

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  $D_{Mn}$  values only mentioned in the text so that I strongly encourage the authors to provide this data in tables. In the case of  $D_{Mn}$  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

### **Comments by page and line number:**

#### **major comments:**

#### **page 5: concerning the methods used**

l.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?

l.6: which mass was measured for Mg? (it is not in the list in l. 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?

l.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?

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 NIST610 calibration values used? Could this data be provided in a supplementary table?

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?

#### **page 6**

l. 29: please provide table with Mn/Ca measurements (and also for calculated DMn for stations 6,8,10)

#### **page 8**

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.

l.27/1.28: 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.

#### **page 9**

l.19-29: since the  $D_{Mn}$  values are not listed in the paper (no table and no figure) I cannot assess this part, please provide data

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?)

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?

**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.

**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 redoxchemistry, however, only very little focus lies on the paleo implications of this study. Please move the discussion of the TROXCHEM model and the redox chemistrz into a different paragraph.

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

- 1) bottom water oxygenation (where is the data- regressions/ statistics and or figures? e.g. regression of foram Mn and BWO) representing this?
- 2) Mn redox chemistry (where is the data? regressions? statistics)
- 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.

**minor comments:**

**page 1**

l.16: calcium carbonate tests

l.19: define BWO or spell out; what are differences exactly?

l.20: where is this entangling happening in manuscript?

l.24: At each station, Mn/Ca (omit "the")

also Mn/Ca is a ratio of concentrations, not a concentration

l.31: the forams are not the tools, but carry the proxy -> rephrase

l.32: has a high...

## **page 2**

l.4: have been shown to reflect carbonate chemistry (omit "the")

l.18: are oxygenated and sediments are anoxic... add "and sediments are anoxic"

l.27: omit "the" before shallow

l.28: than not then

l.32: why 33 (random?) also omit "the" before foraminifera and change to foraminiferal

## **page 3**

l.17: change to sth. like this as it is confusing otherwise: "At each site, three separate..."

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?

l.25: Whole sample centrifuged or subsample?

l.30: how much HCl was added? final conc.? What samples were used for storage? Were they acid cleaned?

## **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?

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?

l.13: Change title so it is more precise: e.g. "Foraminifera: sampling an elemental concentrations"

l.14 et al.

l.17: Plummer slides? Are they micropaleoslides?

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?

**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?

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.

**page 6**

l.6: what exactly is pore water chemistry? which parameters?

l.8: in-sediment depth? what depth is this?

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)").

**page 7**

l. 28: lowest **average** (?) Mn/Ca values

**page 8:**

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?

**page 9:**

please add references to figures and tables (also the "new" one with the Mn/Ca and  $D_{Mn}$  values)

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

l. 26: delete "are"

**page 10:**

l. 20: fluxes must still be relatively

l.32 remove "study" at end of sentence

**page 11:**

l.6: fig 2 not fig1

last paragraph: good discussion of Mn redox chemistry and availability, but maybe move up in the manuscript, as it is in general relevant for the incorporation of Mn into foraminifera and not necessarily part of the "paleo implications only".