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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 field study sites focusing on foraminiferal Mn / Ca and redox chemistry, therefore allowing further resolution of previously observed trends. The Mn / Ca ratios were analysed using laser ablation inductively coupled plasma-mass spectrometer (ICP-MS), allowing single-chamber determination of Mn / Ca. The 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 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 at greater depth, 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 palaeoceanographic reconstructions as their microhabitat exposes them to higher variability in pore water Mn, thereby making them relatively sensitive recorders of redox conditions and/or bottom water oxygenation.

1 Introduction

Benthic foraminifera, single-celled, testate eukaryotes, are common proxies used in palaeoceanographic 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 isotopic and elemental composition) reflects various physical and chemical conditions of the

calcification environment, thereby allowing the 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, 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 oxic conditions Mn is present in the 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 the build-up of bioavailable 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 concentrations (Munsel et al., 2010). Exceptions are environments such as 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, the incorporation of 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 and 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 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, the test chemistry of species with different microhabitat preferences, i.e. living and/or calcifying at different sediment depths with varying Mn redox chemistry, is 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 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 $\geq 33\,\mu mol\,L^{-1}$) in northern Japan. The incorporation of Mn into foraminiferal test carbonate is evaluated in the context of microhabitat distributions and foraminiferal ecology, which have been described previously (Fontanier et al., 2014) for this area, and compared to 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, the Kuroshio Current and the 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 200 m water depth, the North Pacific Intermediate Water (NIPW) mixes gradually with saline Deep Pacific Water (DPW), entering this area between a water depth of 800 and 3000 m. The development of a dysoxic water mass approximately between water depths of 700 and 1400 m is related to both high surface water productivity, resulting in enhanced remineralisation 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 multicorer equipped with eight Plexiglas tubes with an internal diameter of 82 mm (Barnett et al., 1984). This type of coring device allows the recovery of undisturbed sediments with an intact sediment–water interface. Sediment for faunal analyses was collected over a transect spanning the oxygen minimum zone (OMZ), whereas pore water chemistry was determined from material collected at three selected sites within this transect (Fig. 1, Table 1). Separate cores were collected for pore water and foraminiferal analyses and oxygen profiling; all of these cores were derived from the same multicore cast. In addition to coring, a conductivity–temperature–
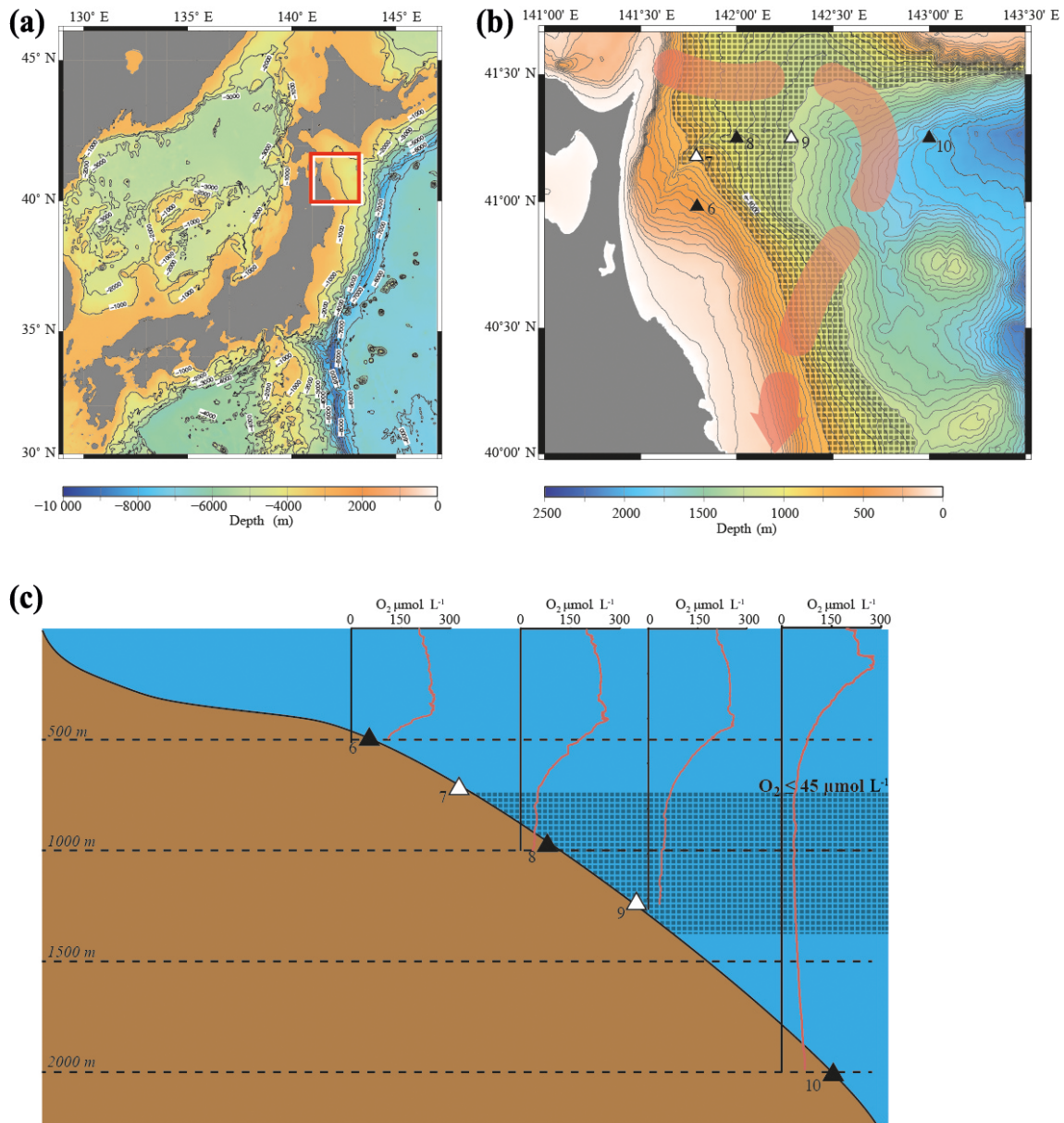
Figure 1. (a) Regional map of the study area. **(b)** Bathymetric map of the study region, showing the position of the Tsugaru Warm Current (Oguma et al., 2002) and multicore sampling sites. **(c)** Schematised study transect with water column profiles of dissolved oxygen. The dysoxic water column ($O_2 < 45 \, \mu mol \, L^{-1}$), located approximately between 750 and 1400 m, is indicated by a grey-square pattern. Black triangles indicate stations where pore water parameters were measured. White triangles are stations where pore water data were not obtained.

depth (CTD) cast (Sea-Bird Electronics, S/N 860; SBE9plus) equipped with an 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 multicore 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 2 cm had intervals with a resolution of 0.5 cm; between 2 and 10 cm, samples were taken at 1 cm intervals; and from 10 cm down-

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

Station	Latitude (N)	Longitude (E)	Depth (m)	BWO (μmol L^{-1})	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

wards, they had 2 cm intervals. Sediment samples were centrifuged in 50 mL tubes for 20 min at 2800 rpm. The supernatant was removed and filtered over 0.45 µm TeflonTM filters under N_2 atmosphere and divided into subsamples for various analyses. The nutrient samples were stored at $-20\,^{\circ}$C until analyses, and back in the laboratory nitrate concentrations were measured with a Bran-Luebbe AA3 autoanalyser, and ammonium was measured spectrophotometrically using phenol-hypochlorite (Helder and De Vries, 1979). Samples for pore water elemental analyses were acidified with Suprapur HCl 37 % (10 µL per millilitre of sample) and subsequently stored at 4 °C until analysis 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 less than 3 %.

2.4　Oxygen micro-profiles

The oxygen micro-profiles were recorded in a custom-built incubation chamber, allowing the regulation of temperature and oxygen content of overlaying water, and have been previously published in Fontanier et al. (2014). A brief summary is as follows: 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 stabilise for a minimum of 9 h 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^{-1}. Afterwards, the oxygen micro-profiles 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, at 1 cm interval from 4 to 6 cm depth and

at 2 cm intervals down to 10 cm depth in sediment. Samples were preserved and stained with rose bengal dissolved in 95 % ethanol (1 g L^{-1}). Stained (living) foraminifera in the > 150 µm fraction were wet picked, identified and stored on micropalaeontological 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).

A 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 (top 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); this was done by placing the foraminifera in Eppendorf tubes and rinsing them three times in ultrapure water (100 µL). This was followed by three rinses in methanol (100 µL) and finally three more rinses in ultrapure water (100 µL). Between the methanol rinses, foraminifera were placed in an ultrasonic bath for approximately 5 s. 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 setups, 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 based on averaging measured concentrations during each ablation after selecting the non-contaminated part of the ablation profile, which was recognised by elevated counts of Al, Mg and Mn at the beginning, and occasionally the 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 less than 5 s) were excluded from the data, and only longer ablation profiles, typically ranging between 10 and 30 s in length, were used.
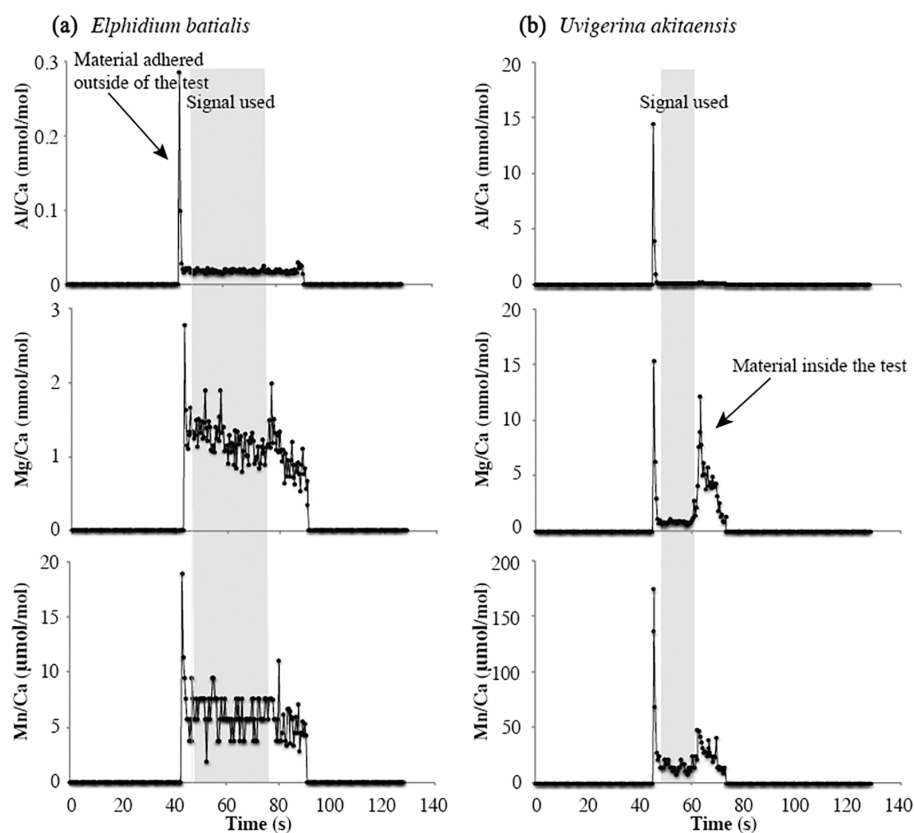
Figure 2. Laser ablation profile for Al / Ca, Mg / Ca and Mn / Ca measured in **(a)** *Elphidium batialis* (station 8, 0–0.5 cm depth) and **(b)** *Uvigerina akitaensis* (station 7, 0–0.5 cm depth) benthic foraminifera. The selected signal for the elemental composition is indicated by the grey shading. 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.

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 s, of which the first 45 s consisted of background. Ablation craters were circular with a diameter of 80 µm; the 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 s. 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 the 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. The 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., 2010).

Some samples were measured at the Royal NIOZ (Netherlands Institute for Sea Research) using a comparable, but slightly different setup. This configuration consists of an NWR193UC (New Wave Research) laser, containing a dual-volume ablation cell and an ArF excimer laser (Existar) with deep UV 193 nm wavelength and less than 4 ns pulse duration, connected to a quadrupole ICP-MS (iCAP-Q, Thermo Scientific). The energy density of the ablation was also set to 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 Utrecht University. Helium was used as a carrier gas with a flow rate of 0.8 L min^{-1} for cell gas and 0.3 L min^{-1} for cup gas. From the laser chamber to the ICP-MS, the He flow was mixed with ~ 0.4 L min^{-1} neb-

uliser Ar and 0.0025 mL min^{-1} N$_2$. Before measuring the samples, the nebuliser gas, extraction lense, CCT (collision cell technology) focus lense and torch position were automatically tuned for the highest sensitivity to ^{238}U, ^{139}La, ^{59}Co and low ThO / Th ratios (less than 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 s, of which the first 20 s consisted of a background. The cycle length through all masses was 0,12 s. Intensity data were integrated, background subtracted, standardised 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 – NIOZ foraminifera house standard) were used for quality control and measured every 10 foraminiferal samples. 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). 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 BWO content varied from 112 µmol L^{-1} at station 6 to 33 µmol L^{-1} measured at station 9 (Table 1). Stations 7 and 8 were also bathed in dysoxic (< 45 µmol L^{-1}) 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 less than 2 mm at station 6.

Pore water chemistry, including dissolved oxygen, nitrate, ammonium and manganese, was measured at sites 6, 8 and 10 (Fig. 3). Nitrate concentrations always peaked in the bottom waters (approximately 40 µmol L^{-1}), 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^{-1} 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^{-1}.

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^{-1} (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^{-1}): 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^{-1} 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 the umbo in *Elphidium batialis*. Selected data of single chamber measurements are presented in Fig. 4, showing *E. batialis*, *Uvigerina akitaensis* and *Bolivina spissa* from stations with the highest numbers of specimens measured across a range of chambers. In addition, single specimen measurements, in which four or more chambers were measured, are shown in Supplement Fig. S1. For none of the species, or for individual profiles shown in Fig. S1, was there 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 Table S1 in the Supplement), confirming the absence of a relation between shell size and Mn / Ca. An example of *Nonionellina labradorica* is not shown in Fig. 4 as a relatively low number of total measurements ($n = 18$) was 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 analysed, 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 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^{-1} (Fig. 5). The highest concentrations were measured in *N. labradorica* (ranging from 23.4 to 277.0 µmol mol^{-1}). *E. batialis* also showed least variability in measurements per sample with the average standard error of all measurements per station ranging between 0.2 and 7.4 µmol mol^{-1}.

Most of the measurements were performed on specimens collected from surface sediments; however, for *Uvigerina* spp., *B. spissa*, *N. labradorica* and *C. fimbriata*, specimens were also measured 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 tests with *N.*
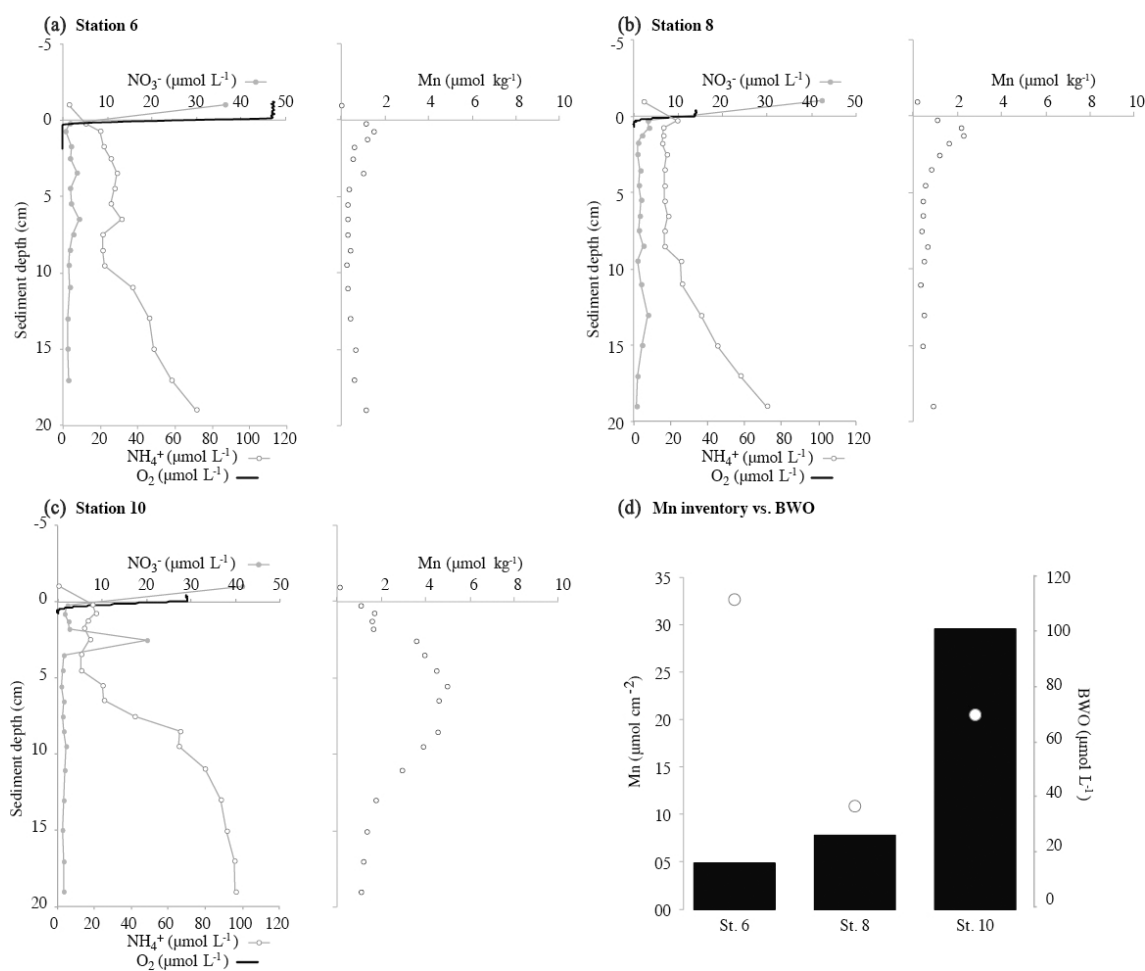
Figure 3. Pore water profiles of dissolved oxygen, nitrate, ammonium and manganese at stations 6 **(a)**, 8 **(b)** and 10 **(c)**. **(d)** Pore water manganese inventory in the top 10 cm of sediment and bottom water oxygen content (white symbols).

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	

labradorica and *C. fimbriata* are of limited value due to the low total number of specimens measured at these sites.

The average living depth of all species analysed was calculated after Jorissen et al. (1995). The shallowest living depth was noted for *E. batialis* and was generally encountered in the upper 1 cm of the cores (Fig. 6). At site 10, a 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* – stations 7, 8 and 9) was found at slightly greater depth, with an ALD ranging from 1.0 cm at station 9 to 2.1 cm at station 7. *B. spissa* was consistently found living at greater depth 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 centred at 4 cm depth in sediment, except at station 7 where the ALDs
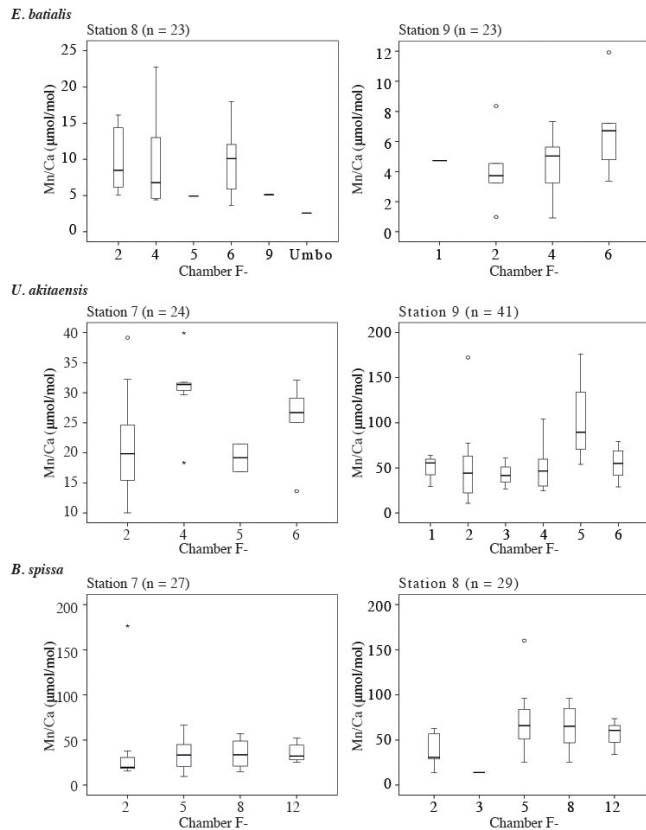
Figure 4. Box plots showing chamber-to-chamber variability in Mn / Ca. Error bars display the full range of data variation (data within 1.5 interquartile (IQ) range). Data outliers are represented with a white circle (between 1.5 and 3 IQ range), and extreme data outliers are indicated by an asterisk (above 3 IQ range).

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.

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

of these species were 2.9 and 2.3 cm, respectively. Overall, a systematic distribution of foraminiferal microhabitats was observed with the shallow infaunal microhabitat represented by *E. batialis*. An intermediate infaunal habitat was occupied by *Uvigerina* spp. and *B. spissa*, and the deep infaunal habitat was inhabited 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*, fol-

lowed 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 the deep infaunal species *N. labradorica* and not in the deeper-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 approximately 1 cm, whereas the 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 were available (Fig. 7, Table S1). 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 none of the other taxa were systematic, statistically significant trends observed between BWO content and Mn / Ca.
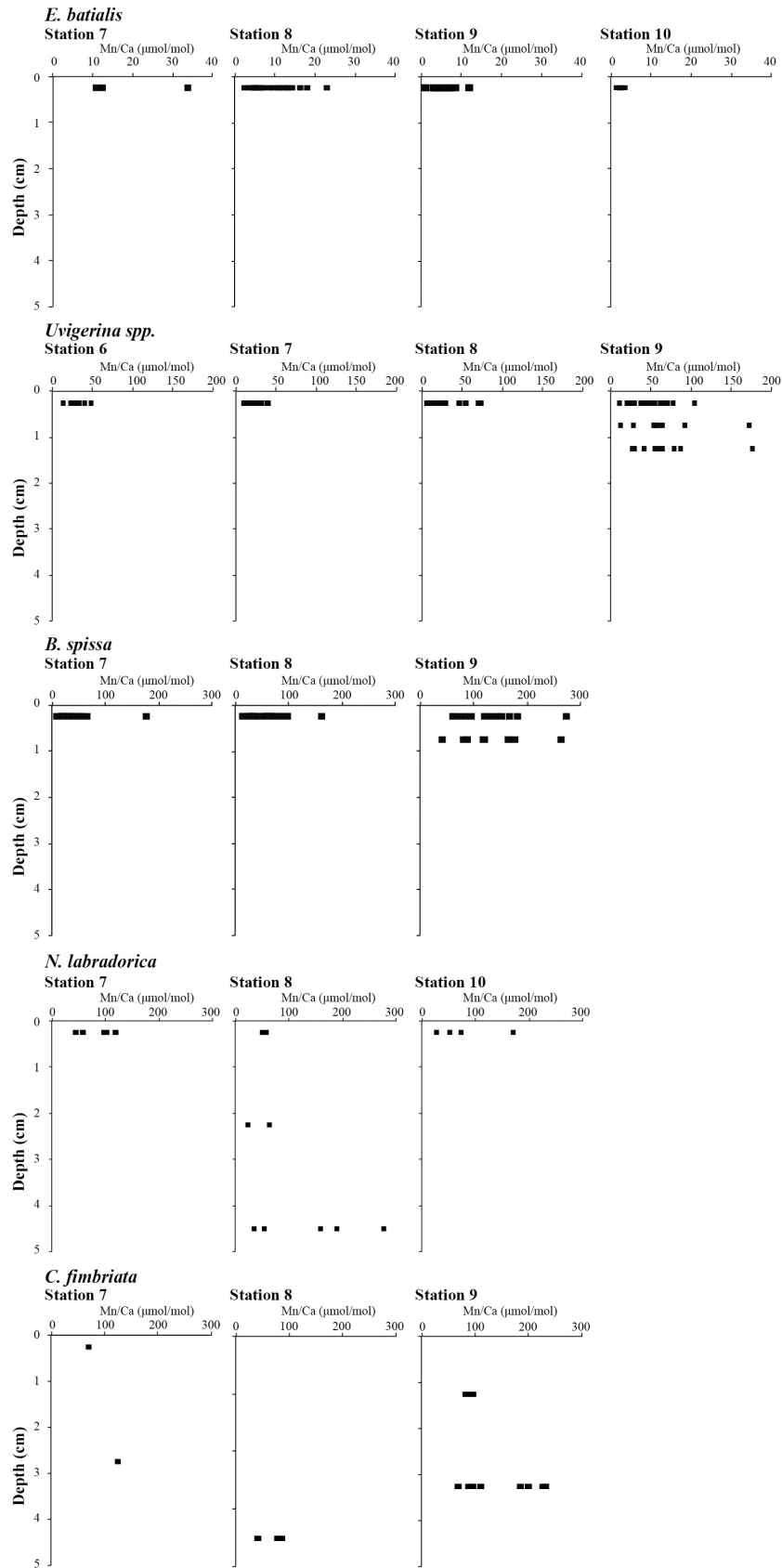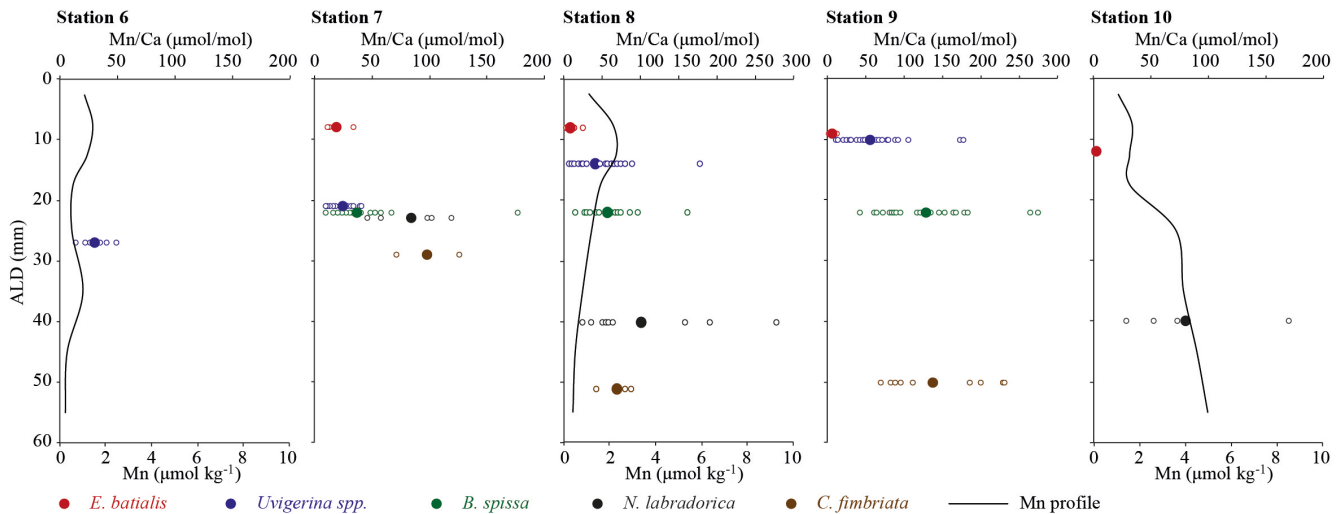
Figure 5. Individual laser ablation measurements of Mn / Ca in foraminifera versus sediment depth where the specimens were collected.

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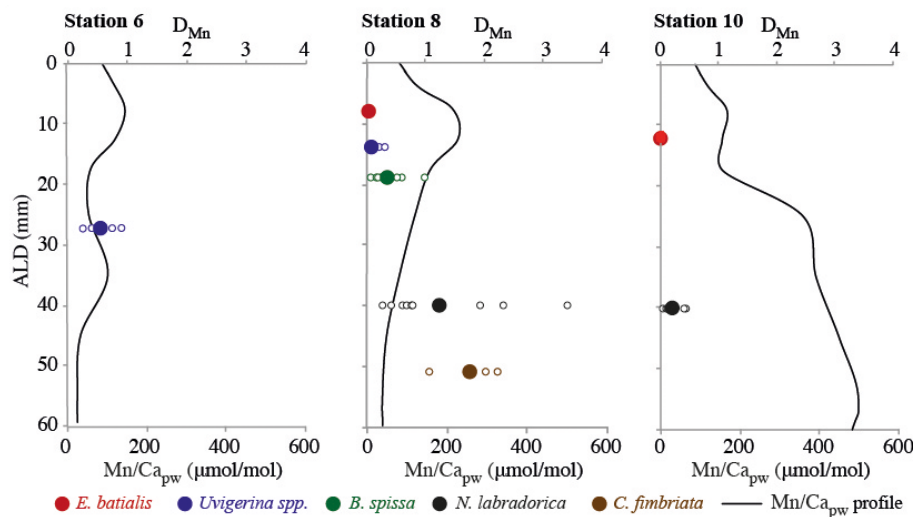
Figure 7. Manganese partition coefficient DMn in foraminifera as a function of average living depth of each species. In addition, the pore water (pw) Mn / Ca profile is shown.

4 Discussion

4.1 Intrashell variability in Mn / Ca ratios

Traditionally, Mn / Ca in foraminiferal test carbonate is used to indicate the 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 (laser ablation)-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 con-

taminants were excluded from data. In addition, all specimens analysed 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, the 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 or growth. In this study no systematic variations were noted in the Mn / Ca ratios and chamber stages of any foraminifera (Fig. 4, Fig. S1). These observations are consistent with work of Dueñas-
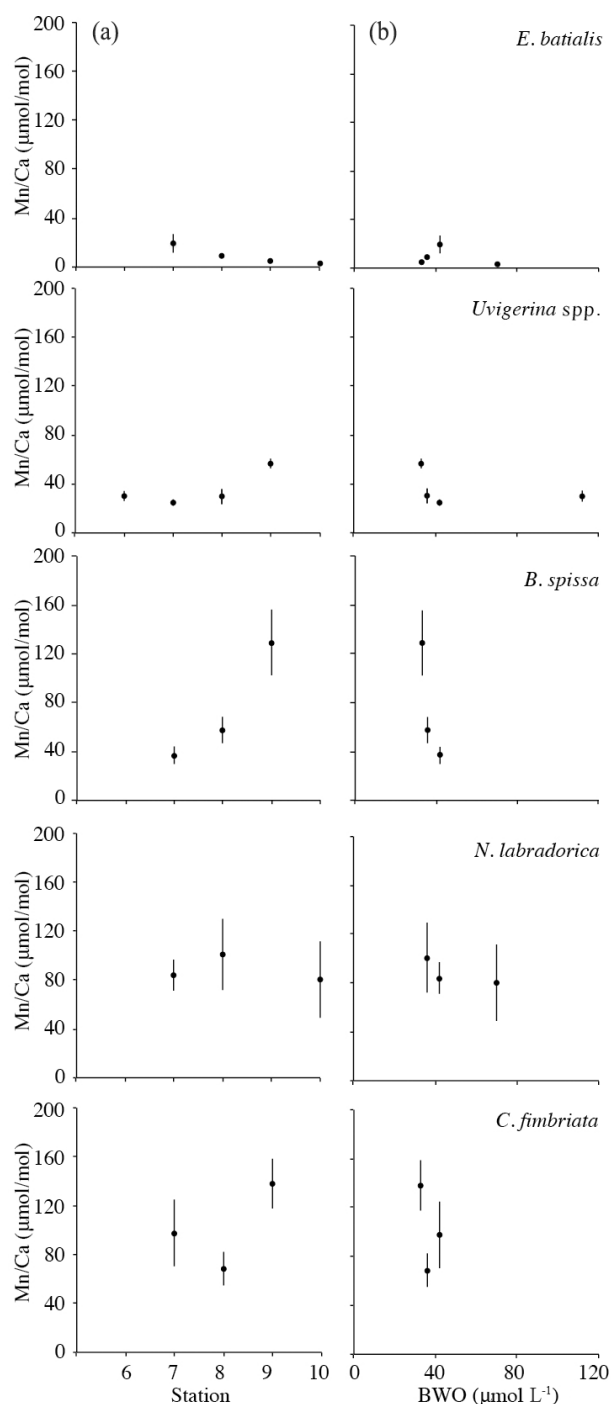
Figure 8. Variability in average Mn / Ca ratios of each species plotted against the study transect from station 6 to station 10 **(a)** and along the bottom water oxygenation **(b)**. The error bars represent the standard error of the measurements.

Bohórquez (2010), who also noted no clear trend in the Mn / Ca ratios with chamber stages of *Cibicidoides pachyderma*. Therefore, it appears that Mn / Ca ratios in benthic foraminifera are not substantially influenced by ontogenetic processes, as it 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 a 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, whereas elevated Mn / Ca ratios were measured in deep infaunal *Globobulimina turgida*. Moreover the results from the western 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 conditions, 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 (namely station 10), 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 stations 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 a 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 the case of ALD calculations. However, this does not explain the discrepancy observed at station 8 as the modes of maximum density and ALD of *N. labradorica* were alike: 4.5 and 4.0 cm, respectively.

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) have also 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 even be 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} less than 1 based on their calculated ALD might calcify at a somewhat shallower depth where Mn concentrations are lower or actually have substantially lower D_{Mn} values.

Foraminifera are known to migrate in the sediment and laboratory experiments have shown that changes in the sediment oxygenation typically result in the 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 a relatively wider range of sediment depths (Fontanier et al., 2014). Therefore, foraminiferal migration may resolve some of the discrepancies seen in the foraminiferal D_{Mn} values and explain part 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 result in relatively large changes in the ambient pore water Mn content, which would be reflected in the test chemistry during calcification. Furthermore, a closer observation of Mn / Ca ratios of sediment-dwelling foraminifera shows that both intermediate and deep infaunal species showed relatively higher range of Mn / Ca values at each station (Figs. 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 a range of chambers, including younger and older ones (Fig. 4), whereas pore water profiles represent a snapshot in time. Therefore, some mismatch can be expected to result 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 actively grow 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 the deep infaunal taxa studied here have also adapted to 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 to form new chambers. Here we show that Mn / Ca ratios in benthic foraminifera can also be measured to identify calcification under such conditions.

4.3 Implications for palaeoceanographic reconstructions

In recent years, efforts have been made to develop new bottom water oxygenation proxies via the 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 our 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^{-1}). 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^{-1} (Koho et al., 2015). These observations give further confidence that intermediate infaunal species may be the 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 microhab-

itat to the zone of Mn reduction, leading to higher sensitivity for recording changes in redox conditions.

By contrast with 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 the hampering of the any redox signal. Therefore, our data suggest that shallow infaunal taxa may not be suitable for the 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 $46\,\mathrm{mmol\,C^{-1}\,m^{-2}\,d^{-1}}$, Yokouchi et al., 2007) than in the northern Arabian Sea (annual average $111\,\mathrm{mmol\,C^{-1}\,m^{-2}\,d^{-1}}$, 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 is lower, and subsequently Mn reduction occurs deeper in the sediment, an influence on deeper infauna may be more significant. In palaeo-studies where large changes in the carbon fluxes are foreseen, Mn / Ca ratios in multiple species, including 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 implication for palaeoceanographic 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 the availability of Mn oxides in the sedimentary environments (e.g. Van der 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 depth, where the maximum dissolved Mn^{2+} concentrations were only $1.4\,\mathrm{\mu mol\,L^{-1}}$ 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 $5.0\,\mathrm{\mu mol\,L^{-1}}$, occurring at a sediment depth of 5.5 cm. This pore water $[Mn^{2+}]$ increase, which is also reflected in the foraminiferal Mn / Ca, may, in 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 the 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 higher BWO conditions at the deeper station might have allowed Mn being shuttled there. In addition, although BWO content was higher than $33\,\mathrm{\mu mol\,L^{-1}}$ 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 stations 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 observed to penetrate into the overlying oxic water column in a 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 occurs well within the sediment (at depths of 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). Palaeoceanographic reconstructions applying Mn / Ca ratios as a proxy for changes in redox chemistry therefore need to take into account changes in the availability of Mn oxides, which could influence sediment biogeochemistry and the incorporation of Mn into foraminiferal test carbonate.

5 Conclusions

Here we show that Mn / Ca ratios in benthic foraminifera reflect their microhabitat distribution, with Mn / Ca ratios increasing with deeper in-sediment habitat. Although appreciable differences between species in Mn partitioning were present, the overall higher Mn / Ca measured in some intermediate and deep-infaunal foraminifera suggest that these taxa actively grow and calcify 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 regard to palaeoceanographic reconstructions, the application of Mn / Ca ratios in intermediate 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.

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