

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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Received and published: 18 June 2013

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 2

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. Groen-
C2848

eveland and H. L. Filipsson

Anonymous Referee #2

Dear Editor, After careful judgment of manuscript number bg-2013-28, I recommend to publish this work in Biogeosciences. The results are novel and this manuscript fits the scope of Biogeosciences. However, there are a number of issues that need to be resolved before acceptance. In addition, I found many minor things that need to be addressed before acceptance, all of which are listed below.

General 1. Do I understand correctly that for every sample moment, only 1 group of 3-20 specimens were analyzed for Mg/Ca and Mn/Ca? Since we know that Mg/Ca can display relatively large inter-specimen variability, the values reported here may not necessarily be representative for all specimens living at that place and time. I think the authors need to discuss what this small sample volume may mean for the reported Mg/Ca and Mn/Ca, and uncertainties therein.

Yes, due to the aim of collecting living specimens the absolute numbers were quite low. We agree with the reviewer that this could have led to less-representative results. We have this now included into the methods as well as potential size effects. Additionally, we have now added three non-stained core top samples from the Gullmar location. Three samples of *G. turgida* were picked with 22-40 specimens per sample and cleaned according to standard procedures to give representative values. The average Mg/Ca is 3.47 mmol mol⁻¹ (range 2.86-3.78 mmol mol⁻¹). Two of the samples have Mn/Ca between 5.2-6.2 mmol mol⁻¹, the third one 0.9 mmol mol⁻¹. These new results suggest that the results from the stained samples are representative. (Lines 171-174; Section 3)

2. The discussion hints to the use of Mn/Ca as a proxy for pore water manganese content/ redox state/ oxygenation. However, the lack of pore water Mn/Ca prevents accurate interpretation of the benthic foraminiferal Mn/Ca. Therefore, the authors need to stress the qualitative nature of their dataset and should include the outlook that

linking pore water [Mn²⁺] to foraminiferal Mn/Ca is the only way to develop a proxy for redox conditions.

Section 4.2 on Mn/Ca and the Mn part of 4.3 have been adapted to a more careful setup. 4.3 now ends with: "...or combining living specimens with in-situ pore water measurements are necessary to determine if Mn/Ca can indeed be developed as a proxy for dissolved oxygen content." (Section 4.2; Lines 484-488)

3. Are the authors sure that Mn/Ca is not affected by diagenesis? With the potential long lifespan of benthic foraminifers, Mn/Ca at the surface may be altered before the end of the foraminifer's life. To test the homogeneity of Mn/Ca throughout the test wall, either depth resolved-laser ablation data or mapping of a sectioned test wall should be included. If not available, please state explicitly the possibility of surface-enriched Mn/Ca.

We agree (see also previous comments) that we cannot be sure that no diagenesis has taken place. Some studies exist on calcitic algae (e.g. Hover et al., 2001) which found alteration on nm scale in the older parts of living calcitic algae. We have changed throughout the text our statement that using CTG prevents diagenesis to a more careful assumption that the use of CTG most likely minimizes the impact of diagenesis (and is assumed not to be present in the results) but that it cannot be completely excluded. For ongoing studies this will indeed be a necessary component to check by high-resolution mapping of the tests. (e.g. Lines 165-168)

4. The text of this manuscript can be condensed considerably. Particularly the Discussion is too long for its information content. I think that the discussion can be reduced by at least 50%!

Following the comments below and from the other reviewer the text was significantly condensed.

Title Since the manuscript only reports values for Mg and Mn, I suggest to change the

C2850

title of this manuscript from 'Trace metal/Ca ratios: : : ' to 'Mg/Ca and Mn/Ca ratios: : : '.

Done

Abstract

Lines 19-20: please mention that there may be practical problems when translating 'open ocean' isotope and element-calibrations to foraminifera living in coastal environments. Apart from species-specific offsets in calibrations, elements and isotopes in foraminifera from shallow areas should just as well reflect ambient temperature, pH, etc. The real 'problem' is caused by small-scale environmental variability (seasonal, daily), but is not a calibration- or proxy-based problem.

Changed to "...conditions can change much faster compared to the open-ocean".

Lines 29-30: I think 'carbonate ion saturation state' is incorrect. Seawater is either (under)saturated with respect to calcite/ aragonite, or carbonate ion concentrations may be very low (affecting the CaCO₃ saturation state).

We think we agree with this comment, although a literature search did not show a consistent answer to this. Nevertheless, we have changed this term throughout the manuscript.

Line 31: change into 'Mn/Ca ratios from Globobulimina: : : ' or 'Mn/Ca ratios from the calcite of Globobulimina: : : '.

Changed to "Mn/Ca ratios from Globobulimina"

Lines 37-38: please change to something like ': : :but inorganic carbon chemistry may additionally impact foraminiferal Mg/Ca and Mn/Ca in these regions.'

Sentence was rewritten as: "an additional impact of the inorganic carbonate chemistry cannot be excluded". (Lines 39-40)

Introduction Line 41: proxies themselves are not 'open ocean', but instead, often ap-

C2851

plied to or calibrated in, open ocean settings.

Rephrased as: "Traditional proxies, which for example are based on the calcite shells of marine organisms like foraminifera and generally calibrated with respect to open-ocean conditions". (Lines 43-46)

Lines 45-46: change 'local and regional patterns' to 'local from regional signals' and remove 'which hampers: : :'.
Done

Done

Line 60: please change 'going down' to 'decreasing'

Done

Line 63: I don't understand use of 'intensifying'. If the natural variability is amplified (i.e. extremes occur more often/ extremes become extremer), can't that in itself be of anthropogenic cause?

Rephrased as: "...are part of the natural variations or intensified by anthropogenic causes".

Lines 83-93: this paragraph can be condensed considerably. E.g.: 'Since incorporation of many elements is shown to be species-specific, calibrations for species may not be easily translated to those dominant in coastal environments and call for field calibrations for shallow-water species.'

Paragraph was rewritten as: "As the incorporation of trace metals into calcite shells is species-specific, and typical benthic foraminiferal faunas in shallow and more brackish environments like the Skagerrak and the Gullmar Fjord are very different from open-ocean settings, it is necessary to develop new calibrations to allow the reconstruction of environmental conditions like temperature, dissolved oxygen, or inorganic carbonate chemistry." (Lines 85-89)

Methods Line 162: change 'a much higher accuracy is needed' to something like:

C2852

'distinguishing living from dead specimens requires a more accurate method'.

Changed to: "more accurate method is needed to distinguish between dead and living specimens".

Lines 169-170: with a potential long lifespan for foraminifera, couldn't diagenesis affect the (surface) geochemistry of living specimens too? Do the authors have any idea about the rate at which Mn/Ca can be altered in foraminifera? How does this compare to the lifespan of benthic foraminifers?

The sentence was changed 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) So, yes, in calcitic algae it has been shown that while the organism was still living first diagenetic alterations on nm scale already occurred in the older parts of the tests. So this would potentially also be possible in benthic foraminifera, especially when they are living for extended periods under these specific conditions, and would definitely complicate efforts to extract a primary signal for redox related elements. We are not aware on published rates of diagenesis but it seems likely that this occurs significantly faster than the total lifespan of these organisms.

Lines 190-194: I don't understand why the analytical precision is different for the two species/ locations. I could see how the variability in Mg/Ca and/or Mn/Ca is different for the two species or locations, but not why this is based on different analytical precision.

The analytical precision used here is purely based on the precision of the single measurements (ie for each sample) consisting of three replicates per sample. This can be given as an average for all, or split up for the specific parts. We have split them up here to allow species-specific numbers, and per location as the amount of material available has the biggest impact if a precise measurement can be done or not. As the Mn-concentration is much lower than Mg, the precision was also less. And in general, the Skagerrak samples were larger/higher numbers, so that the measurements were

C2853

also more precise. But to conclude, none of these differences is large enough to have a significant impact on any of the interpretations.

Lines 206 and 209: what are the standard deviations for these seawater Mg/Ca ratios? To avoid confusion between foraminiferal Mg/Ca and seawater Mg/Ca, I suggest using Mg/Casw for the latter.

Sd was added and sea water quoto was added to the Mg/Ca values for sea water. (Lines 197-203)

Results (Lines 209-250)

Line 216: rephrase so that it doesn't sound as if 5 specimens of *B. marginata* were measured.

Changed to: "Four samples with enough specimens of *B. marginata* are from the top centimeter of the sediment, one sample is from 1-2 cm depth".

Line 216-217: does this mean that no specimens of *B. marginata* were found in the 1-2 cm interval? Table 2a seems to suggest so, but better to mention this also in the text.

Changed to: "Four samples with enough specimens of *B. marginata* are from the top centimeter of the sediment, one sample is from 1-2 cm depth".

Lines 218-229: is discussion and does not belong to this section.

Cut and pasted to the beginning of section 4.1.1.

Line 230: rephrase so that it doesn't sound as if 8 specimens of *G. turgida* were measured.

Changed to: "The samples for *G. turgida* are evenly distributed between the 0-1 cm and 1-2 cm sediment depths".

Line 232: change 'systematic' to 'significant'.

Done

C2854

Line 233: remove either 'in general' or 'significant'.

Changed to "systematically".

Lines 232-241: is discussion and should be cut and paste to next section.

Deleted; section 4.1.2. already contains the same info.

Line 244: add uncertainties to average values (also in the rest of this section).

Errors and uncertainties are already presented in the methods, so we do not see the need to repeat them here.

Discussion Line 292: change 'chapters' into 'sections'.

done

Lines 298-306: delete.

Done and replaced with the moved section from the results.

Lines 337-351: this can be stated in 1-2 sentences.

The paragraph was re-written as follows: Salinity has been shown to increase foraminiferal Mg/Ca, especially in high-salinity settings like the Red Sea or the Mediterranean (e.g. Nürnberg, 1995; Lea et al., 1999; Kisakürek et al., 2008; Ferguson et al., 2008; Groeneveld et al., 2008; Mathien-Blard and Bassinot, 2009; Hoogakker et al., 2009; Dissard et al., 2010; Van Raden et al., 2011; Diz et al., 2012). Salinity in the deep Skagerrak is very stable throughout the year (35.0-35.3) both similar to open-ocean settings and to the culturing experiments of Hintz et al. (2006a). The impact of low-salinity (20-30) surface water coming from the Baltic proper, via the Baltic Current, does not reach the deep Skagerrak. Thus, it can be excluded that salinity is having a significant impact on our Mg/Ca results. (Lines 317-324)

Lines 357-380: these values probably refer to bottom water conditions. In-sediment saturation states (where benthic forams calcify) may be (much) lower and hence affect

C2855

Mg/Ca.

Exactly, although this difference in bottom water conditions should at least account for a similar difference in the shallowest/early part of the sediment, i.e. difference in the pre-condition. We have added the following sentence into the discussion to point this out: "keeping in mind that the infaunal habitat of *G. turgida* might not be directly comparable with bottom water conditions." (Lines 363-364)

Line 418: 'foraminifera' should be 'calcite'.

Done

Lines 439-443: take into account the longevity of benthic forams, and the potential of 'diagenesis' in living specimens under low oxygen conditions.

See also previous comments; the following was added to the sentence: "and, thus, are assumed to be not significantly affected by diagenetic coatings yet".

Lines 452-457: doesn't look significantly different to me. Either test with appropriate statistics or remove these lines. If there would be differences in Mn/Ca between individuals from the same species, would that mean that part of the population is adapted to a deeper habitat?

This statement was toned down and rephrased as follows: "Accordingly, Mn-concentrations in the pore water increase to values of 50-100 $\mu\text{mol L}^{-1}$ below the oxic zone in the sediment (Bakker and Helder, 1993). This might suggest that *G. turgida* specimens which are living deeper in the sediment are incorporating more Mn into their calcite." (Lines 434-435)

Lines 485-489: since there is no pore water Mn data, and vertical migration may cause a variable habitat depth, calculation of partition coefficients does not make sense. Please remove.

Agree and deleted

C2856

Tables Table 1: place units to the first column. Most of the notes can then be placed right after the values. Also put note '4' after CO₂-, _CO₂-, etc.

The Table was corrected accordingly.

Figures Figures 3 and 4: change symbols from stars to dots or diamonds.

Done

Figure 4a: how many specimens were analyzed per sample? What is the difference between replicate measurements?

We added the number of specimens used for the different sample groups in the results section. Due to low absolute numbers no replicate samples could be done. However, we have added three multi-specimen (22-40 specimens per sample) core top samples of *G. turgida* from the Gullmar to the paper to show how representative our results are.

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

C2857