Dear Editor,

We would like to thank you for your comment. In your comment you point out a common misconception, in which the depth at which organisms are recovered is mistakenly interpreted as also being the depth at which they calcify. As you rightfully indicate this is not necessarily so. This is also one of the main rationales underlying our study and we hoped that this is clear throughout the manuscript. Already at lines 67 and 68 of the original manuscript we hence tried to highlight the difference between living depth and calcification depth. This sentence is somewhat rephrased now to make this more clear and now reads: "Linking foraminiferal test chemistry with pore water chemistry requires in-depth knowledge of, 1) how early diagenesis in sediments affects pore water chemistry, 2) the habitat preference of the foraminiferal species, 3) foraminiferal migration (and the depth at which they calcify) within the uppermost sediment layer."

You also pointed out the differences in living depth between *Uvigerina peregrina* and *U. mediterranea*. At lines 366 and 368 we referred to *U. mediterranea* living deeper than *U. peregrina*, similar to your comment. This is now emphasized in the revised version at lines 359-361: "Both *Uvigerina mediterranea* and *M. barleeanus* were in the Gulf of Lyons found to occupy shallow to intermediate infaunal habitat, with *U. peregrina* having a somewhat shallower infaunal habitat (Fontanier et al., 2008)". This is based on existing literature and counts on living foraminifera, which we do not dispute. We fully agree that the difference observed is more likely due to a difference in calcification depth. We indicated this at lines 372-374 of the original manuscript. See also lines 412-413 of the original manuscript, pertaining to the same.

For *Melonis barleanus* Mn uptake is fully in line with its deeper habitat, and depth habitat and calcification depth probably coincide. See also lines 386-387 and 450-452 of the original manuscript. Although we suggest that *M. barleanus* potentially "travels" more along a depth gradient in the sediment (lines 469-470), this would still be consistently deeper than the depth habitats of both *U. peregrina* and *U. mediterranea*. In the revised manuscript this is therefore now changed to: "This is in line with the depth habitat of *M. barleeanus* being consistently deeper and this species traveling more actively through the redox zones than *U. mediterranea* or *U. peregrina*."

In the revised version we now also added at lines 390-394: "*Melonis barleeanus*, generally considered an intermediate-infaunal species (Fontanier et al., 2002, 2008), contains the highest concentrations of Mn in its test, which is in line with the deepest habitat of the species studied here", to better reflect this fact.

We hope that our answers and the additional changes convince the editor to forward our manuscript.

Many thanks, also on behalf of all other co-authors,

Gert-Jan Reichart

Original review:

Dear Editor,

We are glad to have received two helpful sets of comments. Below we have copied the reviewer's comments one at the time and indicate how we have addressed them or (in a few cases) argue why we respectfully disagree. We would like you to consider the revised manuscript for publication in Biogeosciences.

Anonymous Referee #1

Received and published: 2 April 2018

This study looks at the potential for the Mn/Ca of benthic foraminiferal calcite to act as a proxy for pore water oxygenation and labile organic matter. In order to do this, the authors have measured the pore water chemistry as well as the Mn/Ca geochemistry of 4 species of benthic foraminifera from a depth transect of cores in the Mediterranean. Analysis focuses on the living foraminifera recovered from the upper 10 cm of each of these core sites. Ni Fhlaithearta et al., find that the Mn/Ca of benthic foraminifera reflects the pore water environment from which they calcified and the flux of organic material to the site. However, the amount of incorporation and variability in Mn/Ca incorporation is governed by species specific KD as well as ecological and depth preferences in addition to environmentally controlled pore-water conditions.

Overarching comments/questions: The authors analyzed select foraminifera species from specific core depths, however much of the article relies on speculation and inferences from existing literature as to the calcification or habitat depth of these same species. This is clearly extremely relevant to the interpretation of any pore water proxy. Is there a reason that species abundances with depth (at least for the relevant species) has not been included here? It would seem that inclusion of this could clarify some questions of habitat preference, and the degree to which this varies between sites.

Author's response: As referee 1 states, the species abundances with depth have not been added to this manuscript as they were published before already. Included in the manuscript is a brief reference to the average living depth (ALD_{10}), for *U. mediterranea* and *U. peregrina* (line 363-364). The species abundances in these samples have previously been reported in Fontanier et al., (2008). We are aware that it was recently published that partitioning with respect to Mn may vary between species (Barras et al., in press). This was not known at the time the discussion paper was submitted. We now added this to the discussion and refer to the recent paper by Barras et al. (in press) and added to the text:

New Lines 429-434: "Recently Barras et al. (2018), also using controlled growth experiments, showed however that Mn partitioning in B. marginata differs from that in *A. tepida*, with that in *B. marginata* being close to one and that of A. tepida being 4 times lower. Inter-specific differences are considerable and hence an impact of biomineralization on Mn incorporation can not be disregarded."

Authors's changes to the manuscript: A summary of the species abundances, based on Fontanier et al., (2008) table 5 of that paper, has been added to the text at lines 348-350: 'Both *Uvigerina mediterranea* and M. barleeanus were in the Gulf of Lyons found to occupy shallow to intermediate infaunal habitat, with *U. peregrina* having a somewhat shallower infaunal habitat (Fonatnier et al., 2008).'

It seems to me that the greatest barrier to application of these results to the fossil record is the issue of preservation. The authors discuss this clearly. However, I wonder if the research could not be even more impactful with a statement as to how this could be circumvented (at least in some environments). For example, did the authors undertake any comparative analyses of non-living and potentially altered specimens from the same cores? Could Mn-rich coatings be identified using the same LA techniques applied here to living foraminifera?

Author's response: One way to circumnavigate issues with preservation of the original Mn signal and hence the possibility to apply our approach to the fossil record, is by specifically targeting *H. elegans* for Mn/Ca measurements. The aragonitic nature of this organism prevents overgrowths. Such an approach was previously applied for the reconstruction of the paleo-environment during deposition sapropel S1 in the Mediterranean (Ni Fhlaithearta et al., 2010).

For the other species (*Uvigerina mediterranea, Uvigerina peregrina* and *Melonis barleeanus*) studied in this paper it would potentially be possible to analyse fossil specimens using selection criteria (for example, degree of visible alteration, diagenetic Fe incorporation, etc.). With laser ablation measurements it is furthermore possible to adjust the analytical window in such a way as to exclude diagenetic coatings (based on the trace metal signature within the test wall), which has been described in several papers (e.g. Reichart et al., 2003).

Author's changes in the manuscript: We added to the discussion a sentence describing this potential approach at lines 307-312 'The fact that this study was based on living foraminifera circumvents potential complications due to Mn-rich coatings. Such coatings would likely not affect the aragonitic shell of *H. elegans* (Ní Fhlaithearta et al., 2010), but might interfere when analyzing fossil calcite shells. Still, a spatially resolved analytical technnique like LA-ICP-MS allows detecting such coatings also in fossil specimens.'

27 – and 52-53 – "surface and bottom water" – consider rephrasing surface (pelagic or near-surface?), as most planktic foraminifera do not actually reflect surface conditions

Author Response: No reference to 'surface and bottom water' is seen at line 27. In line 52-53, 'surface' has been changed to 'pelagic'.
Author's changes to the manuscript: 52-53: 'Both pelagic and bottom water conditions…'

262 – What was the detection limit and how was it established?

The detection limit differs for each ablation and is a combination of the number of scans collected (acquisition time) and the background for a certain element. These levels are hence calculated using data reduction software for each single ablation profile. For Mn/Ca in the foraminiferal shells analysed here detection limits were on the order of 1.2 umol/mol. This is indicated in figure 6 of the manuscript.

367 – peregrina
Author Response: changed accordingly.

407 – what is the p value? If the correlation is not significant, is it still meaningful? Also for Fig. 7, can you include the p values?

The exact p-values is not calculated. The fact that it is over 0.05 indicates that, in view of the number of samples, it is not significant. This is stated in the manuscript. The correlation is indeed included as the high value hint towards a relationship. This is included because although a high p-value implies that a statistical significant correlation cannot be proven, it does not exclude a relation may still exist.

412-413- where was U. peregrina actually found in these sample? In relation to U. mediterranea?

Uvigerina mediterranea has indeed been classified as intermediate to shallow infaunal and *U. peregrina* as shallow infaunal at this location (Fontanier et al., 2008). The somewhat different incorporation of Mn in U. peregrina indeed suggests that it calcifies somewhat more shallow, which is in line with the microhabitat study. This is now clarified in the revised manuscript (lines 416-417).

Anonymous Referee #2

Received and published: 27 May 2018

This manuscript aims to understand Mn incorporation into benthic foraminifera and explore its potential use for reconstructing pore water redox condition and organic matter content of sediments. Although the topic is potentially very interesting I have serious concerns about the analytical side of Laser ablation measurements. The authors should clarify these issues before 'interpretation/discussion' part of the manuscript can be evaluated. Therefore, I recommended major revision for this work. Below, I summarised the questions for the analytical part of the work. 1- Detection limits for Mn/Ca measurements. Mn values in ontogenetic (i.e. not altered)foraminiferal calcite is very low (umol/mols) which make it challenging to accurately quantify with laser ablation measurements. Usually in our lab we use large laser spot size and energy to get sufficient signal to noise ratio (>100). The authors in this study
provided very basic description of analytical procedures in the method section, which overshadows the result and discussion as there is no assurance on the quality of the measurements.

We agree with the reviewer that the analyses of Mn in foraminiferal test is analytically challenging. We have invested much effort in improving this type of analyses since they were published for the first time (Reichart et al., 2003). Currently we are able to not only analyse Mn/Ca in benthic foraminifera, but are now also able to reliably analyse Mn/Ca in planktonic foraminifera (e.g. Steinhardt et al., 2014). The analytical procedures have been

described in detail in several publications, which we refer to (e.g. Koho et al., 2015; 2017). Matrix matched standards were used to verify the analytical procedures and consistency.

The main concern I have is lack of any estimation on detection limits of their method. Fig 2 shows typical ablation profile BUT the Mn signal to noise ratio is very low (<10). Such low noise to signal ratios usually correspond to very noisy measurements (large error bars), which in fact is a common feature of the data presented in this work (figs 5,6,7). In fig 6a, there are labels 'LD' which I presume indicate detection limits and they are 1umol/mol. If this is true detection limit then majority of the data presented in this work (in exception of data for Melonis) has very little analytical base. Simply it is too close to detection limits compared to error bars and therefore statistically indistinguishable from noise. The authors should really accurately estimate their errors in the background (LD = 2SD of the variance in the background signal) and also variance in the signal itself. This is crucial for interpretation of the data. For example, the summary in fig 7 as it presented now shows no trends as the errors are huge and horizontal line is the best solution for these plots. Note, if 1 umol/mol is the detection limit, then more than 60% of the data is within the error bar from the noise.

We are very much aware of the fact the analyses are close to the detection limit. For each profile the detection limit was calculated already according to the procedure suggested by the reviewer. We also know that part of the inter species variability will be due to analytical issues, which is exactly why we have discussed this as a separate issue. We have tried to rephrase this somewhat to accommodate the referees concern. Lines 480-482: 'Although the analyses of foraminiferal test Mn/Ca is challenging, which adds to the inter-specimen variability, we observe systematic differnces between species in Mn/Ca variability.'.

2- Inappropriate standards for calibration. The authors used NIST610 for Mn/Ca calibration. This standard has _400ppm of Mn, which is >10,000 times higher than typical foraminifera values. It is advisable to use Nist 612,614 pair for this kind of application to avoid artefacts/noise in calibration. The typical LA-ICPMS will give 3-5% reproducibility on NIST glass. Considering that calibration is one point calibration and 0=blank, the 5% variability at 400ppm will result in large variance at few ppbs level. Considering very low noise/signal ratio (see above) all propagated errors will case huge variance in the resulting data. I am afraid this has to be fixed before discussing the science behind Mn incorporation into foraminifera.

When we would do these analyses today we might follow a different analytical approach. The reason for using the NIST610 standard at that time was the large range between species and with depth we had observed already. Moreover, studies into the fundamentals of laser ablation ICP-MS analyses at the ETH had at the time shown that the absorption behaviour of the lower concentrated NIST lead to significant different particle size distributions, which could influence results, especially when analyzing foraminiferal tests.
We agree that for the lower concentrations pressed powders or an alternative matrix-matched standard might have been better. These analyses are, however, already performed some time ago and to our opinion we did all possible effort at that time to make sure we included as much cross-checks as possible. We used for instance a matrix-matched carbonate standard which we also analysed off line to check our results. The analyses have been performed in two independent laboratories (ETH, Switserland and Utrecht University, The Netherlands), with different machines (Micromass Platform and Elan 6100) and using different software packages (Glitter and LamTrace). Results of cross calibrated samples were identical as well as the results of the matrix matched standard. The error is admittedly larger than what it would be when we do these analyses these days, but in view of the large observed differences they still are very useful.
We have now added several lines to the methods section explaining the followed procedure and potential caveats at lines 181-185: 'For Mn this standard showed a precission better than 3% over all analyses, at ETH and UU, and with an offset of less than 5% from an off line determined (solution ICP-AES) concentration analyzing discrete sub-samples. The matrix matched standard is routinely included in the analyses and has been monitored since 2010 (Duenas Bohorquez et al., 2011).'

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Minor comments
- Measurements in the lab should be validated by their lab publication/s therefore sections 211-215 cannot assure the accuracy of the measurements. It has been mentioned in lines 181-182 that calcite standard were analysed for consistence. Data for this reproducibility will be the best indication of accuracy and reproducibility of the method and has to be reported.

The publications we refer to in lines 211-215 are actually from our lab. This is now indicated in this section and also a reference to Duenas Bohorquez et al. (2011), which gives data on the long time accuracy of standards. The accuracy for the matrix-matched calcite standard has been added to the manuscript at lines 181-185

- Section 2.5/2.5.1/2.5.2 (lines 217-239). It is necessary to break this down in sections if there are only 2 sentences in each section?
These sections have been combined into a single section 2.5.

Manganese incorporation in living (stained) benthic foraminiferal shells: A bathymetric and in-sediment study in the Gulf of Lions (NW Mediterranean).

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Keywords: Benthic foraminifera, minor/trace metals, calibration study, Gulf of Lions, Mn/Ca

Abstract

Manganese geochemistry in deep-sea sediments is known to vary greatly over the first few centimeters, which overlaps with the in-sediment depth habitats of several benthic foraminiferal species. Here we investigated manganese incorporation in benthic foraminiferal shell carbonate across a 6-station depth transect in the Gulf of Lions, NW Mediterranean to unravel the impacts of foraminiferal ecology and Mn pore water geochemistry. Over this transect water depth increases from 350 to 1987 m, while temperature (~13˚C) and salinity (~38.5) remained relatively constant. Manganese concentrations in the tests of living (Rose Bengal stained) benthic foraminiferal specimens of *Hoeglundina elegans*, *Melonis barleeanus, Uvigerina mediterranea*, *Uvigerina peregrina* were measured using laser ablation inductively coupled mass spectrometry (laser ablation ICP-MS). Pore water manganese concentrations show a decrease from shallow to deeper waters, which corresponds to a generally decreasing

organic matter flux with water depth. Differences in organic matter loading at the sediment water interface affects oxygen penetration depth into the sediment and hence Mn pore water profiles. Mn/Ca values for the investigated foraminiferal species reflect pore water geochemistry and species-specific microhabitat in the sediment. The observed degree of variability within a single species is in–line with know ranges in depth habitat and gradients in redox conditions. Both Mn/Ca ratio and inter-specific variability hence reflect past Mn cycling and related early diagenetic processes within the sediment, making this a potential tool for bottom-water oxygenation and organic-matter fluxes. Dynamics of both in-sediment foraminiferal depth habitats and Mn cycling, however, limit the application of such a proxy to settings with relatively stable environmental conditions.

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1. Introduction

Reconstructing past climate and environmental change largely depends on so-called proxies. These proxies relate measurable variables in the geological record to target parameters, such as e.g. temperature, biological productivity and bottom water oxygenation. The carbonate shells of unicellular protists, foraminifera, are one of the most utilized signal carriers for reconstructing past environments. Both the census data of foraminifera and the geochemical composition of the shells are used in this context. The geochemical composition of the shells is investigated for their stable isotopic composition as well as for their trace and minor element incorporation. Both pelagic and bottom water conditions are reconstructed this way, using planktonic and benthic foraminiferal species respectively.

Most existing calibrations of trace element uptake in foraminiferal test carbonate are based on comparing their composition with bottom water conditions

(Elderfield et al., 2006; Nürnberg et al., 1996; Yu and Elderfield, 2007). Many benthic foraminiferal species live, however, within the sediment and precipitate their calcium carbonate test in contact with pore water. As a result, the trace metal composition of pore water exerts a control on the uptake of trace metals in their test. This effectively links benthic foraminiferal microhabitat preference and pore water chemistry. On the one hand, this creates complications when using foraminiferal trace metal ratios for reconstructing bottom water conditions, whereas on the other hand, it offers the possibility to develop proxies of pore water chemistry in the past.

Linking foraminiferal test chemistry with pore water chemistry requires in-depth knowledge of, 1) how early diagenesis in sediments affects pore water chemistry, 2) the habitat preference of the foraminiferal species, 3) foraminiferal migration (and the depth at which they calcify) within the uppermost sediment layer. In principle, the chemical composition of living (stained) benthic foraminifera will reflect all these processes.

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For many elements an important inter-specific difference in uptake of trace metals has been observed (Hintz et al., 2006; Wit et al., 2012; Barras et al., 2018), a so-called vital effect. This implies that in addition to ecology and pore water geochemistry, trace metal partitioning also needs to be taken into consideration. This requires a comparative study between locations where all three of these aspects have been quantified.

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Reconstructing past pore water trace metal profiles is important since it provides valuable information on organic carbon degradation and recycling of nutrients at the seafloor (Van Cappellen and Wang, 1996; De Lange, 1986). Such diagenetically controlled trace metal profiles are used in quantitative models constraining oceanic

carbon fluxes and burial (Wang and Van Cappellen, 1996). Knowledge of such profiles in the past could thus help to reconstruct past carbon cycles.

Benthic foraminiferal species have a specific preference for their depth-habitat (Jorissen et al., 1995). Some benthic foraminiferal species are limited to a very narrow environmental in-sediment range, for example, along redox fronts, whereas others have a wider distribution, thriving under variable conditions and consequently occupy a broader niche. These differences in depth-habitat preferences could be related to the presence of different types of metabolism (Koho et al., 2011; Risgaard-Petersen et al., 2006). As such, trace metal profiles and foraminiferal in-sediment depth habitat can be related, such as recently proposed in a conceptual (TROXCHEM^3) model for the redox sensitive element, manganese, by Koho et al. (2015). Studying the interplay between benthic foraminiferal habitat preference and incorporation of redox-sensitive trace elements is key to verifying such models.

Studying manganese bound in foraminiferal shell carbonate lies at the intersection of foraminiferal ecology and early diagenesis in sediments. Manganese is a redox sensitive element and exists as Mn- (hydr)oxides in the presence of oxygen. As oxygen concentrations in the sediment decreases due to ongoing organic matter remineralization, Mn-(hydr)oxides are reduced to aqueous Mn^{2+}, (Froelich et al., 1979). Manganese in sediments cycles continuously between solid and aqueous state as a result of upward diffusion of Mn^{2+} and consequent remineralization to Mn-(hydr)oxides. Hence proxy studies must account for both ecological controls, like foraminiferal habitat preference, as well as geochemical controls like oxygen concentrations and organic matter loading (Glock et al., 2012; Groeneveld and Filipsson, 2013; Koho et al., 2015, 2017; McKay et al., 2015; Reichart et al., 2003). Notably, both benthic foraminifera and trace metal geochemistry react to organic matter recycling and bottom

water oxygenation (Jorissen et al., 1995). This implies that locations with contrasting conditions, both low and high bottom-water oxygenation as well as low and high productivity, are required for testing. Whereas most of these studies focused on the role of bottom water oxygenation in relatively oxygen poor settings, here we focus on the well-oxygenated western Mediterranean.

In this study we combine pore water geochemistry, foraminiferal habitat preference and test geochemistry in an area characterized by well-oxygenated bottom water conditions and average productivity. Results are compared with earlier studies from high productivity regimes and low-oxygen conditions at the sediment-water interface (e.g. Arabian Sea, Koho et al., 2015 and Mediterranean sapropel deposition, Ní Fhlaithearta et al., 2010). Specifically, we investigate the link between manganese incorporation and benthic foraminiferal ecology and compare this to the recently proposed TROXCHEM^3 model (Koho et al., 2015). Four species of living (stained) foraminifera were sampled along a 6-station bathymetric transect in the Gulf of Lions, NW Mediterranean. Individuals were picked from a series of in-sediment depths and analyzed by laser ablation ICP-MS, enabling multiple analyses of single specimens.

2. Material and methods

2.1 Study area and sediment sampling

Cores were collected with a classical Barnett multicorer (Barnett et al. 1984) at 6 stations in the Gulf of Lions (NW Mediterranean) during the August-September 2006 BEHEMOTH cruise (Fig. 1, Table 1). The 6 stations describe a bathymetric transect from 350m to 1987m depth. The shallowest site, station F, is bathed in Mediterranean Intermediate Water (MIW). Stations E (552 m) and D (745 m) are positioned at the

transition of MIW and Western Mediterranean Deep Water (WMDW). Stations C (980 m), B (1488 m) and A (1987 m) are bathed by the WMDW. Bottom water temperature is stable through the part of the water column studied here (~13.1°C) (Xavier Durrieu de Madron, pers. com.). Salinity ranges between 38.4 and 38.5. The multicorer allowed sampling of the first decimeters of the sediment, the overlying bottom waters, and an undisturbed sediment-water interface. Cores were sliced for foraminiferal studies with a 0.5-cm resolution down to 4 cm, followed by 1 cm slices down to 10 cm depth. Sediments were put in an ethanol-Rose Bengal mixture (95% ethanol with 1g/l Rose Bengal), in order to identify living (stained) specimens. For more detailed information about methods, please consult Fontanier et al., (2008).

2.2 Pore water geochemistry

Sediment sampling for pore water extraction was carried out under an inert atmosphere (N_2). Hereafter, samples were centrifuged at 3500 rpm for 20 min. The supernatant was filtered and acidified (HNO_3 *s.p.*) for analyzing dissolved metals. Dissolved Mn concentrations were determined with flame atomic absorption spectrometry (Perkin Elmer AA 300). Precision for this method is ± 5%. A pore water subsample was also analyzed for Mn using ICP-MS (Agilent 7500 Series). Relative precision for this method is 3%. Total alkalinity of pore water was measured at Utrecht University using an automated titrator (702 SM Titrino, Metrohm) making Gran plots. Dissolved Inorganic Carbon (DIC) was measured using a Dissolved Carbon Analyser (Shimadzu, Model TOC-5050A). Carbonate ion concentrations were calculated using the CO2SYS software (version 01.05; Lewis and Wallace, 1998). Analytical uncertainty for the alkalinity is about 10 μeq, relative standard deviation for the DIC analyses is 0.8%.

158 Oxygen concentration profiles were determined using Clark-type
159 microelectrodes (Unisense©, Denmark). Labile organic matter was derived from the
160 sum of lipids, amino acids and sugars measured in the top cm of sediment; for details,
161 see Fontanier et al., 2008.
162
163 **2.3 Foraminiferal trace metal geochemistry**
164 Foraminiferal trace element concentrations were determined using two laser ablation
165 ICP-MS systems. Prior to laser ablation, all samples were gently cleaned in methanol
166 (x1) and UHQ water (x4). Between each rinse, the samples were placed in a sonic bath
167 for several seconds to thoroughly clean the tests. Benthic foraminifera from 745 m
168 (station D), 980 m (station C), 1488 m (station B) and 1987 m (station A) were
169 measured at Utrecht University using a deep UV (193nm) ArF excimer laser (Lambda
170 Physik) with GeoLas 200Q optics. Ablation was performed at a pulse repetition rate of
171 10 Hz, and energy density of 1.4 J/cm^2, with a crater size of 80μm. Ablated particles
172 were measured by a quadrupole ICP-MS (Micromass Platform) equipped with a
173 collision and reaction cell. Such a collision and reaction cell improves carbonate
174 analyses by eliminating interferences on mass 44. Scanned masses included ^{24}Mg, ^{26}Mg,
175 ^{27}Al, ^{42}Ca, ^{43}Ca, ^{55}Mn, ^{88}Sr, ^{137}Ba, ^{138}Ba, ^{208}Pb. Benthic foraminifera from stations F (350
176 m) and E (552 m) were analyzed at ETH-Zurich (due to laboratory renovations at
177 Utrecht University). The laser type and ablation parameters were identical to those
178 detailed above. The ablated particles were measured using a quadrupole ICP-MS
179 (ELAN 6100 DRC, Perkin-Elmer). In both cases, calibration was performed using an
180 international standard (NIST610) with Ca as an internal standard (Jochum et al. 2011).
181 The same masses as measured in Utrecht were monitored, in addition to ^{7}Li, ^{23}Na, ^{47}Ti,
182 ^{60}Ni, ^{61}Ni and ^{89}Y. Inter-laboratory compatibility was monitored using a matrix-matched

calcite standard. For Mn this standard showed a precission better than 3% over all analyses, at ETH and UU, and with an offset of less than 5% from an off line determined (solution ICP-AES) concentration analyzing discrete sub-samples. The matrix matched standard is routinely included in the analyses and has been monitored since 2010 (Duenas Bohorquez et al., 2011).

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Analytical error (equivalent to 1 sigma), based on repeated measurement of an external standard, was <5% for reported elements. Each laser ablation measurement was screened for contamination by monitoring Al and Pb. On encountering surface contamination, the data integration interval was adjusted to exclude any Al or Pb enrichment. Cross-plots between Al and Pb versus Mn showed that they are unrelated, confirming accuracy of the integrations.

During the laser ablation analyses the different trace elements were monitored with respect to time, thus representing a cross section of the test wall. This allows not only quantification of the different trace metals of interest, but also to observe variability within individual tests. Each species has a distinct test-wall thickness, permitting the study of intra-test variability. A typical ablation profile for *H. elegans* is shown in Fig. 2.

2.4 Analyses of manganese in foraminiferal tests

Contamination and presence of secondary Mn-rich coatings on benthic foraminiferal tests has been a longstanding challenge in trace metal analyses of benthic foraminifera (Boyle 1983, Lea and Boyle 1989). In this study the trace metal data are based exclusively on living (Rose Bengal stained) foraminifera, which effectively rules out the impact of Mn-rich coatings on trace metal concentrations. At the time of sampling, the collected tests were still enveloped by foraminiferal cytoplasm,

preventing the formation of extraneous inorganic precipitates. Although benthic foraminifera live within the sediment, their test is physically separated from the environment as they are enveloped in an organic sheath (Ní Fhlaithearta et al., 2013). In case a recently deceased foraminifer was mistakenly analyzed (still with sufficient protoplasm to stain with Rose Bengal) the Mn oxide would not only have had limited time to develop, but it would also show up as a Mn spike at the start of a laser ablation profile. The ablation profiles confirm that no Mn-rich phases are present at the test surfaces (Fig. 2).

Comparing LA-ICP-MS data with traditional solution analyses for foraminiferal Mg/Ca values showed that data are directly comparable (Rosenthal et al., 2011). Also for trace metals such as Ni^{2+}, Cu^{2+} and Mn^{2+}, cross-calibration of LA-ICP-MS and micro-XRF shows those analytical results are robust (Munsel et al., 2010).

2.5 Benthic foraminiferal Mn/Ca

Manganese incorporation in benthic foraminiferal test carbonate was analyzed from 4 different species (*Hoeglundina elegans, Melonis barleeanus, Uvigerina mediterranea, Uvigerina peregrina*), from 6 coring sites, for up to 9 depths in the sediment. Sample coverage for all stations is described in Table 2. Descriptive statistics are presented in Table 3.

From the largest taxon, *Uvigerina mediterranea*, 3-4 analyses were routinely carried out per test, and no trend in Mn/Ca values was seen in consecutive growth stages. From the other species two analyses were performed per test. The resolution of the ablation profiles themselves does not allow quantifying changes in trace metals within the test wall. Still, comparing the data within individual ablation profiles shows that the intratest variability is generally limited for Mn (Table 4). As the ablation profiles target

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2.5.1 Intra-individual variability ¶

one chamber mostly, this does not include the full potential range. Comparing different ablation profiles between chambers in a single shell would circumvent this, but this data is somewhat limited.

Boxplots are used to describe the range of Mn/Ca values and how the distribution, median, average and skewness compares between species. All ICP-MS measurements are included, and as such represent both intra- and inter-individual variation.

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2.5.2 Distribution characteristics of Mn/Ca in benthic foraminiferal calcite¶

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3. Results

3.1 Pore water data

Pore water dissolved manganese (Mn^{2+}) concentrations were measured at all six stations. Manganese concentrations increase below the oxygen penetration depth at stations C and D (Fig. 3), with the highest in-sediment Mn^{2+} concentrations reached at station D. At stations E and F manganese concentrations remain low after crossing the oxygen penetration depth. At stations A and B the oxygen penetration depth and MnO_2/Mn^{2+} redox boundary are deeper than 10 cm's. Dissolved inorganic carbon (DIC) and total alkalinity (TA), were measured at stations E, C and B (Fig. 4). At stations D, C and E, DIC concentrations in the top 10 cm have a similar range (2350-2700 μmol/kg). The DIC profile at station B has a narrower range, ranging from 2400-2550 μmol/kg. Total alkalinity values range from 3242 μmol/kg at station E to a minimum of 2774 at station B. Carbonate ion concentrations [CO_3^{2-}] were derived based on TA and DIC values. The [CO_3^{2-}] profiles were relatively similar (Fig. 4) for stations E and C and B. Values for all three stations ranged from a maximum of 419 μmol/kg at station E to a minimum of 192 μmol/kg at station C (Fig. 4).

3.2 Mn/Ca data

3.2.1 Intra-individual variability

For most species some Mn/Ca analyses were below detection limit, except for *M. barleeanus,* which contained measurable quantities of Mn in all shells analyzed. This was most evident for *H. elegans*, where all but three Mn/Ca measurements were below detection limit (dl). *Uvigerina peregrina* had a wider range of Mn/Ca values than *U. mediterranea*. *Melonis barleeanus* exhibited the largest range of Mn/Ca values of the four studied species (Fig. 5). For all species, except *H. elegans,* values are somewhat skewed towards higher values.

3.2.3 Foraminiferal Mn/Ca variation across a depth transect

A trend of decreasing manganese incorporation with increasing water depth (350-1987 m) is most clearly visible in *M. barleeanus* (Fig. 6), except that the maximum values are observed at station E at 552 m. *Melonis barleeanus* shows the highest Mn/Ca values and the largest Mn/Ca variability. Station E registers the broadest Mn/Ca variability, which decreases with increasing water depth. *U. peregrina* also exhibits the largest variability in Mn/Ca values at station E. For *U. peregrina*, Mn^{2+} incorporation decreases from 350 m to 1987 m, except for station D (745 m), where Mn/Ca values (between the 10 – 90^{th} percentile) are approximately equivalent to those at station A (350 m; Fig. 6). For *U. mediterranea* a trend of decreasing Mn incorporation with increasing depth is found in specimens of *U. mediterranea* from the sediments at 552, 745 and 980 m. The highest values are reached at the shallowest station (350 m). Station E is also marked by the highest minimum Mn/Ca values for *U. mediterranea*. At station A only two *U. mediterranea* measurements are above the detection limit. *Hoeglundina elegans* shells from three stations (350 m, 1488 m and 1987 m) were analyzed, however, all but three

measurements were below detection limit (Fig. 6). These slightly elevated values were recorded at the shallowest station (station F). These Mn/Ca values are still very low compared to ranges in Mn/Ca values observed for the other species (Fig. 6).

Variability in Mn/Ca increases together with the overall Mn/Ca concentration within benthic foraminiferal species (Table 4). This suggests that even at those stations and depth levels where the highest Mn concentrations are recorded, individuals with relatively low amounts of Mn in their calcitic test were found. Comparing relative standard deviations, as a measure for the inter-specimen variability, for the different stations and species suggests that with increasing Mn concentration for *M. barleeanus* and *U. mediterranea* variability increases, whereas for *U. peregrina* it decreases.

3.2.4 In-sediment variation

For most species Mn/Ca values are more or less constant with in-sediment depth (Fig. 3). However, *M. barleeanus* shows increasing Mn/Ca values with in-sediment depth. This is most apparent at the shallowest station (station F - 350 m) (Fig. 3d).

4. Discussion

Incorporation of Mn in benthic foraminiferal carbonate depends both on foraminiferal ecology and early diagenesis in sediments. Although other factors such as temperature, sea water carbonate chemistry, growth rate etc., might also affect the uptake of Mn in the shell carbonate (Koho et al., 2017), these effects are most likely several orders of magnitude smaller compared to the large range in dissolved Mn in pore water. Since pore water Mn is the dominant factor controlling Mn incorporation, studies must account for ecological controls, like foraminiferal depth habitat preference, as well as

for geochemical controls like oxygen concentrations and organic matter fluxes (Koho et al., 2015; De Lange, 1986; Reichart et al., 2003). The fact that this study was based on living foraminifera circumvents potential complications due to Mn-rich coatings. Such coatings would likely not affect the aragonitic shell of *H. elegans* (Ní Fhlaithearta et al., 2010), but might interfere when analyzing fossil calcite shells. Still, a spatially resolved analytical technnique like LA-ICP-MS allows detecting such coatings also in fossil specimens.

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4.1 Impact of redox conditions and foraminiferal habitat preference on Mn incorporation

In general, flux of organic matter arriving at the sea floor decreases with increasing water depth, due to ongoing degradation during settling (Arndt et al., 2013 and references theirein). Consequently, redox boundaries within the sediment generally also deepen as a function of water depth, as oxygen consumption in the sediment decreases. Such a fundamental organic matter-depth relation is in line with the much deeper oxygen penetration depths at stations A and B compared to the more shallow stations. At station F the relative shallow oxygen penetration depth observed is in line with its' relative shallow water depth, although the organic matter which arrives here at the seafloor apparently undergoes winnowing (Fontanier et al., 2008). The organic matter along the transect studied is concentrated at a so-called depocenter, which largely coincides with the depths of stations C and D (Fontanier et al., 2008). As bottom waters at all stations are well oxygenated, organic matter concentration can be considered the main control for redox conditions at stations F-A, with the amount of organic matter arriving at the seabed being regulated by water depth and sedimentary processes, such as focusing versus winnowing.

At stations C, D and F, the oxygen penetration depth and the Mn^{2+} redox boundaries are at the same depth, as expected. Station F shows the shallowest OPD of all stations, although the organic matter concentration is relatively low. One explanation for this observation is that a lower porosity at F (56% versus 76% and 79 % at stations D and E, respectively) impedes oxygen diffusion through the sediment. Alternatively, the pore water profile reflects an earlier organic matter deposition event, with this organic matter being largely consumed at the time of sampling. The pore water profiles require more time to re-equilibrate to the new conditions (Burdige and Gieskes, 1983). At station E there is a mismatch between oxygen penetration depth and the Mn^{2+} redox boundary as the Mn^{2+} redox boundary is considerably deeper than the OPD. Although this is in line with the observed higher bioirrigation at this station (Fontanier et al., 2008), this might reflect non-equilibrium conditions as well.

The vertical distribution of benthic foraminiferal species varies between stations, in accordance with organic matter concentrations and redox zonation, which is consistent with the TROX model (Jorissen et al., 1995; Fontanier et al., 2008). In case of a shallower redox zone, infaunal benthic foraminifera biomineralize in contact with Mn-enriched pore water, with highest dissolved manganese concentrations occurring just below the oxygen penetration depth at all stations, except for station E (552 m). This is in contrast to low bottom-water oxygen environments often studied in the context of proxy development studies, where pore water Mn^{2+} is released from the pore water (Koho et al., 2015, 2017; Mangini et al., 2001).

The species studied here cover the range of shallow-infauna to intermediate-infauna niches. Both *Uvigerina mediterranea* and M. barleeanus were in the Gulf of Lyons found to occupy shallow to intermediate infaunal habitat, with *U. peregrina* having a somewhat shallower infaunal habitat (Fonatnier et al., 2008). *Hoeglundina*

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363 *elegans*, a typically shallow infaunal species, is often found close to the sediment-water
364 interface (Jorissen et al., 1998; Schönfeld 2001; Fontanier et al., 2002; Fontanier et al.,
365 2008) and contains the lowest concentration of Mn in its test. Only at the shallowest
366 station (350 m) three specimens of *H. elegans* show concentrations above the detection
367 level, with values still low compared to the values observed for the other species (Fig.
368 6). In the Bay of Biscay Reichart et al. (2003) also suggested that elevated Mn
369 concentrations in *H. elegans* were confined to stations with oxygen depleted bottom
370 waters and/or with a shallow oxygen penetration depth. *Uvigerina mediterranea* and
371 *Uvigerina peregrina* are also classed as shallow-infaunal species; they are typically
372 found within the top few centimeters of the sediment column (Fontanier et al. 2002,
373 Fontanier et al. 2008). The calculated average living depth (ALD_{10}) as calculated in
374 Fontanier et al. (2008) is consistently shallower than the ALD_{10} for *U. mediterranea*.
375 This is at odds with previous reports suggesting *U. peregrina* has a slightly deeper
376 microhabitat than *U. mediterranea* (Fontanier et al. 2002; 2006). That *U. peregrina* has
377 a deeper microhabitat is further supported by the usual distinct $\partial^{13}C$ offset in *U.*
378 *peregrina,* which is more depleted compared to *U. mediterranea* (Schmiedl et al., 2004;
379 Fontanier et al, 2002, 2006). The higher Mn/Ca values observed here for *U. peregrina*
380 (Figure 6) supports the idea that it calcifies somewhat deeper in the sediment compared
381 to *U. mediterranea*. Alternatively, *U. peregrina* may migrate downwards within
382 burrows to track food resources, recording redox steepness (Loubere et al., 1995). This
383 could highlight a disparity between the assumed living depth (the depth interval of
384 recovery) and biomineralization depth of foraminifera. Still, this would also result in a
385 higher variability of Mn/Ca values at higher Mn/Ca levels, which is not observed.
386 Hence, more likely the observed disparity between the geochemical signals
387 incorporated into foraminiferal calcite and depth of recovery in *U. peregrina* reflects

388 opportunistic behaviour, with calcification at a shallower in-sediment depth in response
389 to more favourable conditions after e.g. seasonal peaks in organic matter fluxes
390 (Accornero et al., 2003), when the OPD is close to the sediment water interface.
391 *Melonis barleeanus*, generally considered an intermediate-infaunal species
392 (Fontanier et al., 2002, 2008), contains the highest concentrations of Mn in its test,
393 which is in line with the deepest habitat of the species studied here. Manganese
394 incorporation in this species increases with increasing labile organic matter (Fig. 7a).
395 In summary, the habitat preference of the benthic foraminiferal species studied
396 here is reflected in the Mn/Ca values recorded in their tests. This is in contrast with
397 other results showing lower Mn/Ca values in foraminiferal tests with shallower redox
398 fronts (Koho et al., 2015). This, however, critically depends on the Mn being released
399 to the water column, which only occurs when the bottom waters are disoxic. In case of
400 a seasonal organic matter deposition event, an increase of Mn concentration in
401 foraminiferal test carbonate would initially occur in the deeper and ultimately also in
402 the more shallow calcifying foraminifera. This is in line with the conceptual
403 TROXCHEM[3] model, with the conditions studied here falling within the first stage of
404 the temporal succession considered in the model. Bottom water remains well
405 oxygenated (O_2 concentrations at the study area: 199-219 μmol/l (Fontanier et al.,
406 2008)) and organic matter loading is controlling Mn^{2+} concentrations in the sediment.
407 To what extend species are high in Mn/Ca depends on living depth and opportunistic
408 behavior.
409 At a given location, a benthic foraminiferal species' depth preference or
410 biomineralization depth, is reflected in its average Mn/Ca value (Fig. 5). The trend
411 across a depth transect shows a strong correlation to labile organic matter
412 concentrations in the surface sediments (Fig. 7). The strong correlation between labile

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organic matter (i.e. sedimentary lipid content) and Mn incorporation in shallow and intermediate infaunal species *U. mediterranea* ($R^2 = 0.80$ ($p < 0.05$) suggests that test Mn has potential as a proxy for detecting past labile organic matter fluxes. Noteably, *M. barleeanus* has a very strong correlation (0.81), though this correlation lacks statistical significance ($p > 0.05$). In contrast, *U. peregrina* shows a correlation coefficient of only 0.45 (R^2) between test Mn and labile organic matter. *Uvigerina peregrina* is reported to respond opportunistically to the concentration and quality of organic matter produced during bloom events (Fontanier et al., 2003; Koho et al., 2008; Barras et al., 2010). This response is in the form of increased reproduction and growth. Perhaps *U. peregrina* calcifies preferentially at shallower depths and therefore does not capture the full Mn^{2+} gradient.

At low oxygen concentrations Mn is released through the reduction of manganese (oxy)hydroxides. Here we show an increase in Mn/Ca incorporation in several species, from shallow to intermediate-depth infaunal habitats, as a function of oxygen penetration depth. Such a correlation agrees with studies by Ní Fhlaithearta et al. (2010) and McKay et al. (2015) from a down core record of $Mn/Ca_{H. elegans}$ during the formation of sapropel (S1) in the Eastern Mediterranean and a paleoproductivity study of an upwelling system in the NE Atlantic, respectively. Here, a comparison of Mn (oxy)hydroxides in the sediment and foraminiferal Mn^{2+} showed that Mn^{2+} incorporation in an epifaunal to shallow infaunal species was higher during times of enhanced Mn^{2+} remobilization and hence higher pore water Mn^{2+}. Such a correlation, however, requires that the bottom waters remain somewhat oxygenated to retain the dissolved Mn^{2+} in the pore water. With disoxic bottom waters Mn^{2+} escapes the porewater and foraminiferal Mn/Ca values decrease (Koho et al., 2015). However, with high organic matter deposition, which might be concentrated in events, also

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foraminiferal species living at or close to the sediment water interface may show elevated Mn concentrations.

In addition to the here observed changes, biomineralization could affect Mn^{2+} incorporation. In a controlled laboratory study by Munsel et al (2010) Mn incorporation in *Ammonia tepida* increased with increasing Mn^{2+} concentrations in the culture water and the partition coefficient was well above 1. The lack of an appreciable discrimination argues against a major biomineralization impact on Mn^{2+} partitioning. Recently Barras et al. (2018), also using controlled growth experiments, showed, however, that Mn partitioning in *B. marginata* differs from that in *A. tepida*, with that in B. marginat being close to one and that of A. tepida being 4 times lower. Inter-specific differences are considerable and hence an impact of biomineralization on Mn incorporation can not be disregarded.

In summary, Mn incorporation seems primarily controlled by pore water conditions in close proximity to the test, biomineralization and with a secondary control determined by the ability of a foraminifer to seasonally calcify and migrate within the sediment.

4.2 Pore water Mn dynamics and foraminiferal migration within the sediment

Manganese is incorporated in foraminiferal carbonate with a partition coefficient (D) close to 1 or somewhat lower (Munsel et al., 2010; Barras et al., 2018). We calculated Mn partition coefficients for *U. mediterranea*, *U. peregrina* and *M. barleeanus* at stations E, C and B (Table 6) based on average Mn/Ca_{foram} and average $Mn/Ca_{pore\ water}$ values found above the Mn^{2+}-MnO(H) redox boundary. Calculated D_{Mn} agrees with the previously reported D_{Mn} by Munsel et al., (2010), with values varying between ~1-2 for *U. mediterranea* and *U. peregrina*. The Mn partition coefficient for *Melonis barleeanus* ranges from ~4-7. The partition coefficient for this species most likely reflects its

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capacity to calcify under dysoxic conditions, close to or even below the oxygen penetration depth. Still, this calculation is based on two assumptions: (1) the depth foraminifera are recovered from during sampling corresponds with the average depth of calcification and, (2) variation in pore water is limited. Establishing species specific Mn partitioning coefficients using culture experiments might, however, be needed for unlocking the full potential of this proxy (Barras et al., 2018).

A foraminifer calcifying within a steep Mn^{2+} gradient is exposed to a higher range of Mn^{2+} concentrations (over a fixed depth interval) compared to specimens living along a more gradual Mn^{2+} concentration gradient. Since foraminifera can migrate through the sediment as a response to food availability and oxygen concentrations (Alve and Bernhard 1995; Gross, 2000), not only the slope of the Mn gradient, but also the in-sediment depth range (microhabitat) of the foraminifer in relation to the Mn redox boundary, should be considered (Fig. 8). Although the analyses of foraminiferal test Mn/Ca is challenging, which adds to the inter-specimen variability, we observe systematic differences between species in Mn/Ca variability. A shallow-infauna species, with a limited in-sediment range, would be expected to exhibit lower variability than an intermediate- infauna species, which possibly migrates considerably in depth. This is exemplified at station F (350 m) where we note an increase in foraminiferal test Mn/Ca variability at 2 cm depth, consistent with the oxygen penetration depth at that station (Fig. 3). Moreover, the variability in Mn/Ca values increases towards higher Mn/Ca values. This is in line with the depth habitat of *M. barleeanus* being consistently deeper and this species traveling more actively through the redox zones than *U. mediterranea* or *U. peregrina*. Nitrate respiration could be mechanism allowing this dynamic behaviour by *M. barleeanus* in the intermediate depth habitat. However, Pina-Ochao et al. (2010), studying denitrification in foraminifera, reports nitrate storage in

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all three species mentioned here. Notably, nitrate storage in *M. barleeanus* is lower than *U. mediterranea* and *U. peregrina*. Alternatively *M. barleeanus* thrives in habitats with varying oxygenation and hence also varying Mn levels, whereas the stable but high Mn/Ca values in the Uvigerinids are related to their opportunistic behaviour.

With a redox-sensitive element such as Mn, in a dynamic geochemical environment, it is not surprising that foraminifera exhibit high inter-individual variability in their Mn/Ca incorporation. Benthic foraminifera reside in a 3D geochemical mosaic, as reflected by a large spread of Mn values, in addition to undergoing substantial temporal variability. Still, using Mn/Ca as a potential proxy for redox conditions or primary productivity seems promising, as established ecological characteristics of species are reflected by differences in Mn incorporation. Apparently the large variability on both spatial and temporal scales averages out, making Mn into a promising proxy for paleo-redox and organic matter flux.

5. Conclusion

This study investigates the link between benthic foraminiferal habitat preferences and manganese incorporation in their tests. Manganese incorporation increases with bottom-arriving labile organic matter content, driven by enhanced oxygen demand. This results in a more shallow oxygen penetration depth with immediately below it enhanced dissolved Mn levels. Shallow infaunal species calcify under lower concentrations of Mn compared to intermediate infauna, in line with their depth preference. Their depth habitat is related to in-sediment changes in redox conditions. However, these distribution not necessarily vary synchronous with changes in redox zonation as illustrated by the Mn/Ca variability in their tests (Fig. 8). The latter reflects the Mn/Ca porewater composition, which itself is directly related to reactive organic

matter concentration and redox conditions. The foraminiferal Mn/Ca ratio and inter-specimen variability, therefore, provides information on past Mn cycling within the sediment. Consequently, foraminiferal Mn/Ca ratio is a potential proxy for bottom-water oxygenation and organic matter fluxes.

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