77 ± 0.26 (2SD, nAE121=14)		17.77 ± 0.26	15.8 ± 0.4	125 ± 7	2.21 ± 0.01	17 ± 7	0.03 ± 0.01
FC-02a	N. dutertrei	300-400	Ox-Red		-0.55 ± 0.11		17.03 ± 0.31 (2SD, nAE121=11)		18.6 ± 0.4	82 ± 7	2.13 ± 0.01	13 ± 7	0.07 ± 0.01
FC-02a	G. tumida	300-400	Ox-Red	1.64 ± 0.03	-0.28 ± 0.11	16.93 ± 0.26 (2SD, nAE121=14)	16.95 ± 0.26 (2SD, nAE121=14)	16.94 ± 0.18	15.6 ± 0.4	87 ± 7	1.90 ± 0.01	17 ± 7	0.04 ± 0.01
Arabian Sea													
FC-12b	G. ruber (white ss)	250-300	Ox-Red		-2.82 ± 0.11		21.23 ± 0.31 (2SD, nAE121=11)		19.5 ± 0.4			14 ± 7	0.16 ± 0.01
FC-12b	G. sacculifer (s)	300-400	Ox-Red		-2.15 ± 0.11		19.57 ± 0.31 (2SD, nAE121=11)		14.6 ± 0.4	101 ± 7	4.28 ± 0.01	17 ± 7	0.14 ± 0.01
FC-12b	T. sacculifer (w/o sacc)	300-400	Ox-Red		-2.19 ± 0.11		20.37 ± 0.31 (2SD, nAE121=11)		16.7 ± 0.4		4.90 ± 0.01	20 ± 7	0.26 ± 0.01
FC-12b	O. universa	>500	Ox-Red		-1.59 ± 0.11	18.13 ± 0.20 (2SD, nAE121=6)		18.13 ± 0.20	13.6 ± 0.4	103 ± 7	6.91 ± 0.01	10 ± 7	0.06 ± 0.01
FC-12b	P. obliquiloculata	300-400	Ox-Red		-1.58 ± 0.11		16.15 ± 0.26 (2SD, nAE121=14)		16.7 ± 0.4	95 ± 7	3.61 ± 0.01	69 ± 7	0.38 ± 0.01
FC-12b	G. menardii	300-400	Ox-Red		-0.97 ± 0.11	16.2 ± 0.26 (2SD, nAE121=14)	17.73 : 0.24 (25D AF121 10)	16.20 ± 0.26	14.8 ± 0.4	75 ± 7	3.44 ± 0.01	52 ± 7	0.17 ± 0.01
FC-12b	N. dutertrei	300-400	Ox-Red	1.35 ± 0.03	-1.57 ± 0.11	1/.// ± 0.24 (2SD, nAE121=10)	17.73 ± 0.24 (2SD, nAE121=10)	$1/./5 \pm 0.1/$	17.1 ± 0.4	75 ± 7	3.25 ± 0.01	46 ± 7	0.25 ± 0.01
FC-13a	G. ruber (white ss)	250-300	Ox-Red	0.08 ± 0.03	-3.71 ± 0.11	20.27 ± 0.24 (2SD, nAE121=10)	20.15 ± 0.24 (2SD, nAE121=10)	20.21 ± 0.17	16.4 ± 0.4	147 ± 7	4.52 ± 0.01	13 ± 7	0.08 ± 0.01
FC-13a	T. sacculifer (w/o sacc)	300-400	Ox-Red		-2.46 ± 0.11	17.85 ± 0.29 (2SD, nAE121=12)		17.85 ± 0.29	15.7 ± 0.4		5.49 ± 0.01	21 ± 7	0.49 ± 0.01
FC-13a	P. obliquiloculata	300-400	Ox-Red		-0.97 ± 0.11		16.50 ± 0.26 (2SD, nAE121=14)		18.7 ± 0.4	79 ± 7	4.43 ± 0.01	30 ± 7	0.43 ± 0.01
FC-13a	G. menardii	300-400	Ox-Red		-1.07 ± 0.11	16.74 ± 0.20 (2SD, nAE121=6)		16.74 ± 0.20	9.2 ± 0.4	60 ± 7	1.99 ± 0.01	19 ± 7	0.07 ± 0.01
FC-13a	N. dutertrei	300-400	Ox-Red	0.71 ± 0.03	-1.41 ± 0.11	14.43 ± 0.24 (2SD, nAE121=10)	14.40 ± 0.24 (2SD, nAE121=10)	14.41 ± 0.17	15.7 ± 0.4	69 ± 7	1.98 ± 0.01	15 ± 7	0.06 ± 0.01
Pacific Ocean													
WP07-a	G. ruber (white ss)	250-400	Ox-Red			19.12 ± 0.29 (2SD, nAE121=12)		19.12 ± 0.29	14.5 ± 0.4	144 ± 7	4.32 ± 0.01	15 ± 7	0.16 ± 0.01
WP07-a	T. sacculifer (sacc)	250-400	Ox-Red			20.13 ± 0.21 (2SD, nAE121=11)		20.13 ± 0.21	12.7 ± 0.4	92 ± 7	4.44 ± 0.01	22 ± 7	0.05 ± 0.01
WP07-a	T. sacculifer (w/o sacc)	250-400	Ox-Red			18.10 ± 0.31 (2SD, nAE121=11)	18.04 ± 0.31 (2SD, nAE121=11)	18.07 ± 0.22	12.3 ± 0.4		4.51 ± 0.01		0.08 ± 0.01
WP07-a	O.universa	500-630	Ox-Red				17.99 ± 0.26 (2SD, nAE121=14)		11.9 ± 0.4	71 ± 7	7.52 ± 0.01	11 ± 7	0.02 ± 0.01
WP07-a	P. obliquiloculata	250-400	Ox-Red				16.19 ± 0.26 (2SD, nAE121=14)		13.4 ± 0.4	72 ± 7	3.02 ± 0.01	7 ± 7	0.03 ± 0.01
WP07-a	G. menardii	250-400	Ox-Red				14.53 ± 0.26 (2SD, nAE121=14)		13.5 ± 0.4	85 ± 7	2.68 ± 0.01	26 ± 7	0.08 ± 0.01
WP07-a	N. dutertrei	250-400	Ox-Red				16.99 ± 0.31 (2SD, nAE121=11)		21.7 ± 0.4	86 ± 7	3.66 ± 0.01	42 ± 7	0.63 ± 0.01
WP07-a	G. tumida	250-400	Ox-Red			16.45 ± 0.26 (2SD, nAE121=14)	16.32 ± 0.26 (2SD, nAE121=14)	16.39 ± 0.18	10.6 ± 0.4	58 ± 7	2.55 ± 0.01	16 ± 7	0.10 ± 0.01
806A	T. sacculifer (w/o sacc)	250-400	Ox-Red			17.53 ± 0.36 (2SD, nAE121=11)		17.53 ± 0.36	14.40 ± 0.4	77 ± 7	3.89 ± 0.01	7 ± 7	0.15 ± 0.01
807A	T. sacculifer (w/o sacc)	250-400	Ox-Red			18.38 ± 0.21 (2SD, nAE121=11)	18.17 ± 0.21 (2SD, nAE121=11)	18.28 ± 0.15	12.54 ± 0.4	87 ± 7	4.24 ± 0.01	17 ± 7	0.09 ± 0.01
A14	G. ruber (white ss)	250-400	Ox-Red				19.17 ± 0.24 (2SD, nAE121=10)						
A14	T. sacculifer (sacc)	250-400	Ox-Red				19.32 ± 0.24 (2SD, nAE121=10)		12.0 ± 0.4		3.91 ± 0.01	22 ± 7	0.02 ± 0.01
A14	T. sacculifer (w/o sacc)	250-400	Ox-Red			18.93 ± 0.24 (2SD, nAE121=10)	18.84 ± 0.24 (2SD, nAE121=10)	18.88 ± 0.17	12.3 ± 0.4	93 ± 7	3.76 ± 0.01	25 ± 7	0.06 ± 0.01
A14	O. universa	500-560	Ox-Red			17.33 ± 0.26 (2SD, nAE121=14)	17.08 ± 0.26 (2SD, nAE121=14)	17.20 ± 0.18	11.3 ± 0.4	66 ± 7	6.59 ± 0.01	10 ± 7	0.02 ± 0.01
A14	N. dutertrei	250-400	Ox-Red			14.39 ± 0.31 (2SD, nAE121=11)		14.39 ± 0.31	16.9 ± 0.4	75 ± 7	1.99 ± 0.01	35 ± 7	0.04 ± 0.01

^{*} uncertainties given in 1SD (see text)

^{**} When two measurements were carried out uncertaity was calculated with $\Delta a = \sqrt{(1/\Sigma_i(1/\Delta_m)^2)}$; with only one measurement the error was determined on reproducibility of the AE121 standard ***Uncertainty given in 2SD , calculated on the reproducibility of CamWuellestorfi (see text and table S3, ref in Misra et al., 2014)

Table 3

Species	Size fraction (µm)	Material	Instrument (original)	Regression method	$\delta^{11}B_{borate} = f(\delta^{11}B_{calcite})$	n	Calibratio	n number Reference
G. ruber	~380	Culture/core tops/plankton tows	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 9.52 (\pm 2.02)]/0.6 (\pm 0.11)$			Henehan et al., 2013
G. ruber	315-355	Core-tops	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 11.78 (\pm 3.20)]/0.45 (\pm 0.16)$			Raitzsch et al., 2018
T. sacculifer	n.d.	Culture/artificial seawater enriched in B	N-TIMS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 3.94 (\pm 4.02)]/0.82 (\pm 0.22)$			Sanyal et al., 2001 refitted Martinez-Boti et al., 2015
T. sacculifer	315-355	Core-tops	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 8.86 (\pm 5.27)]/0.59 (\pm 0.21)$			Raitzsch et al., 2018
O. universa	no effect	Core-tops/plankton tows/sediment traps	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 0.42 (\pm 2.85)]/0.95 (\pm 0.17)$			Henehan et al., 2016
O. universa	>425	Core-tops	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 5.69 (\pm 7.51)]/1.26 (\pm 0.39)$			Raitzsch et al., 2018
G. bulloides	300-355	Core-top/sediment trap	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 3.440 (\pm 4.584)]/1.074 (\pm 0.252)$			Martinez-Boti et al., 2015
G. bulloides	315-355	Core-tops	MC-ICP-MS		$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 3.81 (\pm 13.17)]/1.13 (\pm 0.72)$			Raitzsch et al., 2018
N. pachyderma	150-200	Core-tops	MC-ICP-MS		$\delta^{11}B_{borate} = \delta^{11}B_{calcite} + 3.38$			Yu et al., 2013
G. ruber	250-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 1.23 (\pm 0.59)]/1.12 (\pm 1.67)$	5	1	This study
G. ruber	250-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 11.73 (\pm 0.83)]/0.46 (\pm 0.34)$	40	2	This study; Foster et al., 2008; Henehan et al., 2016; Raitzsch et al., 2018
T. sacculifer (sacc and w/o sacc)	250-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 6.06 (\pm 0.25)/1.38 (\pm 1.33)]$	11	3	3 This study
T. sacculifer (sacc and w/o sacc)	250-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 4.09 (\pm 0.86)]/0.83 (\pm 0.48)$	27	4	This study; Foster et al., 2008; Raitzsch et al., 2018
N. dutertrei	300-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 0.34 (\pm 1.83)]/0.93 (\pm 0.55)$	5	5	5 This study
N. dutertrei	300-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 3.88 (\pm 0.65)]/0.72 (\pm 0.74)$	9	(This study; Foster et al., 2008
O. universa	400-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 8.01 (\pm 23)]/1.38 (\pm 2.67)$	5	7	7 This study
O. universa	400-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} + 2.08 (\pm 0.59)]/1.06 (\pm 0.13)$	36	8	This study; Henehan et al., 2016; Raitzsch et al., 2018
G. menardii	400-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 5.36 (\pm 1.36)]/0.65 (\pm 0.76)$	5	9	This study
G. tumida	400-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 6.33 (\pm 2.52)]/0.57 (\pm 1.2)$	3	1	0 This study
P. obliquiloculata	300-400	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 5.59 (\pm 4.16)]/0.59(\pm 0.65)$	6	1	1 This study; Henehan et al., 2016
Deep-dweller	300-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 1.99 (\pm 0.13)]/0.82 (\pm 0.27)$	22	1	2 This study
Deep-dweller	300-600	Core-tops	MC-ICP-MS	Bootstrap	$\delta^{11}B_{borate} = [\delta^{11}B_{calcite} - 0.18 (\pm 0.6)]/0.95 (\pm 0.13)$	54	1	This study; Foster et al., 2008; Henehan et al., 2016; Raitzsch et al., 2018

Supplemental information

Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO₂ gradients

Maxence Guillermic^{1,2}, Sambuddha Misra^{3,4}, Robert Eagle^{2,5}, Alexandra Villa^{2,6}, Fengming Chang⁷, Aradhna Tripati ^{1,2,5}

¹ Department of Earth, Planetary, and Space Sciences, UCLA, University of California – Los Angeles, Los Angeles, CA 90095 USA

² Laboratoire Géosciences Océan UMR6538, UBO, Institut Universitaire Européen de la Mer, Rue Dumont d'Urville, 29280, Plouzané, France

³ Indian Institute of Science, Centre for Earth Sciences, Bengaluru, Karnataka 560012, India

⁴ The Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, UK

⁵ Institute of the Environment and Sustainability, Department of Atmospheric and Oceanic Sciences, University of California – Los Angeles, CA 90095, USA

⁶Department of Geology, University of Wisconsin-Madison, Madison, WI 53706 USA

⁷ Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

Supplemental Figures

Figure S1: An example of the impact of seasonality on results. Based on data from GLODAP used for site FC13-a. Seasonality has less of an impact that a change in the depth habitats.

Figure S2: Figure showing the offset $\Delta^{11}B=\delta^{11}B_{carbonate}-\delta^{11}B_{borate}$ versus calcification depth, red symbols are from Arabian Sea, green from Indian Ocean and Blue from the WEP, blue with black line symbols are data from site A14. This figure highlights a decrease of $\delta^{11}B_{carbonate}$ for *T. sacculifer* and *G. ruber* with a deeper depth habitat.

Figure S3: Multi-panels figure showing the correlation between B/Ca and boron geochemistry and different variables. A to C show comparison of B/Ca and A) $[B(OH)_4^-]/[HCO_3^-]$, B) $\delta^{11}B_{carbonate}$ and C) temperature. Panel D) shows the correlation between $\delta^{11}B_{carbonate}$ and temperature. Symbol in brackets is high B/Ca; this point is included in the linear regressions. Linea regression (LR - black line) is when compiling *G. ruber* and *T. sacculifer*, LR of *G. ruber* (dotted line green), *T. sacculifer* (red line – p<0.05), *T. sacculifer* (w/o sacc – red dotted line).

Figure S4: Boron geochemistry against water depth. A) $\delta^{11}B_{carbonate}$ versus water depth, B) B/Ca against water depth and C) $\delta^{11}B_{carbonate}$ versus calcification depth and linear regressions for *G. ruber*, *T. sacculifer* (w/o sacc), *T. sacculifer* (sacc) and *O. universa*.

Figure S5: Figure evaluating the circularity of our reconstructions. It is showing in the y-axis the difference between reconstruction utilizing calibrations derive from the entire dataset and compare to *in-situ* values and in the x-axis the difference between the reconstruction utilizing the species-specific calibrations derived excluding the site of interest (no circularity) compared to *in-situ* values. Results show that difference is not significant between the two reconstruction methods (e.g. following the 1:1 line), validating the method and the calibrations.

Supplemental Tables

Table S1: Elemental ratios of multi-elemental standards utilized in this study.

Table S2: Reproducibility of boron isotope standards.

Table S3: Reproducibility of elemental ratios for CamWuellestorfi standard.

Table S4: Seasonality of foraminifera utilized in this study.

Table S5: Mg/Ca-T calibrations used for reconstructions and $\delta^{18}O_w$ -T calibrations used for calcification depth reconstructions.

Table S6: Calcification depth (CD) calculations from $\delta^{18}O$ (CD1), Mg/Ca (CD2) and literature (CD3).

Table S7: Pre-industrial in-situ parameters estimated using calcification depths for each species and calculated parameters based on analytical results.

Trace element standards

A series of multi-element standards (Table S1) with fixed Ca concentration and variable B, Mg, Sr, Mn, Ba, Zn, Cd, U, Li, Al and Fe concentrations were prepared for elemental ratios analysis in Brest following the method developed by Yu et al., (2005). Multi-element stock standard mixtures were prepared gravimetrically by spiking a 10,000 ppm Ca standard with appropriate amounts of Li, B, Al, Mn, Zn, Sr, Cd and U mono-elemental 1,000 ppm (SCP Science). They were diluted with OPTIMA grade HNO₃ acid and 18.2 MΩ.cm-1water to reach a 0.28M HNO₃ final solution. The stock standards (1500 ppm Ca) were prepared in 500mL cleaned PFA bottles. Working standards were made by diluting the stock solutions to a final concentration of 100 ppm Ca. The multi-element standards were calibrated at the University of Cambridge, elemental ratios are presented in Table S1. An external standard CamWuellestorfi (Misra et al., 2014a) was used in Brest for cross-calibration and reproducibility (Table S3).

Potential contaminations

Possible contamination of samples due to presence of silicate minerals was monitored with the Fe/Mg ratio. Samples with Fe/Mg > 0.1 mol/mol would be rejected due to potential contamination by silicate minerals (Barker et al., 2003). Samples (site E035 excluded) have an average Fe/Mg of 0.03 ± 0.05 mol/mol (2SD, n=42), meaning that silicate minerals have been efficiently removed during our cleaning.

Contribution of Mn-Fe-oxide coatings to Mg/Ca ratio has been calculated to be 0.5 μ mol/mol Mg/Ca (change for 5 μ mol/mol Mn/Ca ratio Barker et al., 2003). The maximum Mn/Ca ratio in our samples is 89 μ mol/mol which can lead to a potential contribution of ~9 μ mol/mol Mg/Ca or in other words a decrease of 0.1°C in our reconstructed temperatures. However, the calibration error is much larger and is estimated to be ~1.4°C (Dekens et al., 2002). The range in Mn/Ca values in our samples is 0.021 \pm 0.033 mmol/mol (2SD, n=42) which allows us to not be ignore *Mn-Fe-oxide* coating related complications. Additionally, no correlations were found between Mg/Ca and Fe/Ca (R²=0.006) or with Mn/Ca (R²=0.008), and between B/Ca ratio and Mn/Ca (R²=0.003) or Fe/Ca (R²=0.062) ratios.

Contamination by clays was monitored with Ti/Ca calculated from blank corrected intensities. Al/Ca ratios were not reliable as we are using an alumina injector for HF matrix in our lab. A minor correlation was found between Ti/Ca and Mg/Ca (R^2 =0.1388) but none with B/Ca (R^2 =0.0887).

Calcification depth determination

The first approach involves comparing measured $\delta^{18}O_c$ with theoretical predictions of $\delta^{18}O_c$ based on vertical profiles of temperature and the $\delta^{18}O$ of seawater ($\delta^{18}O_w$). We assume $\delta^{18}O_c$ is in equilibrium with seawater. First, $\delta^{18}O_w$ was calculated using location-specific $\delta^{18}O_w$ -salinity relationships and salinity profiles. We used salinity values from the World Ocean Atlas database (Boyer et al., 2013). Oxygen isotopes may be affected by both temperature and salinity. As our sites present different hydrographic settings and freshwater inputs, location-specific $\delta^{18}O_w$ -salinity relationship relationships are utilized for accurate $\delta^{18}O_w$ reconstructions. For Site CD107-a, we used a $\delta^{18}O_w$ -salinity relationship of 0.56*S-19.3 (Duplessy et al., 1991). For FC01-a and FC02-a, we used a $\delta^{18}O_w$ -salinity relationship of 0.24*S-7.8 (Sime et al., 2005), and for FC13-a and FC12-b, we used a $\delta^{18}O_w$ -salinity relationship of 0.28*S-9.24-0.27 (Rosteket al., 1993). Then, we used the calculated ambient $\delta^{18}O_w$ in concert with: (1) temperature profiles from the World Ocean Atlas database (Boyer et al., 2013), and (2) published calcite-water oxygen isotope fractionation factors, to calculate theoretical values for $\delta^{18}O_c$. Species-

specific relationships were used when available, including for *T. sacculifer* (Mulitza et al., 2003), *G. ruber* (Mulitza et al., 2003), and *O. universa* (Bemis et al., 2002, medium light). For all other, species we used the calcite equation from Kim and O'Niel (1997), adapted to a quadratic form by Bemis et al., (1998) following the approach of Sime et al., (2005). To take into account the ecology of each species, theoretical $\delta^{18}O_c$ profiles were made for the season of maximum abundance (Table S4). Therefore spring and summer profiles were used for *T. sacculifer*, summer profiles used for *G. ruber*, and winter and annual average profiles was used for *N. dutertrei*. Annual average profiles were used for the other species.

For the two sites WP07-1 and A14, a different approach was necessary because $\delta^{18}O_c$ data is sparse. At these sites, and for our other sites, we utilized Mg/Ca-derived temperatures to estimate calcification depths (Table S6). $T_{Mg/Ca}$ was derived using species-specific Mg/Ca-temperature calibrations (Table S6) along with the Mg/Ca ratios determined in this study. Calcification depth was estimated by comparing $T_{Mg/Ca}$ to modern temperature profiles from the World Ocean atlas database 2013 (Boyer et al., 2013) in light of the ecology (seasonality of growth) of the species of interest. A caveat is that in certain cases $T_{Mg/Ca}$ may be partially biased by a carbonate ion effect or salinity effect (Russell et al., 2004; Elderfield et al., 2006; Ferguson et al., 2008; Arbuszewski et al., 2010; Martinez-Boti et al., 2011). These artifacts on $T_{Mg/Ca}$ may be significant at high-latitude sites such as CD107-a which is located in the North Atlantic Ocean.

Depth habitat

Planktonic foraminifera live in the upper 500 m of the water column. Their preferred depth habitat 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 summer (Deuser et al., 1981) whereas *T. sacculifer* (n or ns) is present in the mixed layer until the midthermocline depth (Farmer et al., 2007) during spring and summer (Deuser et al., 1981, 1989). Specimens of *P. obliquiloculata* and *N. dutertrei* are found during winter (Deuser et al., 1989), in the mixed layer (~60m) for *P. obliquiloculata*, and at mid-thermocline depth for *N. dutertrei* (Farmer et al., 2007). Whereas, *O. universa* tends to record annual average conditions and is living 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) even upper thermocline (Farmer et al., 2007) and records annual temperatures. And specimens of *G. tumida* are found at the lower thermocline or below the thermocline and record annual average conditions (Fairbanks and Wiebe, 1980; Farmer et al., 2007, Birch et al., 2013). Our calcification depth reconstructions are summarized in Table 3, also see Table S6 for comparison.

Atlantic Ocean

Farmer et al., (2007) determined the depth habitat for *O. universa* to be ranging from 0 to 60m (LL, Bemis et al., 1998). Our calculation, through δ^{18} O measurement, suggests a deeper habitat of around 70m (LL, Bemis et al., 1998), 80m (ML, Bemis et al., 2002). Whereas, the Mg/Ca method derived depth habitat calculation yields a depth habitat of 50 m. The lower habitat depth can also come from the different size fractions, as our size fraction is lower than Farmer's. *O.universa* is thought to migrate to shallower depth along its ontogeny (Emiliani et al., 1954) younger individuals are thus living deeper but smaller individuals might also have a

deeper habitat as already suggested by Hönisch and Heming, (2004). Since most of the published studies have used the δ^{18} O-based depth calcification, we will preferentially adopt this method.

Indian Ocean

Calcification depths for the Indian Ocean cores have already been determined for majority of the species by Sime et al., (2005). Additionally, Birch et al., (2013) have reconstructed the depth habitat of multiple species from a core collected in the offshore region of Tanzania (Glow 3). In Indian Ocean specimens of G. ruber is found in the top 50m (Birch et al., 2013) and until 60 m (Sime et al., 2005), T. sacculifer is found in the surface mixed layer (SML) but also in the upper thermocline between 50-70 m for Birch et al., (2013) and between 60 to 80 m for Sime et al., (2005). Our results are consistent with these reported depth habitats. We calculate that specimens of G. ruber, T. sacculifer with and without sac are living in the top 80m; O. universa lives between 50 to 90 m (Sime et al., 2005, Birch et al., 2013). For N. dutertrei we calculate a depth habitat of 90m at site FC01a, calcification depths derived from both δ^{18} O and Mg/Ca methods agree with the 93 m estimate by Sime et al., (2005). At site FC02a the calculated calcification depth based on δ^{18} O method is 65 m, and, the Mg/Ca derived depth is 100m; however, Sime et al., (2005) proposed a calcification depth of 146 m. A deeper depth habitat than site FC01a seems to be in line with the weaker stratification of the water column at site FCO2a. The depth habitat for P. obliquiloculata's was determined to be 106-120m by Sime et al., (2005); however, our calculations predict a lower and narrower depth habitat of 60 - 70m. Calcification depth for G. menardii has been calculated to be 60 - 70m, which is consistent with an upper thermocline depth habitat. Specimens of G.tumida is commonly found at the bottom of the thermocline which is around 200-250m at our Indian Ocean sites, Birch et al., (2013) found this species ranging from 100 to 200 m but our δ^{18} O based habitat reconstruction suggests a shallower depth of 70m at both sites. It seems that the calcification derived Mg/Ca for G. tumida is more realistic than with our $\delta^{18}O_c$ reconstructions, the Mg/Ca based calculation predicts a depth habitat of 100 - 130 m.

Arabian Sea

In the Arabian Sea foraminifera are affected by changes in local hydrology caused by the Indian summer and winter monsoons. The specimens of different species collectively record a shallower habitat during SW monsoon (e.g., upwelling) and a deeper habitat during NE monsoon (Peeters and Brummer, 2002). Except for *N. dutertrei*, our two methods of calcification depth reconstruction closely agree with each other within their respective uncertainties. The depth habitat reconstructions for *G. ruber* and for *T. sacculifer* are consistent with species living in the shallow mixed layer (SML) at a depth of 30m for *G. ruber* and 40 m for *T. sacculifer*. Specimens of *O. universa* are calculated to live at 30m depth; *N. dutertrei* at site FC12-b (water depth 151m) is living around 40m and at 150m at site FC13-b (water depth 3200m), which is consistent with the hydrography at this site (Fig. 4). The depth habitat of *P. obliquiloculata* is calculated to be 50m at both sites. Specimens of *G. menardii* is found at depths of 60m, consistent with Peeters and Brummer, (2002) estimate of 50 – 130m.

Pacific Ocean

For Pacific Ocean samples the Mg/Ca derived calcification depths were used in absence of δ^{18} Oc values. The Sites WP07-01 and A14 are located in the Western Equatorial Pacific with Site WP07-01

characterized by a deep thermocline. At these sites *G. ruber* and *T. sacculifer* have deep depth habitat of around 100m for *G. ruber* (Elderfield and Ganssen, 2000) and around 125m for *T. sacculifer* (Rickaby et al., 2005). The depth habitat for specimens of *O. universa* was determined to be 75m depth at site WP07-01 and at 55m depth at site A14. We calculate that *P. obliquiloculata* is living at 125m deep. Rickaby et al., (2005) estimated the living depth of *N. dutertrei* at 165m in agreement with our calculated depths (~125m). Specimens of *G. menardii* were determined to live at 180m like *G. tumida* (Rickaby et al., 2005).

The data are not consistent with a dissolution effect to explain the low $\delta^{11}B$ T. sacculifer in the WEP

Documented dissolution effects have been attributed to the preferential dissolution of ontogenic calcite relative to the light $\delta^{11}B$ of gametogenic calcite (Ni et al., 2007; Seki et al., 2010; Henehan et al., 2016). *T. sacculifer* (w/o sacc) should be less impacted compared to the *T. sacculifer* (sacc). Hönisch and Hemming, (2004) and Ni et al., (2007) reported a dissolution effect at site 806 (close to our WP07-01 site) for *T. sacculifer* (sacc), however, in our data the $\delta^{11}B_{carbonate}$ for *T. sacculifer* (sacc) is not decreasing with water depth when *T. sacculifer* (w/o sacc) is which suggests that at these sites and at the same size-fraction no dissolution is observed (eg. different water depth). $\Delta^{11}B$ for *T. sacculifer* (w/o sacc) and for *G. ruber* shift to lighter with higher calcification depth, a trend that does not support a dissolution effect. The lethal temperature for *T. sacculifer* is $14^{\circ}C$, which at site WP07-01 corresponds to a $\delta^{11}B_{borate}$ of 17.5 % which makes our low $\delta^{11}B_{carbonate}$ realistic. If no dissolution is observed, a deep depth habitat inducing a respiration-driven microenvironment might explain the low $\delta^{11}B$ of the measured carbonate.

Microenvironment calculations

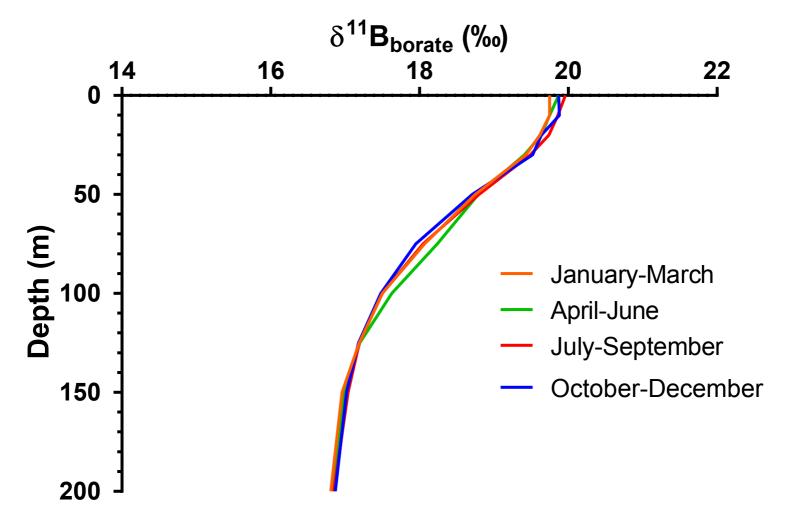
We observe a trend between $\Delta^{11}B$ (eg. $\Delta^{11}B=\delta^{11}B_{carbonate}-\delta^{11}B_{borate}$) with derived calcification depth (Fig. S2). In order to verify why the WEP δ^{11} B_{carbonate} of *T. sacculifer* (w/o sacc) is low and to test the hypothesis of the depth habitat we try to recalculate independently the theoretical water depth habitat based on culture results from Jorgensen et al., (1985) and our microenvironment pH results. A change of microenvironment pH for T. sacculifer will change the theoretical light intensity needed to reach this microenvironment pH. The compensation light intensity (E_c) for T. sacculifer has been calculated by Jorgensen et al., (1985) to be ~30 μ Eistn.m⁻².s⁻¹, E_c corresponds to the energy where photosynthesis compensates respiration or where δ^{11} B_{carbonate} reaches the 1:1 theoretical line. We tested two microenvironment pH, $\Delta pH_1 = -0.04$ and $\Delta pH_2 = -0.06$ (Fig S3). We've recalculated the light energy needed to decrease the pH of ΔpH_1 and ΔpH_2 and apply these changes to the light penetration profile determined with an insolation E₀ 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). A decrease of ΔpH₁ would lead to a decrease of 15 μEistn.m⁻².s⁻¹ and a decrease of ΔpH₂ would lead to a decrease of 24 μEistn.m⁻².s⁻¹ (Jorgensen et al., 1985). These results correspond in our case of a light penetration of 12% to reach Ec, 5% for a decrease of ΔpH₁ and 1% for a decrease of ΔpH_2 . This means that in the WEP if T. sacculifer calcifies below 75m where E_c is reached the $\delta^{11}B_{carbonate}$ is below the theoretical 1:1 line. T. sacculifer (w/o sacc) in the WEP is decreasing its pH of $\sim \Delta pH_1$ which would imply a calcification depth of 110m consistent with the reconstruction of Rickaby et al., (2005).

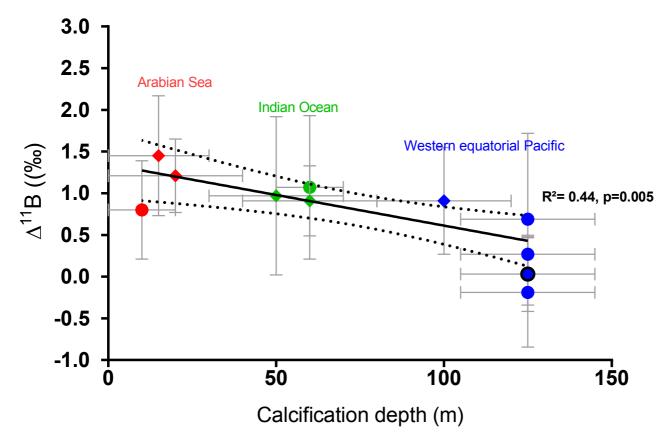
$$\Delta microenvironment~pH = -log(\frac{(\delta 11Bseawater - \delta 11Bcarbonate)~x~Kb*}{\epsilon - \delta 11Bseawater + \delta 11Bcarbonate}) - pHseawater$$

References

- Arbuszewski, J., DeMenocal, P., Kaplan, A. and Farmer, E. C.: On the fidelity of shell-derived δ18Oseawater estimates, Earth Planet. Sci. Lett., 300, 185–196, 2010.
- Barker, S., Greaves, M. and Elderfield, H: A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, Geochemistry, Geophys. Geosystems 4, 1–20, 2003.
- Bemis, B. E., Spero, H. J. and Thunell, R. C.: Using species-specific paleotemperature equations with foraminifera: a case study in the Southern California Bight, Mar. Micropaleontol., 46, 405–430, 2002.
- Bemis, B. E., Spero, H. J., Bijma, J. and Lea, D. W.: Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations, Paleoceanography, 13, 150–160, 1998.
- Birch, H., Coxall, H. K., Pearson, P. N., Kroon, D. and O'Regan, M.: Planktonic foraminifera stable isotopes and water column structure: Disentangling ecological signals, Mar. Micropaleontol., 101, 127–145, 2013.
- Boyer, T.P., J. I. Antonov, O. K. Baranova, C. Coleman, H. E. Garcia, A. Grodsky, D. R. Johnson, R. A. Locarnini, A. V. Mishonov, T.D. O'Brien, C.R. Paver, J.R. Reagan, D. Seidov, I. V. Smolyar, and M. M. Zweng: World Ocean Database 2013, NOAA Atlas NESDIS 72, S. Levitus, Ed., A. Mishonov, Technical Ed.; Silver Spring, 2013
- Dekens, P. S., Lea, D. W., Pak, D. K. and Spero, H. J.: Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, Geochemistry, Geophys. Geosystems, 3, 1–29, 2002.
- Deuser, W.G., Ross, E.H., Hemleben, Ch., Spindler, M.: Seasonal changes in species composition, numbers, mass, size, and isotopic composition of planktonic foraminifera settling into the deep Sargasso Sea, Palaeogeogr., Palaeoclimat., Palaeoecol., 33:103-127, 1981.
- Deuser, W. G. and Ross, E. H., Seasonally abundant planktonic foraminifera of the Sargasso Sea; succession, deep-water fluxes, isotopic compositions, and paleoceanographic implications, J. Foraminifer. Res., 19, 268–293, 1989.
- Duplessy, J., Labeyrie, L., Juilletleclerc, A., Maitre, F., Duprat, J. and Sarnthein, M., Surface salinity reconstruction of the north-atlantic ocean during the last glacial maximum, Oceanol. Acta, 14, 311–324, 1991.
- Elderfield, H., Yu, J., Anand, P., Kiefer, T. and Nyland, B.: Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis, Earth Planet. Sci. Lett., 250, 633–649, 2006.
- Farmer, E. C., Kaplan, A., de Menocal, P. B. and Lynch-Stieglitz, J.: Corroborating ecological depth preferences of planktonic foraminifera in the tropical Atlantic with the stable oxygen isotope ratios of core top specimens, Paleoceanography, 22, 1–14, 2007.
- Fairbanks, R. G., Sverdlove, M., Free, R., Wiebe, P. H. and Bé, A. W. H.: Vertical distribution and isotopic fractionation of living planktonic foraminifera from the Panama Basin, Nature, 298, 841–844, 1982.
- Fairbanks, R. G. and Wiebe, P. H., Foraminifera and Chlorophyll Maximum: Vertical Distribution, Seasonal Succession, and Paleoceanographic Significance, Science, 209, 1524–1526, 1980.
- Ferguson, J. E., Henderson, G. M., Kucera, M. and Rickaby, R. E. M.: Systematic change of foraminiferal Mg/Ca ratios across a strong salinity gradient, Earth Planet. Sci. Lett., 265, 153–166, 2008.
- Henehan, M. J., Foster, G. L., Bostock, H. C., Greenop, R., Marshall, B. J. and Wilson, P. A.: A new boron isotope-pH calibration for Orbulina universa, with implications for understanding and accounting for 'vital effects.', Earth Planet. Sci. Lett., 454, 282–292, 2016.

- Hönisch, B. and Hemming, N. G.: Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: Partial dissolution and shell size effects, Paleoceanography, 19, 1–13, 2004.
- Jørgensen, B. B., Erez, J., Revsbech, P. and Cohen, Y.: Symbiotic photosynthesis in a planktonic foraminiferan, Globigerinoides sacculifer (Brady), studied with microelectrodes, Limnol. Oceanogr. 30, 1253–1267, 1985.
- Kim, S.-T. and O'Neil, J. R.: Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, Geochim. Cosmochim. Acta, 61, 3461–3475, 1997.
- Martínez-Botí, M. A., Mortyn, P. G., Schmidt, D. N., Vance, D. and Field, D. B.: Mg/Ca in foraminifera from plankton tows: Evaluation of proxy controls and comparison with core tops, Earth Planet. Sci. Lett., 307, 113–125, 2011.
- Misra, S., Greaves, M., Owen, R., Kerr, J., Elmore, A. C. and Elderfield, H.: Determination of B/Ca of natural carbonates by HR-ICP-MS, Geochemistry, Geophys. Geosystems, 15, 1617–1628, 2014.
- Mulitza, S., Boltovskoy, D., Donner, B., Meggers, H., Paul, A. and Wefer, G.: Temperature:δ18O relationships of planktonic foraminifera collected from surface waters, Palaeogeogr. Palaeoclimatol. Palaeoecol, 202, 143–152, 2003.
- Ni, Y., Foster, G. L., Bailey, T., Elliott, T., Schmidt, D. N., Pearson, P., Haley, B. and Coath, C.: A core top assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers, Paleoceanography, 22, 2007.
- Peeters, F. J. C. and Brummer, G.-J. a.: The seasonal and vertical distribution of living planktic foraminifera in the NW Arabian Sea, Geol. Soc. London, Spec. Publ., 195, 463–497, 2002.
- Rostek, F., Ruhland, G., Bassinot, F. C., Muller, P. J., Labeyrie, L. D., Lancelot, Y. and Bard, E.: Reconstructing Sea-Surface Temperature and Salinity Using δ18O and Alkenone Records, Nature, 364, 319–321, 1993.
- Russell, A. D., Hönisch, B., Spero, H. J. and Lea, D. W.: Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera, Geochim. Cosmochim. Acta, 68, 4347–4361, 2004.
- Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K. and Pancost, R. D.: Alkenone and boron-based Pliocene pCO2records, Earth Planet. Sci. Lett., 292, 201–211, 2010.
- Sime, N. G., De La Rocha, C. L. and Galy, A.: Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera, Earth Planet. Sci. Lett., 232, 51–66, 2005.
- Yu, J., Day, J., Greaves, M. and Elderfield, H.: Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS, Geochemistry, Geophys. Geosystems 6, 2005
- Rickaby, R. E. M. and Halloran, P.: Cool La Nina During the Warmth of the Pliocene?, Science, 307, 1948–1952, 2005.
- Wang, G., Cao, W., Yang, D. and Xu, D. Variation in downwelling diffuse attenuation coefficient in the northern South China Sea, Chinese J. Oceanol. Limnol., 26, 323–333, 2008.
- Weare, B. C., Strub, P. T. and Samuel, M. D.: Annual Mean Surface Heat Fluxes in the Tropical Pacific Ocean, J. Phys. Oceanogr., 11, 705–717, 1981.



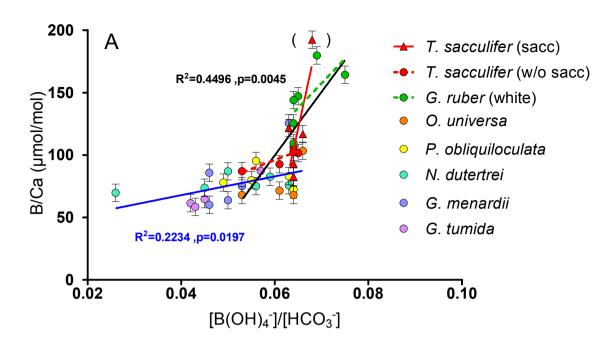


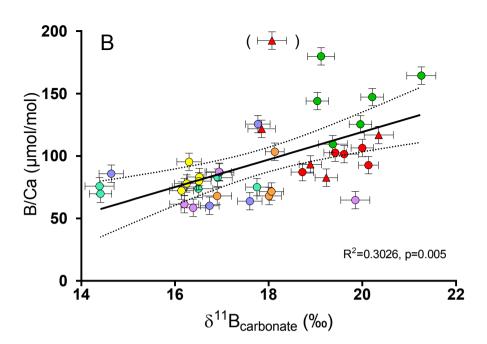
◆ G. ruber (Arabian Sea)

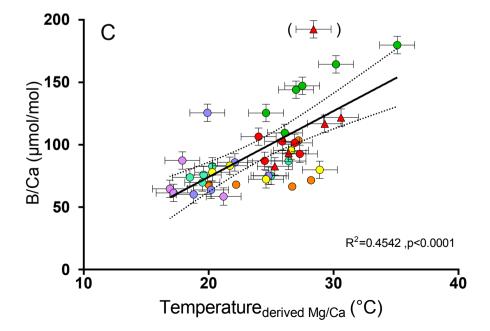
- ◆ G. ruber (WEP)
- T. sacculifer (w/sacc) (Arabian Sea)
- T. sacculifer (w/o sacc) (WEP)

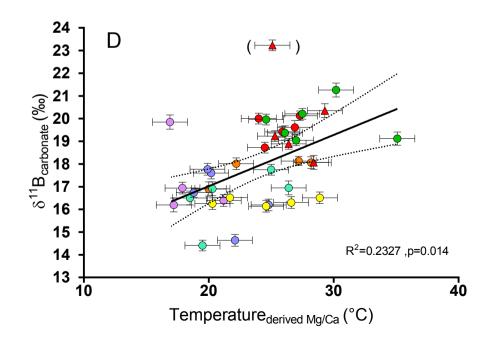
G. ruber (Indian Ocean)

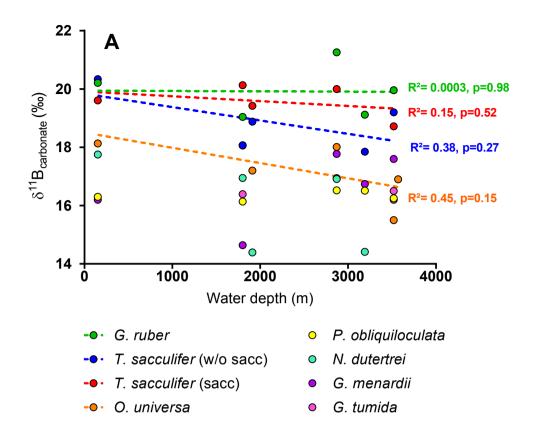
- Linear reg. All
- T. sacculifer (w/o sacc) (Indian Ocean)

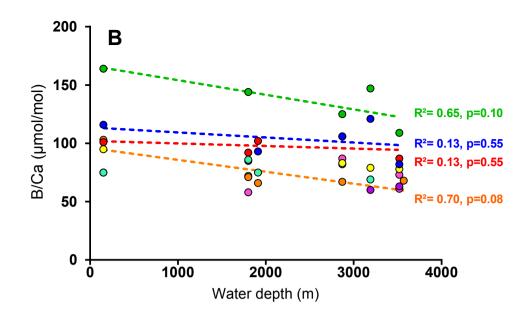


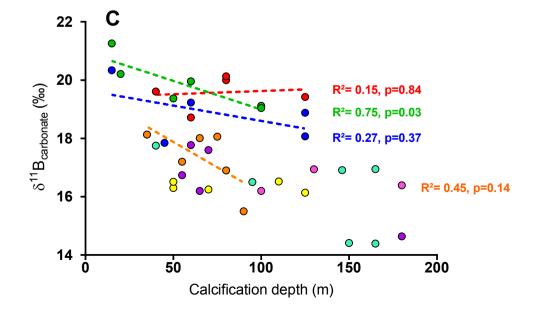


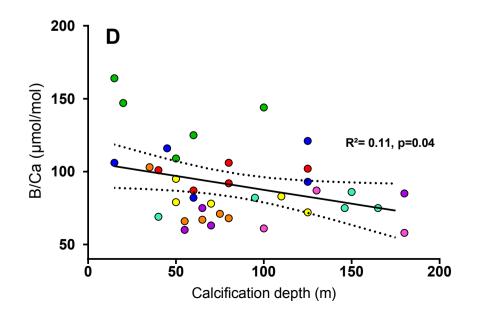












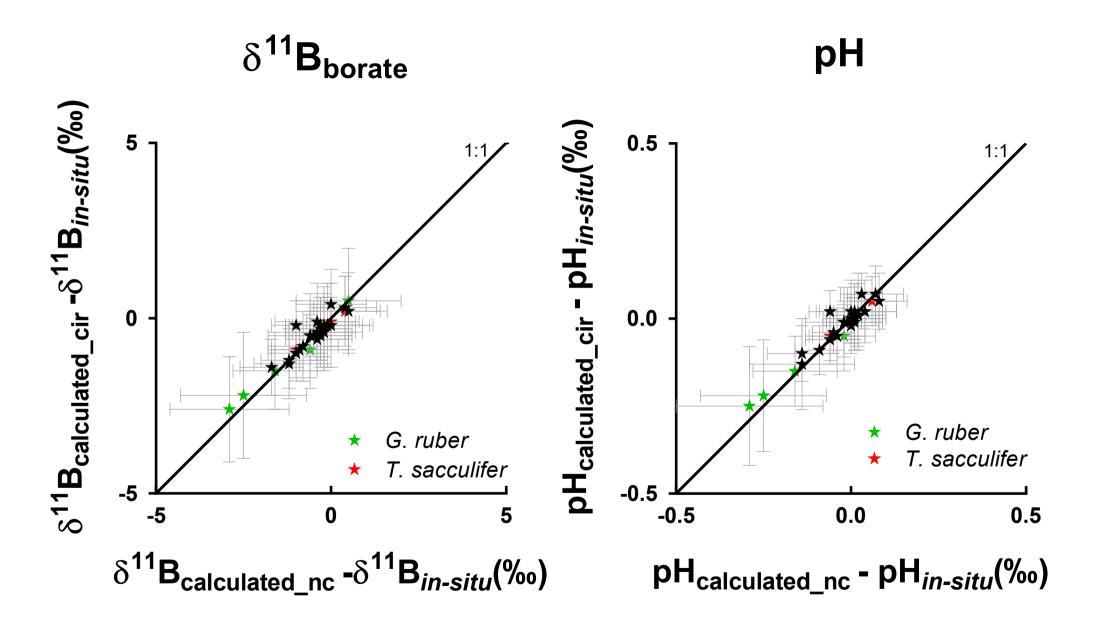


Table S1

Elemental ratios	Li/Ca	B/Ca	Mg/Ca	Al/Ca	Sr/Ca	Cd/Ca	Ba/Ca	U/Ca	Mn/Ca	Fe/Ca
	μmol/mol	μmol/mol	mmol/mol	mmol/mol	mmol/mol	μmol/mol	μmol/mol	nmol/mol	μmol/mol	mmol/mol
Standard solution 0	0.8	9	0.10	0.131	0.00	0.03	0.6	31	1	0.01
Standard solution 1	2.3	38	0.31	0.112	0.49	0.05	1.9	38	12	0.02
Standard solution 3	6.8	108	1.31	0.177	1.06	0.13	3.0	53	39	0.04
Standard solution 5	14.6	216	3.17	0.223	1.57	0.23	5.1	62	129	0.08
Standard solution 6	19.0	278	5.23	0.352	1.97	0.28	5.5	74	196	0.11
Standard solution 8	25.0	281	6.07	0.602	2.99	0.50	20.1	390	501	0.50
Standard solution 9		408			4.89					
Standard solution 10		519			8.01					
Standard solution 11		607			9.93					

Table S2

Standard	$\delta^{11}\mathbf{B}_{1}$ (‰)	2SD _{AE121}	n _{AE121}	$\delta^{11} \mathbf{B}_2 \ (\%)$	2SD _{AE121}	n _{AE121}	Reference
NEP1	25.21	0.25	11	25.22	0.25	11	This study
NEP2	25.00	0.30	12				This study
NEP3	24.70	0.30	12				This study
NEP4	25.40	0.21	11				This study
NEP5	25.32	0.21	11	25.33	0.21	11	This study
NEP6	25.22	0.21	11				This study
NEP7	25.26	0.26	15				This study
NEP8	25.39	0.26	15				This study
NEP9	26.15	0.26	15				This study
NEP10	25.97	0.26	15				This study
NEP11	26.09	0.26	15	26.09	0.26	15	This study
NEP12	26.22	0.26	15	26.29	0.26	15	This study
NEP13	26.19	0.26	15	26.21	0.26	15	This study
NEP14	26.12	0.26	15	26.13	0.26	15	This study
NEP15	26.00	0.26	15				This study
NEP16	26.04	0.26	15				This study
NEP17	26.02	0.29	12				This study
NEP18	25.86	0.29	12	25.86	0.26	14	This study
NEP19	25.78	0.26	14				This study
NEP20	25.42	0.15	3	25.32	0.15	3	This study
NEP21	25.54	0.22	6	26.16	0.22	6	This study
NEP22	26.42	0.22	6				This study
JCP-1-1	24.07	0.10					This study
JCP-1-2	24.17	0.11		24.17	0.10		This study
JCP-1-3	24.01	0.11					This study
JCP-1-4	23.92	0.26					This study
JCP-1-5	24.03	0.26		24.05	0.39		This study
JCP-1-6	24.18	0.36		24.16	0.36		This study
Standard	Average $\delta^{11}B$	2SD	n				Reference
NEP	25.70	0.93	22				This study
NEP	26.20	0.88	27				Holcomb et al., 2015
NEP	25.80	0.89	6				Sutton et al., 2018
JCP-1	24.06	0.20	6				This study
JCP-1	24.37	0.32	57				Holcomb et al., 2015
JCP-1	24.42	0.28	7				Sutton et al., 2018

Table S3

Date of analysis	Standard	Li/Ca µmol/mol	B/Ca µmol/mol	Mg/Ca mmol/mol	Sr/Ca mmol/mol	Cd/Ca µmol/mol	Ba/Ca μmol/mol	U/Ca nmol/mol	Mn/Ca µmol/mol	Fe/Ca mmol/mol	Reference
10/7/17	CamWuel 1	16.0	204	1.22	1.31	0.26	4.6	43	μποι/ποι 67	0.04	This study
10/7/17	CamWuel 2	16.3	209	1.24	1.32	0.28	4.6	45	69	0.04	This study
10/7/17	CamWuel 3	16.3	209	1.23	1.31	0.26	4.6	44	77	0.04	This study
10/7/17	CamWuel 4	16.0	207	1.23	1.32	0.28	4.6	44	74	0.04	This study
10/7/17	CamWuel 5	16.4	210	1.23	1.32	0.27	4.6	42	74	0.04	This study
10/7/17	CamWuel 6	16.0	208	1.24	1.31	0.26	4.6	42	74	0.04	This study
10/7/17	CamWuel 7	16.6	213	1.23	1.32	0.28	4.6	44	74	0.04	This study
11/7/17	CamWuel 1	16.0	203	1.22	1.32	0.26	4.6	41	72	0.04	This study
11/7/17	CamWuel 2	16.1	205	1.22	1.32	0.27	4.6	42	76	0.04	This study
11/7/17	CamWuel 3	16.2	204	1.22	1.32	0.27	4.6	41	72	0.04	This study
11/7/17	CamWuel 4	16.1	205	1.22	1.32	0.27	4.5	41	71	0.04	This study
11/7/17	CamWuel 5	15.8	204	1.21	1.32	0.27	4.6	42	73	0.04	This study
11/7/17	CamWuel 6	16.1	206	1.22	1.32	0.27	4.6	42	68	0.04	This study
11/7/17	CamWuel 7	16.0	207	1.22	1.32	0.26	4.6	43	66	0.04	This study
11/7/17	CamWuel 8	15.9	203	1.21	1.32	0.27	4.6	42	68	0.04	This study
12/7/17	CamWuel 1	16.3	201	1.22	1.31	0.22	4.6	41	66	0.03	This study
12/7/17	CamWuel 2	16.1	203	1.22	1.32	0.23	4.6	42	67	0.03	This study
12/7/17	CamWuel 3	16.4	202	1.22	1.32	0.23	4.6	42	69	0.04	This study
12/7/17	CamWuel 4	16.3	202	1.22	1.31	0.22	4.6	41	68	0.04	This study
12/7/17	CamWuel 5	16.6	202	1.22	1.31	0.23	4.6	44	67	0.03	This study
12/7/17	CamWuel 6	16.6	205	1.22	1.31	0.24	4.5	42	66	0.03	This study
12/7/17	CamWuel 7	16.1	204	1.22	1.31	0.22	4.6	40	67	0.03	This study
12/7/17	CamWuel 8	16.4	204	1.22	1.31	0.23	4.6	43	67	0.03	This study
12/7/17	CamWuel 9	16.4	202	1.22	1.32	0.23	4.6	43	64	0.03	This study
13/7/2017	CamWuel 1	16.2	198	1.22	1.31	0.31	4.6	42	74	0.04	This study
13/7/2017	CamWuel 2	16.4	200	1.22	1.30	0.30	4.6	43	73	0.04	This study
13/7/2017	CamWuel 3	16.2	201	1.23	1.31	0.31	4.7	43	74	0.04	This study
13/7/2017	CamWuel 4	16.3	198	1.22	1.31	0.30	4.6	42	73	0.04	This study
13/7/2017	CamWuel 5	16.6	200	1.23	1.30	0.30	4.6	42	73	0.04	This study
13/7/2017	CamWuel 6	16.5	198	1.22	1.31	0.31	4.6	44	74	0.04	This study
13/7/2017	CamWuel 7	16.1	201	1.22	1.30	0.32	4.7	43	74	0.04	This study
	Average CamWuel	16.2	204	1.22	1.31	0.27	4.6	42	71	0.04	This study
	2SD	0.4	7	0.01	0.01	0.06	0.1	2	7	0.01	,
	n	31	31	31	31	31	31	31	31	31	
	Published CamWuel	16.4	202	1.23	1.30	0.29	4.8	44	71		Misra et al., 2014
	2SD	0.8	7	0.06	0.02	0.02	0.2	2	2		,
	n	180	180	180	180	180	180	180	180		

Table S4

Seasonality
Spring
Spring
Summer
Winter
Annual average
Annual average
Annual average
Winter

Table S5

Species	В	A	Reference	
T. sacculifer (sacc)	0.377	0.090	Anand et al., 2003	
T. sacculifer (w/o sacc)	0.347	0.090	Anand et al., 2003	
G. ruber (white)	0.300	0.089	Dekens et al., 2002	
N. dutertrei	0.600	0.008	Dekens et al., 2002	
G. tumida	0.380	0.090	Anand et al., 2003	
G. menardii	0.360	0.091	Regenberg et al., 2009	
O. universa	0.595	0.090	Anand et al., 2003	
P. obliquiloculata	0.328	0.090	Anand et al., 2003	

Species	A	В	C	dw correction	Condition	Reference	Equation
O. universa	16.500	4.800		-0.27	LL	Bemis et al., 1998	T=A-B* (δ18Oc-δ18Ow)
O. universa	15.700	4.460	0.35	-0.27	ML	Bemis et al., 2002	$T=A-B*(\delta 18Oc-\delta 18Ow)+C*(\delta 18Oc-\delta 18Ow)^2$
O. universa	14.900	4.800		-0.27	HL	Bemis et al., 1998	$T=A-B*(\delta 18Oc-\delta 18Ow)$
T. sacculifer	14.910	4.350		-0.27		Mulitza et al., 2003	$T=A-B*(\delta 18Oc-\delta 18Ow)$
G. ruber	14.200	4.440		-0.27		Mulitza et al., 2003	$T=A-B*(\delta 18Oc-\delta 18Ow)$
All	16.900	4.380	0.1	-0.2		Shackleton et al., 1974	$T=A-B* (\delta 18Oc-\delta 18Ow)+C*(\delta 18Oc-\delta 18Ow)^2$
All	17.000	4.520	0.03	-0.22		Erez and Luz, 1983	$T=A-B* (\delta 18Oc-\delta 18Ow)+C*(\delta 18Oc-\delta 18Ow)^2$
All	16.100	4.640	0.09	-0.27		Kim and O'Neil 1997	$T=A-B*(\delta 18Oc-\delta 18Ow)+C*(\delta 18Oc-\delta 18Ow)^3$

Table S6

FC-01a G. ruber (white ss) 83 ± 20 30 ± 10 50 ± 20 Sime thesis 2006 FC-02a G. ruber (white ss) 56 ± 10 15 ± 10 60 ± 20 Sime thesis 2006 FC-12b G. ruber (white ss) Surface ± 10 -0.30 60 ± 10 Poeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. ruber (white ss) Go ± 10 100±20 Felderfield and Ganssen, 2000 A14 G. ruber (white ss) 48 ± 10 50 ± 10 60 ± 10 Sime et al., 2005 FC-01a T. sacculifier (sacc) 7 ± 10 30 ± 10 80 ± 20 Sime et al., 2005 FC-02b T. sacculifier (sacc) 7 ± 10 30 ± 10 80 ± 20 Fisckaby et al., 2005 FC-01a T. sacculifier (sacc) 15 ± 10 40 ± 10 Fisckaby et al., 2005 FC-01a T. sacculifier (wo sacc) 88 ± 20 50 ± 10 60 ± 10 Sime thesis 2006 (Wind22-b) FC-02a T. sacculifier (wo sacc) 32 ± 10 10 ± 10 80 ± 20 Sime thesis 2006 FC-01a T. sacculifier (wo sacc) 80 ± 20 <t< th=""><th>Core</th><th>Species</th><th>CD₁</th><th>CD₂</th><th>CD₃</th><th>Reference</th></t<>	Core	Species	CD ₁	CD ₂	CD ₃	Reference
FC-12b G. ruber (white ss)	FC-01a	G. ruber (white ss)	83 ± 20	30 ± 10	50 ± 20	Sime thesis 2006
FC-13a G. ruber (white ss)	FC-02a	G. ruber (white ss)	56 ± 10	15 ± 10	60 ± 20	Sime thesis 2006
NP7-01 G. ruber (white ss)	FC-12b	G. ruber (white ss)	Surface ± 10	0-30	60 ± 10	Peeters and Brumer, 2012 (non upwelling station Arabian sea)
A14 G. ruber (white ss)	FC-13a	G. ruber (white ss)	Surface ± 10	20 ± 20	60 ± 10	Peeters and Brumer, 2012 (non upwelling station Arabian sea)
FC-01a	WP7-01	G. ruber (white ss)			100±20	Elderfield and Ganssen, 2000
FC-02a	A14	G. ruber (white ss)		60 ± 10	100±20	Elderfield and Ganssen, 2000
FC-12b	FC-01a	T. sacculifer (sacc)	48 ± 10	50 ± 10	60 ± 10	Sime et al., 2005
WP7-01 T. sacculifer (sacc) S0 ± 20 125 ± 15 Rickaby et al., 2005	FC-02a	T. sacculifer (sacc)	7 ± 10	30 ± 10	80 ± 20	Sime et al., 2006
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	FC-12b	T. sacculifer (sacc)	15 ± 10	40 ± 10		
FC-01a	WP7-01	T. sacculifer (sacc)		80 ± 20	125 ± 15	Rickaby et al., 2005
FC-02a	A14	T. sacculifer (sacc)		60 ± 10	125 ± 15	
FC-12b	FC-01a	T. sacculifer (w/o sacc)		50 ± 10		Sime thesis 2006 (Wind22-b)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	FC-02a	T. sacculifer (w/o sacc)	32 ± 10	10 ± 10		Sime thesis 2006
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	FC-12b		$0-15 \pm 10$	30 ± 10	45 ± 20	Peeters and Brumer, 2012 (non upwelling station Arabian sea)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	WP7-01	T. sacculifer (w/o sacc)		80 ± 20	125 ± 15	Rickaby et al., 2005
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	A14	T. sacculifer (w/o sacc)		60 ± 10	125 ± 15	Rickaby et al., 2005
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					65 ± 10	Birshe et al., 2013
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			35 ± 10			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A14	O. universa		55 ± 15		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$					106 ± 20	Sime et al., 2005
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		P. obliquiloculata				
FC-01a N. dutertrei 95 ± 20 90 ± 20 146 ± 20 Sime et al., 2005 FC-12b N. dutertrei 40 ± 10 50 ± 10 FC-13a N. dutertrei 45 ± 10 150 ± 20			65 ± 10			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	WP7-01	P. obliquiloculata		125 ± 25		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	FC-01a	N. dutertrei		90 ± 20		Sime et al., 2005
FC-13a N. dutertrei 45 ± 10 150 ± 20 Rickaby et al., 2005 MP7-01 N. dutertrei 125 ± 25 165 Rickaby et al., 2005 FC-01a G. menardii 135 ± 20 70 ± 20 FC-02a G. menardii 60 ± 10 60 ± 10 FC-12b G. menardii 65 ± 10 55 ± 15 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. menardii 55 ± 10 70 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) WP7-01 G. menardii 180 ± 20 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-01a G. tumida 70 ± 20 100 ± 10 160 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 160 ± 20 Birshe et al., 2013					146 ± 20	Sime et al., 2005
WP7-01 N. dutertrei 125 ± 25 165 Rickaby et al., 2005 FC-01a G. menardii 135 ± 20 70 ± 20 FC-02a G. menardii 60 ± 10 60 ± 10 FC-12b G. menardii 65 ± 10 55 ± 15 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. menardii 55 ± 10 70 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) WP7-01 G. menardii 180 ± 20 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-01a G. tumida 70 ± 20 100 ± 10 160 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 160 ± 20 Birshe et al., 2013						
A14 N. dutertrei 110 ± 20 165 Rickaby et al., 2005 FC-01a G. menardii 135 ± 20 70 ± 20 FC-02a G. menardii 60 ± 10 60 ± 10 FC-12b G. menardii 65 ± 10 55 ± 15 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. menardii 55 ± 10 70 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) WP7-01 G. menardii 180 ± 20 FC-01a G. tumida 70 ± 20 100 ± 10 160 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 160 ± 20 Birshe et al., 2013			45 ± 10			
FC-01a						
FC-02a G. menardii 60 ± 10 60 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-12b G. menardii 55 ± 10 70 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. menardii 180 ± 20 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-01a G. tumida 70 ± 20 100 ± 10 160 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 160 ± 20 Birshe et al., 2013	A14	N. dutertrei		110 ± 20	165	Rickaby et al., 2005
FC-12b G. menardii 65 ± 10 55 ± 15 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) FC-13a G. menardii 55 ± 10 70 ± 10 60 ± 10 Peeters and Brumer, 2012 (non upwelling station Arabian sea) WP7-01 G. menardii 180 ± 20 Birshe et al., 2013 FC-01a G. tumida 70 ± 20 130 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 Birshe et al., 2013						
FC-13a						
WP7-01						
FC-01a G. tumida 70 ± 20 100 ± 10 160 ± 20 Birshe et al., 2013 FC-02a G. tumida 70 ± 20 130 ± 20 160 ± 20 Birshe et al., 2013			55 ± 10		60 ± 10	Peeters and Brumer, 2012 (non upwelling station Arabian sea)
FC-02a G. tumida 70 ± 20 130 ± 20 Birshe et al., 2013	WP7-01	G. menardii		180 ± 20		
WP7-01 <i>G. tumida</i> 180 ± 20 $210 - 240$ Rickaby et al., 2005			70 ± 20			Birshe et al., 2013
	WP7-01	G. tumida		180 ± 20	210 - 240	Rickaby et al., 2005

 $[\]text{CD}_1\text{:}$ Depth habitat estimated from $\delta^{18}\text{O}_c$

CD₂: Depth habitat estimated from Mg/Ca derived temperature

 $CD_{3:}$ Depth habitat from literature

Table S7

		I	PRE INDUST	ΓRIAL	IN-SIT	U PARA	METERS														CALCU	LATEI) PARA	1ETER:	3						
Core	Species	Depth habitat (m)	Femperature	2sd*	Salinity	2sd*	pH (pre-ind	1) 2sd*	pCO ₂	2sd*	HCO ₃	2sd*	CO ₃ ²⁻	2sd*	DIC	2sd*	ALK	2sd*	$\delta^{11}B_{borat}$	e 2sd*	T _{Mg/Ca} 2s	d pH	δ11B 2sd	* pCO	2sd***	Calibration	рН біів	2sd**	pCO ₂	2sd***	Calibration
	<u> </u>		(°C)																												
Atlantic (Ocean																														
CD107a	O. universa	80 ± 20	12.0	0.3	35.6	0.01	8.19	0.03	274	21	1856	29	192	12	2059	18	2333	1	17.86	0.31	20.0 1.	.4 8.	19 0.0	5 285	39	[8]					
Indian O	cean																														
FC-01a	G. ruber (white ss)	50 ± 20	23.4	5.9	35.0	0.4	8.10	0.04	338	41	1743	138	226	48	1979	93	2299	22	18.40	0.90	26.1 1.	.4 8.0	0.0	387	29	[1]	7.88	0.16	630	42	[2]
FC-01a	T. sacculifer (sacc)	60 ± 10	21.9	5.7	35.1	0.3	8.09	0.03	346	38	1773	126	215	45	1998	84	2303	18	18.15	0.81	24.5 1.	.4 8.0	0.0	400	79	[3]	8.04	0.06	417	82	[4]
FC-01a	T. sacculifer (w/o sacc)	60 ± 10	21.9	5.7	35.1	0.3	8.09	0.03	346	38	1773	126	215	45	1998		2303		18.16	0.82	25.3 1.				49	[3]	8.10	0.05	356	49	[4]
FC-01a	O. universa	90 ± 20	18.2	4.0	35.2	0.0	8.07	0.04		43	1856	94	184	35	2053		2311		17.42	0.61		7.9			63	[8]					
FC-01a	P. obliquiloculata	106 ± 20	20.5	4.6	35.2	0.1	8.09	0.03	353	32	1802	99	204	36	2018		2306		17.91	0.66	20.3 1.				48	[11]					
FC-01a	G. menardii	70 ± 20	20.5	4.6	35.2	0.1	8.09	0.03	353	32	1802	99	204		2018		2306		17.93	0.68	20.2 1.				43	[13]					
FC-01a	N. dutertrei	95 ± 20	17.7	4.0	35.1	0.0	8.06	0.04	380	43	1868	94	180	35	2061		2313		17.26	0.62	18.5 1.				49	[13]					
FC-01a	G. tumida	100 ± 20	17.1	1.6	35.1	0.0	8.06	0.02	386	22	1881	41	175	15	2070	27	2314	3	17.21	0.27	17.2 1.	.4 8.0	0.0	7 400	52	[13]					
FC-02a	G. ruber (white ss)	60 ± 20	20.4	2.4	35.5	0.0	8.19	0.01	268	10	1724	26	246	10			2332		19.06	0.34	24.6 1.				26	[1]	8.03	0.10	428	31	[2]
FC-02a	T. sacculifer (sacc)	80 ± 20	19.3	1.9	35.6	0.1	8.19	0.01	268	7	1741	38	240	15	1989		2333	3	18.89	0.30	24.0 1.		18 0.0	3 286	57	[3]	8.21	0.05	267	54	[4]
FC-02a	T. sacculifer (w/o sacc)	80 ± 20	19.3	1.9	35.6	0.1	8.19	0.01	268	7	1741	38	240	15	1989			3	18.90	0.30	25.1 1.										
FC-02a	O. universa	65 ± 10	20.1	1.1	35.5	0.0	8.19	0.00	268	2	1728	15	245	6	1981	9	2332	1	19.00	0.17	22.2 1.				42	[8]					
FC-02a	P. obliquiloculata	60 ± 10	18.3	0.5	35.6	0.0	8.18	0.01	277	8	1769	17	228	7	2007		2334	1	18.64	0.14	21.7 1.				43	[11]					
FC-02a	G. menardii	60 ± 10	20.4	1.9	35.5	0.0	8.19	0.01	268	10	1724	19	246	7	1979		2332	2	19.05	0.30	19.9 1.				42	[13]					
FC-02a	N. dutertrei	146 ± 20	17.5	1.0	35.6	0.1	8.16	0.02	292	14	1798	31	216		2024		2333	2	18.33	0.27	20.3 1.				46	[13]					
FC-02a	G. tumida	130 ± 20	17.8	0.8	35.6	0.0	8.17	0.02	284	17	1784	32	222	14	2015	19	2334	1	18.47	0.25	17.9 1.	.4 8.1	12 0.0	339	46	[13]					
Arabian S	Sea																														
FC-12b	G. ruber (white ss)	0-30	25.9	0.3	36.6	0.1	8.18	0.05		39	1655	53	292	23	1954		2374		19.81	0.65	30.2 1.				28	[1]	8.20	0.10	265	26	[2]
FC-12b	T. sacculifer (sacc)	40 ± 10	25.3	0.6	36.5	0.0	8.10	0.06	350	64	1756	75	249	31	2015		2369	2	18.71	0.77	26.9 1.				54	[3]	8.10	0.06	366	53	[4]
FC-12b	T. sacculifer (w/o sacc)	15 ± 10	25.9	0.0	36.5	0.1	8.16	0.04		34	1681	45	281		1970		2374	8	19.54	0.50	29.3 1.				50	[3]	8.16	0.06	302	47	[4]
FC-12b	O. universa	35 ± 10	25.5	0.6	36.5	0.0	8.11	0.06	334	56	1738	68	257	28	2004		2369	1	18.90	0.69	27.2 1.				50	[8]					
FC-12b	P. obliquiloculata	50 ± 10	25.0	0.9	36.5	0.1	8.06	0.06	382	69	1794	75	233		2038				18.24	0.67	26.6 1.				58	[11]					
FC-12b	G. menardii	65 ± 10	24.1	1.1	36.4	0.1	8.02	0.06	438	72	1850	75	209	32			2365	4	17.69	0.62	24.8 1.				68	[13]					
FC-12b	N. dutertrei	40 ± 10	25.3	0.6	36.5	0.0	8.10	0.06	350	64	1756	75	249	31	2015	46	2369	2	18.75	0.71	25.0 1.	.4 8.	11 0.0	350	52	[13]					
FC-13a	G. ruber (white ss)	20 ± 20	27.1	1.1	36.7	0.1	8.10	0.03	343	27	1724	43	263		1996		2371		19.00	0.37	27.5 1.		11 0.0	351	29	[1]	8.05	0.09	417	32	[2]
FC-13a	T. sacculifer (w/o sacc)	45 ± 20	25.7	0.7	36.6	0.0	8.07	0.03	380	34	1782	38	239	16	2032	23	2371	2	18.86	0.45	30.6 1.	.4									
FC-13a	P. obliquiloculata	50 ± 10	25.4	1.2	36.6	0.1	8.06	0.05	391	59	1797	66	233	29	2041		2370	4	18.31	0.57	28.9 1.	.4 8.0	0.0		55	[11]					
FC-13a	G. menardii	55 ± 10	25.1	1.3	36.6	0.1	8.04	0.05	409	65	1815	69	225	30			2369		18.04	0.56	18.8 1.				68	[13]					
FC-13a	N. dutertrei	150 ± 20	19.4	2.3	36.0	0.1	7.80	0.03	766	45	2056	37	118	15	2199	25	2348	1	15.37	0.27	19.5 1.	.4 7.1	79 0.0	811	101	[13]					
Pacific O																															
WP07-a	G. ruber (white ss)	100±20	26.1	2.4	35.2	0.4	8.05	0.05	387	51	1753	81	224	31	1988		2305	7	18.21	0.64	27.0 1.				32	[1]	7.80	0.16	778	52	[2]
WP07-a	T. sacculifer (sacc)	80 ± 20	27.4	2.2	35.0	0.5	8.08	0.05	357	56	1708	89	242	33	1960		2303	10	18.68	0.65	27.3 1.				63	[3]	8.13	0.04	324	49	[4]
WP07-a	T.sacculifer (w/o sacc)	125 ± 20	24.7	1.8	35.4	0.2	8.03	0.00	413	30	1797	31	209		2017				17.80	0.23	28.4 1.				58	[3]	7.92	0.08	573	73	[4]
WP07-a	O. universa	75 ± 25	27.7	2.6	34.9	0.6	8.09	0.07	349	68	1696	110	247	39	1953		2303		18.78	0.83	28.2 1.				52	[8]					
WP07-a	P. obliquiloculata	125 ± 25	24.7	3.6	35.4	0.4	8.03	0.02	413	30	1797	80	209	26			2311	18	17.82	0.48	24.6 1.				58	[11]					
WP07-a	N. dutertrei	165 ± 20	20.6	3.8	35.5	0.2	8.03	0.01	408	10	1855	44	189	18			2322		17.34	0.45	26.4 1.				50	[13]					
WP07-a	G. tumida	180 ± 20	18.7	5.0	35.4	0.2	8.04	0.01	403	13	1877	58	180	24	2070	35	2322	0	17.23	0.56	21.2 1.	.4 8.0	0.0	5 406	53	[13]					

^{*} uncertainties calculated using Henehan's 2016 R code

** propagated uncertainty on pH including d11B, temperature, salinity uncertainties

*** propagated uncertainty on pCO2 including d11B, temperature, salinity, Alk uncertainties