



# Mg/Ca and Mn/Ca ratios in benthic foraminifera: the potential to reconstruct past variations in temperature and hypoxia in shelf regions

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**Abstract.** Shelf and coastal regions are exceptionally important for many countries as they provide the main habitat for many economically important fish and shellfish species. With ongoing climate change and human-induced eutrophication the shelf regions are especially affected, resulting in increased temperatures and stratification as well as oxygen depletion of the bottom waters. In order to be able to predict the magnitude of these changes in the future, it is necessary to study how they varied in the past. Commonly used foraminiferal climate and environmental proxies, e.g., stable isotopes and trace metal/Ca ratios, that are applied in open-ocean settings are not necessarily applicable in shelf regions, either as faunas are significantly different or as conditions can change much faster compared to the open ocean. In this study we explore the use of Mg/Ca as paleothermometer and Mn/Ca as a potential proxy for changing dissolved oxygen conditions in bottom water on the benthic foraminifera *Bulimina marginata* and *Globobulimina turgida*. Living specimens were collected from the Skagerrak and the Gullmar Fjord (SW Sweden); the latter is hypoxic for several months a year. As the specimens were alive when collected, we assume it unlikely that any diagenetic coatings have already significantly affected the trace metal/Ca ratios. The Mg/Ca ratios are similar to previously published values but display much larger variation than would be expected from the annual temperature change of less than 2 °C. An additional impact of the difference in the calcite saturation state between the Skagerrak and the Gullmar Fjord could explain the results. Mn/Ca ratios from *G. turgida* can potentially be related to variations in dissolved oxygen of the habitat where

the foraminifera calcify. Samples from the Skagerrak display increased Mn/Ca in specimens that lived deeper in the sediment than those that lived near the surface. *G. turgida* samples from the low-oxygen Gullmar Fjord showed significantly increased Mn/Ca, being highest when bottom water dissolved oxygen was at a minimum. Our study suggests that trace metal/Ca ratios in benthic foraminifera from shelf regions have the potential to record past variations in bottom water temperature and dissolved oxygen concentrations, but an additional impact of the inorganic carbonate chemistry cannot be excluded.

## 1 Introduction

Traditional proxies, which for example are based on the calcite shells of marine organisms like foraminifera and generally calibrated with respect to open-ocean conditions, are applied to a lesser extent in shelf and fjord environments as changes in the water mass conditions vary on a much larger scale than in the open ocean. The larger seasonal variability as well as the higher impacts from terrestrial and anthropogenic factors makes it sometimes difficult to disentangle local from regional patterns.

Shelf and fjord environments, however, are particularly affected by ongoing climate change, and also economically important, being for instance important habitats for many fish and shellfish species. With ongoing climate change, changes in circulation, and as a consequence of eutrophication, dissolved oxygen concentrations are predicted to

decrease in many areas (Sarmiento et al., 1998; Keeling and Garcia, 2002; Meier et al., 2011). Hypoxic conditions ( $< 2 \text{ mL L}^{-1}$  dissolved oxygen) are already widespread in the world's ocean, often occurring naturally under high productivity areas like, for example, in the Arabian Sea (Reichart et al., 1998; Helly and Levin, 2004). But increasingly (seasonal) hypoxic conditions are caused or strengthened by anthropogenically induced eutrophication, especially in semi-enclosed basins like, for example, the Gulf of Mexico (Osterman et al., 2005; Platon et al., 2005), the Baltic Sea (Diaz and Rosenberg, 2008; Conley et al., 2011), and (Scandinavian) fjords (Gustafsson and Nordberg, 2000; Filipsson and Nordberg, 2004a). Ocean general circulation models predict that with ongoing climate change, dissolved oxygen concentrations will decrease as less oxygen can be dissolved into warmer water and thus stratification increases (Keeling and Garcia, 2002; and references therein). A matter of debate is still whether these recent decreases in dissolved oxygen, especially in the Baltic Sea area, are part of the natural variations or intensified by anthropogenic causes (Zillén and Conley, 2010). Zillén and Conley (2010) show that, especially during the last two millennia, phases of hypoxia such as during the early medieval expansion (700–1300 AD) seem to correlate with major changes in population and land use in Scandinavia instead of correlating with natural climate variations. Some of the fjords of southwest Sweden, e.g., the Gullmar Fjord off the Skagerrak, have been studied extensively, especially with respect to changes in hydrography, eutrophication, and oxygen status (Gustafsson and Nordberg, 1999, 2000, 2001; Nordberg et al., 2001; Eriksson et al., 2002; Filipsson and Nordberg, 2004a, b, 2010; Filipsson et al., 2004; Erlandsson et al., 2006; Polovodova et al., 2011; Polovodova Asteman et al., 2013). Due to their relatively small area, fjords provide ideal settings for monitoring changes in water mass conditions. The Gullmar Fjord has been subject to regular environmental monitoring since 1958. The Swedish Meteorological and Hydrological Institute's (SMHI) SHARK hydrographic database provides time series to perform further investigations on. Based on sediment cores covering the last century, using benthic foraminifer assemblages, Filipsson and Nordberg (2004a) indicated that the faunal switches that have taken place between a common Skagerrak–Kattegat fauna and a more low-oxygen-adapted fauna can be correlated to switches in North Atlantic Oscillation (NAO). During positive NAO periods, such as the beginning and the end of the 20th century, strong westerly winds prevented the stagnant water from the Gullmar Fjord from being refreshed, leading to more hypoxic conditions (Nordberg et al., 2000; Filipsson and Nordberg, 2004a).

As the incorporation of trace metals into calcite shells is species-specific, and typical benthic foraminiferal faunas in shallow and more brackish environments like the Skagerrak and the Gullmar Fjord are very different from open-ocean settings, it is necessary to develop new calibrations to allow for the reconstruction of environmental conditions such as

temperature, dissolved oxygen, or inorganic carbonate chemistry.

*Bulimina marginata* is a common, shallow infaunal species of benthic foraminifera occurring in a wide range of settings, from the deep sea to open-shelf areas like the Skagerrak and stratified fjords like the Gullmar Fjord (Conradsen et al., 1994; Gustafsson and Nordberg, 2000). Additionally, it is tolerant to a wide range of microhabitats, from fully oxygenated down to hypoxic or even anoxic (Ohga and Kitazato, 1997; Fontanier et al., 2002), and it is relatively easy to culture (Hintz et al., 2006a, b; Barras et al., 2010; Filipsson et al., 2010). This makes *B. marginata* a very promising candidate to be used more often in paleoceanographic reconstructions.

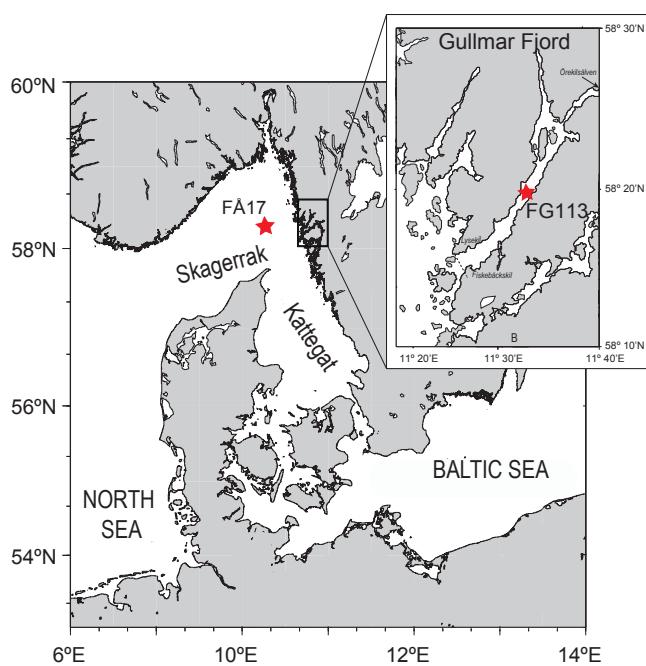
Another common benthic foraminifer species tolerant of low-oxygen contents is *Globobulimina turgida* (Jorissen et al., 1995; Kitazato et al., 2000; Fontanier et al., 2003; Koho and Piña-Ochoa, 2012). Although *Globobulimina* spp. are usually reported as deeper infaunal, *G. turgida* in the Gullmar Fjord is mostly found at  $< 2 \text{ cm}$  depth in the sediment (Risgaard-Petersen et al., 2006; Koho et al., 2008). In general, the chemocline in the Gullmar Fjord is located shallower in the seasonally hypoxic fjord's sediment, which explains the shallower habitat depth of *G. turgida* in the fjord compared to more oxygenated open-ocean settings.

In this study we explore the potential of using Mg/Ca and Mn/Ca in the benthic foraminiferal species *B. marginata* and *G. turgida* from the Skagerrak and the Gullmar Fjord as proxies for reconstructing changes in sea water temperature and dissolved oxygen content.

## 1.1 Hydrography

The Skagerrak is located between Denmark, Sweden, and Norway forming the connection between the North Sea in the west and the Kattegat in the south, which then continues on towards the Baltic Sea (Fig. 1). Water masses enter the Skagerrak both from the south and the northwest. The brackish Baltic Current (salinity  $\sim 20$ ) usually follows the Swedish west coast, transporting surface water from the Baltic Sea northwards. The Northern Jutland Current enters the Skagerrak from the west, consisting of water masses from the North Sea (salinity of 31–35) as well as from the Atlantic (salinity  $> 35$ ). These two water masses mix into the Norwegian Coastal Current, which leaves the Skagerrak in the northwest creating a cyclonic circulation pattern (Rodhe, 1996).

The Gullmar Fjord is located in southwestern Sweden off the Skagerrak (Fig. 1). The fjord is connected to the Skagerrak by a sill at 42 m water depth. The fjord itself is almost 30 km long and 1–2 km wide. The maximum water depth reaches 120 m. The water masses in the fjord can be divided into three separate layers: a brackish surface layer consisting of low-saline Baltic Current and river water, an intermediate layer from 15 to 50 m that is in connection with the Skagerrak having salinities of 32–33, and a deep ( $> 50 \text{ m}$ ) layer



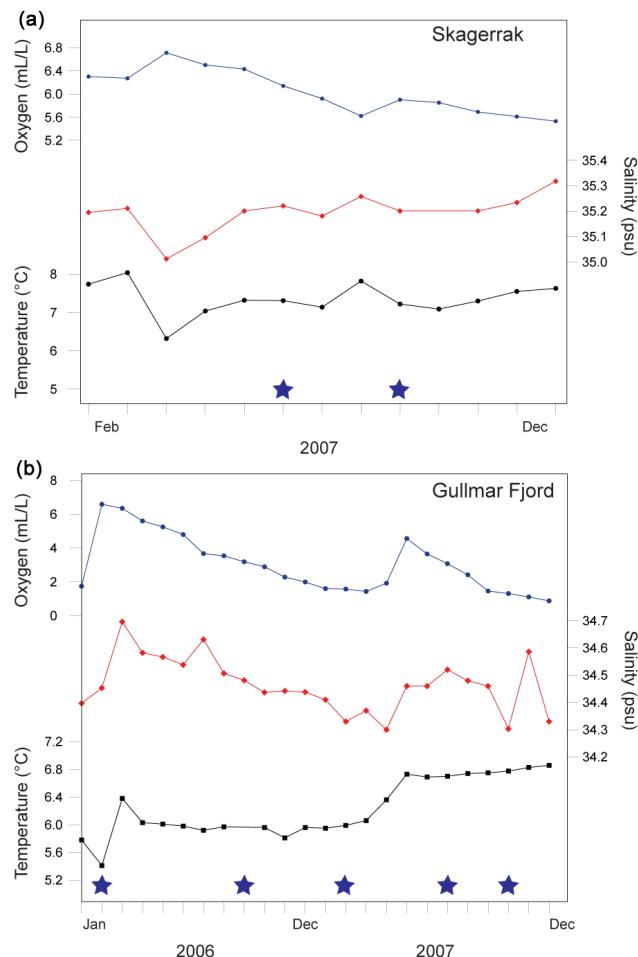
**Fig. 1.** Map showing the locations of sites FÅ17 and FG113 (inset) where samples were collected. Site FÅ17 is located in the Skagerrak, while site FG113 is from the deepest central part of the Gullmar Fjord.

with salinities of 34–35 that is blocked from free exchange with the Skagerrak by the sill. Usually the deep water is renewed once a year in late winter/early spring (Filipsson and Nordberg, 2004a), bringing the oxygen concentration back to open Skagerrak values of  $\sim 6 \text{ mL L}^{-1}$  (Fig. 2b). After the spring bloom, oxygen concentrations start to decrease, reaching minimum, hypoxic values of less than  $2 \text{ mL L}^{-1}$  towards the end of the year (Filipsson and Nordberg, 2004a).

## 2 Material/methods

### 2.1 Samples

The samples were collected from site FÅ17 (SMHI site Å17), from the NE Skagerrak ( $58^{\circ}16.50\text{ N}, 10^{\circ}30.80\text{ E}$  – 330 m water depth) and from site FG113 from the deepest part of the Gullmar Fjord ( $58^{\circ}19.40\text{ N}, 11^{\circ}32.8\text{ E}$  – 118 m water depth) by a Gemini corer (Fig. 1). The stations were visited in June 2006 (called no. 1), August 2006 (no. 2), January 2007 (no. 3), June 2007 (no. 4), and September 2007 (no. 5), using R/V *Arne Tiselius*. Additionally, a core top was collected with R/V *Skagerak* in October 2012 from site FG113. At each station two replicate cores were recovered, labeled A and B. The uppermost 2 cm of the sediment cores were sectioned into 1 cm slices. The vital fluorogenic probe Cell-Tracker Green CMFDA (hereafter CellTracker Green) (final concentration  $1 \mu\text{M}$  in ambient sea water) was added to all



**Fig. 2.** (a) Annual cycle of temperature, salinity, and dissolved oxygen at 300 m water depth at the location of site FÅ17 in the Skagerrak for 2007. (b) Temperature, salinity, and dissolved oxygen at 110 m water depth at the location of site FG113 in the Gullmar Fjord for 2006 and 2007. Stars (lila) indicate the month of sampling of the living foraminifera.

samples (station no. 1 was Rose-Bengal-stained; the October 2012 core top was not stained); the CellTracker Green samples were incubated for 12 h at  $7^{\circ}\text{C}$  following the protocol of Bernhard et al. (2006). The samples were preserved using 3.8 % borax-buffered formalin. At the time of analysis an aliquant of the sediment was carefully sieved over a  $63 \mu\text{m}$  screen, and selected foraminiferal species were wet-picked under an epifluorescence stereo microscope (Nikon SMZ 1500, filters 485-nm excitation, 520-nm emission) and air-dried for geochemical analysis.

Traditionally, Rose Bengal staining of the samples is used to identify living foraminifera as it fixes onto proteins and colors the protoplasm pink (Walton, 1952; Bernhard, 2000). However, the use of Rose Bengal often results in an overestimation of the number of living specimens (Bernhard et al., 2006). This can particular be an issue in low-oxygen

environments, where the foraminiferal protoplasm is either slowly or not at all remineralized, leading to the occasional staining of dead specimens. In seasonal and short-term studies, as presented here, where comparisons are made to in situ measurements of the environmental conditions, a more accurate method is needed to distinguish between dead and living specimens. Therefore, we used the CellTracker Green method (Bernhard et al., 2006; Pucci et al., 2009), which is a non-terminal method, meaning it can be applied during the life stage without killing the specimens. This is not only important in allowing for comparison with water mass conditions during the time of sampling but also for interpreting the geochemical results. Especially for Mn/Ca, high values are commonly associated with Mn oxyhydroxides and Mn carbonates, which form on the test of buried foraminifera (Boyle, 1983; Barker et al., 2003). Use of the CellTracker Green method aimed to minimize the impact of diagenetic coatings on the Mn/Ca values in this study, even though diagenesis cannot be completely excluded (Hoover et al., 2001).

## 2.2 Mg/Ca and Mn/Ca

Between 3 and 20 tests of *B. marginata* and *G. turgida* were selected from the stained samples as well as 20–40 specimens from the non-stained samples, and then gently crushed. Due to the low number of living specimens available the size range of the selected specimens was not restricted, possibly introducing a bias on the results (Hintz et al., 2006b). The shell fragments were cleaned according to the standard cleaning protocol for foraminiferal Mg/Ca analyses (Barker et al., 2003). Samples were centrifuged for 10 min (6000 rpm) to exclude any remaining insoluble particles from the analyses. Samples were diluted with Seralpur water and analyzed with an ICP-OES (Agilent Technologies, 700 Series with autosampler (ASX-520 Cetac) and micro-nebulizer) at the MARUM – Center for Marine Environmental Sciences, University of Bremen, Germany. Instrumental precision of the ICP-OES was monitored by analysis of an in-house standard solution with Mg/Ca of 2.93 mmol mol<sup>-1</sup> after every five samples (long-term standard deviation of 0.026 mmol mol<sup>-1</sup> or 0.91 %). To allow interlaboratory comparison we analyzed an international limestone standard (ECRM752-1) with reported Mg/Ca of 3.75 mmol mol<sup>-1</sup> (Greaves et al., 2008). The long-term average of the ECRM752-1 standard, which is routinely analyzed twice before each batch of 50 samples in every session, is 3.78 mmol mol<sup>-1</sup> ( $1\sigma = 0.066$  mmol mol<sup>-1</sup>). Analytical precision based on three replicate measurements of each sample for *B. marginata* and *G. turgida* was 0.39 % ( $1\sigma = 0.009$  mmol mol<sup>-1</sup>) and 0.43 % ( $1\sigma = 0.016$  mmol mol<sup>-1</sup>) for Mg/Ca, respectively; for *G. turgida* Mn/Ca the analytical precision was 1.02 % ( $1\sigma = 0.06$  mmol mol<sup>-1</sup>) for the Gullmar Fjord, and 5.52 % ( $1\sigma = 0.001$  mmol mol<sup>-1</sup>) for the Skagerrak. Due to the low number of specimens no replicates were measured.

Mn/Ca of the samples was corrected based on analyses of the ECRM752-1 standard with a published Mn/Ca of 0.132 mmol mol<sup>-1</sup> (Greaves et al., 2008).

Sea water samples of the Skagerrak and the Gullmar Fjord were either collected during the same sampling occasion as the sediment collection or in conjunction with the monthly monitoring program from the Swedish Environmental Protection Agency executed by SMHI. The water samples were collected in glass bottles after rinsing with water from the same depth and being cold-stored. For the analysis of Mg/Ca<sub>sw</sub> and Mn/Ca<sub>sw</sub> a subsample was taken and diluted with quality distilled (QD) HNO<sub>3</sub> to a 1 % HNO<sub>3</sub> solution. Samples were measured on the same ICP-OES as the foraminiferal samples. The average Mg/Ca<sub>sw</sub> for the Skagerrak is 5.04 mol mol<sup>-1</sup> ( $\sigma = 0.012$  mol mol<sup>-1</sup>), confirming average open-ocean values to be between 5.00 and 5.20 mol mol<sup>-1</sup> (e.g., Wilson, 1975; Broecker and Peng, 1982). The water samples from the Gullmar Fjord were taken between July and September 2007, giving an average Mg/Ca<sub>sw</sub> value of 5.00 mol mol<sup>-1</sup> ( $\sigma = 0.010$  mol mol<sup>-1</sup>). Sea water Mn concentrations in the Skagerrak were below the detection limit. In the Gullmar Fjord, Mn concentrations of the bottom water varied between 3.7 and 10.3 µmol L<sup>-1</sup>.

## 3 Results

### 3.1 Mg/Ca

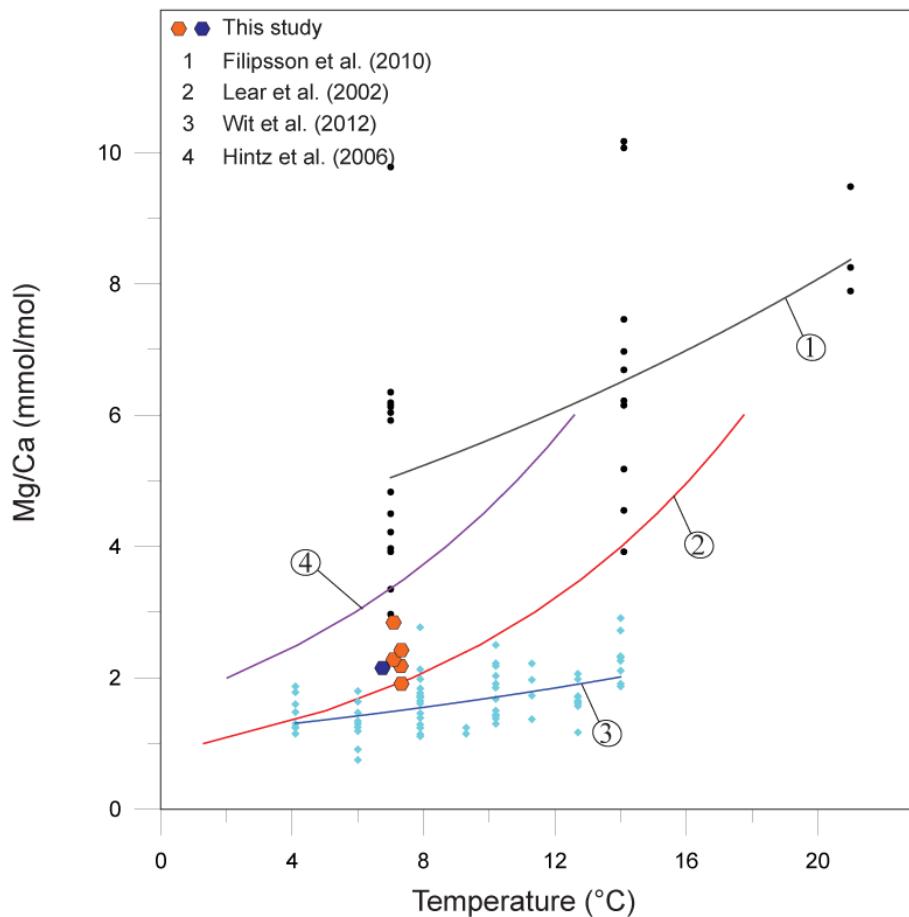
#### 3.1.1 Skagerrak

Four samples with enough specimens (6–15) of *B. marginata* are from the top centimeter of the sediment; one sample is from 1 to 2 cm depth. The Mg/Ca values vary between 1.90 and 2.85 mmol mol<sup>-1</sup> (Fig. 3a). The samples for *G. turgida* (4–20 specimens per sample) are evenly distributed between the 0–1 cm and 1–2 cm sediment depths. Mg/Ca varies between 3.41 and 4.96 mmol mol<sup>-1</sup> (Fig. 3b), but no significant difference between the two depths is present. Our results confirm that *Globobulimina* Mg/Ca values are systematically higher (Table 2a) than those of commonly used benthic genera like *Cibicidoides*, *Uvigerina*, or also *Bulimina* (Lear et al., 2002; Raitzsch et al., 2008; Huang et al., 2012), but similar to *Globobulimina affinis* (Skinner et al., 2003).

#### 3.1.2 Gullmar Fjord

Only one sample from the slightly shallower location at 70 m water depth yielded enough specimens ( $n = 10$ ) of *B. marginata* to analyze. Mg/Ca of this sample was 2.15 mmol mol<sup>-1</sup>, similar to the Mg/Ca from the Skagerrak samples. The in situ temperature during June 2007 when the samples were collected was 6.7 °C, similar to the temperatures from the Skagerrak.

Three out of eight stained samples for *G. turgida* yielded enough material (3–9 specimens per sample) for reliable



**Fig. 3a.** Mg/Ca vs. temperature for *B. marginata* from this study (hexagons: orange (Skagerrak), blue (Gullmar Fjord)) in comparison with published data for *B. marginata/aculeata* (Filipsson et al., 2010; “1”), multiple species (Lear et al., 2002; “2”); *B. marginata* (Wit et al., 2012; “3”), and *B. marginata* (Hintz et al., 2006a; “4”). Single measurements of Filipsson et al. (2010) and Wit et al. (2012) were included to show the scatter when laser ablation is used on single specimens/chambers in comparison with our bulk measurements. Note that the results of the lowest temperature experiment of Filipsson et al. (2010) are omitted from the figure. Error bars are too small to be displayed (see Methods section).

Mg/Ca values (Table 2b). In situ temperatures at the time of sampling varied between 5.4 and 6.0 °C, slightly lower than the Skagerrak temperatures. Mg/Ca values varied between 2.80 and 2.97 mmol mol<sup>-1</sup>, i.e., significantly lower than those from the Skagerrak samples. Mg/Ca in the three non-stained samples from Oct 2012 varied between 2.86 and 3.78 mmol mol<sup>-1</sup> (Fig. 3b; Table 2b).

### 3.2 Mn/Ca

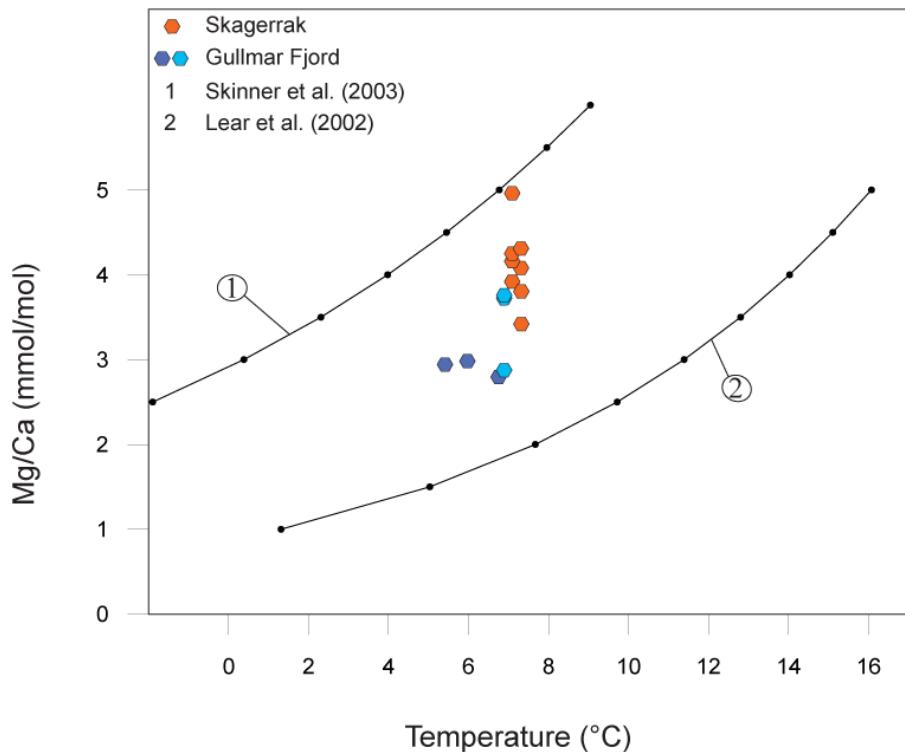
#### 3.2.1 Skagerrak

Measurable Mn concentrations were only present in *G. turgida*. Mn/Ca for *G. turgida* varied between 0 and 0.09 mmol mol<sup>-1</sup> with the samples from 1 to 2 cm depth having higher Mn/Ca than the samples from 0 to 1 cm depth sampled at the same time (Fig. 4a). Oxygen concentrations between 5.5 and 6.5 mL L<sup>-1</sup> confirm that the bottom water in

the Skagerrak was well oxygenated throughout the year. An extensive collection of pore water profiles from the Skagerrak shows that oxygen penetration generally occurs down to 5–20 mm sediment depth (Bakker and Helder, 1993).

#### 3.2.2 Gullmar Fjord

Mn/Ca for *G. turgida* in the Gullmar samples was significantly higher than for the samples from the Skagerrak. Mn/Ca varied between 0.20 and 5.8 mmol mol<sup>-1</sup> (Fig. 4b), while two additional samples, which yielded Mn/Ca of 7.94 and 10.58 mmol mol<sup>-1</sup>, are likely to be biased by a matrix effect (Table 2b). Mn/Ca in the three non-stained samples from Oct 2012 varied between 0.91 and 6.26 mmol mol<sup>-1</sup> (Table 2b). Bottom water oxygen concentrations in 2006 and 2007 followed the common pattern for the fjord, which includes one annual deep-water exchange with subsequent replenished dissolved oxygen content (5–6 mL L<sup>-1</sup>) (Fig. 4b).



**Fig. 3b.** Mg/Ca vs. temperature for *G. turgida* from this study from the Skagerrak (hexagons: orange) and the Gullmar Fjord (hexagons: dark blue represents stained, and light-blue non-stained samples) in comparison with the calibrations for *G. affinis* (Skinner et al., 2003; “1”), and for multiple species (Lear et al., 2002; “2”). Note that the points in the two calibrations do not represent samples. Error bars are too small to be displayed (see Methods section).

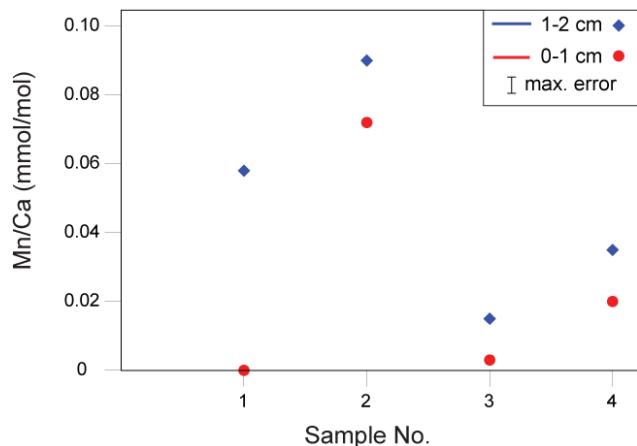
The oxygen concentrations decrease for the remainder of the year again towards hypoxic values. The water samples with the highest Mn/Ca were collected during the time with the lowest oxygen concentrations (January 2007 and April 2007).

#### 4 Discussion

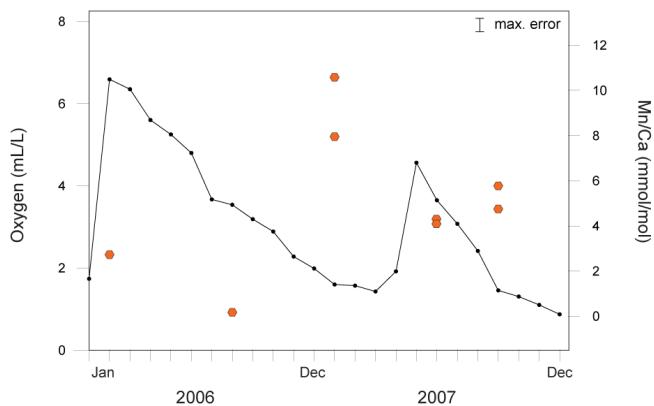
Before the trace metal/Ca results are discussed, it is necessary to consider the life cycle of *B. marginata* and *G. turgida*. Unlike shallow-dwelling planktonic foraminifera that live and calcify only for two to four weeks, many benthic foraminifer species survive much longer (Murray, 1991). It is essential to know for the discussion of any geochemistry data, especially those acquired from benthic foraminifera from variable environments, when the used species calcify as this determines the geochemical signal. Culturing experiments under anoxic conditions showed that *G. turgida* survived for several months, utilizing their internal nitrogen pool (Risgaard-Petersen et al., 2006; Piña-Ochoa et al., 2010). A remaining question is, however, if the specimens also calcify during the anoxic conditions. Reproduction and increased abundances often seem to follow peaks in food supply (Gustafsson and Nordberg, 1999, 2000, 2001;

Kitazato et al., 2000; Fontanier et al., 2003; Filipsson et al., 2004; Koho and Piña-Ochoa, 2012). In the Havstens and Gullmar fjords a strong correlation between the occurrence of the benthic foraminifera *Stainforthia fusiformis* and chlorophyll *a* concentrations was found, which was also imprinted onto the  $\delta^{13}\text{C}$  values (Filipsson et al., 2004). Austin et al. (2006) argue that the period of reproduction directly after a bloom is also the time of the year when the water column (mainly temperature) changes markedly. This would suggest that the geochemical signal that is actually recorded in the foraminiferal tests is the average for a restricted period directly after maximum food supply.

Due to the low number of living specimens available for analyses we combined all size fractions, possibly introducing a bias. Hintz et al. (2006b) showed a significant size effect on Mg/Ca of single specimens of *Bulimina aculeata* in the mid-range size (150–225  $\mu\text{m}$ ) having much higher values. Mg/Ca of the bulk results of Hintz et al. (2006b), however, showed no apparent size trend, which was also suggested by Wit et al. (2012) for *B. marginata*. In order to exclude a possible size effect we analyzed three non-stained, multi-specimen ( $n = 22\text{--}40$ ) *G. turgida* samples from the Gullmar Fjord, showing an average Mg/Ca of 3.47  $\text{mmol mol}^{-1}$  vs. 2.90  $\text{mmol mol}^{-1}$  in the stained samples of the Gullmar Fjord. This indicates that the stained samples with the low



**Fig. 4a.** Mn/Ca of *G. turgida* for the Skagerrak for 0–1 cm (circles, red) and 1–2 cm (diamonds, blue) sediment depth, showing higher values deeper in the sediment corresponding to lower dissolved oxygen concentrations deeper in the sediment. Maximum error corresponds to the largest analytical error for the displayed samples.



**Fig. 4b.** Mn/Ca of *G. turgida* (hexagons, orange) from the Gullmar Fjord vs. dissolved oxygen concentrations in the water column for 2006 and 2007. When bottom water dissolved oxygen decreases, Mn/Ca in *G. turgida* increases. Maximum error corresponds to the largest analytical error for the displayed samples.

number of living specimens are probably not affected by a size effect bias.

In the following sections we discuss the analyzed variations in Mg/Ca and Mn/Ca for *B. marginata* and *G. turgida* with respect to proposed impact factors like temperature, salinity, carbonate system, and dissolved oxygen concentration.

#### 4.1 Mg/Ca

##### 4.1.1 Mg/Ca in *B. marginata*

For *B. marginata* two studies of Mg/Ca vs. temperature have been published based on culturing experiments, and one study combining core top and culturing data (Hintz et al.,

**Table 1.** Water mass conditions, including temperature, salinity, carbonate system parameters, Mg/Ca<sub>SW</sub>, and Mn/Ca<sub>SW</sub> for the Skagerrak (site FÅ17) and the Gullmar Fjord (site FG113).

	Skagerrak	Gullmar Fjord
Temperature (°C)	7.3	6.2
Salinity	35.21	34.46
Dissolved Oxygen (mL L <sup>-1</sup> )	6.03	0.9–6.6
Total Alkalinity (μmol kg <sup>-1</sup> )	2319 <sup>1</sup>	2300 <sup>2</sup>
Dissolved Inorganic Carbon (μmol kg <sup>-1</sup> )	2151 <sup>1</sup>	2225 <sup>2</sup>
CO <sub>3</sub> <sup>=3</sup> (μmol kg <sup>-1</sup> )	120.6	70.6
Δ(CO <sub>3</sub> <sup>=3</sup> ) <sup>3</sup> (μmol kg <sup>-1</sup> )	77.1	29.1
Omega <sup>3</sup>	2.77	1.7
pH <sup>3</sup>	8.15	7.91
Mg/Ca <sub>SW</sub> (mol mol <sup>-1</sup> )	5.04	5.00
Mn/Ca <sub>SW</sub> <sup>4</sup> (μmol mol <sup>-1</sup> )	n.a.	6.07

<sup>1</sup> Hjalmarsson et al. (2010).

<sup>2</sup> Ulfso, MSc, Univ. Göteborg (2009).

<sup>3</sup> Carbonate system parameters were calculated using the CO<sub>2</sub>SYS (Pierrot et al., 2006) with the constants of Mehrbach et al. (1973) and pH on the sea water scale.

<sup>4</sup> Mn concentrations were below the detection limit for the Skagerrak and 3.7–10.3 μmol L<sup>-1</sup> for the Gullmar Fjord.

2006a; Filipsson et al., 2010; Wit et al., 2012). Although analyses in both culturing experiments were done with laser ablation ICP-MS, the resulting calibrations are different from each other and also from the core top study (Fig. 3). Another option to calculate temperatures is the multi-species calibration of Lear et al. (2002) as it also includes analyses of *Bulimina* spp. Temperature fluctuations in the Skagerrak at 300 m water depth during 2007 were less than 2 °C with an average of 7.3 °C (Fig. 2a; SMHI). Applying the different calibrations gives average Mg/Ca-based temperatures of 9.0 °C (Lear et al., 2002), 16.4 °C (Wit et al., 2012), and 3.4 °C (Hintz et al., 2006a), respectively. Comparing our core top Mg/Ca data with the results of cultured *B. marginata* of Filipsson et al. (2010) would suggest temperatures below zero.

One possible reason for the large spread in Mg/Ca could be the heterogeneous Mg distribution between and within shells from the same sample (e.g., Egginis et al., 2003; Allison and Austin, 2003; Rathmann et al., 2004; Hathorne et al., 2009). Hintz et al. (2006a) showed a range in the distribution coefficient of Mg from 0.5 to  $15.1 \times 10^{-3}$ . It is therefore necessary to include a sufficient number of shells when analyzing Mg/Ca to obtain a representative average value for the sample. Although this would explain the scatter in the data, which results from using laser ablation, it does not explain why absolute values between the different studies have different ranges. It is likely that the data from Filipsson et al. (2010) included excess Mg due to the presence of either organic material or an amorphous calcium carbonate phase (Barker et al., 2003; Addadi et al., 2003; Hathorne et al., 2009). Due to the fragility of the cultured tests no cleaning was performed before raster analyses on the newly grown

**Table 2a.** Water mass characteristics during sample collection in the Skagerrak and Mg/Ca and Mn/Ca for *B. marginata* and *G. turgida*.

Sample <sup>1</sup>	Sediment depth (cm)	Temperature (in situ, °C)	Salinity	Oxygen (mL L <sup>-1</sup> )	<i>B. marginata</i> Mg/Ca (mmol mol <sup>-1</sup> )	<i>B. marginata</i> Mn/Ca (mmol mol <sup>-1</sup> )	<i>G. turgida</i> Mg/Ca (mmol mol <sup>-1</sup> )	<i>G. turgida</i> Mn/Ca (mmol mol <sup>-1</sup> )
4A	0–1	7.31	35.22	6.14	1.90	b.d.l. <sup>2</sup>	3.41	b.d.l.
4B	0–1	7.31	35.22	6.14	2.18	b.d.l.	4.07	0.072
5A	0–1	7.09	35.20	5.85	2.85	b.d.l.	4.15	0.003
5B	0–1	7.09	35.20	5.85	2.27	b.d.l.	4.96	0.020
4A	1–2	7.31	35.22	6.14	2.42	b.d.l.	3.79	0.058
4B	1–2	7.31	35.22	6.14	n.a. <sup>3</sup>	n.a.	4.30	0.090
5A	1–2	7.09	35.20	5.85	n.a.	n.a.	3.94	0.015
5B	1–2	7.09	35.20	5.85	n.a.	n.a.	4.25	0.035

<sup>1</sup> Samples 4A and 4B were collected June 2007; samples 5A and 5B were collected September 2007.<sup>2</sup> b.d.l. = Mn concentrations below the detection limit.<sup>3</sup> n.a. = No *B. marginata* specimens were available in these samples.**Table 2b.** Water mass characteristics during sample collection in the Gullmar Fjord and Mg/Ca and Mn/Ca for *G. turgida*.

Sample	Date of collection	Temperature (in situ, °C)	Salinity	Oxygen (mL L <sup>-1</sup> )	Ca conc. (ppm)	<i>G. turgida</i> Mg/Ca (mmol mol <sup>-1</sup> )	<i>G. turgida</i> Mn/Ca (mmol mol <sup>-1</sup> )
2	Feb 2006	5.41	34.45	6.59	59.55	2.93	2.73
8	Aug 2006	5.97	34.50	3.54	28.68	2.97	0.20
13	Jan 2007	5.95	34.41	1.6	0.82 <sup>1</sup>		10.58 <sup>1</sup>
13	Jan 2007	5.95	34.41	1.6	1.88 <sup>1</sup>		7.94 <sup>1</sup>
18	Jun 2007	6.69	34.46	3.7	7.65 <sup>1</sup>		4.30 <sup>1</sup>
18	Jun 2007	6.69	34.46	3.7	3.38 <sup>1</sup>		4.16 <sup>1</sup>
21	Sep 2007	6.75	34.46	1.5	4.89 <sup>1</sup>		5.80 <sup>1</sup>
21	Sep 2007	6.75	34.46	1.5	13.01	2.80	4.76
18	Jun 2007	6.69	34.43	3.6	17.51	2.15 <sup>2</sup>	b.d.l.
12–1	Oct 2012	6.83	34.39	1.78	56.57	3.78	5.26
12–2	Oct 2012	6.83	34.39	1.78	102.45	2.86	6.26
12–3	Oct 2012	6.83	34.39	1.78	104.06	3.76	0.91

<sup>1</sup> Due to the matrix effect on very small samples, Mg/Ca on samples with Ca concentrations lower than 5–10 ppm are considered to be biased; Mn/Ca on samples with Ca concentrations lower than 3 ppm are considered to be biased. The two samples with highest Mn/Ca and lowest Ca concentrations are considered to be underestimated based on a matrix experiment using the ECRM752-1 standard of Greaves et al. (2008).<sup>2</sup> From 70 m water depth (site FG70) one sample yielded enough *B. marginata* ( $n = 10$ ) for analysis.

calcite, resulting in Mg/Ca being higher than in any of our samples (Fig. 3a). The data of Wit et al. (2012), on the other hand, are all lower than our results apart from the specimens grown at 14 °C. The number of specimens used for our bulk analyses ranged between 6 and 15, providing an average signal that should be representative of the water mass temperature (7.1–7.3 °C) at the time of collection. The variation in Mg/Ca, however, suggests a spread of 3.9–6.0 °C depending on the choice of calibration, which is significantly larger than the error commonly associated with benthic Mg/Ca vs. temperature calibrations of 0.5–1.5 °C (e.g., Lear et al., 2002; Huang et al., 2012).

Salinity has been shown to increase foraminiferal Mg/Ca, especially in high-salinity settings such as the Red Sea or the Mediterranean (e.g., Nürnberg et al., 1996; Lea et al., 1999;

Kisakürek et al., 2008; Groeneveld et al., 2008; Hoogakker et al., 2009; Dissard et al., 2010; Van Raden et al., 2011; Diz et al., 2012). Salinity in the deep Skagerrak is very stable throughout the year (35.0–35.3), both similar to open-ocean settings and to the culturing experiments of Hintz et al. (2006a). The impact of low-salinity (20–30) surface water coming from the Baltic Proper, via the Baltic Current, does not reach the deep Skagerrak. Thus, it can be excluded that salinity is having a significant impact on our Mg/Ca results.

A factor known to be significant in the deep sea is the carbonate ion effect (Elderfield et al., 2006; Raitzsch et al., 2008). Especially at water temperatures < 3–4 °C the change in the carbonate ion concentration dominates over the influence of temperature on Mg/Ca, mainly caused by increasing water depth, i.e., pressure, and the impact of water masses

with a different calcite saturation state, e.g., North Atlantic Deep Water vs. Antarctic Bottom Water (Raitzsch et al., 2008). Conditions in the deep Skagerrak show oversaturated values with  $\Omega = 2.77$  and a carbonate saturation state of  $77.1 \mu\text{mol kg}^{-1}$  (values calculated with CO<sub>2</sub>SYS; Pierrot et al., 2006; Table 1). In combination with a water temperature of  $\sim 7^\circ\text{C}$  this does not directly suggest a significant impact on the Mg/Ca results.

#### 4.1.2 Mg/Ca in *Globobulimina turgida*

Our Mg/Ca results on *G. turgida* are among the first data available for *Globobulimina* spp. covering the same range of values as for *G. affinis* between 2.2 and  $4.9 \text{ mmol mol}^{-1}$  (Skinner et al., 2003; Fig. 3). The Mg/Ca calibration of *G. affinis* (Skinner et al., 2003), however, was defined for a temperature range between  $-1.8^\circ\text{C}$  and  $\sim 3.5^\circ\text{C}$ . Applying the Skinner et al. (2003) calibration equation would result in an average temperature for the Skagerrak of  $4.2^\circ\text{C}$  and for the Gullmar Fjord of  $\sim 0^\circ\text{C}$ , while in situ temperatures at the time of collection were  $7.3^\circ\text{C}$  and  $6.2^\circ\text{C}$ , respectively (Fig. 2a). Due to generally higher Mg/Ca ratios of *Globobulimina* spp. the multi-species calibration of Lear et al. (2002) gives overestimated temperatures of  $10\text{--}14^\circ\text{C}$ . As with *B. marginata* the lack of available published data for comparison makes it difficult to determine if the Mg/Ca is indeed showing temperature or also showing the influence of other factors. The spread in the Skagerrak *G. turgida* Mg/Ca data is as large as for *B. marginata* (Fig. 3b). Even though the bottom water mass characteristics between Skagerrak and the Gullmar Fjord concerning temperature and salinity are similar (Table 1), there is a significant difference in Mg/Ca of *G. turgida*. Average foraminiferal Mg/Ca in the Skagerrak is  $4.11 \text{ mmol mol}^{-1}$  vs.  $2.90 \text{ mmol mol}^{-1}$  in the Gullmar Fjord, while the average Mg/Ca of the non-stained samples from the Gullmar Fjord is  $3.47 \text{ mmol mol}^{-1}$ . This difference cannot be explained by the small temperature difference of  $1.1^\circ\text{C}$ , implying that another factor is present.

Bottom water temperature in the Gullmar Fjord is higher ( $6.2^\circ\text{C}$ ) than the threshold of  $3\text{--}4^\circ\text{C}$  suggested for the calcite saturation state to have a major influence on Mg/Ca (Elderfield et al., 2006; Raitzsch et al., 2008). Nevertheless, the parameters of the carbonate system are different in the deep Gullmar Fjord when compared to the deep Skagerrak. The carbonate ion concentration is significantly lower, leading to less saturated bottom water with respect to calcite ( $\Omega = 1.7$  and  $\Delta(\text{CO}_3^{\pm}) = 29.1 \mu\text{mol kg}^{-1}$ ; values calculated with CO<sub>2</sub>SYS; Pierrot et al., 2006; Table 1). If we hypothetically study the differences between the deep water in the Gullmar Fjord and the Skagerrak using existing dependencies for benthic foraminifera, the difference in Mg/Ca of *G. turgida* from the Skagerrak and the Gullmar Fjord could be explained as a combined effect of temperature and  $\Delta(\text{CO}_3^{\pm})$  (keeping in mind that the infaunal habitat of *G. turgida* might not be directly comparable with bottom

water conditions). The difference in temperature of  $1.1^\circ\text{C}$  would account for a  $\Delta(\text{Mg/Ca})$  of  $0.35\text{--}0.45 \text{ mmol mol}^{-1}$  (Lear et al., 2002; Skinner et al., 2003). Using the dependency of  $\Delta(\text{Mg/Ca})$  on  $\Delta(\text{CO}_3^{\pm})$  determined on *Cibicidoides mundulus* and *Planulina wuellerstorfi* (Raitzsch et al., 2008) the difference in Mg/Ca is  $0.48\text{--}0.82 \text{ mmol mol}^{-1}$ . Taken together, the expected difference between Mg/Ca in the Skagerrak and Gullmar Fjord would be  $0.83\text{--}1.27 \text{ mmol mol}^{-1}$ . This would be sufficient to explain the observed difference for *G. turgida* Mg/Ca of  $1.21 \text{ mmol mol}^{-1}$ .

Additionally, a bottom water mass characteristic that is also significantly different between the Skagerrak and the Gullmar Fjord is the low dissolved oxygen content during most of the year in the fjord. *Globobulimina turgida* is a foraminifera species that is able to respire nitrate through denitrification via an internal nitrate pool (Risgaard-Petersen et al., 2006; Piña-Ochoa et al., 2010), allowing its survival in low-oxygen environments. But although it was shown in culturing experiments that *G. turgida* maintains its metabolic activity, it remains unclear if the foraminifera also calcify and reproduce under these conditions (Piña-Ochoa et al., 2010). Elderfield et al. (1996) hypothesized that there is a direct link between growth rate and partitioning coefficients of trace metal incorporation into calcite, although this was not shown explicitly for Mg. We speculate that in a lower oxygen environment the lower metabolic activity might also decrease the distribution coefficient of Mg, which could potentially have contributed to the lower *G. turgida* Mg/Ca in the Gullmar Fjord compared with the Skagerrak.

#### 4.2 Mn/Ca as a potential proxy for oxygen concentration

Traditionally, Mn/Ca in foraminifera is used as an indicator for the presence of diagenetic Mn oxyhydroxides and Mn carbonates, which can contain significant concentrations of other trace metals like Cd and Mg (Boyle, 1983; Barker et al., 2003). Typical Mn/Ca in cleaned foraminifera, which are unaffected by coatings, is  $< 0.1 \text{ mmol mol}^{-1}$  (Barker et al., 2003). For the development of Mn/Ca as proxy for oxygen concentrations it is essential to determine where the Mn is located in the calcite, either incorporated into the tests or as coating. Manganese is a redox-sensitive element, mainly present as Mn<sup>2+</sup> in sea water but precipitating as a Mn oxyhydroxide under oxygenated conditions. However, under low-oxygen conditions the Mn oxyhydroxide is reduced and the Mn<sup>2+</sup> concentration increases (Tribouillard et al., 2006). Especially pore water can become supersaturated with respect to Mn under low-oxygen conditions, resulting in inorganic precipitation of Mn carbonate (MnCO<sub>3</sub> or rhodochrosite). Thus, when benthic foraminifera live and precipitate calcium carbonate under lower oxygen conditions, more Mn will be incorporated into their calcite tests and Mn/Ca may therefore be used as a proxy for low-oxygen conditions. Based on theory and precipitation experiments of

inorganic calcite, the variation in distribution coefficients for Mn in inorganic calcite varies between 1 and 1700 (e.g., Pinigore, 1978; Franklin and Morse, 1983), and laser ablation measurements on benthic foraminifera from the Arabian Sea and the Gulf of Biscay have confirmed the incorporation of Mn into foraminiferal calcite (Reichart et al., 2003). The large spread in distribution coefficients for Mn is also suggested for benthic foraminifera, which display a large variation of Mn/Ca. A laser ablation study on the aragonitic *Hoeglundina elegans* from the Mediterranean showed Mn/Ca between 1 and  $10 \mu\text{mol mol}^{-1}$  (Ní Fhlaithearta et al., 2010), similar to Mn/Ca in the calcitic *Uvigerina peregrina* and *Bolivina spissa* from below the oxygen minimum zone (OMZ) off the coast of Peru determined by secondary ion mass spectrometry (SIMS; Glock et al., 2012). Mn/Ca of *U. peregrina* from below the OMZ in the eastern tropical North Pacific, on the other hand, varied from 0.05 to  $0.2 \text{ mmol mol}^{-1}$ , analyzed using flow-through time-resolved analysis (Klinkhammer et al., 2009). The different analytical techniques used in these studies all aimed at preventing Mn-related diagenetic coatings being included in the analyses. This is also the reason why the specimens used in this study were labeled by CellTracker Green: ensuring that they were alive during collection, and thus they are assumed to be not significantly affected by diagenetic coatings yet.

#### 4.2.1 Mn/Ca in the Skagerrak

Bottom water in the Skagerrak is well oxygenated throughout the year, with oxygen concentrations varying between 5.5 and  $7 \text{ mL L}^{-1}$  (Fig. 2a; SMHI, 2007, 2008). The Mn concentrations in the bottom water were all below the detection limit. *B. marginata* tends to live closer to the sediment surface, where abundant oxygen is available (e.g., Gustafsson and Nordberg, 2000), while *G. turgida* extends its microhabitat down into the sediment (e.g., Jorissen et al., 1995). The lack of Mn in the bottom water translates to negligible Mn/Ca in the tests of *B. marginata* (Table 2). For *G. turgida*, on the other hand, all samples from 1 to 2 cm have higher Mn/Ca than their respective samples from 0 to 1 cm (Fig. 4a; Table 2). Bakker and Helder (1993) analyzed oxygen concentrations in pore water profiles from a collection of sediment cores from the Skagerrak. Typical profiles show oxygen penetration into the sediment from < 5 mm for the shallower locations to 15–20 mm for deeper locations. Comparing their profiles with the water depth of our study location suggests that oxygen penetrated the sediment down to ~ 5 mm. Accordingly, Mn concentrations in the pore water increase to values of  $50\text{--}100 \mu\text{mol L}^{-1}$  below the oxic zone in the sediment (Bakker and Helder, 1993). This might suggest that *G. turgida* specimens that are living deeper in the sediment are incorporating more Mn into their calcite.

#### 4.2.2 Mn/Ca in Gullmar Fjord

Mn/Ca in the Gullmar Fjord samples is significantly different from the Skagerrak samples with partially extremely high foraminiferal Mn/Ca values (Fig. 4b; Table 2). As the deeper water in the Gullmar Fjord only gets renewed once a year usually during late winter/early spring, oxygen concentrations decrease during the rest of the year, being lower than  $2 \text{ mL L}^{-1}$  during autumn and winter (Fig. 2b). As dissolved Mn is not directly precipitated as it is under lower oxygenated conditions, higher Mn concentrations occur in the bottom water of the Gullmar Fjord than in the Skagerrak, reaching concentrations between  $3.7$  and  $10.3 \mu\text{mol L}^{-1}$ , rapidly increasing to  $30\text{--}250 \mu\text{mol L}^{-1}$  in the pore water (Goldberg et al., 2012). Due to the already low bottom water oxygen concentrations, *G. turgida* tends to live near the sediment surface (Risgaard-Petersen et al., 2006). The Mn/Ca values in *G. turgida* vary between  $0.2$  and  $6.26 \text{ mmol mol}^{-1}$ , significantly higher than those in the Skagerrak (Table 2). Although the shallow habitat of *G. turgida* in the Gullmar Fjord could suggest a direct link between Mn/Ca in the bottom water and in the foraminiferal calcite, the lack of pore water chemistry data prevents calculation of possible distribution coefficients (Goldberg et al., 2012).

### 4.3 Potential as paleoproxies

#### 4.3.1 Mg/Ca

The Mg/Ca results in this study are difficult to align with currently existing Mg/Ca vs. temperature calibrations. Likely reasons for this are the different ways the various studies have achieved their results, from laser ablation analyses on chamber parts of cultured specimens to bulk analyses on specimens from core tops. The conditions in the Skagerrak are similar to open-ocean conditions, suggesting, especially for *B. marginata*, that the application of Mg/Ca as paleothermometer as hitherto commonly applied has the potential to work. What is needed though is an effort to establish a Mg/Ca vs. calcification temperature calibration based on multi-specimen samples with a narrow size fraction from a wide range of core top settings. In the case of *G. turgida* the significant difference between the samples from the Skagerrak and the Gullmar Fjord can be explained by a significant impact of differences in the carbonate system between the Skagerrak and the Gullmar Fjord. Additionally, we speculate that the low-oxygen conditions might have an additional impact on the distribution coefficient of Mg in foraminifer tests.

#### 4.3.2 Mn/Ca

Mn/Ca in benthic foraminifera that are tolerant of low-oxygen conditions, such as *G. turgida*, has the potential to be developed as an indirect proxy to variations in low dissolved oxygen conditions. Our results show an increase in foraminiferal Mn/Ca with increasing Mn concentrations in

the bottom water due to low-oxygen conditions. The redox behavior of Mn, however, provides some issues for reconstructing downcore records. The specimens used in this study were alive when collected, and thus were assumed not to be significantly affected by diagenetic coatings. But after burial in the sediment the tests can be covered with diagenetic coatings either resulting from oxidizing (Mn oxyhydroxides) or reducing conditions (Mn carbonates) (Boyle, 1983; Klinkhammer et al., 2009). Thus, not only is it necessary to determine when and/or where in the sediment the foraminifera incorporate the Mn signal into their tests, this primary signal also needs to be extracted without including the additional Mn from any coatings. The traditional reduction step for cleaning foraminiferal samples only removes the Mn oxyhydroxides (Boyle, 1983; Barker et al., 2003). Different techniques have made an effort to exclude the Mn carbonate from the analyses, although the resulting Mn/Ca in the foraminifera still varied by several orders of magnitude (Klinkhammer et al., 2009; Ní Fhlaithearta et al., 2010; Glock et al., 2012). To determine whether this range in values is indeed primary or an artifact of the analytical techniques, culturing experiments under varying oxygen conditions or combining living specimens with in situ pore water measurements are necessary to determine if Mn/Ca can indeed be developed as a proxy for dissolved oxygen content.

## 5 Conclusions

In this study we have explored variations of Mg/Ca and Mn/Ca in live benthic foraminifera, *Bulimina marginata* and *Globobulimina turgida* with respect to changes in bottom water temperature and dissolved oxygen content in shelf regions. Foraminifera and water samples were collected from the Skagerrak and the Gullmar Fjord (SW Sweden) over a 2 yr period. Staining with CellTracker Green ensured that the specimens were alive when collected, and thus were assumed to be only minimally affected by diagenetic coatings.

The range in Mg/Ca of 1.90–2.85 mmol mol<sup>-1</sup> for *B. marginata*, and 2.80–4.96 mmol mol<sup>-1</sup> for *G. turgida* is similar to other studies. However, Mg/Ca results for both species show much more variation than would be expected from the influence of the annual temperature change of less than 2 °C using existing Mg/Ca vs. temperature calibrations. Taking differences in the carbonate ion system between the Skagerrak and the Gullmar Fjord into account would explain these results.

Mn/Ca results on *G. turgida* show potential to record variations in dissolved oxygen content of the habitat where they calcify. Samples from the Skagerrak show increased Mn/Ca (on average 0.05 mmol mol<sup>-1</sup>) in specimens that lived deeper in the sediment (1–2 cm) compared to those that lived near the surface (on average 0.02 mmol mol<sup>-1</sup>; 0–1 cm). *G. turgida* samples from the lower oxygen Gullmar

Fjord showed significantly increased Mn/Ca, being highest (10.58 mmol mol<sup>-1</sup>) when dissolved oxygen was lowest.

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