Click Here for Full Article

Reassessing Mg/Ca temperature calibrations of *Neogloboquadrina pachyderma* (sinistral) using paired $\delta^{44/40}$Ca and Mg/Ca measurements

Reinhard Kozdon
Leibniz-Institut für Meereswissenschaften an der Universität Kiel (IFM-GEOMAR), D-24148 Kiel, Germany

Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel, D-24118 Kiel, Germany

Now at Department of Geology and Geophysics, University of Wisconsin−Madison, Madison, Wisconsin 53706, USA (rkozdon@geology.wisc.edu)

Anton Eisenhauer
Leibniz-Institut für Meereswissenschaften an der Universität Kiel (IFM-GEOMAR), D-24148 Kiel, Germany

Mara Weinelt
Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel, D-24118 Kiel, Germany

Marius Y. Meland
Bjerknes Centre for Climate Research, N-5007 Bergen, Norway

Dirk Nürnberg
Leibniz-Institut für Meereswissenschaften an der Universität Kiel (IFM-GEOMAR), D-24148 Kiel, Germany

[1] The Mg/Ca temperature calibration of the polar to subpolar planktonic foraminifera *Neogloboquadrina pachyderma* (sinistral) (sinistral indicates left coiling) was refined by a multiproxy approach combining hydrographic temperature and salinity data with Mg/Ca, $\delta^{44/40}$Ca, and δ^{18}O values from Holocene Nordic seas core top samples. Reliable Mg/Ca-based temperature estimates are limited to foraminiferal tests that calcified in water masses with temperatures above ∼3°C at habitat depth. In these samples, Mg/Ca and $\delta^{44/40}$Ca values are positively correlated (Mg/Ca (mmol/mol) = 0.77 (±0.22) × $\delta^{44/40}$Ca (‰ SRM 915a) + 0.52 (±0.12); n = 20, R^2 = 0.76). Both Mg/Ca- and $\delta^{44/40}$Ca-derived temperatures projected onto their corresponding depth intervals reveal that the "apparent" calcification depth of *N. pachyderma* (sinistral) averaging the specimens' whole life cycle is bound to an isopycnal layer defined by water densities (σ_t) between 27.7 and 27.8. This implies that *N. pachyderma* (sinistral) prefers gradually deeper habitats with increasing sea surface temperatures, thus counterbalancing absolute temperature variations. Consequently, the total temperature range recorded in this foraminiferal species is restricted and only partly reflects environmental changes. On the basis of the new Mg/Ca, $\delta^{44/40}$Ca, and δ^{18}O multiproxy data set, we propose a linear Mg/Ca temperature relation for high-latitude *N. pachyderma* (sinistral): Mg/Ca (mmol/mol) = 0.13 (±0.037) T (°C) + 0.35 (±0.17); T > 3°C. In core top samples from polar waters with peak summer temperatures below ∼3°C, the temperature response in the Mg/Ca and $\delta^{44/40}$Ca proxy signal is

inversed and poorly correlated. Both Mg/Ca- and $\delta^{44/40}$Ca-derived temperature estimates pretend significantly higher calcification temperatures than maximum summer sea surface temperatures of these water masses.

1. Introduction

[2] Although foraminiferal Mg/Ca has proven to be an useful proxy for the reconstruction of past sea surface temperatures (SSTs) in subtropical to tropical regions, its application at high latitudes is limited, mainly because of the low sensitivity of the Mg incorporation into foraminiferal calcite at low temperatures. To date, several multi and single species Mg/Ca temperature calibrations as well as multiproxy comparisons are published from transitional to tropical foraminiferal provinces, but data from higher latitudes remain sparse. In fact, the commonly applied Mg/Ca temperature calibrations for polar to subpolar planktonic foraminiferal species [*Mashiotta et al.*, 1999; *Elderfield and Ganssen*, 2000] were reusing the Mg/Ca data set of *Nürnberg* [1995] that was derived by electron microprobe analysis of North and South Atlantic core top specimens of *N. pachyderma* (sinistral). However, aside from a small number of recent studies using laser ablation MC-ICP-MS, electron microprobe instruments or other high-resolution techniques [e.g., *Eggins et al.*, 2003; *McKenna and Prell*, 2004; *Sadekov et al.*, 2005], most Mg/Ca data for palaeoceanographic applications were routinely determined by the solution-based ICP-OES technique. Unfortunately, only few systematic cross calibrations between these different analytical approaches were reported [*Nürnberg et al.*, 2000]. Hence, Mg/Ca ratios derived by ICP-OES were routinely converted to absolute temperature estimates by calibrations that are, on their low temperature end, based on data from a different analytical approach.

[3] An additional inherent weakness of high-latitude core top calibrations is the large uncertainty regarding the "reference" calcification temperatures selected for each sample location. In this respect, the *N. pachyderma* (sinistral) calibration of *Nürnberg* [1995] is based on reference temperatures compiled from hydrographic databases [*Dietrich*, 1969; *Koltermann and Lüthje*, 1989; *Thiede and Hempel*, 1991; *Pfannkuche et al.*, 1993], assuming a planktonic summer bloom and a constant average calcification depth. However, later studies revealed that the correlation between modern Mg/Ca inferred temperatures and their corresponding hydrographic data is poor [*Meland et al.*, 2006; *Nyland et al.*, 2006]. Furthermore, various authors [e.g., *Kohfeld et al.*, 1996; *Stangeew*, 2001; *Simstich et al.*, 2003] found that the water depth of chamber formation and encrustation of *N. pachyderma* (sinistral) is related to the stratification of the water column and therefore highly variable. The cumulative isotope signal of foraminiferal tests averages the whole depth range they inhabited, indicating "apparent" calcification depths of up to 250 m off Norway, but only about 50 m in the Arctic domain [*Simstich et al.*, 2003]. Hence, temperature calibrations based on empirical data from constant habitat depths may be reconsidered. In order to avoid these uncertainties regarding the specimens' calcification habitat, seasonality and life cycle, *Elderfield and Ganssen* [2000] cross-calibrated foraminiferal Mg/Ca ratios with calcification temperatures inferred from the oxygen isotopic differences between foraminiferal calcite and seawater. Apparently, still in the temperature range of 0°C to 7°C, the data set of *Nürnberg* [1995] was reused without any correction for δ^{18}O-inferred calcification temperatures. This is mainly because Mg/Ca calibrations in this temperature range could not be further improved by cross calibrations to oxygen isotopes, as the
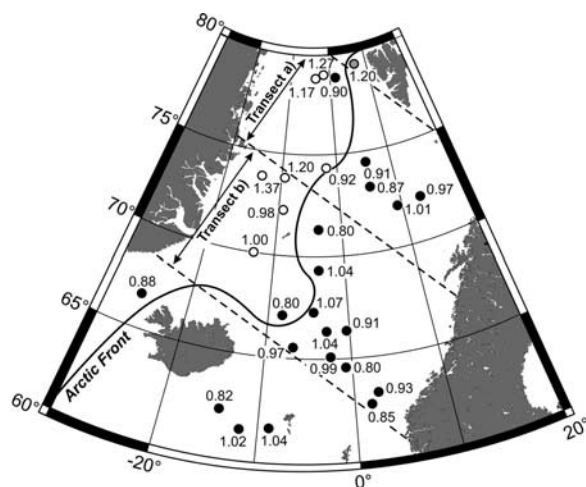
Figure 1. Station chart of Late Holocene sediment surface samples of *N. pachyderma* (sinistral) and their corresponding Mg/Ca ratios (mmol/mol). The dashed lines mark transects a and b discussed in the text and in Figure 5. Stations with a positive correlation of their Mg/Ca:$\delta^{44/40}$Ca proxy pair and consistent calcification temperature estimates are marked black, and core locations with an obscured proxy to temperature relationship are shown in white. The Mg/Ca:$\delta^{44/40}$Ca proxy pair of core 23233-1 west of Svalbard (see Table 1) shows this aberrant proxy behavior in warmer waters and is marked in gray.

δ^{18}O-temperature relationship is most likely superimposed by meltwater discharges and salinity variations.

[4] With respect to recent proxy developments and modern analytical possibilities, the objective of this study was to reassess the Mg/Ca temperature response in core top samples of *N. pachyderma* (sinistral) from high northern latitudes, using solution-based ICP-OES technology. In order to constrain the calcification habitat of *N. pachyderma* (sinistral), independent calcification temperatures were calculated from paired $\delta^{44/40}$Ca measurements which are found to have a temperature sensitivity of 0.17‰ C^{-1} in core top samples of this foraminiferal species [*Hippler et al.*, 2009]. Furthermore, these data were compared to δ^{18}O-inferred calcification temperatures and modern summer temperatures provided by *Conkright et al.* [2002].

2. Material and Methods

2.1. The $\delta^{44/40}$Ca and Mg/Ca Measurements

[5] Both $\delta^{44/40}$Ca and Mg/Ca measurements were performed on the polar to subpolar planktonic

foraminifer *N. pachyderma* (sinistral) from core top samples which were previously used by *Meland et al.* [2006] for paired Mg/Ca:δ^{18}O measurements and by *Hohnemann* [1996], *Horwege* [1987], and *Simstich et al.* [2003] for the determination of δ^{18}O values (Figure 1). AMS ^{14}C ages of 35 adjacent core top samples were given by *Simstich et al.* [2003]. Except for three samples, all core top sediments are significantly younger than ~3000 years and therefore represent modern oceanographic conditions. For each paired Mg/Ca:$\delta^{44/40}$Ca measurement, approximately 60 to 80 foraminiferal tests in the size fraction 125 to 250 μm were hand picked, gently crushed between glass plates, and subsequently cleaned using an oxidative cleaning procedure slightly modified after *Barker et al.* [2003]. After cleaning, the test fragments were dissolved in ultrapure 2.5 N HCl. About 80% of the sample solution was separated for the determination of Mg/Ca ratios, the rest was used for $\delta^{44/40}$Ca analysis.

[6] For Mg/Ca measurements, the sample solution was dried down, dissolved in ultrapure 0.075 M nitric acid and diluted to Ca concentrations of about 30 to 70 ppm. Analyses were performed on a simultaneous radially viewing ICP-OES (Ciros CCD SOP, Spectro A.I., Germany) following standard procedures [*Nürnberg et al.*, 2000]. During the course of the measurements, the total drift was less than 0.2% as determined by analyzing an internal consistency standard after every five samples. Replicate analyses of foraminiferal tests from the same core top sample, which were cleaned and analyzed during different sessions, showed a standard deviation of 0.08 mmol/mol.

[7] Samples labeled "HM" were already prepared and analyzed for Mg/Ca at the Department of Earth Sciences, University of Cambridge, UK [*Meland et al.*, 2006]. These foraminiferal tests were purified following identical cleaning protocols [*Barker et al.*, 2003] and measured using an ICP-OES with a relative precision of <0.3% [*de Villiers et al.*, 2002]. For additional $\delta^{44/40}$Ca determinations, approximately 20 tests from each core top in the size fraction 150–212 μm were hand picked from the remaining sample material and measured at IFM-GEOMAR (Kiel, Germany). Mg/Ca ratios from adjacent core tops reflecting identical water masses measured in Cambridge and Kiel are within analytical error indistinguishable from each other. Moreover, the Mg/Ca to $\delta^{44/40}$Ca relationship is consistent between these groups, implying that

there are no systematic offsets due to measurements in different laboratories.

[8] For the determination of $\delta^{44/40}$Ca values, an isotopically well defined ^{43}Ca/^{48}Ca double-spike [*Heuser et al.*, 2002] was added to an aliquot of the sample solution to correct for isotope fractionation during the course of the Ca isotope analysis. The sample-spike mixture was dried down in order to guarantee a homogenous distribution and later recovered in 2 μl of ultrapure 2.5 N HCl. Following the method published by *Birck* [1986], the mixture was subsequently loaded with a Ta$_2$O$_5$ activator solution onto a previously outgassed, zone refined rhenium single filament using the ''sandwich technique'' (activator-sample-activator). After evaporating to dryness, the filament with the sample-spike mixture was briefly glowed. The total amount of Ca loaded on the filament (spike and sample) was about 300 ng. Ca isotope measurements were performed on a Thermo Scientific TRITON thermal ionization mass spectrometer at IFM-GEOMAR. The isotopic variations are expressed as $\delta^{44/40}$Ca values ($^{44/40}$Ca$_{sample}$/$^{44/40}$Ca$_{standard}$ − 1) × 1000 [*Eisenhauer et al.*, 2004] using NIST SRM 915a CaCO$_3$ reference powder as standard material. In order to monitor the long-term reproducibility, an additional CaF$_2$ standard previously used by *Nägler et al.* [2000] and further discussed by *Hippler et al.* [2003] was repeatedly measured.

2.2. Calculation of Mg/Ca, $\delta^{44/40}$Ca, and δ^{18}O Inferred Calcification Temperatures

[9] The preferred habitat depth of planktonic foraminifera as well as their main calcification period is species specific and varies between sample locations. Thus, available regional and monospecific temperature calibrations should be chosen in the first place. For this study, Mg/Ca temperature estimates were calculated using the Mg/Ca:temperature equation of *Mashiotta et al.* [1999] that is based on *N. pachyderma* (sinistral) from North Atlantic core tops:

$$\text{Mg/Ca(mmol/mol)} = 0.549 \exp 0.099 \, \text{T}(°\text{C}). \quad (1)$$

[10] $\delta^{44/40}$Ca inferred temperatures were calculated by the calibration of *Hippler et al.* [2009]:

$$\delta^{44/40} \text{Ca (‰ NIST SRM 915a)} = 0.17(\pm 0.02)\text{T}(°\text{C})$$
$$- 0.22(\pm 0.08). \quad (2)$$

[11] Oxygen isotope ratios were converted to calcification temperatures by the calcite tempera-

ture: δ^{18}O relation of *Shackleton* [1974], modified after *O'Neil et al.* [1969]:

$$\text{T}(°\text{C}) = 16.90 - 4.38\left(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}\right)$$
$$+ 0.10\left(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}\right)^2 \quad (3)$$

applying a δ^{18}O vital effect of 0.6‰ in core top samples of *N. pachyderma* (sinistral) and the salinity to δ^{18}O$_{\text{water}}$ relation of

$$\delta^{18}\text{O}_{\text{water}}(\text{VSMOW}) = -12.17 + 0.36 \times \text{S} \quad (4)$$

as proposed by *Simstich et al.* [2003] for the central and eastern Nordic seas. S refers to salinity, δ^{18}O$_{\text{calcite}}$ to the oxygen isotope value of foraminiferal calcite and δ^{18}O$_{\text{water}}$ to ambient seawater δ^{18}O values. Most palaeoceanographic studies based on *N. pachyderma* (sinistral) as proxy carrier still use the equation of *Shackleton* [1974] that was modified from *O'Neil et al.* [1969]. However, newer determinations of the $CO_2 - H_2O$ and the phosphoric acid − CO_2 fractionation factors lead to a slightly different calibration of the calcite − water fractionation factor [*Dibrov et al.*, 1997]. In order to maintain comparability with previous publications, we applied the equation of *Shackleton* [1974].

[12] A correction factor to convert δ^{18}O$_{\text{water}}$ values from the VSMOW to the PDB scale is necessary to compare measured δ^{18}O values of CO_2 produced by the reaction of calcite with phosphoric acid to δ^{18}O values of CO_2 equilibrated with water. The equation of *Shackleton* [1974] is tied to a correction factor of −0.2‰ as determined by *Craig and Gordon* [1965] that differs slightly from the most recent δ^{18}O water correction of −0.27‰ [*Hut*, 1987] (see discussion by *Bemis et al.* [1998]).

[13] In order to obtain proxy-independent hydrographic parameter, temperature and salinity data for the months of July to September, characterizing the main planktonic bloom in the Nordic seas [cf. *Kohfeld et al.*, 1996; *Jensen*, 1998; *Schröder-Ritzrau et al.*, 2001], were extracted with a vertical resolution of 25 m from the hydrographic database given by *Conkright et al.* [2002]. This database contains objectively analyzed ocean variables at 1° spatial resolution that are interpolated to 33 standard depth levels.

3. Results and Discussion

3.1. High-Latitude Mg/Ca-$\delta^{44/40}$Ca-δ^{18}O Relation

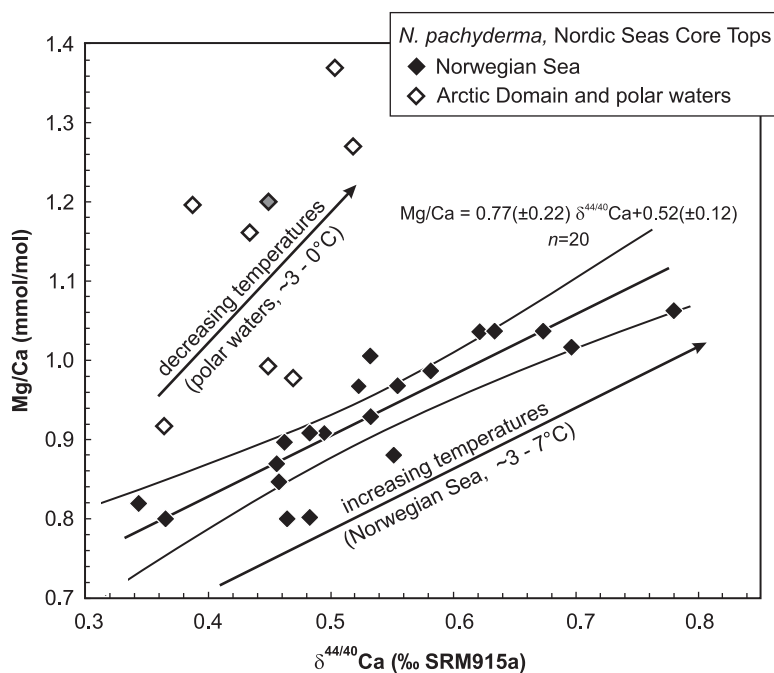[14] The measured $\delta^{44/40}$Ca values were plotted as a function of their corresponding Mg/Ca ratios

Figure 2. Mg/Ca ratios versus $\delta^{44/40}$Ca values from core top *N. pachyderma* (sinistral) originating from the Nordic seas. In Norwegian Sea samples, Mg/Ca and $\delta^{44/40}$Ca values are positively correlated, whereas in the cold (<3°C), low saline Arctic domain and polar waters, the temperature response in the Mg/Ca and $\delta^{44/40}$Ca proxy signal is inversed and poorly correlated. Both Mg/Ca- and $\delta^{44/40}$Ca-derived temperature estimates pretend significantly higher calcification temperatures than maximum sea surface temperatures of these water masses. Core 23233-1 west of Svalbard (see Table 1) is marked gray as it is located in warmer waters east of the Arctic domain but shows a Mg/Ca:$\delta^{44/40}$Ca proxy pair that is indistinguishable from polar samples.

(Figure 2). Tests of *N. pachyderma* (sinistral) can be subdivided into two groups which differ significantly in their suitability as temperature proxy recorder. The distinctive feature between these two groups is their calcification habitat. In foraminiferal test which calcified in the Norwegian Sea east of the Arctic domain with summer temperatures of at least 2.5°C in combination with salinities above 34.5‰, Mg/Ca and $\delta^{44/40}$Ca values are positively correlated (Figure 2):

$$\text{Mg/Ca(mmol/mol)} = 0.77(\pm 0.22) \times \delta^{44/40}\text{Ca(SRM 915a)}$$
$$+ 0.52(\pm 0.12)\left(n = 20, R^2 = 0.76\right) \quad (5)$$

This consistency demonstrates that Mg/Ca and $\delta^{44/40}$Ca values in the Norwegian Sea are predominantly controlled by the same environmental parameters. However, the "cold limit" for reliable Mg/Ca and $\delta^{44/40}$Ca inferred temperatures is specified by Mg/Ca ratios of ~0.80 mmol/mol and $\delta^{44/40}$Ca values of ~0.35‰ (SRM 915a), associated to foraminiferal tests that calcified at the boundary between the Norwegian See and the Arctic domain (Figure 1). At this boundary, water masses are characterized by peak summer surface

temperatures of 3 to 4°C and maximum summer surface salinities of ~34.5‰ [*Weinelt et al.*, 2001]. In the second group of foraminiferal tests that calcified at summer temperatures below 2.5°C associated with salinities of 34.5‰ or less, the temperature response in the Mg/Ca and $\delta^{44/40}$Ca proxy signal is inversed and poorly correlated (Figure 2). However, foraminiferal tests picked from one core tops west of Svalbard (core 23233-1, Figure 1 and Table 1), show this proxy behavior in slightly warmer, more saline waters.

[15] In Figure 3, the positively correlated Mg/Ca and $\delta^{44/40}$Ca values from Norwegian Sea core top samples are plotted as a function of their corresponding δ^{18}O values. Lines of equal temperatures were calculated using the Mg/Ca:temperature equation (1) of *Mashiotta et al.* [1999], the $\delta^{44/40}$Ca:temperature calibration (2) for *N. pachyderma* (sinistral) by *Hippler et al.* [2009] and the calcite temperature:δ^{18}O relation (3) of *Shackleton* [1974], applying a foraminiferal vital effect in δ^{18}O of 0.6‰ and the salinity to δ^{18}O$_{\text{water}}$ relation (4) as proposed by *Simstich et al.* [2003]. In contrast to the high degree of correlation ($R^2 = 0.76$) for the Mg/Ca:$\delta^{44/40}$Ca relationship, the δ^{18}O signal in *N.*

Table 1. Core Locations; $\delta^{44/40}$Ca, Mg/Ca, and δ^{18}O Records of *N. pachyderma* (sinistral); and Proxy Temperature Estimates

Core Number	Core[a]	Latitude (°N)	Longitude (°W/°E)	T_{WOA},[b] 0–200 m (°C)	S_{WOA},[b] 0–200 m (‰)	Mg/Ca[c] (mmol/mol)	$\delta^{44/40}$Ca[d] (‰ SRM 915a)	$\delta^{18}O_{Nps}$[e] (‰ PDB)	$\delta^{18}O_{water}$[f] (‰ SMOW)	$T_{\delta18O}$[g] (°C)	$T_{Mg/Ca}$[h] (°C)	$T_{\delta44/40Ca}$[i] (°C)
1	HM16130	65.10	−2.42	5.9	35.0	0.99	0.58 ± 0.11	2.40	0.44	5.6	6.0	4.7
2	HM16132	64.57	−0.72	6.9	35.1	0.80	0.46 ± 0.18	2.58	0.47	5.0	3.8	4.0
3	HM16142	63.25	2.60	8.4	35.1	0.93	0.53 ± 0.07	1.83	0.47	7.9	5.3	4.4
4	HM49-15	66.34	−0.36	6.5	35.1	0.91	0.49 ± 0.18	2.23	0.46	6.3	5.1	4.2
5	HM52-18	62.27	−14.14	9.1	35.2	0.82	0.34 ± 0.08	3.09	0.50	3.2	4.1	3.3
6	HM52-39	65.57	−6.79	4.2	34.9	0.97	0.52 ± 0.06	2.73	0.41	4.2	5.7	4.4
7	HM52-42	66.34	−2.80	5.5	35.0	1.04	0.62 ± 0.06	2.38	0.43	5.6	6.5	4.9
8	HM57-11	67.12	−8.30	2.7	34.9	0.80	0.48 ± 0.06	3.19	0.38	2.4	3.8	4.1
9	HM57-16	67.28	−4.37	4.4	35.0	1.07	0.78 ± 0.09	2.59	0.43	4.8	6.7	5.9
10	HM57-20	62.65	1.67	8.6	35.1	0.85	0.46 ± 0.05	2.92	0.48	3.8	4.4	4.0
11	HM71-17	70.00	−13.02	0.9	34.6	1.00	0.45 ± 0.11	3.40	0.29	0.6	6.0	3.9
12	HM71-22	69.34	−3.61	4.2	35.0	1.04	0.67 ± 0.06	2.44	0.41	5.3	6.5	5.2
13	HM80-43	72.25	−9.19	0.8	34.6	0.98	0.47 ± 0.08	3.50	0.29	0.3	5.9	4.0
14	HM94-12	71.32	−3.55	2.5	34.8	0.80	0.36 ± 0.09	3.23	0.37	2.2	3.8	3.4
15	HM94-16	73.23	5.37	3.2	35.0	0.87	0.45 ± 0.06	3.32	0.43	2.1	4.7	4.0
16	HM94-18	74.50	5.70	2.8	35.0	0.91	0.48 ± 0.13	3.47	0.42	1.6	5.1	4.1
17	HM94-30	74.38	−2.00	0.6	34.8	0.92	0.36 ± 0.03	3.67	0.36	0.2	5.2	3.4
18	HM133-21	61.62	−8.86	8.9	35.2	1.04	0.63 ± 0.09	–	–	–	6.5	5.0
19	HM133-24	61.42	−11.87	9.1	35.2	1.02	0.70 ± 0.03	–	–	–	6.2	5.4
20	23231-2	78.90	−3.99	0.5	34.2	1.17	0.43 ± 0.16	3.06	0.14	1.7	7.6	3.8
21	23232-1	79.03	−1.62	0.9	34.4	1.27	0.52 ± 0.08	3.37	0.21	1.8	8.5	4.3
22	23233-1	79.41	6.88	2.6	34.8	1.20	0.45 ± 0.09	2.90	0.36	3.2	7.9	3.9
23	23235-1	78.87	1.39	1.6	34.6	0.90	0.46 ± 0.07	3.03	0.29	2.6	5.0	4.0
24	23259-3	72.02	9.3	5.8	35.0	1.01	0.53 ± 0.05	2.50	0.41	5.1	6.1	4.4
25	23261-2	72.18	13.11	5.8	35.0	0.97	0.55 ± 0.11	2.55	0.45	5.0	5.7	4.5
26	23508-1	73.86	−9.40	0.4	34.6	1.20	0.38 ± 0.20	3.35	0.29	1.3	7.9	3.5
27	23509-1	73.83	−13.50	0.2	34.2	1.37	0.50 ± 0.08	3.41	0.19	0.9	9.3	4.2
28	23514-3	66.67	−25.95	4.1	34.5	0.88	0.55 ± 0.08	3.48	0.23	0.8	4.7	4.5

[a] Samples 1 to 19 were provided from *Meland et al.* [2006]; samples 20 to 28 were provided from *Simstich et al.* [2003, and references therein].

[b] Averaged salinities and summer temperatures (July–September) in 0–200 m water depth from *Conkright et al.* [2002] (http://www.nodc.noaa.gov/OC5/WOA01/pr_woa01.html).

[c] Mg/Ca ratio measurements for samples 1 to 19 were performed in Cambridge, UK. Mg/Ca ratios of samples 20 to 28 were measured in Kiel, Germany.

[d] Analytical uncertainty 2SEM = $2\sigma/n^{0.5}$ of the calcium isotope ratios, calculated from repeated measurements.

[e] δ^{18}O values were taken from *Hohenegger* [1996], *Horvege* [1987], *Meland et al.* [2006], and *Simstich et al.* [2003].

[f] Calculated after the salinity − δ^{18}O relation of *Simstich et al.* [2003]: $\delta^{18}O_{water}$ (‰ SMOW) = −12.17 + 0.36 × S.

[g] Calculated after *Shackleton* [1974]: T (°C) = 16.90 − 4.38 ($\delta^{18}O_{calcite}$ − $\delta^{18}O_{water}$) + 0.10 ($\delta^{18}O_{calcite}$ − $\delta^{18}O_{water}$)^2 assuming a foraminiferal vital effect of 0.6‰ [*Simstich et al.*, 2003].

[h] Mg/Ca temperature equation of *Mashiotta et al.* [1999]: Mg/Ca (mmol/mol) = 0.549 × exp$^{0.099T}$.

[i] The $\delta^{44/40}$Ca temperature equation of *Hippler et al.* [2009]: $\delta^{44/40}$Ca (‰) = 0.17 (±0.02) × SST (°C) − 0.22 (±0.08).
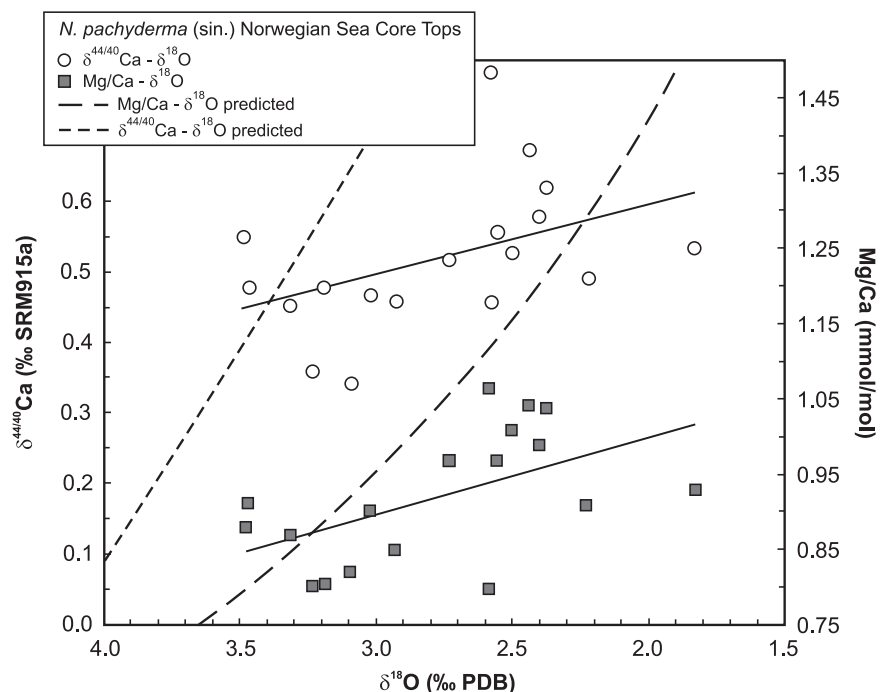
Figure 3. Comparison of measured and predicted Mg/Ca and $\delta^{44/40}$Ca values of *N. pachyderma* (sinistral) versus δ^{18}O. The predicted Mg/Ca-δ^{18}O relation was calculated using the palaeoequation (3) of *Shackleton* [1974] and the Mg/Ca calibration (1) of *Mashiotta et al.* [1999] (Table 1). The $\delta^{44/40}$Ca-δ^{18}O relation is based on the Ca isotope temperature equation (2) of *Hippler et al.* [2009]. A δ^{18}O$_{water}$ of 0.42‰ (SMOW) (averaged from modern data) was assumed for the Norwegian Sea.

pachyderma (sinistral) deviates by up to 1.5‰ from the values predicted by Mg/Ca or $\delta^{44/40}$Ca temperature estimates and is therefore poorly correlated. ($R^2 = 0.29$ for the Mg/Ca:δ^{18}O relationship and $R^2 = 0.20$ for the $\delta^{44/40}$Ca:δ^{18}O relationship).

3.2. Assessing Foraminiferal Calcification Temperatures

[16] Basically all data sets describing the temperature sensitivity of Mg/Ca in planktonic foraminifera are calibrated against estimated calcification temperatures derived either from instrumental data or by the combination with δ^{18}O measurements. While both approaches reveal fairly consistent results in tropical to subtropical oceans, the assignment of "true" calcification temperatures remains one of the major issues for high-latitude core top calibrations because of the distinctive seasonality and the strong stratification of high-latitude water masses [cf. *Barker et al.*, 2005]. In Figure 4, the new Mg/Ca data set of Norwegian Sea core top samples measured by ICP-OES was plotted against calcification temperature estimates deduced from three different approaches:

[17] 1. Mg/Ca is plotted against δ^{18}O-derived temperatures calculated by equations (3) and (4), following the multispecies calibration of *Elderfield and Ganssen* [2000]. A δ^{18}O vital effect of 0.6‰ as proposed by *Simstich et al.* [2003] for core top samples of *N. pachyderma* (sinistral) was applied.

[18] 2. Mg/Ca is plotted against averaged modern summer temperatures in 0 m to 200 m water depth compiled from *Conkright et al.* [2002] similar to the initial approach of *Nürnberg* [1995] who used various data sources [*Dietrich*, 1969; *Koltermann and Lüthje*, 1989; *Thiede and Hempel*, 1991; *Pfannkuche et al.*, 1993].

[19] 3. Mg/Ca ratios are plotted against $\delta^{44/40}$Ca-derived reference temperatures calculated by the Ca isotope temperature equation (2) of *Hippler et al.* [2009].

[20] The resulting reference temperatures calculated by these three independent approaches vary significantly, showing that the temperature sensitivity in the Mg/Ca proxy signal is mainly a function of the selected calibration approach (Figure 4). Mg/Ca ratios referenced against δ^{18}O-based calcification temperatures that range from ~1°C to ~8°C show
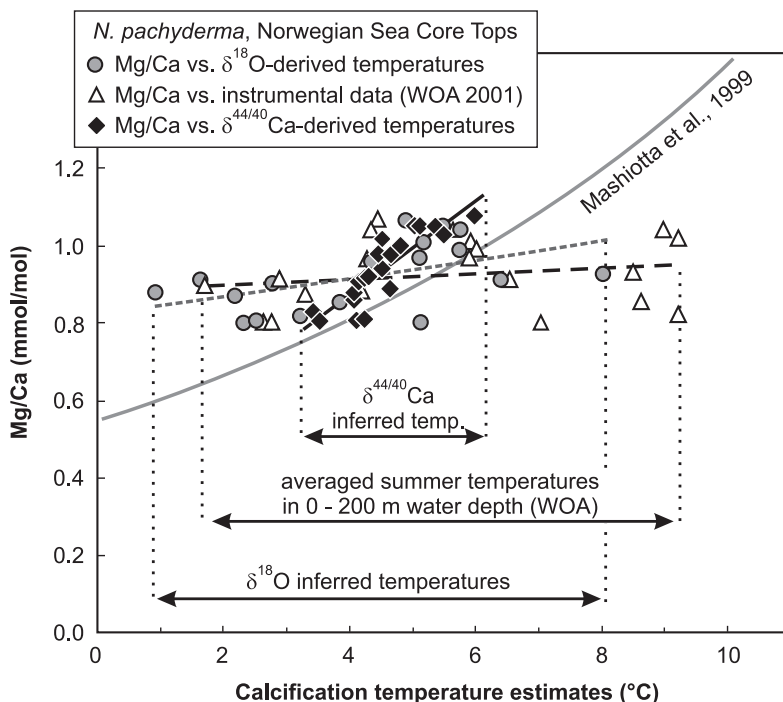
Figure 4. ICP-OES derived Mg/Ca ratios in *N. pachyderma* (sinistral) originating from the Norwegian Sea plotted against calcification temperature estimates derived from (1) modern summer SST (averaged July–September in 0–200 m [*Conkright et al.*, 2002]), (2) δ^{18}O inferred temperatures, and (3) $\delta^{44/40}$Ca temperature estimates. The calculation of the different reference temperatures is explained in detail in section 3.1 and Table 1.

no significant temperature relation and deviate significantly from the Mg/Ca temperature equations of *Mashiotta et al.* [1999] and *Elderfield and Ganssen* [2000]. Assuming a constant calcification habitat corresponding to averaged summer temperatures in 0 m to 200 m water depth, measured Mg/Ca ratios are assigned to water temperatures ranging from about 1.5 to 9.5°C which are on average about 1 to 2°C higher than δ^{18}O-derived temperatures. Similar to the δ^{18}O based calibration, the increase in foraminiferal Mg/Ca with temperature is almost insignificant when referencing against averaged modern summer temperatures. This is in agreement to the study of *Nürnberg* [1995] who found a range in Mg/Ca of only 0.56 to 1.06 mmol/mol in Nordic seas core top samples whereas the exponential temperature equation is mainly supported by North Atlantic core locations reflecting higher water temperatures.

[21] In contrast to the first two approaches, Mg/Ca ratios referenced against $\delta^{44/40}$Ca-derived temperatures calculated by equation (2) reveal a temperature response in the Mg content of foraminiferal calcite that is comparable to the Mg/Ca temperature calibration of *Mashiotta et al.* [1999] and the

multispecies calibration of *Elderfield and Ganssen* [2000]. The calibration of Mg/Ca ratios against $\delta^{44/40}$Ca-derived temperatures is remarkable for two reasons:

[22] 1. For the first time, Mg/Ca ratios from high-latitude planktonic foraminifera are calibrated against a truly independent temperature proxy that is based on sediment surface samples as well as on foraminiferal tests from net catches [*Hippler et al.*, 2009]. Furthermore, $\delta^{44/40}$Ca was measured in an aliquot of the same sample solution that was used for the Mg/Ca runs.

[23] 2. Unlike previous electron microprobe data sets, foraminiferal Mg/Ca ratios used for this calibration study are derived from ICP-OES instruments which is now the common analytical approach in laboratories generating high quantities of Mg/Ca measurements for palaeoceanographic applications. It is notable that in comparison to temperature estimates deduced from foraminiferal δ^{18}O or compiled from *Conkright et al.* [2002] assuming a constant calcification depth, the temperature signal recorded in the $\delta^{44/40}$Ca of Norwegian Sea core top samples reflects a significantly narrower temperature range of only 3°C to 6°C.

According to this, the refined Mg/Ca temperature equation for Norwegian Sea *N. pachyderma* (sinistral) based on $\delta^{44/40}$Ca-derived calcification temperatures (Figure 4) is best described by:

$$Mg/Ca(mmol/mol) = 0.13(\pm0.037)T(°C) + 0.35(\pm0.17) \qquad (6)$$

(n = 20; regression calculated by ISOPLOT [*Ludwig*, 2003]). Despite thermodynamic considerations requiring an exponential temperature dependence of the Mg uptake into foraminiferal calcite [*Mashiotta et al.*, 1999], we assume that in the narrow temperature range occupied by *N. pachyderma* (sinistral), a linear temperature function is also appropriate. The corresponding Mg/Ca temperature estimates are slightly lower than temperatures calculated by the Mg/Ca temperature equations of *Mashiotta et al.* [1999] and *Elderfield and Ganssen* [2000].

3.3. Reassessment of the Calcification Habitat by Mg/Ca:$\delta^{44/40}$Ca Proxy Pairs

[24] Various studies reported that the biological production in the Nordic seas culminates from July to September [cf. *Kohfeld et al.*, 1996; *Jensen*, 1998; *Schröder-Ritzrau et al.*, 2001]. Hence, the temperature signal recorded in tests of *N. pachyderma* (sinistral) from Nordic seas core top sediments most likely reflects summer temperatures from a dedicated depth interval. On the basis of paired oxygen isotope data of *N. pachyderma* (sinistral) and *Turborotalita quinqueloba*, *Simstich et al.* [2003] proposed that "apparent" calcification depths of *N. pachyderma* (sinistral) are bound to pycnoclines, indicating water depth of ~20 to 50 m in the Arctic domain and up to ~250 m off Norway. As a self-consistent confirmation of our data, Mg/Ca and $\delta^{44/40}$Ca proxy temperature estimates (calculated by equations (1) and (2)) projected on corresponding water depths reveal a similar pattern, suggesting that the density-driven water mass stratification is the main factor controlling the habitat depth of this foraminiferal species in the Nordic seas (Figure 5). Both Mg/Ca- and $\delta^{44/40}$Ca-derived temperatures reflect hydrographic conditions strongly bound to the isopycnal layer defined by the potential density σ_t of 27.7 to 27.8 (reduced to atmospheric pressure). This implies that the average habitat depth of *N. pachyderma* (sinistral) in the Nordic seas is either actively or passively controlled by water density. Consequently, this species only partly records subsurface water temperature changes and is dampening the total amplitude of temperature variations one would expect when assuming a constant average calcification depth.

3.4. Implications on Monospecific Multiproxy Approaches

[25] In contrast to the positively correlated $\delta^{44/40}$Ca and Mg/Ca values in Norwegian Sea core top samples, which both reflect average summer temperatures associated to the isopycnal layer defined by a potential density σ_t of 27.7 to 27.8 (reduced to atmospheric pressure), foraminiferal δ^{18}O values deviate significantly from the $\delta^{44/40}$Ca and Mg/Ca proxy signal (Figure 3). Furthermore, δ^{18}O-derived calcification temperatures projected onto their corresponding water depth reveal an inconsistent "apparent" calcification depth (Figure 5). *Nyland et al.* [2006] made similar observations based on paired δ^{18}O:Mg/Ca values in *N. pachyderma* (right coiling) and *N. pachyderma* (sinistral) from high-resolution Norwegian Sea sediment cores spanning the last ~1200 years. They concluded that the large variability in foraminiferal δ^{18}O and hence the discrepancy between foraminiferal Mg/Ca and δ^{18}O is caused by variations in the oxygen isotopic composition of seawater during the Late Holocene. In contrast, *Meland et al.* [2006] hypothesized on the basis of a broad data set comprising paired δ^{18}O:Mg/Ca values, that the vital effect in the δ^{18}O signal of *N. pachyderma* (sinistral) might vary between different water masses.

[26] An important factor that has to be considered when discussing offsets between proxy pairs are intratest variations in the trace element distribution and isotopic composition between the inner ontogenetic calcite and the outer crust. At the final phase of its life cycle, which usually ends after several weeks to months, *N. pachyderma* (sinistral) covers its entire test with a thick calcite layer ("crust"). In some foraminiferal species, this process is known to be associated with gametogenesis [*Bé*, 1980]. The secretion of this outer crust (termed "gametogenetic calcite" for the tropical species *Globigerinoides sacculifer* [*Bé*, 1980]), which may contribute more than 70% of the total test weight of *N. pachyderma* (sinistral) [*Kohfeld et al.*, 1996], takes place in water depths of up to several hundred meters [e.g., *Duplessy et al.*, 1981]. In studies using foraminiferal tests from open ocean conditions, the Mg content in the outer crust usually shows a systematic Mg depletion as predicted by the colder water temperatures at calcification depth [e.g., *Eggins et al.*, 2003]. In contrast, *Nürnberg et al.* [1996] reported a signif-
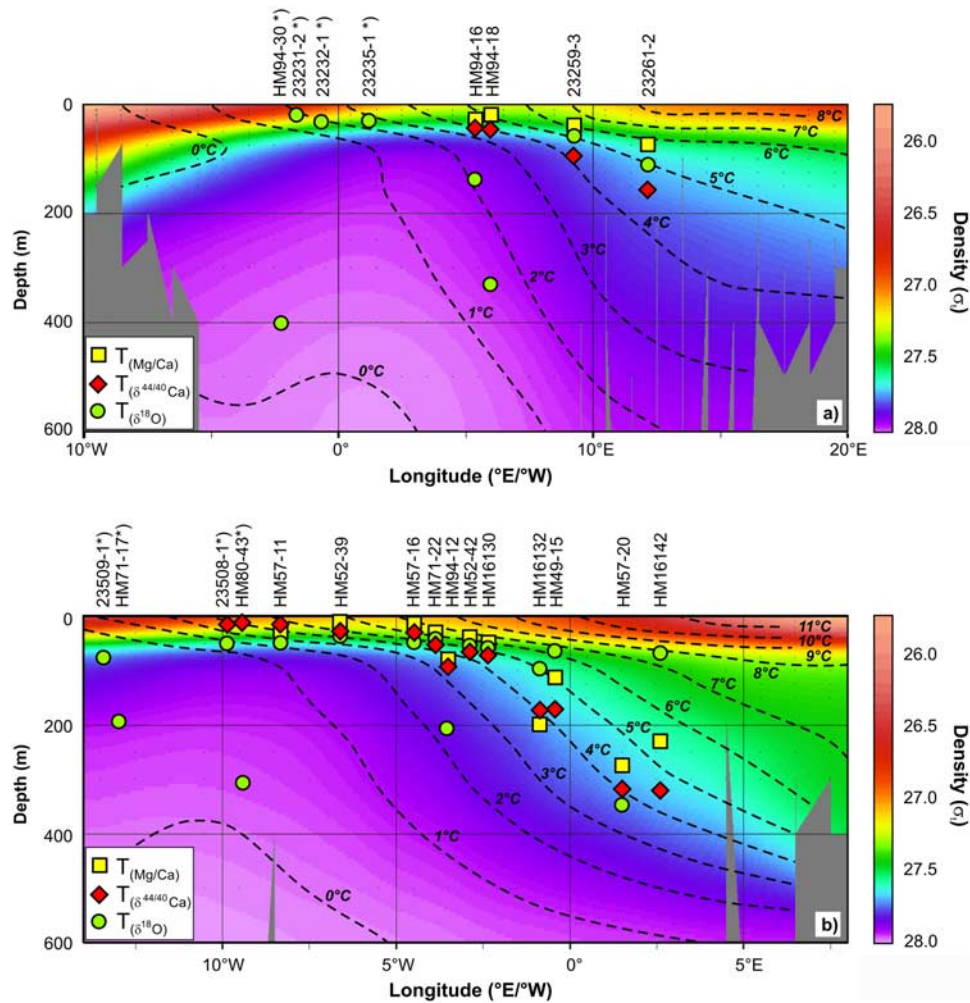
Figure 5. Mg/Ca-, $\delta^{44/40}$Ca-, and δ^{18}O-derived temperatures from the transects shown in Figure 1 projected meridionally to depth intervals with appropriate summer temperatures. (a) Northern and (b) southern transect. The δ^{18}O-derived temperatures predict a wide and unrealistic scatter in average calcification depths, whereas Mg/Ca and $\delta^{44/40}$Ca temperature estimates closely follow the 27.7 isopycne (reduced to sea surface pressure). In Arctic domain and polar waters, Mg/Ca and $\delta^{44/40}$Ca temperature estimates are higher than maximum summer surface temperatures (core labels marked by asterisks). Isopycnals were calculated by ODV (R. Schlitzer, Ocean Data View, 2006, available at http://odv.awi.de) on the basis of data from *Conkright et al.* [2002] (http://www.nodc.noaa.gov/OC5/WOA01/pr_woa01.html). In order to obtain independent Mg/Ca temperature estimates that are not based on $\delta^{44/40}$Ca reference temperatures, Mg/Ca ratios were converted to absolute temperatures by the equation of *Mashiotta et al.* [1999]. Using the new Mg/Ca temperature equation (6), which is cross calibrated with $\delta^{44/40}$Ca values, Mg/Ca inferred temperatures are, on average, about 0.5°C lower.

icantly higher Mg content in the outer crust of *Globigerinoides sacculifer* that have been cultured at constant water temperature. This implies that the Mg/Ca of the outer crust may not be exclusively related to calcification temperature. With respect to $\delta^{44/40}$Ca, the proxy signal recorded in nonencrusted net catches and encrusted core top samples of *N. pachyderma* (sinistral) is within analytical uncertainty identical [*Hippler et al.*, 2009]. Only limited data sets are available for foraminiferal intratest oxygen isotope variations, mainly because the analytical approach is challenging. *Duplessy et al.*

[1981] speculated that the ontogenetic calcite is negatively fractionated in δ^{18}O relative to calcite equilibrated with seawater whereas the crust is secreted at or near equilibrium. This negative fractionation of the ontogenetic calcite was confirmed in a later study by *Spero and Lea* [1996]. Recently, *Kozdon et al.* [2009] determined intratest oxygen isotope variations in *N. pachyderma* (sinistral) using multicollector ion microprobe at 2 to 3 μm spatial resolution. They reported a negative vital effect of −0.5 to −1‰ in the ontogenetic calcite and a positive vital effect of

about +0.8‰ in the final crust. Consequently, whole test δ^{18}O values derived from conventional analytical techniques are highly sensitive to the degree of encrustation.

[27] As most foraminiferal temperature calibrations are based on encrusted core top samples, the chemical heterogeneity of individual foraminiferal tests is already considered in the proxy to temperature calibrations. However, if the addition of the final crust at the end of the foraminiferal life cycle alters the "whole test" bulk value for each temperature proxy in a different way, variations in the degree of test encrustation can produce significant offsets between chemically independent proxies.

3.5. Mg/Ca Temperature Reconstructions in High-Latitude Oceans

[28] It was first reported by *Nürnberg* [1995] and later by *Meland et al.* [2006] that Mg/Ca ratios from sampling sites that are annually covered by sea ice are generally too high. This deviation is even more pronounced in the new ICP-OES data set (Figure 2). In this respect, it is notable that the Mg/Ca calibrations of *Mashiotta et al.* [1999] and *Elderfield and Ganssen* [2000], which are both comprising the electron microprobe data set of *Nürnberg* [1995], are interpolated down to water temperatures of 0°C, implying that Mg/Ca ratios of planktonic foraminifera can be converted to robust temperature estimates in polar waters.

[29] Aberrant proxy signals in foraminiferal tests from polar waters are not restricted to core top samples. *Hippler et al.* [2009] reported that the Ca isotopic ratios of net sampled *N. pachyderma* (sinistral) from polar waters are, similar to core top samples, insensitive to water temperature. In contrast, $\delta^{44/40}$Ca inferred temperatures were found to be reliable in net sampled foraminiferal tests that calcified in cold waters associated with higher salinities. Consequently, the authors described the breakdown of the $\delta^{44/40}$Ca temperature relationship as the "cold-fresh-end" paradox. However, it has yet to be determined if the cold limit for reliable Mg/Ca temperature estimates is different at sampling sites with higher salinities.

[30] On the basis of the current data set, we suggest to apply a new linear Mg/Ca temperature calibration (6) to describe the temperature response in tests of *N. pachyderma* (sinistral) that calcified in water temperatures above ~3°C. Consequently, Mg/Ca ratios associated with almost monospecific foraminiferal assemblages indicating lower water

temperatures should be evaluated carefully. In contrast to previous calibrations, the new equation is based on a self-consistent multiproxy approach combining Mg/Ca ratios with $\delta^{44/40}$Ca temperature estimates from both core top samples and net catches, which are supported by precise instrumental CTD temperature data [*Hippler et al.* 2009]. This new Mg/Ca temperature calibration should be regarded as a refined "cold end" branch of the existing Mg/Ca calibrations of *Mashiotta et al.* [1999] and *Elderfield and Ganssen* [2000], which are both commonly applied for *N. pachyderma* (sinistral).

[31] Our findings that *N. pachyderma* (sinistral) is either actively or passively bound to a narrow isopycnal range enlightens earlier findings of *Meland et al.* [2005, 2006], who observed almost no difference between Glacial and Holocene Mg/Ca ratios for this species. As water density is mainly a function of temperature and salinity, the presumption of a constant habitat depth during glacial-interglacial intervals for the interpretation of high-latitude foraminiferal paleorecords may be misleading. Assuming that *N. pachyderma* (sinistral) can adjust its buoyancy within narrow limits only, the water mass stratification during interglacial periods is likely to provoke a deeper average calcification habitat, partly counterbalancing absolute glacial-interglacial temperature variations. As a result of its alignment to a narrow density band, the total temperature range recorded in the Mg/Ca and $\delta^{44/40}$Ca signal of *N. pachyderma* (sinistral) from Norwegian Sea core tops is restricted to only ~3 to 6°C. In the sedimentary record, similar discrepancies were reported between temperature estimates derived from foraminiferal transfer functions, and δ^{18}O-derived temperatures [*Bond et al.*, 1992]. While the percent abundance data suggest temperature changes of 6° to 8°C, the δ^{18}O signal in *N. pachyderma* (sinistral) indicates little or no change.

[32] The knowledge and understanding of how nonspinose foraminifera as *N. pachyderma* (sinistral) adjust their buoyancy is still limited, mainly because their culturing is challenging compared to spinose foraminifera species [cf. *von Langen et al.*, 2005]. It is assumed that planktonic foraminifera produce low-density lipids or gases to counter gravitational settling [*Furbish and Arnold*, 1997]. In particular, most spinose planktonic foraminifera need an active buoyancy control as they are confined to the photic zone because of their photosynthetic symbionts. In contrast, *N. pachyderma*

(sinistral) is known to be asymbiotic [cf. *Hemleben et al.*, 1989] and therefore probably a passive dweller. This implies that the water mass stratification is preconditioning the habitat of nonspinose or asymbiotic foraminifera more likely than that of spinose and symbiotic foraminifera, which are supposed to have a more effective buoyancy control in order to stay in the photic zone. In this regard, *Anand et al.* [2003] reported a lower temperature response of the Mg/Ca signal in nonspinose foraminifera from the Sargasso Sea than in the spinose group. This effect may become amplified in high latitudes as a result of stronger water mass stratification.

3.6. Aberrant Foraminiferal Mg/Ca at the "Cold End"

[33] Foraminiferal Mg/Ca ratios are lower by an order of magnitude than those predicted by inorganic precipitation from seawater [*Barker et al.*, 2005; *Oomori et al.*, 1987], suggesting a tight biological control on the Mg content. Thus, the organism needs to concentrate Ca^{2+} or alternatively remove Mg^{2+} from the vacuolized seawater that serves as the parent solution from which calcification occurs [cf. *Bentov and Erez*, 2006]. Consequently, a faster calcification rate requires a faster concentration of Ca^{2+} or removal of Mg^{2+} in order to keep the Mg/Ca ratio of the parent solution within certain limits. Available data of the temperature influence on foraminiferal growth rate are very sparse, but indicate that *N. pachyderma* (sinistral) achieves highest calcification rates in cold waters, whereas other foraminiferal species including right coiling *N. pachyderma* (dextral) increase their growth rate with increasing water temperature [*Lombard et al.*, 2009]. It might be possible that under environmental conditions favoring a high growth rate, a chemical modification of the vacuolized seawater beyond certain limits has no further impact on the efficiency of the biomineralization process. Thus, the corresponding Mg/Ca ratios of the precipitated calcite are superimposed by other factors than temperature. This hypothesis could explain the almost parabolic relation between foraminiferal Mg/Ca and water temperature with lowest Mg/Ca ratios of about 0.80 mmol/mol corresponding to water temperatures of ~3°C. However, it is important to emphasize that the entire process of foraminiferal biomineralization is not understood in detail yet [cf. *Erez*, 2003], and the reliability of foraminiferal temperature proxies derived from samples that calcified close to the limits

of their thermal tolerance window is an interesting field for further studies.

4. Conclusion

[34] On the basis of $\delta^{44/40}$Ca and Mg/Ca measurements in Holocene core top samples of *N. pachyderma* (sinistral) from the Norwegian Sea and Arctic domain, we found that the temperature signal recorded in both proxies reflects variable calcification depths associated to a discrete isopycnal band of $\sigma_t = 27.7$ to 27.8 (reduced to atmospheric pressure) and thus counterbalancing absolute temperature variations. As a result, robust cross-calibrated proxy temperature estimates from the Norwegian Sea comprise a range of only ~3 to 6°C, challenging previous temperature calibrations for this foraminiferal species which are based on the assumption of a constant calcification depth. Therefore, we recommend a modified Mg/Ca temperature calibration for high-latitude *N. pachyderma* (sinistral) that is based on independent, cross-calibrated $\delta^{44/40}$Ca temperature estimates: Mg/Ca (mmol/mol) = 0.13 ($\pm$0.037) T (°C) + 0.35 ($\pm$0.17). In contrast, Mg/Ca ratios calibrated against δ^{18}O inferred temperatures or instrumental data according to previous calibration approaches are almost insensitive to temperature variations, emphasizing that the assignment of "true" calcification temperatures is a major issue in high-latitude temperature calibrations. At water temperatures below 2.5°C associated with salinities of 34.5‰ or less, the temperature information in the Mg/Ca and $\delta^{44/40}$Ca proxy signal is lost, implying that common Mg/Ca temperature equations for planktonic foraminifera should not be unambiguously applied to polar waters. This highly nonpassive character of *N. pachyderma* (sinistral) emphasizes the importance of water mass and species specific temperature calibrations.

Acknowledgments

References

Anand, P., H. Elderfield, and M. H. Conte (2003), Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, *18*(2), 1050, doi:10.1029/2002PA000846.

Barker, S., M. Greaves, and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleother-mometry, *Geochem. Geophys. Geosyst.*, 4(9), 8407, doi:10.1029/2003GC000559.

Barker, S., I. Cacho, H. Benway, and K. Tachikawa (2005), Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: A methodological overview and data compila-tion for the Last Glacial Maximum, *Quat. Sci. Rev.*, 24, 821–834, doi:10.1016/j.quascirev.2004.07.016.

Bé, A. W. H. (1980), Gametogenetic calcification in a spinose planktonic foraminifera, *Globigerinoides Sacculifer* (Brady), *Mar. Micropaleontol.*, 5, 283–310, doi:10.1016/0377-8398(80)90014-6.

Bemis, B. E., H. J. Spero, J. Bijma, and D. W. Lea (1998), Reevaluation of the oxygen isotopic composition of plank-tonic foraminifera: Experimental results and revised paleo-temperature equations, *Paleoceanography*, 13, 150–160, doi:10.1029/98PA00070.

Bentov, S., and J. Erez (2006), Impact of biomineralization processes on the Mg content of foraminiferal shells: A bio-logical perspective, *Geochem. Geophys. Geosyst.*, 7, Q01P08, doi:10.1029/2005GC001015.

Birck, J. L. (1986), Precision K-Rb-Sr isotopic analysis: Ap-plication to Rb-Sr chronology, *Chem. Geol.*, 56, 73–83, doi:10.1016/0009-2541(86)90111-7.

Bond, G., et al. (1992), Evidence for massive discharges of icebergs into the North Atlantic Ocean during the last glacial period, *Nature*, 360, 245–249, doi:10.1038/360245a0.

Conkright, M. E., R. A. Locarnini, H. E. Garcia, T. D. O'Brien, T. P. Boyer, C. Stephens, and J. I. Antonov (2002), World Ocean Atlas 2001: Objective analyses, data statistics, and figures, CD-ROM documentation, 17 pp., Natl. Oceanogr. Data Cent., Silver Spring, Md.

Craig, H., and L. I. Gordon (1965), Deuterium and oxygen-18 variations in the ocean and the marine atmosphere, in *Proceedings of a Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures*, edited by E. Tongiorgi, pp. 9–130, Sischi and Figli, Pisa, Italy.

de Villiers, S., M. Greaves, and H. Elderfield (2002), An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES, *Geochem. Geophys. Geosyst.*, 3(1), 1001, doi:10.1029/2001GC000169.

Dibrov, P., J. J. Smith, P. G. Young, L. Fliegel, S.-T. Kim, and J. R. O'Neil (1997), Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, *Geochim. Cosmo-chim. Acta*, 61, 3461–3475, doi:10.1016/S0016-7037(97)00169-5.

Dietrich, G. (1969), *Atlas of the Hydrography of the Northern North Atlantic Ocean*, 140 pp., Conseil Int. Pour L'Explor. de la Mer, Charlottenlund Slot, Denmark.

Duplessy, J.-C., P.-L. Blanc, and A. W. H. Bé (1981), Oxygen-18 enrichment in planktonic foraminifera due to gametogenic calcification below the euphotic zone, *Science*, 231, 1247–1250.

Eggins, S., P. DeDeckker, and A. T. Marshall (2003), Mg/Ca variation in planktonic foraminiferal tests: Implications for reconstructing palaeo-seawater temperature and habitat mi-gration, *Earth Planet. Sci. Lett.*, 212, 291–306, doi:10.1016/S0012-821X(03)00283-8.

Eisenhauer, A., T. F. Nägler, P. Stille, J. Kramers, N. Gussone, B. Bock, J. Fietzke, D. Hippler, and A.-D. Schmitt (2004), Proposal for an international agreement on Ca notation as a result of the discussions from the workshops on stable iso-tope measurements in Davos (Goldschmidt 2002) and Nice (EGS-AGU-EUG 2003), *Geostand. Geoanal. Res.*, 28(1), 149–151, doi:10.1111/j.1751-908X.2004.tb01051.x.

Elderfield, H., and G. Ganssen (2000), Past temperature and δ^{18}O of surface ocean waters inferred from foraminiferal Mg/Ca ratios, *Nature*, 405, 442–445, doi:10.1038/35013033.

Erez, J. (2003), The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies, *Rev. Mineral. Geochem.*, 54, 115–149, doi:10.2113/0540115.

Furbish, D. J., and A. J. Arnold (1997), Hydrodynamic strate-gies in the morphological evolution of spinose planktonic foraminifera, *Geol. Soc. Am. Bull.*, 109, 1055–1072, doi:10.1130/0016-7606(1997)109<1055:HSITME>2.3.CO;2.

Hemleben, C., M. Spindler, and O. R. Anderson (1989), *Mod-ern Planktonic Foraminifera*, Springer, New York.

Heuser, A., A. Eisenhauer, N. Gussone, B. Bock, N. T. Hansen, and T. F. Nägler (2002), Measurement of calcium isotopes (δ^{44}Ca) using a multicollector TIMS technique, *Int. J. Mass Spectrom.*, 220, 385–399, doi:10.1016/S1387-3806(02)00838-2.

Hippler, D., A.-D. Schmitt, N. Gussone, A. Heuser, P. Stille, A. Eisenhauer, and T. F. Nägler (2003), Calcium isotopic composition of various reference materials and seawater, *Geostand. Newsl.*, 27(1), 13–19, doi:10.1111/j.1751-908X.2003.tb00709.x.

Hippler, D., R. Kozdon, K. F. Darling, A. Eisenhauer, and T. F. Nägler (2009), Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.), *Biogeosciences*, 6, 1–14.

Hohnemann, C. (1996), Zur Paläoozeanographie der südlichen Dänemarkstraße, diploma thesis, Geol.-Paläontol. Inst., Christian-Albrechts-Univ., Kiel, Germany.

Horwege, S. (1987), Oberflächentemperaturen (und -strömun-gen) der Norwegisch- Grönländischen See im Abbild stabiler Kohlenstoff und Sauerstoffisotope rezenter planktischer For-aminiferen, diploma thesis, Geol.-Paläontol. Inst., Christian-Albrechts-Univ., Kiel, Germany.

Hut, G. (1987), Stable isotope reference samples for geochem-ical and hydrological investigations, paper presented at Con-sultants Group Meeting, Int. At. Energy Agency, Vienna.

Jensen, S. (1998), Planktische Foraminiferen im Europäischen Nordmeer: Verbreitung und Vertikalfluß sowie ihre Entwick-lung während der letzten 15000 Jahre, *Ber. Sonderforsch.*, 313, 75 pp., Christian-Albrechts-Univ., Kiel Germany.

Kohfeld, K. E., R. G. Fairbanks, S. L. Smith, and I. D. Walsh (1996), *Neogloboquadrina pachyderma* (sinistral coiling) as paleoceanographic tracers in polar oceans: Evidence from Northeast Water Polynya plankton tows, sediment traps, and surface sediments, *Paleoceanography*, 11, 679–699, doi:10.1029/96PA02617.

Koltermann, K. P., and H. Lüthje (1989), Hydrographic atlas of the Greenland and northern Norwegian seas (1979–1987), *Rep. 2328*, Dtsch. Hydrogr. Inst., Hamburg, Germany.

Kozdon, R., T. Ushikubo, N. T. Kita, M. Spicuzza, and J. W. Valley (2009), Intratest oxygen isotope variability in the planktonic foraminifer N. pachyderma: Real vs. apparent vital effects by ion microprobe, *Chem. Geol.*, 258, 327–337, doi:10.1016/j.chemgeo.2008.10.032.

Lombard, F., L. Labeyrie, M. Elisabeth, H. J. Spero, and D. W. Lea (2009), Modelling the temperature dependent growth rates of planktonic foraminifera, *Mar. Micropaleontol.*, 70, 1–7, doi:10.1016/j.marmicro.2008.09.004.

Ludwig, K. R. (2003), Isoplot 3.00: A geochronological toolkit for Microsoft Excel, *Spec. Publ.*, 4, Berkeley Geochronol. Cent., Berkeley, Calif.

Mashiotta, T. A., D. W. Lea, and H. J. Spero (1999), Glacial-interglacial changes in Subantarctic sea surface temperature

and δ^{18}O-water using foraminiferal Mg, *Earth Planet. Sci. Lett.*, *170*, 417–432, doi:10.1016/S0012-821X(99)00116-8.

McKenna, V. S., and W. L. Prell (2004), Calibration of the Mg/Ca of *Globorotalia truncatulinoides* (R) for the reconstruction of marine temperature gradients, *Paleoceanography*, *19*, PA2006, doi:10.1029/2000PA000604.

Meland, M. Y., E. Jansen, and H. Elderfield (2005), Constraints on SST estimates for the northern North Atlantic/Nordic seas during the LGM, *Quat. Sci. Rev.*, *24*, 835–852, doi:10.1016/j.quascirev.2004.05.011.

Meland, M. Y., E. Jansen, H. Elderfield, T. M. Dokken, A. Olsen, and R. G. J. Bellerby (2006), Mg/Ca ratios in the planktonic foraminifer *Neogloboquadrina pachyderma* (sinistral) in the northern North Atlantic/Nordic seas, *Geochem. Geophys. Geosyst.*, *7*, Q06P14, doi:10.1029/2005GC001078.

Nägler, T. F., A. Eisenhauer, A. Müller, C. Hemleben, and J. Kramers (2000), The δ^{44}Ca-temperature calibration on fossil and cultured *Globigerinoides sacculifer*: New tool for reconstruction of past sea surface temperatures, *Geochem. Geophys. Geosyst.*, *1*(9), 1052, doi:10.1029/2000GC000091.

Nürnberg, D. (1995), Magnesium in tests of *Neogloboquadrina pachyderma* (sinistral) from high northern and southern latitudes, *J. Foraminiferal Res.*, *25*, 350–368.

Nürnberg, D., J. Bijma, and C. Hemleben (1996), Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta*, *60*, 803–814, doi:10.1016/0016-7037(95)00446-7.

Nürnberg, D., A. Müller, and R. R. Schneider (2000), Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktic foraminifera: A comparison to sea surface temperature from $U^{K'}_{37}$, oxygen isotopes, and foraminiferal transfer function, *Paleoceanography*, *15*, 124–134, doi:10.1029/1999PA000370.

Nyland, B., E. Jansen, H. Elderfield, and C. Andersson (2006), *Neogloboquadrina pachyderma* (dex. and sin.) Mg/Ca and δ^{18}O records from the Norwegian Sea, *Geochem. Geophys. Geosyst.*, *7*, Q10P17, doi:10.1029/2005GC001055.

O'Neil, J. R., R. N. Clayton, and T. K. Mayeda (1969), Oxygen isotope fractionation in divalent metal carbonates, *J. Chem. Phys.*, *51*(12), 5547–5558, doi:10.1063/1.1671982.

Oomori, T., H. Kaneshima, Y. Maezato, and Y. Kitano (1987), Distribution coefficient of Mg^{2+} ions between calcite and solution at 10–50°C, *Mar. Chem.*, *20*, 327–336, doi:10.1016/0304-4203(87)90066-1.

Pfannkuche, O., J. C. Duinker, G. Graf, R. Henrich, H. Thiel, and B. Zeitschel (1993), Fahrtbericht Nordatlantik 92, Reise Nr. 21, 16. März–31. August 1992, *Meteor Ber.*, *93*, 281 pp., Univ. of Hamburg, Hamburg, Germany.

Sadekov, A. Y., S. M. Eggins, and P. DeDecker (2005), Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping, *Geochem. Geophys. Geosyst.*, *6*, Q12P06, doi:10.1029/2005GC000973.

Schröder-Ritzrau, A., H. Andruleit, S. Jensen, C. Samtleben, P. Schäfer, J. Matthiessen, H. C. Hass, A. Kohly, and J. Thiede (2001), Distribution, export and alteration of fossilizable plankton in the Nordic Sea, in *The Northern North Atlantic: A Changing Environment*, edited by P. Schäfer et al., pp. 81–104, Springer, Berlin.

Shackleton, N. J. (1974), Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus uvigerina: Isotopic changes in the ocean during the last glacial, *Colloq. Int. CNRS*, *219*, 203–209.

Simstich, J., M. Sarnthein, and H. Erlenkeuser (2003), Paired δ^{18}O signals of *Neogloboquadrina pachyderma* (s) and *Turborotalita quinqueloba* show thermal stratification structure in Nordic seas, *Mar. Micropaleontol.*, *48*, 107–125, doi:10.1016/S0377-8398(02)00165-2.

Spero, H. J., and D. W. Lea (1996), Experimental determination of stable isotope variability in *Globigerina bulloides*: Implications for paleoceanographic reconstructions, *Mar. Micropaleontol.*, *28*, 231–246, doi:10.1016/0377-8398(96)00003-5.

Stangeew, E. (2001), Distribution and isotopic composition of living planktonic foraminifera *N. pachyderma* (sinistral) and *T. quinqueloba* in the high latitude North Atlantic, Ph.D. thesis, Math.-Naturwiss. Fak., Christian-Albrechts-Univ., Kiel, Germany. (Available at http://e-diss.uni-kiel.de/diss_464/pp)

Thiede, J., and G. Hempel (1991), Die Expedition ARKTIS-VII/1 of RV "Polarstern" in 1990, *Rep. on Polar Res.*, *80*, 137 pp., Alfred-Wegener-Inst. für Polar- und Meeresforschung, Bremerhaven, Germany.

von Langen, P. J., D. K. Pak, H. J. Spero, and D. W. Lea (2005), Effects of temperature on Mg/Ca in neogloboquadrinid shells determined by live culturing, *Geochem. Geophys. Geosyst.*, *6*, Q10P03, doi:10.1029/2005GC000989.

Weinelt, M., et al. (2001), Paleoceanographic proxies in the Northern North Atlantic, in *The Northern North Atlantic: A Changing Environment*, edited by P. Schäfer et al., pp. 81–104, Springer, Berlin.