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Interactive comment on "Trace metal/Ca ratios in benthic foraminifera: the potential to reconstruct past variations in temperature and hypoxia in shelf regions" *by* J. Groeneveld and H. L. Filipsson

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Dear Editor, We thank both reviewers for their constructive comments and positive feedback. Both reviewers suggest minor revisions. We have corrected our manuscript following the reviewer's comments to our best knowledge and responded to each comment specifically. Below you find our response to both the reviewer's comments in detail.

Yours sincerely, Jeroen Groeneveld and Helena Filipsson

Response to Reviewer 1: Reviewer 1:

Trace metal/Ca ratios in benthic foraminifera: The potential to reconstruct past variations in temperature and hypoxia in shelf regions

Jeroen Groeneveld, Helena L. Filipsson

Summary: The manuscript describes field-based collection methods that attempt to show a link between foraminiferal shell geochemistry of modern bottom water conditions in the Skagerrak and Gullmar Fjord (SW Sweden); this is an important area of research because our current ability to understand the long-term response of these environments to recent change (both natural and anthropogenically forced) is poor and relies on largely qualitative descriptors. The authors are well-respected in the field and have a strong publication track-record for this type of research. The authors set-out the background review and make a clear case for the study; this is useful in that it attempts to broaden the scope and, hopefully, reader interest in the work. The details of the paper are only likely to appeal to a relatively specialized readership; however, the wider implications and potential to reconstruct long-terms changes in these environments are likely to have broader reader appeal. The data are somewhat limited and the inconclusive nature of the results is a little problematic because they do not move us very far forward, although I fully recognize the value of these preliminary data. I am therefore highly supportive of this work and I fully understand the challenges of working with live material and small sample sizes. I recommend revision of the manuscript as follows:

(1) The manuscript could be significantly improved by the inclusion of more geochemical data, otherwise there is a risk that we simply end-up with confusion/uncertainty and potentially undermine the reputation of, in particular, the Mg/Ca proxy for temperature reconstruction.

We have now added extra samples from the same location in the Gullmar Fjord from a cruise last year. The G. turgida specimens in these samples were not stained, which allowed picking of a sufficiently large number of specimens to prevent that Mg/Ca and/or Mn/Ca would have been affected by small-sample size. For each of these samples

we used between 20-40 specimens, opposite to <20, and often <10, specimens which were available from the stained samples. The results from these samples are not significantly different from the stained samples, giving confidence that the results are representative (nevertheless keeping in mind a potential impact of early diagenesis).

(2) Alternatively, it might be possible to restructure the manuscript as a short note, highlighting the potential of Mn/Ca as a proxy in benthic foraminifera for past dissolved oxygen concentration; as noted below, there are difficulties in the interpretation of the Mn/Ca data as they currently stand, but this aspect is novel and its potential as a new tool deserves to be highlighted.

Some specific comments: Line 168-170: "The CellTracker Green method ensures that the Mn/Ca values in this study are part of the foraminiferal test itself and not associated with diagenetic coatings." How so? The possibility of trace-metal contamination is, I agree, minimized in 'live' foraminifera – but I don't see that it 'ensures' 100% absence of coatings?

We agree with both reviewers that the statement on using CTG prevents any diagenetic coatings to be present was too strong. As such we have removed several of the repetitions of this statement from the text and toned done the impact of using CTG. We now use it as a working hypothesis, but meanwhile also realize that early diagenesis in carbonate-based organisms is possible and has indeed already been shown (i.e. Hover et al., 2001). The text was re-phrased to: "Using the CellTracker Green method minimizes the impact of diagenetic coatings on the Mn/Ca values in this study; even though diagenesis cannot be completely excluded (Hover et al., 2001)." (Lines 165-168)

Line 172-174: "Between 3 and 20 tests of B. marginata and G. turgida were selected from each sample and gently crushed. Due to the low number of living specimens available the size range of the selected specimens was not restricted." It is worth highlighting that differences in the numbers of tests analysed can prove problematic in

the comparison of samples measured on the same species – notably where reworking of an unknown number of tests is a possibility (as in any fossil assemblage) or where samples are mixed by bioturbation, bringing specimens from different depths within a geochemical gradient together. To be fair, this is acknowledged and briefly discussed on line 328 ('bias'), but since we know about these problems already – I think they should acknowledge this point sooner.

This sentence was extended with "possibly introducing a bias on the results (Hintz et al., 2006b)". Additionally we added the analysis of a non-stained core top from the Gullmar Fjord with three samples with 22-40 specimens each to give representative bulk values. (Lines 171-174)

Equally, the inclusion of specimens of different sizes can be problematic, given the possibility of ontogenetic changes in habitat-selection and hence shell geochemistry. Again, this issue is discussed in relation to the work of Hintz et al. (2006) around lines 332 – so there is already published evidence to suggest that this is likely to be problematic and so should be highlighted at the outset (i.e. earlier in the manuscript methods)?

See also previous comment; the three new non-stained samples show similar values as the stained samples. Although this does not directly provide evidence for or against a size effect, it does show that the results are not biased because of low sample numbers. This is similar to what has been shown by Hintz et al. (2006) and Wit et al. (2012). (e.g. Lines 270-279)

Line 278-281: "It is essential to know for the discussion of any geochemistry data, especially acquired from benthic foraminifera from variable environments, when the used species calcify as this determines the geochemical signal" – useful to focus on theory of seasonal calcification and e.g. 18O equilibrium calcite calculations in relation to NW European shelf seas (Austin et al., 2006, Holocene).

The text was changed accordingly (Lines 266-268): "Austin et al. (2006) argue that

the period of reproduction directly after a bloom is also the time of the year when the water column (mainly temperature) changes markedly. This would suggest that the geochemical signal which is actually recorded into the foraminiferal tests is the average for a restricted period directly after maximum food supply."

Line 302-306: "Why are these differences in Mg/Ca between the different studies so large assuming that Mg/Ca in B. marginata in the Skagerrak is indeed representative of calcification temperatures? And additionally, why is the scatter in the results much larger than is commonly seen in planktonic or deep sea benthic foraminiferal Mg/Ca?" – these strike me as important and useful questions, which are being raised as a matter of open discussion rather than offering a solution to the problem – this is one reason why manuscript revision to focus on a review-style paper might be better at this stage?

The focus of this part of the discussion has been changed such that it is not presented as a call for a public discussion but rather to present the results of this study and discuss the relative large variations when applying existing calibration studies (Lines 252-269). One of the reasons the spread in the data seems to be larger than what is known from more commonly species/settings is most probably also related to the relative small data set, not only presented here but also as being available. As such, it would be interesting to see how this develops when more extended data sets are produced.

Line 307-309: "One possible reason for the large spread in Mg/Ca could be the heterogeneous Mg distribution between and within shells from the same sample (e.g. Eggins et al., 2003; Rathmann et al., 2004; Hathorne et al., 2009). – misses the work of Allison & Austin (2003, G3 based on ion-probe analyses of benthic foraminifera). Incomplete cleaning, overgrowths etc. may all affect the results – these 'unknowns' are poorly constrained and worrying and one has to consider the value of publishing results (based on a limited data set) that might ultimately undermine this area of research. Have the authors given this careful consideration?

Allison and Austin was added to the text. Cleaning of the tests as in the traditional way of treating foraminiferal samples was successful as indicated by Al/Ca. If additional treatment because of Mn-related overgrowths would have been necessary is indeed not sure. Hence, we have used the CTG method to try to minimize this impact as other studies have used Laser Ablation or SIMS trying to prevent this impact. Obviously, there is no common method yet to avoid potential contamination by these overgrowths; this should also be a major point in future studies to investigate if and how these overgrowths might be present and what their impact on shell chemistry would be. In the current study, we are aware of these issues but consider that this data set gives a valuable addition to further studies. (Lines 298-300)

Lines 407-410: "We speculate that in a lower oxygen environment the lower metabolic activity might also decrease the distribution coefficient of Mg which could potentially have contributed to the lower G. turgida Mg/Ca in the Gullmar Fjord compared with the Skagerrak." – this is highly speculative.

We agree, it is based on the specific setting of the Gullmar Fjord with its low dissolved oxygen concentrations and the study of Elderfield et al. (1996). And as such also phrased as "we speculate. . .." As we do not want to and cannot claim anything more on this yet. (Lines 379-384)

Lines 441-443: "This is also the reason why the specimens used in this study have all been labeled by CellTracker Green ensuring that they were alive during collection and, thus, could not yet have been affected by diagenetic coatings" – again, take care with these bold statements. It seems that the Mn story is very complex and the question of developing a new proxy is still at an early stage? This point needs careful editorial consideration and further discussion with the authors.

See also previous comments. We have toned down the statements relating to the use of CTG excluding any impact of diagenesis on living foraminifera. A study by Hover et al. (2001) (e.g. Lines 165-168) showed that in living specimens of calcitic algae

diagenesis on nm scale already occurred during the life cycle of the organisms in the older parts of its test. It cannot be excluded that this is also the case for longer-living benthic foraminifera, and would require high-resolution SEM studies to determine if benthics are affected too. Nevertheless, we consider that using CTG has at least minimized the impact of diagenetic coatings on the foraminiferal tests.

Lines 480-485: "As CellTracker Green was used to ensure that analysed specimens were alive during collection we can make a direct link between Mn/Ca in the bottom water and in the foraminiferal calcite determining distribution coefficients. A potential bias on the possible distribution coefficients is caused by the lack of pore water chemistry data with likely even higher Mn-concentrations than the bottom water itself (Goldberg et al., 2012)." – this seems a big jump – complexity of bottom-water to pore-water Mn gradients?

We agree and have condensed this section to: "Although the shallow habitat of G. turgida in the Gullmar Fjord could suggest a direct link between Mn/Ca in the bottom water and in the foraminiferal calcite, the lack of pore water chemistry data prevents to calculate possible distribution coefficients (Goldberg et al., 2012)." (Lines 448-451)

Lines 532-533; "Staining with CellTracker Green ensured that the specimens were alive when collected and, thus, were not affected by diagenetic coatings." – I must highlight the problem of this statement – if they want to reach this conclusion, then they need to show data based on the measurement of 'live' and 'dead' specimens, where the 'live' specimens are clearly shown to be diagenetic-free; this is a prime issue in this field and cannot be ignored?

See also previous comments; the sentence was rephrased to "and, thus, were assumed to be only minimally affected by diagenetic coatings".

Lines 540-541: "Mn/Ca results on G. turgida show potential to record variations in dissolved oxygen content of the habitat where they calcify" – this is very encouraging and worth highlighting and publishing.

Ok

Lines 546-549: "Our study shows that trace metal/Ca ratios in benthic foraminifera from shelf regions have the potential to record past variations in bottom water temperature and dissolved oxygen concentrations, but calibration studies based on both core tops and culturing are needed to resolve the possible extend of variation." – in many ways this final sentence of the manuscript (which should be a strong punch-line and take home message) highlights the difficulty of my review – we know this already.

This last sentence was deleted to prevent stating the obvious. The conclusions now state what was specifically achieved for Mg/Ca and Mn/Ca in their own paragraph. (Lines 490-507)

Finally, I consider a revised manuscript well-worth publishing, but some more thought must be given to the rather limited data available at this stage and their use in developing the arguments – a shorter, review style paper would work better at this stage, then collect more data and publish a follow-up? This is an innovative new study and, to my view, the type of paper which is well-suited to the journal and I look forward to follow-up studies in this area.

Interactive comment on Biogeosciences Discuss., 10, 4403, 2013.