**REVIEW 1: NINA KEUL**

The manuscript entitled "Benthic foraminiferal Mn/Ca ratios reflect microhabitat preferences" by Karoliina Koho and colleagues presents foraminiferal Mn/Ca as a potential tool for paleoceanographic reconstructions of the microhabitat, bottom water oxygenation and/or Mn redox chemistry. The research is original and provides novel, interesting data about Mn incorporation into foraminifera for the community. The methods used are state of the art and well suited to answer the research questions posed, however, more details need to be provided concerning the ICPMS measurements, especially since two different ICPMS setups in combination with different signal integration techniques were used, to ensure comparability of the data. The presented data is of appropriate quality, however, foraminiferal Mn/Ca ratios are only represented in Figures and DMn values only mentioned in the text so that I strongly encourage the authors to provide this data in tables. In the case of DMn also in a Figure similar to Fig. 5. In a few cases, I cannot confirm drawn conclusions from the data presented here, an urge the authors to revise those statements (indicated below). Furthermore, I would like the authors to encourage to sharpen the manuscript, that those parameters influencing foraminiferal Mn are more clear. Overall, this is a well written manuscript of an interesting study and I would recommend publication after major revisions have been carried out. I wish the authors good luck with the revisions and remain available for further feedback and discussions.
Best wishes,
Nina Keul

*RESPONSE: The authors thank Nina Keul for thorough review of the manuscript. Her comments have substantially improved the new version of our manuscript. This version now contains an appendix with the Mn/Ca measurements and also the calculated $D_{Mn}$ values. In addition, we added a figure, in which the $D_{Mn}$-values are presented. More details are now provided concerning the LA-ICPMS analyses, and the discussion concerning the parameters influencing foraminiferal Mn has been sharpened.*

**Comments by page and line number:**
**major comments:**
page 5: concerning the methods used
1.1: How long were the measurements on the different species? How long was one cycle of the ICPMS through all masses? Were there any short measurements due to e.g. thin chambers? Where they discarded? How much of the profiles were left out of the integration windows in glitter due to contamination? How many data points were left after this procedure on average? Was the contamination in high Al limited to the beginning and ends of the profiles?
*RESPONSE: Short profiles (typically <5s in length) and profiles containing high Al content contents were excluded from further analysis. A representative profile ranges from 10-30 seconds, depending on species and chamber ablated (final chambers are commonly thinner and hence result in shorter ablation profiles). Some species e.g. N. labradorica and C. fimbriata had relatively short profiles, as their chamber walls are on average thinner. In case of E. batialis longer profiles were obtained due to thicker test calcite.*
*In total, 277 single-chambered measurements were used for our study (Table 2). A new figure (Figure 2) is included, now showing examples of ablation profiles for Al/Ca, Mn/Ca and Mg/Ca. Al contamination was typically observed at the start of the profile (i.e. at the outside surface of the foraminiferal shell), although a very small Al peak was occasionally seen also inside. Often coinciding with these Al-peaks, Mg and Mn contamination peaks were observed inside and outside of the test. The text on the post-processing of the LA-CIP-MS data has been extended by incorporating this information (section 2.5)*

*Regarding a cycle length of the ICPM through all masses, these differ per ICP-MS and masses studied. In NIOZ measurements the cycle length was 0.12 seconds. In Utrecht measurements the cycle length was 0.64 seconds. These are now added to the methods section.*

1.6: which mass was measured for Mg? (it is not in the list in 1. 22)? Were high Mg and Mn and high Al always restricted to the same spot? Could you maybe provide a couple of ablation profiles in the appendix to illustrate this?
*RESPONSE: For magnesium, we measured $^{24}Mg$ and $^{26}Mg$. Two typical ablation profiles have now been added to the methods section. Mg, Mn and Al were usually elevated at the outer surface of the test. With Al, Mg and Mn often peaking at the same time (i.e. depth in ablation profile). A smaller Al peak was also occasionally also observed without the other elements being elevated. The text has been modified and these details have now been included into the manuscript.*

1.10/11: was there no matrix matched in-house standard measured? e.g. GJR or JCP? If not, why not as matrix matched standards are common practice and have been used on the second setup? I do not understand, why the measurements were calibrated against NIST610 values from Jochum et al. 2000 on one machine and against Jochum et al., 2011 on the other machine? Also, in the Jochum et al. 2000 paper cited here I cannot find reported concentrations on NIST610?
*RESPONSE: The reference to Jochum et al. (2000) was a mistake: all references to certified NIST values were supposed to be Jochum et al., 2011. This mistake is now corrected in the text. As already stated in the original version of our manuscript, we also ablated pressed powders JCp-1, MACS-3 and an in-house foraminiferal 'standard', the NFHS (Mezger et al., 2016) to monitor drift and detect any potential offsets caused by switching between matrices and between materials with varying element concentrations.*

l.13: which samples on which machine? Were some samples measured on both systems to ensure comparability? This is especially of importance with the apparently two different NIST610calibration values used? Could this data be provided in a supplementary table?
*RESPONSE: Same NIST610 calibrations (Jochum et al., 2011) were used in both set ups. The mistake regarding "Jochum et al. (2000 versus 2011)" is now corrected. Some specimens were measured on both machines, namely E. batialis and Uvigerina spp. As LA-ICPMS is a destructive technique it is not possible to measure the exact same spot on the foraminifera shell twice, making the analyses not true replica's. Due to within specimen variability in elemental composition, Mn/Ca ratios are expected to vary slightly within specimens. However, as can been seen from comparing the overall distribution and elemental composition of E. batialis (Fig 4 and 5), the elemental composition is relatively consistent regardless of the laser ablation ICP-MS system used. This confirms that results from the two platforms are inter-changeable, not only for the standards used but also the samples themselves. A similar result was also published in De Nooijer et al. (2014a) for which three different systems were used and shown to result in comparable foraminiferal El/Ca. This reference is now cited in section 2.5*

l.23: "consisted of a blank"? I assume the first 20 seconds the laser was not switched on so this was the background and not a blank? Also, so here values were integrated manually and not using Glitter, why?
*RESPONSE: 'Blank' is replaced by 'background'. The use of data reduction software does not mean that the integration windows are not manually selected. The Glitter package was not available on the NWR/iCap platform, but instead the iCap's Qtegra software (Thermo Scientific) was used for data reduction. Both softwares are described in section 2.5, dealing with the laser ablation.*

<u>page 6</u>
l. 29: please provide table with Mn/Ca measurements (and also for calculated DMn for stations 6,8,10)
*RESPONSE: Raw data now provided in appendix, which now also contains the calculated $D_{Mn}$-values.*

<u>page 8</u>
l. 3: was only the correlation with station bottom depth stat. significant or were also other parameters tested? It is mentioned in the abstract and Conclusion that Mn/Ca could be a sensitive recorder of redox conditions and or bottom water oxygenation, so a statistical test of this would be highly valuable.
*RESPONSE: The correlation between Mn/Ca and station depth, as well as bottom water oxygenation (BWO) was tested for all taxa. The Mn/Ca ratios of Uvigerina spp. and B. spissa increased with water depth and were statistically significant (Section 3.4). Another statistically significant trend was found for Mn/Ca in B. spissa and BWO (Statistics are listed in Section 3.4). The correlations were tested for all taxa but these were the only significant trends within our dataset. Due to relatively few data points, correlations for deep infauna were very limited. In the results presented in Koho et al. (2015), a significant trend between Mn/Ca and BWO was also found for the intermediate infaunal species, Melonis barleeanus.*
*Correlation of Mn/Ca in B. spissa and BWO imply that intermediate infaunal species may be the most prominent recorders of BWO in the setting studied here. This is consistent with the conclusion in Koho et al. (2015) based on the TROXCHEM³ model. Furthermore, although no statistical trends were found for other species and BWO, this study clearly illustrates systematic variations in Mn/Ca with foraminiferal microhabitat, coinciding with changes in pore water redox chemistry. Foraminifera inhabiting more oxygenated sediment layers (i.e. E. batialis) systematically showed low Mn/Ca ratios and more infaunal foraminiferal species, experiencing more reducing conditions, showed higher Mn/Ca ratios. Abstract and conclusions have now been adapted to reflect these outcomes.*

l.27/l.28: However, some specimen occurred at different depths in the sediment at the same core location, how likely is it, that they also calcify at the same depth (ideally the ALD) for the species to be a good proxy (e.g. B. spissa at station 9)? Since in the upper few cm, vast changes wrt redox chemistry occur, potentially influencing foraminiferal Mn/Ca.
*RESPONSE: Yes it is true that foraminifera are not found only at their ALD and some specimens are found above and below this depth. The low $D_{Mn}$-values also suggests that for example E. batialis may calcify at slightly shallower depth than their inferred ALD suggests, whereas $D_{Mn}$- values of deep infaunal species (e.g. C. fimbricata) imply that it was found close to its calcification depth (Discussed in section 4.2). However, no systematic ontogenetic trends were seen in this study, where for example Mn/Ca ratios were systematically either higher or lower in the younger or older chambers, or vice versa. We observed no correlation between chamber number and Mn/Ca (See also new appendix 1). Still, variations in the overall Mn/Ca ratios for example in B. spissa shells may be due to migration or changes in the ambient pore water conditions during the lifespan of the foraminifera. The influence of migration on foraminiferal Mn/Ca is now discussed in section 4.2, 4th paragraph.*

<u>page 9</u>
l.19-29: since the DMn values are not listed in the paper (no table and no figure) I cannot assess this part, please provide data
*RESPONSE: $D_{Mn}$ values are now given in appendix 1*

l. 29/ 30: "implies that these taxa are actively growing in dysoxic sediments…" B. spissa in station 9 also has high Mn values, similar to C. fimbriata, please discuss (high Mn values do the not necessarily exclusively occur in deep infaunal species?)

*RESPONSE: Unfortunately it is not possible to calculate $D_{Mn}$ value for B. spissa at station 9 as no pore water Mn data is available for this station. At station 8 the $D_{Mn}$ was low (0.36), suggesting that B. spissa is calcifying shallower than were it was found here. However, it is true that at station 9 the Mn/Ca ratios of B. spissa are similar to that of deep infaunal species. This is now added to discussion.*

Also, please discuss: As shown from the Mn porewater profiles (Fig. 5) and since most of the sediment is dysoxic after 1 cm depth (Fig. 2), the porewater concentrations in Mn are very different between station 6 (more or less constant Mn), Stn. 8 (Mn maximum at ca. 10 mm) and station 10 (Mn increases with depth) so in my interpretation of the data high Mn does not necessarily indicate only dysoxic environments, since this is the case in all the calcification environments and must be the signature of some other parameter?

*RESPONSE: It is true that pore water Mn concentrations are variable between stations and that the highest concentrations are found at the station 10 where bottom waters are relatively well ventilated. We suggest that this is due to variations in the availability of the Mn-oxides between the stations. This (and its implications for paleostudies) is discussed in depth in section 4.3 ($3^{rd}$ paragraph). At the deepest station (with the highest BWO content) Mn-oxides are accumulating in the sediments. As BWO content is relatively high, Mn is trapped and not able to escape into the water column, which may possibly occur at station 6 and 8. In addition it is possible that Mn-oxides are transported along slope, hence accumulating at the deeper and more ventilated areas. Although at each station some Mn-reduction was taking place, as shown by subsurface peaks in Mn, the pool of total dissolved Mn is likely to be related to availability of Mn-oxides in the sediment.*

page 10:
l. 11" deeper in the sediment where higher Mn conc. are present": I do see the increase in Mn with depth only at station 10, not the others, so this statement in my opinion cannot be drawn. "a clear increase in foraminiferal Mn is observed as well": In this case, it would be very valuable to show a regression of foraminiferal Mn to porewater Mn to underline this statement.

*RESPONSE: Indeed the largest increase in the pore water Mn with sediment depth is observed at station 10. At the other stations Mn-reduction is more limited, however, a small dissolved  Mn- peak is also present at station 6 (at depth of 0.8 cm) and 8 (at depth of 1.3 cm), implying that Mn- reduction occurs in the sediment. Nevertheless, at station 10, where a clear peak in Mn is present this is also reflected in the foraminiferal Mn/Ca ratios, as we see very low concentrations in the surface dwelling E. batialis and high concentrations in deep living N. labradorica.  The sentence is now modified to make clear that this refers specifically to station 10. In addition, "clear" is omitted. Unfortunately species-specific regressions of foraminiferal Mn to pore water Mn are not possible due to limited pore water data.*

page 11:
section (4.3). should be revised- at the moment, the paleographic implications from the measurements presented here (Mn/Ca in foraminifera and Mn in porewaters), should be the main focus in addition to comparison to literature values (this part is included). However, the present version discusses the relevance of the Troxchem model at length in addition the Mn redox chemistry, however, only very little focus lies on the paleo implications of this study. Please move the discussion of the TROXCHEM model and the redox chemistry into a different paragraph.

*RESPONSE: Section 4.3 has been revised and the main paragraph dealing with the TROXCHEM model has been moved to section 4.2. However, we have decided to keep the discussion on Mn-redox chemistry as part of 4.3 as it has direct implications for the application of Mn/Ca down core. Our data shows that foraminiferal Mn/Ca is not only reflecting redox conditions but is also influenced by availability of Mn-oxides and hence Mn to be potentially released upon reduction. The availability of Mn-oxides, and hence the MnOx-reduction potential of the sediment, as shown by our results, is recorded in the foraminifera along our study transects. Therefore, paleoceanographic studies should take into account changes in the supply of Mn-oxides as well as changes in sediment oxygenation, as the former is also an important parameter in regulating pore water Mn-concentrations.*

Furthermore, I am having a hard time to discern the key messages of the study wrt to what influences foraminiferal Mn/Ca. I agree with conclusion, that deeper fauna displays higher Mn/Ca, and that the deeper species must be calcifying under dysoxic conditions, but from the data presented I am having a hard time to see that "Mn incorporation" reflects
*RESPONSE: conclusions have been modified*
1)bottom water oxygenation (where is the data- regressions/ statistics and or figures? e.g. regression of foram Mn and BWO) representing this?
*RESPONSE: A statistically significant correlation was observed between BWO and Mn/Ca ratios in B. spissa (Results: section 3.4). Also statistically significant increases in the Mn/Ca ratios were observed along the study transect for Uvigerina spp. and B. spissa (Results: section 3.4).  No regression analyses were carried as there is not sufficient pore water data (i.e. each species was not present at all three sites with available pore water data) to support this.*

2) Mn redox chemistry (where is the data? regressions? statistics)
*RESPONSE: Mn pore water data was collected at three stations only and maximum of 2 taxa were measured at stations with pore water Mn-data. Hence unfortunately there is not sufficient Mn pore water data to carry out such analyses. Conclusions have now been modified to reflect this.*

3) no ontogenetic influence (as argued above, it could be that interspecies variability masks this, since on most specimen, only 2,3 chambers are measured. However, I am positive that data can be easily presented in a revised version to be able to make this statement.
*RESPONSE: the reviewer likely refers to intraspecies variability, not interspecies variability. It is true that most specimens of Uvigerina spp. were measured two or three times, however, this is not true for B. spissa, which was measured 4 times in 14 out of 23 specimens. In addition, E. batialis was measured twice 5 times and once 6 times.  None of these specimens showed systematic, statistically significant ontogenetic trends (now added to the appendix 1). Therefore, we can further conclude that no ontogentic trends were observed in our data. This is now clarified in results section 3.2. with a reference to Appendix 1.*

***minor comments:***
page 1
l.16: calcium carbonate tests
*RESPONSE: ok, done*
l.19: define BWO or spell out; what are differences exactly?
*RESPONSE: ok, done*
l.20: where is this entangling happening in manuscript?
*RESPONSE: changed "further resolving"*

l.24: At each station, Mn/Ca (omit "the")
*RESPONSE: ok, done*
also Mn/Ca is a ratio of concentrations, not a concentration
*RESPONSE: ok, changed to ratio*
l.31: the forams are not the tools, but carry the proxy -> rephrase
*RESPONSE: changed to proxies used in paleoceanographic studies.*
l.32: has a high…
*RESPONSE: ok, done*

page 2
l.4: have been shown to reflect carbonate chemistry (omit "the")
*RESPONSE: ok, done*
l.18: are oxygenated and sediments are anoxic… add "and sediments are anoxic"
*RESPONSE: changed to "In sediments, where bottom waters and surficial sediments are oxygenated and deeper sediments are anoxic…"*
l.27: omit "the" before shallow
*RESPONSE: ok, done*
l.28: than not then
*RESPONSE: ok, done*
l.32: why 33 (random?) also omit "the" before foraminifera and change to foraminiferal
*RESPONSE: 33 is not random this is the lowest BWO content along the study transect, so BWO was always higher than this. "The" is now omitted.*

page 3
l.17: change to sth. like this as it is confusing otherwise: "At each site, three separate…"
*RESPONSE: "Separate cores were collected for pore water- and foraminiferal analyses, and oxygen profiling, all of which were derived from the same multicore cast."*
l.19: company that produced CTD (seabird?), what is the error of the oxygen microsensor? Is it also called a "micro"sensor when it is attached to a CTD?
*RESPONSE: The CTD is SBE9plus (Sea-Bird Electronics, S/N 860) and it was equipped with SBE3 thermometer (S/N 4378), SBE4 conductivity sensor (S/N 3307) and SBE43 oxygen sensor (S/N 0781). The details of the equipment are now added into the manuscript (section 2.2). "Oxygen microsensor" replaced with "oxygen sensor". The accuracy specifications of the oxygen sensor are typically within 2% of true value*

l.25: Whole sample centrifuged or subsample?
*RESPONSE: Changed to "Sediment samples were centrifuged…" In general the whole samples were centrifuged. In case of the deepest sediment intervals where the slice thickness was 2 cm, some sediment may have been disregarded.*
l.30: how much HCl was added? final conc.? What samples were used for storage? Were they acid cleaned?
*RESPONSE: Text modified "Samples for pore water elemental analyses were acidified with suprapur HCl 37% (10μl per ml of sample) and subsequently stored at 4°C until analyses at Utrecht University."*
 *The foraminiferal samples were not cleaned other than was indicated in the original manuscript.*

page 4
l.1: I assume cps were measured and then converted to conc. via a calibration curve for those elements measured on the ICPMS? What wavelengths were measured in the OES? Which elements were measured on which machine? Which isotopes were measured on the ICPMS?
*RESPONSE: Sentence modified to "Seawater elemental concentrations of $^{55}$Mn were measured with an inductively coupled plasma-mass spectrometer (ICP-MS, ThermoFisher*

*Scientific Element2-XR)."* Part about the OES is deleted as only ICP-MS data is reported in *this article.*

l.5 - 12: As I am unfamiliar with the methods and the custom built incubation chamber please provide a few more details to clarify:
I assume the subsample taken with the syringe was analyzed? Stabilization of what? temp. and oxygen? How were the fluctuations in oxygen conc. assessed? Were the stabilization times similar between cores (ca. 9hrs)? Were the oxygen profiles taken continuously or at certain depths?
*RESPONSE: The O2 profiles have been published previously in Fontanier et al. (2014) with details of the employed methods. A citation has been added here.*
*Each time a core was left to stabilize under insitu $O_2$ and temperature conditions for 9hrs (as these parameters are likely to change during core recovery). $O_2$ conditions were monitored with a microsensor, with no syringe being used. $O_2$ profiles were made at 100µm resolution.*

l.13: Change title so it is more precise: e.g. "Foraminifera: sampling an elemental concentrations"
*RESPONSE: changed to "Foraminifera: sampling and elemental composition"*

l.14 et al.
*RESPONSE: ok done*

l.17: Plummer slides? Are they micropaleoslides?
*RESPONSE: ok done*

l.30: So if the crater is 80µm I assume all foraminiferal chambers measured are bigger than that to make sure, that only one chamber is ablated per measurement?
*RESPONSE: The word "generally" was added. In general always single chamber was ablated, however, it can not be completely excluded that in few rare cases two chambers were ablated at once. This would mainly concern small individuals of B. spissa, which has very small older chambers.*

page 5
l. 26: NFHS: has the homogeneity of this standard been published somewhere? Were JCP21 MACS3 and NFHS all used as the form of pressed powder tablets?
*RESPONSE: Yes: all these $CaCO_3$ powders were pressed into tablets. The relative standard deviation in element/Ca based on multiple measurements on the NFHS is comparable to that of other standards (Mezger et al., 2016). A reference to this study is added (section 2.5 $5^{th}$ paragraph)*

l.30: I assume seawater= porewater? where is DMn reported?
Knowing the good quality of data that usually is published from the Utrecht setup used, I assume that the methods have been written up by two different co-authors, I would strongly encourage the authors to rewrite section 2.5 so that the same details are given for both setups used.
*RESPONSE: DMn values are all given now in Appendix 2.*
*Yes, seawater changed to pore water.*
*We have carefully checked section 2.5 to check for consistency and modifications have been made. However, the differences in setups and controls of the ICP-MS's used inherently cause the descriptions to differ. For example, tuning of the quadrupole and SF-ICP-MS differ and also the way they cycle through the elements analysed differs fundamentally. Still, all relevant parameters are described in each of the paragraphs.*

<u>page 6</u>
l.6: what exactly is pore water chemistry? which parameters?
*RESPONSE: Sentence modified to "Pore water chemistry, including dissolved oxygen, nitrate, ammonium and manganese, was measured at sites 6, 8 and 10 (Figure 2)."*

l.8: in-sediment depth? what depth is this?
*RESPONSE: Sentence modified to" In all cores, nitrate was rapidly depleted within surficial sediments"*

l. 23: App. 1 is missing, I contacted the first author for App. 1, the excel file I received looks like there was mostly 2-3 chambers measured on each specimen, so that I doubt that this is enough to support that "there is no correlation between shell size and Mn/Ca" as it could be that interspecies variability masked potential ontogenetic trends in Mn/Ca, if only 2 or 3 chambers were measured on one specimen. I would encourage the authors to provide a figure in the appendix to demonstrate intra-species variability and also to calculate inter- versus intra-species variability for all species studied and provide data in a table. Also I do not see statistical analyses in App. 1 (L. 23: "The statistical analyses were carried out on all data (App.1)").
*RESPONSE Appendix is now added, containing all raw data. This is labeled now as appendix 2. In addition, appendix 1 is now supplied where profiles of B. spissa and E. batialis are shown, based on Mn/Ca ratios in single specimens.*
*Pearson correlation coefficients were calculated, however, all correlations were insignificant with two-tailed significance always being >0.05. This is added to results section 3.2.. Please also consider the response on this same topic earlier in the review.*

<u>page 7</u>
l. 28: lowest average (?) Mn/Ca values
*RESPONSE: Nina Keul was contacted regarding this comment, as it was not clear to the authors what she originally meant with it. In her response she stated " I was wondering whether average shell Mn/Ca is in station 6 the lowest for that species or whether it is actually lower in shells from the same species in station 8, where porewater Mn was higher? (Sorry for the kryptic comment...) If that's the case it should be discussed somewhere.*
*Our response to this comment: The average Mn/Ca ratio at station 6 is 30,1 and at station 8 30,6, so it is little bit higher at station 8 than 6, as should be due to slightly higher pore water Mn-content at station 8. However, the difference is not statistically significant. Based on this comment, it was noted that the standard error is missing in Figure 8 for Uvigerina spp (station 8) this is now added to the figure. For station 7 the error bar is so small (1,7) that it is hidden under the data label, and thus hardly visible.*

<u>page 8</u>
l.16: "excluded from data": show also in exemplary profile (see comment above)
"Due to the nature of the specimens..." does this refer to the fact that living foraminifera most likely do not have diagenetic coatings or some other factor?
*RESPONSE: representative laser ablation profiles are now provided (figure 2). Indeed as specimens were very recent, diagenetic coatings are unlikely. This is now added into the sentence.*

<u>page 9:</u>
please add references to figures and tables (also the "new" one with the Mn/Ca and DMn values)
*RESPONSE: new figure with $D_{Mn}$ made and referred to. Values also given in Appendix 2.*

l.15/16: bimodal distribution - which species here shows a bimodal distribution?

*RESPONSE: B. spissa at station 7 and Uvigerina spp. station 7 and 8 (Fontanier et al. 2014). This is now added into the sentence.*

l. 26: delete "are"
*RESPONSE: Modified to "…it seems that deep infaunal foraminifera, based on their Mn incorporation, are calcifying…"*

*page 10:*
l. 20: fluxes must still be relatively
*RESPONSE: ok, done*

l.32 remove "study" at end of sentence
*RESPONSE: ok, done. This section has also now moved up into the start of section 4.3*

page 11:
l.6: fig 2 not fig1
*RESPONSE: reference to figure corrected.*

Last paragraph: good discussion of Mn redox chemistry and availability, but maybe move upin the manuscript, as it is in general relevant for the incorporation of Mn into foraminifera and not necessarily part of the "paleo implications only".
*RESPONSE: As outlined earlier in the response to the review, we feel that this has direct implications for paleo studies as it shows that the Mn/Ca ratios in foraminfera do not only depend on oxygenation, or redox chemistry, but also on supply of manganese oxides in sediment. Therefore, we have kept this section as part of 4.3.*

---END OF REVIEW 1-----

**REVIEW 2: Anonymous referee#2**

The manuscript "Benthic foraminiferal Mn/Ca ratios reflect microhabitat preferences" by Koho et al. presents new data on the link between pore water Mn concentrations which are related to dissolved oxygen content, and benthic foraminiferal Mn/Ca. Mn/Ca is receiving a lot of attention recently as it may be a suitable proxy to reconstruct past dissolved oxygen concentrations in the water column/pore water. Using several different species and linking the data with pore water measurements has resulted in a very nice dataset, which partly provides evidence for existing ideas but also points out some issues that still exist. Especially the discussion on these possible issues could still use some more extensive consideration as described below in detail. But in general, the manuscript is well-written, easy and clear to follow, and definitely fitting within the scope of Biogeosciences. I recommend that this manuscript is suitable for publication after moderate revisions have been made.
*RESPONSE: The authors thank reviewer#2 for the time spent reviewing the manuscript and the positive feedback on the study.*

My main issue is that I feel that the discussion on the part where pore water Mn/oxygen and Mn/Ca in the forams are not fitting, can be explored further. Currently, it is partly contradicting, i.e. living labradorica and fimbriata were found at 0-1 cm but are generally deeper-living species (unless maybe in conditions where the bottom water is already close to anoxic), so that would imply habitat migration. But then the lack of a trend in Mn/Ca in the chambers would indeed point to no migration. In station 8, both species have the highest Mn/Ca again and are deepest, but there is no Mn in the pore water. So under the anoxic conditions all the available Mn has either diffused upwards

when reduction took place or it precipitated as MnCO3. How then can the forams have high Mn/Ca? For me this either means that they did migrate and picked up the Mn at a shallower depth; or that pore water oxygen and thus Mn are changing through the seasons, having higher pore water Mn when the forams calcified (assuming they were not calcifying at the moment of collection); or finally that the test Mn/Ca is biased by MnCO3 precipitation. You did write that contamination on in- and outside bits (high Al and or Mn) was discarded, but it would be interested to know if especially in these deep station 8 forams there was indeed a Mn-coating. Because if a coating forms, crystals may as easily form somewhere inside the test to bias the bulk Mn/Ca.

*RESPONSE: A discussion dealing with the influence of foraminiferal migration has been added to section 4.2, 4th paragraph. Although, no systematic ontogenetic migration was observed, it is possible that foraminifera move in the sediment during their life. As the study of Fontanier et al (2014) shows some deep infaunal foraminifera, including N. labradorica, are also found in low abundances at surface sediments, although their ALD and maximum density is deeper. The migration of intermediate and deep infauna foraminifera in sediment may also explain the larger scatter seen in the Mn/Ca ratios of these species, whereas specimens from the surface dwelling E. batialis had relatively similar Mn/Ca ratios.*
*Two typical laser ablation profiles are now given in new Figure 2. In all cases any contamination was excluded, and specimens with relatively high final Al content were discarded prior to further statistical analyses. In addition, all specimens used in the study were rose Bengal stained and therefore alive at the time of sampling, or dead very recently. Hence, high Mn/Ca ratios due to diagenetic coatis can be neglected.*

Even though that in general the relation between oxygen and Mn/Ca seems to follow the expected trends, the species-specific correlations are not very good or non-existing. What do you think could be the reason for that? How could the impact of habitat migration be determined? Seasonality may be resolved of course by extra sampling, which is always welcome. As a side note, I do like to point out that it would have been great to have had pore water profiles for stations 7 and 9 too.

*RESPONSE: We suspect that part of this is due to lack of pore water data. Unfortunately the team responsible for the pore water analyses could handle only three stations within the time available. The oxygen free sampling (slicing), porewater extraction and subsampling of porewaters is very labor intensive, resulting in the sampling of pore waters from 3 stations only. In addition, foraminiferal migration and seasonal changes in pore water could explain some of the discrepancies seen in the data. This is now discussed in section 4.2 4th paragraph.*

Minor Comments: 2.1 add some of the main currents and water masses to figure 1.
RESPONSE: The pathway of Tsugaru warm current (based on Oguma et al., 2002) is now added to the Figure 1. As the position of the currents shifts during the year, we do not feel confident placing the Oyashio current on the map. The dysoxic water mass is indicated in figure 1. As the North Pacific intermediate Waters (NIPW) mixes gradually with saline Deep Pacific Water (DPW), entering this area between a water depth of 800-3000 m, it is not possible to accurately place the water mass boundaries on the Figure 1C.

p.4, 16: part of the previously mentioned loop of possible explanations why not everything fits. Could it be that some of the deeper specimens in the anoxic sediment are stained despite being dead? They would still classify as recently-alive, but that may be enough to have them buried a couple of cms.
*RESPONSE: It is true that foraminifera could be recently dead, and hence buried. However, it should be noted that the pore water profiles provide a snap shot in time, and hence the*

*conditions may have been slightly different at the time when the foraminifera calcified. This is now discussed in section 4.2 4th paragraph.*

p.5, 6: Mg? Mg/Ca data would of course also be interesting to present. But to stick to redox elements, were any other redox elements like Fe or U analyzed?
*RESPONSE: Focus of this study is Mn/Ca. Fe was analyzed but the data does not seem good enough for any robust inferences. Measuring Fe with laser ablation is challenging due to interferences with other masses (e.g Ar-O). This can be overcome by measuring the samples at intermediate resolution with the SF-ICP-MS, but is not possible with the quadrupole.*
*Uranium was measured. However, previous studies have also shown it to vary with carbonate saturation (e.g. Raitzsch et al. 2011 G³). Thus, adding U-data to the manuscript would reduce the focus of the paper.*

p.5, 26: Internal reproducibility is good, but how was the comparison between both lasers?
*RESPONSE: As shown earlier, these systems provide consistent results (De Nooijer et al., 2014a). We have added this reference to the manuscript (Section 2.5. paragraph 3), which is also reflected by the similarity in precision/ accuracy of the ablated standards at both instruments.*

p.6, 23: shell size; can a trend in different chambers automatically be related to shell size? I am not sure if this is a correct way of naming it.
*RESPONSE: Chamber number refers to the ontogenetic stage, F- being most recent, F-1 being penultimate chamber and so on.*

p.7, 29: rations, delete n
*RESPONSE: mistake not found on p. 7 line 29 or elsewhere in the document.*

p.10, 20: where the TROXCHEM, add the; still be, add be
*RESPONSE: done*

p.12, 2: foraminferal
*RESPONSE: done*

table 2: change comma's for decimals to points.
*RESPONSE: done*

Figure 1: add currents and watermasses
*RESPONSE: The pathway of Tsugaru warm current (based on Oguma et al., 2002) is now added to the Figure 1. As the position of the currents shifts during the year, we do not feel confident placing the Oyashio current on the map. The dysoxic water mass is indicated in figure 1. As the North Pacific intermediate Waters (NIPW) mixes gradually with saline Deep Pacific Water (DPW), entering this area between a water depth of 800-3000 m, it is not possible to accurately place the water mass boundaries on the Figure 1C.*

Figure 5 caption: in indicated, change to is
*RESPONSE: done*

Figure 6 caption: this is exactly the same as the one for figure 5, which I assume should not be the case.
*RESPONSE: done*

---END OF REVIEW 2-----

# Benthic foraminiferal Mn/Ca ratios reflect microhabitat preferences

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**Abstract.** The Mn/Ca of calcium carbonate tests of living (rose Bengal stained) benthic foraminifera (*Elphidium batialis*, *Uvigerina* spp., *Bolivina spissa*, *Nonionellina labradorica* and *Chilostomellina fimbriata*) were determined in relation to pore water manganese (Mn) concentrations for the first time along a bottom water oxygen gradient across the continental slope along the NE Japan margin (western Pacific). The local bottom water oxygen (BWO) gradient differs from previous

20  field study sites focusing on foraminiferal Mn/Ca and redox chemistry, therefore allowing further resolving previously observed trends. The Mn/Ca ratios were analyzed using laser ablation ICP-MS, allowing single-chamber determination of Mn/Ca. Incorporation of Mn into the carbonate tests reflects environmental conditions and is not influenced by ontogeny. The inter-species variability in Mn/Ca reflected foraminiferal in-sediment habitat preferences and associated pore water chemistry, but also showed large interspecific differences in Mn partitioning. At each station, Mn/Ca ratios were always

25  lower in the shallow infaunal *E. batialis*, occupying relatively oxygenated sediments, compared to intermediate infaunal species, *Uvigerina* spp. and *B. spissa*, which were typically found deeper under more reducing conditions. The highest Mn/Ca was always recorded by the deep infaunal species *N. labradorica* and *C. fimbriata*. Our results suggest that although partitioning differs, Mn/Ca ratios in the intermediate infaunal taxa are promising tools for paleoceanographic reconstructions as their microhabitat exposes them to higher variability in pore water Mn, thereby making them relatively sensitive recorders

30  of redox conditions and/or bottom water oxygenation.

## 1 Introduction

Benthic foraminifera, single-celled, testate eukaryotes, are common proxies used in paleoceanographic studies. Many species make a shell, or a test, of calcium carbonate that has a high preservation potential. The chemistry of the carbonate test (i.e. its

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isotopic and elemental composition) reflects various physical and chemical conditions of the calcification environment, thereby allowing reconstruction of past environmental and climatic conditions. One of the most commonly applied geochemical foraminifera-based proxies is the Mg/Ca ratio of the test carbonate, which has been shown to primarily reflect seawater temperatures (e.g. Nürnberg et al. 1996, Elderfield et al. 2006). Other elemental ratios, such as B/Ca and U/Ca,

5 have been shown to reflect carbonate chemistry (e.g. Yu and Elderfield 2007, Yu et al. 2010, Keul et al. 2013). Previous studies have also highlighted the potential of reconstructing bottom water oxygenation (BWO) and/ or sediment redox chemistry, using Mn/Ca ratios in benthic foraminifera (Reichart et al. 2003, Glock et al. 2012, Groeneveld and Filipsson 2013, Koho et al. 2015, McKay et al. 2015). The relationship between Mn incorporation into foraminiferal test carbonate and oxygenation is based on the combination of Mn availability and redox chemistry, which is typically linked to BWO. Under

10 oxic conditions Mn is present in form of solid (hydr)oxides, i.e $MnO_2$ or MnOOH, on coatings on sediment particles (e.g. Finney et al. 1988). Therefore, foraminifera calcifying under oxic condition are likely to incorporate no, or very low amounts of Mn (Koho et al. 2015). In contrast, in the absence of oxygen the solid Mn-(hydr)oxides are reduced to aqueous $Mn^{2+}$ (Froelich et al. 1979), subsequently leading to build up of bio-available $Mn^{2+}$ in pore water. Foraminifera calcifying under such conditions are expected to show elevated Mn/Ca ratios, the concentration depending on the actual in situ aqueous Mn-

15 concentrations (Munsel et al. 2010). Exceptions are environments, like oxygen minimum zones, where bottom waters have been oxygen-deprived for extended periods. In such cases, aqueous $Mn^{2+}$ has diffused upwards and was released into the overlying water, leaving pore waters (and sediments) depleted in $Mn^{2+}$ (e.g. Van der Weijden 1998, Law et al. 2009). In such settings, foraminiferal test calcite is expected to contain no Mn (Koho et al. 2015).  In sediments, where bottom waters and surficial sediments are oxygenated and deeper sediments are anoxic, and hence Mn is retained in sediments, incorporation of

20 Mn in different species of foraminifera is expected to depend on the species-specific in-sediment living depth.

Benthic foraminifera are traditionally divided into four categories based on their microhabitat: epifauna, shallow-, intermediate- and deep infauna (Corliss 1985, Jorissen et al. 1995). This depth distribution is tightly controlled by species-specific responses to environmental redox chemistry and food supply (e.g. Jorissen et al. 1995, Koho et al. 2008, Koho and Piña-Ochoa 2012). Epi- and infauna, living above the sediment water interface and in surficial sediments respectively, are

25 typically found under oxic conditions with increasing living depth corresponding to increasing oxygen depletion and redox stress (e.g. Koho et al. 2008, Koho and Piña-Ochoa 2012). Therefore, test chemistry of species with different microhabitat preferences, i.e. living and/or calcifying at different sediment depths with varying Mn redox chemistry, are expected to display different Mn/Ca. This was confirmed in a study of Koho et al (2015), showing that shallow infaunal species consistently had lower Mn/Ca ratios than species living at the same location, but found deeper in the sediment. This resulted

30 in a conceptual model linking bottom water oxygenation, organic matter supply and microhabitat effects (Koho et al. 2015). However, this model is currently based on a limited set of oceanic conditions and theoretical considerations.

Here we present Mn/Ca ratios in benthic foraminifera with various microhabitat preferences collected from a depth transect across a dysoxic-to-oxic zone (BWO always ≥33μmol/L) in northern Japan. The incorporation of Mn into foraminiferal test

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carbonate is evaluated in the context of microhabitat distributions and foraminiferal ecology, which is described previously (Fontanier et al. 2014) for this area, and compared against measured bottom- and pore water chemistry.

## 2 Materials and Methods

### 2.1 Study Area

The sampled transect is located at the continental slope of NE Japan, off Hachinohe (Fig. 1). Surface waters in the area are dominated by three major currents: the Tsugaru Warm Current, Kuroshio Current and Oyashio Current. The convergence of these current systems results in a number of hydrological fronts sustaining high productivity in this area (Saino et al. 1998, Itou et al. 2000). Below 200m water depth, the North Pacific intermediate Waters (NIPW) mixes gradually with saline Deep Pacific Water (DPW), entering this area between a water depth of 800-3000 m. The development of a dysoxic water mass between water depths of 700-1500 meters is related to both high surface water productivity, resulting in enhanced remineralization of organic matter and associated oxygen consumption, and poor intermediate water ventilation at depth (Nagata et al. 1992).

### 2.2 Sampling

Sediment samples were collected in August 2011 onboard of R/V *Tansei Maru* (Atmosphere and Ocean Research Institute, University of Tokyo/JAMSTEC) with a Barnett-type multi-corer equipped with eight Plexiglas tubes with an internal diameter of 82 mm (Barnett et al. 1984). This type of coring device allows recovery of undisturbed sediments with an intact sediment-water interface. Sediment for faunal analyses was collected over a transect spanning the OMZ, whereas pore water chemistry was determined from material collected at 3 selected sites within this transect (Fig. 1, Table 1). Separate cores were collected for pore water- and foraminiferal analyses, and oxygen profiling, all of which were derived from the same multicore cast. In addition to coring, a Conductivity-Temperature-Depth (CTD) cast (Sea-Bird Electronics. S/N 860; SBE9plus) equipped with SBE3 thermometer (S/N 4378), SBE4 conductivity sensor (S/N 3307) and SBE43 oxygen sensor (S/N 0781) was taken at every site to record water column properties. The accuracy specifications of the oxygen sensor are typically within 2% of true value.

### 2.3 Pore water analyses

Immediately upon arrival on board, bottom water samples were taken from overlying multi-core water after which the core was transferred via a table with a closely fitted hole into a $N_2$-purged glove bag for sequential slicing (atmospheric $O_2$ within the glove bag never exceeding 1%). The core was subsequently sliced down to 20 cm depth: the first two centimeters with a resolution of 0.5 cm intervals, between two to ten centimeters, samples were taken at 1 cm intervals and from ten centimeter downward with 2 cm intervals. Sediment samples were centrifuged in 50 ml tubes for 20 minutes at 2800 rpm. The supernatant was removed and filtered over 0.45 μm TeflonTM filters under $N_2$ atmosphere, and divided into subsamples for

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various analyses. The nutrient samples were stored at -20°C until analyses, and back in the laboratory nitrate concentrations were measured with a Bran-Luebbe AA3 autoanalyser and ammonium spectrophotometrically using phenol-hypochlorite (Helder and De Vries, 1979). Samples for pore water elemental analyses were acidified with suprapur HCl 37% (10μl per ml of sample) and subsequently stored at 4°C until analyses at Utrecht University. Seawater elemental concentrations of $^{55}$Mn were measured with an inductively coupled plasma-mass spectrometer (ICP-MS, ThermoFisher Scientific Element2-XR). Replicate analyses and an in-house standard indicated that the relative error for analyses of pore water element concentrations was generally <3%.

## 2.4 Oxygen microprofiles

The oxygen microprofiles were recorded in a custom-built incubation chamber, allowing regulation of temperature and oxygen content of overlaying water, and have been previously published in Fontanier et al (2014). Here in short: upon retrieval on board, one core (from stations 6,8 and 10 only) was immediately subsampled with a piston device made of a 50 ml syringe, and subsequently placed into the incubation chamber filled with bottom water collected with Niskin bottles. Every core was left to stabilize for minimum of nine hours, while the temperature and oxygen concentrations were kept at *in situ* conditions. Any fluctuations in the oxygen concentrations were less than 0.5 μmol/l. After the oxygen microprofiles were measured with an OX-50 Unisense microsensor and a motor controller (step size of 100 μm).

## 2.5 Foraminifera: sampling and elemental composition

The details of benthic foraminiferal processing and analyses are described in Fontanier et al. (2014). In summary, cores for faunal analyses were sliced at 0.5 cm intervals down to 4 cm, from four to six centimeter depth at 1 cm interval and at 2 cm intervals down to 10 cm depth in sediment. Samples were preserved and stained with rose Bengal dissolved in 95% ethanol (1g/L). Stained (living) foraminifera in the >150 μm fraction were wet picked, identified and stored on micropaleontological slides. From the census data of Fontanier et al (2014), the average living depth (ALD) of selected species was calculated based on the equation in Jorissen et al (1995).

Few species occurring in high relative abundance and representing various microhabitats were selected for Mn/Ca measurements (Table 2). Most of the specimens came from surficial sediments (0-0,5 cm) but for some taxa, specimens from deeper sediment intervals were measured additionally (Table 2.) Prior to analyses, all foraminifera were thoroughly cleaned to remove sediment contamination (Barker et al 2003) by placing the foraminifera in Eppendorf tubes and rinsing them 3 times in ultrapure water (100μl). This was followed by 3 rinses in methanol (100μl), and finally 3 more rinses in ultrapure water (100μl). Between the methanol rinses foraminifera were placed in an ultra sonic bath for approximately 5 seconds. After these steps, specimens were dried and stored until geochemical analyses.

Trace element content was measured generally on single foraminiferal chambers (Table 2) with two different laser ablation ICP-MS set ups, which have been shown to produce comparable foraminiferal elemental/Ca results (de Nooijer et al. 2014). In all cases, shells were ablated from the outside towards the inside (Fig. 2) in He environment and element ratios were

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based on averaging measured concentrations during each ablation after selecting the non-contaminated part of the ablation profile, which was recognized by elevated counts of Al, Mg, Mn at the beginning, and occasionally end of, the ablation profile (Fig. 2). Although all tests were carefully cleaned, test surfaces of foraminifera can still be contaminated with adhered particles containing elevated concentrations of Mg and Mn in combination with elevated Al. These parts of the ablation profiles were excluded from further consideration (Fig. 2). Short ablation profiles (generally <5s) were excluded from the data, and only longer ablation profiles, typically ranging between 10-30 seconds in length, were used. Measurements carried out at Utrecht University were done with a deep-ultraviolet wavelength laser (193 nm) using a Lambda Physik excimer system with GeoLas 200Q optics (Reichart et al., 2003). Every ablation lasted approximately 130 seconds, of which the first 45 seconds consisted of a background. Ablation craters were circular with a diameter of 80 μm, pulse repetition rate was 5 Hz and the energy density at the sample surface approximately 1 J/cm$^2$. Element to calcium ratios were quantified using counts for $^{27}$Al, $^{43}$Ca, $^{44}$Ca, $^{24}$Mg, $^{26}$Mg and $^{55}$Mn and their relative natural abundances on a sector field-ICP-MS (Element2, Thermo Scientific). The cycle length through all masses was 0,64 seconds. Raw counts were converted to element concentrations and integration windows were set using the computer program Glitter (developed by the ARC National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC) and CSIRO Exploration and Mining). Calibration was performed against international NIST SRM 610 glass standard (using concentrations from Jochum et al., 2011) at a higher energy density (5 J/cm$^2$), which was ablated twice every 12 samples. Calibration of element/calcium ratios in calcium carbonate samples using a NIST glass standard has been demonstrated to be accurate for many elements when using a 193 nm laser (Hathorne et al., 2008). Switching energy density between carbonate sample and glass standard has been shown not to affect the concentration of the relevant elements (Dueñas-Bohórquez et al. 2011).

Some samples were measured at the Royal NIOZ using a comparable, but slightly different setup. This configuration consists of a NWR193UC (New Wave Research) laser, containing a dual volume ablation cell and an ArF Excimer laser (Existar) with deep UV 193 nm wavelength and <4 ns pulse duration, connected to a quadrupole ICP-MS (iCAP-Q, Thermo Scientific). Energy density of the ablation was also set at 1 J/cm$^2$, the ablation spot was 60 μm in diameter and the repetition rate was 6 Hz for the foraminiferal samples. Calibration to the NIST610 standard was identical to that performed at the Utrecht University. Helium was used as a carrier gas with a flow rate of 0.8 L/min for cell gas and 0.3 L/min for cup gas. From the laser chamber to the ICP-MS, the He flow was mixed with ~0.4 L/min nebulizer Ar and 0.0025 mL/min N$_2$. Before measuring the samples, the nebulizer gas, extraction lens, CCT focus lens and torch position were automatically tuned for the highest sensitivity of $^{238}$U, $^{139}$La, $^{59}$Co and low ThO/Th ratios (<1%) by laser ablating NIST SRM 610 glass. Masses monitored included $^{27}$Al, $^{43}$Ca, $^{44}$Ca, $^{24}$Mg, $^{26}$Mg and $^{55}$Mn. Every ablation lasted approximately 100 seconds, of which the first 20 seconds consisted of a background. The cycle length through all masses was 0,12 seconds. Intensity data were integrated, background subtracted, standardized internally to $^{43}$Ca and calibrated against the NIST SRM 610 signal using Thermo Qtergra software and reference values from Jochum et al. (2011), assuming 40% Ca weight for the foraminiferal samples. JCp-1, MACS-3 and an in-house (foraminiferal) calcite standard (NFHS) were used for quality control and measured every 10 foraminiferal samples. The relative standard deviation in element/Ca based on multiple measurements on

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the NFHS is comparable to that of other standards (Mezger et al., 2016). Internal reproducibility of the analyses was all better than 10%, based on the three different carbonate standards.

The resulting Mn and Ca concentrations in foraminiferal test carbonate were used to calculate partition coefficients (D) according to the following equation:

$$D_{Mn} = (Mn/Ca)_{calcite} / (Mn/Ca)_{pore water}.$$

## 3 Results

### 3.1 Bottom water chemistry and pore water profiles

The oxygen The BWO content varied from 112 µmol/l at station 6 to 33 µmol/l measured at station 9 (Table 1). Stations 7 and 8 were also bathed in dysoxic (<45 µmol/l) bottom water. These low BWO contents were reflected in the shallow oxygen penetration depths (Fig. 3), measuring less than 5 mm at all sites and reaching a minimum of <2 mm at station 6.

Pore water chemistry, including dissolved oxygen, nitrate, ammonium and manganese, was measured on sites 6, 8 and 10 (Fig. 3). Nitrate concentrations always peaked in the bottom waters (approximately 40 µmol/l), implying an influx of nitrate from the overlying water into the sediments. In all cores, nitrate was rapidly depleted within surficial sediments. Only at station 10, a small subsurface peak was noted in nitrate between 2 and 3 cm depth. The decline in pore water oxygen and nitrate was accompanied with an increase in ammonium, typically reaching close to 100 µmol/l at 20 cm depth. However, in the top 5 cm, where most of the foraminifera were located (Fontanier et al. 2014), ammonium concentrations were always below 30 µmol/l.

A subsurface peak was observed in pore water Mn concentrations at all sites, suggesting that manganese reduction was taking place within the sediments. However, at station 6 the Mn concentrations were generally low and did not exceed 1.4 µmol/l (0.5-1 cm depth interval). At station 8 the subsurface peak was somewhat more developed but the concentrations still remained low (~2 µmol/l), between 0.5 and 1.5 cm depth in sediment. At station 10, the subsurface manganese front was much broader, extending from 2 to 12 cm depth with a maximum concentration of 5.0 µmol/l in the 5-6 cm depth interval.

### 3.2 Mn/Ca ratios in single foraminiferal chambers

Mn/Ca ratios were measured in multiple foraminiferal chambers, ranging from chambers F-1 and F-2 (penultimate or pre-penultimate) to F-12, and to umbo in *Elphidium batialis*. Selected data of single chamber measurements is presented in Fig. 4, showing *E. batialis*, *Uvigerina akitaensis* and *Bolivina spissa* from stations with highest numbers of specimens measured across a range of chambers. In addition, single specimen measurements, in which 4 or more chambers were measured, are shown in Appendix 1. For none of the species, or for individual profiles shown in Appendix 1, there was any trend in Mn/Ca ratios with chamber number (Pearson correlation where two-tailed significance was always >0.05). The statistical data analyses were carried out on all data (see all Mn/Ca data in Appendix 2), confirming the absence of a relation between shell size and Mn/Ca. An example of *Nonionellina labradorica* is not shown in Fig. 4 as relatively low number of total

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measurements (n=18) were performed on this species and hence statistical tests are not robust. Further, due to test configuration of *Chilostomellina fimbriata*, only the final chamber (F-0) was analyzed and hence a potential size-related effect could not be determined.

Since no trend was present between Mn/Ca and chamber number, all data were combined for interpretation in the following
5  sections.

**3.3 Mn/Ca ratios in test calcite and foraminiferal microhabitat distribution**

Foraminiferal Mn/Ca ratios were generally low in *E. batialis*, ranging from 0.9 to 33.8 µmol/mol (Fig. 5). The highest concentrations were measured in *N. labradorica* (ranging from 23.4 to 277.0 µmol/mol). *E. batialis* also showed least variability in measurements per sample with average standard error of all measurements per station ranging between 0.2-7.4
10  µmol/mol.

Most of the measurements were performed on specimens collected from surface sediments, however, for *Uvigerina* spp., *B. spissa*, *N. labradorica* and *C. fimriata* specimens were measured also from deeper sediment intervals (Fig. 5). However, no statistical correlations were observed between the depths where foraminifera were found and their Mn/Ca ratios (Table 3). However, statistical test with *N. labradorica* and *C. fimriata* are of limited value due low total number of specimens
15  measured at these sites.

Average living depth of all species analyzed was calculated after Jorissen et al. (1995). The shallowest living depth was noted for *E. batialis* and was generally encountered in the upper cm of the cores (Fig. 6). At site 10 few isolated specimens were found deeper in sediment resulting in an overall average living depth of 1.2 cm. *Uvigerina* spp. (*U. cf. graciliformis* station 6, *U. akitaensis station* 7, 8 and 9) was found slightly deeper with an ALD ranging from 1.0 cm at station 9 to 2.1 cm
20  at station 7. *B. spissa* was consistently found living deeper than *Uvigerina* spp. with an average living depth close to 2 cm. Of the two deep living taxa, the average living depth of *C. fimbriata* was around 5 cm depth whereas *N. labradorica* was centered at 4 cm depth in sediment, except at station 7 where the ALD of these species were 2.9 and 2.3 cm, respectively. Overall, a systematic distribution of foraminiferal microhabitats was observed with shallow infaunal microhabitat represented by *E. batialis*. Intermediate infaunal habitat was occupied by *Uvigerina* spp. and *B. spissa*, and the deep infaunal
25  habitat was resided by *N. labradorica* and *C. fimbriata*.

Systematic changes were noted in Mn/Ca ratios with respect to foraminiferal microhabitat (Fig. 6). Lowest Mn/Ca values were found in the shallow infaunal *E. batialis*, followed by intermediate infaunal species *Uvigerina* spp. At stations 7, 9 and 10, foraminiferal Mn/Ca rations continued to increase with increasing habitat depth or their ALD. However, an exception was noted at station 8, where the highest Mn/Ca was recorded for deep infaunal species *N. labradorica* and not in the deeper
30  living *C. fimbriata*.

Despite the clear pattern between foraminiferal Mn/Ca with respect to microhabitat distribution, the Mn/Ca concentrations from the average living depth do not exactly match the pore water profiles (Fig. 6), although direct comparisons are not possible for stations 7 and 9. At station 8, for example, the peak in the pore water Mn/Ca is found at a depth of

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approximately 1 cm, whereas highest foraminiferal Mn/Ca ratios are found in *N. labradorica* with an ALD of 4.0 cm. At station 10, however, where pore water Mn content is clearly increasing with sediment depth, foraminiferal Mn/Ca ratios show a similar trend. At station 6 where pore water Mn content is generally low, foraminiferal Mn/Ca ratios are also low.

Partitioning coefficients of Mn ($D_{Mn}$) for each taxon were calculated for stations 6, 8 and 10 where pore water data was available (Fig. 7, Appendix 2). Calculations were based on pore water Mn concentrations at the ALD of each species, and their average Mn/Ca ratios. The $D_{Mn}$ of *E. batialis* was very low, ranging from 0.02 at station 10 to 0.03 at station 8. The $D_{Mn}$ of *Uvigerina* spp. was slightly higher, ranging from 0.18 to 0.56; and that of *B. spissa* was similar with an average $D_{Mn}$ of 0.36. The deep infaunal taxa generally had higher $D_{Mn}$, with a coefficient for *N. labradorica* of 1.24 and of 1.77 for *C. fimbriata*. However, at station 10 the calculated $D_{Mn}$ for *N. labradorica* was also low (0.18).

**3.4 Foraminiferal Mn/Ca ratios along the study transect**

The Mn/Ca ratios of *Uvigerina* spp. and *B. spissa* increased with water depth (Fig. 8). Both of these trends were statistically robust with Pearson correlation coefficients of 0.43 (*p<0.01;* n=100) and 0.65 (*p<0.01;* n=79) for *Uvigerina* spp. and *B. spissa*, respectively. Average Mn/Ca ratios of *E. batialis* on the other hand declined slightly along the study transect (Pearson correlation coefficient -0.64 p<0.01 n=65), whereas no trends in Mn/Ca with water depth were found for *N. labradorica* or *C. fimbriata.*

Only the Mn/Ca ratios of *B. spissa* correlated significantly with measured BWO content (Pearson correlation coefficient -0.59; p<0,01; n=79). For *Uvigerina* spp. the highest Mn/Ca ratios coincided with the lowest BWO content. For any of the other taxa no systematic, statistically significant trends were observed between BWO content and Mn/Ca.

**4 Discussion**

**4.1 Intrashell variability in Mn/Ca ratios**

Traditionally, Mn/Ca in foraminiferal test carbonate is used to indicate presence of diagenetic Mn oxyhydroxides and Mn carbonates (e.g. Boyle et al. 1983, Barker et al. 2003). However, studies applying techniques such as LA-ICP-MS, allow circumventing surface contamination by a high depth-resolution during the measurement (e.g. Hathorne et al. 2003, Reichart et al. 2003, Koho et al. 2015). In our study all measurements were also conducted with application of LA-ICP-MS, hence all surficial Mn-contaminants were excluded from data. In addition, all specimens analyzed here were stained with rose Bengal, implying that they were alive, or very recently alive, when collected. Due to the nature of the specimens being very recent, presence of any diagenetic coatings is unlikely and Mn/Ca ratios reflect true Mn-incorporation into the shell walls.

Another advantage of LA-ICP-MS is that it allows measurements of individual foraminiferal chambers, providing information on the changes in the elemental composition in relation to foraminiferal ontogeny/growth. In this study no systematic variations were noted in the Mn/Ca ratios and chamber stages of any foraminifera (Fig. 4, Appendix 1). These observations are consistent with work of Dueñas-Bohórquez (2010) who also noted no clear trend in the Mn/Ca ratios with

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chamber stages of *Cibicidoides pachyderma*. Therefore, it appears that Mn/Ca ratios in benthic foraminifera are not substantially influenced by ontogenetic processes, which is occasionally reported for other elements e.g. Mg and B (e.g. Raitzsch et al. 2011), but are primarily driven by environmental changes, such as redox conditions, affecting the concentration of Mn in pore waters. This implies that these foraminifera did not consistently calcify different chambers at different in-sediment depths, with contrasting Mn concentrations. Effectively this rules out systematic ontogenetic migration across oxygen gradients in the benthic foraminiferal species studied here.

**4.2 Mn/Ca ratios as function of microhabitat**

Foraminifera from three microhabitats (shallow-, intermediate- and deep infauna) were included in this study (Fig. 6): *E. batialis* representing the shallow infaunal microhabitat, *Uvigerina* spp. and *B. spissa* representing the intermediate microhabitat, and *N. labradorica* and *C. fimbriata* representing the deep infaunal microhabitat. At all stations, the lowest Mn/Ca ratios were measured in the shallow dwelling *E. batialis*. In general with deeper microhabitat distribution, the Mn/Ca ratios appeared to increase (Fig. 6). The only exception seemed to be *C. fimbriata* at station 8 with the average Mn/Ca ratio slightly lower than that of the other deep-infaunal taxa *N. labradorica*. These results are in a good agreement with previous studies on foraminiferal Mn/Ca ratios. In the Baltic Sea, for example, Groeneveld and Filipsson (2013) showed that specimens of the shallow dwelling *Bulimina marginata* were found to contain no or very small amounts of manganese in their carbonate test, where as elevated Mn/Ca ratios were measured in deep infaunal *Globogulimina turgida*. Moreover the results from the West Pacific presented here are in a good agreement with the TROXCHEM[3] model, a conceptual three-dimensional model, linking foraminiferal Mn uptake, bottom water oxygenation and organic flux (Koho et al., 2015). Based on this model under relatively eutrophic condition, where the bottom waters are still oxygenated very low Mn-concentrations are found in shallow infaunal species. Deeper in the sediment where higher concentrations of aqueous Mn are present in the pore water (station 10 namely), an increase in foraminiferal Mn/Ca is observed.

Pore water Mn profiles and Mn/Ca ratios in foraminifera in combination with their ALD match relatively closely at station 6 and 10. At station 6, pore water Mn concentrations were generally low, hence the Mn/Ca ratio in the *Uvigerina* spp. was also low. At station 10 where the greatest increase in the pore water Mn content was noted, the deep infaunal *N. labradorica* also showed much higher Mn/Ca ratios than shallow dwelling *E. batialis*. At station 8, however, where Mn/Ca ratios peaked at just below 1 cm depth in sediment the highest Mn/Ca ratios were noted in *N. labradorica* with an ALD of 4.0 cm. The apparent mismatch between the pore water profiles and Mn/Ca ratios in foraminifera from their ALD suggests that foraminifera may not always calcify at their observed ALD. As the foraminiferal ALDs represent the average depth where foraminifera are found they may be skewed by few individuals recovered from deeper or shallower depth intervals. In addition, bimodal distributions, which were seen for *B. spissa* at station 7 and *Uvigerina* spp. at stations 7 and 8 (Fontanier et al. 2014), can be considered problematic, in case of ALD calculations. However, this does not explain the discrepancy observed at station 8 as the mode of maximum density and ALD of *N. labradorica* were alike, 4.5 cm and 4.0 cm respectively.

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Calculated Mn partitioning coefficients (based on pore water concentrations at ALDs) showed a large range in values, ranging from 0.02 for *E. batialis* to 1.77 for *C. fimbriata*. This could imply large offsets between ALD and calcification depths, but partition coefficients for Mn and other elements (e.g. Mg) also have been shown to vary between species (e.g. Toyofuku et al. 2011, Wit et al. 2012, Koho et al. 2015). Previous field-based estimates suggest that the $D_{Mn}$ for benthic foraminifera is generally close to 1 (Glock et al. 2012, Koho et al. 2015), whereas controlled growth experiments of Munsel et al. (2010) estimated that Mn/Ca ratios could be even above 1, with 2.6-10 times higher ratios than in seawater. Irrespective of the observed differences in $D_{Mn}$-values of the species coming from similar depth habitats, it seems that deep infaunal foraminifera, based on their Mn incorporation, are calcifying in or close to the pore waters where they were collected from. The shallow and intermediate infaunal species having $D_{Mn}$ <1 based on their calculated ALD, might calcify somewhat shallower depth where Mn concentrations are lower, or really have substantially lower D-values.

Foraminifera are known migrate in the sediment and laboratory experiments have shown that changes in the sediment oxygenation, typically result in migration of foraminifera to their preferred microhabitat (Gross 2000, Geslin et. al. 2004). Although, no systematic ontogenetic migration was seen in this study, foraminiferal migration is anticipated as all of the studied taxa were found in relatively wider range of sediment depths (Fontanier et al. 2014). Therefore, foraminiferal migration may explain some of the discrepancies seen in the foraminiferal $D_{Mn}$-values, and explain some of the discrepancies between the foraminiferal Mn/Ca ratios and Mn pore water concentrations. Even relatively small scale migration of intermediate and deep infaunal taxa could results in relatively large changes in the ambient pore water Mn content, which would be reflected in their test chemistry during calcification. Furthermore, a closer observation of Mn/Ca ratios of in-sediment dwelling foraminifera shows that both intermediate and deep infaunal species showed relatively higher range of Mn/Ca values at each station (Fig. 4, 6). In contrast, the shallow living *E. batialis*, which is expected to mainly inhabit the surficial more oxygenated sediments, displayed relatively low variability. This suggests that the deeper habitat depth exposes foraminifera to greater variations in pore water Mn concentration. Alternatively, it should be noted that the foraminiferal Mn/Ca measurements were carried out in range of chambers, including younger and older ones (Fig. 4), where as pore water profiles represent a snap shot in time. Therefore, some mismatch can be expected to results from variation in pore water conditions through time.

The relatively high Mn measured in deep-infaunal foraminifera, and for *B. spissa* at station 9 only, further implies that these taxa are actively growing in dysoxic sediments where pore water Mn-concentrations are higher. Although not shown for the species studied here, foraminifera are known to be capable of denitrification (e.g. Risgaard-Petersen et al. 2006, Piña-Ochoa et al. 2010a) and prolonged survival under anoxic conditions (Piña-Ochoa et al. 2010b). Therefore, it is very likely that also the deep-infaunal taxa studied here have adapted similar life strategies. Foraminiferal calcification in the absence of oxygen was also recently demonstrated by Nardelli et al. (2014), whose experimental approach demonstrated that three benthic foraminiferal species *Ammonia tepida*, *Bulimina marginata* and *Cassidulina laevigata* were not only able to survive under anoxic conditions but also form new chambers. Here we show that Mn/Ca ratios in benthic foraminifera can also be measured to identify calcification under such conditions.

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**4.3 Implications for paleoceanographic reconstructions**

In recent years, efforts have been made to develop new bottom water oxygenation proxies via application of foraminiferal Mn/Ca ratios (Glock et al. 2012, Groeneveld and Filipsson 2013, McKay et al. 2015, Koho et al. 2015). To date, direct statistically significant correlations between bottom water oxygenation and foraminiferal Mn/Ca ratios have been noted only for the intermediate to deep infaunal *M. barleeanus* (Koho et al. 2015). In this study a statistically significant correlation between Mn/Ca ratio and BWO was also measured in the intermediate infaunal foraminifera *B. spissa* (Pearson correlation coefficient: -0.59, $p<0.01$, n=79). Similarly in the study of Glock et al. (2012) Mn/Ca ratios measured in *B. spissa* from the Peruvian margin seemed to respond to BWO and associated changes in Mn-redox chemistry, although the observed trend was not statistically significant. However, in the case of the other intermediate infaunal species studied here, namely *Uvigerina* spp., no robust statistical correlation with BWO was observed, although the highest Mn/Ca ratios still coincided with the lowest BWO content (33 µmol/l). Consistent with this observation, the highest Mn/Ca ratios in *Uvigerina peregrina* from the Arabian Sea were measured at sites with BWO contents of 20-40 µmol/l (Koho et al. 2015). These observations give further confidence that intermediate infaunal species may be most suitable proxies for BWO and redox reconstructions in the productivity regimes studied here and the study of Koho et al., 2015. Their suitability is most likely related to the vicinity of their microhabitat to the zone of Mn reduction, leading to higher sensitivity for recording changes in redox conditions.

On contrary to intermediate infauna, no clear trends were observed along the study transect in the Mn/Ca ratios of deep or shallow infaunal species (Fig 8). The Mn/Ca ratios were relatively, constantly low in shallow infaunal *E. batialis* or relatively high in deep infaunal species. In the case of the shallow infauna, the surficial microhabitat does not seem to expose foraminifera to pore water Mn, leading to hampering of the any redox signal. Therefore, our data suggests that shallow infaunal taxa may not be suitable for reconstruction of past redox conditions, in line with the results presented in Koho et al (2015). However, the exact response of deep versus intermediate infauna to changes in bottom water oxygenation is most likely to depend on the intricate interplay with organic matter loading. Although productivity at our study site is anticipated to be relatively lower (annual average around 46 mmol/C/m$^2$/d, Yokouchi et al. 2007) than in the Northern Arabian Sea (annual average 111 mmol/C/m$^2$/d, Barber et al. 2001), where the TROXCHEM$^3$ model was developed, fluxes must still be relatively high, as shown by shallow nitrate penetration depth and relatively high ammonium content in the pore waters (Fig. 3). Therefore, influence on the intermediate infauna may also be anticipated here. However, if the carbon loading would be lower, and subsequently Mn-reduction would occur deeper in the sediment, an influence on deeper infauna may be more significant. In paleostudies where large changes in the carbon fluxes are foreseen, Mn/Ca ratios in multiple species, included both intermediate and deep infaunal taxa, should be measured simultaneously.

Along the study transect, the total pore water Mn-inventory did not correlate with BWO content (Fig. 3), having a direct implications for paleoceanographic studies aiming to combine the two. In addition to sedimentary redox chemistry, the total potential pool of Mn in the pore water is related to availability of Mn-oxides in the sedimentary environments (e.g. Van der

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Weijden et al. 1999, Law et al. 2009). In this study both intermediate infaunal taxa (*B. spissa* and *Uvigerina* spp.) showed consistent variability in their Mn/Ca ratios along the study gradient (Fig. 8), with ratios increasing with water depth. Therefore, these trends are likely to reflect an increase in the pore water Mn along our study transects as also shown by the pore water Mn profiles (Fig. 3). Concentrations of $Mn^{2+}$ were generally low at station 6, located at around 500 m water

5 depth, where the maximum dissolved $Mn^{2+}$ concentrations were only 1.4 μmol/l at sediment depths of 0.75 cm. With increasing water depth, both, the total depth of the in-sediment zone containing elevated dissolved $Mn^{2+}$ and total concentrations of dissolved manganese increased. At station 10, at a water depth of 2000 m, relatively elevated pore water manganese concentrations were found at sediment depths between 2 and 10 cm with a maximum of 5.0 μmol/l, occurring at the sediment depth of 5.5 cm. This pore water $[Mn^{2+}]$ increase, which is also reflected in the foraminiferal Mn/Ca, may in

10 addition to bottom water oxygenation also be related to an increase in Mn-oxides in the sediment with increasing water depth. Such changes could be due to sustained Mn-recycling, which with no Mn escaping to the water column over time results in the accumulation of high Mn oxides close to the sediment water interface. Alternatively, manganese "shuttling", or downslope transport and focusing of Mn-oxides, is well described in literature (e.g. Schulz et al. 2013, Jilbert et al. 2013), typically explaining spatial differences in the distribution of solid phase manganese along BWO gradients. The slightly

15 higher BWO conditions in the deeper station might have allowed Mn being shuttled there. In addition, although BWO content was higher than 33 μmol/L at all sites during our expedition, at some sites manganese may be able to escape the sedimentary environment at times, leading to relatively Mn depleted pore waters. This may be the case especially at the station 6 and 8, where the Mn-reduction was taking place very close to the sediment surface at the time (Fig 3). Moreover, kinetics of manganese oxidation are known to be relatively slow and subsequently in some aqueous settings $Mn^{2+}$ has been

20 observed to penetrate to the overlying oxic water column in metastable form (e.g. Balzer 1982, Pakhomova et al. 2007), resulting in $Mn^{2+}$ escaping the sedimentary system and diagenetic recycling. At station 10, where the highest pore water $[Mn^{2+}]$ values are noted, Mn oxide reduction is occurring well within the sediment (at depths between 5 and 7 cm). Thus here the internal cycling of Mn-(hydr)oxides is likely to be more efficient, resulting in $Mn^{2+}$ being efficiently trapped within the system (Van der Weijden 1999, Law et al. 2009). Paleoceanographic reconstructions applying Mn/Ca ratios as a proxy

25 for changes in redox chemistry therefore need to take into account changes in availability of Mn-oxides, which could influence sediment biogeochemistry and incorporation of Mn into foraminiferal test carbonate.

**5 Conclusions**

Here we show that Mn/Ca ratios in benthic foraminifera reflect their microhabitat distribution, Mn/Ca ratios increasing with deeper in-sediment habitat. Although appreciable differences between species in Mn partitioning were present, the overall

30 higher Mn/Ca measured in some intermediate and deep-infaunal foraminifera suggest that these taxa are actively growing and calcifying in dysoxic-anoxic sediments where pore water Mn-concentrations are also higher. We also show that Mn incorporation into foraminiferal carbonate appears to reflect the ambient environmental conditions and is not influenced by ontogenetic processes. With regards to paleoceanographic reconstructions, the application of Mn/Ca ratios in intermediate

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infaunal foraminifera, such as *B. spissa,* which showed a statistically significant correlation between BWO and Mn/Ca, seems most promising, as their microhabitat appears to expose them to systematic and broad variations in pore water manganese in response to environmental changes.

## 6 Acknowledgements

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**Table 1. Station details including latitude, longitude, water depth and bottom water oxygen (BWO) content. In addition sites, where pore water and foraminifera were collected, are indicated.**

| Station | Latitude (N) | Longitude (E) | Depth (m) | BWO (µmol/l) | Foraminifera | Pore water |
|---|---|---|---|---|---|---|
| 6 | 40° 58.891' | 141° 47.572' | 496 | 112 | Yes | Yes |
| 7 | 41° 10.647' | 141° 47.348' | 760 | 42 | Yes | No |
| 8 | 41° 15.003 | 142° 00.028 | 1033 | 36 | Yes | Yes |
| 9 | 41° 14.982' | 142° 16.969' | 1249 | 33 | Yes | No |
| 10 | 41° 14.918 | 142° 59.989 | 1963 | 70 | Yes | Yes |

**Table 2. Total number of laser ablation measurements and number of foraminifera ablated. In addition, the depth intervals of specimens per station are indicated.**

| Species | Measurements | Specimens | Depth intervals of foraminifera (cm) | | | | |
|---|---|---|---|---|---|---|---|
| | | | ST 6 | ST7 | ST8 | ST9 | ST10 |
| *E. batialis* | 65 | 44 | 0-0.5 | 0-0.5 | 0-0.5 | 0-0.5 | 0-0.5 |
| *Uvigerina* spp. | 100 | 66 | 0-0.5 | 0-0.5 | 0-0.5 | 0-0.5 | 0-0.5; 0.5-1; 1-1.5 |
| *B. spissa* | 79 | 23 | | 0-0.5 | 0-0.5 | 0-0.5; 0.5-1 | |
| *N. labradorica* | 18 | 18 | | 0-0.5 | 0-0.5; 2-2.5; 4-5 | | 0-0.5 |
| *C. fimbriata* | 15 | 15 | | 0-0.5 | 4-5 | 1-1.5; 3-3.5 | |

**Table 3. Pearson correlation coefficients and significance values for Mn/Ca ratios of *Uvigerina* spp. (St 9), *B. spissa* (St 9). *N. labradorica* (St 8) and *C. fimbriata* (St 9) versus sediment depth from where foraminifera were collected from.**

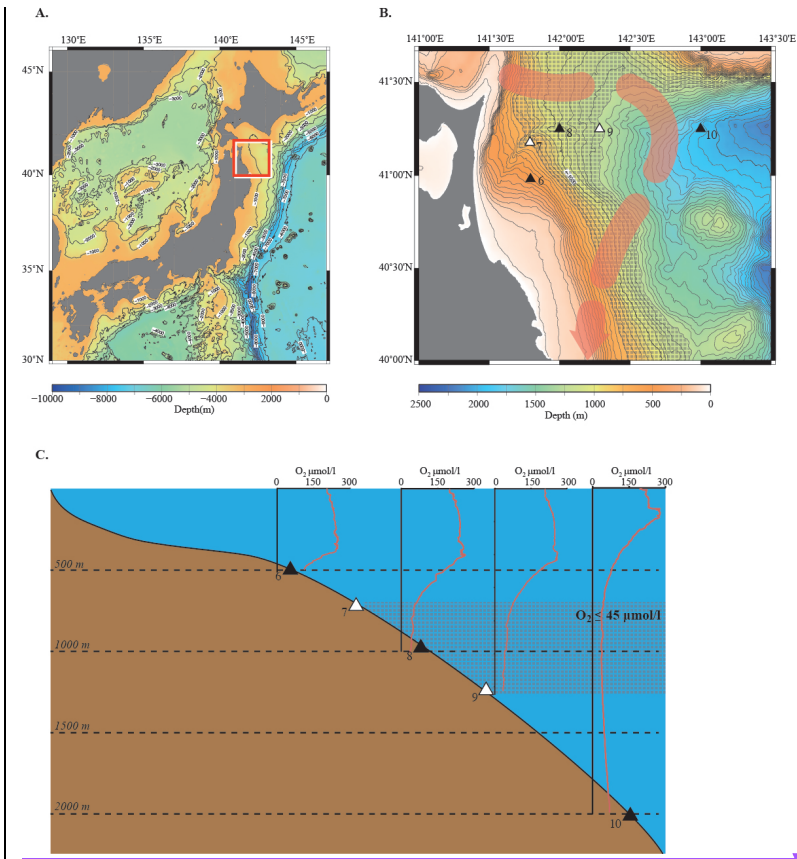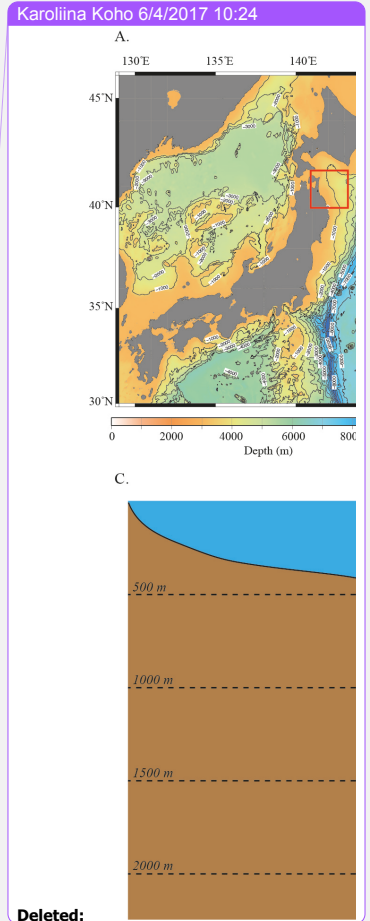| Species | Pearson correlation | Significance | N |
|---|---|---|---|
| *Uvigerina* spp. | 0.267 | 0.91 | 41 |
| *B. spissa* | 0.017 | 0.937 | 23 |
| *N. labradorica* | 0.512 | 0.159 | 9 |
| *C. fimbriata* | 0.404 | 0.247 | 10 |

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**Figure 1**: A Regional map of the study area B: Bathymetric map of the study region, showing the position of Tsugaru warm current (Oguma et al., 2002) and multicore sampling sites. C: Schematized study transect with water column profiles of dissolved oxygen. The dysoxic water column (O2<45 μmol/l) is indicated with gray-square pattern.

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**A.** *Elphidium batialis*

**B.** *Uvigerina akitaensis*
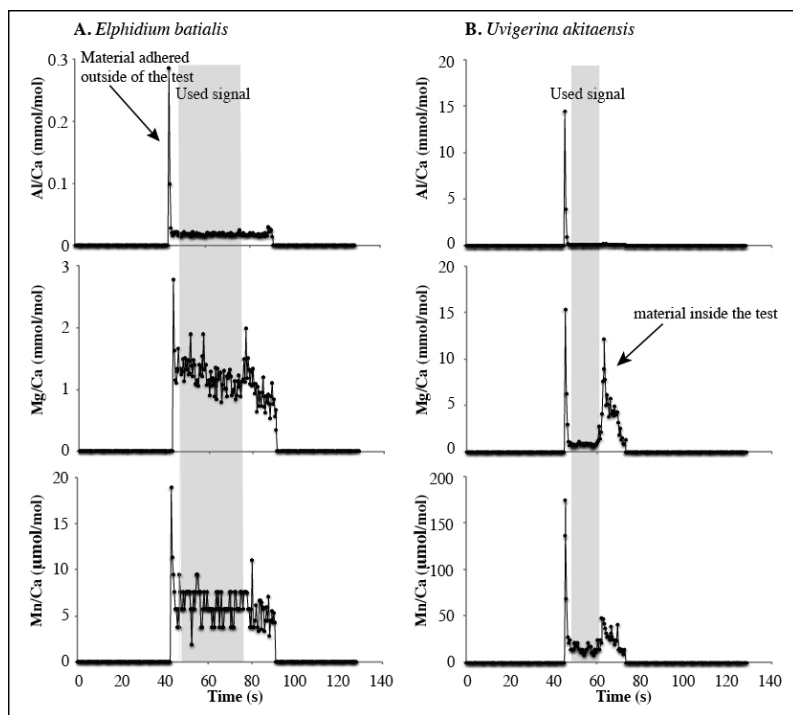
**Figure 2: Laser ablation profile for Al/Ca Mg/Ca and Mn/Ca measured in (A) *E. batialis* (station 8, 0-0.5 cm depth) and (B) *Uvigerina akitaensis* (station 7, 0-0.5 cm depth) benthic foraminifera The selected signal for the elemental composition is indicated with the gray shading. Parts of the profile with elevated surface ratios, especially Al/Ca, are removed. In addition, the elevated concentrations, following the ablation through the foraminiferal test are not included in the averaged elemental ratios. Note the different scale bars for elemental ratios.**
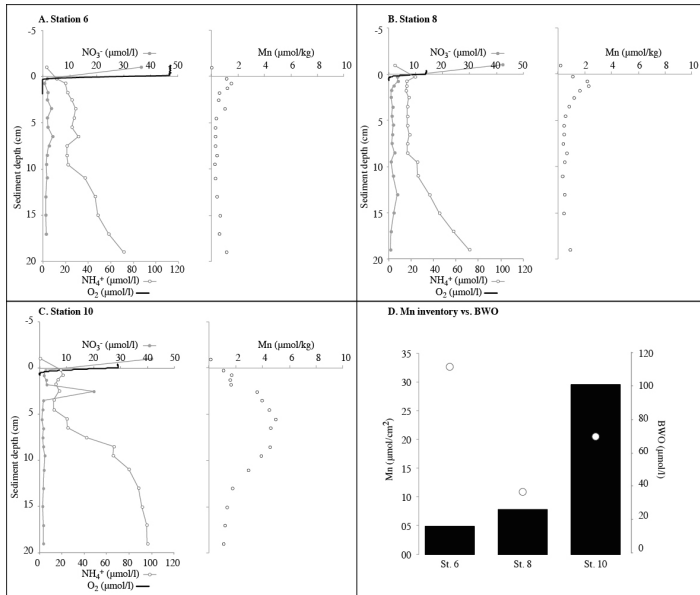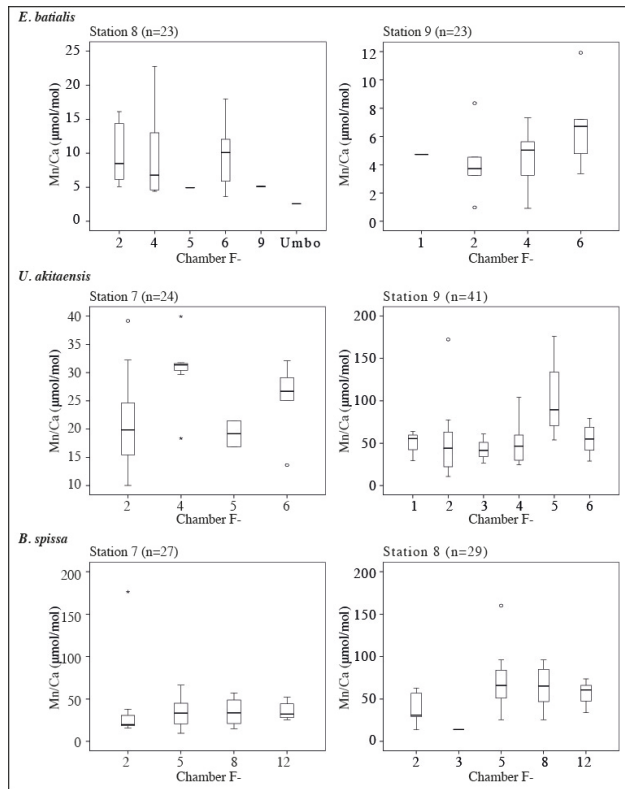
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**Figure 2:** Pore water profiles of dissolved oxygen, nitrate, ammonium and manganese at station 6 (A), 8 (B) and 10 (C). (D) Pore water manganese inventory in the top 10 cm of sediment and bottom water oxygen content (white symbols).

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**Figure 4: Box-plots showing chamber-to-chamber variability of Mn/Ca. Error bars display the full range of data variation (from minimum to maximum). Data outliers are represented with an astrix.**

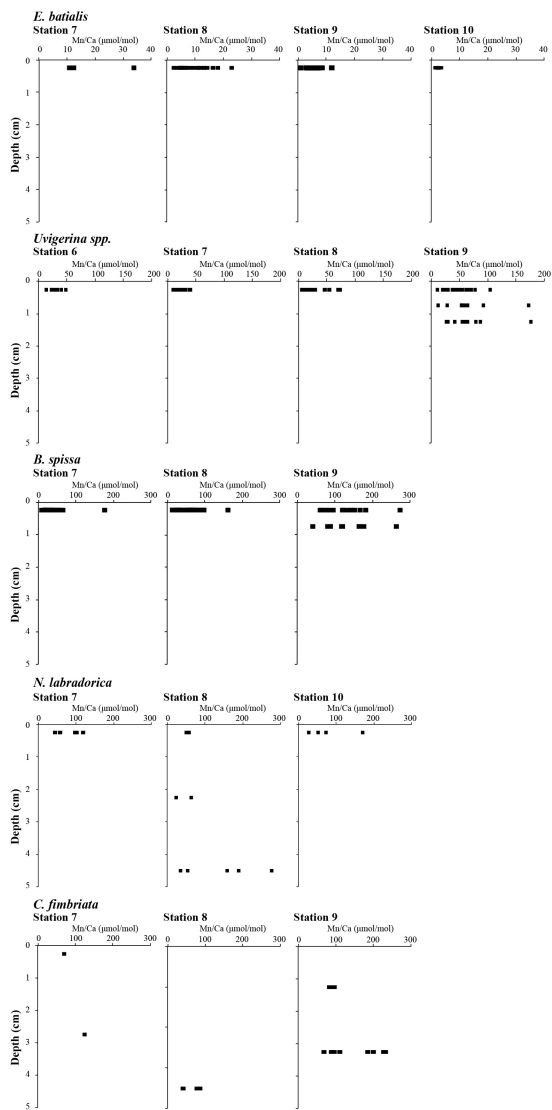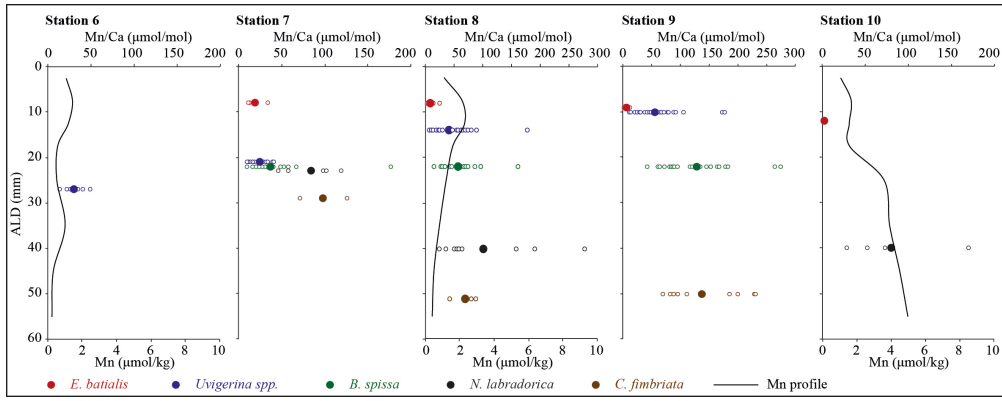**Figure 5: Individual laser ablation measurements of Mn/Ca in foraminifera versus sediment depth where the specimens were collected.**

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Figure 6: **Mn/Ca ratios in foraminifera as a function of the average living depth of each species. The average of all measurements is indicated with a solid symbol and the individual measurements with open symbols. In addition the pore water profile of Mn is shown in all sites where it was measured.**
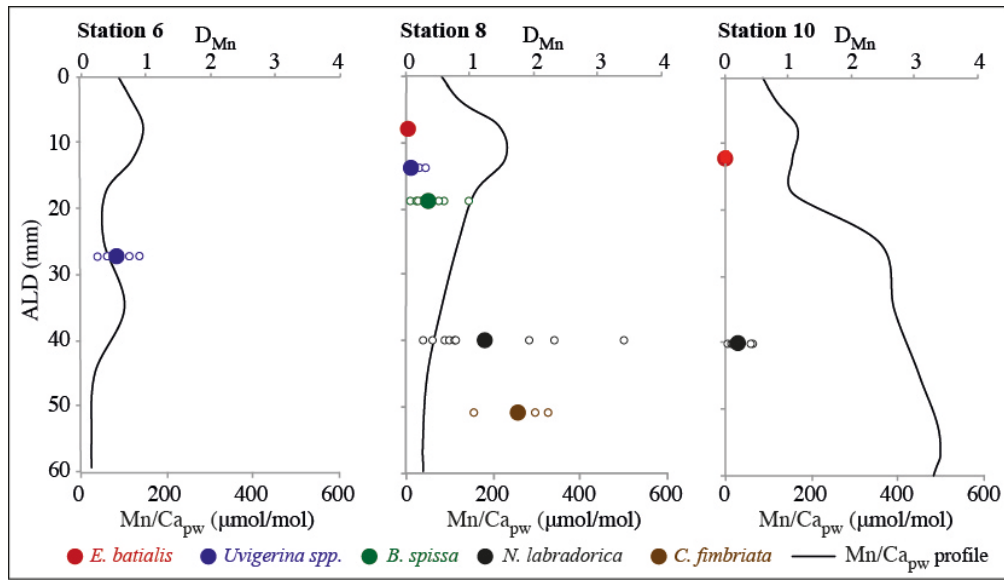
**Figure 7: Manganese partition coefficient DMn in foraminifera as a function of average living depth of each species. In addition, the pore water (pw) Mn/Ca profile is shown.**
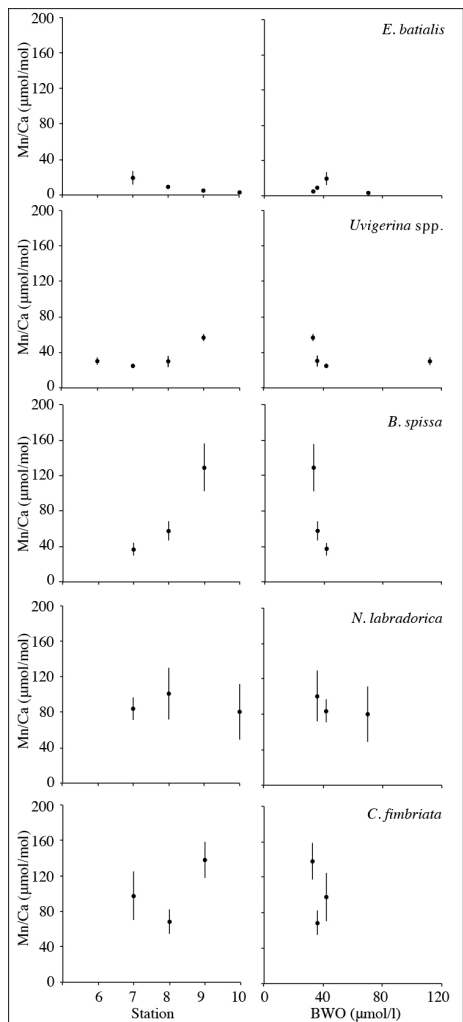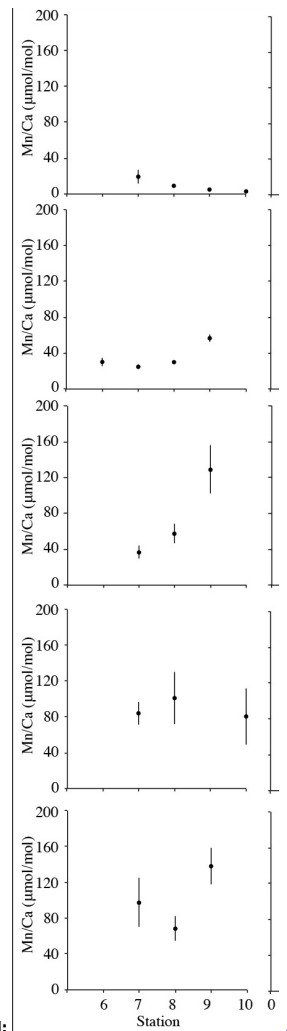
5

**Figure 8: Variability of average Mn/Ca ratios of each species plotted against the study transect from station 6 to station 10 (left), and along the bottom water oxygenation (right). The error bars represent the standard error of the measurements.**
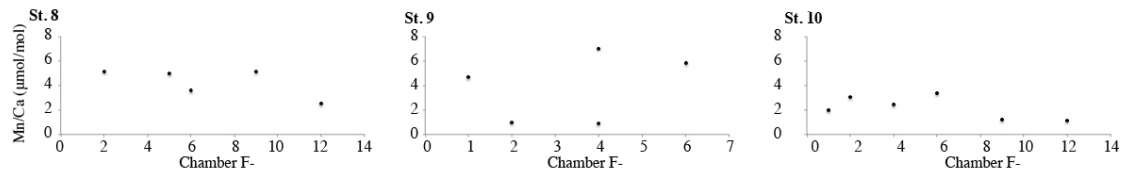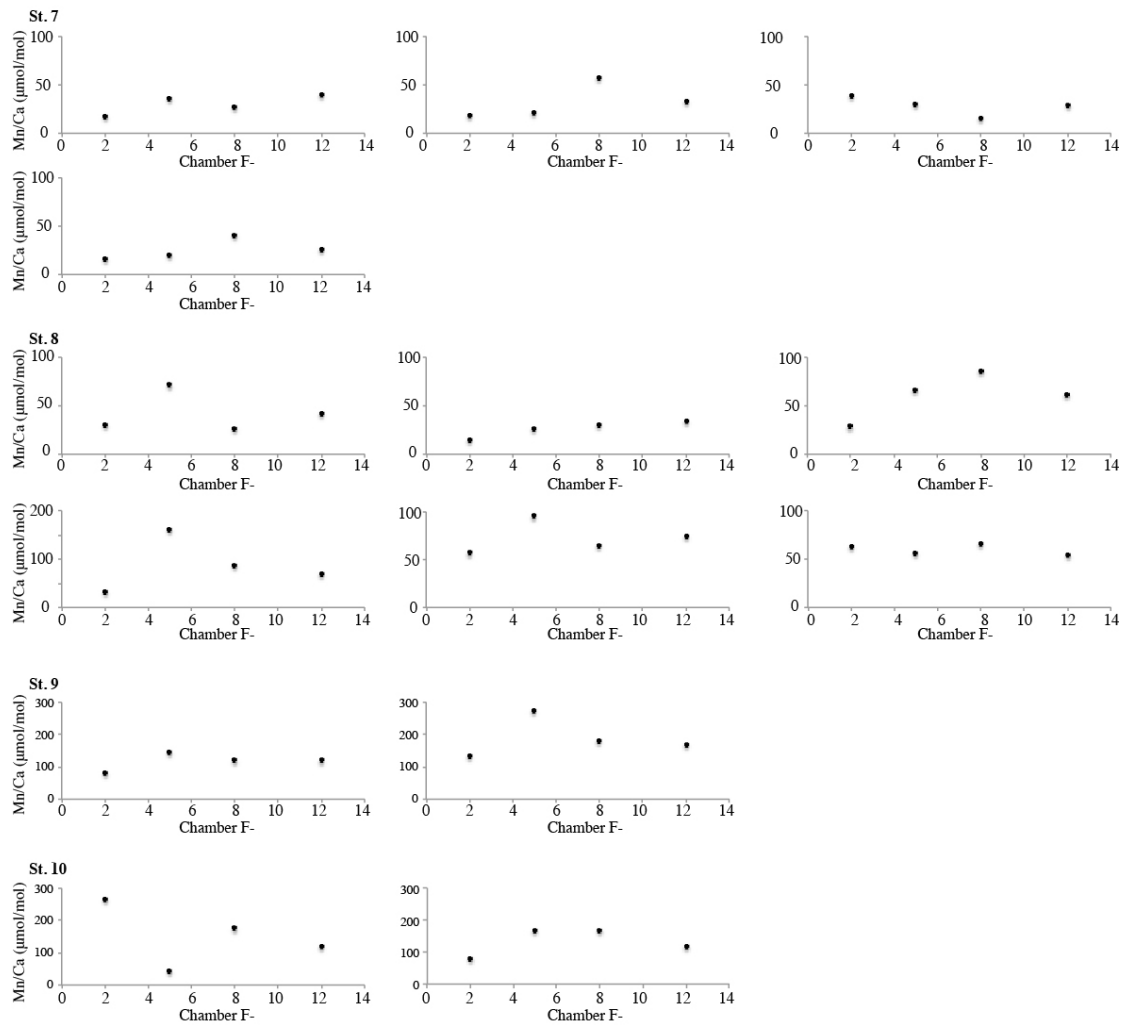
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Appendix I. Mn/Ca ratios in individual foraminiferal chambers.

*E. batialis*



*B. spissa*

APPENDIX 2: Raw data

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | DMn | Dmn average per station |
|---|---|---|---|---|---|---|---|---|---|
| 30 | E. batialis | 7 | 4 | 0-0,5 | 12,58 | 0,4 | no data | | |
| 30 | E. batialis | 7 | 2 | 0.-0.5 | 33,78 | 0,4 | no data | | |
| 30 | E. batialis | 7 | 6 | 0.-0.5 | 10,85 | 0,4 | no data | | |
| 31 | E. batialis | 8 | 4 | 0-0,5 | 4,41 | 0,8 | 212,3 | 0,02 | 0,04 |
| 31 | E. batialis | 8 | 2 | 0.-0.5 | 14,36 | 0,8 | 212,3 | 0,07 | |
| 31 | E. batialis | 8 | 6 | 0.-0.5 | 9,39 | 0,8 | 212,3 | 0,04 | |
| 32 | E. batialis | 8 | 4 | 0-0,5 | 22,78 | 0,8 | 212,3 | 0,11 | |
| 32 | E. batialis | 8 | 6 | 0.-0.5 | 6,97 | 0,8 | 212,3 | 0,03 | |
| 33 | E. batialis | 8 | 4 | 0-0,5 | 13,00 | 0,8 | 212,3 | 0,06 | |
| 33 | E. batialis | 8 | 6 | 0.-0.5 | 17,98 | 0,8 | 212,3 | 0,08 | |
| 34 | E. batialis | 8 | 4 | 0-0,5 | 6,77 | 0,8 | 212,3 | 0,03 | |
| 34 | E. batialis | 8 | 2 | 0.-0.5 | 8,48 | 0,8 | 212,3 | 0,04 | |
| 34 | E. batialis | 8 | 6 | 0.-0.5 | 12,96 | 0,8 | 212,3 | 0,06 | |
| 35 | E. batialis | 8 | 5 | 0-0,5 | 4,93 | 0,8 | 212,3 | 0,02 | |
| 35 | E. batialis | 8 | 9 | 0-0,5 | 5,12 | 0,8 | 212,3 | 0,02 | |
| 35 | E. batialis | 8 | 12 | 0-0,5 | 2,56 | 0,8 | 212,3 | 0,01 | |
| 35 | E. batialis | 8 | 2 | 0.-0.5 | 5,10 | 0,8 | 212,3 | 0,02 | |
| 35 | E. batialis | 8 | 6 | 0.-0.5 | 3,62 | 0,8 | 212,3 | 0,02 | |
| 36 | E. batialis | 8 | 4 | 0-0,5 | 4,62 | 0,8 | 212,3 | 0,02 | |
| 36 | E. batialis | 8 | 2 | 0.-0.5 | 6,17 | 0,8 | 212,3 | 0,03 | |
| 36 | E. batialis | 8 | 6 | 0.-0.5 | 5,88 | 0,8 | 212,3 | 0,03 | |
| 37 | E. batialis | 8 | 6 | 0.-0.5 | 10,96 | 0,8 | 212,3 | 0,05 | |
| 38 | E. batialis | 8 | 6 | 0.-0.5 | 5,10 | 0,8 | 212,3 | 0,02 | |
| 39 | E. batialis | 8 | 6 | 0.-0.5 | 10,79 | 0,8 | 212,3 | 0,05 | |
| 40 | E. batialis | 8 | 2 | 0.-0.5 | 16,13 | 0,8 | 212,3 | 0,08 | |
| 40 | E. batialis | 8 | 6 | 0.-0.5 | 12,07 | 0,8 | 212,3 | 0,06 | |
| 41 | E. batialis | 9 | 4 | 0-0,5 | 3,10 | 0,9 | no data | | |
| 41 | E. batialis | 9 | 2 | 0.-0.5 | 3,26 | 0,9 | no data | | |
| 41 | E. batialis | 9 | 6 | 0.-0.5 | 3,37 | 0,9 | no data | | |
| 42 | E. batialis | 9 | 4 | 0-0,5 | 5,04 | 0,9 | no data | | |
| 42 | E. batialis | 9 | 6 | 0.-0.5 | 6,59 | 0,9 | no data | | |
| 43 | E. batialis | 9 | 4 | 0-0,5 | 3,25 | 0,9 | no data | | |
| 43 | E. batialis | 9 | 2 | 0.-0.5 | 8,35 | 0,9 | no data | | |
| 43 | E. batialis | 9 | 6 | 0.-0.5 | 7,23 | 0,9 | no data | | |
| 44 | E. batialis | 9 | 4 | 0-0,5 | 4,93 | 0,9 | no data | | |
| 44 | E. batialis | 9 | 2 | 0.-0.5 | 4,53 | 0,9 | no data | | |
| 44 | E. batialis | 9 | 6 | 0.-0.5 | 6,84 | 0,9 | no data | | |
| 45 | E. batialis | 9 | 4 | 0-0,5 | 5,59 | 0,9 | no data | | |
| 45 | E. batialis | 9 | 2 | 0.-0.5 | 3,73 | 0,9 | no data | | |
| 45 | E. batialis | 9 | 6 | 0.-0.5 | 3,71 | 0,9 | no data | | |
| 46 | E. batialis | 9 | 4 | 0-0,5 | 7,32 | 0,9 | no data | | |
| 46 | E. batialis | 9 | 6 | 0.-0.5 | 11,92 | 0,9 | no data | | |
| 47 | E. batialis | 9 | 4 | 0-0,5 | 5,63 | 0,9 | no data | | |
| 47 | E. batialis | 9 | 6 | 0.-0.5 | 7,15 | 0,9 | no data | | |
| 48 | E. batialis | 9 | 4 | 0-0,5 | 0,92 | 0,9 | no data | | |
| 48 | E. batialis | 9 | 1 | 0-0,5 | 4,74 | 0,9 | no data | | |
| 48 | E. batialis | 9 | 4 | 0-0,5 | 7,08 | 0,9 | no data | | |
| 48 | E. batialis | 9 | 2 | 0.-0.5 | 0,98 | 0,9 | no data | | |
| 48 | E. batialis | 9 | 6 | 0.-0.5 | 5,86 | 0,9 | no data | | |
| 49 | E. batialis | 10 | 9 | 0-0,5 | 1,24 | 1,2 | 154,8 | 0,01 | 0,02 |
| 49 | E. batialis | 10 | 1 | 0-0,5 | 2,00 | 1,2 | 154,8 | 0,01 | |
| 49 | E. batialis | 10 | 4 | 0-0,5 | 2,51 | 1,2 | 154,8 | 0,02 | |
| 49 | E. batialis | 10 | 12 | 0-0,5 | 1,13 | 1,2 | 154,8 | 0,01 | |
| 49 | E. batialis | 10 | 2 | 0.-0.5 | 3,06 | 1,2 | 154,8 | 0,02 | |
| 49 | E. batialis | 10 | 6 | 0.-0.5 | 3,39 | 1,2 | 154,8 | 0,02 | |
| 50 | E. batialis | 10 | 4 | 0-0,5 | 2,22 | 1,2 | 154,8 | 0,01 | |
| 50 | E. batialis | 10 | 2 | 0.-0.5 | 1,51 | 1,2 | 154,8 | 0,01 | |
| 50 | E. batialis | 10 | 6 | 0.-0.5 | 2,18 | 1,2 | 154,8 | 0,01 | |
| 51 | E. batialis | 10 | 4 | 0-0,5 | 3,57 | 1,2 | 154,8 | 0,02 | |
| 51 | E. batialis | 10 | 6 | 0.-0.5 | 3,06 | 1,2 | 154,8 | 0,02 | |
| 52 | E. batialis | 10 | 4 | 0-0,5 | 3,41 | 1,2 | 154,8 | 0,02 | |
| 52 | E. batialis | 10 | 2 | 0.-0.5 | 2,33 | 1,2 | 154,8 | 0,02 | |
| 52 | E. batialis | 10 | 6 | 0.-0.5 | 3,49 | 1,2 | 154,8 | 0,02 | |
| 53 | E. batialis | 10 | 4 | 0-0,5 | 1,79 | 1,2 | 154,8 | 0,01 | |
| 53 | E. batialis | 10 | 6 | 0.-0.5 | 2,31 | 1,2 | 154,8 | 0,01 | |

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | DMn | DMn average per station |
|---|---|---|---|---|---|---|---|---|---|
| 44 | B. spissa | 7 | 2 | 0-0,5 | 17,83 | 2,2 | no data | | |
| 44 | B. spissa | 7 | 5 | 0-0,5 | 36,28 | 2,2 | no data | | |
| 44 | B. spissa | 7 | 8 | 0-0,5 | 27,00 | 2,2 | no data | | |
| 44 | B. spissa | 7 | 12 | 0-0,5 | 39,70 | 2,2 | no data | | |
| 45 | B. spissa | 7 | 2 | 0-0,5 | 19,23 | 2,2 | no data | | |
| 45 | B. spissa | 7 | 5 | 0-0,5 | 22,01 | 2,2 | no data | | |
| 45 | B. spissa | 7 | 8 | 0-0,5 | 57,29 | 2,2 | no data | | |
| 45 | B. spissa | 7 | 12 | 0-0,5 | 32,21 | 2,2 | no data | | |
| 46 | B. spissa | 7 | 2 | 0-0,5 | 38,09 | 2,2 | no data | | |
| 46 | B. spissa | 7 | 5 | 0-0,5 | 30,47 | 2,2 | no data | | |
| 46 | B. spissa | 7 | 8 | 0-0,5 | 15,07 | 2,2 | no data | | |
| 46 | B. spissa | 7 | 12 | 0-0,5 | 28,81 | 2,2 | no data | | |
| 47 | B. spissa | 7 | 2 | 0-0,5 | 15,73 | 2,2 | no data | | |
| 47 | B. spissa | 7 | 5 | 0-0,5 | 19,65 | 2,2 | no data | | |
| 47 | B. spissa | 7 | 8 | 0-0,5 | 40,36 | 2,2 | no data | | |
| 47 | B. spissa | 7 | 12 | 0-0,5 | 25,62 | 2,2 | no data | | |
| 48 | B. spissa | 7 | 2 | 0-0,5 | 23,37 | 2,2 | no data | | |
| 48 | B. spissa | 7 | 5 | 0-0,5 | 9,61 | 2,2 | no data | | |
| 49 | B. spissa | 7 | 2 | 0-0,5 | 19,23 | 2,2 | no data | | |
| 49 | B. spissa | 7 | 5 | 0-0,5 | 37,67 | 2,2 | no data | | |
| 49 | B. spissa | 7 | 12 | 0-0,5 | 27,29 | 2,2 | no data | | |
| 50 | B. spissa | 7 | 2 | 0-0,5 | 176,40 | 2,2 | no data | | |
| 50 | B. spissa | 7 | 5 | 0-0,5 | 52,07 | 2,2 | no data | | |
| 50 | B. spissa | 7 | 12 | 0-0,5 | 48,70 | 2,2 | no data | | |
| 51 | B. spissa | 7 | 2 | 0-0,5 | 19,99 | 2,2 | no data | | |
| 51 | B. spissa | 7 | 5 | 0-0,5 | 66,24 | 2,2 | no data | | |
| 51 | B. spissa | 7 | 12 | 0-0,5 | 52,07 | 2,2 | no data | | |
| 52 | B. spissa | 8 | 2 | 0-0,5 | 29,70 | 1,9 | 158,8 | 0,19 | 0,36 |
| 52 | B. spissa | 8 | 5 | 0-0,5 | 72,02 | 1,9 | 158,8 | 0,45 | |
| 52 | B. spissa | 8 | 8 | 0-0,5 | 25,65 | 1,9 | 158,8 | 0,16 | |
| 52 | B. spissa | 8 | 12 | 0-0,5 | 41,17 | 1,9 | 158,8 | 0,26 | |
| 53 | B. spissa | 8 | 2 | 0-0,5 | 29,27 | 1,9 | 158,8 | 0,18 | |
| 53 | B. spissa | 8 | 5 | 0-0,5 | 65,83 | 1,9 | 158,8 | 0,41 | |
| 53 | B. spissa | 8 | 8 | 0-0,5 | 85,07 | 1,9 | 158,8 | 0,54 | |
| 53 | B. spissa | 8 | 12 | 0-0,5 | 61,47 | 1,9 | 158,8 | 0,39 | |
| 54 | B. spissa | 8 | 2 | 0-0,5 | 56,79 | 1,9 | 158,8 | 0,36 | |
| 54 | B. spissa | 8 | 5 | 0-0,5 | 96,07 | 1,9 | 158,8 | 0,60 | |
| 54 | B. spissa | 8 | 8 | 0-0,5 | 64,18 | 1,9 | 158,8 | 0,40 | |
| 54 | B. spissa | 8 | 12 | 0-0,5 | 73,67 | 1,9 | 158,8 | 0,46 | |
| 55 | B. spissa | 8 | 2 | 0-0,5 | 13,82 | 1,9 | 158,8 | 0,09 | |
| 55 | B. spissa | 8 | 5 | 0-0,5 | 25,61 | 1,9 | 158,8 | 0,16 | |
| 55 | B. spissa | 8 | 8 | 0-0,5 | 29,69 | 1,9 | 158,8 | 0,19 | |
| 55 | B. spissa | 8 | 12 | 0-0,5 | 33,77 | 1,9 | 158,8 | 0,21 | |
| 56 | B. spissa | 8 | 2 | 0-0,5 | 32,35 | 1,9 | 158,8 | 0,20 | |
| 56 | B. spissa | 8 | 5 | 0-0,5 | 160,07 | 1,9 | 158,8 | 1,01 | |
| 56 | B. spissa | 8 | 8 | 0-0,5 | 85,01 | 1,9 | 158,8 | 0,54 | |
| 56 | B. spissa | 8 | 12 | 0-0,5 | 68,27 | 1,9 | 158,8 | 0,43 | |
| 57 | B. spissa | 8 | 2 | 0-0,5 | 62,74 | 1,9 | 158,8 | 0,40 | |
| 57 | B. spissa | 8 | 5 | 0-0,5 | 56,12 | 1,9 | 158,8 | 0,35 | |
| 57 | B. spissa | 8 | 8 | 0-0,5 | 65,33 | 1,9 | 158,8 | 0,41 | |
| 57 | B. spissa | 8 | 12 | 0-0,5 | 54,11 | 1,9 | 158,8 | 0,34 | |
| 58 | B. spissa | 8 | 3 | 0-0,5 | 14,04 | 1,9 | 158,8 | 0,09 | |
| 58 | B. spissa | 8 | 8 | 0-0,5 | 96,10 | 1,9 | 158,8 | 0,61 | |
| 58 | B. spissa | 8 | 12 | 0-0,5 | 63,73 | 1,9 | 158,8 | 0,40 | |
| 59 | B. spissa | 8 | 5 | 0-0,5 | 45,63 | 1,9 | 158,8 | 0,29 | |
| 59 | B. spissa | 8 | 12 | 0-0,5 | 59,80 | 1,9 | 158,8 | 0,38 | |
| 60 | B. spissa | 9 | 2 | 0-0,5 | 83,05 | 2,2 | no data | | |
| 60 | B. spissa | 9 | 5 | 0-0,5 | 144,96 | 2,2 | no data | | |
| 60 | B. spissa | 9 | 8 | 0-0,5 | 121,06 | 2,2 | no data | | |
| 60 | B. spissa | 9 | 12 | 0-0,5 | 119,73 | 2,2 | no data | | |
| 61 | B. spissa | 9 | 2 | 0-0,5 | 133,37 | 2,2 | no data | | |
| 61 | B. spissa | 9 | 5 | 0-0,5 | 273,02 | 2,2 | no data | | |
| 61 | B. spissa | 9 | 8 | 0-0,5 | 181,53 | 2,2 | no data | | |
| 61 | B. spissa | 9 | 12 | 0-0,5 | 165,67 | 2,2 | no data | | |
| 63 | B. spissa | 9 | 8 | 0-0,5 | 62,66 | 2,2 | no data | | |
| 63 | B. spissa | 9 | 12 | 0-0,5 | 71,88 | 2,2 | no data | | |
| 64 | B. spissa | 9 | 5 | 0-0,5 | 152,53 | 2,2 | no data | | |
| 64 | B. spissa | 9 | 8 | 0-0,5 | 94,90 | 2,2 | no data | | |
| 64 | B. spissa | 9 | 12 | 0-0,5 | 60,20 | 2,2 | no data | | |
| 65 | B. spissa | 9 | 2 | 0,5-1 | 264,03 | 2,2 | no data | | |
| 65 | B. spissa | 9 | 5 | 0,5-1 | 41,21 | 2,2 | no data | | |
| 65 | B. spissa | 9 | 8 | 0,5-1 | 177,07 | 2,2 | no data | | |
| 65 | B. spissa | 9 | 12 | 0,5-1 | 118,65 | 2,2 | no data | | |
| 67 | B. spissa | 9 | 2 | 0,5-1 | 79,88 | 2,2 | no data | | |
| 67 | B. spissa | 9 | 5 | 0,5-1 | 163,35 | 2,2 | no data | | |
| 67 | B. spissa | 9 | 8 | 0,5-1 | 164,15 | 2,2 | no data | | |
| 67 | B. spissa | 9 | 12 | 0,5-1 | 116,29 | 2,2 | no data | | |
| 68 | B. spissa | 9 | 2 | 0,5-1 | 88,22 | 2,2 | no data | | |
| 68 | B. spissa | 9 | 12 | 0,5-1 | 88,00 | 2,2 | no data | | |

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | DMn | DMn average per station |
|---|---|---|---|---|---|---|---|---|---|
| 6 | U. cf. graciliformis | 6 | 2 | 0-0,5 | 26,15 | 2,7 | 53,6 | 0,49 | 0,56 |
| 6 | U. cf. graciliformis | 6 | 4 | 0-0,5 | 22,35 | 2,7 | 53,6 | 0,42 | |
| 7 | U. cf. graciliformis | 6 | 1 | 0-0,5 | 13,30 | 2,7 | 53,6 | 0,25 | |
| 7 | U. cf. graciliformis | 6 | 4 | 0-0,5 | 40,03 | 2,7 | 53,6 | 0,75 | |
| 8 | U. cf. graciliformis | 6 | 4 | 0-0,5 | 30,96 | 2,7 | 53,6 | 0,58 | |
| 9 | U. cf. graciliformis | 6 | 1 | 0-0,5 | 25,32 | 2,7 | 53,6 | 0,47 | |
| 9 | U. cf. graciliformis | 6 | 3 | 0-0,5 | 32,69 | 2,7 | 53,6 | 0,61 | |
| 11 | U. cf. graciliformis | 6 | 2 | 0-0,5 | 48,08 | 2,7 | 53,6 | 0,90 | |
| 11 | U. cf. graciliformis | 6 | 4 | 0-0,5 | 32,66 | 2,7 | 53,6 | 0,61 | |
| 12 | U. cf. graciliformis | 6 | 1 | 0-0,5 | 27,36 | 2,7 | 53,6 | 0,51 | |
| 12 | U. cf. graciliformis | 6 | 4 | 0-0,5 | 33,91 | 2,7 | 53,6 | 0,63 | |
| 62 | U. cf. graciliformis | 6 | 1 | 0.-0.5 | 28,40 | 2,7 | 53,6 | 0,53 | |
| 64 | U. akitaensis | 7 | 4 | 0-0,5 | 18,36 | 2,1 | no data | | |
| 64 | U. akitaensis | 7 | 2 | 0.-0.5 | 39,13 | 2,1 | no data | | |
| 65 | U. akitaensis | 7 | 4 | 0-0,5 | 31,72 | 2,1 | no data | | |
| 65 | U. akitaensis | 7 | 2 | 0.-0.5 | 20,62 | 2,1 | no data | | |
| 66 | U. akitaensis | 7 | 4 | 0-0,5 | 29,64 | 2,1 | no data | | |
| 66 | U. akitaensis | 7 | 6 | 0.-0.5 | 13,63 | 2,1 | no data | | |
| 67 | U. akitaensis | 7 | 4 | 0-0,5 | 31,34 | 2,1 | no data | | |
| 67 | U. akitaensis | 7 | 2 | 0.-0.5 | 24,63 | 2,1 | no data | | |
| 67 | U. akitaensis | 7 | 6 | 0.-0.5 | 26,12 | 2,1 | no data | | |
| 68 | U. akitaensis | 7 | 4 | 0-0,5 | 31,19 | 2,1 | no data | | |
| 68 | U. akitaensis | 7 | 2 | 0.-0.5 | 19,86 | 2,1 | no data | | |
| 68 | U. akitaensis | 7 | 6 | 0.-0.5 | 27,27 | 2,1 | no data | | |
| 69 | U. akitaensis | 7 | 4 | 0-0,5 | 31,49 | 2,1 | no data | | |
| 69 | U. akitaensis | 7 | 2 | 0.-0.5 | 32,20 | 2,1 | no data | | |
| 69 | U. akitaensis | 7 | 6 | 0.-0.5 | 29,12 | 2,1 | no data | | |
| 70 | U. akitaensis | 7 | 4 | 0-0,5 | 39,90 | 2,1 | no data | | |
| 70 | U. akitaensis | 7 | 2 | 0.-0.5 | 15,47 | 2,1 | no data | | |
| 70 | U. akitaensis | 7 | 6 | 0.-0.5 | 32,11 | 2,1 | no data | | |
| 71 | U. akitaensis | 7 | 5 | 0.-0.5 | 21,48 | 2,1 | no data | | |
| 71 | U. akitaensis | 7 | 2 | 0.-0.5 | 15,64 | 2,1 | no data | | |
| 72 | U. akitaensis | 7 | 2 | 0.-0.5 | 13,32 | 2,1 | no data | | |
| 72 | U. akitaensis | 7 | 6 | 0.-0.5 | 25,05 | 2,1 | no data | | |
| 73 | U. akitaensis | 7 | 2 | 0.-0.5 | 10,03 | 2,1 | no data | | |
| 73 | U. akitaensis | 7 | 5 | 0.-0.5 | 16,87 | 2,1 | no data | | |
| 74 | U. akitaensis | 8 | 4 | 0-0,5 | 53,69 | 1,4 | 227,4 | 0,24 | 0,13 |
| 74 | U. akitaensis | 8 | 2 | 0.-0.5 | 73,59 | 1,4 | 227,4 | 0,32 | |
| 74 | U. akitaensis | 8 | 5 | 0.-0.5 | 69,33 | 1,4 | 227,4 | 0,30 | |
| 75 | U. akitaensis | 8 | 4 | 0-0,5 | 29,72 | 1,4 | 227,4 | 0,13 | |
| 75 | U. akitaensis | 8 | 6 | 0.-0.5 | 54,70 | 1,4 | 227,4 | 0,24 | |
| 76 | U. akitaensis | 8 | 2 | 0.-0.5 | 26,98 | 1,4 | 227,4 | 0,12 | |
| 76 | U. akitaensis | 8 | 6 | 0.-0.5 | 28,80 | 1,4 | 227,4 | 0,13 | |
| 77 | U. akitaensis | 8 | 4 | 0-0,5 | 9,51 | 1,4 | 227,4 | 0,04 | |
| 77 | U. akitaensis | 8 | 2 | 0.-0.5 | 8,46 | 1,4 | 227,4 | 0,04 | |
| 77 | U. akitaensis | 8 | 6 | 0.-0.5 | 45,80 | 1,4 | 227,4 | 0,20 | |
| 78 | U. akitaensis | 8 | 2 | 0.-0.5 | 23,01 | 1,4 | 227,4 | 0,10 | |
| 78 | U. akitaensis | 8 | 6 | 0.-0.5 | 23,39 | 1,4 | 227,4 | 0,10 | |
| 79 | U. akitaensis | 8 | 4 | 0-0,5 | 22,02 | 1,4 | 227,4 | 0,10 | |
| 79 | U. akitaensis | 8 | 2 | 0.-0.5 | 24,39 | 1,4 | 227,4 | 0,11 | |
| 79 | U. akitaensis | 8 | 6 | 0.-0.5 | 46,83 | 1,4 | 227,4 | 0,21 | |
| 80 | U. akitaensis | 8 | 2 | 0.-0.5 | 6,28 | 1,4 | 227,4 | 0,03 | |
| 80 | U. akitaensis | 8 | 5 | 0.-0.5 | 12,29 | 1,4 | 227,4 | 0,05 | |
| 81 | U. akitaensis | 8 | 4 | 0-0,5 | 27,20 | 1,4 | 227,4 | 0,12 | |
| 81 | U. akitaensis | 8 | 2 | 0.-0.5 | 24,41 | 1,4 | 227,4 | 0,11 | |
| 82 | U. akitaensis | 8 | 2 | 0.-0.5 | 17,27 | 1,4 | 227,4 | 0,08 | |
| 82 | U. akitaensis | 8 | 6 | 0.-0.5 | 18,29 | 1,4 | 227,4 | 0,08 | |
| 83 | U. akitaensis | 8 | 4 | 0-0,5 | 26,71 | 1,4 | 227,4 | 0,12 | |
| 83 | U. akitaensis | 8 | 6 | 0.-0.5 | 18,49 | 1,4 | 227,4 | 0,08 | |
| 13 | U. akitaensis | 9 | 1 | 1-1,5 | 63,84 | 1 | no data | | |
| 13 | U. akitaensis | 9 | 3 | 1-1,5 | 41,44 | 1 | no data | | |
| 13 | U. akitaensis | 9 | 5 | 1-1,5 | 175,96 | 1 | no data | | |
| 14 | U. akitaensis | 9 | 1 | 1-1,5 | 29,24 | 1 | no data | | |
| 14 | U. akitaensis | 9 | 3 | 1-1,5 | 26,91 | 1 | no data | | |
| 14 | U. akitaensis | 9 | 6 | 1-1,5 | 79,43 | 1 | no data | | |
| 15 | U. akitaensis | 9 | 1 | 1-1,5 | 55,41 | 1 | no data | | |
| 15 | U. akitaensis | 9 | 3 | 1-1,5 | 60,78 | 1 | no data | | |
| 15 | U. akitaensis | 9 | 5 | 1-1,5 | 87,37 | 1 | no data | | |
| 84 | U. akitaensis | 9 | 4 | 0-0,5 | 29,65 | 1 | no data | | |
| 84 | U. akitaensis | 9 | 6 | 0.-0.5 | 45,43 | 1 | no data | | |
| 85 | U. akitaensis | 9 | 4 | 0-0,5 | 46,63 | 1 | no data | | |
| 85 | U. akitaensis | 9 | 2 | 0.-0.5 | 77,71 | 1 | no data | | |
| 85 | U. akitaensis | 9 | 6 | 0.-0.5 | 62,51 | 1 | no data | | |
| 86 | U. akitaensis | 9 | 4 | 0-0,5 | 24,45 | 1 | no data | | |
| 86 | U. akitaensis | 9 | 2 | 0.-0.5 | 61,07 | 1 | no data | | |
| 86 | U. akitaensis | 9 | 6 | 0.-0.5 | 67,69 | 1 | no data | | |
| 87 | U. akitaensis | 9 | 4 | 0-0,5 | 30,02 | 1 | no data | | |
| 87 | U. akitaensis | 9 | 2 | 0.-0.5 | 24,52 | 1 | no data | | |
| 87 | U. akitaensis | 9 | 6 | 0.-0.5 | 28,87 | 1 | no data | | |
| 88 | U. akitaensis | 9 | 4 | 0-0,5 | 104,08 | 1 | no data | | |
| 88 | U. akitaensis | 9 | 2 | 0.-0.5 | 20,10 | 1 | no data | | |
| 89 | U. akitaensis | 9 | 4 | 0-0,5 | 54,55 | 1 | no data | | |
| 89 | U. akitaensis | 9 | 2 | 0.-0.5 | 37,77 | 1 | no data | | |
| 89 | U. akitaensis | 9 | 6 | 0.-0.5 | 38,01 | 1 | no data | | |
| 90 | U. akitaensis | 9 | 2 | 0.-0.5 | 41,16 | 1 | no data | | |
| 90 | U. akitaensis | 9 | 6 | 0.-0.5 | 55,19 | 1 | no data | | |
| 91 | U. akitaensis | 9 | 2 | 0.-0.5 | 65,51 | 1 | no data | | |
| 91 | U. akitaensis | 9 | 6 | 0.-0.5 | 50,95 | 1 | no data | | |
| 92 | U. akitaensis | 9 | 2 | 0.-0.5 | 10,79 | 1 | no data | | |
| 92 | U. akitaensis | 9 | 6 | 0.-0.5 | 70,93 | 1 | no data | | |
| 93 | U. akitaensis | 9 | 2 | 0.-0.5 | 47,44 | 1 | no data | | |
| 93 | U. akitaensis | 9 | 6 | 0.-0.5 | 70,19 | 1 | no data | | |
| 94 | U. akitaensis | 9 | 5 | 0,5-1 | 91,65 | 1 | no data | | |
| 94 | U. akitaensis | 9 | 2 | 0.5-1 | 12,72 | 1 | no data | | |
| 94 | U. akitaensis | 9 | 6 | 0.5-1 | 54,61 | 1 | no data | | |
| 95 | U. akitaensis | 9 | 5 | 0,5-1 | 53,94 | 1 | no data | | |
| 95 | U. akitaensis | 9 | 2 | 0.5-1 | 172,32 | 1 | no data | | |
| 95 | U. akitaensis | 9 | 6 | 0.5-1 | 28,94 | 1 | no data | | |
| 96 | U. akitaensis | 9 | 4 | 0,5-1 | 64,88 | 1 | no data | | |
| 96 | U. akitaensis | 9 | 2 | 0.5-1 | 58,96 | 1 | no data | | |

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | D$_{Mn}$ | D$_{Mn}$ average per station |
|---|---|---|---|---|---|---|---|---|---|
| 11 | N. labradorica | 7 | 4 | 0-0,5 | 45,20 | 2,3 | no data | | |
| 9 | N. labradorica | 7 | 4 | 0-0,5 | 101,06 | 2,3 | no data | | |
| 42 | N. labradorica | 7 | 5 | 0-0,5 | 57,37 | 2,3 | no data | | |
| 43 | N. labradorica | 7 | 1 | 0-0,5 | 118,84 | 2,3 | no data | | |
| 43 | N. labradorica | 7 | 6 | 0-0,5 | 97,63 | 2,3 | no data | | |
| 14 | N. labradorica | 8 | 4 | 0-0,5 | 57,32 | 4 | 81,1 | 0,71 | 1,24 |
| 15 | N. labradorica | 8 | 1 | 0-0,5 | 50,31 | 4 | 81,1 | 0,62 | |
| 16 | N. labradorica | 8 | 3 | 2-2,5 | 23,40 | 4 | 81,1 | 0,29 | |
| 17 | N. labradorica | 8 | 4 | 2-2,5 | 63,18 | 4 | 81,1 | 0,78 | |
| 18 | N. labradorica | 8 | 1 | 4,0-5,0 | 276,98 | 4 | 81,1 | 3,41 | |
| 21 | N. labradorica | 8 | 4 | 4,0-5,0 | 157,87 | 4 | 81,1 | 1,95 | |
| 22 | N. labradorica | 8 | 3 | 4,0-5,0 | 189,49 | 4 | 81,1 | 2,34 | |
| 23 | N. labradorica | 8 | 4 | 4,0-5,0 | 35,09 | 4 | 81,1 | 0,43 | |
| 25 | N. labradorica | 8 | 4 | 4,0-5,0 | 54,58 | 4 | 81,1 | 0,67 | |
| 26 | N. labradorica | 10 | 3 | 0-0,5 | 27,58 | 4 | 391,3 | 0,070 | 0,20 |
| 27 | N. labradorica | 10 | 3 | 0-0,5 | 51,45 | 4 | 391,3 | 0,131 | |
| 28 | N. labradorica | 10 | 4 | 0-0,5 | 72,33 | 4 | 391,3 | 0,185 | |
| 29 | N. labradorica | 10 | 1 | 0-0,5 | 169,29 | 4 | 391,3 | 0,433 | |

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | D$_{Mn}$ | D$_{Mn}$ average per station |
|---|---|---|---|---|---|---|---|---|---|

| Specimen id | Species | Station | Chamber F= | Sed depth (cm) | Mn/Ca umol/mol | Average living depth cm | Mn/Ca$_{pw}$ at ALD umol/mol | DMn | DMn average per station |
|---|---|---|---|---|---|---|---|---|---|
| 17 | C. fimbriata | 7 | 1 | 0-0,5 | 70,03 | 2,7 | no data | | |
| 19 | C. fimbriata | 7 | 1 | 2,5-3 | 124,65 | 2,7 | no data | | |
| 23 | C. fimbriata | 8 | 1 | 4,0-5,0 | 41,42 | 5,1 | 38,9 | 1,07 | 1,77 |
| 23 | C. fimbriata | 8 | 1 | 4,0-5,0 | 78,80 | 5,1 | 38,9 | 2,03 | |
| 24 | C. fimbriata | 8 | 1 | 4,0-5,0 | 86,32 | 5,1 | 38,9 | 2,22 | |
| 29 | C. fimbriata | 9 | 1 | 1-1,5 | 94,98 | 5 | no data | | |
| 30 | C. fimbriata | 9 | 1 | 1-1,5 | 81,85 | 5 | no data | | |
| 31 | C. fimbriata | 9 | 1 | 3-3,5 | 199,08 | 5 | no data | | |
| 32 | C. fimbriata | 9 | 1 | 3-3,5 | 228,21 | 5 | no data | | |
| 33 | C. fimbriata | 9 | 1 | 3-3,5 | 69,26 | 5 | no data | | |
| 34 | C. fimbriata | 9 | 1 | 3-3,5 | 95,37 | 5 | no data | | |
| 35 | C. fimbriata | 9 | 1 | 3-3,5 | 184,99 | 5 | no data | | |
| 36 | C. fimbriata | 9 | 1 | 3-3,5 | 231,29 | 5 | no data | | |
| 37 | C. fimbriata | 9 | 1 | 3-3,5 | 110,20 | 5 | no data | | |
| 38 | C. fimbriata | 9 | 1 | 3-3,5 | 86,94 | 5 | no data | | |

**PORE WATER**

| Station | sedm depth cm | mid depth cm | Mn umol/l |
|---|---|---|---|
| 10 | bottom water | bottom water | 0,1 |
| | 0-0.5 | 0,25 | 1,1 |
| | 0.5-1 | 0,75 | 1,7 |
| | 1-1.5 | 1,25 | 1,5 |
| | 1.5-2 | 1,75 | 1,6 |
| | 2-3 | 2,5 | 3,6 |
| | 3-4 | 3,5 | 3,9 |
| | 4-5 | 4,5 | 4,5 |
| | 5-6 | 5,5 | 5,0 |
| | 6-7 | 6,5 | 4,6 |
| | 8-9 | 8,5 | 4,5 |
| | 9-10 | 9,5 | 3,8 |
| | 10-12 | 11 | 2,9 |
| | 12-14 | 13 | 1,7 |
| | 14-16 | 15 | 1,3 |
| | 16-18 | 17 | 1,2 |
| | 18-20 | 19 | 1,1 |
| | | | |
| 8 | bottom water | bottom water | 0,1 |
| | 0-0.5 | 0,25 | 1,1 |
| | 0.5-1 | 0,75 | 2,1 |
| | 1-1.5 | 1,25 | 2,3 |
| | 1.5-2 | 1,75 | 1,6 |
| | 2-3 | 2,5 | 1,2 |
| | 3-4 | 3,5 | 0,8 |
| | 4-5 | 4,5 | 0,5 |
| | 5-6 | 5,5 | 0,4 |
| | 6-7 | 6,5 | 0,4 |
| | 7-8 | 7,5 | 0,4 |
| | 8-9 | 8,5 | 0,6 |
| | 9-10 | 9,5 | 0,4 |
| | 10-12 | 11 | 0,4 |
| | 12-14 | 13 | 0,4 |
| | 14-16 | 15 | 0,4 |
| | 16-18 | 17 | |
| | 18-20 | 19 | 0,9 |
| | | | |
| 6 | bottom water | bottom water | 0,0 |
| | 0-0.5 | 0,25 | 1,1 |
| | 0.5-1 | 0,75 | 1,4 |
| | 1-1.5 | 1,25 | 1,2 |
| | 1.5-2 | 1,75 | 0,6 |
| | 2-3 | 2,5 | 0,5 |
| | 3-4 | 3,5 | 1,0 |
| | 4-5 | 4,5 | 0,3 |
| | 5-6 | 5,5 | 0,3 |
| | 6-7 | 6,5 | 0,3 |
| | 7-8 | 7,5 | 0,3 |
| | 8-9 | 8,5 | 0,4 |
| | 9-10 | 9,5 | 0,2 |
| | 10-12 | 11 | 0,3 |
| | 12-14 | 13 | 0,4 |
| | 14-16 | 15 | 0,6 |
| | 16-18 | 17 | 0,6 |
| | 18-20 | 19 | 1,1 |