



# Combining benthic foraminiferal ecology and shell Mn/Ca to deconvolve past bottom water oxygenation and paleoproductivity

K.A. Koho<sup>a,b,\*</sup>, L.J. de Nooijer<sup>b</sup>, G.J. Reichart<sup>a,b</sup>

<sup>a</sup> University of Utrecht, Department of Earth Sciences, Faculty of Geosciences, Budapestlaan 4, 3584CD Utrecht, The Netherlands

<sup>b</sup> Netherlands Institute of Sea Research, Department of Marine Geology and Chemical Oceanography, Landsdiep 4, 1797 SZ 't Horntje, The Netherlands

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## Abstract

The Mn/Ca of carbonate tests of living deep-sea foraminifera (*Hoeglundina elegans*, *Bulimina aculeata*, *Uvigerina peregrina* and *Melonis barleeanus*) were determined together with pore water manganese along a bottom water oxygen gradient across the lower boundary of the Arabian Sea oxygen minimum zone. Although Mn has long been considered an indicator for contamination, new cleaning protocols and high-resolution laser ablation ICP-MS now allow the reliable analyses of test-associated Mn. Within locations, Mn incorporation between species varies as a function of their in-sediment depth preferences and associated pore water chemistry. Under well-oxygenated bottom water conditions, shallow infaunal species incorporate little Mn in their test, whereas the species collected from deeper habitats show elevated Mn concentrations. With decreasing oxygen contents pore water Mn concentrations and benthic foraminiferal in-sediment distribution change. Whereas Mn/Ca in shallow infaunal species responds moderately to bottom water oxygenation, Mn/Ca of the infaunal species *M. barleeanus* correlates well to oxygenation. Although high productivity results in a shallower redox cline within the sediment, pore water Mn is retained as long as the bottom water remains oxygenated. Under reduced bottom water oxygen conditions, Mn escapes to the overlying water column and test-associated Mn/Ca decreases also in the infaunal species. By combining pore water chemistry of Mn, calcitic Mn/Ca and foraminiferal ecology, a new conceptual model is presented (TROXCHEM<sup>3</sup>) that provides a framework for deconvolving past organic matter input and bottom water oxygenation. © 2015 Elsevier Ltd. All rights reserved.

## 1. INTRODUCTION

Bottom-water oxygenation is an important parameter in oceanography since it plays an essential role in regulating organic carbon cycling and preservation (e.g. Hedges and Keil, 1995; Hartnett et al., 1998; Dauwe et al., 2001; Koho et al., 2013) and in controlling structure and biodiversity of

benthic ecosystems (e.g. Levin, 2003; Levin et al., 2009). Moreover, large-scale changes in bottom-water oxygenation, such as expansion or reduction in the extent of oxygen minimum zones (OMZs), may have global consequences by altering atmospheric CO<sub>2</sub> content through modification of nutrient availability by denitrification (Altabet et al., 1995, 2002). Due to the importance of bottom-water oxygenation for Earth's climate, a number of proxies have been developed to reconstruct seawater or pore water oxygen content. Some of these proxies are relatively robust, but have the disadvantage of recording general state, i.e. oxic versus dysoxic, rather than resulting in a quantitative estimate (Den Dulk et al.,

\* Corresponding author at: University of Helsinki, Department of Environmental Sciences, Viikinkaari 1, Helsinki, Finland. Tel.: +358 504487276.

E-mail address: [karoliina.koho@helsinki.fi](mailto:karoliina.koho@helsinki.fi) (K.A. Koho).

2000; Tribovillard et al., 2006). Quantitative reconstructions may be based on e.g. uranium stable isotope ratios in Fe–Mn crusts (e.g. Goto et al., 2014), but yield information of global oceanic state rather than local conditions.

In foraminiferal research, bottom-water oxygen concentrations have traditionally been reconstructed using transfer functions, which are based on relative abundance of specific marker species (e.g. Kaiho, 1994, 1999). However, these reconstructions are problematic as research shows that there are no distinct marker species for anoxic bottom waters (Jorissen et al., 2007). In addition, new insights into ecology of benthic foraminifera indicate that some species do not rely on aerobic respiration (e.g. Risgaard-Petersen et al., 2006; Piña-Ochoa et al., 2010; Koho et al., 2011) and are able to calcify in the absence of oxygen (Nardelli et al., 2014). Still, extending foraminiferal-based proxies to include pore-water information shows that the stable carbon isotopic difference between epi- and infaunal benthic foraminifera provides an indirect measure for bottom water oxygen (McCorkle and Emerson, 1988; Hoogakker et al., 2014). Also pore-water Mn-concentrations reflect bottom-water oxygen and organic carbon flux to the sea floor (e.g. Froelich et al., 1979; Van Cappellen and Wang, 1996) and reconstructing such profiles in the past would potentially provide important constraints on past redox conditions.

When bottom waters are oxygenated, Mn is transported to the seafloor in the form of (hydr)oxides ( $\text{MnO}_2$  or  $\text{MnOOH}$ ) as coatings on sediment particles (e.g. Finney et al., 1988). Deeper in the sediment, where pore water oxygen is diminished by ongoing organic matter remineralization, the Mn-(hydr)oxides are reduced to aqueous  $\text{Mn}^{2+}$  (Froelich et al., 1979). In turn, pore water  $\text{Mn}^{2+}$  diffuses upwards, reprecipitating in the oxygenated zone of the sediment (e.g. Burdige and Gieskes, 1983). In this way, continued cycling of Mn can increase the build-up of pore water  $\text{Mn}^{2+}$ . In contrast, in low-oxygen, high productivity settings where Mn (hydr)oxides are oxidized already in the water column,  $\text{Mn}^{2+}$  present in the pore water will escape. Subsequently, the sedimentary environment and pore waters in permanently low-oxygen settings, such as oxygen minimum zones, remain depleted in  $\text{Mn}^{2+}$  (Van der Weijden et al., 1998; Law et al., 2009). Benthic foraminifera incorporate available  $\text{Mn}^{2+}$  and may thus record oxygenation of the pore water. The advantage of foraminiferal test chemistry (i.e. Mn/Ca ratios) over Mn concentrations from bulk sediment analyses is that once precipitated, the Mn concentration remains fixed into the foraminiferal shell and is not prone to reduction or oxidation, as would be the case in sedimentary Fe–Mn records (Schenau et al., 2002).

During calcification foraminifera can incorporate many (trace/minor) elements, including manganese, present in seawater or pore water into their calcium carbonate crystal lattice (e.g. Boyle, 1981; Munsel et al., 2010). However, incorporation of manganese in foraminiferal tests has not been studied extensively since post mortem Mn-rich coatings (Boyle, 1983) potentially interfere with traditional trace metal analyses. Therefore, such coatings need to be removed prior to dissolving the test using a cleaning

protocol after which Mn (and Fe) are generally monitored as indicators for contamination (Barker et al., 2003). Analyses of trace metals in test carbonate obtained with LA-ICP-MS analysis now allow distinguishing between trace metals associated with coatings from their concentrations in the test carbonate (e.g. Reichart et al., 2003; Munsel et al., 2010; Wit et al., 2010).

To date, only few field studies (Reichart et al., 2003; Glock et al., 2012; Groeneveld and Filipsson, 2013) have attempted to link Mn/Ca ratios in benthic foraminifera to ambient seawater Mn-concentrations and hence potentially bottom-water oxygenation. In addition, two paleoceanographic studies (Klinkhammer et al., 2009; Ni Fhlaithearta et al., 2010) have applied Mn/Ca ratios in planktonic and benthic foraminifera to reconstruct terrestrial input and oxidation–reduction reactions in past environments. Previous studies on foraminiferal Mn/Ca appear promising but a detailed calibration with dissolved oxygen and soluble Mn concentrations, which is crucial for accurate reconstructions, is lacking to date.

Here we report Mn/Ca data on multiple species of living (rose Bengal-stained) benthic foraminifera with variable but well-known microhabitat preferences. It is commonly reported that different benthic foraminiferal species prefer specific in-sediment niches (e.g. Jorissen et al., 1995; Koho et al., 2008). Infaunal foraminifera like *Melonis barleeanus* for example, are typically found below the oxygen penetration depth and associated to the zone of denitrification (e.g. Koho et al., 2008). In contrast, shallow infaunal species like *Hoeglundina elegans*, prefer oxygenated surface sediments (Koho et al., 2008). Therefore, the geochemical gradients present in the microhabitat and foraminiferal calcification environment should be recorded differently in foraminiferal test carbonate of species with different depth habitats.

Here we present results from samples collected along a depth transect in the Arabian Sea OMZ, in which bottom water oxygen concentrations are below  $2 \mu\text{M}$  in its core (e.g. Cowie and Levin, 2009; Koho et al., 2013). The OMZ is sustained through high, monsoon-driven surface water primary productivity and relatively weak bottom water ventilation (Olson et al., 1993). The vertical extent of the OMZ at the study site reaches approximately from 125 m down to 1350 m water depth (Wyrki, 1971, 1973). The depth of the upper boundary of the OMZ varies seasonally, whereas the vertical change in oxygen concentrations marking the OMZ's lower boundary is minimal and its depth is thus stable over the year (Cowie and Levin, 2009). Our study transect covers a prominent shift in bottom-water oxygen content from nearly depleted (less than  $2 \mu\text{M}$  of  $\text{O}_2$ ) to relatively well-oxygenated ( $77 \mu\text{M}$  of  $\text{O}_2$ ) bottom waters beyond the direct influence of the OMZ (Table 1). The incorporation of Mn in foraminiferal test calcite is evaluated in the context of benthic foraminiferal ecology (Caille et al., 2014) and pore water Mn-content with associated changes in bottom water oxygen content. The results are summarized in a conceptual model (TROXCHEM<sup>3</sup>) providing a framework for deconvolving past organic matter input and bottom water oxygenation.

## 2. MATERIALS AND METHODS

Sediment samples (for living foraminifera and pore-water chemistry) were recovered from 10 stations (Table 1), spanning a depth transect with varying oxygen concentrations at the Murray Ridge (Fig. 1). Samples were collected in January 2009 with a MUC 8 + 4 multiple corer (Oktopus, GmbH), equipped with eight sample tubes with a diameter of 6 cm and four with a diameter of 10 cm. Using a multi corer generally allows recovery of less disturbed sediment samples, including the fluffy top layer (if present). For foraminiferal analyses, the smaller cores with a diameter of 6 cm were used, while pore water was sampled from sediment retrieved with the larger (diameter of 10 cm) cores. Cores for foraminiferal and pore water chemical analyses were always retrieved from the same multicore cast. A Conductivity-Temperature-Depth (CTD) – profiler was employed to measure physical properties of the seawater overlying each station. The CTD was also equipped with

an oxygen sensor (Sea-Bird SBE43, accuracy 2%) to obtain water-column and bottom water oxygen measurements. Bottom water oxygenation was also measured using micro-Winkler titrations and cross-calibrated using an optode oxygen sensor fitted to the multicorer frame.

### 2.1. Samples for living foraminifera

Two cores were sampled for foraminifera from every station. Upon retrieval, sediment samples for living foraminiferal analyses were sliced and subsequently stored in a solution of rose Bengal in ethanol (1 g/L). Foraminifera were sampled from the top 10 cm of sediment. The slicing was done in steps of 0.5 cm for top 2 cm of sediment, and in steps of 1 cm between 2 and 6 cm. Sediment depths between 6 and 10 cm were sampled in slices of 2 cm each. Upon return in the laboratory, samples were washed and sieved over a 150  $\mu\text{m}$  mesh. Well-stained specimens (brightly pink, staining complete except last chamber) were picked and sorted on Chapman slides. Although staining specimens with rose Bengal has its limitations (e.g. Bernhard, 1988; Corliss and Emerson, 1990; De Nooijer et al., 2006), limited transport of sediment and stability of the OMZ boundary at the sampled stations will not compromise the relation between recorded sediment pore water chemistry and foraminiferal test chemistry.

Species were chosen for element analyses based on their contrasting habitat preferences and their availability along the studied transect and included *H. elegans*, *Bulimina aculeata*, *Uvigerina peregrina* and *M. barleeanus*. These species were sufficiently abundant at all stations and represent different ecological groups: *H. elegans* (producing aragonite) and *B. aculeata* (producing calcite) represent a group that predominantly lives relatively shallow in the sediment. This allows resolving a potential difference related to calcite

Table 1  
Station position, longitude, latitude, water depth, bottom water oxygen (BWO) content and bottom water temperature (Temp).

Station	Longitude PASOM- (°N)	Latitude (°E)	Water depth (m)	BWO ( $\mu\text{M}$ )	Temp. (°C)
1B	22°32.9'	64°02.4'	885	2.1	10.1
2	22°33.9'	64°03.8'	1013	2.6	8.8
3	22°19.9'	63°36.0'	1172	5.1	7.9
4	22°18.0'	63°36.0'	1306	13.8	6.8
5	22°09.3'	63°12.8'	1379	16.8	6.6
6	22°04.7'	63°04.5'	1495	26.8	5.6
7	22°18.5'	63°24.5'	1791	45.2	4.1
8	22°08.7'	63°01.1'	1970	56.9	3.4
9	22°06.3'	62°53.7'	2470	66.3	2.1
10	21°55.6'	63°10.6'	3010	76.9	1.8

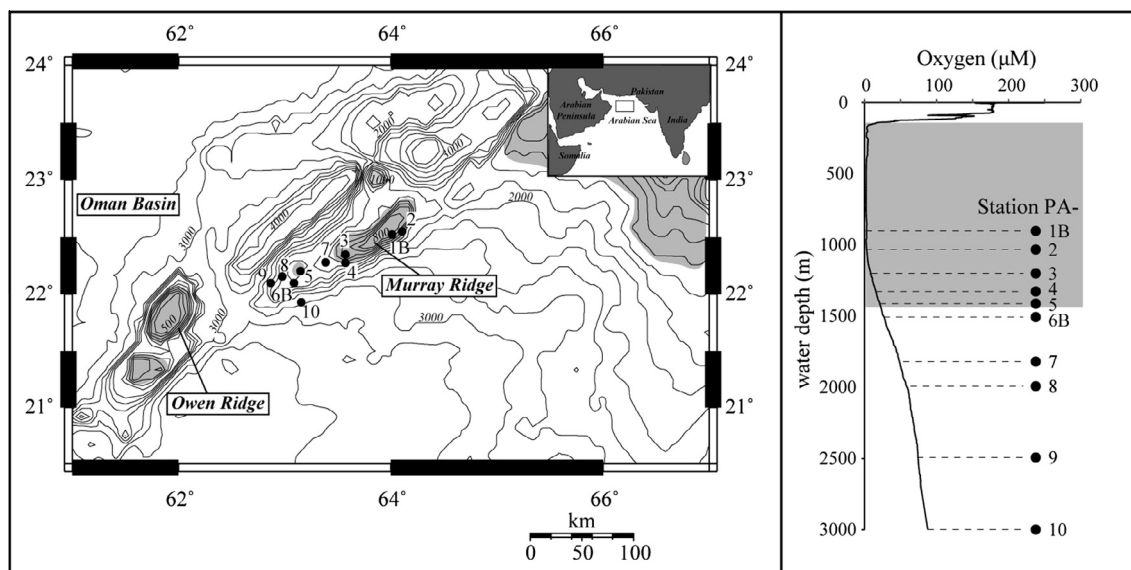


Fig. 1. Left: Bathymetric map of Arabian Sea, showing the multicore station locations at Murray Ridge. The gray shading indicates where the OMZ makes contact with sediment. On top right, an annex of the Arabian Sea with the location of Murray Ridge indicated with a square. Right: a typical water column profile of dissolved oxygen in the study area. In gray: oxygen minimum zone where bottom water  $\text{O}_2$  content is  $<21 \mu\text{M}$ .

mineralogy. These species are compared with *U. peregrina*, representing a group that lives at shallow to intermediate depths and *M. barleeanus*, representing the intermediate to deep infaunal foraminifera (e.g. Koho et al., 2008). Prior to analyses, all foraminifera were thoroughly cleaned in order to remove any sediment contamination (Barker et al., 2003) by placing in Eppendorf tubes and rinsing 3 times in ultra-pure water (100  $\mu$ l). This was followed by 3 rinses in methanol (MeOH; 100  $\mu$ l) and finally with 3 more rinses in ultra-pure water (100  $\mu$ l). Between each rinse, specimens were placed in ultra sonic bath for approximately 5 s. Finally, specimens were dried and stored until (geochemical) analyses.

## 2.2. Pore water samples

At every station, the sediment core used for pore water analyses was immediately capped with a rubber stopper upon recovery. This core was subsequently transferred to a N<sub>2</sub>-purged glovebox, placed in a temperature-controlled laboratory allowing all sampling to be done at *in situ* temperature. After sampling the overlying bottom water and siphoning off the remaining water, sediment was sliced at 0.5–2 cm intervals, resolution decreasing with sediment depth. However, in some samples it was not possible to extract sufficient volumes of pore water from a single sediment slice for the geochemical analyses. In such cases pore water samples were combined with adjacent shallower ones prior to analyses.

For each sediment slice, a subsample of the wet sediment was directly transferred into a 15 ml glass vial and stored in an air-tight glass jar at –20 °C before further geochemical analyses. The remaining sediment was transferred into 50 ml plastic centrifuge tubes, which were centrifuged for 20 min at 4500 rpm outside the glovebox. The centrifuge tubes were then transferred back into the glovebox where supernatant pore water was filtrated (0.45  $\mu$ M) and divided into subsamples for various uses, including elemental analyses. Subsamples for element analyses were acidified with suprapure HCl and stored at 4 °C until analyses at Utrecht University, The Netherlands. Seawater element concentrations were measured with an inductively coupled plasma-mass spectrometer (ICP-MS, ThermoFisher Scientific Element2-XR) and inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer Optima 3000). Replicate analyses indicated that the relative error for analyses of the pore-water element concentrations was generally <10%.

## 2.3. Laser ablation ICP-MS

Trace metal concentrations were measured on single foraminiferal chambers (Table 2) using laser ablation ICP-MS at Utrecht University. In most cases, a foraminiferal specimen was ablated once, preferably the pre-penultimate (F-2) chamber. All tests were ablated from the outside toward the inside. In cases where chamber walls were very thin and hence ablation profiles very short, foraminiferal specimens were ablated twice.

All ablation was carried out in a He environment with a deep-ultraviolet wavelength laser (193 nm) using a Lambda Physik excimer system with GeoLas 200Q optics (Reichert et al., 2003). Ablation crater diameter was 80 or 120  $\mu$ m, pulse repetition rate was 5 Hz and the energy density at the sample surface approximately 1 J/cm<sup>2</sup>. In most cases, ablations took >30 s to penetrate the foraminiferal chamber wall. Element to calcium ratios were quantified using counts for <sup>27</sup>Al, <sup>24</sup>Mg, <sup>26</sup>Mg, <sup>43</sup>Ca, <sup>44</sup>Ca and <sup>55</sup>Mn and their relative natural abundances on a sector field-ICP-MS (Element2, Thermo Scientific). Raw counts were converted to element concentrations using computer software (Glitter). Element ratios were based on averaging measured concentrations during each ablation after selecting the non-contaminated part 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, Mn and/or Al. Therefore care was taken to avoid that such elevated element concentrations affect the calculated average chamber wall element/Ca (Fig. 2). Calibration was performed against international NIST SRM 610 glass standard (using concentrations from Jochum et al., 2000) at a higher energy density (~5 J/cm<sup>2</sup>) which was ablated twice every 12 samples. Calibration of element/calcium ratios in calcium carbonate samples using a NIST glass standard has been demonstrated to be accurate for many elements when using a 193 nm laser (Hathorne et al., 2008). Switching energy density between carbonate sample and glass standard has been shown not to affect the concentration of the relevant elements (Dueñas-Bohórquez et al., 2011).

Laser ablation analyses of foraminiferal calcite were also compared against in-house matrix matched calcite standard (GJR; Wit et al., 2010) and a powder pellet of the JCT-1 carbonate reference material (Inoue et al., 2004), ablated at low energy density every 8–12 foraminiferal samples. The elemental data for Mn yielded robust measurements with relative standard error (RSE) for <sup>55</sup>Mn in GJR being smaller than 2.

## 3. RESULTS AND DISCUSSION

### 3.1. Mn incorporation into foraminiferal test carbonate: relation to pore water Mn content and bottom water oxygenation

In general, Mn/Ca ratios in the species *H. elegans*, which lives at or close to the sediment–water interface, were relatively low (<5.6  $\mu$ mol/mol) with slightly elevated

Table 2  
Number of laser ablation measurements and number of foraminifera used in this study for each taxa. See Section 2.3 for more details on the measurements.

Species	Number of measurements	Number of specimens
<i>H. elegans</i>	17	17
<i>B. aculeata</i>	18	16
<i>U. peregrina</i>	60	56
<i>M. barleeanus</i>	60	54



concentrations ( $18.6 \mu\text{mol/mol}$ ) in specimens retrieved from the lower boundary of the OMZ (Fig. 3). Mn/Ca ratios were also generally low in specimens of the shallow infaunal species *B. aculeata*, with again slightly elevated values ( $23.8 \mu\text{mol/mol}$ ,  $n = 1$ ) in Mn/Ca ratios from samples collected from the lower OMZ boundary (Fig. 3). Mn/Ca ratios of infaunal *U. peregrina* and *M. barleeanus* were generally higher than that of *B. aculeata* and *H. elegans*. Highest Mn/Ca values in *U. peregrina*

( $55.0 \pm 19.5 \mu\text{mol/mol}$ ,  $n = 16$ ) were observed at the lower boundary of the OMZ, at the transition to more ventilated bottom waters. In the tests of *M. barleeanus* a general increase in Mn/Ca values was observed with increasing water depth and thus bottom water oxygenation (min =  $6.7 \pm 1.8 \mu\text{mol/mol}$ ,  $n = 8$ ; max =  $64.4 \mu\text{mol/mol} \pm 15.0$ ,  $n = 2$ ) (Fig. 3).

Previous work of Munsel et al. (2010) showed that increased ambient dissolved Mn results in higher Mn/Ca ratios in shallow-water benthic foraminiferal tests in a laboratory culture experiment. Along the here studied transect Mn-availability is tightly coupled to redox chemistry (Fig. 4). Inside the core of the OMZ bottom water oxygen content is around, or less than  $2 \mu\text{M}$ . This results in escaping  $\text{Mn}^{2+}$  to the water column, resulting in pore waters depleted in  $\text{Mn}^{2+}$  (Van der Weijden et al., 1998; Law et al., 2009). Hence all foraminifera calcifying in the core of the OMZ are expected to have low Mn/Ca ratios. In the lower boundary of the OMZ, in the transition zone to more oxic conditions,  $\text{MnO}_2$  accumulates in the most superficial sediment layers and thus little  $\text{Mn}^{2+}$  is found in the surface pore waters. Here surface dwelling foraminifera, like *H. elegans* and *B. aculeata*, are therefore expected to accumulate some Mn in their test. With increasing oxygenation more  $\text{MnO}_2$  accumulates in surface and subsurface sediments and recycling of Mn will lead to build up of  $\text{Mn}^{2+}$  in the pore waters (Fig. 4, Appendix A). Under oxic conditions, only infaunal species will incorporate Mn in their calcite. In settings where the Mn dynamics are not in steady state, occurrence of double solid phase  $\text{MnO}_2$  peaks have been observed (e.g. Froelich et al., 1979; Burdige, 1993), leading to release of  $\text{Mn}^{2+}$  deeper in sediment below the active zone of manganese reduction. Such double peaks may result, for example, from a sudden change in oxygenation and/or organic matter burial rate (Froelich et al., 1979). If oxygen concentrations would drop dramatically over a short time period some  $\text{Mn}^{2+}$  may diffuse into the oxic zone. However, pore water profiles of  $\text{Mn}^{2+}$  have been shown to reestablish themselves generally fast, in order of month(s) (Froelich et al., 1979; Van der Zee et al., 2003). Although this would potentially impact the distribution of the low Mn concentrations of the shallow infaunal species, it does not affect Mn incorporation in the deep infaunal species. When low Mn concentrations in the deep infaunal species are observed, such as in the core of the OMZ, the Mn has escaped to the water column. This somewhat limits robust application of the here proposed proxy to low oxygen settings (low Mn in both shallow and deep infaunal species), whereas application to more oxygenated settings requires additional information on stability of redox zonation. In addition the analyses of multiple single specimens potentially could provide insight in stability of this redox zone, looking at the range in Mn/Ca between specimens of the same species. In the Arabian Sea the lower zone of the OMZ does not fluctuate seasonally (Cowie and Levin, 2009), although the organic matter flux is known to be seasonal (Kabanova, 1968). This might explain the observed variability in Mn incorporation observed for some of the shallow infaunal species (Figs. 3 and 5).

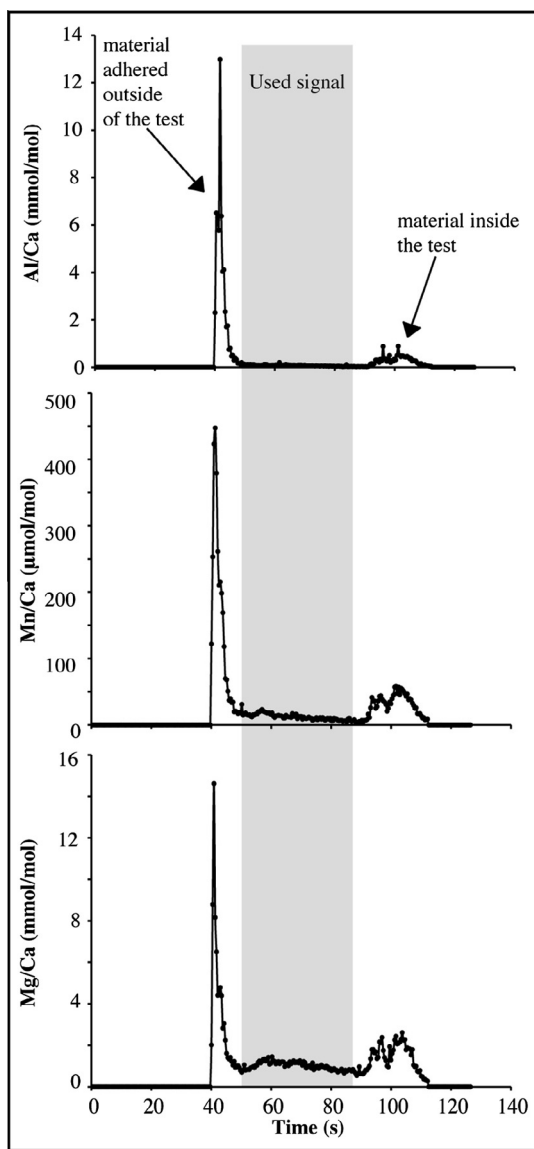


Fig. 2. Laser ablation profile for Al/Ca and Mn/Ca measured in benthic foraminifera *Uvigerina peregrina* (Station 8 found at 0.5–1.0 cm depth in sediment). In addition Mg/Ca profile is shown for comparison to illustrate the stable elemental composition in the foraminiferal test calcite. The selected signal for the elemental composition is indicated with the gray shading. Parts of the profile with elevated surface ratios, especially Al/Ca, are removed. In addition, the elevated concentrations, following the ablation through the foraminiferal test are not included in the averaged elemental ratios.

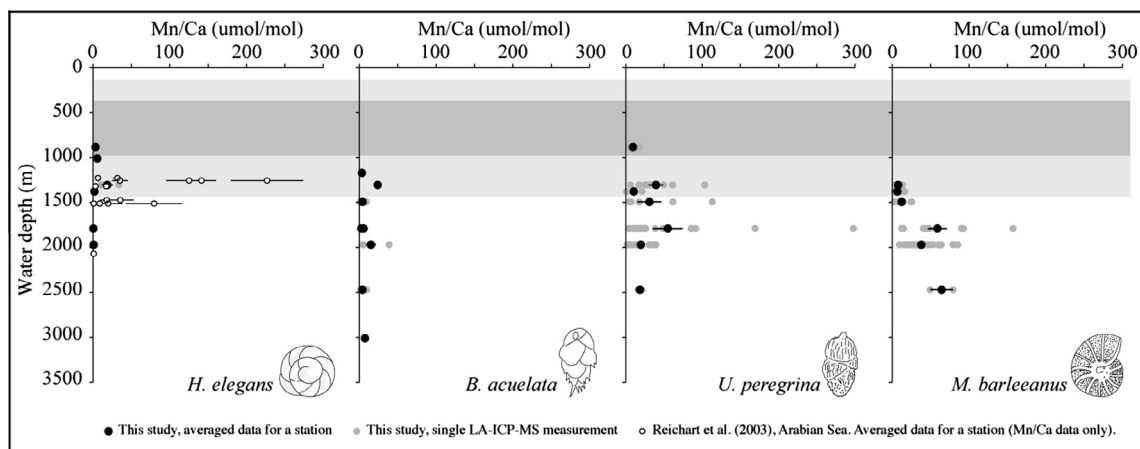


Fig. 3. Foraminiferal Mn/Ca ratios along the study transect. Black symbols are the average ratios for each site and associated error bars represent the standard error. Light gray symbols show the individual laser ablation measurements. Mn/Ca data of *H. elegans* of Reichart et al.

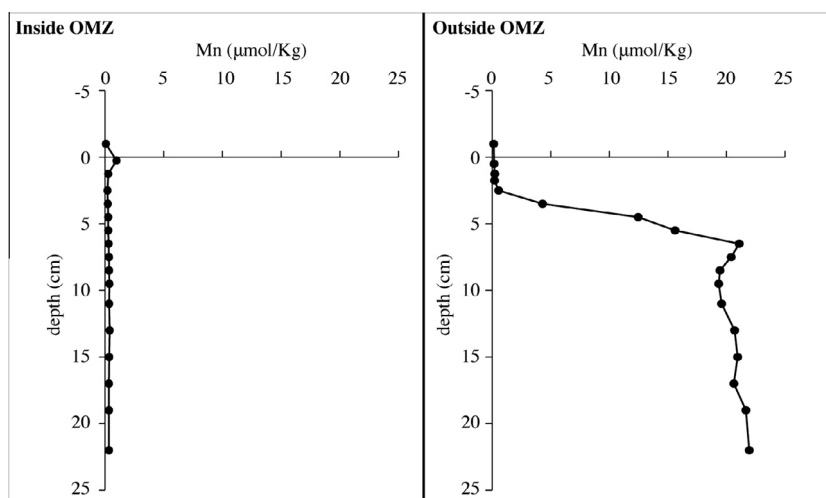


Fig. 4. Examples of pore water profiles of Mn in the oxygen minimum zone (Station 1B; BWO: 2  $\mu\text{mol/l}$ ) and outside (Station 8; BWO: 57  $\mu\text{mol/l}$ ).

In our data set the availability of pore water  $\text{Mn}^{2+}$  and its relation to bottom water oxygenation is most clear in the foraminiferal Mn/Ca ratios of *M. barleeanus* (Fig. 5). When comparing pore water  $[\text{Mn}^{2+}]_{\text{aq}}$  concentrations from the average in-sediment living depth of *M. barleeanus* (calculated after Jorissen et al., 1995; also known as the Average Living Depth, ALD) to Mn/Ca ratios in this species, a statistically significant trend is apparent (raw data: Pearson correlation 0.513,  $p < 0.01$ ,  $n = 60$ ; the averaged Mn/Ca values: Pearson correlation 0.812,  $p < 0.05$ ,  $n = 6$ ). Furthermore, the ratio between foraminiferal and pore water Mn/Ca is similar to, albeit somewhat lower than the partitioning coefficient ( $D_{\text{Mn}}$ ) calculated by Munsel et al. (2010). Based on controlled growth experiments they suggested foraminiferal Mn/Ca to be about 2.6–10 times elevated with respect to that ratio in seawater. Our results and those of Munsel et al. (2010) show a partitioning coefficient considerably lower than the  $D_{\text{Mn}}$  of approximately

50 observed in inorganically precipitated carbonate (Lorens, 1978). Precipitation rate potentially offsets  $D_{\text{Mn}}$ , with higher precipitation rates resulting in a  $D_{\text{Mn}}$  closer to 1 (Lorens, 1981; Tesoriero and Pankow, 1996; Rimstidt et al., 1998). Although growth of a foraminifer as such may be relatively slow, chamber addition in benthic species occurs within a few hours (De Nooijer et al., 2009, 2014). The relation between Mn/Ca and ALD  $[\text{Mn}^{2+}]_{\text{aq}}$  appears to vary somewhat between the different deep-sea species shown here (Fig. 5). Also for other elements (e.g. Mg), partitioning coefficients are known to vary between species (e.g. Toyofuku et al., 2011; Wit et al., 2012). The somewhat higher  $D_{\text{Mn}}$  for *A. tepida* (Munsel et al., 2010) compared to the species studied here might be due to similar species-specific offsets. The  $D_{\text{Mn}}$  estimated in the study of Glock et al. (2012) for deep-sea foraminifera, *Bolivina spissa*, was close to 1.0 and is thus in line with our results. Furthermore, the consistent incorporation of pore water

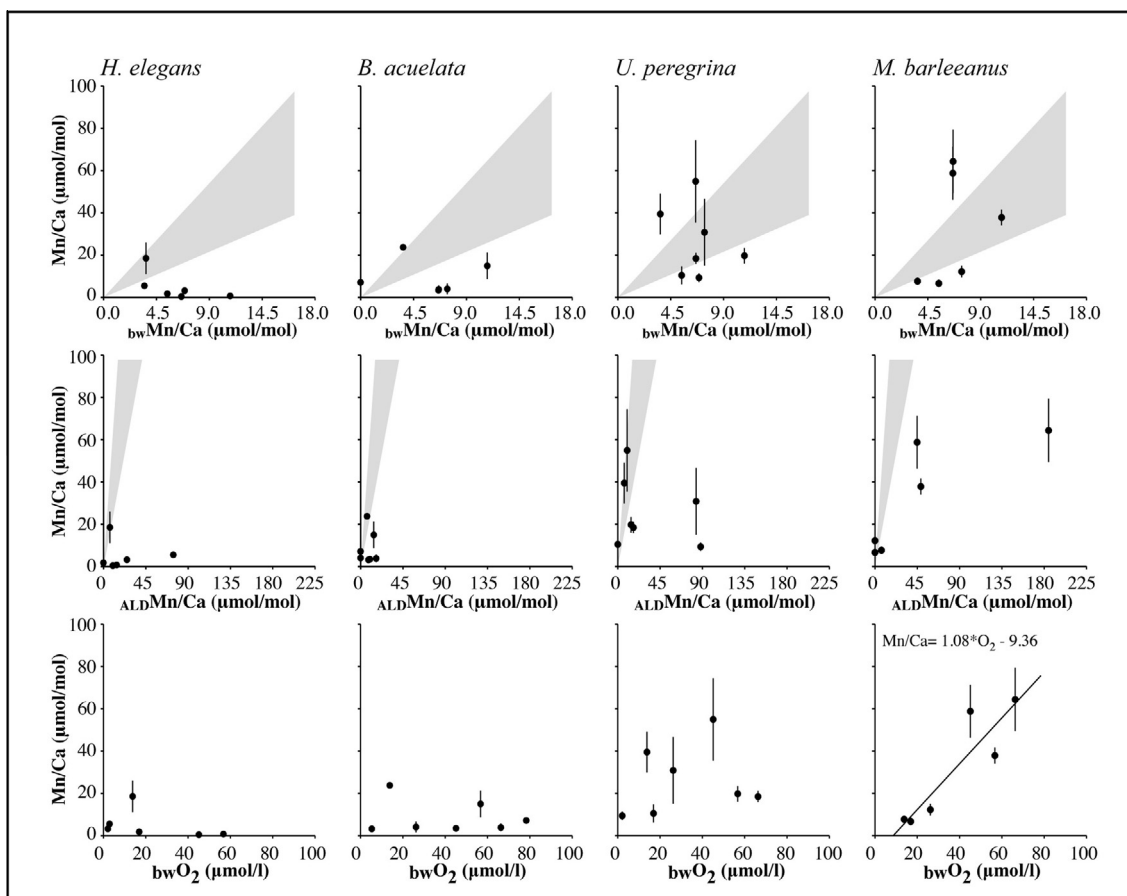


Fig. 5. Foraminiferal Mn/Ca ratios versus bottom water Mn content ( $_{bw}Mn$ ; top row), the manganese content of the average living depth of foraminifera ( $_{ALD}Mn$ ; middle row) and bottom water oxygen content ( $_{bw}O_2$ ; bottom row). The average living depth of each species for each site was calculated after Jorissen et al. (1995) and foraminiferal counts are based on the field study of Cauille et al. (2014). The samples used in this study are included in the study of Cauille et al. (2014). Error bars in our data represent the standard error of measurements for each site and species. The light gray shading (triangle) in the top rows indicates the window of  $D_{Mn}$  values reported in Munsel et al. (2010), see main body of text for more details.

Mn into test carbonate, suggests that *M. barleeanus* is growing and calcifying within a relatively narrow and stable microhabitat, below the oxygen penetration depth. Moreover, deeper in the sediment pore water profiles are less affected by seasonal variability in organic matter flux, resulting in more stable  $Mn^{2+}$  concentrations.

Although compared to *M. barleeanus* the other species studied here showed limited variability in their Mn/Ca, the observed changes are in line with their ecology and pore water chemistry. For example, *H. elegans* and *B. aculeata* recorded low Mn/Ca throughout the studied transect, corresponding to the low pore water Mn concentrations of the near surface in-sediment depth habitat where these species were found. Only at the lower boundary of the OMZ where Mn-reduction takes place close to the sediment–water interface a moderate increase in Mn-content is recorded for both *H. elegans* and *B. aculeata*. Similarly, large variability observed in the Mn/Ca of *U. peregrina* is in line with the variable microhabitat preference of this species (Cauille et al., 2014) and the potentially more variable Mn concentrations closer to the sediment–water interface.

The Mn/Ca in this species is low close to the OMZ and increases with increasing water depth, where Mn is retained within the pore water due to elevated bottom water oxygenation.

The Mn/Ca ratios in the infaunal foraminifera *M. barleeanus* also shows a very promising, statistically significant trend with bottom water oxygenation (raw data: Pearson correlation 0.536,  $p < 0.01$ ,  $n = 60$ ; the averaged Mn/Ca values: Pearson correlation 0.903,  $p < 0.05$ ,  $n = 6$ ). Although *M. barleeanus* is living deeper in the sediment, the availability of pore water  $Mn^{2+}$  is directly coupled to bottom water oxygenation in the OMZ. It seems that the infaunal lifestyle of this species provides it with best opportunity to track the reduction of  $MnO_2$  to  $Mn^{2+}$  as this typically takes place in the sediment. For the other species, no such clear trend is observed. This is likely related to the low  $Mn^{2+}$  availability in the surface sediments where these shallow infaunal species (*B. aculeata* and *H. elegans*) live. In our samples the highest Mn/Ca ratios for infaunal *U. peregrina* are recorded where bottom water  $O_2$  contents are between 20 and 45  $\mu M$ . We suggest that at these oxygen

concentrations relatively more  $Mn^{2+}$  is incorporated into *U. peregrina* test calcite as the  $MnO_2$  reduction occurs close to its calcification environment and thus more  $Mn^{2+}$  can diffuse into the foraminiferal microenvironment. When bottom water (and associated pore water) oxygen content increases the  $MnO_2$  reduction moves deeper into the sediment outside the common habitat of *U. peregrina* and hence calcitic Mn/Ca ratios also decrease.

### 3.2. Conceptual model: TROXCHEM<sup>3</sup>

The results outlined above are combined into a conceptual model, building upon the existing TROX-models from Jorissen et al. (1995) and Van der Zwaan et al. (1999): TROXCHEM<sup>3</sup> (three dimensional trophic level, bottom water oxygenation and pore water chemistry model, Fig. 6). This provides the first step toward the use of foraminiferal Mn/Ca as a function of both food supply and bottom water oxygenation. TROXCHEM<sup>3</sup> is based on data presented here and Mn/Ca in recent deep-sea benthic foraminifera in literature (Reichert et al., 2003; Glock et al., 2012), illustrating the relationships between organic flux, oxygenation, pore water Mn-content and foraminiferal test Mn/Ca (Fig. 6), but also sets the stage for including other redox sensitive elements and elements sensitive to carbon flux.

In well-ventilated benthic habitats, such as on most continental margins, oxygen typically penetrates deep into the sediment and results in increasing dissolved pore water Mn with sediment depth. In such environments, only intermediate to deep infaunal foraminifera are subject to elevated Mn concentrations, resulting in higher calcitic Mn/Ca of their tests. In contrast, shallow infaunal foraminifera like *H. elegans* will not incorporate Mn under such conditions (Reichert et al., 2003). If oxygen penetration into the sediment reduces due to enhanced remineralization, but bottom-waters remain oxic, also shallow infaunal species (tolerant to low oxygen conditions) are subject to elevated pore water Mn-concentrations and thereby incorporate more Mn into their carbonate skeletons (Reichert et al., 2003).

In settings permanently depleted from oxygen (like within the Arabian Sea OMZ and the Peruvian OMZ; Glock et al., 2012) no or very little Mn is incorporated into foraminiferal carbonate tests, as pore water  $Mn^{2+}$  escapes into the water column (Fig. 6). However, as bottom water oxygenation increases and Mn-(hydr)oxides can form in surface sediments, leading to their subsequent reduction, (deep/intermediate) infaunal species show a trend with low Mn-incorporation under oxygen deprived bottom water conditions and a higher Mn-incorporation with increasing bottom water ventilation (Figs. 5 and 6). Shallow infaunal species seem to rather respond to organic matter loading, having higher Mn concentrations when the redox cline moves up and Mn concentrations in the pore waters near the sediment water increase. In contrast, Mn concentrations of oxyphillic, epifaunal/shallow infaunal species show no response to bottom water oxygenation, as they never calcify in environment where aqueous  $Mn^{2+}$  is present.

A prerequisite for application of the TROXCHEM<sup>3</sup> model is that microhabitat preferences of species are constrained. The four species studied here represent four groups with different micro-habitat preferences. The *H. elegans* and *B. aculeate*, living in surficial sediments, display similar Mn/Ca, indicating that the mineralogy does not affect the amount of Mn incorporated in the shells. For many species, the microhabitat distribution is well documented (e.g. Jorissen et al., 1995; Koho et al., 2008). In addition, experimental studies have also demonstrated that foraminifera actively migrate and seek for their preferred microhabitat if their distribution in sediment is disturbed (Geslin et al., 2004; Koho et al., 2013). These well constrained microhabitat distributions, confirmed by patterns in Mn-incorporation, also allow studying impact of differences in pore water chemistry of elements suggested to co-vary with carbonate chemistry.

In future studies, the conceptual TROXCHEM<sup>3</sup> model may be extended by including other redox sensitive elements, as well as shifts in pore water carbonate chemistry related to ongoing early diagenesis. For this, however, more data are needed for especially for shallow infaunal but also for deeper infaunal species and from more contrasting settings. Particularly elements of which the chemical speciation depends on pore water redox chemistry, or associated organic matter cycling, (e.g. B, Fe, Mo, U) could provide a useful extension of the TROXCHEM<sup>3</sup> model. If indeed related to pore water chemistry, the combined measurement of these elements in foraminiferal species with a well-constrained depth habitat will allow a quantitative reconstruction of pore water oxygenation levels.

### 3.3. The proxy value of Mn/Ca ratios in benthic foraminifera and application of TROXCHEM<sup>3</sup> in paleoenvironmental reconstructions

Few studies have attempted to apply Mn/Ca ratios measured in benthic foraminifera to reconstruct bottom water oxygenation or redox conditions in past sedimentary environments (Klinkhammer et al., 2009; Ni Fhlaithearta et al., 2010). In the latter of these two studies, Mn/Ca ratios were measured in the shallow infaunal species *H. elegans*, and obtained ratios were used to reconstruct changes in redox conditions during deposition of the youngest sapropel (S1) in the eastern Mediterranean (10.8–6.1 kyrs B.P., De Lange et al., 2008). Mn/Ca ratios in the test carbonate of *H. elegans* increased from  $<2 \mu\text{mol/mol}$  prior to the onset of the S1 deposition up to  $8.2 \mu\text{mol/mol}$  during deposition of S1 under suboxic conditions, corresponding to  $Mn^{2+}$  mobilization from the sediment during the deposition of S1. The total change in Mn/Ca of *H. elegans* over this time period, during which major changes were taking place in the bottom water oxygenation, however, was relatively small ( $\Delta \pm 6 \mu\text{mol/mol}$ ). The relatively low sensitivity of Mn/Ca in *H. elegans* to sediment redox conditions corresponds well with our observation of Mn/Ca measured for this taxa in the Arabian Sea OMZ. Furthermore, in line with the TROXCHEM<sup>3</sup> model (Fig. 6), a shallow infaunal species such as *H. elegans* occupies niches where oxygen is present (Koho et al., 2008) and thus rarely inhabits



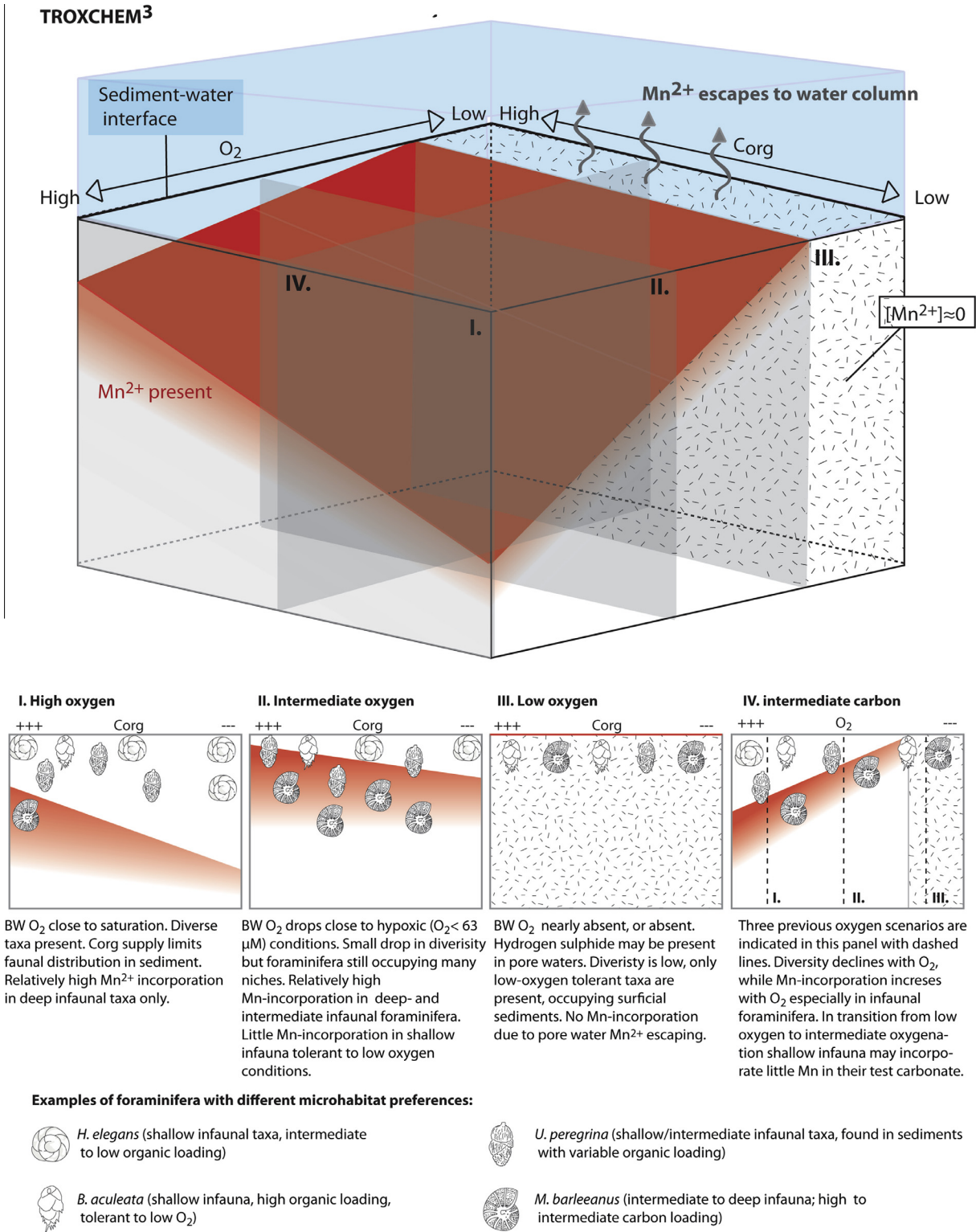


Fig. 6. A conceptual TROXCHEM<sup>3</sup> model illustrates the relationships between organic loading, oxygenation, pore water Mn-content and their influence on Mn-incorporation into benthic foraminiferal tests. Four two-dimensional model transects are shown to further highlight how the environmental conditions influence Mn-incorporation into foraminifera with various microhabitats. See main body of text (Section 3.2) for further details.

sediments with high soluble  $Mn^{2+}$  content. At the onset of S1 bottom water  $O_2$  content decreased and the  $MnO_2$  reduction front migrated upwards. When bottom waters became suboxic, some  $Mn^{2+}$  may have entered into the habitat of *H. elegans* and was subsequently incorporated in the test carbonate. Furthermore, in heavily reducing and/or anoxic sediments, *H. elegans* is unlikely to be present at all, or contribute only marginally to the total assemblage (Koho et al., 2008).

Klinkhammer et al. (2009), measured Mn/Ca ratios in infaunal species *U. peregrina* from the ODP site 1242 in order to reconstruct Mn dynamics in the OMZ sediments of the Eastern Tropical North Pacific (ETNP). The ETNP OMZ is similar to the Arabian Sea, in that it is also fueled by upwelling driven high primary productivity, leading to an extended OMZ (Karstensen et al., 2008). Furthermore, like the Arabian Sea OMZ, the ETNP OMZ is a relatively stable paleoceanographic feature, which persisted on geological times scales.

In the study of the Klinkhammer et al. (2009), Mn/Ca ratios in *U. peregrina* were shown to be below during the glacial and deglaciation, albeit not entirely in phase with changes in the water column based on Mn/Ca ratios measured on *N. dutertrei*. In turn a peak in Mn/Ca ratios was noted around 10 ka. The low glacial Mn/Ca ratios in *U. peregrina* are consistent with high productivity estimates of Klinkhammer et al. (2009), implying that the Mn escaped to the water column, which is in line with the TROXCHEM<sup>3</sup> model. For the same core Martinez and Robinson (2010) showed that at the time of the peak in the Mn/Ca ratios measured in *U. peregrina* (10 ka) sedimentary organic carbon and nitrogen values were lower, probably due to lower export production. Lower export production, possibly in combination with changes in the bottom water circulation, would have retained the Mn within the sediment and hence increased Mn incorporation from pore water into the infaunal benthic foraminifera. The interpretations are consistent with our observations in the Arabian Sea OMZ, where highest Mn/Ca ratios in *U. peregrina* are associated with the lower boundary of OMZ, where oxygen was still sufficient to prevent  $Mn^{2+}$  from escaping the sediments. The lower Mn/Ca ratios at about 15 ka would hence imply that the ETNP OMZ was more intense and subsequently became slightly more oxygenated toward values of about 60  $\mu\text{mol}$ , based on our Arabian Sea calibration, at 10 ka. Other, deeper infaunal species, would be needed to better constrain the oxygenation history of the ETNP.

The reconstruction of Mn dynamics and bottom water oxygenation using foraminiferal Mn uptake depends on how well the ecology of the foraminiferal species and their in-sediment depth habitat is known. Our observations in the Arabian Sea OMZ show that the intermediate to deep infaunal foraminifera (e.g. *M. barleeanus*) are the most suitable species to base reconstructions on (Fig. 5). Application of a shallow infaunal species, such as *H. elegans* in the study of Ni Fhlaithearta et al. (2010) is possible, although the

change in Mn/Ca is likely to be much smaller than for intermediate or deep infaunal species. Sensitivity of Mn/Ca in epi to shallow infaunal species as a function of bottom water oxygenation is much less than that of deeper living fauna, and small changes in oxygenation may hence go undetected. In addition, a shallow infaunal species may not be present in assemblages when oxygen levels decrease below the critical level for that species.

Reconstruction of Mn dynamics and redox conditions in sedimentary environments could be further improved using the TROXCHEM<sup>3</sup> model, integrating the microhabitat distribution of different benthic foraminifera, each with its own in-sediment depth habitat and thus Mn/Ca response (Fig. 6). Based on the here presented model (Fig. 6, panel III), when no Mn is recorded in both shallow and deeper living infauna, sedimentary conditions must be very reducing, with bottom water oxygen content close to zero and  $Mn^{2+}$  escaping into the water column. Instead, if  $Mn^{2+}$  is incorporated only in deep infauna but not in shallow infauna, bottom waters must be relatively well oxygenated (Fig. 6 panel I).

#### 4. CONCLUSIONS

Here we show that Mn-analyses in foraminiferal test carbonate obtained with LA-ICP-MS analysis produce reliable Mn/Ca data. The Mn/Ca ratios can be used to reconstruct redox changes in sedimentary environments. When relying on a single species our data suggest that infaunal foraminifera are best suited for reconstructing BWO. Our data also set the stage for a new conceptual model: TROXCHEM<sup>3</sup>, which combines foraminiferal ecology and test trace element chemistry with pore water geochemistry and sediment carbon loading. Using Mn incorporation this model explains the observed differences in between species with contrasting micro-habitats. Application of the TROXCHEM<sup>3</sup> model provides a first step toward deconvolving past organic matter input and bottom water oxygenation, potentially allowing their independent quantification in paleosediment records.

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#### APPENDIX A. PORE WATER MN DATA

Mn ( $\mu\text{mol/kg}$ )	Station											
	Bottom	Average	PASOM-1B	PASOM-2	PASOM-3	PASOM-4	PASOM-5	PASOM-6	PASOM-7	PASOM-8	PASOM-9	PASOM-10
Bottom water	–1	0.08	0.04	0.34	0.04	0.06	0.08	0.07	0.12	0.07	0.00	0.00
0	0.5	0.25	0.98	0.82	0.09	0.08	0.00	0.00	0.11	0.16	0.18	0.00
0.5	1	0.75									0.19	0.00
1	1.5	1.25	0.28	3.94	0.19	0.00	1.84	0.93	0.50	0.21	0.14	0.00
1.5	2	1.75								0.19	0.15	
2	3	2.5	0.21	5.31	0.61	4.60	4.61	8.31	15.37	0.54	2.05	0.00
3	4	3.5	0.24	5.35	0.88	5.52		12.95	24.66	4.29	24.97	0.92
4	5	4.5	0.28	5.36	1.12	5.52	9.19	14.80		12.46	51.21	11.98
5	6	5.5	0.28	4.63	1.22	6.46	9.04	12.02		15.61	74.54	
6	7	6.5	0.30	4.19	1.37	5.52	8.30	12.93		21.09	57.98	17.51
7	8	7.5	0.34	3.56	1.21	5.53		10.14		20.41	78.82	
8	9	8.5	0.35	2.49	1.45	5.52	7.36	9.24		19.45	86.36	42.38
9	10	9.5	0.37	3.06	1.56	5.53		8.29		19.34		

## REFERENCES

- Altabet M. A., Francos R., Murray D. W. and Prell W. L. (1995) Climate-related variations in denitrification in the Arabian Sea from sediment  $^{15}\text{N}/^{14}\text{N}$  ratios. *Nature* **373**(6514), 506–509.
- Altabet M. A., Higginson M. J. and Murray D. W. (2002) The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric  $\text{CO}_2$ . *Nature* **415**(6868), 159–162.
- Barker S., Greaves M. and Elderfield H. (2003) A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochem. Geophys. Geosyst.* **4**(9).
- Bernhard J. M. (1988) Postmortem vital staining in benthic foraminifera; duration and importance in population and distributional studies. *J. Foraminifer. Res.* **18**, 143–146.
- Boyle E. A. (1981) Cadmium, zinc, copper, and barium in foraminifera tests. *Earth Planet. Sci. Lett.* **53**, 11–35.
- Boyle E. A. (1983) Manganese overgrowths on foraminifera tests. *Geochim. Cosmochim. Acta* **47**, 1815–1819.
- Burdige D. J. (1993) The biogeochemistry of manganese and iron reduction in marine sediments. *Earth Sci. Rev.* **35**, 249–284.
- Burdige D. J. and Gieskes J. M. (1983) A pore water/solid phase diagenetic model for manganese in marine sediments. *Am. J. Sci.* **283**, 29–47.
- Caulle C., Koho K. A., Mojtahid M., Reichart G. J. and Jorissen F. J. (2014) Live (Rose Bengal stained) foraminiferal faunas from the northern Arabian Sea: faunal succession within and below the OMZ. *Biogeosciences* **11**, 1155–1175.
- Corliss B. H. and Emerson S. (1990) Distribution of Rose Bengal stained deep-sea benthic foraminifera from the Nova Scotian continental margin and Gulf of Maine. *Deep Sea Res. Part A* **37**, 381–400.
- Cowie G. L. and Levin L. A. (2009) Benthic biological and biogeochemical patterns and processes across an oxygen minimum zone (Pakistan margin, NE Arabian Sea). *Deep-Sea Res. Pt. II* **56**(6–7), 261–270.
- Dauwe B., Middelburg J. J. and Herman P. M. J. (2001) Effect of oxygen on the degradability of organic matter in subtidal and intertidal sediments of the North Sea area. *Mar. Ecol. Prog. Ser.* **215**, 13–22.
- De Lange G. J., Thomson J., Reitz A., Slomp C. P., Speranza Principato M., Erba E. and Corselli C. (2008) Synchronous basin-wide formation and redox-controlled preservation of a mediterranean sapropel. *Nat. Geosci.* **1**(9), 606–610.
- Den Dulk M., Reichart G. J., Van Heyst S., Zachariasse W. J. and Van Der Zwaan G. J. (2000) Benthic foraminifera as proxies of organic matter flux and bottom water oxygenation? A case history from the northern Arabian Sea. *Palaeogeogr. Palaeocli.* **161**(3–4), 337–359.
- De Nooijer L. J., Duijnste I. A. P. and Van der Zwaan G. J. (2006) Novel application of MTT-reduction: a viability assay for temperate, shallow-water benthic foraminifera. *J. Foramin. Res.* **36**, 195–200.
- De Nooijer L. J., Langer G., Nehrke G. and Bijma J. (2009) Physiological controls on seawater uptake and calcification in the benthic foraminifer *Ammonia tepida*. *Biogeosciences* **6**, 2669–2675.
- De Nooijer L. J., Spero H. J., Erez J., Bijma J. and Reichart G.-J. (2014) Biomineralization in foraminifera. *Earth Sci. Rev.* **135**, 48–58.
- Dueñas-Bohórquez A., Raitsch M., de Nooijer L. J. and Reichart G.-J. (2011) Independent impacts of calcium and carbonate ion concentration on Mg and Sr incorporation in cultured benthic foraminifera. *Mar. Micropal.* **81**, 122–130.
- Finney B. P., Lyle M. W. and Heath G. R. (1988) Sedimentation at MANOP site H (eastern Equatorial Pacific) over the past 400,000 years: climatically induced redox variations and their

- effects on transition metal cycling. *Paleoceanography* **3**, 169–189.
- Froelich P. N., Klinkhammer G. P., Bender M. L., Luedtke N. A., Heath G. R., Cullen D., Dauphin P., Hammond D., Hartman B. and Maynard V. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**(1075), 1090.
- Geslin E., Heinz P., Jorissen F. and Hemleben C. (2004) Migratory responses of deep-sea benthic foraminifera to variable oxygen conditions: laboratory investigations. *Mar. Micropaleontol.* **53**, 227–243.
- Glock N., Eisenhauer A., Liebetrau V., Wiedenbeck M., Hensen C. and Nehrke G. (2012) EMP and SIMS studies on Mn/Ca and Fe/Ca systematics in benthic foraminifera from the Peruvian OMZ: a contribution to the identification of potential redox proxies and the impact of cleaning protocols. *Biogeosciences* **9**(1), 341–359.
- Goto K. T., Anbar A. D., Gordon G. W., Romaniello S. J., Shimoda G., Takaya Y., Tokumaru A., Nozaki T., Suzuki K., Machida S., Hanyu T. and Usui A. (2014) Uranium isotope systematics of ferromanganese crusts in the Pacific ocean: implications for the marine  $^{238}\text{U}/^{235}\text{U}$  isotope system. *Geochim. Cosmochim. Acta* **146**, 43–58.
- Groeneveld J. and Filipsson H. L. (2013) Mg/Ca and Mn/Ca ratios in benthic foraminifera: the potential to reconstruct past variations in temperature and hypoxia in shelf regions. *Biogeosciences* **10**, 5125–5138.
- Hartnett H. E., Keil R. G., Hedges J. I. and Devol A. H. (1998) Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature* **391**(6667), 572–574.
- Hathorne E. C., James R. H., Savage P. and Alard O. (2008) Physical and chemical characteristics of particles produced by laser ablation of biogenic calcium carbonate. *J. Analyt. Atom. Spectro.* **23**, 240–243.
- Hedges J. I. and Keil R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49**, 81–115.
- Hoogakker B. A. A., Elderfield H., Schmiedl G., McCave I. N. and Rickaby R. E. M. (2014) Glacial-interglacial changes in bottom-water oxygen content on the Portuguese margin. *Nat. Geosci.* **8**, 40–43.
- Inoue M., Nohara M., Okai T., Suzuki A. and Kawahata H. (2004) Concentrations of trace elements in carbonate reference materials coral JCp-1 and giant clam JCT-1 by inductively coupled plasma-mass spectrometry. *Geostand. Geoanal. Res.* **28**(3), 411–416.
- Jochum K. P., Dingwell D. B., Rocholl A., Stoll B., Hofmann A. W., Becker S., Besmehn A., Bessette D., Dietze H.-J., Dulski P., Erzinger J., Hellebrand E., Hoppe P., Horn I., Janssens K., Jenner G. A., Klein M., McDonough W. F., Maetz M., Mezger K., Munker C., Nikogosian I. K., Pickhardt C., Raczek I., Rhede D., Seufert H. M., Simakin S. G., Sobolev A. V., Spettel B., Straub S., Vincze L., Wallianos A., Weckwerth G., Weyer S., Wolf D. and Zimmer M. (2000) The preparation and preliminary characterisation of eight geological MPI-DING reference glasses for in-site microanalysis. *Geostand. Newslett.* **24**, 87–133.
- Jorissen F. J., de Stigter H. C. and Widmark J. G. V. (1995) A conceptual model explaining benthic foraminiferal microhabitats. *Mar. Micropaleontol.* **26**(1–4), 3–15.
- Jorissen F. J., Fontanier C. and Thomas E. (2007) Chapter seven paleoceanographical proxies based on deep-sea benthic foraminiferal assemblage characteristics. *Dev. Mar. Geol.* **1**, 263–325.
- Kabanova Y. G. (1968) Primary production in the northern part of the Indian Ocean. *Oceanology* **8**, 214–225.
- Kaiho K. (1994) Benthic foraminiferal dissolved-oxygen index and dissolved-oxygen levels in the modern ocean. *Geology* **22**, 719–722.
- Kaiho K. (1999) Effect of organic carbon flux and dissolved oxygen on the benthic foraminiferal oxygen index (BFOI). *Mar. Micropaleontol.* **37**, 67–76.
- Karstensen J., Stramma L. and Visbeck M. (2008) Oxygen minimum zones in the eastern tropical Atlantic and Pacific oceans. *Prog. Oceanogr.* **77**, 331–350.
- Klinkhammer G. P., Mix A. C. and Haley B. A. (2009) Increased dissolved terrestrial input to the coastal ocean during the last deglaciation. *Geochim. Geophys. Geosyst.* **10**(3).
- Koho K. A., García R., de Stigter H. C., Epping E., Koning E., Kouwenhoven T. J. and van der Zwaan G. J. (2008) Sedimentary labile organic carbon and pore water redox control on species distribution of benthic foraminifera: a case study from Lisbon-Setúbal Canyon (southern Portugal). *Prog. Oceanogr.* **79**, 55–82.
- Koho K. A., Piña-Ochoa E., Geslin E. and Risgaard-Petersen N. (2011) Vertical migration, nitrate uptake and denitrification: Survival mechanisms of foraminifera (*Globobulimina turgida*) under low oxygen conditions. *FEMS Microbiol. Ecol.* **75**(2), 273–283.
- Koho K. A., Nierop K. G. J., Moodley L., Middelburg J. J., Pozzato L., Soetaert K., Van Der Plicht J. and Reichart G.-J. (2013) Microbial bioavailability regulates organic matter preservation in marine sediments. *Biogeosciences* **10**(2), 1131–1141.
- Law G. T. W., Shimmield T. M., Shimmield G. B., Cowie G. L., Breuer E. R. and Martyn Harvey S. (2009) Manganese, iron, and sulphur cycling on the Pakistan margin. *Deep-Sea Res. Pt. II* **56**, 305–323.
- Levin L. A. (2003) Oxygen minimum zone benthos: adaptation and community response to hypoxia. *Oceanogr. Mar. Biol. Annu. Rev.* **41**, 1–45.
- Levin L. A., Whitcraft C. R., Mendoza G. F., Gonzalez J. P. and Cowie G. (2009) Oxygen and organic matter thresholds for benthic faunal activity on the Pakistan margin oxygen minimum zone (700–1100 m). *Deep-Sea Res. Pt. II* **56**, 449–471.
- Lorens R. B. (1978) A study of biological and physical controls on the trace metal content of calcite and aragonite. Ph. D. dissertation, Univ. of Rhode Island.
- Lorens R. B. (1981) Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochim. Cosmochim. Acta* **45**, 553–561.
- Martinez P. and Robinson R. S. (2010) Increase in water column denitrification during the last deglaciation: the influence of oxygen demand in the eastern equatorial Pacific. *Biogeosciences* **7**, 1–9.
- McCorkle D. C. and Emerson S. R. (1988) The relationship between pore water carbon isotopic composition and bottom water oxygen concentration. *Geochim. Cosmochim. Acta* **52**(5), 1169–1178.
- Munsell D., Kramar U., Dissard D., Nehrke G., Berner Z., Bijma J., Reichart G.-J. and Neumann T. (2010) Heavy metal incorporation in foraminiferal calcite: results from multi-element enrichment culture experiments with *Ammonia tepida*. *Biogeosciences* **7**, 2339–2350.
- Nardelli M. P., Barras C., Metzger E., Mouret A., Filipsson H. L., Jorissen F. and Geslin E. (2014) Experimental evidence for foraminiferal calcification under anoxia. *Biogeosciences* **11**, 4029–4038.



- Ni Fhlaithearta S. N., Reichart G.-J., Jorissen F. J., Fontanier C., Rohling E. J., Thomson J. and De Lange G. J. (2010) Reconstructing the seafloor environment during sapropel formation using benthic foraminiferal trace metals, stable isotopes, and sediment composition. *Paleoceanography* **25**(4).
- Olson D. B., Hitchcock G. L., Fine R. A. and Warren B. A. (1993) Maintenance of the low-oxygen layer in the central Arabian Sea. *Deep Sea Res.* **40**, 673–685.
- Piña-Ochoa E., Høglund S., Geslin E., Cedhagen T., Revsbech N. P., Nielsen L. P., Schweizer M., Jorissen F., Rysgaard S. and Risgaard-Petersen N. (2010) Widespread occurrence of nitrate storage and denitrification among Foraminifera and Gromiida. *PNAS* **107**, 1148–1153.
- Reichart G.-J., Jorissen F., Anschutz P. and Mason P. R. D. (2003) Single foraminiferal test chemistry records the marine environment. *Geology* **31**(4), 355–358.
- Rimstidt J. D., Balog A. and Webb J. (1998) Distribution of trace elements between carbonate minerals and aqueous solutions. *Geochim. Cosmochim. Acta.* **62**, 1851–1863.
- Risgaard-Petersen N., Langezaal A. M., Ingvarsdén S., Schmid M. C., Jetten M. S. M., Op Den Camp H. J. M., Derksen J. W. M., Piña-Ochoa E., Eriksson S. P., Nielsen L. P., Revsbech N. P., Cedhagen T. and van der Zwaan G. J. (2006) Evidence for complete denitrification in a benthic foraminifer. *Nature* **443**(7107), 93–96.
- Schenu S. J., Reichart G. J. and de Lange G. J. (2002) Oxygen minimum zone controlled Mn redistribution in Arabian Sea sediments during the late quaternary. *Paleoceanography* **17**(4), 10–11.
- Tesoriero A. J. and Pankow J. F. (1996) Solid solution partitioning of Sr<sup>2+</sup>, Ba<sup>2+</sup>, and Cd<sup>2+</sup> to calcite. *Geochim. Cosmochim. Acta.* **60**, 1053–1063.
- Toyofuku T., Suzuki M., Suga H., Sakai S., Suzuki A., Ishikawa T., de Nooijer L. J., Schiebel R., Kawahata H. and Kitazato H. (2011) Mg/Ca and δ<sup>18</sup>O in the brackish shallow water benthic foraminifer *Ammonia beccarii*. *Mar. Micropal.* **78**, 113–120.
- Tribouillard N., Algeo T. J., Lyons T. and Riboulleau A. (2006) Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* **232**, 12–32.
- Van Cappellen P. and Wang Y. (1996) Cycling of iron and manganese in surface sediments; a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese. *Am. J. Sci.* **296**, 197–243.
- Van der Weijden C. H., Reichart G. J. and Visser H. J. (1998) Enhanced preservation of organic matter in sediments deposited within the oxygen minimum zone in the northeastern Arabian Sea. *Deep-Sea Res. Pt. I* **46**, 807–830.
- Van Der Zee C., Van Raaphorst W., Helder W. and De Heij H. (2003) Manganese diagenesis in temporal and permanent depositional areas of the north sea. *Cont. Shelf Res.* **23**, 625–646.
- Van der Zwaan G. J., Duijnste I. A. P., Den Dulk M., Ernst S. R., Jannink N. T. and Kouwenhoven T. J. (1999) Benthic foraminifers: proxies or problems? A review of paleoecological concepts. *Earth Sci. Rev.* **46**, 213–236.
- Wit J. C., Reichart G.-J., Jung S. J. A. and Kroon D. (2010) Approaches to unravel seasonality in sea surface temperatures using paired single-specimen foraminiferal δ<sup>18</sup>O and Mg/Ca analyses. *Paleoceanography* **25**, PA4220.
- Wit J. C., De Nooijer L. J., Barras C., Jorissen F. J. and Reichart G.-J. (2012) A reappraisal of the vital effect in cultured benthic foraminifer *Bulimina marginata* on Mg/Ca values: assessing temperature uncertainty relationships. *Biogeosciences* **9**(9), 3693–3704.
- Wyrski K. (1971) *Oceanographic Atlas of the International Indian Ocean Expedition*. National Science Foundation, Washington, DC, 531p.
- Wyrski K. (1973) Physical oceanography of the Indian Ocean. In *The Biology of the Indian Ocean*, vol. 3 (ed. B. Zeitzschel), pp. 18–36. Ecological Studies. Springer, Berlin.

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