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Interactive comment on "A comparison of benthic foraminiferal Mn/Ca and sedimentary Mn/Al as proxies of relative bottom water oxygenation in the low latitude NE Atlantic upwelling system" *by* C. L. McKay et al.

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Dear editor, Please find enclosed our final author comments. We thank the referees for their constructive comments which we address here and also enclose the revised manuscript as a supplement with changes tracked in red text.

Thank you for considering our manuscript. We are looking forward to the next stage.

Kind regards, Claire McKay, Jeroen Groeneveld, Helena Filipsson, David Gallego-Torres, Martin Whitehouse, Takashi Toyofuku and Oscar Romero

Reviewer 1: Glock

"One flaw of the manuscript I see is that it's not emphasized in a proper way that E. exilis is an infaunal species and that this fact severely affects the Mn/Ca ratios. Usually dissolved Mn2+ should be higher in the pore water at the living depth of the foraminifera than in the bottom water, if the oxygen penetration depth is not very deep. An exception would be if the bottom water already is anoxic. Furthermore, infaunal species are able to migrate within the sediment column and probably experience variable pore water conditions within their lifetime. I don't see this fact as a big disadvantage and would rather use infaunal species for this proxy by myself since they probably incorporate more Mn than epifaunal species. These facts are already introduced in the manuscript but discussed only very sparse and very late (page 18; line 18)."

Response: We agree with this statement Action: We have now emphasized these points in the introduction section (lines 155-160).

"Another point is a major problem with foraminiferal Mn/Ca ratios itself: Diagenetic overprinting by Mn (oxyhydr)oxide coatings. If I look at your data I do not think you have a problem with these, but not every reader is familiar with details of SIMS analyses and, since in the foraminiferal community Mn/Ca ratios are usually used as tracer for contamination, I think it is worth to be discussed in a bit more detail. Regarding this point there is a mistake in a sentence referring to the paper Glock et al. (2012). At page 8, line 19 you wrote "Therefore, we employed a rigorous pre-treatment cleaning technique to remove possible diagenetic coatings following the method of Glock et al. (2012)." Probably I know these details since I'm the author of the paper: If you used the cleaning method from this paper you did not remove possible diagenetic coatings. In this study I just used oxidative cleaning to get rid of organic contamination. Beforehand I showed that the specimens were generally free from diagenetic oxide coatings with element mapping done by EMP. Please correct this sentence! Furthermore, I am not sure if you used reductive cleaning during your flow through analyses, thus it would be nice to provide some more details about this in the methods section. As I already

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mentioned I do not think that you have a problem with diagenetic coatings if you chose your SIMS spots within the massive centre of the test walls. Furthermore, I guess if there would be an influence of diagenetic coatings on the foraminiferal bulk analyses the results would be much higher than the SIMS results."

Response: We agree with this statement that not every reader will be familiar with the details of SIMS analyses and acknowledge the mistake.

Action: We have now addressed these points by explaining in more detail how contamination was avoided. and have corrected the mistake regarding organic contamination and stated that the massive centres of the test walls were measured in order to avoid diagenetic coatings (lines 192 – 196 and 253-256). Regarding reductive cleaning, this has now been addressed in lines 278-284.

Page 4, line 3: I would suggest not to write "trace elemental to foraminiferal calcite" ratios and rather write "trace element to calcium ratios". The trace elements are also incorporated into the foraminiferal calcite and thus part of it.

Response: agreed. Action: amended (line 61).

Page 4, line 14: "You wrote "…. gained more interest is Mn/Ca both as a measure in biogenic foraminiferal calcite and in bulk sediment samples…". As far as I understood you measured Mn/Al ratios in bulk sediment and not Mn/Ca ratios. Response: True, Mn/Al was analysed, however in the literature Mn alone has also been analysed in sediments (Lenz et al. 2014). It is true that most geochemical data in bulk sediments are presented as Mn/Al, but eventually, core scanner XRF data (being semiquantitative) might be presented as Mn/Ca (maybe even Mn/Ti, but I am not sure right now if this is frequent at all). In any case, both Al and Ca are used as normalization factor, so it makes sense to use Al for bulk sediment normalization and Ca for foram test normalization.

Action: amended so that there is a clear difference between foraminiferal Mn/Ca and

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bulk (lines 70-72).

Page 5, line 3: “On the other hand, under anoxic conditions the Mn either diffuses upwards and into the overlying water column or when pore waters become supersaturated with respect to Mn, precipitation of MnCO3 (rhodochrosite) occurs (Froelich et al., 1979; Pedersen and Price, 1982; Tribovillard et al., 2006).” I do not understand the argument that under these conditions Mn/Ca should be very low in the forams. Even if all Mn diffuses out of the pore water it is available for the forams during that process. Only within the sediment you probably won’t find any accumulation.

Response: We now realise this statement is unclear. We have to assume that Mn abundance affects Mn content in E. exilis tests, and this is what we want to highlight. Otherwise, all variations in Mn/Ca would be related to vital effect, and our data does not support this. Action: We have clarified this by stating the expected Mn/Ca under different redox conditions (lines 91-93).

Page 5 line 15: “Mn/Ca signatures of the ambient bottom water are recorded by benthic foraminifera, for instance, culture experiments have confirmed that the species Ammonia tepida incorporates Mn into the test (Munsel et al., 2010).” I would suggest to reformulate this sentence. Maybe even divide it into two sentences. Furthermore, it might be good to emphasize that “Ammonia tepida incorporates Mn into the test proportional to the concentration in the ambient water masses (Munsel et al., 2010).

Response: agreed. Action: sentence has now been reformulated to clarify our meaning and divided into two sentences to emphasize this point (lines 101-104).

Page 11 line 2: “With cautious positioning of the primary beam on the test walls, such detrital material and potential contaminants were avoided and therefore only the elements actually incorporated into the calcitic tests were measured.” How did you do this? I guess it’s easy to avoid macroscopic contaminations which are easy to see optically, but a lot of contaminants you won0t see like this. You wrote that you checked the Ca counts and thus assured that you measured within massive calcite which is already

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good. Do you have any other evidence? Like watching the element distributions during the measurements, for instance (Mn hotspots would probably indicate contaminats), or any pictures which show that you hit the massive centre of the test walls?

Response: Yes we observed the element distributions during measurements and therefore Mn hotspots could be annulled. Action: these details have now been added to this paragraph (lines 253-256).

Page 14 Line 8: “The slightly higher Mn/Ca determined by FT-ICP-OES in comparison to SIMS derived Mn/Ca perhaps highlights the issue of comparing bulk foraminiferal samples with individual tests comprising of only 6–10 analytical targets. Overall, when a sufficient number (minimum weight of 0.1 mg) of benthic foraminiferal specimens are not available in sediment samples for solution-based analyses (in this case from 35–18 ka), SIMS has the potential to provide reliable results from a few individuals to compensate for this.” I just can say it again: This is a great result! You should emphasize it a bit more (maybe in the conclusions), because it0s not trivial that SIMS Mn/Ca ratios on only a few specimens are indeed comparable with foram bulk samples. You won’t find this for every element.

Response: agreed. Action: We have now expanded on this great result and emphasized it in more detail in the conclusion (lines 499-503).

Page 15 line 8: “overlying water column immediately above” I would suggest to remove either “overlying” or “immediately above” because it basically describes the same.

Response: Agreed. Action: Removed "overlying" (line 371)

Page 15 line 9: “Concurrently, these low Mn/Ca results adhere to the benthic foraminiferal response of a low abundance (ca. 2 specimens cm3) of low oxygen tolerant E. exilis (McKay et al., 2014)” Why concurrently? Both proxies indicate into the same direction (higher oxygen concentrations).

Response: Perhaps "concurrently" was not the best word to use. Action: This has

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now been amended to clarify that the Mn/Ca results agree with the faunal data (line 372-373).

Line 15, line 22: “Dissolved Mn available for the precipitation of Mn hydroxides” It would be a bit more correct to speak from Mn (oxyhydr)oxides. Please check the paper to keep at one formulation.

Response: agreed. Action: amended throughout the paper where applicable.

Page 15, line 24: “Based on this increase in sedimentary Mn/Al coinciding with relatively low foraminiferal Mn/Ca, we therefore infer that the Mn/Al enrichment occurred immediately below the oxygenrich pore waters during late H3 and throughout the period 30–25 ka, delimiting the oxygen penetration front and the upward diffusion of Mn.” If I understood right you suggest that the oxygen penetration depth is very deep and thus Mn is precipitating already below the living depth of E. exilis. What is the typical living depth in the sediment for B. exilis? If it doesn’t only follow the oxygen gradient maybe it is even possible to reconstruct the minimum oxygen penetration depth like this or at least to give a rough estimate.

Response: Agreed. E. exilis has been shown to live at 1-2 cm sediment depth (Caulle et al., 2014) which might give a rough estimate of oxygen penetration front. Action: A sentence has now been added to this paragraph for this detail (line 390-392).

Page 16, line 11: “We interpret this greater range in Mn/Ca as a relative decrease in oxygen within the pore water from earlier times within the record” What if you indeed see oxygen fluctuations over the lifetime of the specimens or between different specimens? Could it be that oxygen indeed was highly variable during the LGM at this location? Did you check if there was a trend in Mn/Ca from older chambers until the younger ones?

Response: We agree that the greater range in Mn/Ca could be due to oxygen being more variable. We checked if there were any trends in Mn/Ca from the older to the

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younger chambers, however we found no trends or systematic shifts in values. Action: The interpretation of the greater range of Mn/Ca has now been amended (lines 401-404).

Page 16, line 24: During H1, the increase in foraminiferal Mn/Ca; both the greater variability within the individual tests (Fig. 3) and the higher average Mn/Ca per sample depth (Fig. 4) indicate lower oxygen conditions in the pore waters (Fig. 5c)" This sentence is hard to read.

Response: This refers to our two lines of evidence for lower oxygen conditions. Action: We have reworded this sentence and divided it into two sentences to more clearly express our intended meaning (lines 415-417).

Page 17, line 14: "We interpret this similarity in oxygen conditions as being due to comparable. . .." Being what? I think you forgot a word in this sentence.

Response: there is no word missing Action: the tense has now been amended to make this sentence clearer (lines 433-434)

Page 18, line 6: "As MnO2 is rapidly reduced to soluble Mn2+ in hypoxic pore waters (Glock et al., 2012). . .." I would suggest to give another reference here. . .. Response: reference has now been amended (line 452).

Page 18, line 8: "causes low bottom water oxygen concentrations or even anoxia within millimetres of the sediment-water interface, we can expect a high accumulation of redox sensitive trace metals" Different redox sensitive elements react different under variable oxygen concentrations. Vanadium vor example accumulates under anoxic conditions, while Manganese does accumulate under oxic conditions. You cannot generalize "redox sensitive trace metals" within this sentence.

Response: Agreed that this statement is too general as different elements precipitate under different conditions. Action: This sentence has now been amended and made more specific (Mn/Ca opposed to "redox sensitive elements") (line 454).

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Page 19, line 18: “Therefore, whilst high phytodetritus export typically causes low bottom water oxygen concentrations and benthic faunal studies are indicative of such a scenario, redox trace elemental test composition presents a more comprehensive interpretation.” I would suggest to rewrite this sentence.

Response: Agreed Action: This sentence has been made shorter for better clarification (lines 490-492).

Table 1: Just for clarification: Write 1sd instead of just sd. Is it possible to provide the precision as well?

Response: Agreed. Action: 1 sd has now been written which is the precision.

Figure 4: The figure is hard to read. Maybe it would be better to present it in horizontal format.

Response: Agreed and I would prefer it in landscape format. Action: The editor will be informed.

Figure 5: This figure is great and provides all the interpretations of your multiproxy approach in one graphic. Unfortunately it is hard to understand if the reader does not jump between the discussion part and figure. I would suggest to extend the figure caption and to give a short explanation for every time interval and the reason for the interpretation.

Response: We agree with this suggestion. Action: We have now extended the figure caption to provide a better explanation for each time interval to link with our interpretations.

Reviewer 2: Limburg

“Figure 4 is quite difficult to read”

Response: Agreed Action: as previously stated, figure 4 should be placed in landscape layout so it can be enlarged on a separate page.

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“The author’s findings are consistent with recent work on fish otoliths”

Response: we were aware of these publications but since our work is on infaunal foraminifera, we did not directly compare with fish otoliths or other biota living within the water column. Action: We have however, cited Limburg et al., (2011) when discussing MnO_2 in hypoxic waters (line 449).

“Perhaps eventually there will emerge a consensus about carbonate-based bio proxies of hypoxia?”

Response: we hope that our data here contributes to such a future consensus.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C4175/2015/bgd-12-C4175-2015-supplement.pdf

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