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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.

N. Glock (Referee)

nglock@geomar.de

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General comment on the manuscript:

The manuscript of McKay et al. reports a study on Mn/Ca ratios in fossil tests of the benthic foraminiferal species Eubuliminella exilis. Mn/Ca ratios have been determined downcore a sediment core from the NE Atlantic Upwelling System over the last 35 kyrs. Results from Secondary Ion Mass Spectrometry (SIMS) on single specimens were compared to bulk measurements done by Flow-Through Inductively Coupled Plasma

Optical Emission Spectroscopy (FT-ICP-OES) and appear to be in good agreement. Different scenarios of changes in bottom and pore water oxygen concentrations were reconstructed for several time intervals by comparing the Mn/Ca ratios to bulk sediment Mn content, changes in foraminiferal assemblages and the abundance of diatoms.

The results are new, very exciting, will be an important contribution and are definitely worth to be published in Biogeosciences. Actually it is great to see that the Mn/Ca ratios determined by SIMS on just a few specimens are indeed comparable with bulk samples of more specimens. The manuscript is well structured and written, the introduction gives a detailed overview about previous studies and existing literature is referred well. The data is presented very detailed in a good way and is thoughtfully discussed. The interpretation of the Mn/Ca ratios in respect to the other proxies and thus the schematic reconstruction of the oxygen pore water profiles is excellent in my opinion. I only suggest some minor revisions but otherwise I would be happy to see this manuscript published!

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).

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 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.

Below you can find some points of minor revision:

Introduction:

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.

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.

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.

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)".

Methods

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 won't see like this. You wrote that you checked the Ca counts and thus assured that you measured within massive calcite which is already 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?

Discussion:

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 su cient 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 it's 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.

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.

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).

Page 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.

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.

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?

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.

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.

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. . .

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.

Page 19 line 18: "Therefore, whilst high phytodetritus export typically causes low bottom wateroxygen 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.

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

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

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.

Interactive comment on Biogeosciences Discuss., 12, 7335, 2015.