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A comparison of benthic foraminiferal Mn/Ca and sedimentary Mn/Al as proxies of relative bottom water oxygenation in the low latitude NE Atlantic upwelling system

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Abstract

Trace element incorporation into foraminiferal shells (tests) is governed by physical and chemical conditions of the surrounding marine environment and therefore foraminiferal geochemistry provides a means of palaeoceanographic reconstructions. With the availability of high spatial resolution instrumentation with high precision, foraminiferal geochemistry has become a major research topic over recent years. However, reconstructions of past bottom water oxygenation using foraminiferal tests remain in their infancy. In this study we explore the potential of using Mn/Ca determined by Secondary Ion Mass Spectrometry (SIMS) as well as by Flow-Through Inductively Coupled Plasma Optical Emission Spectroscopy (FT-ICP-OES) in the benthic foraminiferal species *Eubuliminella exilis* as a proxy for recording changes in bottom water oxygen conditions in the low latitude NE Atlantic upwelling system. Furthermore, we compare the SIMS and FT-ICP-OES results with published Mn/Al in the bulk sediment from the same sediment core. This is the first time that benthic foraminiferal Mn/Ca is directly compared with Mn/Al in the bulk sediment, which largely agree on the former oxygen conditions. Samples were selected to include different productivity regimes related to Marine Isotope Stage 3 (35–28 ka), the Last Glacial Maximum (28–19 ka), Heinrich Event 1 (18–15.5 ka), Bølling Allerød (15.5–13.5 ka) and the Younger Dryas (13.5–11.5 ka). Foraminiferal Mn/Ca determined by SIMS and FT-ICP-OES are comparable. Mn/Ca was higher during periods with high primary productivity, such as during the Younger Dryas which indicates low oxygen conditions. This is further supported by the benthic foraminiferal faunal composition. Our results highlight the proxy potential of Mn/Ca in benthic foraminifera from upwelling systems for reconstructing past variations in oxygen conditions of the sea floor environment as well as the need to use it in combination with other proxy records such as faunal assemblage data.

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1 Introduction

Foraminifera, being extensively distributed and highly abundant in most marine environments, are essential proxies for reconstructing the chemical and physical properties of past oceans. Several trace elemental to foraminiferal calcite (Ca) ratios have been developed as proxies in the last decades. Perhaps one of the most conventional approaches is the reconstruction of seawater temperatures using Mg/Ca (e.g. Nürnberg et al., 1996; Elderfield et al., 2006). Other established trace elemental proxies also include Ba/Ca to trace salinity changes due to continental runoff (Lea and Boyle, 1989; Hönisch et al., 2011) and Cd/Ca to reconstruct water masses (Marchitto and Broecker, 2006). Whilst there is a wealth of research applying the geochemistry of foraminiferal calcite for palaeoceanographic reconstruction and copious sedimentary redox proxies have been developed (e.g. Gooday et al., 2009), utilising the trace elemental composition of foraminiferal shells (tests) to reconstruct oxygen conditions is still in its infancy. One proxy variable which has recently gained more interest is Mn/Ca both as a measure in biogenic foraminiferal calcite and in bulk sediment samples (Reichart et al., 2003; Glock et al., 2012; Groeneveld and Filipsson, 2013; Lenz et al., 2014). Here we aim to explore the potential of Mn/Ca by analysing both benthic foraminiferal tests and bulk sediment samples from an upwelling record to determine if changes in oxygen conditions during different primary productivity regimes are detectable by these methods.

At the sediment-water interface, the concentration of dissolved redox sensitive elements such as Mn vary significantly between oxic and hypoxic (hypoxia defined as $< 1.42\,\mathrm{mL\,L^{-1}}$ O_2 following Levin et al., 2009) settings. In seawater, redox sensitive Mn is mainly present as Mn^{2+} which under oxic conditions precipitates as Mn oxyhydroxide (Burdige, 1993; Glasby, 2006). The Mn flux across the sediment-water interface is driven by reductive dissolution of reactive Mn oxyhydroxide (Froelich et al., 1979).

Under oxic conditions, dissolved O_2 is present in the pore waters and thus benthic foraminiferal tests are expected to incorporate less Mn into their test. In contrast,

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under low oxygen conditions, Mn oxyhydroxide is reduced and the Mn^{2+} concentration increases (Tribovillard et al., 2006), becoming available to be incorporated in the foraminiferal tests. On the other hand, under anoxic conditions the Mn either diffuses upwards and into the overlying water column or when pore waters become supersaturated with respect to Mn, precipitation of $MnCO_3$ (rhodochrosite) occurs (Froelich et al., 1979; Pedersen and Price, 1982; Tribovillard et al., 2006). Therefore, under hypoxic conditions, benthic foraminifera will incorporate more Mn into their calcite tests and hence foraminiferal Mn/Ca has potential to be used as a proxy of hypoxic conditions. Accordingly, we expect bulk Mn to be depleted in the sediment and exhibit the opposite trend.

Whilst benthic foraminiferal Mn/Ca has been conventionally used as an indicator of contamination by Mn oxyhydroxide or Mn carbonate (Boyle, 1983; Barker et al., 2003) new studies are pioneering Mn/Ca as a potential proxy of related changes in bottom/pore water oxygen and redox conditions (Ní Fhlaithearta et al., 2010; Glock et al., 2012; Groeneveld and Filipsson, 2013). Mn/Ca signatures of the ambient bottom water are recorded by benthic foraminifera, for instance, culture experiments have confirmed that the species *Ammonia tepida* incorporates Mn into the test (Munsel et al., 2010). Thus, during benthic foraminiferal calcification under hypoxic conditions, more Mn will be assimilated into their calcite tests, whereas under anoxic or oxic conditions Mn is expected to decrease (Pena et al., 2005). Hence Mn/Ca used in this study could provide a reliable means of reconstructing the former seafloor oxygen settings at the time of deposition opposed to sediment bulk measurements which can continue to oxidise and be mobilised post deposition.

Traditionally, trace element/Ca is analysed on solution based samples containing larger numbers of foraminifera specimens to give a representative result (Groeneveld and Filipsson, 2013). When a sufficient amount of specimens is not available for solution based techniques, or if diagenesis has affected the tests, a micro-analytical technique upon single specimens such as Secondary Ion Mass Spectrometry (SIMS) is a valuable tool. From an analytical perspective SIMS has enhanced our ability to de-

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termine how trace elements are distributed within foraminiferal tests at high spatial resolution and precision on individual foraminifera specimens (Allison and Austin, 2003; Bice et al., 2005; Kunioka et al., 2006; Glock et al., 2012). Recently, SIMS determined Mn/Ca of benthic foraminifera has been found to be representative of Mn/Ca in the top cm of the pore water, confirming that the foraminiferal calcite composition relates to the level of oxygen depletion (Glock et al., 2012).

Where a sufficient amount of foraminiferal specimens were available, we additionally used Flow-Through Inductively Coupled Plasma Optical Emission Spectroscopy (FT-ICP-OES; Haley and Klinkhammer, 2002). Flow-Through analysis is a means of determining elemental composition from samples of foraminiferal tests which permits complete monitoring of the effects of cleaning and dissolution (Haley and Klinkhammer, 2002). However, due to the small size of *Eubuliminella exilis*, a larger number (up to 50 specimens in this case) of foraminiferal tests from the same core sample is required to give a representative average signal. Therefore we utilise both SIMS and FT-ICP-OES to explore the potential of Mn/Ca for interpreting down core oxygen studies.

To explore how Mn/Ca works as a potential proxy for bottom/pore water oxygen conditions, we study a site from the low latitude NE Atlantic Upwelling System. Upwelling systems are an ideal environment as they are renowned for high export rates of labile organic matter from surface waters which provokes severe oxygen depletion in the underlying intermediate waters and at the seafloor (Böning et al., 2004). We study core GeoB7926-2 from the upwelling region off coastal NW Africa (Fig. 1) and compare foraminiferal and sedimentary Mn with published diatom and benthic foraminiferal species composition (Romero et al., 2008; Filipsson et al., 2011; Kim et al., 2012; McKay et al., 2014). In general, coastal upwelling systems are the most productive of the world ocean resulting in vulnerability to oxygen minima within the water column and underlying seafloor (Helly and Levin, 2004; Bakun et al., 2010). At present, the benthic environment of this particular upwelling system is not especially susceptible to low oxygen conditions and is well ventilated with bottom water oxygen of ca. 5 $mL\,L^{-1}$ (Goretski and Koltermann, 2004). However, based on benthic foraminiferal faunal stud-

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ies, there is evidence of previous periods of oxygen depletion at the sea floor during the Younger Dryas (YD, 13.5–11.5 ka) and Heinrich Event1 (H1, 18–15.5 ka) in particular. This is inferred from the predominance of the low oxygen tolerant benthic foraminiferal species *Eubuliminella exilis* (synonymised taxa: *Bulimina exilis*) (Filipsson et al., 2011; McKay et al., 2014). Therefore, we selected samples allocated to late Marine Isotope Stage 3 (MIS3, 35–27 ka), the Last Glacial Maximum (LGM), Heinrich Event 1 (H1), Bølling Allerød (BA) and the Younger Dryas (YD) to reconstruct past bottom water oxygen. These climatic intervals were chosen in order to test if Mn/Ca can confirm the low oxygen conditions during different productivity regimes as reported by previous studies from this particular sediment core (Filipsson et al., 2011; McKay et al., 2014). We focus on utilising SIMS and compare this method with FT-ICP-OES where a sufficient number of *E. exilis* specimens were available. We also present Mn/Al sediment bulk measurements from the same sediment for further comparison.

The low oxygen tolerant, infaunal benthic foraminiferal species *Eubuliminella exilis* occurs in a range of settings. Abundant populations of this taxon are reported from coastal upwelling sites, sapropels, oxygen minimum zones and other environments for example in the Bering Sea and the Mississippi River mouth (Caralp, 1989; Jorissen, 1999; Jannink et al., 1998; Rasmussen et al., 2002; Khusid et al., 2006). Thus *E. exilis* has potential to be a useful proxy for other marine environments susceptible to strong oxygen deficiency and high fluxes of organic export. *Eubuliminella exilis* has been found to correlate with diatom accumulation rate and clearly dominates the foraminiferal fauna during very high diatom input (Caralp, 1984; Filipsson et al., 2011; McKay et al., 2014, 2015). Therefore *E. exilis*, being present (albeit in considerably varying abundance) throughout the GeoB7926-2 record is an ideal candidate to record oxygen changes in the environment in which they lived and also provide an opportunity to test if export productivity is causing low oxygen conditions opposed to the dominance of this species merely being a fresh phytodetritus diet signal (Caralp, 1989).

We hypothesise that higher foraminiferal Mn/Ca will occur during times of high diatom accumulation rate and lower bottom water oxygen concentrations and accord-

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ingly higher *E. exilis* abundance, with the opposite effect during times of low surface productivity.

2 Method

Gravity core GeoB7926-2 from the NE Atlantic Upwelling System (20°13′ N, 18°27′ E, 2500 m water depth) was recovered during R/V *Meteor* cruise M53/1 (Meggers and Cruise Participants, 2003). The age model for the core was published by Kim et al. (2012) and the timing and duration of the climatic intervals were adopted from the δ^{18}O of NGRIP (NGRIP Members, 2004) and Sánchez Goñi and Harrison (2010). We selected well-preserved foraminiferal specimens based on the criteria of high and low surface productivity regimes as demonstrated from diatom abundance (Romero et al., 2008). Details of sample preparation for benthic foraminiferal faunal analysis have previously been published (Filipsson et al., 2011; McKay et al., 2014).

2.1 SIMS analysis

From the > 150 µm size fraction, a total of 48 specimens of the benthic foraminifera species *Eubuliminella exilis* were hand-picked under a binocular microscope for SIMS analysis (Table 1). We acknowledge that the presence of Mn-rich authigenic coatings (e.g. Mn (oxy) hydroxides and Mn carbonates) can be problematic for trace elemental analysis of foraminifera (Boyle, 1983; Pena et al., 2005; Klinkhammer et al., 2009). Therefore, we employed a rigorous pre-treatment cleaning technique to remove possible diagenetic coatings following the method of Glock et al. (2012).

For the SIMS analysis, foraminifera from individual sample depths were rinsed over a 63 µm sieve with milliQ water. After this rinsing step, the foraminifera were transferred into vials and sonicated for 20 s. Subsequently, the foraminifera were rinsed with methanol and sonicated again for 1 min. Any residual methanol was then removed with milliQ water. An oxidative cleaning step consisted of mixing the following reagent:

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100 µL 30 % H_2O_2 to 10 mL of 0.1 M NaOH solution. 350 µL of this reagent was added to each individual vial and the vials were put into a water bath at 92 °C for 20 min. Afterwards another 20 s sonic bath was undertaken; the foraminifera samples were rinsed again with milliQ water in the 63 µm sieve to remove any residues. For the final step, the specimens were transferred back into their respective vials and 250 µL of 0.001 M HNO_3 was added to each vial. The vials were put into a sonic bath for 20 s and finally rinsed one last time with milliQ water. After the cleaning procedure, the specimens were checked under a binocular microscope to ensure sufficient cleaning and that the tests remained intact.

Foraminifera specimens were embedded in low viscosity epoxy resin at JAMSTEC, Japan. The foraminifera were then ground to expose a cross-section across the test wall using 16 µm silicon carbide paper at the Department of Geosciences, University of Edinburgh, UK. Resin pieces were mounted into low viscosity epoxy resin disks (Struers) at the NORDSIM laboratory, Laboratory for Isotope Geology at the Swedish Museum of Natural history, Stockholm, Sweden. The mounts were polished using a Struers Rotopol-2 at 150 rpm for 1 min, first with 3 µm diamond suspension and again with 1 µm diamond suspension. Between each grinding and polishing step, mounts were cleaned with ethanol. Each cross-sectioned foraminifera test was examined under high power reflected light microscopy to evaluate the quality of the carbonate and to assist in assessing the progress of polishing until the cross sections were clear. Subsequently, the mounts were cleaned in high purity ethanol and coated in a 20 nm thick high purity Au coat.

The reference material used for the SIMS was a polished piece of OKA calcite crystal supplied from Geomar, Kiel University, Germany (E. Hathorne, personal communication, 2013). This standard was obtained from a matrix matched specimen for which Mn/Ca has been reported by solution ICP-MS (Glock et al., 2012). During calibration, the OKA was analysed n = 16 times, yielding a high sensitivity with 1 SD repeatability of 1.2 % for Mn concentration.

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The Mn/Ca analyses of the test cross-sections were performed using a Cameca IMS 1270 ion microprobe at the NORDSIM laboratory at the Swedish Museum of Natural history, Stockholm, Sweden. Analysis used a $^{16}O_2^-$ ion beam accelerated at 23 kV impact energy (−13 kV primary beam, +10 kV secondary beam). It is vital to only analyse Mn which is located internally within the original test wall to attain most representative Mn/Ca for developing it as a redox proxy. Therefore, a 50 µm aperture in the primary column was used to shape a slightly elliptical 5 µm spot on the sample surface, which, together with careful placement, reduced the effects of sample contamination from the test wall outer surface. Prior to each analysis, the analytical location was pre-sputtered for 2 min with the ion beam rastered over 10 µm × 10 µm raster to remove the Au coat and any remaining surface contamination. During the initial pre-sputtering, the ^{44}Ca distribution was monitored using the ion imaging system of the instrument and maximised to ensure high precision beam targeting on the fine foraminiferal test walls. The mass spectrometer was operated at a mass resolution of M/Δ M ∼ 6000 to resolve the ^{55}Mn peak from nearby molecular interferences. A 400 µm contrast aperture was employed for maximum transmission together with a 60 µm entrance slit, a 2001 µm field aperture restricting the field of view on the sample to an area of ca. 12 µm × 12 µm at the transfer magnification of ca. 160×, and a 45 eV wide energy window; all of which combined to yield adequately flat topped peaks on the species of interest. Each analysis comprised of 16 cycles of ^{44}Ca (1 s integration cycle^{-1}) and ^{55}Mn (2 s). Each analysis lasted approximately 9 min. Secondary ions were measured using a low noise (< 0.01 cps) ion counting electron multiplier. Multiple analysis points were undertaken upon each individual test of *E. exilis* (ca. 6–10 targets per individual specimen) starting from the aperture and taking measurements alternating between the outer wall and internal walls. For the best targets, programming was performed manually to ensure that widest chamber walls and "*t*" junctions were targeted since they provide a wider test wall for the analyses (Fig. 2). Furthermore, at such high spatial resolution and precision, it is easy to visually observe and avoid encrusting prior to selecting analysis targets via the connected screen and avoid measuring secondary calcite or authigenic clays which

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would otherwise affect measurements. With cautious positioning of the primary beam on the test walls, such detrital material and potential contaminants were avoided and therefore only the elements actually incorporated into the calcitic tests were measured. As an additional prerequisite to this, analyses with Ca values > 500 kcps were classified as being reliable. Mn/Ca was first normalised to those determined in the OKA standard and subsequently converted to the true value in the OKA based on the Glock et al. (2012) value for Mn/Ca of 4920 µmol mol^{-1}.

The advantage of SIMS is that it is non-destructive and as the foraminiferal cross sections are preserved within the mounts, they can be stored for further analyses. Mounts are archived at the NORDSIM laboratory.

2.2 FT-ICP-OES analysis

For FT-ICP-OES, 20–50 specimens per sample depth of *E. exilis* from the GeoB7926-2 record were selected from samples corresponding to H1, BA and the YD for comparisons with the SIMS data. These three climatic intervals encompassed the only samples where a sufficient number of pristine *E. exilis* individuals were present. The tests were gently crushed in a 0.5 mL vial and fragments were transferred into a PTFA filter with 0.45 µm mesh.

For analysis, the filters were connected to a Flow-Through – Automated Cleaning Device (Klinkhammer et al., 2004; Haarman et al., 2011). Automatic cleaning prevents the loss of material which occurs with traditional cleaning allowing the analysis of very small samples (~ 20 µg). The Flow-Through was then connected to an ICP-OES (Agilent Technologies, 700 Series with autosampler (ASX-520 Cetac) and micro-nebulizer). Time Resolved Analysis (TRA) was used to analyze the samples at MARUM, University of Bremen, Germany. After an initial rinse (5 min) with buffered Seralpur water to remove clays, the samples were slowly dissolved using an acid ramp formed by mixing of Seralpur with 0.3 M QD HNO_3. Starting with pure Seralpur the acid contribution was stepwise increased every minute to 100 % acid after 30 min. The flow speed of the solution was 250 µL L^{-1}. Mn/Ca was determined by identifying the TRA interval which

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showed a consistent linear relationship between Mn and Ca counts. Mn/Ca was then calibrated using the characteristic slope of this linear relationship of a known in-house standard solution analyzed on the same acid ramp. The average standard error on the determination of the slope for Mn/Ca was 0.75 %. We analysed an international limestone standard (ECRM752-1) for Mg/Ca to validate the results following the same FT-protocol. The average Mg/Ca of the ECRM752-1 ($n = 4$) was 3.76 mmol mol^{-1}, which compares well with an average published value of 3.75 mmol mol^{-1} (Greaves et al., 2008).

2.3 Mn bulk measurements

For geochemical bulk analyses, samples were dried and ground in an agate mortar and homogenised. Total dissolution of samples was undertaken using HF and HNO_3 following the standard procedures of Gallego-Torres et al. (2007). Mn and Al content for samples corresponding to 35–10 ka was determined by Atomic Absorption Spectrometry, using Re and Rh as internal standards at the Analytical Facilities at the University of Granada, Spain. Mn being redox sensitive was normalised to Al content in order to correct for detrital variations (Van Der Weijden, 2002). Mn/Al data corresponding to 25–10 ka has previously been published (Gallego-Torres et al., 2014) and here we extend the Mn/Al record to 35 ka.

3 Results

3.1 SIMS and FT-ICP-OES data

Overall, Mn/Ca determined by SIMS varied between 2 and 750 µmol mol^{-1}. Average values ranged from 6.5 to 260 µmol mol^{-1} throughout the record and displayed a decreasing trend down core (Figs. 3 and 4, Table 1).

Mn/Ca was lowest in foraminiferal tests from MIS3 and the LGM with values ranging from 25–68 µmol mol^{-1} (average 50 µmol mol^{-1}) and 2–225 µmol mol^{-1} (average

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70 µmol mol^{-1}) respectively. Foraminifera from samples derived from the H1 and the BA exhibited a slightly elevated range of Mn/Ca at 50–380 µmol mol^{-1} (average 117 µmol mol^{-1}) and 27 to 280 µmol mol^{-1} (average 133 µmol mol^{-1}) respectively. Highest Mn/Ca occurred in foraminiferal tests from the YD (average 175 µmol mol^{-1}) period ranging from 23 to 750 µmol mol^{-1} (Fig. 3, Table 1).

In order to determine statistically significant differences between samples from different productivity regimes, Kruskal–Wallis tests were run and showed a statistically significant difference between the mean Mn/Ca values (per individual foraminifera specimen) between all five climatic intervals (p = 0.003). By testing the mean Mn/Ca of each foraminifera between each climatic interval individually in turn, using Post hoc (Mann Whitney U) tests, significant differences lay between climatic intervals with high and low export productivity regimes (based on diatom accumulation rate). Namely, significant differences in Mn/Ca were evident between the YD interval and the LGM and MIS3 (Table 2).

Mean SIMS derived Mn/Ca per sample depth compare well with FT-ICP-OES results (Table 1), agreeing with maximum differences of 15–24 µmol mol^{-1} (Fig. 4). Mn/Ca from the FT-ICP-OES on bulk foraminiferal samples tended to be slightly higher compared to the mean ratios obtained from the SIMS microanalyses for the same sediment depth (for example 140 µmol mol^{-1} compared to 116 µmol mol^{-1} during the YD).

3.2 Mn bulk data

Bulk sedimentary Mn/Al showed highest values during MIS3 at 30–24 ka as well as during 19–17.5 ka and the YD. The YD was characterised by a sharp Mn/Al increase at 12.3 ka, coinciding with maximum diatom productivity (Fig. 4). Relatively low Mn values occurred during 35–32 ka and during the LGM Mn was below the level of detection (< 0.06 %). Between 32 ka and the onset of the LGM, a progressive increase was observed.

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4 Discussion

4.1 Comparison of analytical methods

Our results indicate that Mn/Ca in benthic foraminifera might prove to be a valuable proxy for oxygen in the bottom and pore waters. The downcore variability in foraminiferal Mn/Ca at site GeoB7926-2 displays a consistent agreement between the mean SIMS determined Mn/Ca of each sample depth and the bulk foraminifera Mn/Ca measured by FT-ICP-OES. In general, the agreement in values suggests that the SIMS determined Mn/Ca is likely to be a true signal within our reconstruction. The slightly higher Mn/Ca determined by FT-ICP-OES in comparison to SIMS derived Mn/Ca perhaps highlights the issue of comparing bulk foraminiferal samples with individual tests comprising of only 6–10 analytical targets. Overall, when a sufficient number (minimum weight of 0.1 mg) of benthic foraminiferal specimens are not available in sediment samples for solution-based analyses (in this case from 35–18 ka), SIMS has the potential to provide reliable results from a few individuals to compensate for this.

Recent culturing experiments on benthic foraminifera demonstrate that calcification can occur even under anoxic conditions (Nardelli et al., 2014). This is key for the discussion of trace elemental data derived from the foraminiferal tests, as not only does the timing of the calcification determine the geochemical signature, it also shows that the signature is recorded in a wide range of oxygen conditions.

When comparing foraminiferal Mn/Ca to previously published sediment measurements of Mn/Al (Fig. 4) for site GeoB7926-2 (Gallego-Torres et al., 2014), in general we do not find a continuous relationship in trends throughout the record, but overall they largely agree on the former oxygen conditions. This is most likely due to diagenetic processes and migration of redox fronts through the sediment which redistributes the bulk Mn after deposition, whereas the foraminiferal tests record the Mn concentration at the time of calcification. In fact, bulk sediment Mn concentrations are often interpreted as being related to diagenetic (post-production) oxidation fronts and less often to the syn-sedimentary environment (e.g. Thomson et al., 1995; de Lange et al.,

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2008). Thus, two different processes govern Mn fixation in sediment and foraminifera tests respectively and consequently we can expect an offset between the two signals.

4.2 Reconstruction of bottom water oxygen conditions: late MIS3 to the Younger Dryas (35–11.5 ka)

4.2.1 Late MIS3 – late LGM (35–19 ka)

Foraminiferal Mn/Ca derived from SIMS measurements were comparably low and exhibited less variability within individual tests (Fig. 3) during episodes of low diatom export between 35 and 19 ka. The lower Mn/Ca indicates that the pore waters and overlying water column immediately above were oxygenated (Fig. 5a). Concurrently, these low Mn/Ca results adhere to the benthic foraminiferal response of a low abundance (ca. 2 specimens cm^{-3}) of low oxygen tolerant *E. exilis* (McKay et al., 2014) to the extent that not enough well preserved specimens were available for FT-ICP-OES analysis. Such low Mn/Ca and lack of low oxygen dwellers is to be expected since benthic foraminifera living in an environment where productivity export does not fluctuate at great magnitudes are potentially less exposed to a wide range of oxygen conditions and according Mn concentrations in the pore waters during their growth. This stable and relatively low export productivity is not only exhibited by diatom accumulation but also carbonate ($CaCO_3$ = 30–45 %) during late MIS3 to late LGM (Romero et al., 2008; McKay et al., 2014).

However, by late Heinrich Event 3 (H3: 32.5–29 ka), whilst foraminiferal Mn/Ca is low, there is an increase in bulk sediment Mn/Al, suggesting penetration of oxygen-rich bottom waters within the upper centimetres of the sediment column. Dissolved Mn available for the precipitation of Mn hydroxides would most likely be sourced by diffusion from underlying sediments where anoxic conditions prevail (Burdige, 1983). Based on this increase in sedimentary Mn/Al coinciding with relatively low foraminiferal Mn/Ca, we therefore infer that the Mn/Al enrichment occurred immediately below the oxygen-rich pore waters during late H3 and throughout the period 30–25 ka, delimiting the

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oxygen penetration front and the upward diffusion of Mn (Fig. 5a). As both foraminiferal and sedimentary Mn results correspond to low relative abundances (< 5 %) of the low oxygen indicator *E. exilis* and low diatom input (Romero et al., 2008; McKay et al., 2014), this reinforces our interpretation of more oxygenated conditions at the sea floor during H3. It associates with the scenario that during low primary productivity export, oxygen levels are not lowered by the decomposition of large amounts of fresh phytodetritus.

During the LGM, Mn/Ca show a greater range between specimens (three specimens exhibit consistent Mn/Ca in the order of 4–16 µmol mol^{-1} whilst others suggest a greater intra-test variability of 16–230 µmol mol^{-1}) than samples from MIS3 (Fig. 3) despite diatom input being relatively low and stable during this interval. We interpret this greater range in Mn/Ca as a relative decrease in oxygen within the pore water from earlier times within the record (Fig. 5b), but not to the extent of hypoxia since *E. exilis* abundance remains low (McKay et al., 2014). Simultaneously, Mn/Al remains low (Mn content < 0.06 %) which could relate to bottom water masses since Mn can be transported to deep waters via scavenging (Glasby, 2006). In particular, Gallego-Torres et al. (2014) suggested that site GeoB7926-2 was under the influence of Antarctic Bottom Water (AABW) during the LGM. AABW contains lower Mn concentrations relative to North Atlantic water masses (Statham et al., 1998; Idrus, 2013). Mn is scavenged from AABW as it flows north and thus when reaching site GeoB7926-2 is Mn-impoverished. However, we propose that low Mn fixation in the sediment during the LGM is due to export production leading to relatively more Mn being located in the water column.

4.2.2 Heinrich Event 1 – Younger Dryas (18–11.5 ka)

During H1, the increase in foraminiferal Mn/Ca; both the greater variability within the individual tests (Fig. 3) and the higher average Mn/Ca per sample depth (Fig. 4) indicate lower oxygen conditions in the pore waters (Fig. 5c). The comparably lower oxygen conditions are consistent with our hypothesis which stemmed from the benthic foraminiferal faunal assemblage composition (Filipsson et al., 2011; McKay et al., 2014)

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whereby the dominance of *E. exilis* indicated low oxygen conditions at the seafloor as a result of high primary productivity and export flux.

Bulk Mn/Al is moderate-low (below average of 3.4×10^{-2} at the corresponding sample depth of the benthic foraminifera analysed by SIMS) when compared to the rest of the record, despite high diatom accumulation rate. The combined interpretation of Mn, Mo and U to Al ratios presented in Gallego-Torres et al. (2014) evidenced that the H1 period experienced suboxic ($< 0.1\,mL\,L^{-1}$ O_2 as defined by Morrison et al., 1998) to anoxic bottom water conditions. Under these conditions, the redoxcline would have been very shallow or even located at the sediment-water interface, so that Mn was not preferentially fixed in the sediment. Furthermore, the sedimentary layer might have acted as a source of reduced dissolved Mn to the water column and/or the uppermost pore waters, allowing for higher Mn availability for incorporation into benthic foraminiferal tests.

During the BA, foraminiferal Mn/Ca determined by SIMS exhibit a similar range of values and intra-test variability as during H1 (Fig. 3). We interpret this similarity in oxygen conditions as being due to comparable diatom accumulation rates during both climatic intervals. Previously, from the relative decrease in *E. exilis* abundance during the BA, the bottom water oxygen concentrations were interpreted to have increased in comparison to H1 and the YD (Filipsson et al., 2011). Despite this benthic faunal response to productivity export, the diatom input itself was relatively higher at the core depth sampled for SIMS analysis within the BA than the one in H1. Subsequently, our SIMS derived Mn/Ca results do not suggest vast redox shifts between the two climatic intervals generally the values follow the diatom input. This emphasizes that whilst the benthic foraminiferal community composition is a reliable indicator of past environmental conditions, the trace elemental composition of foraminiferal tests has potential to reveal a more detailed palaeoenvironmental interpretation. Furthermore, the foraminiferal Mn/Ca coincides with the lack of Mn enrichment in the bulk sediment and Mn/Al does not substantially differ from the previous climatic interval either. Mo and U suggest prevailing suboxic conditions during the BA (Gallego-Torres et al., 2014)

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and further, we infer that the redoxcline would be shallow within the sediment which is similar scenario to H1.

From both SIMS and FT-ICP-OES, the highest foraminiferal Mn/Ca and greatest Mn variability within individual tests are found during the YD (Fig. 3). This consistent pattern of Mn enrichment coincides with high primary productivity, high export flux and the dominance of low oxygen tolerant *E. exilis*. As MnO_2 is rapidly reduced to soluble Mn^{2+} in hypoxic pore waters (Glock et al., 2012) and since high phytodetritus export typically causes low bottom water oxygen concentrations or even anoxia within millimetres of the sediment-water interface, we can expect a high accumulation of redox sensitive trace metals (Hunt, 1983; McKay et al., 2005) as represented in Fig. 5d. Furthermore, the sediment accumulation rate during the interval is the highest of the record (350 cm ka^{-1}, Fig. 4) which can also intensify the low oxygen concentrations and promote Mn enrichment (McKay et al., 2005). This confirms our hypothesis that Mn/Ca values in *E. exilis* respond to the oxygen deficiency instigated by the large increase in diatom input. Furthermore, the redox front would also vary in position during this oxygen depleted period with diatom export fluctuating at such great magnitude. Therefore the strong intra-test variability (Fig. 3) may be representative of actual changes in oxygenation of the habitat during test growth, due to amplified seasonal fluctuations in diatom export. Moreover, since *E. exilis* is an infaunal species, it is influenced by the microhabitat of the pore waters. Therefore, the sediment depth at which this species resided and possibly migrated to during calcification in such low oxygen conditions could further explain the greater Mn/Ca variability during the YD.

We emphasise that the benthic foraminiferal Mn/Ca seems to represent a more regional signal due to diatom input opposed to being generated by deep bottom water formation and poor ventilation. However, whilst we interpret that the sheer level of diatom input provoked O_2 deficiency in the bottom and pore waters, we acknowledge that even in the modern ocean, it is difficult to separate the effects of productivity and deep-water oxygen concentrations since they are inter-related. Gallego-Torres et al. (2014) interpret the YD as a phase of reduced ventilation coinciding with reduced Atlantic

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Meridional Overturning Circulation (AMOC), promoted by intense export productivity. Both effects provided dissolved Mn available for incorporation into the foraminiferal calcite lattice. Therefore, whilst Mn/Ca has potential for oxygen level reconstruction, additional proxies are required in order to determine the precise factor driving the conditions.

5 Conclusions

Our study contributes to the development of Mn/Ca in benthic foraminiferal calcite as a proxy for reconstructing past oxygen conditions. The results based on data from the low latitude NE Atlantic Upwelling System indicate that shifts in oxygen levels occurred during different productivity regimes between 35 and 11.5 ka and thus foraminiferal Mn/Ca can assist our understanding of the past environment in the region studied. The foraminiferal Mn/Ca results are supported by benthic foraminiferal faunal data.

The highest foraminiferal Mn/Ca and greatest Mn variability within individual tests were obtained during the YD and indicate Mn enrichment which coincides with very high primary productivity and the dominance of low oxygen tolerant benthic foraminifera *Eubuliminella exilis*. The results confirm our hypothesis that Mn/Ca in *E. exilis* can be applied as a proxy for oxygen deficiency, in this case instigated by the increase in diatom input. Therefore, whilst high phytodetritus export typically causes low bottom water oxygen concentrations and benthic faunal studies are indicative of such a scenario, redox trace elemental test composition presents a more comprehensive interpretation. Our initial down-core dataset raises the implication of calibrations. Once developed, Mn/Ca determined by the SIMS method in particular may have the potential to be applied to other study regions and foraminiferal species for reconstructing former bottom water oxygen conditions.

Furthermore, we conclude that SIMS determined Mn/Ca upon individual tests is comparable with bulk foraminiferal Mn/Ca measured by FT-ICP-OES. However, due to the processing time required to program and target delicately thin foraminiferal test

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walls, SIMS may not be practical for Mn/Ca studies where large numbers of samples must be processed. Nevertheless, where a sufficient number of individual benthic foraminiferal specimens are not present in sediment samples for solution-based bulk analyses, SIMS has a large potential to provide reliable results from just a few individuals and is in addition non-destructive. In contrast, foraminiferal Mn/Ca data does not continuously exhibit a consistent trend with Mn/Al determined from bulk sediment measurements. The reason for this discrepancy is that Mn related to redox fronts within the sediment provides a diagenetic signal and thus it continues to react and shift after deposition, whereas foraminiferal tests record the Mn concentration at the time of calcification.

Author contributions. H. L. Filipsson initiated the project; C. L. McKay designed the sampling plan and carried out sample selection and preparation with assistance from T. Toyofuku. J. Groeneveld performed FT-ICP-OES analyses, C. L. McKay and M. Whitehouse performed SIMS analyses. D. Gallego-Torres and O. E. Romero provided Mn/Al and diatom data. C. L. McKay prepared and wrote the manuscript with contributions from all co-authors.

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Table 1. Sample list: climatic intervals, export productivity according to diatom export, average foraminiferal Mn/Ca for different samples determined by SIMS and FT-ICP-OES.

Sample no.	Depth (cm)	Age (ka)	Climatic interval	Export productivity	SIMS: average Mn/Ca (μmol mol^{-1})	SD (μmol mol^{-1})	SIMS: average Mn/Ca (μmol mol^{-1}) per sample depth	FT-ICP-OES: average Mn/Ca (μmol mol^{-1})
YD A	170	12.2	YD	High	138	62	198	220
YD B	170	12.2	YD	High	191	116		
YD C	170	12.2	YD	High	321	251		
YD D	170	12.2	YD	High	141	56		
YD E	270	12.7	YD	High	178	82	164	160
YD F	270	12.7	YD	High	96	53		
YD G	270	12.7	YD	High	117	48		
YD H	270	12.7	YD	High	164	120		
YD I	270	12.7	YD	High	183	51		
YD J	270	12.7	YD	High	111	27		
YD K	270	12.7	YD	High	261	275		
YD L	270	12.7	YD	High	204	78		
BA A	365	13.5	BA	Moderate-high	155	37	Only 1 specimen available	280
BA B	430	15.1	BA	Moderate-high	242	42	130	110
BA C	430	15.1	BA	Moderate-high	63	51		
BA D	430	15.1	BA	Moderate-high	217	51		
BA E	430	15.1	BA	Moderate-high	49	18		
BA F	430	15.1	BA	Moderate-high	179	88		
BA G	430	15.1	BA	Moderate-high	175	87		
BA H	430	15.1	BA	Moderate-high	67	149		
BA I	430	15.1	BA	Moderate-high	47	27		
H1 A	500	16.7	H1	High	57	17	117	140
H1 B	500	16.7	H1	High	154	36		
H1 C	500	16.7	H1	High	186	81		
H1 D	500	16.7	H1	High	191	142		
H1 E	500	16.7	H1	High	76	57		
H1 F	500	16.7	H1	High	92	37		
H1 G	500	16.7	H1	High	62	19		
H1 H	500	16.7	H1	High	116	36		
LGM A	723	20.7	LGM	Low	27	14	74	
LGM B	723	20.7	LGM	Low	146	28		
LGM C	723	20.7	LGM	Low	115	71		
LGM D	723	20.7	LGM	Low	7	4		Insufficient no.
LGM E	773	22.7	LGM	Low	7	3	65	of specimens
LGM F	773	22.7	LGM	Low	10	3		
LGM G	773	22.7	LGM	Low	70	49		
LGM H	773	22.7	LGM	Low	175	91		
MIS3 A	928	29.9	MIS3	Low	38	13	43	
MIS3 B	928	29.9	MIS3	Low	48	38		Insufficient no.
MIS3 C	928	29.9	MIS3	Low	45	24		of specimens
MIS3 D	1058	34.0	MIS3	Low	67	23	61	
MIS3 E	1058	34.0	MIS3	Low	55	62		

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Table 2. Post hoc test (Mann Whitney U) *z* values between the mean foraminiferal Mn/Ca (per individual) between climatic intervals. Significant differences are highlighted in bold.

	YD	BA	H1	LGM	MIS3
YD					
BA	−1.14				
H1	−1.93	−0.19			
LGM	**−2.7**	−1.83	−1.68	−1.68	
MIS3	**−3.16**	**−2.07**	0	0	

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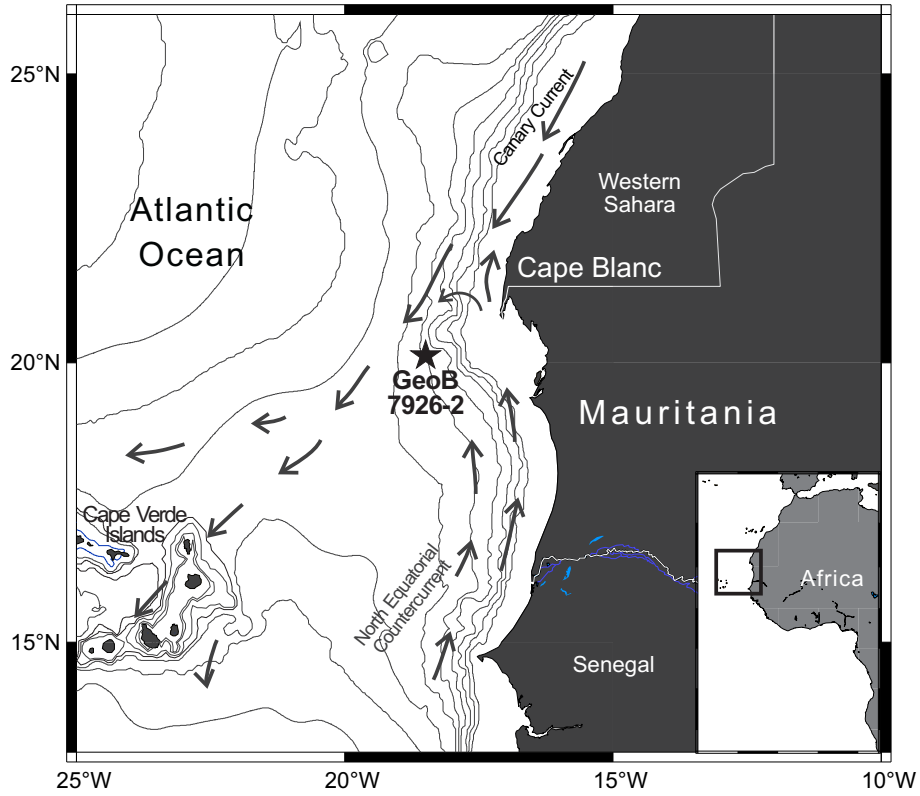

Figure 1. Locality of gravity core GeoB7926-2 (black star) in the low latitude NE Atlantic upwelling area. Arrows indicate the major oceanic currents in the study area. Inset: Location of the study area off coastal NW Africa. Modified after Romero et al. (2008).

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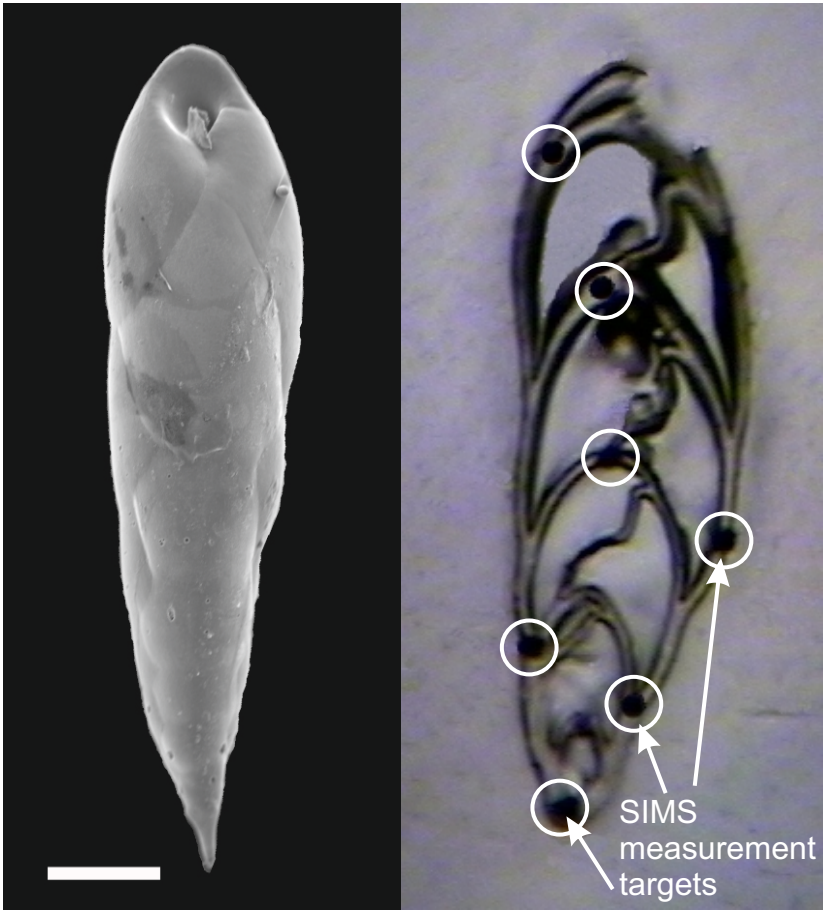

Figure 2. SEM image (scale bar: 100 µm) and cross section image during SIMS analysis of a single *Eubuliminella exilis* specimen. Black spots indicated by the white circles are examples of selected locations for SIMS analyses, measuring 5 µm in diameter.

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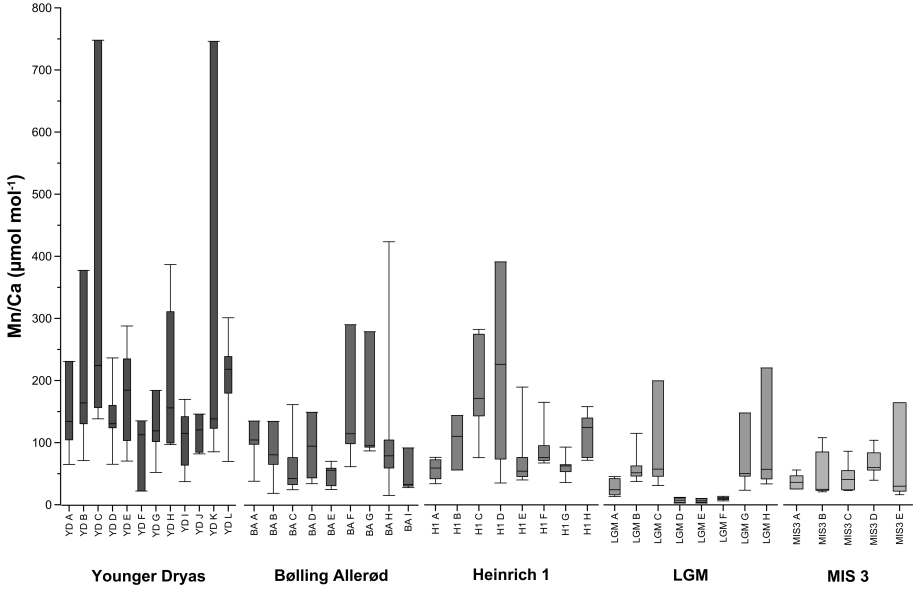

Figure 3. The Mn/Ca ($\mu mol\,mol^{-1}$) variability within each individual *Eubuliminella exilis* specimen for each climatic interval (labelled on the *x* axis), determined by SIMS.

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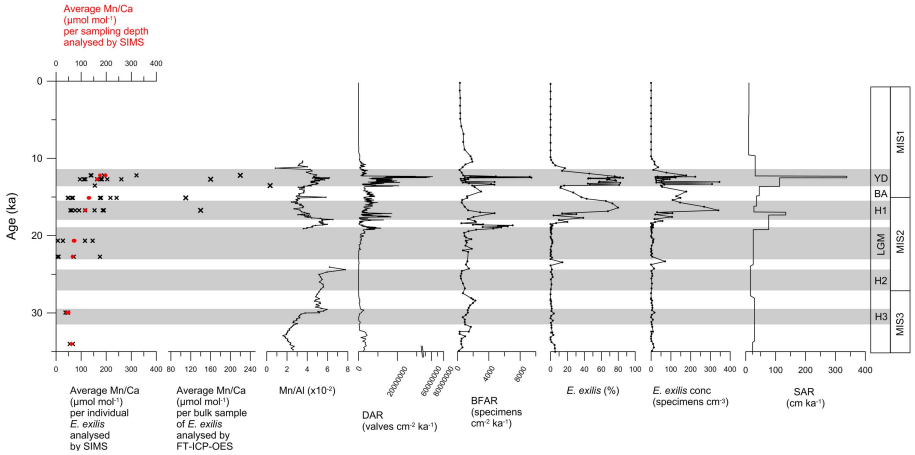

Figure 4. Foraminiferal Mn/Ca (µmol mol^{-1}) determined by SIMS (black crosses: average per specimen, red circles: average per depth) and FT-ICP-OES, bulk sediment Mn/Al (Gallego-Torres et al., 2014), diatom accumulation rate (DAR; Romero et al., 2008), relative abundance and concentration of low oxygen indicating *Eubuliminella exilis* and sediment accumulation rate (SAR) of core GeoB7926-2.

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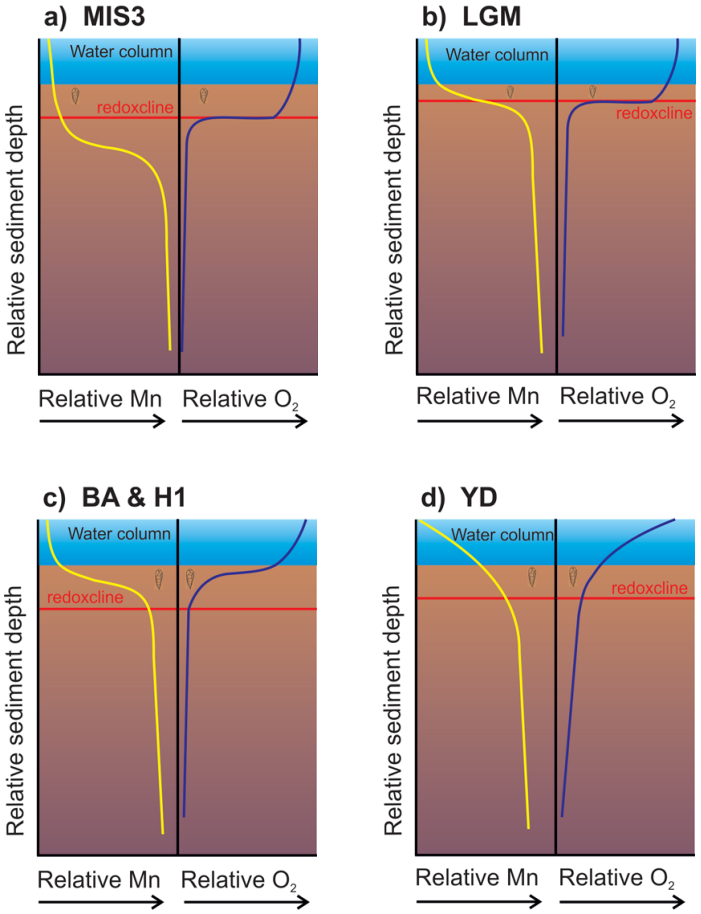

Figure 5. Idealised schematic pore water Mn and oxygen profiles for the climatic intervals studied: **(a)** MIS3, **(b)** LGM, **(c)** BA and H1 and **(d)** YD from the GeoB7926-2 record. The red line represents the redoxcline.

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