



## A $\delta^{11}\text{B}$ -pH calibration for the high-latitude foraminifera species *Neogloboquadrina pachyderma* and *Neogloboquadrina incompta*.

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25 **Abstract.** The boron isotopic composition of planktonic foraminifera is a powerful tool to reconstruct ocean pH  
and CO<sub>2</sub> in the past. Applications to the high-latitude and polar oceans are however limited as robust calibrations  
between the  $\delta^{11}\text{B}$  of foraminifera and ocean pH in these regions are lacking. Here, we present a new empirical  
calibration for the high latitude Arctic species *Neogloboquadrina pachyderma* and the sub-polar to temperate  
species *Neogloboquadrina incompta* using towed specimens from the Labrador Sea, Baffin Bay, and the Nordic  
30 Seas. When paired with in situ hydrographic data, this approach allows us to avoid key assumptions used in  
traditional core top calibrations that are required to link shell geochemical composition to hydrographic conditions  
during their formation. We show that the foraminifera  $\delta^{11}\text{B}$  of the species analysed is well correlated with the  $\delta^{11}\text{B}$   
of seawater borate ion. Further, the foraminiferal  $\delta^{11}\text{B}$  values are consistently lower than seawater equilibrium  
borate values, consistent with the interpretation of more acidic seawater in the microenvironment due to  
35 respiration. However, unlike published calibrations for non-spinose species to date the slope of the  $\delta^{11}\text{B}$   
foraminifera to  $\delta^{11}\text{B}$  borate calibration is  $>1$ . We discuss several drivers of this higher sensitivity to pH and  
describe the possible role of vital effects in determining the boron isotopic composition of *N. pachyderma* and *N.*



*incompta*. Finally, we apply the tow calibration to core top samples from the Nordic Seas to validate the calibration for use in the paleorecord.

## 40 1 Introduction

The northern North Atlantic and the Southern Oceans are areas of strong vertical mixing and convection and as a result play a major role in air-sea gas exchange, including the release or storage of deep ocean CO<sub>2</sub> (Takahashi et al., 2009; Ezat et al., 2017; Shuttleworth et al., 2021). The North Atlantic, the Nordic Seas, the Labrador Sea, and Baffin Bay in particular are areas of deep-water formation and contribute to the formation of North Atlantic  
45 deep waters (NADW), a key component of the Atlantic Meridional Overturning Circulation (AMOC). Today, NADW ventilates 26% of the global deep ocean (Johnson, 2008) and carries dissolved CO<sub>2</sub> to depth making the Nordic and Labrador Seas major sinks of atmospheric CO<sub>2</sub>. The extent to which CO<sub>2</sub> is taken out of the atmosphere in these regions is dependent on several factors including temperature, the strength of the AMOC (Schmittner and Galbraith, 2008), sea-ice extent (Rysgaard et al., 2009), and biological productivity (Raven and Falkowski, 1999).  
50 Understanding the variability and magnitude of changes in surface ocean pH and CO<sub>2</sub> fluxes in the high latitudes is critical to understand its contribution to regulate the ocean carbon cycle and global climate.

Whilst the knowledge of global atmospheric CO<sub>2</sub> over the last 800 kilo annum (ka) is known with confidence from bubbles of ancient air trapped in Antarctic ice cores (Bereiter et al., 2015), our understanding of regional  
55 oceanic CO<sub>2</sub> fluxes, their magnitude and temporal variability relies on marine CO<sub>2</sub> proxy records (e.g., Martínez-Botí et al., 2015; Shuttleworth et al., 2021; Si et al., 2024). One commonly applied proxy of marine CO<sub>2</sub> relies on the boron isotopic composition ( $\delta^{11}\text{B}$ ) of foraminifera shells that tracks ocean pH (Cenozoic CO<sub>2</sub> Proxy Integration Project Foster and Rae, 2016; Consortium et al., 2023). This proxy has been extensively applied at low and mid latitudes using species from cultures, tows, and core tops where their  $\delta^{11}\text{B}$ -pH relationship has been well  
60 calibrated (Henehan et al., 2016; Raitzsch et al., 2018; Guillermic et al., 2020), and thoroughly tested against the CO<sub>2</sub> record from ice cores in areas where the ocean is in equilibrium with the atmosphere (Henehan et al., 2013; Chalk et al., 2017; de la Vega et al., 2023). However, reconstructing CO<sub>2</sub> at high latitudes is particularly challenging due to the lower species diversity living in areas of the surface ocean where temperature is <5 degrees Celsius (°C) and the lack of well constrained  $\delta^{11}\text{B}$  calibrations in such species (Yu et al., 2013; Ezat et al., 2017).  
65 One such species is the non-spinose planktonic foraminifera *Neogloboquadrina pachyderma*. It is found in abundance at latitudes above 55-60°N and exclusively in surface waters colder than 4 °C. Considering these oceanographic regions are important areas of CO<sub>2</sub> uptake via NADW formation over the observational period, it is critical to constrain how the  $\delta^{11}\text{B}$  in this species records changes in pH and CO<sub>2</sub>.

70 Although the boron isotope system has a relatively well understood theoretical basis (e.g., Foster and Rae, 2016), calibrations are required to account for “vital effects” – offsets from the expected  $\delta^{11}\text{B}$  value caused by foraminiferal physiology (e.g., Henehan et al., 2016; Hönisch et al., 2003). In general, geochemical calibrations rely on at least one of these three approaches: (1) the culturing of foraminifera in a controlled laboratory environment (e.g., Gray and Evans, 2019; Lea et al., 1999), (2) the collection of foraminifera from Holocene-aged  
75 core tops or sediment traps (e.g., Anand et al., 2003; Erez and Honjo, 1981; Dekens et al., 2002) and (3) the collection of living specimen using plankton tows (e.g., Martínez-Botí et al., 2011; Mortyn and Charles,



2003; Winkelbauer et al., 2023). Whilst the culturing approach has the merit of knowing the exact seawater chemistry in which the foraminifera grew, it doesn't fully represent the environment experienced in the open ocean, such as ontogenetic vertical migration (Meilland et al., 2021), changes in biological productivity, nutrient  
80 abundance, sea ice cover, or secondary diagenetic processes such as precipitation or dissolution in the water column and sediments. Culturing foraminifera is also a time consuming and specialist activity requiring ready access to live foraminifera and careful maintenance of culture conditions, which can be challenging. The approach using core top samples accounts for all secondary alterations of the primary signal as the foraminifera is incorporated in the sedimentary archive and is thus well-suited for application in the paleoclimatic record.  
85 However, it is challenged by the difficulty to find a natural modern range of upper ocean pH (reflected by the  $\delta^{11}\text{B}$  of borate) that is sufficiently large to define a reliable calibration (e.g., Yu et al., 2013) and there remains considerable uncertainty in determining the seawater carbonate chemistry the foraminifera calcified in, especially in regions like the northern North Atlantic where there has been significant invasion of anthropogenic  $\text{CO}_2$  (Yasunaka et al., 2023). Finally, there can be uncertainty in core top sample age making the determination of  
90 seawater temperature and anthropogenic carbon contribution more uncertain.

To date, only one study has attempted to construct a  $\delta^{11}\text{B}$  calibration (Yu et al., 2013) using *N. pachyderma* from core top samples from the Labrador and Irminger Sea covering a relatively narrow range of pH and assuming a constant habitat depth of 50 m. Several attempts have been made to constrain the habitat depth of *N. pachyderma*  
95 and it is often stated that this species is a subsurface dweller (e.g., Kohfeld et al., 1996; Simstich et al., 2003) that is migrating to deeper waters prior to calcifying a thick outer crust. However, more recent direct observations of *N. pachyderma* habitat across the Arctic and polar oceans show that the habitat depth of *N. pachyderma* is variable, can be shallow (i.e. < 20 m) and is primarily controlled by sea ice cover and chlorophyll intensity (Pados and Spielhagen, 2014; Greco et al., 2019) and not by diel vertical migration or the lunar phase (Greco et al., 2019).  
100 When sea-ice cover is reduced and/or when chlorophyll at the surface is low, the habitat generally deepens to 75–150 m (Greco et al., 2019). Critically, these studies have shown that heavily crusted *N. pachyderma* specimens can be found at any depth including the top 0–50 m (Tell et al., 2022) suggesting that there is no systematic ontogenetic vertical migration associated with reproduction or “crusting” for *N. pachyderma* (Manno and Pavlov, 2014; Tell et al., 2022). The considerable variability in habitat depth across the top 200 m of the surface ocean  
105 complicates the attribution of a single depth to core top calibrations and potentially results in large uncertainties when attributing modern pH and thereby  $\delta^{11}\text{B}$  of borate to foraminiferal  $\delta^{11}\text{B}$ .

To avoid the assumptions associated with traditional core top calibrations we present here a calibration using living *N. pachyderma* and *N. incompta* specimens (e.g., cytoplasm intact, no crust) collected via plankton tows  
110 from across a large range of pH in the Labrador Sea, Baffin Bay, and the Nordic Seas. This approach allows us to compare the foraminiferal  $\delta^{11}\text{B}$  with the pH of seawater and hence  $\delta^{11}\text{B}$  of seawater borate from the exact same depth at which the tows of *N. pachyderma* and *N. incompta* were collected. While this approach provides the most accurate hydrographic data for the calibration effort, the tow depth range, in some cases, integrates a large gradient in seawater carbonate chemistry and temperature, which introduces some uncertainties (reported in Table 1).  
115 Further, the  $\delta^{11}\text{B}$  composition of non-crusted specimens analysed here may be different to crusted specimen found in marine climate archives.



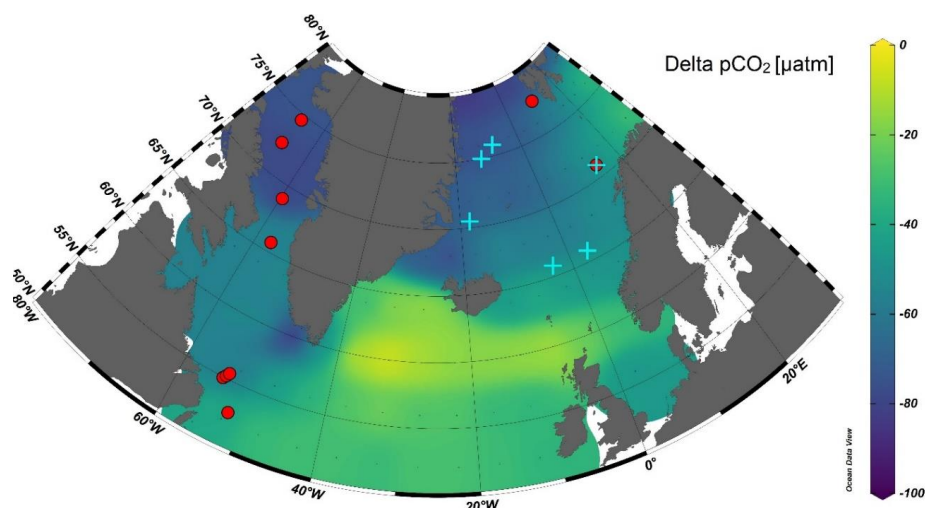
Whilst *N. pachyderma* and *N. incompta* were historically considered as two morphotypes of the same species (*N. pachyderma* sinistral and dextral respectively), they are now considered two separate species based on genetics, biogeography and ecological distinctions (Darling et al., 2006; Cifelli, 1961). They are however closely related; both are non-spinose species and live in polar or subpolar environments. *N. pachyderma* is typically found in cold open ocean waters and is the only species present in waters below 4 °C (e.g., Baffin Bay, Labrador Sea, Greenland Sea) and *N. incompta* dominates warmer subpolar waters of the eastern Norwegian Seas, and subpolar North Atlantic. The large geographical area of the polar North Atlantic allows us to cover a wide range of temperature, convection and CO<sub>2</sub> flux, and as a result a large gradient of pH in this calibration. In order to assess the validity of the calibration we construct, we then apply the tow-based calibration to a series of high latitude core tops alongside existing data from the literature to evaluate its application to the paleorecord.

## 2 Methods

### 2.1 Oceanographic setting

The dataset presented here was collected from the Nordic Seas, constituting the Greenland, Icelandic and Norwegian Seas (also sometimes called in conjunction with the Arctic Sea, the Arctic Mediterranean Sea), and the Labrador Seas. At the surface, the North Atlantic Drift enters the Nordic Seas (as “inflow”) mainly through the Iceland-Scotland ridge, and to a lesser extent the Denmark Strait (Hansen and Østerhus, 2000; Østerhus et al., 2019). North of the Iceland-Scotland ridge the North Atlantic Drift becomes the Norwegian Current, a warm and saline current that gradually cools via air-sea exchanges as it flows northward. From the Arctic Ocean surface outflow through the Fram Strait feeds the East Greenland Current, and through the Canadian Archipelago the Baffin Island Current. Once in the Nordic Seas the East Greenland Current follows the Greenland coast and becomes the West Greenland Current entering the Labrador Seas and subsequently the Baffin Bay. This current partly mixes with the Irminger current, a branch of the North Atlantic Drift, which increases its salinity. Together, the West Greenland and Irminger Currents flow northward into the Baffin Bay before recirculating southward alongside the surface Labrador Current. The Arctic waters that enter the Baffin Bay through the Canadian Archipelago travel via various sounds and straits southward and are of surface and subsurface origin (Azetsu-Scott et al., 2010). Along the way they mix with low salinity waters from precipitation, river, and sea ice meltwater before contributing to the low-density Baffin Island Current on the Western margin of the bay. The Baffin Island Current then mixes with the outflow water from the Hudson Bay and merges with the Labrador Current.

This complex system of water masses influences seawater pH in all regions. Mainly, the cold waters of Arctic origins are characterized by low pH due to the strong temperature dependent solubility of CO<sub>2</sub> at lower temperatures. Conversely, the warmer and saline waters feeding the Norwegian margin, the Labrador Sea, and the southern part of the Baffin Bay are characterized by higher pH. These strong gradients in surface water pH also result in a large range of CO<sub>2</sub> offsets between the surface ocean and the atmosphere (Figure 1). As a result, this wide geographic spread and diversity in water masses allows for the large range of > 0.2 seawater pH (Table 1) and diverse foraminifera habitat included in this calibration effort.



**Figure 1.** Map of the partial pressure of CO<sub>2</sub> in seawater (in units of micro atmospheres) at sea surface temperature (Takahashi et al., 2019) and location of stations where plankton tows (red circles) and core top samples (light blue crosses) were collected. Delta pCO<sub>2</sub> for the Baffin Bay was calculated using pCO<sub>2</sub> values reported in (Nickoloff et al., 2024). Map made with Ocean Data View (Schlitzer, 2002).

## 2.1. Sample material

Specimens collected via plankton tows include 15 *N. pachyderma* samples from the Labrador Sea and Baffin Bay collected during RV Maria S. Marian cruises MSM09 in 2008, MSM44 in 2015, and MSM66 in 2017. In addition, 5 tows containing *N. incompta* and 5 core top samples (containing *N. pachyderma*) were collected from the Nordic Seas during cruise CE20009 in August 2020 (Figure 1). Towed samples were collected from 100 μm mesh multi-nets, brought on board, and either immediately frozen at -80 °C or immediately picked into slides and frozen at -80 °C to preserve the foraminiferal cytoplasm. Frozen tows were thawed onshore and between 0.7 and 2 mg of uncrusted specimens with intact cytoplasm were hand-picked for δ<sup>11</sup>B and trace elemental to calcium analysis. The average size fraction of tow samples from the Labrador Sea ranged between 182-248 μm determined using a Keyence HX 6000 digital microscope, however all specimen sizes available were included in analysis including specimen >100 and <300 μm to ensure enough material was available. Core tops were collected from multicores recovered during cruise CE20009 (September 2020) and cruise CAGE-ARCLIM (June 2022). The multicores were immediately processed onboard and sliced at 0.5 to 1 cm resolution, and subsequently frozen at -20 °C. On land, multicore tops were thawed or freeze-dried and wet-sieved at 63 μm. 1-2 mg of *N. pachyderma* were picked in the 200-250 μm size fraction. When possible morphotype II was favoured when picking specimens from core tops to minimize potential depth habitat variability with morphotypes following the classification of Altuna et al. (2018, Plate 1). All specimens from core tops were encrusted and while we selected specimens from a very narrow size fraction, we did not perform a systematic analysis of the degree of encrustation of *N. pachyderma* in the core top samples. Therefore, we cannot exclude that post-mortem depositional processes including the precipitation of inorganic calcite, dissolution, or recrystallization impact the thickness or geochemical composition of the crust as the tests sink through the water column and settle at the seafloor. In Table S2 we list core tops that were radiocarbon dated. Accelerator mass spectrometry (AMS) radiocarbon (<sup>14</sup>C) was measured at the Keck Carbon



Cycle Accelerator Mass Spectrometry facility at UC Irvine, USA. The samples for radiocarbon dating consist of the planktonic foraminifera *N. pachyderma*. Individuals were picked at from the 0.0-0.5cm interval for each core top (Table S2).

## 2.2. Estimates of $\delta^{11}\text{B}$ of borate

CTD (conductivity, temperature, depth) casts with Niskin bottles were deployed at each station for cruise CE20009 and water samples were collected for total alkalinity (TA) and dissolved inorganic carbon (DIC) analysis (described in Morley et al., 2024). This allows the carbonate chemistry of seawater to be fully constrained at exactly the same depth as where the tows were collected.  $\delta^{11}\text{B}$  of borate was calculated from pH (derived from TA and DIC) and derived using the following equation:

$$\delta^{11}\text{B}_{\text{B(OH)}_4^-} = \frac{\delta^{11}\text{B}_{\text{sw}}[\text{B}]_{\text{sw}} - \epsilon_{\text{B}}[\text{B(OH)}_3]}{[\text{B(OH)}_4^-] - \alpha_{\text{B}}[\text{B(OH)}_3]} \quad (\text{eq. 1})$$

Where the total boron in seawater  $[\text{B}]_{\text{sw}} = 432.6 \times (\text{salinity}/35) \mu\text{mol/kg}$  (Lee et al., 2010),  $\epsilon_{\text{B}}$  is the fractionation factor between the two boron species expressed as  $\epsilon_{\text{B}} = (\alpha_{\text{B}} - 1) \times 1000$ , the isotopic fractionation factor  $\alpha_{\text{B}}$  between  $\text{B(OH)}_3$  and  $\text{B(OH)}_4^-$  is 1.0272 as determined by Klochko et al. (2006) and the  $\delta^{11}\text{B}$  of seawater is 39.61 ‰ (Foster et al., 2010). For stations in the Labrador Sea and the Baffin Bay the water chemistry was determined using nearby cruise data collected at the same time or the same month of the year as the tow samples (Table S1). For the towed samples, the  $\delta^{11}\text{B}$  of borate was determined using the median of the hydrographic parameters within the towed sample depth interval.

For core top samples we estimate  $\delta^{11}\text{B}$  of borate using the traditional core top approach to constrain calcification depth based on paired  $\delta^{18}\text{O}$  measurements (e.g., Ravelo and Hillaire-Marcel, 2007). Briefly, we constrained calcification depth by calculating the  $\delta^{18}\text{O}$  of *N. pachyderma* and *N. incompta* projected onto the equilibrium  $\delta^{18}\text{O}$  of calcite using modern hydrographic profiles and the paleotemperature equation derived by Shackleton (1974) as follow:

$$\delta^{18}\text{O}_{\text{calcite.eq.PDB}} = \delta^{18}\text{O}_{\text{sw.SMOW}} - \left( \frac{4.38 - \sqrt{4.38^2 - 4 \times 0.1(16.9 - T)}}{0.2} \right) \quad (\text{eq. 2})$$

Seawater temperature in degrees Celsius (T),  $\delta^{18}\text{O}_{\text{calcite.eq.PDB}}$  is the equilibrium  $\delta^{18}\text{O}$  of calcite on the PDB scale and  $\delta^{18}\text{O}_{\text{sw.SMOW}}$  is the  $\delta^{18}\text{O}$  of seawater on the SMOW scale, either directly measured from CTD bottles or derived from salinity using the regional salinity– $\delta^{18}\text{O}_{\text{sw}}$  of Simstich et al. (2003). This approach yields a depth estimate for the core top foraminifera between 25 and 91 meters and an average of 65 meters (Morley et al., 2024, Supplementary Table 4). As in Morley et al. (2024) we did not apply a systematic correction for a vital effect on  $\delta^{18}\text{O}$  values because there isn't consensus in the literature on the offset recorded in *N. pachyderma* collected from core top samples. Briefly, the negative  $\delta^{18}\text{O}_c$  offset from equilibrium measured in living (uncrusted) *N. pachyderma* collected from plankton tows is highly variable within a region, across regions, seasons, and on interannual timescales (Stangeew, 2001; Volkman and Mensch, 2001; Pados and Spielhagen, 2014; Livsey et al., 2020). Furthermore, the addition of crust, typical for specimens recovered from core tops, increases the  $\delta^{18}\text{O}_c$  signal because crust is isotopically heavier than ontogenetic calcite (Kozdon et al., 2009; Mikis et al., 2019).



Variations in the degree of encrusting can therefore either “lower”, completely “mask”, or shift the vital effect towards positive values depending on the degree of encrustation (Kozdon et al., 2009). As a result, there remains considerable uncertainty in the exact value to use when correcting for the competing signals of vital effects and crust in *N. pachyderma*, with studies reporting both calcification in equilibrium (Jonkers et al., 2010; Jonkers et al., 2013; Mikis et al., 2019; Jonkers et al., 2022) and out of equilibrium with seawater (Kohfeld et al., 1996; Bauch et al., 1997; Simstich et al., 2003; King and Howard, 2005). By not applying a correction for vital effects or the contribution of crust calcite we avoid biasing calcification depth estimates towards deeper depths and lower  $\delta^{11}\text{B}_{\text{borate}}$  values. This approach is also consistent with sediment trap studies from both the North and South Atlantic where  $\delta^{18}\text{O}_c$  values measured on crusted *N. pachyderma* are in equilibrium with measured water column  $\delta^{18}\text{O}$  (Jonkers et al., 2013; Mikis et al., 2019).

The pH and  $\delta^{11}\text{B}_{\text{borate}}$  for core tops samples was calculated by applying a correction for anthropogenic carbon on DIC (using the anthropogenic DIC of Glodapv2, 2016 ranging ~35 to 50  $\mu\text{mol/kg}$  in the Nordic Sea stations in the upper 200 meters (Lauvset et al., 2022). For core tops dated with AMS radiocarbon dates younger than 550 years we did not apply a correction for anthropogenic carbon (Table S2). The uncertainty for calcification depth was defined as the minimum and maximum within a  $\pm 20$ -meter interval around the central value. We note that this approach yields an average depth of the foraminifera population signal, and that despite both species being observed to live throughout the upper 200 m of the water column (Greco et al., 2019), we assume the inferred depth is representative of where the majority of the population lives and calcifies. The  $\delta^{11}\text{B}_{\text{foram}}$  and corresponding  $\delta^{11}\text{B}_{\text{borate}}$  were fitted with a York regression (York et al., 2004) that accounts for the uncertainty in both the x and y axis.

### 2.3. Elemental and $\delta^{11}\text{B}$ analysis

#### 2.3.1 Samples from cruise CE20009

Foraminifera from tows and core tops were cleaned using a modified version of the established foraminifera method to account for higher organic content in plankton tow samples (Henehan et al., 2016; Barker et al., 2003). All foraminifera were gently crushed between two glass slides to facilitate cleaning and clay removal was carried out through sequential Milli-Q rinses and brief ultrasonication to agitate the samples (core top samples only). Both core top and tow samples were oxidatively cleaned with a solution of  $\text{H}_2\text{O}_2$  (30% by weight) buffered with 0.1M  $\text{NH}_4\text{OH}$  (3.4% of peroxide in the final oxidative mix). Samples were placed in a hot bath for 3x5 min for core tops and 3x20 min for tows to ensure the removal of additional organics, separated by brief 15-seconds ultrasonication. Samples were then weak acid-leached (in 0.0005 M  $\text{HNO}_3$ ) for 30 seconds and dissolved in ~300  $\mu\text{l}$  of 0.15 M  $\text{HNO}_3$ . An aliquot of 20  $\mu\text{l}$  (diluted in 130  $\mu\text{l}$  0.5M  $\text{HNO}_3$ ) was kept for elemental analysis, and the remainder kept for boron sample preparation and analysis.

Elemental analysis was performed on an Thermo Element Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Centre for Earth Research and Analysis Southampton (CERAS) at the University of Southampton and element-to-calcium ratios measured with  $^{43}\text{Ca}$  and  $^{48}\text{Ca}$  and referenced against in house mixed element standards. Bracketing standards were measured at the same concentration as samples, including samples with  $[\text{Ca}]$  below 1 mmol/L to account for drift in Elemental to Calcium (El/Ca) ratios. El/Ca ratios measured included B, Na, Mg,



Al, Mn, Sr, Cd, Ba, U and Fe. Based on the reproducibility of our in-house standards, the uncertainty for most elemental ratios is ~5 % (at 95 % confidence; Henahan et al. 2015). Samples for boron analysis were first purified for boron by anion exchange chromatography in the boron-free class 100 laboratory of CERAS following the procedure of Foster (2008). A total procedure blank (TPB) was conducted for all batches of ~10 columns and ranged 31 to 92 pg (equivalent to 1-5% of the sample total boron). Samples were subsequently corrected using a long term  $\delta^{11}\text{B}$  of TPB of -7.27 ‰ from long term measurement at the University of Southampton. This gave a  $\delta^{11}\text{B}$  correction of 0.1 to 1.1 ‰. The purified sample was analysed for  $\delta^{11}\text{B}$  at CERAS on a Thermo Neptune Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) with  $10^{12} \Omega$  amplifier resistors, using a standard-bracketing technique with NIST SRM 951 (Foster, 2008; Foster et al., 2013). All other sample preparation, elemental and boron isotope analysis for the samples were conducted in class 100 clean laboratories at the University of Southampton belonging to the CERAS facility.

The uncertainty on foraminifera  $\delta^{11}\text{B}$  was empirically determined based on the uncertainty around the long-term measurement of JCp-1 Coral (*Porites* sp.) that has undergone the same chemical purification. The uncertainty is dependent on the boron content (Rae et al., 2011), i.e. the intensity of the  $^{11}\text{B}$  signal. It is defined by the following equation (Anagnostou et al., 2019):

$$2\sigma = 12960e^{-212 \times [^{11}\text{B}]} + 0.3385e^{-1.544 \times [^{11}\text{B}]}, \text{ (eq. 3)}$$

where  $[^{11}\text{B}]$  is the intensity of  $\delta^{11}\text{B}$  signal in volts. Carbonate and boric acid samples were measured at CERAS and AWI and are in good agreement. The long-term  $\delta^{11}\text{B}$  of JCp-1, AE120 and AE121 at CERAS are (at  $1\sigma$ ) 24.21  $\pm$  0.12‰, 20.2  $\pm$  0.19‰ and 19.59  $\pm$  0.28‰ respectively, which are comparable with values measured at AWI of 24.28  $\pm$  0.3‰ (Raitzsch et al., 2018), -19.85  $\pm$  1.57‰ (n=4) and 19.5  $\pm$  0.79‰ (n=10), respectively. Samples with substantial TPB corrections have lower confidence due to higher uncertainty in the  $\delta^{11}\text{B}$  of TPB samples (given the low boron content). Applying a long term  $\delta^{11}\text{B}$  of TPB of -7.27 ‰ may not be representative of the true value. As a result, for samples with substantial TPB correction, the uncertainty of  $\delta^{11}\text{B}_{\text{TPB}}$  was propagated into the corrected  $\delta^{11}\text{B}$  value measured on foraminifera samples (e.g.,  $\delta^{11}\text{B}_{\text{foram}}$ ).

### 2.3.2. Samples from the Labrador Sea and Baffin Bay

Boron (B) isotope ratios for samples from the Labrador Sea were measured following Raitzsch et al. (2018). Briefly, the cleaned samples were dissolved in 60  $\mu\text{L}$  of 1 N  $\text{HNO}_3$  and loaded on a Savillex teflon lid then closed and turned upside to be micro-distilled on a hotplate to separate boron from the carbonate matrix. The micro-distillation method in Ca-rich matrix samples such as foraminifera yields a B recovery of ~100 %, a low procedural blank, and accurate results, even at low B concentrations (Gaillardet et al., 2001; Wang et al., 2010; Misra et al., 2014; Raitzsch et al., 2018). The procedural blank contribution during this study was 10–50 pg B, which equates to ~0.2 %–0.8 % of the total [B] in the micro-distillation vial. The distillate containing only boron was diluted with 2%  $\text{HNO}_3$  and analysed for boron isotopic composition in triplicate using a Nu Plasma II multi-collector inductively coupled plasma mass spectrometry (ICPMS) at AWI (Bremerhaven, Germany) that is equipped with a customized detector array of 16 Faraday cups and 6 secondary electron multipliers (SEM), also termed ion counters (IC), where high-mass IC5 was used for  $^{11}\text{B}$  and IC0 for  $^{10}\text{B}$ .



300 A standard-sample-bracketing technique was used to correct for the instrumental mass bias and drift using the boron reference material NBS 951 and frequent analysis of control standard AE121 with an isotopic composition similar to that of foraminifera was monitored to ensure measurement accuracy. Measurement uncertainties are reported as 2 standard deviations ( $2\sigma$ ) derived from triplicate measurements or as  $\pm 0.30\%$  determined from long-term reproducibility ( $2\sigma$ ) of the control standard, whichever is larger. Each micro-distilled sample was analysed in triplicate where at least two measurements were used for averaging the  $\delta^{11}\text{B}$  value measured. We specify the error as  $2\sigma$  of the mean derived from the replicates, accounting for  $\sim 95\%$  of the data.

For elemental to calcium (El/Ca) ratios the Labrador Sea and Baffin Bay samples were analysed using a Nu AttoM high-resolution double-focusing inductively coupled plasma mass spectrometer (ICP-MS) at the AWI. Five 310 replications were carried out for each sample, where the average repeatability for El/Ca among the five replicates was  $0.95 \pm 0.47\%$  (relative standard deviation). Long-term reproducibility of Mg/Ca analyses is monitored by regular analysis of the carbonate standard. JCP-1, yielding  $3.94 \pm 0.15$  ( $2\sigma$ )  $\text{mmol.mol}^{-1}$  over a period of about two years.

#### 315 2.4. Core top samples.

To evaluate the validity of the tow-based  $\delta^{11}\text{B}$ -pH calibration the core tops were considered as unknown paleo samples by applying the calibration equation derived from the plankton tows together with the revised Mg/Ca temperature calibration recently published by Morley et al. (2024). We applied this scheme to core tops from various location in the North Atlantic, cruise CE20009 and CAGE-ARCLIM (Nordic seas, this study), RAPID-35-25B (North Atlantic, (Yu et al., 2013; Moffa-Sánchez et al., 2014)), and JM-FI-19PC (Norwegian sea, (Ezat et al., 2017)). The foraminiferal  $\delta^{11}\text{B}$  data from Ezat et al. (2017) measured with negative thermal ionization mass spectrometry (N-TIMS) was corrected for offsets in analytical techniques (using a correction of  $-1\%$  defined by the foraminifera data of Farmer et al. (2016) to align with our data sets measured with MC-ICPMS. We calculate  $\delta^{11}\text{B}$ -derived pH (eq 1.) and atmospheric  $\text{CO}_2$  and correct for  $\text{CO}_2$  differences between foraminifera habitat depth and sea surface (from CTD or Glodap V2  $\text{pCO}_2$  profiles) as well as local air-sea  $\text{CO}_2$  disequilibrium (Takahashi et al., 2019), and compare our result to the ice core  $\text{CO}_2$  record (Bereiter et al., 2015) over the last 500 years. Unlike comparing core tops to modern  $\text{pH}/\delta^{11}\text{B}_{\text{borate}}$  profiles that do not account for possible sediment age variations, this approach allows for: (1) comparison of  $\delta^{11}\text{B}$ -derived  $\text{CO}_2$  with an independent record from the ice core; and (2) the knowledge of  $\text{CO}_2$  variations in the recent past to evaluate the range of  $\text{CO}_2$  (and pH) possibly 330 recorded by the  $\delta^{11}\text{B}$  of core top foraminifera of variable ages.

For this calculation we use the constant fractionation factor determined by Klochko et al. (2006); eq. 1). We use a  $\delta^{11}\text{B}$  of seawater of  $39.61\%$  (Foster et al., 2010), and use alkalinity as a second carbonate parameter in the  $\text{CO}_2$  calculation (Zeebe and Wolf-Gladrow, 2001). Aqueous  $\text{CO}_2$  was determined as follow:

$$CO_2 = \frac{TA - \frac{K_B \cdot B_T}{K_B + [H^+]} - \frac{K_W}{[H^+]} + [H^+]}{\frac{K_1}{[H^+]} + \frac{2K_1 K_2}{[H^+]^2}} \quad (\text{eq. 4})$$



TA is the total alkalinity measured from CTD bottle profiles. To account for uncertainty in habitat depth TA uncertainty was estimated by integrating the total range of TA within the upper 100 meters of the water column.

340  $K_B$  is the equilibrium constant of boron species in seawater (a function of temperature  $T$ , salinity  $S$  and pressure  $P$ , (Dickson, 1990)),  $B_T$  the concentration of boron in seawater ( $432.6 \mu\text{mol kg}^{-1}$ , (Lee et al., 2010),  $[H^+]$  the concentration of  $H^+$  determined from  $\text{pH} = -\log[H^+]$  (total scale),  $K_w$  the dissociation constant of water (function of  $T$ ,  $S$  and  $P$ ), and  $K_1$  and  $K_2$  the first and second dissociation constants of carbonic acid (function of  $T$ ,  $S$  and  $P$ , (Sulpis et al., 2020)). The partial pressure of  $\text{pCO}_2$  (in parts per million, ppm) is determined as:

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$$\text{pCO}_2 = [\text{CO}_2]_{\text{sw}}/K_0$$

With  $[\text{CO}_2]_{\text{sw}}$ , the aqueous  $\text{CO}_2$  concentration (eq 4), and  $K_0$  Henry's law constant (Weiss, 1974). The  $\text{pCO}_2$  uncertainty was determined with a Monte Carlo simulation (10,000 realisations) to account for the uncertainty of

350 all input parameters (all with a normal distribution). An error envelope was calculated at 1 and 2  $\sigma$  based on the 68% and 95% distribution of all the realisations.

### 3-Results

#### 3.1 Tow samples

355 The  $\delta^{11}\text{B}$  of towed *N. pachyderma* and *N. incompta* samples from the Labrador and Nordic Sea (e.g.,  $\delta^{11}\text{B}_{\text{foram}}$ ) are compared to seawater  $\delta^{11}\text{B}$  borate (e.g.,  $\delta^{11}\text{B}_{\text{borate}}$ ) in Figure 2a. The  $\delta^{11}\text{B}_{\text{foram}}$  of both species overlaps and both are offset to lower  $\delta^{11}\text{B}$  than ambient borate. The regression for these data, using a constant  $\alpha_B$  (Klochko et al., 2006) is best described by the following equation (with  $1\sigma$  uncertainty, Figure 2a, Table 1), with a mean square weighted deviation (mswd) of 0.58 (and  $p=0.28$ ):

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$$\delta^{11}\text{B}_{\text{foram}} = 1.58 (\pm 0.38) * \delta^{11}\text{B}_{\text{borate}} - 11.09 (\pm 5.9)$$

The slope of 1.58, being larger than unity, shows that at lower ambient  $\delta^{11}\text{B}_{\text{borate}}$  (lower pH), the  $\delta^{11}\text{B}_{\text{foram}}$  is more offset from equilibrium than at higher  $\delta^{11}\text{B}_{\text{borate}}$ . The slope lies below the 1:1  $\delta^{11}\text{B}_{\text{foram}} : \delta^{11}\text{B}_{\text{borate}}$  line and the regression equation when considering all tows (both species *N. pachyderma* and *N. incompta*) and *N. pachyderma*-only (i.e. from the Labrador Sea) show a steeper slope (1.82) than when considering the regression with only *N. pachyderma*, yet both slopes and intercept are within error of each other (Table 2). We do not attempt to define a slope for *N. incompta*-only due to the narrow range of  $\text{pH}/\delta^{11}\text{B}_{\text{borate}}$  covered for these samples.

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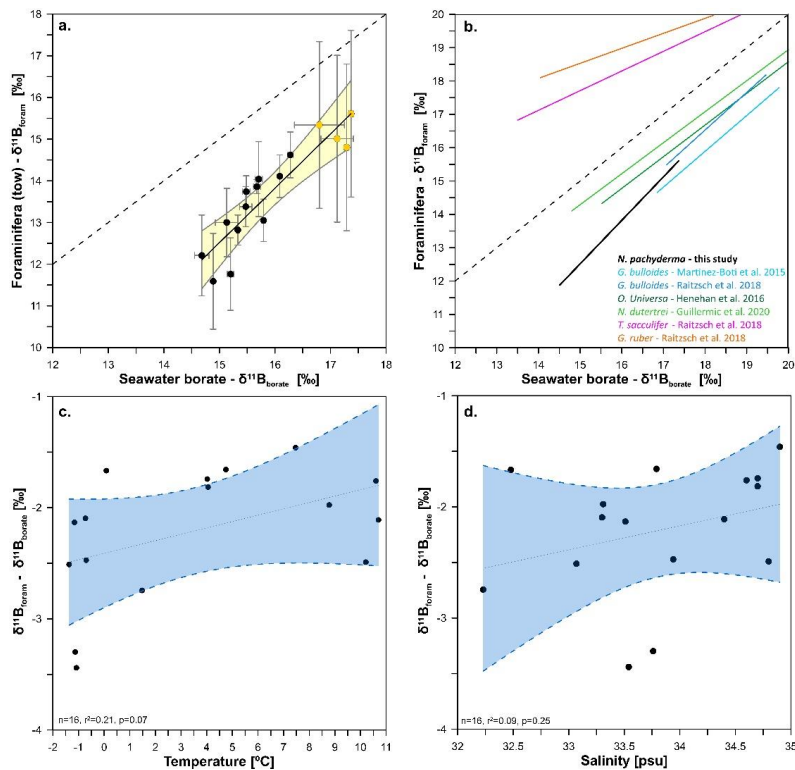


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Table 1. Hydrographic data,  $\delta^{11}\text{B}_{\text{foram}}$  and B/Ca measured on living *N. pachyderma* and *N. incompta* from plankton tows. See also Fig. 2

| Region              | Cruise  | Station     | Tow depth | Species             | Depth | pH         | Temp       | Sal   | $\delta^{11}\text{B}_{\text{bor}}$ | $\delta^{11}\text{B}_{\text{foram}}$ | Ba/Ca         |                                         |      |        |      |        |
|---------------------|---------|-------------|-----------|---------------------|-------|------------|------------|-------|------------------------------------|--------------------------------------|---------------|-----------------------------------------|------|--------|------|--------|
|                     | ID      | ID          | [m]       |                     | [m]   | 1 $\sigma$ | 1 $\sigma$ | [psu] | err (lw)                           | err (up)                             | err ( $\pm$ ) | [ $\mu\text{mol}\cdot\text{mol}^{-1}$ ] |      |        |      |        |
| NE Norwegian Sea    | CE20009 | 2a          | 0-10      | <i>N.incompta</i>   | 5     | 5          | 8.14       | NA    | 10.7                               | 34.44                                | 17.12         | 0.29                                    | 0.29 | 15.01* | 2.00 | 601.80 |
|                     | CE20009 | 2b          | 10-20     | <i>N.incompta</i>   | 15    | 5          | 8.16       | NA    | 10.6                               | 34.63                                | 17.37         | 0.04                                    | 0.04 | 15.61* | 2.00 | 525.70 |
|                     | CE20009 | 2c          | 20-30     | <i>N.incompta</i>   | 25    | 5          | 8.16       | NA    | 10.2                               | 34.80                                | 17.29         | 0.04                                    | 0.04 | 14.8*  | 2.00 | 530.80 |
| Fram Strait         | CE20009 | 5           | 0-40      | <i>N.incompta</i>   | 20    | 20         | 8.14       | NA    | 7.5                                | 34.90                                | 16.80         | 0.56                                    | 0.33 | 15.34* | 2.00 | 328.70 |
| Davis Strait        | MSM44   | GeoB19913-2 | 0-100     | <i>N.pachyderma</i> | 50    | 50         | 8.12       | 0.009 | 0.1                                | 32.48                                | 15.70         | 0.40                                    | 0.10 | 14.04  | 0.90 | 2.97   |
|                     | MSM44   | GeoB19913-2 | 100-200   | <i>N.pachyderma</i> | 150   | 50         | 8.04       | 0.033 | -1.2                               | 33.51                                | 15.13         | 0.15                                    | 0.10 | 13.00  | 0.82 | 2.93   |
| Northern Baffin Bay | MSM44   | GeoB19929-3 | 80-100    | <i>N.pachyderma</i> | 90    | 10         | 8.00       | 0.001 | -1.1                               | 33.76                                | 14.89         | 0.02                                    | 0.10 | 11.59  | 1.15 | 2.05   |
|                     | MSM44   | GeoB19929-3 | 100-200   | <i>N.pachyderma</i> | 150   | 50         | 7.95       | 0.024 | -0.7                               | 33.94                                | 14.67         | 0.15                                    | 0.10 | 12.21  | 0.97 | 2.02   |
| Southern Baffin Bay | MSM09/2 | GeoB455     | 80-100    | <i>N.pachyderma</i> | 90    | 10         | 8.05       | 0.009 | -1.1                               | 33.54                                | 15.20         | 0.11                                    | 0.10 | 11.76  | 0.87 | 2.90   |
| Southern Labrador   | MSM09/2 | GeoB415     | 20-40     | <i>N.pachyderma</i> | 30    | 10         | 8.11       | 0.005 | 1.5                                | 32.23                                | 15.79         | 0.02                                    | 0.30 | 13.05  | 0.51 | 10.46  |
|                     | MSM09/2 | GeoB415     | 40-60     | <i>N.pachyderma</i> | 50    | 10         | 8.09       | 0.016 | -0.7                               | 33.30                                | 15.48         | 0.02                                    | 0.30 | 13.38  | 0.48 | 20.63  |
| Labrador Sea        | MSM09/2 | GeoB433     | 100-150   | <i>N.pachyderma</i> | 125   | 25         | 8.01       | 0.010 | 4                                  | 34.70                                | 15.48         | 0.02                                    | 0.30 | 13.74  | 0.38 | 17.18  |
|                     | MSM09/2 | GeoB434     | 0-20      | <i>N.pachyderma</i> | 10    | 10         | 8.05       | 0.001 | 8.8                                | 33.31                                | 16.08         | 0.02                                    | 0.30 | 14.11  | 0.51 | 15.00  |
|                     | MSM09/2 | GeoB434     | 20-40     | <i>N.pachyderma</i> | 30    | 10         | 8.12       | 0.006 | 4.8                                | 33.79                                | 16.28         | 0.02                                    | 0.30 | 14.62  | 0.55 | 20.80  |
|                     | MSM09/2 | GeoB435     | 100-150   | <i>N.pachyderma</i> | 125   | 25         | 8.04       | 0.000 | 4.1                                | 34.70                                | 15.65         | 0.02                                    | 0.30 | 13.86  | 0.17 | 6.46   |
| Baffin Bay          | MSM09/2 | GeoB460     | 40-60     | <i>N.pachyderma</i> | 50    | 10         | 8.08       | 0.004 | -1.4                               | 33.07                                | 15.33         | 0.30                                    | 0.30 | 12.82  | 0.36 | 9.44   |

\* Total procedure blank corrected



**Figure 2.** Relationship between the  $\delta^{11}\text{B}$  of towed *N. pachyderma* (black circles) and *N. incompta* (yellow circles) with the  $\delta^{11}\text{B}$  of seawater borate. Panel a shows  $\delta^{11}\text{B}$  of towed specimens against  $\delta^{11}\text{B}$  of seawater borate without a temperature correction on  $\alpha\text{B}$  on the calculation of  $\delta^{11}\text{B}$  of borate. We fitted the data with a York regression (black line) and a 95% confidence envelope (light yellow shade). The 1:1 line is shown by the black dashed line. Panel b shows calibration equations for other planktonic foraminifera next to the tow-based calibration equation derived here for *N. pachyderma*. panels c and d show the regression between  $\delta^{11}\text{B}_{\text{foram}} - \delta^{11}\text{B}_{\text{borate}}$  offset and temperature ( $n=16$ ,  $p=0.07$ ,  $r^2=0.22$ ) and salinity ( $n=16$ ,  $p=0.25$ ,  $r^2=0.10$ ) respectively.

**Table 2.** Boron Isotope Calibration equation for *N. pachyderma* and *N. incompta*

| Sample Type                                        | Slope( $\pm 1\sigma$ ) | Intercept( $\pm 1\sigma$ ) | mswd |
|----------------------------------------------------|------------------------|----------------------------|------|
| Tows ( <i>N. pachyderma</i> + <i>N. incompta</i> ) | 1.58( $\pm 0.38$ )     | -11.09( $\pm 5.9$ )        | 0.58 |
| Tows ( <i>N. pachyderma</i> only)                  | 1.82( $\pm 0.5$ )      | -14.95( $\pm 7.77$ )       | 0.58 |

### 3.2. Relationship between $\delta^{11}\text{B}$ , temperature and salinity.

The foraminifera  $\delta^{11}\text{B}$  exhibit a significant correlation with temperature (Fig S1,  $r^2=0.58$ ,  $p<<0.05$ ) and salinity (Fig. 2e,  $r^2=0.24$ ,  $p=0.017$ ), which is likely due to covariance between carbonate system parameters, temperature, and salinity. To evaluate the influence of temperature and salinity on the proxy system we plot them against the offset between  $\delta^{11}\text{B}_{\text{foram}}$  and predicted  $\delta^{11}\text{B}_{\text{borate}}$  (Figures 2c and 2d) and in both cases the correlation is not significant (i.e.  $p<0.05$ ).



### 3.3. Applying the calibration to core top samples.

Whilst tows provide information about the original signal imprinted in well constrained calcifying environments, the application in the paleorecord relies on sediment samples with foraminifera that incorporate the calcification depth during ontogeny and post depositional environment processes in terms of sedimentation rate, corrosiveness of porewaters etc. The tow-based foraminifera  $\delta^{11}\text{B}$  calibration equation based on temperatures calculated from the Mg/Ca- $\delta^{18}\text{O}$  correction scheme (Morley et al., 2024) yields reconstructed atmospheric  $\text{pCO}_2$  concentrations that span the pre-industrial (280 ppm) to modern range (420 ppm)

## 4 Discussion

*N. pachyderma* and *N. incompta* are both non-spinose asymbiotic genetically sister species inhabiting the high latitude oceans (Darling et al., 2006). While their geographic distribution in the North Atlantic overlaps slightly at temperatures between 6-10 °C (Darling et al., 2006) each species inhabits distinct environmental conditions: warm Atlantic waters at subpolar latitudes of high pH for *N. incompta*, and cold polar waters of lower pH for *N. pachyderma*. Combining them in our study therefore allows us to cover a wider range of pH, and hence  $\delta^{11}\text{B}_{\text{borate}}$ , improving the overall calibration. The minor difference in the calibration slopes when considering *N. pachyderma* alone or if both species are combined (Table 1) further support this approach.

### 4.1. Potential drivers of $\delta^{11}\text{B}$ sensitivity and alteration of microenvironment.

Our new calibration shows that the  $\delta^{11}\text{B}_{\text{foram}}$  recorded by *N. pachyderma* and *N. incompta* is lower than the  $\delta^{11}\text{B}$  of seawater borate (1:1 line, Figure 2). This result is in agreement with other published calibrations of the non-spinose species, *Globoconella inflata*, the symbiont-bearing spinose species *O. universa* (Henehan et al., 2016), and the symbiont-barren spinose species *G. bulloides* (Martínez-Botí et al., 2015). Further we observe that the slope of the regression is  $>1$  (Figure 4e, Table 1). This observation contrasts with previously published  $\delta^{11}\text{B}$  calibrations that show either a slope close to unity in line with the expected pH sensitivity from  $\delta^{11}\text{B}$  of borate in seawater such as that found for epifaunal benthic foraminifera (Rae et al., 2011), *G. bulloides* (Martínez-Botí et al., 2015), and *O. universa* (Henehan et al., 2016), or a slope  $<1$  like the spinose symbiont-bearing species *G. ruber* (Henehan et al., 2013) and *T. sacculifer* (Sanyal et al., 2001; Martínez-Botí et al., 2015).

Interpretations of a weaker sensitivity (i.e. slope  $<1$ ) to pH for *G. ruber* and *T. sacculifer* invoke photosymbiont activity, calcification and/or foraminifera metabolism, altering the pH of the diffusion-controlled microenvironment immediately surrounding the living foraminifera (e.g. (Henehan et al., 2016; Hönisch et al., 2003; Zeebe et al., 2003). In this scenario, lower pH in the microenvironment relative to ambient seawater immediately surrounding *N. pachyderma* and *N. incompta* specimens could arise from the  $\text{CO}_2$  flux from foraminiferal respiration and calcification, which is offset/compensated for by  $\text{CO}_2$  drawdown by symbionts in the photosymbiont bearing spinose foraminifera (Zeebe et al., 1999; Rink et al., 1998). Alternative explanations for the patterns seen in photosymbiont bearing foraminifera invoke the incorporation of the isotopically heavy  $\text{B}(\text{OH})_3$  at slower calcification rates at lower pH, suggested to increase  $\delta^{11}\text{B}_{\text{foram}}$  resulting in a shallow  $\delta^{11}\text{B}_{\text{foram}} - \delta^{11}\text{B}_{\text{borate}}$  slope (Uchikawa et al., 2015; Farmer et al., 2019). Whether or not calcification rates impact  $\delta^{11}\text{B}_{\text{foram}}$  in *N. pachyderma* in this way remains to be determined because little is known about the exact foraminiferal calcification rates in their natural environment. Inferred calcification rates based on laboratory culturing



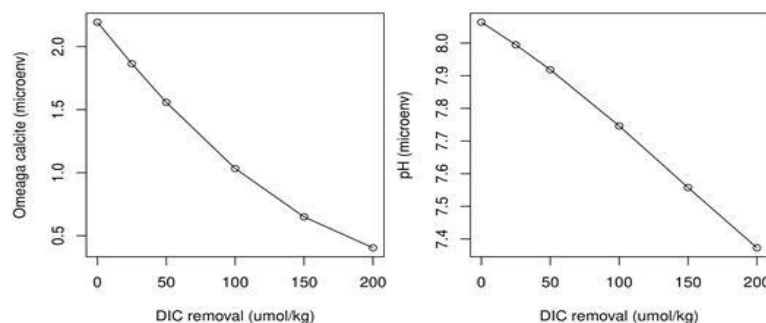
experiments and temperature dependent modelling suggest that *Neogloboquadrinoids* have lower calcification rates overall than other planktonic foraminifera species (Lombard et al., 2011). Furthermore, recent advances in three-dimensional imaging techniques (microCT scans) propose that growth patterns of *Neogloboquadrinoids* through ontogeny follow a distinct growth trajectory that unlike other spinose species slows at maturity for the final whorl of chambers (Burke et al., 2020), which constitute 70% or more of the total pre-gametogenic  $\text{CaCO}_3$ . Whole-shell measurements of non-crusted tows, such as those here, are likely dominated by the isotopic composition recorded in these terminal chambers. In this scenario, if boric acid incorporation at low pH is responsible for  $<1$  slopes in some species of foraminifera, it is unlikely to play a role in the *Neogloboquadrinoids* data presented here as low growth rates are associated with elevated  $\delta^{11}\text{B}$  above borate rather than below borate (Figure 2b; (Farmer et al., 2019; Uchikawa et al., 2015)).

In the following sections we explore additional mechanisms that could explain the lower-than-expected  $\delta^{11}\text{B}_{\text{foram}}$  values and high sensitivity of *N. pachyderma* to low seawater borate (slope  $<1$ ).

#### 4.1.1. Foraminiferal microenvironment and calcification

Non-spinose foraminifera are generally devoid of photosynthetic symbionts; the pH of the micro-environment around such foraminifera is expected to be more acidic than the ambient seawater. The respiration and calcification of foraminifera both release  $\text{CO}_2$  into the microenvironment during these processes, which have been suggested as the main drivers explaining the lower-than-expected  $\delta^{11}\text{B}_{\text{foram}}$  values in symbiont-barren species (Foster, 2008; Hönisch et al., 2003; Martínez-Botí et al., 2015; Yu et al., 2013).

To assess the calcification environment for *N. pachyderma* we estimated microenvironmental pH and the calcite saturation state ( $\Omega_{\text{calcite}}$ ) for our plankton tow dataset. Briefly, we derived  $\Omega_{\text{calcite}}$  at calcification depth using hydrographic profiles (TA and DIC) which yields on average  $\Omega_{\text{calcite}} = 2.2$ . One way to approximate the conditions within the micro-environment of a living foraminiferal, without turning to complex diffusion-reaction modelling (e.g., Zeebe et al., 2003), is to simply model the effect of removing TA and DIC in a 2:1 ratio to simulate the influence of calcification (c.f. Hönisch et al., 2019). Following Hönisch et al. (2019) we modelled the progressive removal of up to 200 and 400  $\mu\text{mol kg}^{-1}$  from the ambient DIC and TA, respectively (as in Hönisch et al., 2019; Figure 3). Taking the  $\delta^{11}\text{B}$  values of the *N. pachyderma* and *N. incompta* at face value, this treatment implies an average pH of 7.4 in the microenvironment with  $\Omega_{\text{calcite}} = 0.4$ . This suggests that *N. pachyderma* calcifies in waters undersaturated with respect to calcite.





455 **Figure 3.** Effect of DIC removal (and TA in a 2:1 ratio) on Omega calcite and pH

Calcification in foraminifera, like in many marine carbonates (Gilbert et al., 2022), takes place in a “privileged” internal space within a fluid, the calcifying fluid, that is ultimately modified from ambient seawater carbonate chemistry (de Nooijer et al., 2014 and references therein). Benthic foraminifera have been observed to upregulate the pH in their calcifying fluid as high as 9 (de Nooijer et al., 2009) by the removal of protons via a Ca-ATPase enzymatic pump (Toyofuku et al., 2017) and/or alkalinity elevation of seawater vacuoles to facilitate calcification (Bentov et al., 2009). It is likely that DIC is also elevated in the calcifying fluid by passive CO<sub>2</sub> diffusion and active HCO<sub>3</sub><sup>-</sup> pumping (Ujjié et al., 2023). Indeed, genes relating to these processes were recently identified in foraminifera by Ujjié et al. (2023).

Whether or not *N. pachyderma* upregulates its internal pH remains to be determined, however, active proton pumping as a mechanism for *N. pachyderma* calcification aligns well with the recent biomineralization model proposed for Mg incorporation in *N. pachyderma* outlined in Morley et al. (2024). Briefly, they demonstrated that the preferential exclusion of Mg<sup>2+</sup> into *N. pachyderma* is compromised in unfavourable calcification environments (e.g., at low seawater [CO<sub>3</sub><sup>2-</sup>] and SST >5 °C) in order to maintain energy for proton removal (see also (Evans et al., 2018; Zeebe and Sanyal, 2002). This observation invokes two important processes: (1) the generation and transport of bicarbonate and protons across the calcifying membrane and (2) that proton pumping may be less efficient for *N. pachyderma* at temperatures below 5 °C and low sea water [CO<sub>3</sub><sup>2-</sup>]. The latter process may provide an explanation for the steep  $\delta^{11}\text{B}_{\text{foram}} : \delta^{11}\text{B}_{\text{borate}}$  slope observed here in equation 1, considering that the samples collected from the coldest and most acidic environments lead to the largest offset from a slope = 1 (Figure 2c).

Assuming *N. pachyderma* upregulate their internal pH, the lower-than-expected  $\delta^{11}\text{B}_{\text{foram}}$  values, suggesting a calcification fluid that is undersaturated with respect to calcite, remain puzzling. Following Gagnon et al. (2021) these observations could be reconciled if we consider boric acid diffusion into the calcifying fluid as part of the biomineralization process. If the diffusion of boric acid between the calcifying fluid and the microenvironment around the foraminifera is fast, while the exchange of seawater between the two is slow, it is possible for the concentration of boric acid internally to be the same as that in the micro-environment. Since the  $\delta^{11}\text{B}$  of each aqueous boron species is set by their relative proportions, this sets the  $\delta^{11}\text{B}$  of borate in the calcifying fluid to be equal to the  $\delta^{11}\text{B}$  of borate externally, even if the pH internally is >> than the micro-environment. While this model reconciles the upregulation of pH in the calcifying fluid enabling calcification with  $\delta^{11}\text{B}_{\text{foram}}$  values representative of the (undersaturated) microenvironment surrounding the foraminifera, it awaits direct determination of the calcifying fluid pH in *N. pachyderma* to validate it.

#### 485 **4.1.2 The effect and impact of temperature on the boron isotope fractionation factor $\alpha_B$**

The influence of temperature on the aqueous boron isotope fractionation factor  $\alpha_B$  has been the subject of debate (Hönisch et al., 2019) even though there is a theoretical thermodynamic basis for  $\alpha_B$  to be influenced by temperature (Zeebe, 2005), its magnitude is uncertain and it has not been conclusively demonstrated experimentally. So far, the fractionation  $\alpha_B$  has been determined at 25 and 40 °C at a salinity of 35 (Klochko et al., 2006). However, large uncertainties prevent a conclusive quantification of the temperature dependence of  $\alpha_B$ , which has been used to argue against a significant temperature sensitivity of  $\alpha_B$  over the temperature range used in most  $\delta^{11}\text{B}$ -pH calibrations and paleo-pH studies (Foster and Rae, 2016). In Figure 2, we show the calibration

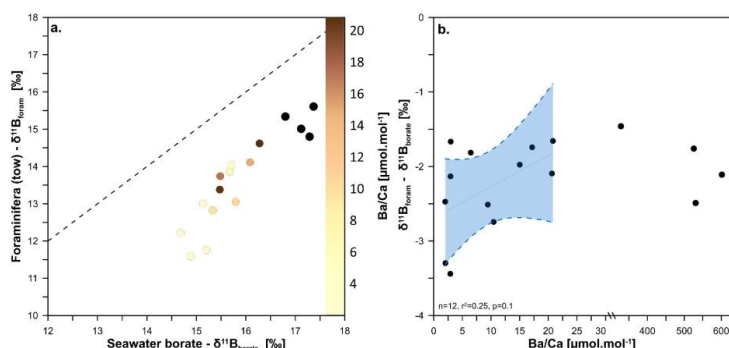


equation with constant  $\alpha_B$  as defined in Klochko et al. (2006) and in Figure S1c with a temperature dependent  $\alpha_B$  as defined in Hönisch et al. (2019).

495 Due to the large temperature gradient in our dataset,  $\alpha_B$  corrected for temperature has a significant effect on the slope and intercept (Figure S1b and S1c). Like in other symbiont-barren planktonic foraminifera the temperature correction, when applied to *N. pachyderma*, reduces the large negative offset between  $\delta^{11}\text{B}_{\text{foram}}$  and predicted  $\delta^{11}\text{B}_{\text{borate}}$  however the microenvironmental pH remains slightly below the predicted  $\delta^{11}\text{B}_{\text{foram}}$ :  $\delta^{11}\text{B}_{\text{borate}}$  line. Therefore, even with a temperature dependent  $\alpha_B$  *N. pachyderma* would still require manipulation of  
500 microenvironmental pH to reconcile the disequilibrium isotopic offset from seawater values. Furthermore, there is no significant correlation between the offsets of *N. pachyderma*  $\delta^{11}\text{B}$  from  $\delta^{11}\text{B}_{\text{borate}}$  and temperature (Figure 2c), arguing against a strong influence of a temperature dependent  $\alpha_B$ . Thus, although a temperature dependence on the fractionation factor is likely to exist, our data suggests that it is not significant over the temperature range relevant for *N. pachyderma*.

#### 505 4.2. The marine aggregate habitat hypothesis.

It has been recently suggested that some non-spinose foraminifera live in marine aggregate (also referred to as marine snow or particulate organic matter). This has been indirectly observed in laboratory culture for *N. pachyderma* (Davis et al., 2020), *G. truncatulinoides* (Richey et al., 2022) and from plankton net for *G. menardii* and *N. dutertrei* (Fehrenbacher et al., 2018). Geochemical analysis of the shells of these species tend to show  
510 elevated Ba/Ca (Fehrenbacher et al., 2018; Richey et al., 2022; Fritz-Endres et al., 2022; Hupp and Fehrenbacher, 2023) compared to species that have not been observed in marine aggregates, and well above Ba/Ca values expected if precipitating in seawater given coefficient partition defined from laboratory experiment (e.g., Hönisch et al., 2011). Barium sulphate  $\text{BaSO}_4$  (barite) in pelagic environment is thought to precipitate via microbial activity (e.g., González-Munoz, 2003; Martínez-Ruiz et al., 2020) or through supersaturation of barium and sulphur in  
515 microenvironment that promotes precipitation abiotically (Dehairs, 1980; Bishop, 1988; Horner and Crockford, 2021 and references therein). Hence foraminifera calcifying in such a microenvironment would have their shell enriched in barium compared to the bulk seawater. Such a microenvironment could be a concern for paleo-pH reconstructions as we expect variable pH alteration in marine aggregates. Marine aggregates dominated by algae can result in a pH increase if the signal is dominated by photosynthesis (e.g., Ploug et al., 1999) whilst aggregates  
520 dominated by organic matter degradation will release  $\text{CO}_2$  and decrease pH by 0.22-0.91 (Alldredge and Cohen, 1987). Due to the technical challenges to collect intact marine aggregates from the water column and to measure pH with microelectrodes on sometimes floating aggregates, studies on pH alterations in marine aggregates are rare (Alldredge and Cohen, 1987) and further constraints are needed to quantify pH changes on multiple aggregates where *N. pachyderma* and *N. incompta* are observed to live.



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**Figure 4.** Relationship between the  $\delta^{11}\text{B}$  of towed *N. pachyderma* (coloured circles) and *N. incompta* (black circles) with the  $\delta^{11}\text{B}$  of seawater borate in relation to calcite Ba/Ca ratio. Panel a. shows  $\delta^{11}\text{B}$  of towed specimens against  $\delta^{11}\text{B}$  of seawater borate while the colour gradient is showing the respective Ba/Ca values. the 1:1 line is shown by the black dashed line. Panel b. is showing the regression between  $\delta^{11}\text{B}_{\text{foram}} - \delta^{11}\text{B}_{\text{borate}}$  offset of towed *N. pachyderma* specimens and Ba/Ca values ( $n=12$ ,  $p=0.1$ ,  $r^2=0.25$ ). The data are fitted with a linear regression (black line) and a 95% confidence envelope (blue shade).

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If barium concentration is an accurate metric to trace this behaviour in *N. pachyderma* and *N. incompta* we would expect samples with high Ba/Ca to record a distinct pH/ $\delta^{11}\text{B}$  from samples with low-Ba/Ca samples. Figure 4a shows some samples have higher barium than what is predicted by seawater following the partition coefficient  $D_{\text{Ba}} = 0.11$  of other non-spinose foraminifera (Fehrenbacher et al., 2018), yet do not show any anomalous  $\delta^{11}\text{B}$  compared to low-Ba/Ca samples. The elevated Ba/Ca results ( $> 30 \mu\text{mol}/\text{mol}$ ) need to be caveated by the fact that samples were not treated for barite removal during the cleaning process (as in Fehrenbacher et al., 2018), as this would lead to unacceptable sample loss for  $\delta^{11}\text{B}$  measurement. The Ba/Ca ratio in *N. incompta* is distinct from *N. pachyderma*, with a range of 328-779  $\mu\text{mol}/\text{mol}$  (vs. 1-21  $\mu\text{mol}/\text{mol}$  for *N. pachyderma*). The species difference and trend of Ba/Ca values is observed in both tows and core tops. This striking contrast between the two species points towards a distinct behavioural difference between the two species, potentially suggesting *N. incompta* is more prone to live in marine aggregates or has a specific feeding behaviour that would favour Ba enrichment during calcification. The lack of any deviation in  $\delta^{11}\text{B}$  space for these high-Ba samples (Figure 4b) suggest that the Ba enrichment observed did not result in a pH-altered microenvironment in marine aggregates influencing the  $\delta^{11}\text{B}_{\text{foram}}$  and instead that Ba increase may be caused by other processes (e.g. feeding behaviour). In the absence of direct evidence of aggregate environment associated with high Ba/Ca for these two species, we conclude that the observed increase in Ba/Ca, either does not result in significant pH change or if it does, it does not compromise the  $\delta^{11}\text{B}$  proxy in the species examined here. The hypothesis that these species live in marine aggregate, and the link with Ba-enrichment requires further investigation through direct observation of intact marine aggregates in the water column (e.g. collected with a marine snow catcher) or newly formed in cultures, as well as direct measurement of pH change in the interstitial fluid of the aggregates and Ba/Ca in foraminifera shells.

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#### 4.3. $\delta^{11}\text{B}$ -derived $\text{CO}_2$ for core top values.

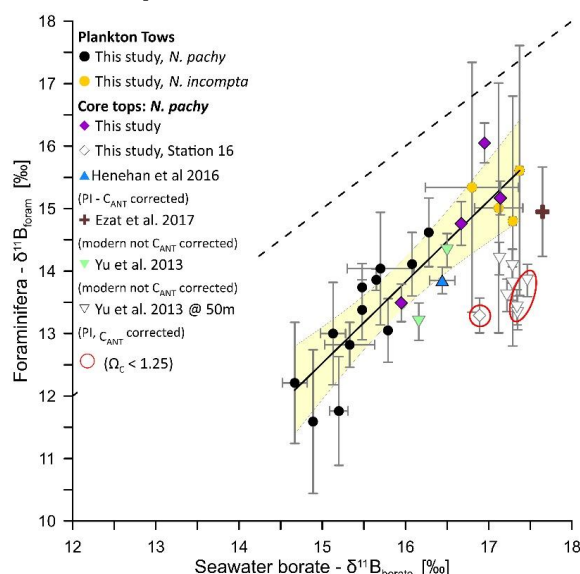
A comparison of available  $\delta^{11}\text{B}_{\text{foram}}$  values measured on *N. pachyderma* from previously published cores tops (Ezat et al., 2017; Henehan et al., 2016; Yu et al., 2013) with our tow-based calibration dataset shows that there is generally good agreement between *N. pachyderma* collected from tows and core tops (Figure 5). We note here

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that we recalculated seawater borate for the Yu et al. (2013) dataset using Glodap V2 at 50 m instead of CARINA that was used in the original study. We used an anthropogenic DIC correction ( $C_{ANT}$ ) on  $\delta^{11}B_{borate}$  values for all core tops pre-dating the onset of anthropogenic  $CO_2$  emissions (see Table S2 and S4). The core tops analysed in this study fall within the calibration uncertainties of the tow-based calibration equation except for Station 16. Further, the majority of the Yu et al. (2013) data falls below the calibration equation derived using the plankton

tows. There could be several reasons for the offsets between calibration studies. First, the estimated calcification depth of 50m for these samples may be too shallow. A shift to a deeper depth habitat (e.g. 75-150m) would reduce  $\delta^{11}B_{borate}$  and thereby result in a better overall fit with the tow dataset (Figure S2). However, in the absence of stable isotopes we cannot constrain habitat depth with better accuracy. Further, the modern water column data including the correction factor for anthropogenic carbon to estimate seawater borate may not represent the actual calcification environment of *N. pachyderma* preserved in core tops. For example, when the correction factor for anthropogenic carbon is removed for the Yu et al. (2013) dataset, the offset to the tow based calibration dataset is resolved. However, the pre-industrial ages for all but one core top in this dataset would strongly argue for the use of the correction factor for anthropogenic carbon. For station 16, it is possible that the sample from the MUC top 0-0.5cm is modern or partially modern and should not be corrected for anthropogenic carbon. This is supported by the age model for gravity core M23411 (Baumann, 2007) collected at the same location as Station 16 providing Holocene sedimentation rates of 143 years per 0.5cm. Therefore, the top 0-0.5cm of sediments at this station could include a significant contribution of specimens grown after the onset of fossil fuel burning. However, in the absence of a date from the multicore top we cannot confirm it.



**Figure 5. Compilation of plankton tows and core top  $\delta^{11}B_{foram}$  versus  $\delta^{11}B_{borate}$ .** Here we plot our tow and core top results together with all available  $\delta^{11}B_{foram}$  values measured on *N. pachyderma* (Henehan et al., 2016; Ezat et al., 2017; Yu et al., 2013). The 1:1 line is shown by the black dashed line, and the solid black line shows the York regression of the tow dataset as shown



in Figure 2 with the 95% confidence envelope (light yellow shade). The Yu et al., (2013) data is plotted with  $\delta^{11}\text{B}_{\text{borate}}$  values estimated at 50 m. Please view Figure S2 for  $\delta^{11}\text{B}_{\text{borate}}$  values estimated at 150 m.

585 Alternatively, the lower than expected  $\delta^{11}\text{B}_{\text{foram}}$  values from the Yu et al. (2013) dataset may result from different size fractions used in the analysis. Here, core tops were sieved at a narrow size fraction of 200–250  $\mu\text{m}$ , while Yu et al. (2013) used a larger range of 150–250  $\mu\text{m}$ . Indeed, the offsets of *N. pachyderma*  $\delta^{11}\text{B}_{\text{foram}}$  from  $\delta^{11}\text{B}_{\text{borate}}$  are much larger for the Yu et al. (2013) dataset that includes smaller specimens. However, we note that our core tops are not offset from our plankton tow dataset which includes all size fractions. This would argue against a size  
590 effect. However, the apparent size effect could be reconciled if it is placed in the context of dissolution. For example, it has been observed that small foraminifera are more affected by dissolution than larger individuals as a result of their higher surface area to volume ratio (Berger and Piper, 1972; Berger et al., 1982). The cumulative effect of smaller size fractions and partial dissolution may therefore explain the apparent offset in the Yu et al. (2013) dataset (Ni et al., 2007).

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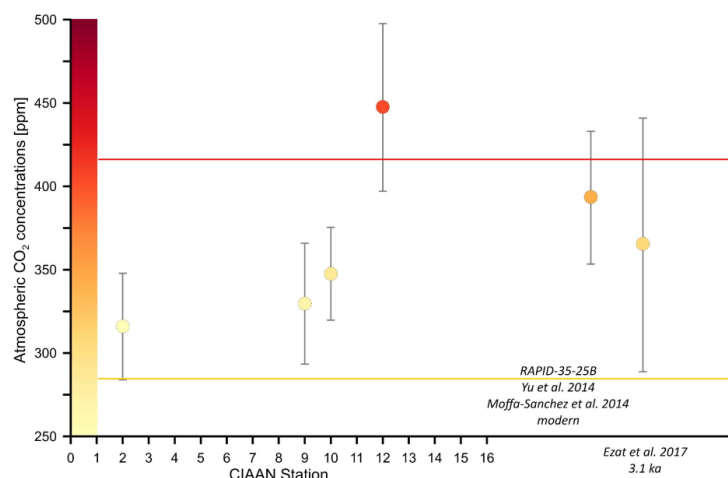
Finally,  $\delta^{11}\text{B}$  values recorded in crust calcite may be lower than in ontogenetic calcite. This has previously been suggested for *T. sacculifer*, where crust calcite is lower in  $\delta^{11}\text{B}$  relative to ontogenetic calcite because symbionts are expelled or digested before gametogenic calcification begins (Ni et al., 2007). This loss of photosymbionts decreases the local pH due to the lack of photosynthetic activity and the  $\delta^{11}\text{B}_{\text{borate}}$  of the microenvironment would  
600 be lower than ambient seawater values. Consequently, the crust calcite will be isotopically lighter than the ontogenetic calcite (Ni et al., 2007). However, *N. pachyderma* is asymbiotic and modern ecological observations would argue against a habitat migration to deeper depth during gametogenesis (Tell et al., 2022; Manno and Pavlov, 2014; Greco et al., 2019) and therefore it is unlikely that a difference in hydrographic conditions would be responsible for a geochemical signature difference between ontogenetic and crust calcite. These ecological  
605 observations are supported by geochemical analysis of living (no crust) and dead (crust) *N. pachyderma* specimens collected from the same plankton nets (Hupp and Fehrenbacher, 2023), *N. incompta* and *N. dutertrei* specimen grown and crusted in culture under constant temperatures (Davis et al., 2017; Westgård et al., 2023; Fehrenbacher et al., 2017) and *N. pachyderma* specimen from sediment traps (Jonkers et al., 2016).

610 The mechanisms responsible for the geochemical offsets observed in ontogenetic and crust calcite for *N. pachyderma* (e.g.,  $\text{Mg}/\text{Ca} \approx 15\%$  and  $\delta^{18}\text{O}_c$  up to 2 ‰), remain unresolved, but are more likely linked to changes in the biomineralization process than hydrography. For example, faster calcification rates during the formation of crust calcite relative to the last whirl of chambers could result in variable kinetic fractionation during ontogeny and therefore variation in the degree of isotopically heavy  $\text{B}(\text{OH})_3$  incorporated into the foraminiferal calcite in  
615 crusted specimen (Uchikawa et al., 2015; Farmer et al., 2019). If so, the degree of crusting would be an additional factor to consider when preparing specimens for analysis. Furthermore, the more soluble ontogenetic calcite (Wycech et al., 2018), could be prone to preferential dissolution (water column and sediments) relative to crust calcite, leaving core top *N. pachyderma* from sites close to undersaturation depleted in  $\delta^{11}\text{B}$  values (Hönisch and Hemming, 2004; Ni et al., 2007; Seki et al., 2010). Indeed, we note that the low  $\delta^{11}\text{B}$  values from Station 16 and  
620 from some stations of the Yu et al. (2013) dataset have low bottom water



$\Omega_c < 1.25$  values (Figure 4a, Table S4). Unfortunately, calcification rates are difficult to determine in culture for *N. pachyderma* as temperature control, especially at low temperatures, prevents prolonged periods of observations. Furthermore, there is no systematic  $\delta^{11}\text{B}$  offset between crusted and uncrusted specimens preventing us at this stage from estimating a geochemical offset value between ontogenetic and crust calcite (e.g., Kozdon et al., 2009). Ongoing developments in  $\delta^{11}\text{B}$  single shell analysis vs MC-ICPMS laser ablation (Standish et al., 2019; Mayk et al., 2020; Raitzsch et al., 2020) *N. pachyderma* may provide enhanced spatial resolution to address the foraminifera test isotopic heterogeneity.

To assess whether the tow-based calibration can be used to estimate past pH and atmospheric  $\text{CO}_2$  concentrations beyond these caveats we now treat the core tops as if they were an unknown paleo-sample.  $\delta^{11}\text{B}$  derived  $\text{CO}_2$  estimates from core tops in this study (except for station 16) provide  $\text{CO}_2$  values that are consistent with atmospheric  $\text{CO}_2$  observations made post 1900 (Figure 6). These results suggest that despite the low sedimentation rates; a proportion of modern foraminifera shells capture the anthropogenic  $\text{CO}_2$  signal within the top 0–0.5 cm of surface sediments in the Nordic Seas. We also calculated atmospheric  $\text{CO}_2$  using published core tops from Ezat et al. (2017) (which has larger uncertainties due to the additional uncertainties linked to differing analytical methods) and one core top from Yu et al. (2013) that we were able to pair with Mg/Ca values from the same multicore top published in Moffa-Sánchez et al. (2014). The highest reconstructed  $\text{CO}_2$  values consistent with modern atmospheric  $\text{CO}_2$  were measured in core tops that were confirmed modern by AMS  $^{14}\text{C}$  dating (e.g., Station 12 and RAPID-35-25B).



**Figure 6.** Atmospheric  $\text{CO}_2$  concentration [ppm] derived using boron isotopes, Mg/Ca and  $\delta^{18}\text{O}_c$  from CE20009 core tops collected from the Nordic Seas (except station 16). Also shown are two core tops that have paired Mg/Ca and  $\delta^{18}\text{O}_c$  values for *N. pachyderma* available. One from the Yu et al. (2013) dataset that we paired with Mg/Ca and  $\delta^{18}\text{O}$  from Moffa-Sánchez et al. (2014) and the other is from Ezat et al. (2017). The  $\text{CO}_2$  uncertainty was calculated with a Monte Carlo simulation (see methods) See also Table S4.

## 5. Conclusion



Here we present the first tow-based open ocean  $\delta^{11}\text{B}$  calibration of the non-spinose foraminifera *N. pachyderma* and *N. incompta* in the North Atlantic, complemented by core tops from similar locations. The use of tows allows us to precisely constrain the water chemistry in which foraminifera grew, bypassing the assumptions of foraminifera habitat depth and water chemistry typically encountered in core-top-based calibrations. We show that the signal recorded by these species is consistently below what is predicted by aqueous  $\delta^{11}\text{B}_{\text{borate}}$ , in line with other non-spinose foraminifera and that there is little evidence to support a strong influence of a temperature dependent  $\alpha_{\text{B}}$ .

We propose instead that the lower-than-expected  $\delta^{11}\text{B}_{\text{foram}}$  values are a result of active proton pumping during calcification raising the pH in the calcification fluid while the microenvironment surrounding the cell is undersaturated with respect to calcite as a result of respiration and calcification. The seemingly opposing signals can be reconciled when considering rapid boric acid diffusion between the calcifying fluid and the microenvironment around the foraminifera (Gagnon et al., 2021).

The addition of core top samples in the calibration does not significantly alter the slope of the calibration, giving confidence in the application of this tow-based calibration equation in downcore sediments. This is further supported when combining the  $\delta^{11}\text{B}$  calibration with the Mg/Ca- $\delta^{18}\text{O}$  correction scheme to reconstruct past atmospheric  $\text{CO}_2$  concentrations. Given the rapid rise in recent atmospheric  $\text{CO}_2$  concentrations, highly resolved marine archives when independently dated (e.g.  $^{210}\text{Pb}$ ), may be used to reconstruct ocean surface  $\text{CO}_2$  and air-sea  $\text{CO}_2$  fluxes over the past 200 years/the last glacial cycles and thereby provide crucial insight into ocean-atmosphere carbon fluxes since the onset of anthropogenic carbon emissions over deepwater formation regions. The application of the  $\delta^{11}\text{B}$  calibration to recent marine archives may therefore allow us to answer critical open questions about the role of the Nordic Seas as a carbon sink when deepwater formation was reduced (stronger) and sea ice extend was greater (reduced).

#### Data and materials availability

All data needed to evaluate the conclusions in the paper are presented in the paper and/or the Supplementary Materials.

#### Author contributions

E.D.L.V. carried out palaeoceanographic sample preparation and geochemical analysis of plankton tows and core tops from expedition CE20009, compiled and analysed all datasets, and wrote the original draft of the manuscript. A.M. conceptualized the project, acquired funding, carried out palaeoceanographic sample preparation of plankton tows from the Labrador Sea, coordinated the input of all co-authors and finalized the manuscript for publication. M.R. performed trace element and boron isotope analysis on *N. pachyderma* plankton tow samples from the Labrador Sea. J.B. supervised A.M. at the Alfred Wegner Institute and oversaw trace element and boron isotope analysis. U.N. oversaw all stable isotope analyses of water and foraminifera samples from CE20009 and contributed to the final version of this manuscript. G.F. oversaw trace element and boron isotope analysis on *N. pachyderma* plankton tow samples from CE20009 and contributed to the final version of this manuscript. M.K. advised A.M. during project conceptualization, supervised her during her MSCA-IF at MARUM, University of



Bremen, and contributed to the final version of this manuscript. T.B. provided support to E.D.L.V. during boron  
690 isotope analysis and contributed to the final version of this manuscript. J.C.B. carried out palaeoceanographic  
sample preparation of plankton tows from expedition CE20009. M.E. provided sample material and contributed  
to the final version of this manuscript.

### Competing interests

695 The contact author has declared that neither they nor their co-authors have any competing interests.

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