

# Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.)

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**Abstract.** The accurate reconstruction of sea surface temperature (SST) history in climate-sensitive regions (e.g. tropical and polar oceans) became a challenging task in palaeoceanographic research. Biogenic shell carbonate SST proxies successfully developed for tropical regions often fail in cool water environments. Their major regional shortcomings and the cryptic diversity now found within the major high latitude proxy carrier *Neogloboquadrina pachyderma* (sin.) highlight an urgent need to explore complementary SST proxies for these cool-water regions. Here we incorporate the genetic component into a calibration study of a new SST proxy for the high latitudes. We found that the calcium isotopic composition ( $\delta^{44/40}\text{Ca}$ ) of calcite from genotyped net catches and core-top samples of the planktonic foraminifera *Neogloboquadrina pachyderma* (sin.) is related to temperature and unaffected by genetic variations. The temperature sensitivity has been found to be  $0.17 (\pm 0.02)\%$  per  $1^\circ\text{C}$ , highlighting its potential for downcore applications in open marine cool-water environments. Our results further indicate that in extreme polar environments, below a critical threshold temperature of  $2.0 (\pm 0.5)^\circ\text{C}$  associated with salinities below  $33.0 (\pm 0.5)\%$ , a prominent shift in biomineralization affects the  $\delta^{44/40}\text{Ca}$  of genotyped and core-top *N. pachyderma* (sin.), becoming insensitive to temperature. These findings highlight the need of more systematic calibration studies on single planktonic foraminiferal species in order to unravel species-specific factors influencing the temperature sensitivity of Ca isotope fractionation and to validate the proxies' applicability.

## 1 Introduction

The geochemical signatures of carbonate skeletal remains, i.e. foraminifers, corals, and bivalves, provide a valuable source of information for palaeo-reconstruction of changes in physical and chemical oceanographic conditions. In particular, sea surface temperatures (SSTs) contribute a vital element to our understanding of past and future climate dynamics (Broecker, 1997). Changes in SST strongly impact upon the global thermohaline circulation, a major driver of global climate variability on both millennial and orbital timescales (Broecker, 1998). In this context, the polar oceans are of major importance as they represent sensitive key locations of hydrographic activity within the system. The accurate reconstruction of the SST history is therefore essential for climate modelling (Rahmstorf, 2002). Yet, reliable high-latitude proxies for SST remain elusive.

The growing consensus on the reliability of biostatistical and geochemical SST proxies successfully utilized in the tropics (Rühlemann et al., 1999; Lea et al., 2003; Visser et al., 2003) contrasts markedly with their application in (sub-) polar oceans. The interpretation of  $\delta^{18}\text{O}$ -values in planktonic foraminiferal test calcite is complicated by the fact that seawater  $\delta^{18}\text{O}$  is altered significantly by frequent meltwater discharges related to the complex ice-sheet dynamics in this region (Jones and Keigwin, 1988). Moreover, planktonic foraminiferal Mg/Ca ratios show little response to temperature in the Nordic Seas (Meland et al., 2006). This is thought to be due to the difference in seawater carbonate chemistry specifically associated with Arctic and polar water masses. These regions are characterised by low salinities and annual sea ice cover. Alkenone proxies overestimate Last Glacial Maximum (LGM) temperatures for these



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regions (Rosell-Mele et al., 1999), possibly due to ice-rafted ancient alkenones masking the autochthonous biomarker signal (Weaver et al., 1999). Temperature overestimations are also a common problem in all transfer functions calculated from the near-monospecific assemblages found in polar regions (Pflaumann et al., 1996; Huber et al., 2000; Kucera et al., 2005). These inherent shortcomings highlight the need to develop complementary SST proxies for high latitude oceans, especially as they are known to act as pacemaker for glacial-interglacial climate dynamics (Sarnthein et al., 2001).

In high latitudes, left-coiling *Neogloboquadrina pachyderma* (*N. pachyderma* (sin.=sinistral)) dominates planktonic foraminiferal assemblages (Kucera et al., 2005; Pflaumann et al., 1996), especially at temperatures below 7–9°C (e.g. Bé and Tolderlund, 1971). Due to its preference for cold-water high-latitude settings on both hemispheres, *N. pachyderma* (sin.) constitutes the major ecological and geochemical proxy carrier in these cooler water environments of palaeoceanographic interest. Recently published phylogenetic studies, however, have revealed that the morphospecies *N. pachyderma* (sin.), in fact, represents several highly divergent genetic types (genotypes) over the Atlantic and Southern Ocean with different biogeographical distributions and environmental adaptations (Stewart et al., 2001; Darling et al., 2000, 2004, 2006). It could be shown that the North Atlantic Ocean is inhabited by one genotype (Type I) only, whereas the South Atlantic Ocean and the Southern Ocean represent the habitat of four different genotypes (Type II to V). It was shown by Bauch et al. (2003), who found apparent single species records of North Atlantic *N. pachyderma* (sin.) to contain a change in species concurrent with environmental change, that the understanding of genetic diversity could be important for precise palaeographic reconstructions. Therefore, current SST proxies based on *N. pachyderma* (sin.) might require reassessment or potential genetic diversity within proxy carrier species should be considered if new proxies are developed.

### 1.1 The temperature sensitivity of $\delta^{44/40}\text{Ca}$ in marine carbonates

Early investigations of Zhu and Macdougall (1998) indicated species-dependent variations in calcium isotopic composition in planktonic foraminifera potentially related to temperature. For cultured and field-collected specimens of the tropical foraminifer *Globigerinoides sacculifer* (*G. sacculifer*), the intra-species variability in  $\delta^{44/40}\text{Ca}$  of approximately 2‰ could be attributed to differences in ambient seawater temperature (Nägler et al., 2000; Hippler et al., 2006). Based on these findings, the species-specific temperature relationship of *G. sacculifer* has now been successfully quantified and applied as palaeothermometer in the eastern tropical Atlantic Ocean on glacial-interglacial timescale (Nägler et al., 2000; Hippler et al., 2006). Furthermore, it has been applied to a Caribbean Sea down-core record to reconstruct SST and

salinity changes in response to the Pliocene closure of the Central American Gateway (Gussone et al., 2004). Contrary to the latter findings, several studies have reported a small response of Ca isotopic composition to temperature. Gussone et al. (2003) and Griffith et al. (2008) exhibited a small temperature sensitivity of 0.02‰ per 1°C for cultured planktonic foraminifera *Orbulina universa*, and seven planktonic foraminifera species taken from core-top sediments, respectively. Moreover, Böhm et al. (2006) found the temperature sensitivity for cultured and open ocean scleractinian corals to be similar. These relationships are almost an order of magnitude lower than for *G. sacculifer*, but show strong similarities to the slope of temperature-related Ca isotope fractionation in inorganic calcite and aragonite precipitates (Gussone et al., 2003; Lemarchand et al., 2004; Marriott et al., 2004). The reason for this species-dependent bimodal behaviour is still inexplicit pointing to unique and species-related calcification processes, which might be the consequence of the species' adaptation to a specific ecological niche. The results of Sime et al. (2005) who analysed 12 species of planktonic foraminifera from core-top sediments, and Griffith et al. (2008) who also analysed four planktonic foraminifera species from a sediment trap, have further stimulated the discussion about the temperature sensitivity of  $\delta^{44/40}\text{Ca}$ , since these results showed a considerable amount of scatter and no consistent temperature-dependent fractionation. Both studies included *G. sacculifer*, though not *N. pachyderma* (sin.). The major conclusion of Sime et al. (2005) is that the theoretically expected relationship between the Ca enrichment factor and temperature can be obscured by, as yet, unquantified metabolic and physiological processes in nature. The modelling approach of Griffith et al. (2008), however, suggests that foraminiferal calcite is precipitated from an internal Ca reservoir, which is approximately –0.8‰ offset from seawater. Ca isotope fractionation by Rayleigh distillation from this biomineralization reservoir could likely explain their foraminiferal Ca isotope data. Nevertheless, recently, high-resolution in situ measurements of the Ca isotopic composition by ion microprobe revealed variations in  $\delta^{44/40}\text{Ca}$  of 1.7‰ within two single tests of 2.8 Ma old *Globorotalia inflata* from Shatsky Rise, ODP leg 198 (Rollion-Bard et al., 2007). They attributed the intra-test variations to several processes, such as ontogenetic effects, differences between primary and secondary calcite, and temperature. Hence, with respect to existing data, it is important to differentiate between foraminiferal records from cultures, plankton tows, sediment traps, core-tops and sediment cores, in order to extract the factors and processes (e.g. temperature, vital effects, seawater composition) influencing the Ca isotopic signature of foraminiferal tests.

Thus, the goal of this study is (1) to examine the Ca isotope fractionation in genotyped *N. pachyderma* (sin.) and to compare these results to Ca isotope data obtained from core-top samples of the same species by following two different analytical approaches, and (2) to investigate the potential of Ca

isotope signatures of *N. pachyderma* (sin.) as a complementary tool for multi-proxy SST reconstruction in high-latitude settings. This study should further improve the understanding of how species-dependent temperature sensitivity might be related to different biomineralization processes as a consequence of biological adaptation.

## 2 Material and methods

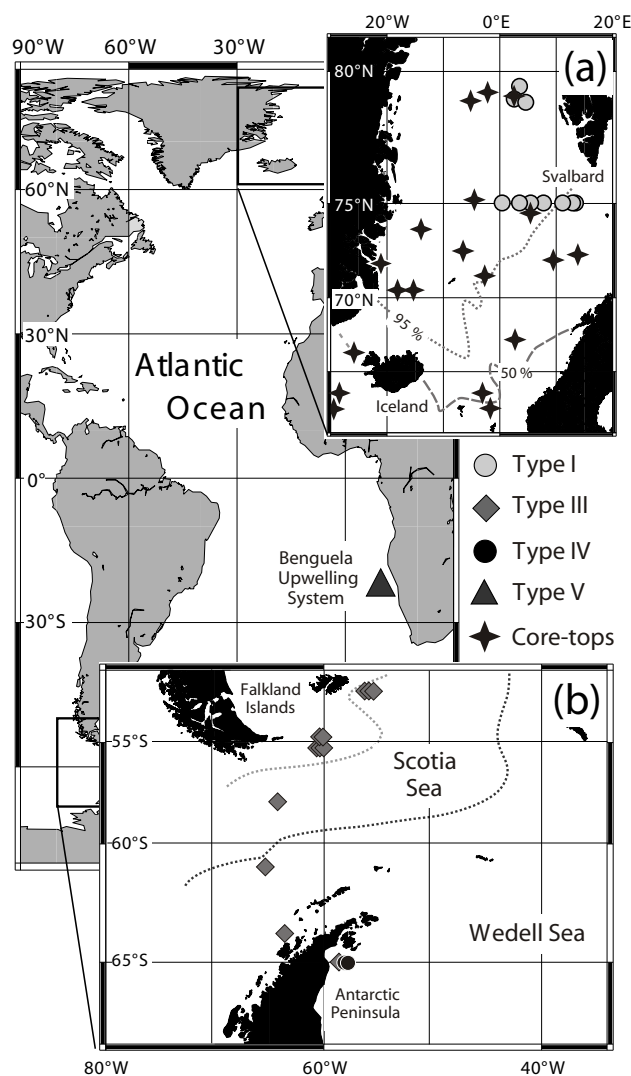
### 2.1 Sample locations and material

In this  $\delta^{44/40}\text{Ca}$ -temperature calibration study, we attempt to eliminate the genetically induced uncertainties by using genetically characterised individuals of *N. pachyderma* (sin.). Samples were collected in the northern North Atlantic at 75° N (from 13° W to 13° E). South Atlantic samples were collected along transects between the Falkland Islands (53°21' S, 58°20' W) and the Antarctic Peninsula (65°36' S, 77°39' W), and samples from the Benguela system were taken offshore Namibia (23° S) (Fig. 1). Samples were obtained either by pumping continually from the surface water layer (6 m, 63- $\mu\text{m}$  filter), or from vertical plankton tows ( $\leq 100$  m, 63  $\mu\text{m}$  mesh). Samples chosen for genetic determinations were taken from the 125–250  $\mu\text{m}$  size fraction. On-site SST and salinity data were obtained by CTD measurements and ranged between  $-1.0$  and  $14.0^\circ\text{C}$  and 32.5 and 35.0‰, respectively. For a more detailed description see Darling et al. (2004).

The study further involved core-top samples of *N. pachyderma* (sin.) from different stations in the Nordic Seas. Sampling sites represent the Norwegian Current, Arctic Domain and polar waters (Fig. 1a). Four of the core-tops included in this study belong to a group of adjacent core-tops ( $n=35$ ) that were dated by AMS  $^{14}\text{C}$  (compilation of all data in Simstich et al., 2003) and corrected for a  $^{14}\text{C}$  reservoir effect of 400 years (Bard et al., 1994) (Table 2). Most of these core-top dates ( $n=31$ ) are younger than 2500 years before present and can therefore be considered to represent modern conditions, assuming that the major hydrographic parameters in the Nordic seas did not change significantly over this time span (Koç et al., 1993, Sarnthein et al., 2001).

### 2.2 Core-top temperature estimates

High-latitude core top proxy calibrations are limited in their accuracy by several restrictions in “true” calcification temperature estimates, mainly caused by the lack of additional independent and robust temperature proxies in these regions. Recently, Nyland et al. (2006) have shown in a paired  $\delta^{18}\text{O}$  to Mg/Ca proxy approach applied to a sediment core collected in the Norwegian Sea that the  $\delta^{18}\text{O}$ -inferred temperatures are poorly correlated to Mg/Ca ratios, presumably due to short-term variations in  $\delta^{18}\text{O}$  water. Furthermore, the relationships between salinity and  $\delta^{18}\text{O}$  of seawater in



**Fig. 1.** Sampling localities of genotyped and core-top samples of left-coiling (sin.) *N. pachyderma*. Symbols are displayed in the legend, and remain the same in all following figures. Inlet (a): sampling localities of *N. pachyderma* (sin.) type I (grey circles) and of the core-top sites (stars) in the northern North Atlantic. The contours denote the sediment “core-top” coiling ratio (% left-coiling), delineating the modern *N. pachyderma* (sin.) provinces (Pflaumann et al., 1996). Inlet (b): sampling sites of *N. pachyderma* (sin.) type III (grey diamond) and type IV (black circle) in the subpolar/polar Antarctic Ocean. The contours delineate the approximate position of the Subantarctic Front (grey) and the Polar Front (black). The main map highlights the sampling site of *N. pachyderma* (sin.) type V (black triangles) from the Benguela upwelling system.

the central and eastern Nordic Seas is affected by a significant scatter at low salinities (Simstich, 1999; Simstich et al., 2003), disqualifying  $\delta^{18}\text{O}$ -derived temperatures as a robust reference for core top calibrations. In addition, Mg/Ca ratios derived from planktonic foraminifers of the Nordic Seas are surprisingly insensitive to temperature variations

(Meland et al., 2006). Hence, we found that core top calcification temperatures can be best described by modern hydrographic data (e.g. temperature, salinity), which, according to Koç et al. (1993) and Sarnthein et al. (2001), have not basically changed in the Nordic Seas over the last 2500 years. Average calcification depths were estimated using the  $\Delta\delta^{18}\text{O}$ -difference between shallow-dwelling *Turborotalita quinqueloba* and deeper-dwelling *N. pachyderma* (sin.):  $\Delta\text{depth [m]} = -86 + \Delta\delta^{18}\text{O} \times 300$  (Simstich, 1999). The corresponding temperature and salinity data for the months of July to September, which characterise the main planktonic bloom in this region (Kohfeld et al., 1996; Schröder-Ritzrau et al., 2001), were extracted from the hydrographic database “World Data Atlas 2001” (Conkright et al., 2002) using the software “Ocean Data View” (Schlitzer, 2007).

### 2.3 Molecular determinations

Living individuals of polar to subpolar planktonic foraminifera *N. pachyderma* (sin.) were selected for molecular determinations. DNA extraction, amplification by polymerase chain reaction (PCR), cloning and automated sequencing of a  $\sim 1000$ -b.p. region of terminal 3' end of the foraminiferal small subunit ribosomal RNA (SSU rRNA) gene were performed as described previously (Darling et al., 2000).

### 2.4 Ca isotope analysis

Ca isotope analyses on genetically characterised material were carried out on single tests of *N. pachyderma* (sin.) that were already dissolved in the course of the pre-treatment related to the molecular determination methods. An important advantage of the Ca isotope method applied in both laboratories is the ability to measure very small quantities of Ca (200–500 ng) (see below). This sensitivity allows replicate analyses of single tests and thus the innovative approach of performing genetic determination and Ca isotope analysis on the same individual. On the other hand, the analysis of Ca isotopes is a fairly time-consuming method with a limited sample throughput. Therefore, only two or three individuals could be chosen as representatives for a certain temperature. Concerning the core-top samples, approximately 60–80 hand-picked specimens in the 125 to 250  $\mu\text{m}$  size fraction were selected for isotopic analyses. In this approach, potential inter-individual differences become negligible. These tests were crushed between glass plates, cleaned using the Mg-cleaning protocol of Barker et al. (2003) and subsequently dissolved in ultrapure 2.5 N HCl.

Only the pre-treated genotyped samples were processed through ion chromatography. The dissolved samples were loaded onto one-way polyethylene microcolumns containing 10  $\mu\text{l}$  of AP-MP-50 ion exchange resin. The microcolumns have been pre-cleaned with Mili-Q® water, ammoniumacetate and 6 M HCl, and were subsequently conditioned with

1.5 M HCl. The chemical extraction procedure was exclusively based on 1.5 M HCl. The Ca fraction was collected in the second elution step, evaporated to dryness and re-dissolved in 2.5 M HCl for mass spectrometry. The procedure showed a  $>95\%$  yield on standard solutions and total procedural blanks were below 1 ng, thus have no effect on the isotopic data. Since genetically characterised samples were treated with an EDTA-buffer solution, it was essential that samples were treated with a  $\text{HNO}_3\text{-H}_2\text{O}_2$  solution prior to and after column chemistry to remove the residual organic compounds (Hippler, 2004).

Ca isotope analyses of genotyped samples were carried out on a modified single collector AVCO® thermal ionization mass spectrometer (TIMS) at the University of Bern (CH), following the method described in Nægler et al. (2000), Hippler (2004) and Hippler et al. (2006). Moreover, Ca isotope ratios of the core-top samples were determined on a Finnigan TRITON T1 TIMS at the IFM-GEOMAR, Kiel (D), following the method described in Heuser et al. (2002). Briefly, in both laboratories, after addition of a  $^{43}\text{Ca}\text{-}^{48}\text{Ca}$  double-spike of a precisely known Ca isotopic ratio to correct for isotopic fractionation occurring during the course of analysis, the cleaned and dissolved samples were loaded with a tantalum-based activator on outgassed zone-refined Re single filaments. Measurements on the single collector TIMS were made in peak jumping mode in descending sequence (masses 48, 44, 43, 40) and on the multi-collector TIMS in dynamic mode in two cycles, respectively. In each case, signal intensity during acquisition was 2–4 V (Bern) and 4–5 V (Kiel) for  $^{40}\text{Ca}$ . Ca isotope variations are expressed in the  $\delta$ -notation:  $\delta^{44/40}\text{Ca} [\text{‰}] = \left\{ \frac{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}}{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}}} - 1 \right\} \times 1000$ , where the standard is NIST SRM 915a (Hippler et al., 2003; Eisenhauer et al., 2004). Throughout the analysis period, standard measurements of an in-house  $\text{CaF}_2$  standard and the  $\text{CaCO}_3$  standard NIST SRM 915a were performed. A detailed compilation of various reference materials is available (Hippler et al., 2003). Both laboratories achieve a long-term analytical reproducibility of the standard  $\delta^{44/40}\text{Ca}$  in the order of 0.2‰ ( $2\sigma$ ). The  $2\sigma$  standard deviation of replicate analyses was even lower.

## 3 Results

### 3.1 The Ca isotopic composition of genotyped and core-top samples

The  $\delta^{44/40}\text{Ca} [\text{‰}]$  values of *N. pachyderma* (sin.) varied between  $-0.12$  and  $1.07$  in Arctic specimens (Type I), and between  $0.17$  and  $1.05$  in Antarctic specimens (Type III, IV). Samples of the Benguela system (Type V) yielded values near  $1.75$ . Core-top  $\delta^{44/40}\text{Ca} [\text{‰}]$  values of *N. pachyderma* (sin.) ranged from  $0.36$  to  $1.05$ . All Ca isotopic data are presented in Tables 1 and 2. The overall intra-species variability

**Table 1.** Calcium isotopic composition of genotyped *N. pachyderma* (sin.).

Northern Atlantic Ocean, Polarstern (ARK XV/1, 1999)									
Station	No.	Latitude [° N]	Longitude [° E/W]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
A5	3	79 3.73	4 17.08 E	Type I	33.5	1	0.51	0.13	2
	4	79 3.73	4 17.08 E	Type I	33.5	1	0.67	0.2	1
B5	1	79 7.14	2 31.00 E	Type I	33.4	2	0.04	0.19	1
	2	79 7.14	2 31.00 E	Type I	33.4	2	-0.01	0.16	1
C5	3	79 7.14	2 31.00 E	Type I	33.4	2	-0.04	0.21	1
	4	79 7.14	2 31.00 E	Type I	33.4	2	-0.12	0.18	1
D5	1	79 28.15	2 59.71 E	Type I	33.7	2	-0.04	0.19	1
F5	2	74 59.49	12 44.72 W	Type I	32.7	2.5	0.27	0.13	1
	3	74 59.49	12 44.72 W	Type I	32.7	2.5	0.36	0.3	1
H5	3	75 0.08	7 23.80 W	Type I	34.8	4	0.45	0.23	1
I5	2	75 0.84	3 33.82 W	Type I	34.8	4	0.54	0.22	1
J5	2	75 0.21	0 22.17 E	Type I	34.7	3.5	0.14	0.2	2
K5	5	75 1.06	5 9.05 E	Type I	35	6.5	1.07	0.24	1
L5	1	74 59.66	10 37.25 E	Type I	35.1	6.5	1.07	0.2	1
M5	1	75 0.39	12 33.57 E	Type I	35	6	0.87	0.18	1
Southern Atlantic Ocean, British Antarctic Survey James Clark Ross (JR 48, 2000)									
Station	No.	Latitude [° S]	Longitude [° W]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
8	69	54°81'	60°53'	Type III	34.1	7	0.89	0.25	1
	71	54°81'	60°53'	Type III	34.1	7	1.05	0.16	1
10	121	55°22'	60°79'	Type III	33.9	6	0.88	0.25	1
	129	55°22'	60°79'	Type III	33.9	6	0.92	0.08	2
13	165	57°98'	64°31'	Type III	33.9	4	0.53	0.24	1
17	223	61°00'	65°32'	Type III	33.7	3.5	0.47	0.2	1
23	265	63°92'	63°74'	Type III	33.7	2	0.17	0.3	1
30	297	62°63'	58°45'	Type III	34.3	2.5	0.27	0.3	1
36	309	64°74'	59°61'	Type IV	32.4	0	0.67	0.19	1
	313	64°74'	59°61'	Type IV	32.4	0	0.57	0.21	1
85	321	64°74'	59°61'	Type III	32.4	0	0.52	0.14	1
	649	52°21'	56°75'	Type III	34	8.5	0.80	0.01	2
	651	52°21'	56°75'	Type III	34	8.5	0.91	0.15	1
Benguela System (offshore Namibia), RV Welwitscha (2001)									
Station	No.	Latitude [° S]	Longitude [° E]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
10	13	23	14 13.26	Type V	35	13.5	1.67	0.22	1
	23	23	14 23.26	Type V	35	13.5	1.79	0.26	1
20	35	23	14 02.45	Type V	35	14	1.85	0.29	1

<sup>a</sup> $\delta^{44/40}\text{Ca}$  values are given in [‰] relative to NIST SRM 915a. Samples were collected either by pumping continually from the surface water layer (6 m, 63- $\mu\text{m}$  filter) or from vertical plankton tows ( $\leq 100$  m, 63  $\mu\text{m}$  mesh).

in  $\delta^{44/40}\text{Ca}$  of 1.2‰ was six times the uncertainty of the measurements and clearly demonstrated that the Ca isotopic composition of *N. pachyderma* (sin.) is not unique. Given the observations that Ca isotopic composition of seawater is homogeneous throughout modern oceans (Zhu and Mac-

dougall, 1998; Schmitt et al., 2001; Hippler et al., 2003), due to the residence of Ca in the ocean ( $\tau=1$  Ma), which is long in comparison to the ocean mixing time of approximately 1500 years, these variations do not reflect regional differences in seawater Ca isotopic composition. Small-scale

**Table 2.** Calcium isotopic composition of *N. pachyderma* (sin.) from Holocene core-tops, Nordic Seas.

Nordic Seas (Norwegian Current) core tops samples										
Core <sup>a</sup>	Latitude [° N]	Longitude [° E/W]	Water depth [m]	$\Delta\delta^{18}\text{O}_{\text{Nps-}}\text{-}$ quinqueloba <sup>b</sup>	Inferred depth [m] <sup>b</sup>	SAL [‰] <sup>c</sup>	SST [°C] <sup>c</sup>	$\delta^{44/40}\text{Ca}$ [‰] <sup>d</sup>	<i>n</i> <sup>e</sup>	2SEM <sup>f</sup>
23071-1	67 04.80	2 54.60 E	1306	0.53	150–200 m	35.1	6.1	0.64	11	0.11
23259-3	72 01.20	9 18.00 E	2518	0.66	150–200 m	35.1	4.8	0.65	4	0.03
23261-2	72 10.80	13 06.60 E	1667	0.44	100–150 m	35.0	5.1	0.54	4	0.21
23514-3	66 40.20	25 57.00 W	713	−0.05	0–50 m	33.8	4.8	0.55	2	0.14
23523-3	62 15.00	30 13.20 W	2156	1.88	>250 m	35.1	6.3	1.05	2	0.16
23528-3	63 09.60	28 50.40 W	1632	1.79	>250 m	35.0	6.4	0.63	2	0.11
23538-1	62 00.60	2 10.20 W	1667	1.32	>250 m	35.2	7.1	0.87	7	0.39
23540-2	62 46.20	2 30.60 W	1126	1.19	>250 m	35.1	5.8	0.60	4	0.04
HM94-12	71 19.20	3 33.00 W	1816	0.63*	150–200 m	35.0	2.4	0.36	2	0.09
HM94-18	74 30.00	5 42.00 W	2469	0.52*	150–200 m	35.0	4.0	0.48	3	0.20
Nordic Seas (Arctic Domain and polar waters) core top samples										
23231-2	78 54.00	3 59.40 W	1979	0.17	0–50 m	34.0	0.2	0.43	2	0.23
23232-1	79 01.80	1 37.20 W	2642	0.64	150–200 m	34.9	1.1	0.44	2	0.03
23235-1	78 52.20	1 23.40 E	2500	0.24	50–100 m	34.7	1.5	0.46	4	0.06
23347-4	70 26.40	16 04.80 W	1375	−0.05	0–50 m	33.8	1.4	0.53	3	0.02
23348-2	70 25.20	18 57.00 W	737	−0.33	0–50 m	33.3	0.5	0.56	2	0.13
23506-1	72 23.40	7 36.00 W	2670	0.15	0–50 m	34.2	2.3	0.46	2	0.16
23509-1	73 49.80	13 30.00 W	2576	0.11	0–50 m	33.2	0.6	0.50	6	0.08
23549-9	75 03.60	4 36.00 W	3624	−0.05	0–50 m	34.1	1.6	0.47	2	0.27
PS2638-6	72 05.40	22 45.00 W	428	–	0–50 m	31.7	−1.0	0.44	3	0.08

<sup>a</sup> Source: see references (Meland et al., 2006 and Simstich et al., 2003). <sup>b</sup> Average calcification depths are estimated using the  $\delta^{18}\text{O}$ -difference between shallow-dwelling *T. quinqueloba* and deep-dwelling *N. pachyderma* (sin.):  $\Delta\text{depth} = -86 + \Delta\delta^{18}\text{O} * 300$  following the study of Simstich (1999). Negative values are set to 0–50 m. \*  $\Delta\delta^{18}\text{O}_{\text{Nps}}$  ratios from adjacent cores 23 277 and 23 254, see (Simstich et al., 2003). <sup>c</sup> Summer salinities and SSTs are averaged using depth corresponding hydrographic data from July–September (main planktonic bloom in the Nordic Seas (Kohfeld et al., 1996)) from the World Ocean Atlas, NOAA, 2001 ([http://www.nodc.noaa.gov/OC5/WOA01/pr\\_woa01.html](http://www.nodc.noaa.gov/OC5/WOA01/pr_woa01.html)). <sup>d</sup>  $\delta^{44/40}\text{Ca}$  values are given in [‰] relative to NIST SRM 915a. <sup>e</sup> Number of repeated measurements of each sample. <sup>f</sup>  $2\text{SEM} = 2\sigma/n^{0.5}$ .

variations of seawater Ca isotopic composition observed in the Early Pleistocene and Late Pliocene of  $\pm 0.2\text{‰}$  compared to the modern seawater value (Fantle and DePaolo, 2005; Heuser et al., 2005; Sime et al., 2007) are within the analytical uncertainty and therefore negligible for the purpose of this study.

As mentioned before, the morphospecies *N. pachyderma* (sin.) could have been subdivided in five highly divergent genotypes, which appear to be adapted to certain environmental conditions (Fig. 1). In order to evaluate whether the magnitude of Ca isotope fractionation varies between genotypes of the same morphotype, the Ca isotopic compositions of all genotyped samples were compared to each other (Fig. 2). This figure clearly indicates that the Ca isotopic composition is not related to a certain genotype. Particularly, the respective mean  $\delta^{44/40}\text{Ca}$ -values for genotypes I, III and IV, representing temperatures between 0 and 8.5°C, are within uncertainties indistinguishable from each other. In addition, the large and similar intra-genotype variability

in  $\delta^{44/40}\text{Ca}$  of type I (net catches and core-tops) and type III emphasizes that the Ca isotopic composition has to be independent from the genotype, but has been likely influenced by an additional, environmental factor. Type V has not been included in the comparison of the mean  $\delta^{44/40}\text{Ca}$ -values, since the samples from the Benguela upwelling region represent mid-latitude environmental conditions, with particularly much higher temperatures, which significantly differ from the high-latitude temperatures, characterising the other samples.

### 3.2 The $\delta^{44/40}\text{Ca}$ -temperature relationship of genotyped samples

We observed that the Ca isotopic composition of most genotyped samples of *N. pachyderma* (sin.), representing SSTs between 2 and 15°C, is steadily increasing towards higher temperatures (Fig. 3). This positive correlation, thus including samples of genotype I, III and V, was defined by linear

regression using the comprehensive statistics software package for quantitative data analysis SPSS 12:

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.15(\pm 0.01) \times \text{SST}[\text{°C}] - 0.15(\pm 0.06)$$

$$r = 0.956, N = 26 \text{ (Type I, III, V, SST} \geq 2\text{°C)}, p < 0.001 \quad (1)$$

Only the Ca isotopic composition of five genotyped samples did not show a considerable response to their respective SSTs and would plot offset from the latter linear regression line (Eq. 1). These samples, however, originate from polar waters, which are characterized by temperatures below  $2.0 \pm 0.5\text{°C}$  and salinities below  $33.0 \pm 0.5\text{‰}$ , and are herein after referred to as samples collected at the “cold-fresh-end”.

Given the apparent threshold temperature of  $2.0 \pm 0.5\text{°C}$  and the genetic diversity of the morphospecies *N. pachyderma* (sin.), the temperature-dependent Ca isotope fractionation was further assessed separately for genotype I and III. The quantity of samples of genotype IV ( $N=2$ ) and V ( $N=3$ ) was too small to evaluate their temperature sensitivity to the same degree.

For modern specimens of *N. pachyderma* (sin.) of the northern North Atlantic (Type I) sampled from the water column, the  $\delta^{44/40}\text{Ca}$ -temperature relationship can be therefore expressed as follows,

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.23(\pm 0.02) * \text{SST}[\text{°C}] - 0.45(\pm 0.08)$$

$$r = 0.963, N = 13 \text{ (Type I, SST} \geq 2\text{°C)}, p < 0.001 \quad (2)$$

and for high-latitude South Atlantic specimens of *N. pachyderma* (sin.) (Type III), it can be expressed as

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.12(\pm 0.02) * \text{SST}[\text{°C}] + 0.06(\pm 0.12)$$

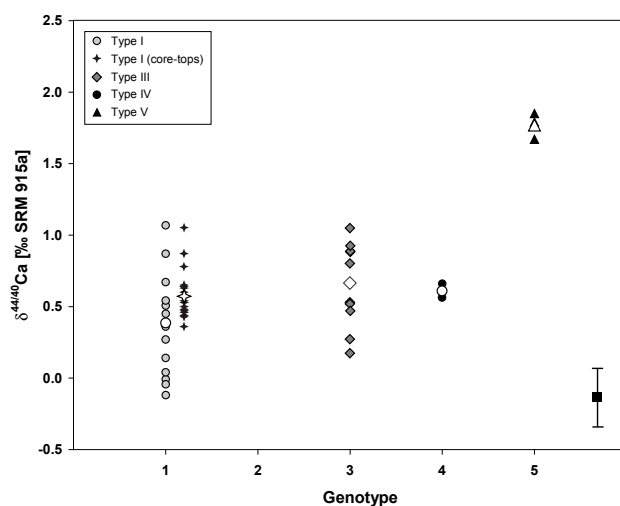
$$r = 0.891, N = 10 \text{ (Type III, SST} \geq 2\text{°C)}, p = 0.001 \quad (3)$$

To date, the determination of the foraminiferal genotype is restricted to living organisms. However, down-core studies are based on fossil material, which could be determined only on the morphospecies level. In consideration of the fact that it would be desirable to develop a morphospecies-based  $\delta^{44/40}\text{Ca}$ -thermometer for high-latitude SST reconstructions, which would be valid down to temperatures of  $2.0 \pm 0.5\text{°C}$ , we further determined the  $\delta^{44/40}\text{Ca}$ -temperature relationship for pooled high-latitude specimens from both hemispheres.

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.17(\pm 0.02) * \text{SST}[\text{°C}] - 0.22(\pm 0.08)$$

$$r = 0.911, N = 23 \text{ (Type I, III, SST} \geq 2\text{°C)}, p < 0.001 \quad (4)$$

Here, the three specimens from the Benguela system are purposely excluded, since they depict a rather small set of samples and might represent different water mass properties (nutrients, carbonate ion concentration) of a mid-latitude setting. Including samples of genotype IV in the calculation



**Fig. 2.** Genotypes of *N. pachyderma* (sin.) plotted vs. Ca isotope composition showing that genotype has a no considerable effect on  $\delta^{44/40}\text{Ca}$ . The mean  $\delta^{44/40}\text{Ca}$  values for each genotype are presented as open symbols. Note that within uncertainties, the mean  $\delta^{44/40}\text{Ca}$  values for genotype I, III and IV are indistinguishable from each other. The uncertainty on the  $\delta^{44/40}\text{Ca}$  values is given in the right corner.

would comply with Eq. (1), highlighting that the two regressions are in overall agreement within calculated uncertainties.

### 3.3 Core-top $\delta^{44/40}\text{Ca}$ -temperature relationship

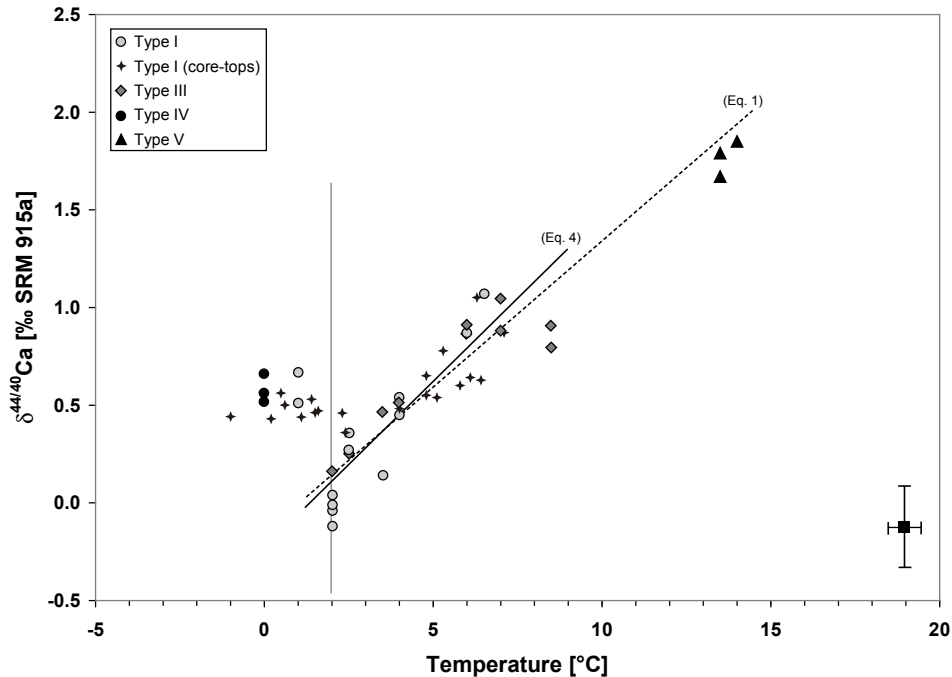
Similar to genotyped foraminiferal tests sampled in the water column, the Ca isotopic composition of core-top *N. pachyderma* (sin.) samples is positively correlated to their corresponding estimated calcification temperatures ( $T_{\text{WOA}}$ ). The temperature sensitivity, defined by linear regression, however, is much weaker than for genotyped samples.

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.05(\pm 0.01) * \text{SST}[\text{°C}] + 0.42(\pm 0.05)$$

$$r = 0.703, N = 19, p = 0.001 \quad (5)$$

Based on the studies of Darling et al. (2000, 2004) we can assume that Holocene core-top specimens of *N. pachyderma* (sin.) collected from the North Atlantic Ocean represent only one genotype, which in turn implies that the inter-sample variability in Ca isotopic composition can not be biased by genetic reasons. As mentioned in 2.1, however, the overall core-top sample set consists of samples collected in the Norwegian Current and in the Arctic Domain, two sites that are characterized by different water mass properties (Weinelt et al., 2001; Simstich et al., 2003). Therefore, the temperature sensitivity was re-assessed separately.

Samples from the Norwegian Current with corresponding estimated temperatures ( $T_{\text{WOA}}$ ) ranging from 2.5 to 7.0



**Fig. 3.** The Ca isotope composition of genotyped and core-top specimens of *N. pachyderma* (sin.) in relation to their corresponding seawater temperatures. Symbols are displayed in the legend in the left corner. Note that for most genotyped and core-top samples, particularly from open marine settings,  $\delta^{44/40}\text{Ca}$  values increase with increasing temperatures. The black line represents the  $\delta^{44/40}\text{Ca}$ -temperature relationship for the morphospecies *N. pachyderma* (sin.), with a temperature gradient of  $0.17\text{‰}/^\circ\text{C}$  (Eq. 4). The dashed line represents the  $\delta^{44/40}\text{Ca}$ -temperature relationship, including samples of type V from a mid-latitude setting (Benguela; Eq. 1), which is within errors indistinguishable from Eq. 4. Only the samples left of the grey perpendicular line, representing samples from the “cold-fresh-end”, which is characterised by  $T=2.0\pm 0.5^\circ\text{C}$  and  $\text{SAL}=33.0\pm 0.5\text{‰}$  show no considerable relationship with temperature. The uncertainty on the  $\delta^{44/40}\text{Ca}$  values and temperature (the latter for samples from surface waters) is given in the right corner.

( $\pm 1.0$ ) $^\circ\text{C}$  showed a stronger temperature sensitivity in their Ca isotope fractionation.

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.11(\pm 0.03) * \text{SST} [^\circ\text{C}] + 0.06(\pm 0.17)$$

$$r = 0.774, N = 10, p = 0.009 \quad (6)$$

In contrast,  $\delta^{44/40}\text{Ca}$ -values of core-top samples originated from polar and Arctic Domain waters, characterised by temperatures below  $2.0\pm 0.5^\circ\text{C}$  and/or salinities  $< 33.0\pm 0.5\text{‰}$ , are not related to ambient seawater temperature. This is shown in the slope of the respective linear regression, which is not significantly different from 0:

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.01(\pm 0.02) * \text{SST} [^\circ\text{C}] + 0.47(\pm 0.02)$$

$$r = 0.126, N = 9, p = 0.75 \quad (7)$$

The fact that Ca isotope fractionation appears to behave different in these extreme environments is further clarified by applying Eq. (4), to the Ca isotope ratios of the core-top samples. For the Norwegian Current core-top samples the calculated temperatures ( $T_{\delta^{44/40}\text{Ca}}$ ) are found to be within uncertainties similar to the local temperatures ( $T_{\text{WOA}}$ ). In contrast,

calculated temperatures based on the  $\delta^{44/40}\text{Ca}$ -ratios of polar and Arctic Domain core-tops ( $T_{\delta^{44/40}\text{Ca}}$ ) would overestimate local temperatures ( $T_{\text{WOA}}$ ) as far as  $4^\circ\text{C}$ . Our data indicate that the breakdown of the  $\delta^{44/40}\text{Ca}$ -temperature relationship is likely restricted to these extreme low-temperature and low-salinity environments.

#### 4 Discussion

Our approach to study the Ca isotopic composition of *N. pachyderma* (sin.) in relation to SST indicates that it is important to account both for the collection depth within the water column (plankton tow sampling vs. core-top sampling), as well as for the hydrography at the collection site (high-latitude sites vs. extreme “cold-fresh” sites (e.g. Arctic Domain)). Particularly, the attempt to assess the overall data, as pooled and independent data sets, might shed light in the complexity of Ca isotope fractionation in foraminiferal calcite. Accordingly, the latter approach allows exploring if genotyped samples taken from the surface water column are really recording the same signal as the core-top samples or whether any superficial relationship (e.g. the  $\delta^{44/40}\text{Ca}$ -



temperature relationship) is muted in between the surface water column and the seafloor.

#### 4.1 Genetic coherences

The determination of the genotype and  $\delta^{44/40}\text{Ca}$  on the same test of *N. pachyderma* (sin.) provides direct evidence that genotype has a negligible influence on the temperature sensitivity of Ca isotope fractionation. Albeit the slope of the  $\delta^{44/40}\text{Ca}$ -temperature regression of Type I samples appears slightly steeper than the slope of the  $\delta^{44/40}\text{Ca}$ -temperature regression based on Type III samples, the temperature-sensitivity for both genotypes is best described by Eq. (4). Within the calculated uncertainties, the extrapolation of the relationship, up to 15°C, also covers the samples of the mid-latitude Benguela genotype. The interpretation of  $\delta^{44/40}\text{Ca}$ -values of the two Type IV samples in relation to SST is unlike ambiguous. First, the two samples represent the same temperature (below 1°C) and second, this genotype has only been found in extreme cool environments, including sea ice (Darling et al., 2004). Therefore these samples clearly belong to the “cold-fresh-end”. Thus, whether the insignificant temperature response is a direct genotype effect, is rather unlikely.

The most significant consequence of the genotype-independency is the global validity of the  $\delta^{44/40}\text{Ca}$ -temperature calibration for down-core studies in non-extreme environments, where sample classifications can only be carried out on the morphospecies level. Thus, even if there would be more than one genotype in the Arctic realm, genotype differences or shifts would have no or only a negligible impact on temperature reconstructions from core-top or down-core studies.

#### 4.2 Preservation of test material

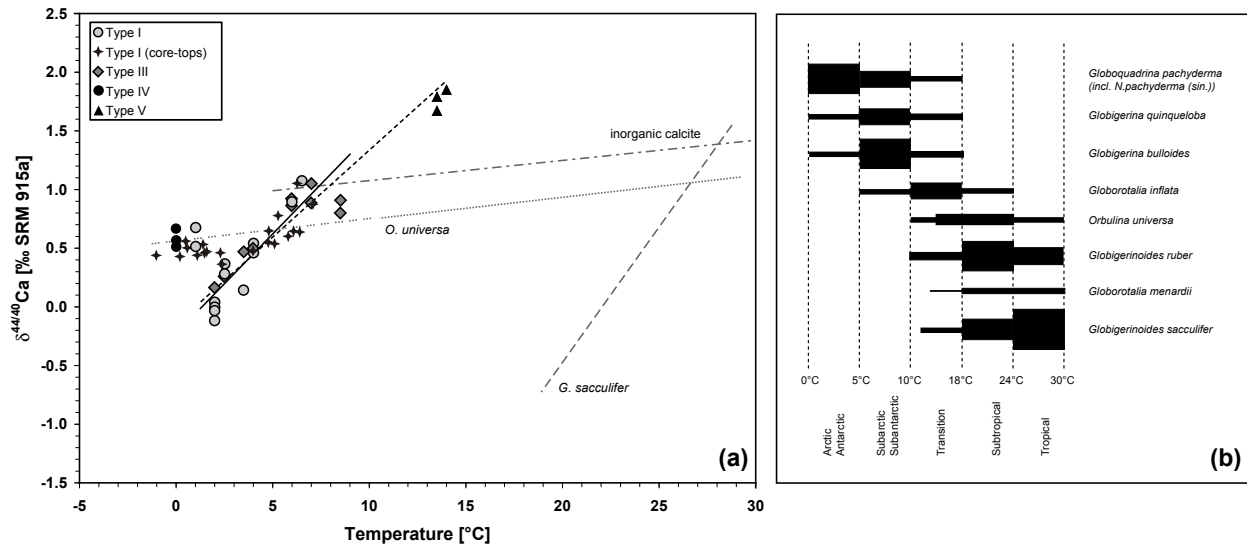
In contrast to pristine genotyped foraminifer tests, core-top tests could incorporate secondary information since they could have been exposed to post-dying or post-depositional processes. The consistency of  $T_{\text{WOA}}$  and  $T_{\delta^{44/40}\text{Ca}}$  of core-top test samples from the Norwegian Current confirms that the Ca isotopic composition of foraminiferal calcite is well preserved in these samples and records the primary temperature signal. Particularly crucial for the fossil record, our findings support earlier observations on the preservation potential of *N. pachyderma* (sin.). Investigating foraminiferal distribution and ecology, Martinez et al. (1998) found *N. pachyderma* (sin.) resistant to dissolution. Further evidence of primary signal retention is provided by partial dissolution experiments performed on tests of *N. pachyderma* (sin.) demonstrating that the degree of dissolution has no significant impact on the  $\delta^{44/40}\text{Ca}$  values (Hönisch et al., 2002).

#### 4.3 Calcification depth vs. sea surface temperature

Most observations suggest that *N. pachyderma* (sin.) calcifies at depth similar to other morphospecies used as recorders of SST. There is a general consensus that the vertical distribution of *N. pachyderma* (sin.) is related to local hydrography. An early study of the depth habitat of *N. pachyderma* (sin.) demonstrated that it lives above 100 m depth north of 83°N in the Arctic Ocean (Carstens and Wefer, 1992). Peak abundances of *N. pachyderma* (sin.) were observed in the surface 20–80 m in the Northeast Water Polynya (East Greenland Current), in conjunction with the chlorophyll maximum zone (Kohfeld et al., 1996), which is in agreement with  $\delta^{18}\text{O}$  signatures suggesting that *N. pachyderma* (sin.) calcifies in the upper 25 m of the water column offshore Greenland (Simstich, 1999). The assumption of a depth habitat by proxy is the inherent weakness in core-top calibrations where summer SSTs for the respective core locations are calculated using estimated calcification depths. Furthermore, core-top calibrations suffer from the sites' natural variability integrated over several hundred years. In order to minimise these uncertainties, the average calcification depths were calculated by an independent approach according to the findings of Simstich (1999). The author reported that the  $\Delta\delta^{18}\text{O}$ -difference between shallow-dwelling *Turborotalita quinqueloba* and deeper-dwelling *N. pachyderma* (sin.) can be converted to calcification depth estimates that closely resemble data from high latitudes plankton tow studies (Table 2). Subsequently, empirical data from the World Ocean Atlas 2001 (Conkright et al., 2002) for the calculated water depths were used as reference temperatures for the core top  $\delta^{44/40}\text{Ca}$ -temperature calibration. The recalculation of calcification temperatures of core-top specimens of *N. pachyderma* (sin.) by using the  $\delta^{44/40}\text{Ca}$ -temperature relationship based on genotyped specimens (Eq. (4)), independently reassesses these estimated calcification temperatures and provides strong evidence that they are within the correct range.

#### 4.4 Interspecies comparison of genotyped *N. pachyderma* (sin.)

The observed  $\delta^{44/40}\text{Ca}$ -temperature sensitivity of genotyped *N. pachyderma* (sin.) collected from surface waters is similar to the one recently reported for modern specimens of planktonic foraminifera *G. sacculifer* (Hippler et al., 2006) (Fig. 3), which has been successfully applied to down core records in the eastern tropical Atlantic (Hippler et al., 2006) and in the Caribbean Sea (Gussone et al., 2004) to reconstruct temperature and salinity changes on two different geological timescales (Pleistocene and Paleogene). The respective trendlines of the temperature sensitivity, however, are significantly offset (Fig. 4a), which emphasise the importance of species-specific calibrations for absolute temperature reconstruction. These findings render potential evidence that biocalcification in these two species is related to comparable



**Fig. 4.** Comparison of the temperature sensitivity between three planktonic foraminifera species, *N. pachyderma* ((sin.); Eqs. 1 and 4 of this study), *G. sacculifer* (Hippler et al., 2006), *O. universa* (Gussone et al., 2003) and inorganic calcite (Marriott et al., 2004) obtained in systematic calibration studies (a), and foraminifera preferred sea surface temperature habitats (b). Width of lines indicates relative abundance (modified from Boersma, 1978). Note, that samples from the “cold-fresh-end” appear to fall on the *O. universa*- $\delta^{44/40}\text{Ca}$ -temperature relationship extrapolated to lower temperatures.

biochemical mechanisms controlling Ca isotope fractionation.

Although *N. pachyderma* (sin.) and *G. sacculifer* have different ecologies demonstrated particularly in opposite temperature preferences (Zaric et al., 2005), the occurrence of both species is restricted to narrow temperature habitats (Fig. 4b). According to the SST ranges of some contemporary planktonic foraminifera, illustrating their preferred temperature habitat, *N. pachyderma* (sin.) shows highest relative abundances at the lower temperature limit, corresponding to high-latitude environments, whereas *G. sacculifer* represents the upper temperature limit characteristic for tropical environments. The species’ adaptation and specialization to either the lower (cold-end) or the upper temperature limit (warm-end) might explain the development of similar calcification strategies. In order to unravel the yet speculative causes and links of these observations, more elaborated studies, involving geochemists and microbiologists are required.

#### 4.5 Interspecies comparison of core-top *N. pachyderma* (sin.)

The interpretation of the  $\delta^{44/40}\text{Ca}$ -temperature sensitivity of *N. pachyderma* (sin.) collected from core-tops, in contrast, appears ambiguous. First, the  $\delta^{44/40}\text{Ca}$ -temperature dependence of core-top samples collected from the Norwegian Current (Eq. 6), with a slope of 0.11‰ per °C, is similar to the one observed for the morphospecies *N. pachyderma* (sin.) (Eq. 4). However, specimens collected from the Arctic Domain and polar waters appear insensitive to ambient

temperatures. These samples from the “cold-fresh-end” tend to fall on the *O. universa*- $\delta^{44/40}\text{Ca}$ -temperature relationship of Gussone et al. (2003), extrapolated to lower temperatures (Fig. 4).

Most planktonic foraminifera species studied so far, dwelling in subpolar to subtropical temperate waters, exhibit a shallow slope for their temperature sensitivity (e.g. Gussone et al., 2003; Heuser et al., 2005; Sime et al., 2005, 2007; Griffith et al., 2008). A detailed study on the temperature sensitivity of cultured *Orbulina universa* resulted in a temperature gradient one-order-of-magnitude smaller than that of *N. pachyderma* (sin.) and *G. sacculifer* (Gussone et al., 2003) but similar to the gradient observed for inorganic precipitates. According to the latter authors, foraminiferal species could be divided in two distinct groups using different calcification mechanisms. The different Ca fractionation behaviour has been explained by different modes of Ca transport to the site of calcification, either as hydrated  $\text{Ca}^{2+}$  ions in the case of *O. universa* or as dehydrated  $\text{Ca}^{2+}$  ions in the case of *G. sacculifer*. Another theory favoured equilibrium dynamics for Ca isotope fractionation, which is based solely on the results obtained for inorganic calcite precipitates (Marriott et al., 2004). These authors attributed the similarity of Ca isotope fractionation in inorganic precipitates and *O. universa* to similar equilibrium processes. The stronger temperature dependence of *G. sacculifer* was interpreted as the result of superimposed additional biological fractionation effects assuming different biomineralization processes for both species.

The temperature sensitivity of Ca isotopes has also been investigated in other important proxy carriers (e.g. coccoliths and corals). Gussone et al. (2006) studied the cellular calcium pathways and isotope fractionation in *Emiliana huxleyi*. They concluded that the main factor influencing Ca isotopes in coccoliths is the isotopic composition of seawater. The second parameter that affects Ca isotope fractionation ( $\delta^{44/40}\text{Ca}$ ) is temperature, with a sensitivity of 0.027‰ per °C. They further suggested that small variations in Ca isotopic composition of coccoliths might be introduced by changes in ambient  $[\text{CO}_3^{2-}]$  or  $p\text{CO}_2$ , which can be neglected for palaeoceanographic reconstruction purposes. Studying cultured and open ocean scleractinian corals, Böhm et al. (2006) found coral Ca isotope composition positively correlated to temperature, with the temperature sensitivity similar to that of inorganic aragonite. However,  $\delta^{44/40}\text{Ca}$  of the coral aragonite was significantly offset from inorganic aragonite, which was explained by biologically induced fractionation, as corals actively transport calcium to the site of calcification.

Insensitivity of Ca isotope fractionation to temperature was recently reported for 12 species of planktonic foraminiferal species collected from core-top sediments (Sime et al., 2005). *N. pachyderma* (sin.) was not included in their study. The authors concluded that any temperature relationship is obscured by yet “unquantified metabolic and physiological processes in nature”. Samples were collected from a suite of box-cores from site between 60° N and 30° S in the North Atlantic and the West Indian oceans. SSTs ranging from 9 to 27°C were inferred from  $\delta^{18}\text{O}_{\text{calcite}}$  values of the tests and estimated  $\delta^{18}\text{O}_{\text{seawater}}$  values for the respective core locations, and therefore incorporate a higher degree of uncertainty ( $\pm 2^\circ\text{C}$ ). Given the broad temperature range, the interspecies variability in  $\delta^{44/42}\text{Ca}$  of 0.6‰ obtained by MC-ICP-MS, as well as the minor intra-species variability of  $\leq 0.1\%$  (e.g. *O. universa*, *G. sacculifer* and *G. inflata*), could not be attributed to inferred SSTs.

Recently, the core-top planktonic foraminifera samples of Griffith et al. (2008) collectively exhibited a temperature-dependent fractionation of 0.013‰ per °C, which is in agreement with already discussed and published estimates for most species of planktonic foraminifera obtained from core-tops, as well as for biogenic and inorganic calcite and aragonite. Sediment trap data, which were also included in their study showed a considerable amount of scatter resulting in no consistent temperature dependent fractionation. Griffith et al. (2008) thus proposed that likely other factors than temperature likely influence Ca isotope fractionation in planktonic foraminifera samples collected at shallow depth in the water column. In order to constrain the isotopic composition of the original biomineralization Ca reservoir, the latter authors run a one-box model, in which Ca was allowed to fractionate by Rayleigh distillation from an internal Ca pool. This model indicates that the Ca isotopic composition of the biomineralization reservoir was offset from seawater by approximately

–0.8‰, which explains most of the foraminiferal Ca isotope data.

Unexpectedly, their findings are inconsistent with recent studies on *G. sacculifer*, for which a strong temperature response has been reported in cultures, catches and sediments (Nägler et al., 2000; Hippler et al., 2006). Further evidence for the temperature sensitivity of Ca isotope fractionation comes also from ODP site 999 in the Caribbean Sea (Gussone et al., 2004) and from the western equatorial Pacific box core ERDC92 (2° 13.5' S, 156° 59.9' E Java plateau) (Zhu and Macdougall, 1998), the latter reporting a difference in  $\delta^{44/40}\text{Ca}$  of 0.6‰ between Holocene and Last Glacial Maximum (LGM) tests of *G. sacculifer*. Applying the  $\delta^{44/40}\text{Ca}$ -temperature calibration based on *G. sacculifer* (Hippler et al., 2006) this value would correspond to a temperature change of  $2.7 \pm 0.6^\circ\text{C}$  between the LGM and the Holocene. Furthermore, a consistent SST change for this period of  $2.8 \pm 0.7^\circ\text{C}$  has been estimated for the equatorial Pacific (including data from Ontong Java plateau ODP core 806B at 0° 19.1' N, 159° 21.7' E) based on Mg/Ca ratios in foraminifera (Lea et al., 2000) rendering strong support for a preserved temperature signal in the *G. sacculifer* data (Zhu and Macdougall, 1998).

The reasons for these contrasting Ca isotope fractionation patterns observed in different planktonic foraminiferal species and other marine calcifiers remain a highly interesting challenge for future research. Studying single species both from cultures, different levels of the water column (e.g. surface layer, sediment traps) and sediment deposits (e.g. core-tops, down-core records) might help to unravel, which environmental or physiological factor contributes most to the Ca isotope signal that is finally recorded and preserved in the foraminiferal tests. Furthermore, as Griffith et al. (2008) recently quoted, biomineralization pathways should be studied in detail (e.g. residence time of Ca within the internal pool) in order to constrain their influence on Ca isotope fractionation in foraminifera. Especially, recent technical achievements have demonstrated that the discussion is not yet brought to an end. Using an ion microprobe, high-resolution in-situ measurements of Ca isotope composition have yielded  $\delta^{44/40}\text{Ca}$  values between 0.3 and 2.0‰ within two single tests of planktonic foraminifera *Globorotalia inflata*, dated 2.8 Ma from Shatsky Rise (ODP leg 198, Rollion-Bard et al., 2007). The authors attributed the observed intratest variations to several processes such as temperature variation, ontogenetic effects or differences between primary and secondary calcite, precipitated by different biomineralization processes.

#### 4.6 The “cold-end” or “cold-fresh-end” paradox

$\delta^{44/40}\text{Ca}$  values from both genotyped specimens sampled in polar surface waters and core-top samples from the low saline Arctic Domain, which are characterised by temperatures below  $2.0 \pm 0.5^\circ\text{C}$  and lower salinities ( $< 33\%$ ), were found to deviate from the trendline of the  $\delta^{44/40}\text{Ca}$

temperature relationship (Eq. (4)). Calculated calcification temperatures for core-top samples, using Eq. (4), seem to become ambiguous and overestimate temperatures in comparison to  $T_{\text{WOA}}$ . Similar to that,  $\delta^{44/40}\text{Ca}$  inferred temperatures from genotyped specimens are significantly higher than measured water temperatures at the sample location. Our data indicate that the breakdown of the  $\delta^{44/40}\text{Ca}$ -temperature relationship only occurs in these extreme low-temperature and low-salinity environments. Therefore, the apparent “cold-end” paradox is better described as a “cold-fresh-end” paradox. The observation that the breakdown of the  $\delta^{44/40}\text{Ca}$ -temperature relationship can be most likely attributed to distinct changes in water mass properties, particularly associated with lower salinities, however, do not fully explain the failure of *N. pachyderma* (sin.) as proxy carrier in these extreme environments.

A speculative indication for the observed findings could be provided by the parallel study of Kozdon (2007) applying a multi-proxy approach ( $\delta^{44/40}\text{Ca}$ , Mg/Ca,  $\delta^{18}\text{O}$ ) to *N. pachyderma* (sin.) tests from Holocene core-tops from different regions of the Nordic Seas. On the basis of the chemical signatures, tests of *N. pachyderma* (sin.) have been subdivided into two groups which differ significantly in their suitability as temperature proxy carrier. In the first set of samples from the Norwegian Sea,  $\delta^{44/40}\text{Ca}$  values and Mg/Ca ratios are positively correlated with temperature. Furthermore,  $\delta^{44/40}\text{Ca}$ - and Mg/Ca-inferred temperatures show similar trends, assuming a  $\delta^{44/40}\text{Ca}$ -temperature sensitivity of  $0.17\text{‰}\text{°C}^{-1}$ . By contrast, the  $\delta^{44/40}\text{Ca}$  and Mg/Ca proxy signal in foraminiferal tests from the low saline Arctic Domain is insensitive to water temperature and pretends higher calcification temperatures than actual peak summer temperatures in this region. In a first attempt, to explain these data, the final test chemistry of *N. pachyderma* (sin.) has been described by the temperature-mediated mixture of two calcite endmembers (cf. Bentov and Erez, 2006) with a different initial Mg/Ca and  $\delta^{44/40}\text{Ca}$  composition, indicating two pathways of biomineralization. This temperature-mediated mixing of two calcite endmembers is the main factor controlling the final test chemistry in samples from the Norwegian Sea. However, in tests originating from the “cold-fresh-end”, the temperature information in the Mg/Ca and the  $\delta^{44/40}\text{Ca}$  signal is lost, indicating that one pathway of biomineralization is more effective in these environments and hence dominates the final test composition. However, in order to constrain the yet speculative causes and links to these observations, more elaborated studies are required. For instance, comprehensive culturing experiments of certain foraminiferal species (including *N. pachyderma* (sin.) and *G. sacculifer*) could provide important information on how external stimuli, like temperature, salinity, pH and carbonate ion concentration directly affect the Ca isotopic composition (e.g. Kisakürek et al., 2007). Furthermore, advanced modelling studies could provide new insights on the theoretical relationships of elemental and isotope pathways. The study of Griffith et

al. (2008) marks an important step in this respect. Finally, in order to unravel the complex processes during biomineralization, more high-resolution geochemical methods should be applied, as done by Rollion-Bard et al. (2007). Comparative studies on the geochemistry of foraminiferal species dwelling in open ocean conditions vs. species adapted to the specific environments of ecological niches could further result in achieving a mechanistic understanding of how the calcification strategy might be related to the adaptation to a species-specific habitat.

## 5 Conclusions

Conducting systematic Ca isotope analyses on tests of *N. pachyderma* (sin.) covering a temperature range between 0 and 14°C possibly provide a new complementary SST proxy for open marine high-latitude oceans. This is supported by evidence from both genotyped plankton and core-top sediment. A change in  $\delta^{44/40}\text{Ca}$  [‰] of 0.17 ( $\pm 0.02$ ) corresponds to a temperature change of 1°C. The temperature sensitivity is independent of genetic variation observed within the major high-latitude proxy carrier, highlighting its potential for down-core applications in open marine cool-water environments. We propose to validate the  $\delta^{44/40}\text{Ca}$ -temperature relationship, with  $\delta^{44/40}\text{Ca}$  [‰]=0.17 ( $\pm 0.02$ )\*SST [°C]-0.22 ( $\pm 0.08$ ), in a well-documented down-core study. The strong temperature sensitivity of Ca isotope fractionation observed above a critical threshold temperature of  $2.0 \pm 0.5$  °C and salinity of  $33.0 \pm 0.5\text{‰}$  is in excellent agreement with the temperature sensitivity obtained for tropical planktonic foraminifera *G. sacculifer*. Therefore our findings render strong evidence that biocalcification in these two species is likely related to comparable biochemical mechanisms controlling Ca isotope fractionation. The failure of *N. pachyderma* (sin.) as proxy carrier at the “cold-fresh-end” might be attributed to shifts in elemental and isotopic processing (uptake and removal) during biomineralization and seems to be restricted to extreme polar environments. Therefore, Ca isotope fractionation in planktonic foraminifera should be studied in respect of elemental and isotopic biomineralization pathways, in order to understand, whether Ca isotope fractionation is controlled by specific biological processes, if foraminifera are adapted to an ecological niche.

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