

Author comment (response to reviewers' comments) on: **The B/Ca proxy for past seawater carbonate chemistry reconstructions-laser ablation based calibrations for *C. mundulus*, *C. wuellerstorfi* and its morphotype *C.cf. wuellerstorfi*** by F. Kersten, R. Tiedemann, J. Fietzke and M. Frische

We thank both reviewers for their thorough reviews and helpful comments, which will aid in significantly improving the manuscript. The reviewers' comments are given below in italics and our replies are given in bold. Where not referred to, technical corrections will be included directly in the revised manuscript.

**Anonymous referee #2, cpd-9-C2194-2013**

*Major points that need to be addressed:*

*The linear regressions are missing uncertainties and some interpretations may change if these standard errors overlap.*

**Uncertainties will be included in the revised manuscript. Revised equations are as follows:**

**C.cf. wuellerstorfi**

$$\text{B/Ca} = 2.27 \pm 0.362 (\Delta[\text{CO}_3^{2-}]) + 152.5 \pm 11.19 (R^2 = 0.76, \text{p-value} < 0.0001).$$

**C. wuellerstorfi**

$$\text{B/Ca} = 1.39 \pm 0.048 (\Delta[\text{CO}_3^{2-}]) + 175.5 \pm 1.43 (R^2 = 0.87, \text{p-value} < 0.0001).$$

**C. mundulus**

$$\text{B/Ca} = 0.80 \pm 0.054 (\Delta[\text{CO}_3^{2-}]) + 114.5 \pm 1.82 (R^2 = 0.79, \text{p-value} < 0.0001).$$

*There are places where linear regression has not been carried out and the significance (or not) seems to be purely speculative (e.g. p4430 line 24).*

**Linear regression has been carried out and the p-values indicate that correlations are significant (see above).**

*The "B/Ca-DCO32- range" is referred to throughout the manuscript but this should just be the DCO32- range as B/Ca is measured as a proxy for DCO32-. If the manuscript discussed changes in seawater B/Ca this would make sense but this is not the case.*

**Point taken. Will be changed.**

*The discussion of ontogenetic variability (NOT profiles through shells) is based on two individual shells and no C. cf. wuellerstorfi specimens had many different chambers analysed because of technical problems. I do hope that these technical problems can be resolved and perhaps the ontogenetic variability of the different morphotypes compared? This would be exciting to see.*

**We agree, unfortunately no funding for further measurements is available.**

*The different morphotypes need to be better defined and distinguished. The Hayward reference is not freely available and I was unable to see if the morphotypes are more clearly defined there. I was therefore not able to see the reasoning for calling the morphotype simply “cf.” when in planktonic taxonomy the consensus seems to be distinguish different morphotypes with different species names (e.g. Aurahs et al., 2011, Mar. Micropal. 79, 1). Has anyone looked at the genetics of these benthic foraminifera yet?*

**Little attention has been paid towards this morphotype so far in the literature. We communicated with Bruce Hayward who confirmed our findings that C. cf. wuellerstorfi (or C. dispars) is more abundant in South Pacific sediments than C. wuellerstorfi. The first description of C. dispars is given in: Hayward et al. (1999). They summarised variable recent plano-convex Cibicides morphologies as C. dispars, which they also refer to as C. cf. wuellerstorfi. Further images of C. dispars can be found in Hayward et al. (2003) and Hayward et al. (2001).**

**In this study we focussed on the C. dispars specimen that have a clear resemblance to C. wuellerstorfi and thus follow Bruce Hayward in naming them C. cf. wuellerstorfi. The key characteristic that sets apart C. cf. wuellerstorfi from C. wuellerstorfi are their inflated chambers on the umbilical side. While C. wuellerstorfi is compressed, the C. cf. wuellerstorfi specimen studied here show a clearly convex umbilical side. We will include a more detailed description of C. cf. wuellerstorfi in the revised version of this manuscript.**

**Genotyping of these morphotypes has not been done.**

*The calibration obtained here is compared to the extensive dataset of Yu & Elderfield (2007) but why are the data from Raitzsch et al. (2011) and Rae et al. (2011) also not plotted and included in the compiled calibration?*

**Good point, will be included in the revised version.**

*Detailed points:*

*Introduction. I do not see the need to have separate sections 1.1 and 1.2. In fact section 1.1 fits nicely after page 4427 line 6. Section 1.2 fits nicely after page 4427 line 15.*

**This is a matter of personal style.**

*Also at that point some more references concerning different shell chemistry and morphotypes could be cited, perhaps expanding to the planktonic literature also.*

**Our study focusses on benthic foraminifera.**

*P4427 line 27. Can you cite a reference suggesting HCO<sub>3</sub><sup>-</sup> incorporation into calcite?*

**See text: Hemming and Hanson (1992).**

*P4428 line 21-23. This sentence would fit better in the methods sections.*

**We disagree as it follows directly out of the statements made above.**

*Was there any pre-cleaning of the shells performed, for example the first clay removal step?*

**Shells were pre-ablated to remove superficial coatings. Results with high Al/Ca indicative of clay contamination were discarded from the dataset (p. 4430, lines 6-9).**

*P4430 line 1. Was the instrument used in high resolution mode for the B/Ca measurements? It would probably be more helpful to readers who do not know the AttoM instrument to refer to it as a magnetic sector or sector field ICP-MS.*

**The laser ablation system was coupled to a double-focusing magnetic sector mass spectrometer in low-resolution mode (300 Res, 10% valley definition).**

*P4430 line 3. So there are 12 to 24 data points for each sample? I assume it is the standard deviation of these 12 to 24 data that are providing the sample standard deviation? Please clarify this here and delete the unclear sentence on line 5 to 6.*

**This is correct. The standard deviation per foram includes the analytical uncertainty of B/Ca derived from the standard measurements (done before and after each foram) and the individual spot measurements on the forams (4 per shell). The standard deviation of a given sample (included in the manuscript) was calculated from the standard deviations of individual foram measurements and the intra-sample variability. Sentence will be deleted.**

*P4430 line 3. The NIST 614 and 615 glasses are the same apart from the wafer thickness. It is therefore more common to see NIST 614 used in the literature, including Jochum et al. (2011). What is the B/Ca of the NIST 614 glass?*

**Jochum et al. (2011) give the following compositional data for NIST SRM 614–615: B= 1.49 ppm and CaO=11.9 wt%, B/Ca is then accordingly 65  $\mu\text{mol/mol}$ .**

*P4430 line 5. You should mention that accurate non-matrix matched calibration of B/Ca in carbonate samples has been demonstrated for 193nm laser ablation and cite a reference like Raitzsch et al. (2011) or one of the references in that paper.*

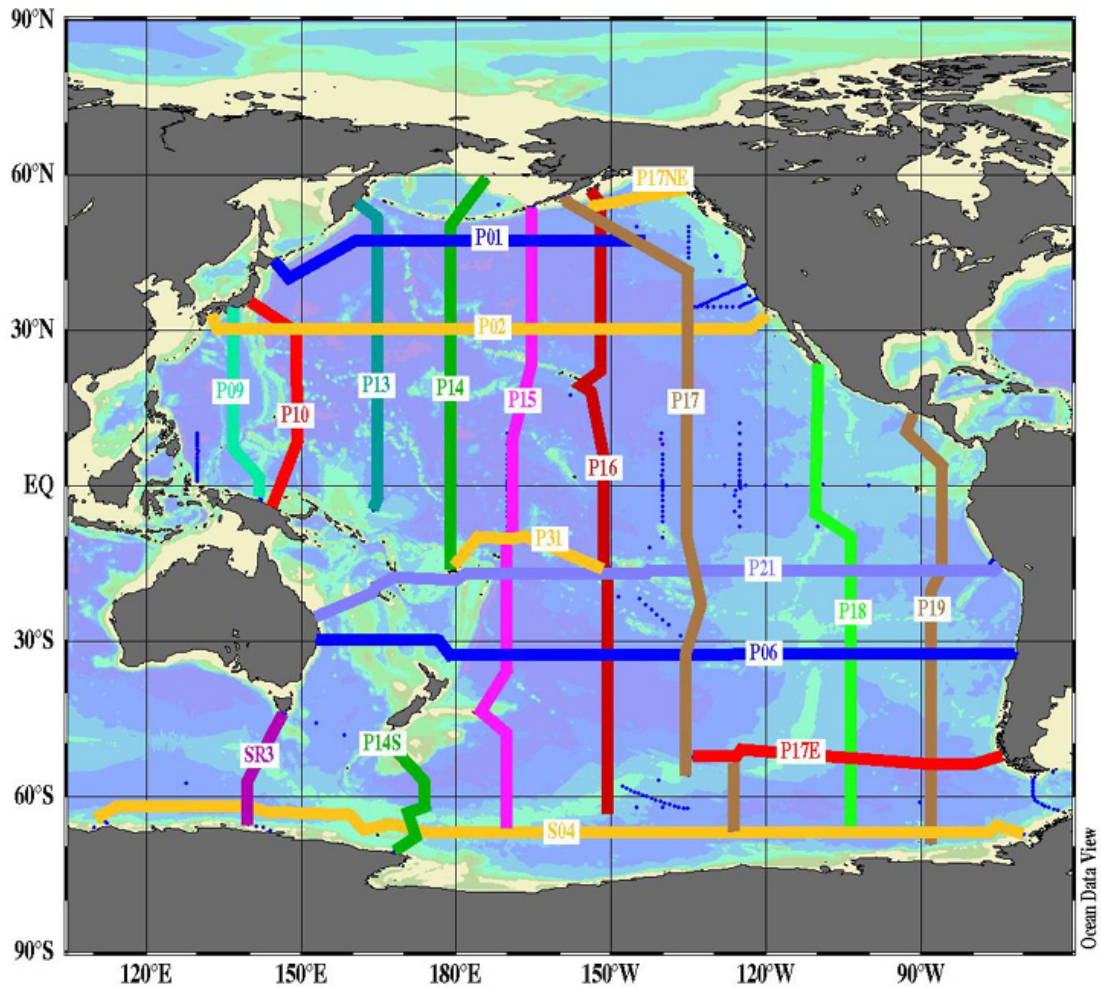
**Ok. A reference for Hathorne et al., (2008) who showed this, will be included in the revised version.**

*P4430 line 9-10. Where were these values for discarding data as being contaminated taken from? Ni et al. (2007) used a cut-off value of 100  $\mu\text{mol/mol}$  Al/Ca to eliminate clay contaminants high in B. What is the basis of the 4 times higher value here?*

**We follow the approach of Elderfield et al. (2010).**

*P4430 line 16. What parameters were taken from the GLODAP sites and how nearby were they to the multi-core locations?*

**Parameters taken from GLODAP were TA, DIC, Si and P, and stem from WOCE profiles P15-P17 (see below, image taken from: [http://cdiac.ornl.gov/oceans/glodap/atlas/pacific\\_map.html](http://cdiac.ornl.gov/oceans/glodap/atlas/pacific_map.html)) from latitudes and water depths that correspond to the herein studied locations.**



*P4431 line 8-9. What is the p value if regression analysis was performed?*

**No regression analysis was performed here.**

*P4433 line 20. I'm not sure if citing yourself in this way is part of the Harvard method and probably should be avoided.*

**Ok.**

*P4434 line 9. Should read "The two specimens chosen for ontogenetic analysis come from water depths. . .". Profiles could be confused with time resolved depth profiles through chamber walls that are not presented here*

**Ok.**

*P4434 line 15. Replace “. . . analogue to. . .” with “. . . as found by previous studies.” What about the intra-shell Mg/Ca variability and references dealing with how many laser ablation analyses of benthic foram Mg/Ca are required to be representative, for example the work of de Nooijer and colleagues?*

**This study focusses on B/Ca and not Mg/Ca.**

*P4435 line 9-25. This should be rephrased to highlight these samples extend the range of DCO32- sampled in the same oceanographic region.*

**Ok.**

*P4436 line 1. Surely such statements should be examined with water data and not proxy calibrations?*

**The statements made here refer to water data (d13C and DCO32-).**

*Section 4.3 is mostly redundant. As the other reviewer mentioned small samples can be analysed by solution ICP-MS.*

**The authors would be very interested to see ICP-MS B/Ca measurements on single species *Cibicides* samples with such low shell counts. We undertook several attempts to measure 4-6 *C. wuellerstorfi* individuals (the maximum amount we found in our samples) on a Thermo Finnigan Element 2 ICP-MS at the University of Bremen, none of which yielded meaningful results. This was the reason why we turned to the laser ablation ICP-MS technique in the first place.**

*The point of a micro-sampling technique like laser ablation is to provide additional spatial information, such as looking at ontogenetic patterns or lack of. This study could be greatly improved by incorporating some additional data for many chambers of more individual shells than the 2 specimens analysed.*

**We agree, however there is no more funding available to extend the discussed database.**

*P4437 line 12. The intra-sample variability is not presented or discussed previously in the paper so why should this suddenly appear in the conclusions?*

**True. Will be revised.**

*If not already there please include a data table in the supplementary material.*

**Data table is already available.**

*Fig 4. Why are there different symbols in (d)?*

**The symbols are the same as defined in Fig. 4a.**

*Fig 5. Which samples are which? Do the downcore samples have the higher B/Ca?*

**Sample 1=PS75/100-4\_12cm, sample 2=PS75/103-1\_38cm; sample 3= PS75/103-1\_52cm, sample 4=PS75/104-2\_2 cm, sample 5= PS75/105-1\_0cm, sample 6= SO213/86-1\_0cm. There is no relationship between depth in core and B/Ca ratios (see Supplemental data table).**

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