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.

<u>Anonymous referee #1, cpd-9-C2109-2013</u>

Points (i) and (iii) have been previous published by Yu & Elderfield (2007) EPSL and Raitzsch et al (2011) Geology, respectively. Point (iii) is somewhat new, but Rae et al (2010) EPSL also noted some morphological impacts on shell B/Ca. Therefore, this study does not present anything truly new. However, no B/Ca data from the South Pacific have been published previously, due to the challenge to obtain core-top samples from this region (mentioned by the authors). Therefore, this study may present some valuable B/Ca data, if the ages of the core-tops can be justified to be within Holocene (<5 ka).

Point (i): the data presented here stem from the South Pacifc, a region that is not included in B/Ca core-top calibrations so far and on top of that they were generated with a different technique than the one used in the Yu and Elderfield (2007) study. Seeing that the C. wuellerstorfi and C. mundulus data presented in this study follow the trends of the calibration by Yu and Elderfield (2007) further increases trust in the overall robustness of the global core-top calibration and shows that laser ablation ICP-MS generated data are comparable with ICP-MS generated data.
Point (ii): the observations of Rae et al. (2011) are referred to on page 4428 (lines 12-14), however Rae et al. (2011) present just a limited comparison of B/Ca ratios between Cibicides morphotypes and present no core-top data for the C. wuellerstorfi morphotype. This clearly leaves room for more work, a major point that is addressed in our study.
Point (iii): as mentioned on page 4428 (lines 16-18) Raitzsch et al. (2011) indeed presented trace element profile data for P. wuellerstorfi (or C. wuellerstorfi). In our study we merely show that the observed trace element patterns are replicated in our C. wuellerstorfi specimen, and in addition we demonstrate that B/Ca and Mg/Ca show a comparable variability throughout C. mundulus, something that has not been shown before.
We the authors thus maintain that our study presents new information and that these data provide a valuable contribution to the current B/Ca core-top database.

Major points:

1. For all core-top samples, we have no age control - this is very critical, and ages for these core-top samples have to be robustly established; otherwise, it would be meaningless to compare benthic B/Ca with modern deep water DCO32-. A new table with ages and sed rates, *etc will be helpful.*

2. In addition to ages, it is highly preferable to provide sedimentation rates for these multi-cores, so that we have some idea about bioturbation effects. Bioturbation influ- ences have been mentioned in a recent study by Yu et al. (2013) QSR. Since only a very limited number of shells were analysed by LA-ICP-MS, a single shells from glacials would bias the ratio very significantly. Thus, an evaluation of bioturbation influence is critical for this work.

1. and 2. This is a good point and will be addressed in the revised version. Stable oxygen isotope data for the studied sediments document that they are Holocene in age, however these data are part of separate upcoming publications of two PhD students (Ronge et al. in prep. and Tapia et al., in prep.) and can thus not be given here. Moreover, Holocene sediments in the studied cores can be clearly distinguished from Glacial sediments based on their respective colors. On top of that, only the upper 3 cm of multi-corer sediments were used for analysis and we are thus confident that our datapoints indeed represent recent environmental conditions.
We do not have 14C data on these cores which would enable us to calculate sedimentation rates.
Bioturbation is recognized as a source of data scatter and we can not completely rule out that it affects the data presented here. However, there were no visible signs of bioturbation in the studied multi-corer sediments.

3. Although some new B/Ca for C. mundulus and C. wuellerstorfi from the S Pacific are valuable, I find it is not the right place to construct a new calibration for C. cf. wuellerstorfi. Such a job could be best done in the Atlantic Ocean, where age models are much easier to constrain and much more samples could be measured (to improve con- fidence with the calibration). At present, we only have 12 core-top C. cf. wuellerstorfi samples whose ages are unknown. Critically, the great sensitivity for C. cf. wuellerstorfi is mainly driven by 4 samples (2 high B/Ca data from PS75/105-1 0cm and 1 cm; two low B/Ca from SO213 68-1 0cm and SO21379-1 0cm). The rest samples plot along the C. wuellerstorfi B/Ca-DCO3 trend. If I were authors, I would make effort to pick additional C. cf. wuellerstorfi from other regions such as the North Atlantic Ocean to ensure that these values/relationships are reproducible.

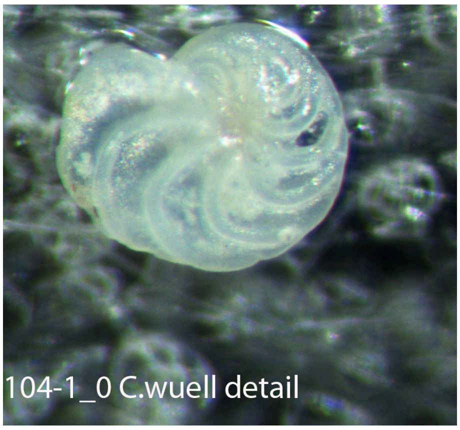
3. We agree that a more extensive database for C. cf. wuellerstorfi (presently there are 15 core-top samples) would improve confidence in the calibration and hopefully future work will address this. The major objective of this study was to allow the application of the B/Ca proxy in the South Pacific, a region where no B/Ca studies have been carried out so far mainly due to the low shell availability. By using a technique that is capable of measuring little material and by establishing a core-top calibration for a morphotype that is abundant in this region but so far understudied (i.e. C. cf. wuellerstorfi) a means to overcome the lack of knowledge about past carbonate ion histories of South Pacific waters is provided. An offset in B/Ca between Cibicides morphotypes has been documented by Rae et al. (2011) and in our study, hence morphotype specific calibrations are necessary.

4. Further descriptions about similarities and differences between C. wuellerstorfi and C. cf. wuellerstorfi are needed. Based on Fig. 3, it appears that C. wuellerstorfi seems to have compressed chambers on the umbilical side and raised/thickened su- tures on both sides, while C. cf. wuellerstorfi shows widely convex chambers and de- pressed/indented sutures on the umbilical side. I would definitely prefer more pictures of C. cf. wuellerstorfi in the text (and supplementary if needed), as this will greatly help the reader out.

4. 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 and more images in the revised version of this manuscript.

5. I am also interested to see C.wuellerstorfi from <1000 m water depths (Fig. 2). Personally, I have never seen any C. wuellerstorfi from such shallow water depths. Please present images of the these shells.

5. Hayward et al. (2003) and Hayward et al. (2010) document that C. wuellerstorfi close to New Zealand have an upper depth limit of 250 to 300 m water depth. Additional SEM images are currently being produced. Below is a photograph of a C. wuellerstorfi specimen from 835 m water depth.



6. For many sensitivity comparisons, the authors make strong claims based on a limited number of measurements. As mentioned above, the greater sensitivity of C. cf. wuellerstorfi B/Ca versus deep water DCO32- (compared to C. wuellerstorfi) heavily dependents on 4 data points from 3 samples whose ages are unknown. They did the same thing for C. wuellerstorfi from DCO32- < ~15 umol/kg (Fig. 7b) and for C. mundulus (Equation 4). No errors are given to the slopes and intercepts. Clearly, robust statistical analyses are needed before any claim can be made. The authors should be more cautious about the limit number of measurements presented, which prevent them from making any robust statement regarding different sensitivities between species. The number of samples is just too limited. Also, what are the uncertainties associated with deep water DCO32- (which should be considered during regression analyses)? Also, the recent paper by Yu et al. (2013) QSR compiles new and *published B/Ca for C. wuellerstorfi and C. mundulus, which should be considered. The authors may plot the new data against data from Yu et al. (2013) QSR, to see any differences/similarities.*

6. Good point, B/Ca errors will be included in Fig. 7. Linear regression has been carried out and the errors on slope and intercept will be given in the revised manuscript (C. cf. wuellerstorfi: B/Ca = 2.27 ± 0.362 ($\Delta[CO_3^{2-}]$) + 152.5 ± 11.19; C. wuellerstorfi: B/Ca = 1.39 ± 0.048 ($\Delta[CO_3^{2-}]$) + 175.5 ± 1.43; C. mundulus: B/Ca = 0.80 ± 0.054 ($\Delta[CO_3^{2-}]$) + 114.5 ± 1.82). P-values are all below 0.0001.
As stated above, we are confident in the Holocene ages of our samples.
Equations (3) and (4) include datapoints from Yu and Elderfield (2007) for C. wuellerstorfi and C. mundulus, respectively and thus represent an overall large number of samples (n= 99 and 59, respectively).
Regarding the C. cf. wuellerstorfi calibration being based on 15 samples, please compare this to the Yu and Elderfield (2007) calibrations on Uvigerina spp. and Hoeglundina elegans on 11 and 5 samples, respectively. The authors furthermore point out that the presented C. cf. wuellerstorfi calibration is not meant to serve as a global core-top calibration. Seeing that the analyzed core-top samples are distributed throughout the South Pacific and cover a large range of water depths and water mass characteristics (S, T, DIC) in this region, we are confident that this calibration can be applied here. If you compare the number of samples from different ocean regions that contribute to the global core-top calibration of Yu and Elderfield (2007), e.g. 8 samples from the Norwegian Sea, 17 samples from the Indian Ocean, we argue that it is appropriate to base a regional calibration on 15 samples.
Nevertheless, the authors agree that further analyses of C. cf. wuellerstorfi samples would be very useful and a global core-top calibration of this morphotype should be attempted in future studies. There is no further funding available to carry out said measurements within the scope of this research project.
According to Yu et al. (2013) uncertainties in Holocene (last 5 ky) deep water DCO32- estimates are ±5-10 μmol/kg.
New core-top data from Yu et al. 2013 will be included in Figure 7 and in the regression equation.

7. I am not convinced by the negative correlations between B/Ca and Mg/Ca in Fig. 6. Cross plots are needed, with statistical analyses (R^2, P value, etc).

7. We here describe observable inverse along-shell trends of B/Ca and Mg/Ca in C. wuellerstorfi (Fig. 6) and thus corroborate previous findings of Raitzsch et al. (2011) who discussed a negative correlation between intra-shell Mg/Ca and B/Ca trends in C. wuellerstorfi. As for the C. mundulus trace element profile, we agree that Mg/Ca and B/Ca do not show as clear of a contrast as in C. wuellerstorfi and will revise p. 4434 lines 1-3 to clarify this. We do not argue for a statistically significant negative correlation between Mg/Ca and B/Ca here, and as is stated on p. 4434 lines 3-4 maintain that an in-depth discussion of these trace element patterns is beyond the scope of this manuscript.

8. I suspect the errors in Fig. 5 are underestimated, especially for sample #1. How many shells in each sample were analysed (I note 3-6 shells/sample, but it would help to be more specific with each sample)? The analytical errors and variances in Fig. 6 for B/Ca are much larger. Why are errors in Fig. 5 so small?

8. Thank you for pointing this out, sigma has been recalculated and you were right about the underestimation. We apologize for the mistake.
3-6 shells were used for all core-top data, in Fig. 5 down-core data are included as well. Sample 1=PS75/100-4_12cm (n=3), sample 2=PS75/103-1_38cm (n=3); sample 3= PS75/103-1_52cm (n=2), sample 4=PS75/104-2_2 cm (n=4), sample 5= PS75/105-1_0cm (n= 3), sample 6= SO213/86-1_0cm (n=4).
Analytical errors varied between different measurement sessions due to ageing of the ion counter (electron multiplier).

9. While acknowledging LA-ICP-MS is a useful technique to obtain data for shell de- pleted samples, this method measures a much smaller quantity of carbonate materials than the traditional bulk/wet ICP-MS method. Are these small quantity of materials rep- resentative of the integrated averages of bulk samples (say, ratios based on 10 shells using wet ICP-MS method)? I am dubious, but we need more data. It is important to make a direct comparison between B/Ca ratios from these two methods at least for some, if not all, samples. This is especially critical for samples that lead to different sensitivities (see above). At present, the authors are comparing B/Ca based on different methods, and it is impossible to exclude analytical offsets as a reason for different sensitivities (in addition to very limited data points used for regressions and poor age controls).

9. It is certainly worthwhile to undertake a study that is aimed at comparing both methods, this was however not feasible here due to low shell availability. Seeing that our data for C. wuellerstorfi and C. mundulus do plot along the trends of the Yu and Elderfield (2007) calibrations (which are based on ICP-MS B/Ca measurements) reveals that laser ablation ICP-MS gives reliable and representative B/Ca results. This is in agreement with Raitzsch et al. (2011) who previously demonstrated that laser ablation ICP-MS analyzed B/Ca in P. wuellerstorfi samples from the Atlantic show a correlation with seawater DCO32- that is similar to the one presented by Yu and Elderfield (2007). In Yu et al. (2013) data obtained via LA-ICP-MS and ICP-MS are combined for core-top calibrations of C. wuellerstorfi and C. mundulus, accordingly we maintain that this is a viable approach.

10. Line 16-17 in Abstract, Section 4.2, and Line 14-16 in Conclusion: provide a cross plot between B/Ca and age of deep waters. Otherwise these statements and Section should be deleted. I am not convinced by the argument.

10. Point taken, the authors agree that this topic would better be addressed in a separate publication and this section will be deleted from this manuscript.

Further points:
1. I do not understand the logic behind "Intra-shell variability equals intra-sample variability, mean sample B/Ca values can thus be reliably calculated from averaged spot results of single specimen" lines 15-17 in Abstract and lines 12-14 in Conclusion.

1. Ok, this sentence will be revised.

2. Line 5-6, P4427: further references are needed - such as Raitzsch et al., (2011) Geology, Yu et al., (2013) QSR, Brown et al., 2011, EPSL.

2. Further references will be included.

3. Line 10-12, p4434: invalid argument - it has been shown that Mg/Ca in C.wuellerstorfi does not reflect changes in BWT. See Elderfield et al., (2006) EPSL, Yu & Elderfield (2008) EPSL.

3. Ok, this argument will be deleted.

4. Line 20-23, p4436: unsupported argument and should be deleted. Nowadays, we can measure ~8 shells and even less (say ~4-5) without any problem!

4. 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.

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