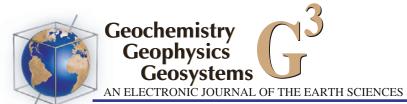
### Paper 3

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# Mg/Ca ratios in the planktonic foraminifer *Neogloboquadrina* pachyderma (sinistral) in the northern North Atlantic/Nordic Seas

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[1] In core top samples in the Nordic Seas, Mg/Ca ratios of *N. pachyderma* (sin.) are generally consistent with previous high-latitude calibration data but do not reflect the modern calcification temperature gradient from 2°C in the northwest to 8°C in the southeast. This is because Mg/Ca ratios in foraminiferal shells from the central Nordic Seas are ~0.4 mmol/mol higher than expected from calibrations of Nürnberg (1995) and Elderfield and Ganssen (2000). The enhanced Mg/Ca ratios are observed in an area with low sedimentation rates (<~5 cm/kyr). Possible factors that may cause this include bioturbation, Holocene variability in old core tops, dissolution, pore water chemistry, occurrence of volcanic ash, and other natural variability. The enhanced foraminiferal Mg/Ca ratios in areas of the Nordic Seas and the northern North Atlantic may also be linked with secondary factors related to the presence of fresher and colder water masses, possibly combined with pore water chemistry in low-sedimentation areas differing from high-sedimentation areas.

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Theme: Development of the Foraminiferal Mg/Ca Proxy for Paleoceanography

Guest Editor: Pamela Martin

#### 1. Introduction

- [2] Mg/Ca in foraminiferal calcite is becoming an established paleotemperature proxy. The potential advantage of foraminiferal Mg/Ca thermometry over other marine paleotemperature proxy methods is that temperature estimates may be obtained from the same foraminiferal sample from which data on oxygen isotopes, also sensitive to temperature, are obtained [e.g., Elderfield and Ganssen, 2000; Lea et al., 1999; Lear et al., 2002; Rosenthal et al., 1997]. There are, however, a number of issues with the methodology that require further clarification, in particular application to cold, near surface, environments at high latitudes where foraminiferal Mg/Ca is low and changes with temperature are small. Under such circumstances it is possible that secondary factors (e.g., salinity, pH, alkalinity, carbonate ion concentration, secondary calcification, dissolution) may have a proportional large influence on Mg/Ca ratios.
- [3] Few investigations of Mg/Ca in planktonic foraminifers have been made in the Nordic Seas and the northern North Atlantic. Previously, *Nürnberg* [1995] showed that there is a temperature dependent Mg/Ca fractionation in *N. pachyderma* (sinistral) in the Nordic Seas, based on electron microprobe analyses of samples compared with water temperatures averaged over 0–200 m depth.
- [4] Several secondary factors may influence measured Mg/Ca ratios in foraminiferal calcite. In this paper we evaluate the potential contributions of such factors for the apparent discrepancy between surface water temperature gradients and Mg/Ca gradients. Secondary factors include pH, salinity [Lea et al., 1999; Nürnberg et al., 1996] and carbonate ion concentration [CO<sub>3</sub><sup>2-</sup>] [Russell et al., 2004]. In the Nordic Seas the [CO<sub>3</sub><sup>2-</sup>] values in the Nordic Seas vary and are mainly below 200 μmol/kg, suggesting that [CO<sub>3</sub><sup>2-</sup>] may potentially influence foraminiferal Mg/Ca ratios. Additionally, dissolution is known to significantly affect Mg/Ca ratios in foraminifera [Dekens et al., 2002].

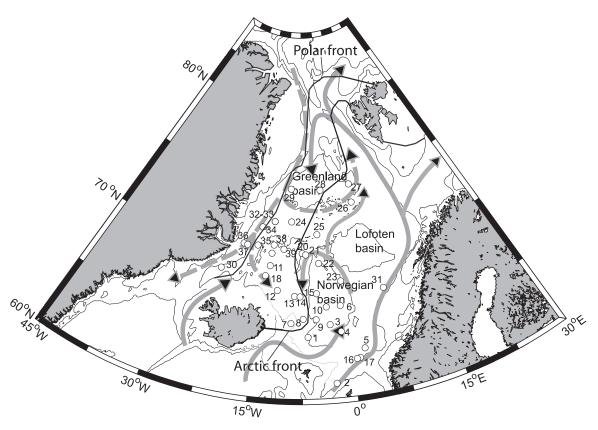
Influences from cleaning protocols and contamination from the clay phase of the sediments may also influence ratios.

[5] In this paper we discuss construction of a temperature calibration, based on core tops from the Nordic Seas. The core tops are shown in Figure 1 and Table 1. Next we discuss foraminiferal Mg/Ca data for the Last Glacial Maximum (LGM) [Meland et al., 2005] in the context of the calibration results and also transient records of Mg/Ca during or near the Dansgaard-Oeschger Interstadial 2, LGM and the last Deglaciation (Younger Dryas-Holocene) from the Faeroe-Shetland core MD99-2284 (0.98°W, 62.37°N, 1500 m water depth).

### 2. Materials and Methods

### 2.1. Sample Selection and Preparation

- [6] The planktonic foraminifer species N. pachyderma (sin.) was picked from the size fraction  $150-212~\mu m$ . Each sample had a weight of  $200-500~\mu g$  before crushing and cleaning, comprising 40-100 foraminifera. If not otherwise stated, foraminifera were cleaned using the "Mg cleaning method" [Barker et al., 2003]. Foraminiferal samples were first gently crushed, using glass plates, to open the chambers. The samples were cleaned to remove clays (water and methanol wash) and organic matter (hydrogen peroxide treatment) followed by a dilute acid polish prior to analysis.
- [7] Elemental analyses were performed with a Varian Vista AX simultaneous inductively coupled plasma atomic-emission spectrometer (ICP-AES) [de Villiers et al., 2002], at the University of Cambridge, UK. At the time of analysis, the instrumental precision of measured Mg/Ca ratios was ±0.01 mmol/mol for a standard solution of Mg/Ca = 5.13 mmol/mol. By comparing 28 duplicate measurements of core top and LGM samples from this work, a standard deviation of the residuals with 56 degrees of freedom indicates reproducibility within ±0.08 mmol/mol where all



**Figure 1.** Map showing the locations of the studied core tops, marked as white circles. The numbered labels point to the cores in Table 1. Main oceanographic features of the upper water masses are indicated. The solid gray lines indicate the flow of warm Atlantic Water, and the dashed gray lines indicate the flow of the cold Polar Water. The solid black lines indicate positions of the Arctic and Polar Fronts.

samples have Fe/Ca < 0.10 mmol/mol, less than the contamination threshold used by *Barker et al.* [2003].

[8] In addition, a few samples were cleaned using the "Cd cleaning method" [Boyle and Keigwin, 1985] at the University of California, Santa Barbara, USA. The main difference from the cleaning method obtained by Barker et al. [2003] is that "Cd cleaning" involves a reductive step aimed at removing the Mn-Fe-oxide coating. The purpose was to determine whether systematic bias exists between the two cleaning methods for these samples.

[9] Oxygen isotope data for *N. pachyderma* (sin.) were measured together with Mg/Ca ratios, to refine calcification temperatures used for core top Mg/Ca calcification temperatures. Available  $\delta^{18}O_{Nps}$  measurements for most of the samples are from *Johannessen* [1992] for *N. pachyderma* (sin.) in the size fraction 125–250  $\mu$ m. Because Mg/Ca ratios in our work showed some size

dependency (see Results below), we conducted additional  $\delta^{18}O_{Nps}$  analyses in the size fraction  $150{-}212~\mu m$  to avoid eventual size dependent differences as far as possible. We performed two measurements for each sample.

[10] Oxygen isotope measurements were performed at the GMS lab, University of Bergen, using a Finnigan MAT 251 equipped with automatic preparation lines ("Kiel device"). Foraminifera were crushed and cleaned with methanol in an ultrasonic bath before analysis. The reproducibility of the analyses was  $\pm 0.07\%$ , based on replicate measurements of carbonate standards. However, 39 duplicate measurements of single core top samples reveal a higher standard deviation of the residuals with 78 degrees of freedom, indicating reproducibility within ±0.13‰. All results are reported as δ<sup>f8</sup>O in ‰ versus PDB, calibrated against NBS 19 and CM03. To achieve the best possible results, each sample had a weight of 60-90 µg before the crushing and cleaning, comprising 12-20 foraminifera.

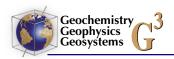


Table 1. Geochemical Data of N. pachyderma (sin.), Including Measured Mg/Ca Ratios in the Size Fraction 150–212 µm, Oxygen Isotope Ratios, Calcification Tanametries and Communication Between Measured and "Expended," Mg/Ca Batios, Datios<sup>a</sup>

| Tempe | Temperatures and Depths, and Comparisons Between | Depths, an | d Comp | arisons     |                                 | Measured and "Expected"                            | ected" Mg/Ca                                 | Mg/Ca Ratios <sup>a</sup>                   |                                   | -        |                                   |                             |                                      |
|-------|--|------------|--------|-------------|---------------------------------|--|--|---|-----------------------------------|----------|-----------------------------------|-----------------------------|--------------------------------------|
|       |  |            |        |             |                                 | ,  | ,  |   |                                   | e        | "Expected"                        |                             | $\delta^{18}$ O <sub>Nps</sub>       |
| Label | Core   | Long.      | Lat.   | Depth,<br>m | Mg/Ca, <sup>b</sup><br>mmol/mol | $\delta^{18}O_{w}$ , ‰<br>Versus SMOW <sup>c</sup> | $\delta^{18}O_{\mathrm{Nps}}$ , % Versus PDB | $\delta^{18}O_{\mathrm{Nps}}^{\mathrm{dT}}$ | Inferred<br>Depth, <sup>e</sup> m | Mg/Ca T, | Calc. Depths,<br>JAS <sup>g</sup> | T Diff., <sup>n</sup><br>°C | Versus PDB<br>Reference <sup>i</sup> |
| 1     | HM133-05 <sup>j</sup>                            | -6.08      | 64.33  | 3310        | 0.93                            | 0.25   | 2.62   | 0.9   | 70                                | 6.2      | 70                                | 0.2                         | 1 <sup>k</sup>                       |
| 2     | $HM133-40^{1}$                                   | -2.15      | 61.14  | 546         | 1.29                            | 0.31   | 2.56   | 6.5   | 300                               | 9.5      | 50                                | 3.0                         | $1^{k}$                              |
| 3     | HM16130  | -2.42      | 65.1   | 3182        | 0.99                            | 0.12   | 2.40   | 6.4   | 09                                | 8.9      | 50                                | 0.4                         | $1^{k}$                              |
| 4     | HM16132  | -0.72      | 64.57  | 2798        | 0.80                            | 0.20   | 2.58   | 0.9   | 150                               | 4.7      | 250                               | -1.3                        | $\frac{1^{k}}{1}$                    |
| 5     | HM16142  | 5.6        | 63.25  | 1100        | 0.93                            | 0.10   | 1.83   | 8.5   | 70                                | 6.2      | 270                               | -2.3                        | 1 <sup>k</sup>                       |
| 9     | HM49-15  | -0.36      | 66.34  | 3260        | 0.91                            | 0.27   | 2.23   | 9.7   | 40                                | 0.9      | 100                               | -1.6                        | т.<br>У                              |
| 7     | HM52-33  | -8.81      | 65.27  | 1002?       | 0.74                            | 0.12   | 3.09   | 3.8   | 100                               | 3.9      | 100                               | 0.2                         | $\frac{1^{k}}{1}$                    |
| ∞     | HM52-39  | -6.79      | 65.57  | 2305        | 0.97                            | 0.15   | 2.73   | 5.2   | 70                                | 9.9      | 40                                | 1.4                         | $\frac{1^{k}}{1^{k}}$                |
| 6     | HM52-41  | -4.63      | 65.52  | 3905        | 0.74                            | 0.16   | 2.55   | 0.9   | 50                                | 3.9      | 160                               | -2.0                        | $\frac{1^{k}}{1}$                    |
| 10    | HM52-42  | -2.8       | 66.34  | 3104        | 1.04                            | 0.17   | 2.38   | 6.7   | 50                                | 7.3      | 40                                | 0.7                         | $1^{k}$                              |
| 11    | HM57-05  | -13.12     | 69.14  | 1892        | 0.93                            | 0.10   | 3.55   | 2.0   | 40                                | 6.2      | "too warm"                        | 4.2                         | $2^{\mathrm{m}}$                     |
| 12    | HM57-09  | -11.4      | 67.47  | 1662        | 0.88                            | 0.11   | 3.32   | 2.9   | 50                                | 5.7      | 20                                | 2.8                         | $1^{k}$                              |
| 13    | HM57-11  | -8.3       | 67.12  | 1617        | 0.80                            | 0.05   | 3.19   | 3.1   | 09                                | 4.7      | 40                                | 1.6                         | $\frac{1^{k}}{1}$                    |
| 14    | HM57-12  | -7.32      | 80.79  | 2093        | 0.88                            | 0.05   | 2.83   | 4.5   | 40                                | 5.7      | 30                                | 1.2                         | $1^{k}$                              |
| 15    | HM57-16  | -4.37      | 67.28  | 2816        | 1.07                            | 0.21   | 2.59   | 0.9   | 40                                | 7.6      | 20                                | 1.6                         | $1^k$                                |
| 16    | HM57-20  | 1.67       | 62.65  | 750         | 0.85                            | 0.10   | 2.92   | 4.3   | 400                               | 5.3      | 340                               | 1.0                         | $1^{k}$                              |
| 17    | HM58-08  | 1.19       | 62.63  | 006         | 0.83                            | 0.13   | 2.31   | 8.9   | 250                               | 5.1      | 340                               | -1.7                        | $\frac{1^{k}}{1^{k}}$                |
| 18    | HM71-12  | -13.87     | 68.43  | 1633        | 0.85                            | 0.04   | 3.49   | 2.0   | 50                                | 5.3      | 0                                 | 3.3                         | 1 <sup>k</sup>                       |
| 19    | HM71-17  | -13.02     | 70.00  | 1460        | 1.00                            | 0.11   | 3.40   | 2.6   | 20                                | 6.9      | "too warm"                        | 4<br>4.                     | 1 <sup>k</sup>                       |
| 20    | HM71-20  | -6.88      | 70.07  | 2005        | 0.84                            | 0.21   | 2.90   | 8.4   | 20                                | 5.2      | 20                                | 0.4                         | 1 <sup>k</sup>                       |
| 21    | HM71-21  | -6.16      | 96.69  | 2612        | 0.79                            | 0.25   | 2.79   | 5.4   | 30                                | 4.6      | 40                                | -0.8                        | х.                                   |
| 22    | HM71-22  | -3.61      | 69.34  | 1833        | 1.04                            | 0.35   | 2.44   | 7.1   | 20                                | 7.3      | 20                                | 0.2                         | 1 <sup>k</sup>                       |
| 23    | HM71-25  | 0.23       | 00.89  | 2850        | 0.79                            | 0.29   | 2.29   | 7.5   | 40                                | 4.6      | 170                               | -2.9                        | 1,<br>,                              |
| 24    | HM80-43  | -9.19      | 72.25  | 2448        | 86.0                            | 0.28   | 3.50   | 2.8   | 10                                | 6.7      | "too warm"                        | 3.9                         | 1 <sup>k</sup>                       |
| 25    | HM94-12  | -3.55      | 71.32  | 1816        | 08.0                            | 0.35   | 3.23   | 4.1   | 30                                | 4.7      | 30                                | 9.0                         | , 1 <sup>*</sup>                     |
| 26    | HM94-16  | 5.37       | 73.23  | 2356        | 0.87                            | 0.22   | 3.32   | 3.3   | 09                                | 5.5      | 20                                | 2.3                         | <del>л</del> .                       |
| 27    | HM94-18  | 5.7        | 74.5   | 2469        | 0.91                            | 0.26   | 3.47   | 2.9   | 50                                | 0.9      | "too warm"                        | 3.1                         | ¥T -                                 |
| 28    | HM94-30  | -2.00      | 74.38  | 3599        | 0.92                            | 0.29   | 3.67   | 2.2   | 30                                | 6.1      | "too warm"                        | 3.9                         | 1.<br>Y                              |
| 29    | HM94-36  | -9.58      | 74.53  | 3217        | 98.0                            | 0.29   | 3.42   | 3.2   | 0                                 | 5.4      | "too warm"                        | 2.3                         | Α                                    |
| 30    | HM94-42  | -22.3      | 68.45  | 1339        | 0.91                            | 0.25   | 3.41   | 3.1   | 10                                | 0.9      | "too warm"                        | 2.9                         | 1 <sub>K</sub>                       |
| 31    | ${ m JM97-948^{n}}$                              | 7.64       | 26.99  | 1048        | 0.82                            | 0.29   | 2.01   | 9.8   | 50                                | 4.9      | 410                               | -3.6                        | 30                                   |
| 32    | M23342   | -13.00     | 72.2   | 1974        | 0.77                            | 0.19   | 3.41   | 2.8   | 0                                 | 4.3      | "too warm"                        | 1.5                         | $\frac{1^{k}}{1}$                    |
| 33    | M23343   | -13.00     | 72.21  | 2400        | 1.02                            | 0.19   | 3.36   | 3.0   | 0                                 | 7.1      | "too warm"                        | 4.1                         | $1^{k}$                              |
| 34    | M23344   | -15.58     | 71.73  | 1080        | 06.0                            | -0.15  | 3.38   | 1.7   | 20                                | 5.9      | "too warm"                        | 4.2                         | $\frac{1^{k}}{1^{k}}$                |
| 35    | M23347   | -16.08     | 70.44  | 1229        | 0.85                            | -0.18  | 3.38   | 1.6   | 20                                | 5.3      | "too warm"                        | 3.7                         | $1^{k}$                              |
| 36    | M23348   | -18.95     | 70.42  | 727         | 0.89                            | -0.34  | 3.24   | 1.5   | 20                                | 5.8      | "too warm"                        | 4.2                         | $1^{k}$                              |
| 37    | M23351   | -18.21     | 70.36  | 1632        | 0.97                            | -0.15  | 3.35   | 1.8   | 20                                | 9.9      | "too warm"                        | 8.4                         | 1 <sup>k</sup>                       |
| 38    | M23353   | -12.72     | 70.57  | 1394        | 0.93                            | 0.14   | 3.30   | 3.1   | 20                                | 6.2      | "too warm"                        | 3.2                         | 1 <sup>k</sup>                       |
| 39    | M23354   | -10.63     | 70.33  | 1747        | 92.0                            | 0.25   | 3.23   | 3.7   | 20                                | 4.2      | 10                                | 0.5                         | $1^{k}$                              |
|       |  |            |        |             |                                 |  |  |   |                                   |          |                                   |                             |                                      |



### 2.2. Age Control and Chronology

- [11] The modern distribution of core top Mg/Ca ratios for N. pachyderma (sin.) in the study area was compiled from cores with Holocene sections, a well-preserved sediment surface, and contents of rose bengal stained living foraminifera. Since bioturbation is active in Nordic Seas sediments, core top samples cannot be regarded as fully modern. Simstich et al. [2003] reported that their core top samples, also located in the Nordic Seas, reflected ages ranging from 100 to 4200 years. Thus our measurements represent an integrated record of some hundred up to a few millennia, or even older, depending on the core location, with the oldest samples originating from the deeper portions of the Nordic Seas and the youngest, one sample from the Voering Plateau, (JM97-948), is inferred to have been deposited close to the calendar year 1985 AD, based on <sup>210</sup>Pb ages [Andersson et al., 2003]. Samples from cores HM133-05 and HM133-40 in the Faeroe-Shetland area contain large amounts of rose bengal stained living foraminifera, indicating that the foraminifera in these samples are close to a modern age.
- [12] The LGM time slice in this work follows the definition of GLAMAP 2000, comprising the interval between 18.0-21.5 cal. ka (15-18 <sup>14</sup>C ka) [Vogelsang et al., 2000], a period known to be relatively stable with minimal meltwater flux [Sarnthein et al., 1995]. Some of the LGM levels were determined using AMS <sup>14</sup>C, while other levels were determined by use of isotope stratigraphy. All of the foraminiferal Mg/Ca analyses for the LGM used the size fraction of 250-300 µm, and were previously published by Meland et al. [2005].

- [13] The age model in core MD99-2284 was constrained by identification of the Vedde ash layer and AMS <sup>14</sup>C data. All of the foraminiferal Mg/Ca analyses for this core were measured in the 150-212 µm size fraction.
- [14] Since the Mg/Ca ratios of the core tops and of the core MD99-2284 were measured in the size fraction 150-212 µm fraction, and the LGM Mg/ Ca ratios were performed in the 250-300 µm fraction, additional analyses were performed to evaluate any size dependency on the Mg/Ca ratios.

### 2.3. Constraints on **Calcification Temperatures**

[15] Since our goal is to calibrate Mg/Ca against the water temperatures in which the foraminifera calcify, we have used oxygen isotope data of N. pachyderma (sin.) ( $\delta^{18}O_{Nps}$ ) (Figure 2a) and the water masses in which they calcify ( $\delta^{18}O_{W}$ , Figure 2b) to calculate calcification temperatures using the paleotemperature equation of Shackleton [1974]:

$$\begin{split} T_{Nps} &= 16.9 - 4.38* \left( \delta^{18} O_{Nps} - \delta^{18} O_{W} \right) \\ &+ 0.1* \left( \delta^{18} O_{Nps} - \delta^{18} O_{W} \right)^{2}, \end{split} \tag{1}$$

where  $T_{Nps}$  is the calcification temperature, and  $\delta^{18}O_{Nps}$  and  $\delta^{18}O_{W}$  are measured against PDB. The calcification temperatures are shown in Figure 2c.

[16] Conversion of  $\delta^{18}O_{water}$  from the Vienna Standard Mean Ocean Water (V-SMOW), scale to  $\delta^{18}O_{w}$  (PDB scale) follows:

$$\delta^{18}O_{w(PDB)} = \delta^{18}O_{water(SMOW)} - 0.27 \eqno(2)$$

Notes to Table 1:

Foraminifera are cleaned using the method of Barker et al. [2003].

Calculated temperatures based on the measured Mg/Ca ratios and assuming that equation (3) in text can be used for the purpose.

h Difference between the  $\delta^{18}O_{Nps}$  calcification temperatures and the "expected" Mg/Ca temperatures. 1, this work; 2, *Johannessen* [1992]; 3, *Andersson et al.* [2003].

<sup>j</sup>Upper 1 cm of a multicore.

<sup>1</sup>Upper 1 cm of a grab.

<sup>&</sup>lt;sup>a</sup> All of the samples are box cores, covering the level of 0-1 cm depth, if not anything else mentioned. See next page for explanations of the footnotes. The labels refer to the numbers in Figure 1.

<sup>&</sup>lt;sup>c</sup>Oxygen isotope values of the water masses in the depths of 20-200 m water depth. The  $\delta^{18}O_w$  values in this table are interpolated values from the map in Figure 1a. <sup>d</sup> Calcification temperatures of N. *pachyderma* (sin.), calculated from equation (1) in text, and the  $\delta^{18}O_{Nps}$  and  $\delta^{18}O_{w}$  values in this table. No vital

effect is assumed by calculation of these temperatures.

Apparent calcification depths. The depths are corresponding to the closest depth with published summer temperatures from the database of Levitus and Boyer [1994].

<sup>&</sup>lt;sup>g</sup>Best fitted calcification depth corresponding to the calculated Mg/Ca temperatures, using published summer temperatures from the database of Levitus and Boyer [1994]. "Too warm" means that the Mg/Ca-calculated temperatures are higher than in the summer sea surface.

<sup>&</sup>lt;sup>k</sup> Picked in the sieve size fraction 150–212 μm.

 $<sup>^{\</sup>rm m}$ Picked in the sieve size fraction 125–250  $\mu$ m.

<sup>&</sup>lt;sup>n</sup>Level 1-2 cm of a multicore.

 $<sup>^{\</sup>rm o}$  Picked in the sieve size fraction >150  $\mu m.$ 



[17] The  $\delta^{18}O_{\rm w}$  data used in this study are taken from various sources (see Figure 2b), and consists of averaged data of the water depths  $20{-}200$  m covering all seasons. The  $\delta^{18}O_{\rm w}$  data through these water depths do not vary more than the instrumen-

tal standard deviation of  $\pm 0.10\%$ , indicating that  $\delta^{18}O_w$  is quite homogenously distributed inside this depth level. The choice of water depth is therefore not critical. Where no  $\delta^{18}O_w$  data exists for the actual core top, interpolation was used.

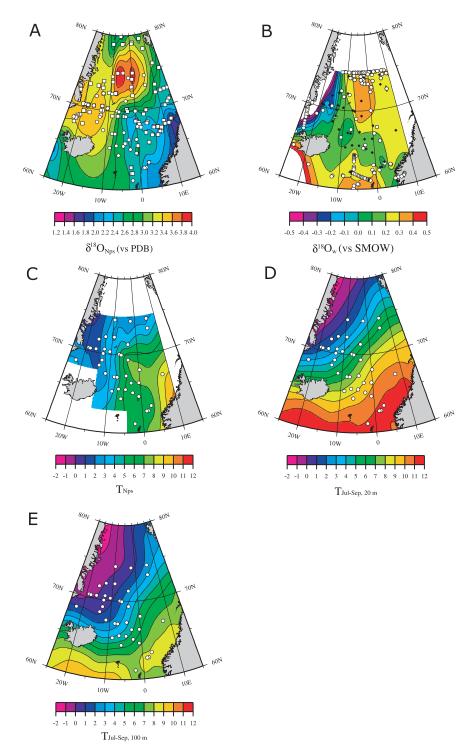
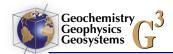


Figure 2



- [18] By calculating the oxygen isotope calcification temperatures in this way, it is not crucial for the results to define the actual water depth and/or season of calcification. The summer average during July September (JAS) is thought to represent the main production season of planktonic foraminifera in the Nordic Seas [Jensen, 1998; Kohfeld, 1996; Schrøder-Ritzrau et al., 2003; von Gyldenfeldt et al., 2000; Weinelt et al., 2001], and we therefore assume that this is the calcifying season. By comparing our calculated temperatures with summer seasonal temperatures from the database of Levitus and Boyer [1994], we find that they correspond to calcification depths of 0-50 m for Arctic and Polar water masses, and 20-300 m for Atlantic water masses (see Table 1 for details).
- [19] To consider the possibility that calcification of *N. pachyderma* (sin.) may have taken place over a wider depth interval of the upper water masses than assumed above, we tested the sensitivity of the calculated calcification temperature to this possibility. As an alternative, we compared Mg/Ca with summer temperatures over the depth range 20 to 200 m, where the temperature distribution at 20 and 100 m depths are shown in Figures 2d–2e. These depth ranges agree with previously interpreted calcifying depths of *N. pachyderma* (sin.) [Kohfeld, 1996; Kuroyanagi and Kawahata, 2004; Simstich et al., 2003].
- [20] We also considered a hypothetical assumption that our Mg/Ca ratios reflect calcification temperatures based on a temperature equation for *N. pachyderma* (sin.) and (dex.), published by *Elderfield and Ganssen* [2000]:

$$Mg/Ca = 0.50 * exp(0.10T),$$
 (3)

where T is the calcification temperature, and Mg/Ca is measured in mmol/mol. These estimated temperatures were used for comparison with oxygen isotope calcification temperatures.

### 3. Results

### 3.1. Mg/Ca Ratios of Core Tops

- [21] Mg/Ca ratios do not reflect the modern calcification temperature gradient (Figures 3a and 2c and Table 1). Comparison of Mg/Ca with alternative modern temperature estimates (20 and 100 m depths) (Figures 2d–2e) and other depths in the range of 20–200 m did not show any temperature dependence either. Mg/Ca ratios are quite similar, with a spatial standard deviation of  $\pm 0.11$  mmol/mol. This is only slightly higher than the average standard deviation of  $\pm 0.08$  mmol/mol, suggesting that Mg/Ca ratios of *N. pachyderma* (sin.) do not vary significantly over the area.
- [22] Comparison of our data with existing temperature equations [Nürnberg, 1995; Elderfield and Ganssen, 2000] shows that many data fall off published calibrations (Figures 3b and 3c). In particular, Mg/Ca ratios with corresponding calcification temperatures below 4°C are much higher than previous data. Additionally, one sample, located at the ridge just north of the Faeroe Islands, have an anomalously high Mg/Ca ratio (Figure 3a).
- [23] Assuming that our measured Mg/Ca ratios, however, reflect calcification temperatures in agreement with equation (3) [Elderfield and Ganssen, 2000], gives the possibility to test how much Mg/Ca derived temperatures deviate from oxygen isotope derived temperatures. Figure 3d shows that the Mg/Ca temperatures are 3–5°C

Figure 2. (a) Oxygen isotope distribution of the planktonic foraminifer species N. pachyderma (sin.) ( $\delta^{18}O_{Nps}$ ), based on interpolation and gridding of  $\delta^{18}O_{Nps}$  data, marked as white squares and circles. The white squares show data from *Simstich* [1999], and the white circles show data from *Johannessen* [1992] and this work (see Table 1 for details). (b) Average distribution of the oxygen isotope values of water masses ( $\delta^{18}O_{w}$ ) in the level of 20-200 m depth, based on interpolation and gridding of  $\delta^{18}O_{w}$  data. The locations of the  $\delta^{18}O_{w}$  data are marked as white circles. The black dots show the locations where Mg/Ca measurements in this work are performed. The  $\delta^{18}O_{w}$  data are from various sources [Azetsu-Scott and Tan, 1997; Bauch et al., 1995; Frank, 1996; Israelson and Buchardt, 1999; Meredith et al., 2001; Mikalsen and Sejrup, 2000; Schmidt et al., 1997; Østbø, 2000; Østlund et al., 1987; Østlund and Grall, 1993]. (c) Calcification temperature distribution of N. pachyderma (sin.) ( $T_{Nps}$ ), based on interpolation and gridding of the  $T_{Nps}$  data in Table 1. The  $T_{Nps}$  data are calculated using the paleotemperature of Shackleton [1974] (equation (1)), where the  $\delta^{18}O_{Nps}$  and  $\delta^{18}O_{w}$  data in Figures 2a and 2b are used for calculation of temperatures. See Table 1 for details about the calcification temperatures. (d) Summer temperature distribution at 20 m water depth. The temperature data are from Levitus and Boyer [1994]. Summer is here defined as the monthly average of the months July, August, and September. The white circles show locations of Mg/Ca ratios performed in this work. (e) Summer is here defined as the monthly average of the months July, August, and September. The white circles show locations of Mg/Ca ratios performed in this work.



"too warm" in northwestern parts of the Nordic Seas. In central parts the Mg/Ca temperatures are similar to the  $\delta^{18}O$  temperatures, while in the southeastern parts they are 1–4°C too cold. If

we also examine the calcification depths implied by the Mg/Ca derived temperatures, we see that many of the cores, especially in central and western parts, get "too warm" (Table 1).

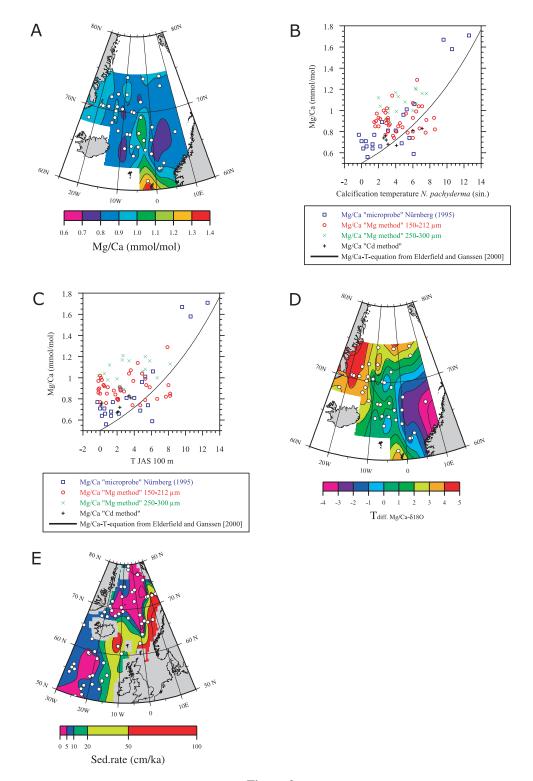


Figure 3



### 3.2. Mg/Ca Ratios of the LGM

[24] Mg/Ca ratios document a clear meridional trend in the eastern sector of the Norwegian Sea for the LGM, with somewhat lower ratios in the eastern Norwegian Sea (0.7-0.8 mmol/mol) than further south, in the North Atlantic west of Ireland (0.8-0.9 mmol/mol) (Figure 4a and Table 2) [Meland et al., 2005]. Ratios are slightly lower than for the core tops. Calcification temperatures (based on equation (3)) decrease from  $5-7^{\circ}$ C south of the Greenland-Scotland ridge to 3-5°C in the eastern Norwegian Sea (Figure 4b and Table 2). In the Greenland and Iceland Seas, temperatures approach 6–10°C, higher than the surface temperatures today (compare Figures 2c-2e versus Figure 4b). This observation contradicts earlier investigations based on foraminiferal transfer functions [Vogelsang et al., 2000; Weinelt et al., 1996, 2003], where SSTs of 3-5°C are proposed.

## 3.3. Mg/Ca Ratios of the Time Slices Interstadial 2, LGM, and the Deglaciation in the Faeroe-Shetland Core MD99-2284

[25] Mg/Ca ratios show some similarities with the subpolar species distribution and the oxygen isotopes of *N. pachyderma* (sin.) (Figures 5a–5d). A distinguishable deviation is that Mg/Ca ratios for the Younger Dryas are almost as high as during the Early Holocene and significantly higher than the LGM Mg/Ca ratios. This contradicts the findings from this and other cores from foraminiferal faunal indices that the Younger Dryas was approximately

as cold as the LGM [Dreger, 1999; Sarnthein et al., 1995; Schulz, 1995; Vogelsang et al., 2000].

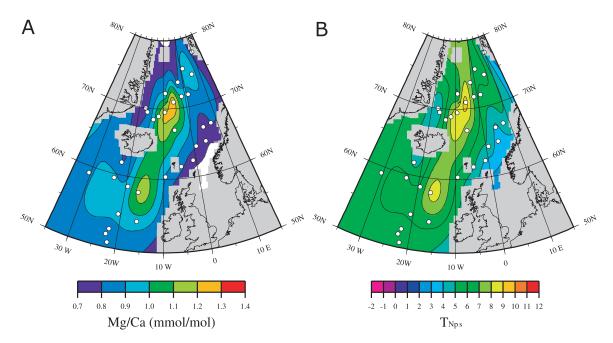
### 3.4. Mg/Ca Ratios Using the "Cd Cleaning Method"

[26] In order to check if Mg/Ca ratios of the core tops and LGM samples in the central Nordic Seas might be contaminated from Fe-Mn coatings, we cleaned samples using the "Cd cleaning method" [Boyle and Keigwin, 1985]. Results show that the Mg/Ca ratios using the two different cleaning methods are correlated, but that the "Cd cleaning method" shows lowered Mg/Ca ratios by 0.20  $(\pm 0.06)$  mmol/mol for 7 core top samples and 0.22 (±0.14) mmol/mol for 8 LGM samples, compared to the "Mg cleaning method" (Figure 6), similar to the pattern seen by Barker et al. [2003]. The overall geographic pattern is not changed, however, suggesting that material removed by the "Cd cleaning method" does not account for the anomalous Mg/Ca ratios. As reported by Barker et al. [2003], a deviation of  $\sim$ 15% between the two cleaning methods seems to be a consistent difference, making unlikely that we would observe a more temperature dependent Mg/Ca fraction, if the "Cd cleaning method" was used for all our samples.

### 3.5. Size-Dependent Mg/Ca Ratios?

[27] A size dependency of Mg/Ca ratios is indicated, at least for the core tops (Figure 7). The  $250-300~\mu m$  size fraction generally contains higher Mg/Ca ratios than the  $150-212~\mu m$  size

Figure 3. (a) Core top Mg/Ca ratios of the planktonic foraminifer species N. pachyderma sinistral in the size fraction 150-212 μm, based on interpolation and gridding of Mg/Ca ratios from 39 samples performed in this study. The samples are marked as white circles. For a more detailed description about Mg/Ca ratios for each core location, see Table 1. (b) Covariance plot between oxygen isotope calcification temperatures and Mg/Ca ratios (mmol/mol), measured on N. pachyderma (sin.). The blue squares mark the Mg/Ca ratios performed in the size fraction 125-250 µm by Nürnberg [1995], using electronmicroprobe analysis. The red circles mark the Mg/Ca ratios performed in the size fraction 150-212 μm in this work, cleaned using the "Mg cleaning method" [Barker et al., 2003] (see also Figure 3a and Table 1). The green crosses mark the Mg/Ca ratios performed in the size fraction 250-300 μm in this work, cleaned using the "Mg cleaning method" [Barker et al., 2003]. The black crosses mark Mg/Ca ratios performed in the size fraction 150–212 μm, cleaned using the "Cd cleaning method" [Boyle and Keigwin, 1985]. For the data from Nürnberg [1995] the temperatures reflect summer at 100 m depth, according to Levitus and Boyer [1994], and not the oxygen isotope calcification temperatures, since  $\delta^{18}O_{Nps}$  data are available only for a few of the cores. (c) Same as Figure 3b, but here the x scale reflects summer temperatures at 100 m depth, according to Levitus and Boyer [1994]. (d) Difference between Mg/Ca calcification temperatures, derived from the Mg/Ca ratios shown in Figure 3a and Table 1, and  $\delta^{18}$ O derived temperatures (Figure 2c). It is assumed that equation (3) in text can be used for this purpose. (e) Sedimentation rates of the LGM (21.5-18 ka) in the Nordic Seas and the northern North Atlantic, based on interpolation and gridding of data from Vogelsang et al. [2000], marked as white circles. In the text, when referring to this figure, it is assumed that the distribution of differing sedimentation rates in the Late Holocene (representative for the core tops) are not much changed compared to the LGM. The gridding and coloring are based only on interpolation of the white circles. The expected higher sedimentation rates along the continental margins are not considered in this figure.



**Figure 4.** (a) Mg/Ca distribution for the Last Glacial Maximum (LGM), based on interpolation and gridding of averaged Mg/Ca ratios (mmol/mol) in Table 2 of *N. pachyderma* (sin.). From *Meland et al.* [2005]. (b) Calcification temperatures of *N. pachyderma* (sin.) calculated using the Mg/Ca ratios in Figure 4a, and assuming that the temperature equation of *Elderfield and Ganssen* [2000] may be used (equation (3) in text).

fraction (Figure 2c). This is in agreement with investigations of *Elderfield et al.* [2002], who suggest that larger shells calcify close to equilibrium with seawater. However, the Mg/Ca ratios in the  $250-300~\mu m$  fraction do not indicate a temperature gradient in the Nordic Seas, from southeast to northwest. Thus the anomalous values are not a size fraction issue.

#### 4. Discussion

# 4.1. Are the Calculated Calcification Temperatures Based on Oxygen Isotopes Representative?

[28] It is important to constrain the oxygen isotope temperatures used for Mg/Ca calibration. There are, however, complications that may limit the use of this approach. If there is a significant vital effect, and if it varies from place to place, it may affect estimated temperatures.

[29] If a vital effect of, e.g., 0.6‰ should be applied [Simstich et al., 2003; Nyland et al., 2006], the assumption would require that N. pachyderma (sin.) calcified at depths of deeper than 500 m in many of the core locations. This seems unlikely as the abundance of living species is very poor at these depths [Kohfeld, 1996; Simstich,

1999]. It should, however, not be excluded that the vital effect may vary between the different water masses. For instance, while the vital effect may be zero in Arctic and Polar water masses, it may be significant in the Atlantic water masses. Nyland et al. [2006] suggest a vital effect of 0.6% at the Voering Plateau (core JM97-948, also studied in this work). This effect will decrease the calcification temperature with almost 3°C here, possibly explaining the measured Mg/Ca ratio here, implying lower temperatures than expected from  $\delta^{18}$ O calcification temperature (Figure 3d). Alternatively, it may be that the pre-exponential constant in the Mg/Ca-T-equation should be lower, at least for Atlantic water masses. Using a preexponential constant of 0.38, in agreement with Anand et al. [2003], gives a Mg/Ca temperature quite similar to the  $\delta^{18}$ O temperature for the core JM97-948.

[30] Another explanation might be that the calcification temperature of *N. pachyderma* (sin.) is approximately the same over whole of the Nordic Seas, explaining the homogenous Mg/Ca ratios. By increasing the pre-exponential constant in equation (3) to about 0.80, the Mg/Ca temperatures in the "too warm" cores in Table 2 may be reliable. However, if this is the case, a calcification depth level of 500 m or deeper in the southeastern part of



**Table 2.** LGM Core Data Used for Studies of Mg/Ca Ratios in the Tests of *Neogloboquadrina pachyderma* (sinistral)<sup>a</sup>

| Core      | Long.  | Lat.  | Water<br>Depth, m | LGM<br>Level 19–21.5 ka<br>Depth, cm | Number of<br>Averaged<br>Trace Element<br>Measurements | Average<br>Mg/Ca,<br>mmol/mol | Calc. T, <sup>b</sup> °C | Reference LGM Level        |
|-----------|--------|-------|-------------------|--------------------------------------|--|-------------------------------|--------------------------|----------------------------|
| BOFS5K    | -21.87 | 50.68 | 3547              | 78-94 <sup>c</sup>                   | 4  | 0.87                          | 5.5                      | Maslin [1992]              |
| BOFS7K    | -22.54 | 51.75 | 2429              | 38 - 40                              | 2  | 0.91                          | 6.0                      | Manighetti et al. [1995]   |
| BOFS8K    | -22.04 | 52.50 | 4045              | 85 - 110                             | 2  | 0.81                          | 4.8                      | Maslin [1992]              |
| BOFS10K   | -20.65 | 54.67 | 2761              | 108 - 114                            | 4  | 0.93                          | 6.2                      | Manighetti et al. [1995]   |
| BOFS14K   | -19.44 | 58.62 | 1756              | 38 - 44                              | 3  | 0.92                          | 6.1                      | Maslin [1992]              |
| BOFS17K   | -16.50 | 58.00 | 1150              | 74-95                                | 4  | 1.16                          | 8.4                      | Maslin [1992]              |
| ENAM94-09 | -9.43  | 60.34 | 1286              | 543-583                              | 3  | 0.89                          | 5.8                      | Lassen et al. [2002]       |
| HM100-7   | -4.72  | 61.67 | 1125              | 71 - 100                             | 4  | 0.83                          | 5.1                      | Sarnthein et al. [1995]    |
| HM52-43   | 0.73   | 64.25 | 2781              | $85-90^{c}$                          | 2  | 0.81                          | 4.8                      | Veum et al. [1992]         |
| HM71-12   | -13.87 | 68.43 | 1547              | 44 - 48                              | 3  | 0.96                          | 6.5                      | Sarnthein et al. [1995]    |
| HM71-15   | -17.43 | 70.00 | 1547              | $38-41^{c}$                          | 4  | 0.71                          | 3.5                      | Roe [1998]                 |
| HM71-19   | -9.51  | 69.48 | 2210              | 42                                   | 1  | 1.22                          | 8.9                      | Vogelsang [1990]           |
| HM79-26   | -5.93  | 66.90 | 3261              | 60                                   | 1  | 1.05                          | 7.4                      | Sarnthein et al. [1995]    |
| HM80-30   | 1.60   | 71.78 | 2821              | 38 - 44                              | 4  | 0.88                          | 5.7                      | Sarnthein et al. [1995]    |
| HM80-42   | -9.23  | 72.25 | 2416              | 57 - 64                              | 4  | 0.90                          | 5.9                      | Sarnthein et al. [1995]    |
| HM80-60   | -11.86 | 68.90 | 1869              | 70 - 76                              | 3  | 1.11                          | 8.0                      | Sarnthein et al. [1995]    |
| HM94-13   | -1.62  | 71.63 | 1946              | 46 - 52                              | 4  | 0.98                          | 6.7                      | Sarnthein et al. [1995]    |
| HM94-18   | 5.70   | 74.50 | 2469              | 28 - 35                              | 2  | 0.96                          | 6.5                      | Sarnthein et al. [1995]    |
| HM94-25   | 1.32   | 75.60 | 2469              | $38-47^{c}$                          | 4  | 0.95                          | 6.4                      | Sarnthein et al. [1995]    |
| HM94-34   | -2.54  | 73.77 | 3004              | 50                                   | 1  | 0.79                          | 4.6                      | Sarnthein et al. [1995]    |
| M23357    | -5.53  | 70.96 | 1969              | 57                                   | 1  | 1.29                          | 9.5                      | Goldschmidt [1994]         |
| MD95-2010 | 4.56   | 66.68 | 1226              | $261 - 373^{c}$                      | 6  | 0.73                          | 3.8                      | Dokken and Jansen [1999]   |
| MD95-2011 | 7.64   | 66.97 | 1048              | 1066-1361 <sup>c</sup>               | 5  | 0.80                          | 4.7                      | Dreger [1999]              |
| MD99-2284 | -0.98  | 62.37 | 1500              | 870 - 1050                           | 5  | 0.74                          | 3.9                      | Jansen and Meland [2001]   |
| MD99-2289 | 4.21   | 64.66 | 1395              | 610 - 690                            | 4  | 0.72                          | 3.6                      | Berstad (unpublished data) |
| MD99-2304 | 9.95   | 77.62 | 853               | $420-512^{c}$                        | 5  | 0.74                          | 3.9                      | Fevang [2001]              |
| NEAP8K    | -23.54 | 59.47 | 2419              | 179 - 192                            | 4  | 0.94                          | 6.3                      | Vogelsang et al. [2000]    |
| PS21842   | -16.52 | 69.45 | 982               | $31-39^{c}$                          | 5  | 0.85                          | 5.3                      | Sarnthein et al. [1995]    |
| SO82-4    | -30.48 | 59.10 | 1503              | $181 - 188^{c}$                      | 1  | 0.89                          | 5.8                      | Moros et al. [1997]        |
| SU90-32   | -22.42 | 61.78 | 2200              | 140 - 170                            | 1  | 0.80                          | 4.7                      | Sarnthein et al. [1995]    |
| V23-81    | -16.14 | 54.03 | 2393              | 260-304°                             | 3  | 0.95                          | 6.4                      | Jansen and Veum [1990]     |

<sup>&</sup>lt;sup>a</sup>The Mg/Ca ratios are analyzed in this study. Modified from *Meland et al.* [2005].

<sup>c</sup> The depths of these LGM levels are determined with use of AMS <sup>14</sup>C.

the Norwegian Sea is required, which we find unlikely. Therefore different calcification depths might only be an explanation for a minor portion of the low geographical Mg/Ca gradients in the Nordic Seas.

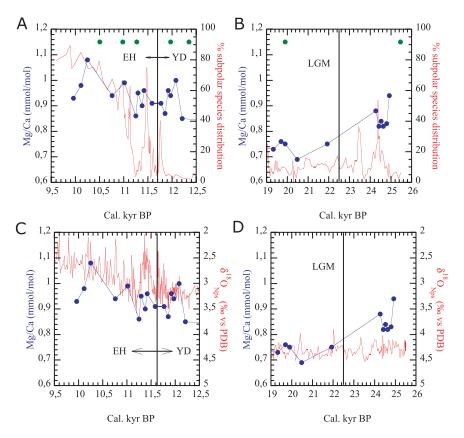
[31] von Langen et al. [2005] show in a culture experiment based on N. pachyderma (dex.) that culture temperature and Mg/Ca ratios are well correlated. When a similar experiment is tested on N. pachyderma (dex.) from shallow plankton tows (0–50 m, Santa Barbara Channel), the authors find a weakened correlation between Mg/Ca and Sea Surface Temperature (SST). They suggest that points below the correlation line likely result from subsurface correlation at different depths. It should not be excluded that this factor also affects

N. pachyderma (sin.). Culturing experiments of N. pachyderma (sin.) could constrain this further.

### 4.2. Possible Sediment Contamination: Influence of Volcanic Ash?

[32] High Mg/Ca ratios in foraminiferal samples may originate from clay or organic material, since these materials may contain significant amounts of magnesium. If the content of magnesium in clay and other contaminants is larger than of iron, this may significantly influence the foraminiferal Mg/Ca ratios, even when the Fe/Ca ratios are below a typical contamination limit of 0.1 mmol/mol [Barker et al., 2003]. As a consequence the anomalously high Mg/Ca ratios in the central and western parts of the Nordic Seas could be due to low Fe/Mg ratios of the bulk sediment. The fact

<sup>&</sup>lt;sup>b</sup>Mg/Ca temperatures, if the equation from *Elderfield and Ganssen* [2000], based on *N. pachyderma* (sin.), is used.



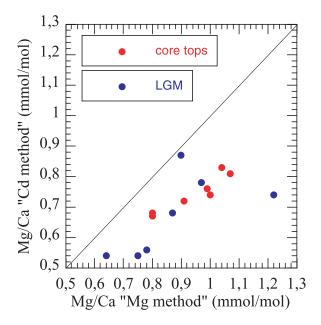
**Figure 5.** Down core Mg/Ca ratios from MD99-2284 located in the Faeroe-Shetland area, compared with subpolar species distribution and oxygen isotopes of *N. pachyderma* (sin.). The blue curve marks Mg/Ca ratios and the red curve marks subpolar foraminiferal species distribution (Figures 5a and 5b) and oxygen isotopes of *N. pachyderma* (sin.) (Figures 5c and 5d). The green dots in Figures 5a and 5b point to chronostratigraphically determined ash layers and AMS <sup>14</sup>C ages. (a) Mg/Ca ratios compared with subpolar foraminiferal species distribution for the Deglaciation on the transition Younger Dryas-Early Holocene. (b) Mg/Ca ratios compared with subpolar foraminiferal species distribution, including the LGM and a time interval close to the Dansgaard-Oeschger Interstadial 2 (IS-2). (c) Mg/Ca ratios compared with oxygen isotopes of *N. pachyderma* (sin.) for the Deglaciation on the transition Younger Dryas-Early Holocene. (d) Mg/Ca ratios compared with oxygen isotopes of *N. pachyderma* (sin.), including the LGM and a time interval close to the Dansgaard-Oeschger Interstadial 2 (IS-2).

that the enhanced foraminiferal Mg/Ca ratios are located near the mid-ocean ridge, with sediment composition influenced of volcanic ash and low terrestrial input, encouraged us also to see if this area contained low sediment Fe/Mg ratios. To test this hypothesis, we examined the Fe/Mg ratios in the bulk sediment. If Fe/Mg is lower than 1 mol/ mol, a fraction of the foraminiferal Mg/Ca ratio may be caused by contamination, even if the Fe/ Ca ratios are low. We used data of Paetsch [1991], who made trace element analyses of surface bulk sediments for 54 core tops in the Nordic Seas, based on X-ray fluorescence. Fe/Mg > 1 mol/mol for approximately whole of the area. The highest sediment Fe/Mg ratios are observed in the central Iceland and Greenland Seas, where also the highest Mg/Ca ratios of N. pachyderma (sin.) are found. In other words, if the data set of

Paetsch [1991] is representative for the contamination phase in our analyzed foraminifera, the anomalously high Mg/Ca ratios in the central and western Nordic Seas cannot be explained by clay contamination. Consequently, it seems like that a location near the mid-ocean ridge cannot explain the elevated Mg/Ca ratios of N. pachyderma (sin.). In addition, when Fe/Ca < 0.1 mmol/mol we do not observe any correlation between Mg/Ca and Fe/Ca ratios in the samples. Sediment contamination is certainly not an important factor explaining elevated planktonic Mg/Ca ratios in the central and western Nordic Seas.

### 4.3. Mg/Ca of the Seawater

[33] Both magnesium and calcium are major constituents of seawater. The Mg/Ca ratio is constant, and thus termed "conservative" [Broecker and



**Figure 6.** Comparison of Mg/Ca ratios obtained by use of "Mg cleaning" [*Elderfield and Ganssen*, 2000] versus "Cd cleaning" [*Boyle and Keigwin*, 1985]. The primary difference between the two procedures is the use of a reductive step in the case of Cd cleaning. Core tops samples are shown in red. LGM samples are shown in blue.

Peng, 1982]. However, since the Nordic Seas is an area with large horizontal and vertical salinity gradients in the upper 200 m ( $\sim$ 33-35 psu), we considered the hypothesis that central and western parts of the Nordic Seas may have higher Mg/Ca ratios in the surface water, explaining the anomalously high foraminiferal core top Mg/Ca ratios. 19 measurements in a transect between 68-75°N, 9°W-6°E, covering the upper 100 meters of both Atlantic and Arctic water masses, shows that the Mg/Ca ratios are homogenous, with a deviation of ±0.78%, only slightly higher than the ICP-AES standard deviation of  $\pm 0.5\%$ . There was no evidence that the Arctic water masses have either higher or lower Mg/Ca ratios compared to Atlantic water masses. Thus we find it unlikely that Mg/Ca ratios of seawater may explain the anomalously high Mg/Ca ratios of the foraminifera in the central and western Nordic Seas.

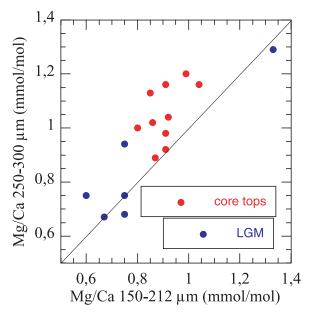
### 4.4. Dissolution and Shell Mass

[34] Previous investigations indicate that calcite dissolution after deposition lowers the Mg/Ca ratios of foraminiferal shells [Brown and Elderfield, 1996; Dekens et al., 2002; Hastings et al., 1998; Rosenthal et al., 1997; Russell et al., 1994]. Even foraminifera deposited well above the lysocline may be influenced by postdepositional dissolution [Brown and

Elderfield, 1996]. Since our highest Mg/Ca ratios for the core tops are found in the deepest water masses (Figure 3a), it first seems unlikely that dissolution may explain our results. Dissolution has also been found to be of minor importance for the modern and the LGM environment in the Nordic Seas [Henrich, 1992]. In the samples we have analyzed there is a tendency for the LGM Mg/Ca ratios to be weakly correlated with shell mass ( $R^2$  = 0.19). This suggests that foraminifera in the samples in the eastern Norwegian Sea may be weakly influenced by dissolution. The possibility that samples close to the eastern continental margin might be influenced by dissolution is supported by Huber et al. [2000]. However, the samples in the western parts of the Nordic Seas should also then be influenced by some dissolution. Since the core top Mg/ Ca ratios are high here, we find it difficult to introduce dissolution as a main mechanism explaining low Mg/Ca ratios in the east. Dissolution is certainly not the dominant influence on variations in foraminiferal Mg/Ca.

### 4.5. Diagenesis and Pore Water Chemistry Associated With Changing Sedimentation Rates

[35] We cannot exclude the possibility that geochemical and post-depositional processes influence the results. There is an overall trend that the



**Figure 7.** Comparison of Mg/Ca ratios of *N. pachy-derma* (sin.) measured in two different sieve size fractions: the  $150-212~\mu m$  and the  $250-300~\mu m$  fractions. The circles in red point to core top samples, while the circles marked in blue point to LGM samples.



differences between  $\delta^{18}O$  and Mg/Ca derived temperatures (Figure 3d) are more or less correlated with sedimentation rates in the Nordic Seas (Figure 3e). Since the sedimentation rates generally are much lower in central and western parts compared to eastern parts of the Nordic Seas, differences in pore water chemistry associated with sedimentation rates and sediment carbonate contents may be secondary factors influencing the foraminiferal Mg/Ca ratios. More investigations have to be done to evaluate this hypothesis.

### 4.6. Core Top Ages, LGM Ages, and Bioturbation

[36] In section 2.2 it was mentioned that the core top samples of Simstich et al. [2003], also located in the Nordic Seas, reflect ages as old as 4000 years. Our core tops in the central and western Nordic Seas may contain foraminifera 4000 years old, or even older, due to low sedimentation rates (<~5 cm/kyr) [Sarnthein et al., 1995; Vogelsang et al., 2000] and potentially high bioturbation. The conditions for upmixing of old sediments might be favorable. In these samples, only a small fraction of the foraminifera were living (rose bengal stained) during the core sampling, indicating that the core tops contain a mix of foraminifera not representing the modern ocean. The Mg/Ca ratios may therefore be influenced by climates several thousand years ago. On the basis of diatoms, several authors found that SSTs in the northern North Atlantic and the Nordic Seas were about 3-5°C higher than today 6000-9000 years ago [Andersen et al., 2004; Birks and Koc, 2002; Koc and Jansen, 1994]. In the central and western Nordic Seas the core tops may therefore contain foraminifera, living during this Mid Holocene Optimum, partly explaining the anomalously high Mg/Ca ratios here. Also for the LGM the highest Mg/Ca ratios in the Nordic Seas are found in low sedimentation areas. A downmixing of "warm" Holocene foraminifera could therefore be a potential contributor to the high Mg/ Ca ratios.

[37] In our view a potential occurrence of "warm" foraminifera is not the main reason explaining the high Mg/Ca ratios in the core tops, for several reasons: First, the oxygen isotopes for the core tops (Figure 2a) and the calcification temperatures (Figure 2c) do not corroborate this pattern. They show the expected decrease in temperature toward the west. Second, the oxygen isotopes for the LGM samples have high and stable values, typical for the LGM [Sarnthein et al., 1995; Meland et al., 2005].

They constrain this time slice well, and document cold temperatures combined with a large global ice-volume. Mixing with Holocene sediments thus seems unlikely.

### 4.7. Seawater Carbonate Chemistry

- [38] On the basis of the Mg/Ca ratios here, it seems that the Mg/Ca proxy in planktonic foraminifers is not applicable as an independent temperature proxy in the cold central and western parts of the Nordic Seas. There is no significant relationship between either Mg/Ca and water depth, or Mg/Ca and salinity.
- [39] One possible hypothesis for this pattern may be that the Mg/Ca ratios in the central and western Nordic Seas may reflect a combination of temperature, salinity and/or seawater chemistry (e.g., pH, carbonate ion concentration, alkalinity). *Nürnberg et al.* [1996] found that foraminiferal Mg/Ca increased by 7% per salinity unit increase, while the corresponding number for *Lea et al.* [1999] was 4%, based on laboratory culture experiments. Using these values, we corrected observed Mg/Ca ratios for salinity but the correlation with temperature was not improved.
- [40] Russell et al. [2004] investigated the sensitivity of Mg/Ca to changes in seawater carbonate ion concentration [CO<sub>3</sub><sup>2-</sup>] and temperature in calcite produced by two planktonic foraminifera species, Orbulina universa and Globigerina bulloides, in laboratory culture experiments. They found that Mg/Ca increased with 0.033 mmol/mol per  $[CO_3^{2-}]$ unit decrease (µmol/kg) for G. bulloides, while the corresponding number for O. universa was 0.019 mmol/mol, as long as  $[CO_3^{2-}] < 200 \mu mol/kg$ . Both species were cultured under constant temperature (22°C). On the basis of measured carbonate ion concentrations in Nordic seas water masses it is clear that for all our samples, with a possible exception of some LGM samples,  $[CO_3^{2-}]$  is below 200 µmol/kg for the calcification conditions of N. pachyderma (sin.).
- [41] Also *Lea et al.* [1999] investigated Mg/Ca ratios of *G. bulloides* and *O. universa* during constant temperature (22°C) and salinity (33 psu), and found that the Mg/Ca ratios increased with lowered pH, and vice versa.
- [42] The hypothesis that foraminiferal Mg/Ca ratios are influenced by  $[CO_3^{2-}]$  [Russell et al., 2004] encouraged us to test if the Mg/Ca ratios in the North Atlantic are influenced by  $[CO_3^{2-}]$ . Since the  $[CO_3^{2-}]$  values in Arctic and Polar water masses are



lower than for Atlantic water masses, this may explain the anomalously high Mg/Ca ratios of the core tops. However, this is very difficult to test because  $[\mathrm{CO}_3^{2-}]$  covaries with temperature, and  $[\mathrm{CO}_3^{2-}]$  values may vary significantly between the surface and water depths of 200 m. Additionally,  $[\mathrm{CO}_3^{2-}]$  values have changed considerably between pre-industrial and industrial time.

### 4.8. Low-Salinity Influences

[43] The close relationship between low salinity and low  $[CO_3^{2-}]$  is a potential cause for the high foraminiferal Mg/Ca ratios in water masses, such as the Arctic and Polar water, where salinities are lower than in the warmer Atlantic water. For example, if low-salinity water masses (e.g., below 35 psu) for some reason tend to raise foraminiferal Mg/Ca ratios, they may explain the anomalously high Mg/Ca ratios of many of the core tops in the Arctic and Polar water masses (Figures 3a), during the LGM (Figures 4a and 4b) in the Greenland and Iceland Seas, and during the YD at the Faeroe-Shetland plateau (Figures 5a and 5c). Assuming that the subpolar species distribution of the core MD99-2284, as shown in Figures 5a and 5b, is a reliable SST proxy, and the oxygen isotopes in the same core reflect a combination of surface/subsurface temperatures and oxygen isotopes/salinities of the water mass, the Mg/Ca ratios of the Early Holocene and the LGM may reconstruct the temperature fairly well, since the salinities are regarded to be high here, based on a combination of the oxygen isotopes and the subpolar species distribution. If the low oxygen isotopes during the YD reflect low salinity rather than high temperature, we suggest that the anomalously high Mg/Ca ratios are linked with secondary factors related to the presence of fresher water masses.

[44] However, the modern salinity gradient between Atlantic and Arctic water masses is only 0.2 to 0.3 PSU, while this water mass boundary is where the most conspicuous deviation between surface water temperature gradients and lack of corresponding Mg/Ca gradient is observed. More investigations need to be done to evaluate any potential low-salinity effect on the Mg/Ca ratios.

### 5. Conclusions

[45] 1. Planktonic foraminiferal Mg/Ca ratios show very little response to temperature in the Nordic Seas in the cold-water areas. The lack of temper-

ature response in the measured samples is not due to contamination, nor to cleaning methods.

- [46] 2. One potential hypothesis for this observation is that foraminiferal Mg/Ca ratios in the Nordic Seas may be significantly influenced by seawater carbonate chemistry (e.g., [CO<sub>3</sub><sup>2-</sup>], alkalinity and/or pH), mainly in water masses with Arctic and Polar characteristics, including lower salinity and partly sea ice cover. This hypothesis may explain parts of the high Mg/Ca ratios in the core tops and the LGM. It may also explain parts of the high Mg/Ca ratios during the Younger Dryas from core MD99-2284 at the Faeroe-Shetland plateau. At the moment this hypothesis cannot be confirmed or disproved.
- [47] 3. Vital effects affecting the oxygen isotopes of *N. pachyderma* (sin.) should be more constrained to give a more precise basis for calculation of oxygen isotope calcification temperatures for correlation of Mg/Ca temperatures. Oxygen isotopes show a consistent temperature trend in the region.
- [48] 4. Different sediment composition in central and western Nordic Seas, for instance caused by location near the volcanic active mid-ocean ridge, is probably not a major factor explaining the elevated Mg/Ca ratios of *N. pachyderma* (sin.) here.
- [49] 5. Calcite dissolution is not considered as a main reason explaining the Mg/Ca ratios observed, but should not be entirely excluded, since both our work and previous work [*Huber et al.*, 2000] indicate weak dissolution near the eastern continental margin of the Nordic Seas today, potentially explaining parts of the low Mg/Ca ratios seen here.
- [50] 6. It cannot be excluded that both core top and LGM samples located in low-sedimentary areas may contain significant amounts of foraminifera 6000-9000 years ago, living during conditions with SSTs 3–5°C higher than today, explaining the anomalously high Mg/Ca ratios in the western and central Nordic Seas. The oxygen isotopes of *N. pachyderma* (sin.), however, do not corroborate this hypothesis.
- [51] 7. A correlation between sedimentation rates (Figure 3e) and differences between oxygen isotope and Mg/Ca derived temperatures (Figure 3d) is observed. The correlation indicates that pore water chemistry and diagenesis related to different sedimentation rates, different amounts of carbonate content and/or different degree of terrestrial input



in the sediment may indirectly explain parts of the foraminiferal Mg/Ca-pattern observed.

[52] 8. At the moment no obvious factor can explain the anomalously high Mg/Ca ratios in the Nordic Seas, for the core top, the LGM and the YD samples (MD99-2284). A combination of the suggestions mentioned above may be the best alternative to explain anomalously high Mg/Ca ratios.

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