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RESEARCH ARTICLE

Relationships Between Temperature, pH, and Crusting on Mg/Ca Ratios in Laboratory-Grown *Neogloboquadrina* Foraminifera

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Abstract Mg/Ca ratio paleothermometry in foraminifera is an important tool for the reconstruction and interpretation of past environments. However, existing Mg/Ca:temperature relationships for planktic species inhabiting middle- and high-latitude environments are limited by a lack of information about the development and impact of low-Mg/Ca ratio "crusts" and the influence of the carbonate system on Mg/Ca ratios in these groups. To address this, we cultured individual specimens of *Neogloboquadrina incompta* and *Neogloboquadrina pachyderma* in seawater across a range of temperature (6°–12°C) and pH (7.4–8.2). We found by laser ablation inductively couple mass spectrometry analyses of shells that culture-grown crust calcite in *N. incompta* had a lower Mg/Ca ratio than ontogenetic calcite formed at the same temperature, suggesting that temperature is not responsible for the low-Mg/Ca ratio of neogloboquadrinid crusts. The Mg/Ca:temperature relationship for ontogenetic calcite in *N. incompta* was consistent with the previously published culture-based relationship, and no significant relationship was found between Mg/Ca ratios and pH in this species. However, the Mg/Ca ratio in laboratory-cultured *N. pachyderma* was much higher than that reported in previous core top and sediment trap samples, due to lack of crust formation in culture. Application of our ontogenetic calcite-specific Mg/Ca:temperature relationships to fossil *N. pachyderma* and *N. incompta* from five intervals in cores from the Santa Barbara Basin and the Bering Sea shows that excluding crust calcite in fossil specimens may improve Mg/Ca-based temperature estimates.

1. Introduction

Planktic foraminifera preserved in sediments are a rich archive of paleoceanographic information, and shell Mg/Ca ratios are an increasingly important component of geochemical paleothermometry (e.g., Barker et al., 2005; Cléroux et al., 2008; Dekens et al., 2008; Elderfield & Ganssen, 2000; Lea et al., 2002; Nürnberg, 1995; Sadekov et al., 2009; Schmidt, Spero, & Lea, 2004; Tripati et al., 2003). For example, Mg/Ca paleothermometry used in conjunction with $\delta^{18}O_{calcite}$ can isolate the contribution of $\delta^{18}O_{seawater}$ to infer changes in the hydrological system or ice volume (e.g., Lea et al., 2002; Mashiotta et al., 1999; Schmidt et al., 2004; Stott et al., 2004). However, Mg/Ca:temperature relationships can be specific to morphospecies (Lea et al., 1999; Mashiotta et al., 1999; Nürnberg et al., 1996; von Langen et al., 2005) and even genotypes (Sadekov et al., 2016) and may be influenced by intrashell variability in Mg/Ca ratios, such as crusting (Sadekov et al., 2009), as well as the inorganic carbon system (Lea et al., 1999; Russell et al., 2004), salinity (Hönisch et al., 2013; Lea et al., 1999), and oceanic Mg/Ca (Evans et al., 2016).

Understanding the history and dynamics of diverse oceanographic regions, especially high latitudes, is critical for placing future global change in a long-term context. Foraminifers of the genus neogloboquadrina, *N. pachyderma* (formerly *N. pachyderma* var. sinistral (Darling et al., 2006)) and *N. incompta* (formerly *N. pachyderma* var. dextral (Darling et al., 2006)), are often well preserved and the dominant species in low-diversity assemblages, making them good candidates for Mg/Ca paleothermometry at high latitudes. *Neogloboquadrina pachyderma* is a morphospecies with a bipolar distribution (Bé & Tolderlund, 1971; Darling & Wade, 2008), comprising several genotypes (Darling et al., 2004; Darling & Wade, 2008). It is often the only abundant species in polar and subpolar faunas (Bauch et al., 2002;

Eynaud, 2011; Eynaud et al., 2009). *Neogloboquadrina incompta* has a wider temperate to subpolar distribution (Darling & Wade, 2008), and both *N. pachyderma* and *N. incompta* have been reported in association with some tropical and temperate upwelling regions (Davis et al., 2016; Naidu & Malmgren, 1996). Whereas the *N. pachyderma* Mg/Ca:temperature relationship has never been established in controlled laboratory experiments, relationships based on core tops (Hendry et al., 2009; Kozdon, Eisenhauer, et al., 2009; Mashiotta et al., 1999; Nürnberg, 1995; Vázquez Riveiros et al., 2016) and sediment traps (Jonkers et al., 2013) have been published. A laboratory-calibrated Mg/Ca:temperature relationship has been developed using combined data from *N. incompta* and *Neogloboquadrina dutertrei* (a subtropical/tropical species) (von Langen et al., 2005), but it is unclear whether this is also applicable to *N. pachyderma*. The temperatures obtained from these relationships are often inconsistent with one another. Possible sources for disagreement between published Mg/Ca:temperature relationships for *N. pachyderma* and *N. incompta* include an unconstrained carbonate ion ($[CO_3^{2-}]$) and/or pH influence and the presence of a thick low-Mg/Ca ratio crust found on the outer portion of neogloboquadrinid shells (Hendry et al., 2009; Jonkers et al., 2013, 2016].

Previous culture experiments have shown that $[CO_3^{2-}]$ can influence Mg/Ca ratios in the spinose planktic foraminifers *Orbulina universa* and *Globigerina bulloides* (Lea et al., 1999; Russell et al., 2004). Varying levels of Mg/Ca ratio sensitivity to the inorganic carbonate system in the form of pH and/or $[CO_3^{2-}]$ have also been established in benthic foraminifera (Dissard et al., 2010; Elderfield et al., 2006; Raitzsch et al., 2010; Rathmann & Kuhnert, 2008; Rosenthal et al., 1997; Yu & Elderfield, 2008), with Mg/Ca ratios in some species insensitive to pH and/or $[CO_3^{2-}]$ (Dissard et al., 2010; Rathmann & Kuhnert, 2008). A substantial pH and/or $[CO_3^{2-}]$ control on Mg/Ca ratios could introduce error into interpretations of the Mg/Ca:temperature signals in fossil foraminifera, especially for morphospecies such as *N. pachyderma* and *N. incompta* which combined have a subtropical to polar distribution (Bé & Tolderlund, 1971; Darling & Wade, 2008) and can live in waters with highly variable $[CO_3^{2-}]$ such as upwelling regions or even at the sea ice-water interface (Dieckmann et al., 1991; Hendry et al., 2009; Spindler & Dieckmann, 1986). This potential influence of pH and/or $[CO_3^{2-}]$ could be a confounding factor in interpreting Mg/Ca ratios and has been evoked as an explanation for low-Mg/Ca:temperature relationship sensitivity (Jonkers et al., 2013), with some authors accounting for $[CO_3^{2-}]$ in the interpretation of their relationships (Hendry et al., 2009).

Crusting presents a further potential complication in interpretation of neogloboquadrinid Mg/Ca:temperature relationships. In all neogloboquadrinids, ontogenetic calcite is formed first and includes new chamber growth followed by gradual thickening, and formation of Mg/Ca banding in *N. pachyderma* (Jonkers et al., 2016) and *N. dutertrei* (Fehrenbacher et al., 2017). A crust is added later, if at all, with some shells acquiring a crusted texture several days prior to gametogenesis (Fehrenbacher et al., 2017; von Langen, 2001). Encrusted fossil foraminifera are characterized by a thicker shell, a distinct euhedral texture, low $\delta^{18}O$, and a relatively low-Mg/Ca ratio (Arikawa, 1983; Bolton & Marr, 2013; Kozdon, Ushikubo, et al., 2009; Sadekov et al., 2005). Analyses of core top and down core neogloboquadrids have been unable to resolve whether the low-Mg/Ca ratio of crust calcite is the result of (1) precipitation in deeper, and hence colder, more CO_2-rich waters than ontogenetic calcite; (2) differing Mg/Ca:temperature sensitivities between the two types of calcite (Bolton & Marr, 2013; de Nooijer et al., 2014; Hathorne et al., 2003; Steinhardt et al., 2015); (3) diagenesis (Branson et al., 2015); or (4) a combination of factors. Recent evidence argues against a temperature trigger for the formation of crust calcite (Jonkers et al., 2016), due to the presence of a low-Mg/Ca ratio crust in shells grown in a deep mixed layer of uniform temperature. Understanding the influence of crusting on Mg/Ca paleotemperature reconstructions is essential in species such as *N. pachyderma* in which such crusts make up as much as 80% of total shell mass (Kohfeld et al., 1996).

We present the results of laboratory culture experiments in the neogloboquadrinid foraminifers *N. incompta* and *N. pachyderma* with the objectives of (a) improving Mg/Ca:temperature relationships for neogloboquadrinid foraminifera by generating culture-based, species-specific relationships based on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses, (b) examining the influence of crust versus ontogenetic calcite on Mg/Ca paleothermometry of cultured neogloboquadrinids, and (c) quantifying the potential influence of covarying parameters pH and/or $[CO_3^{2-}]$ on Mg/Ca ratios in specimens cultured across a range of seawater pH conditions.

Table 1
Composition and Source of Isotopic and Elemental Spikes

Spike	Batch information	Spike isotopic composition	Elemental enrichment after spike addition
^{43}Ca (as CaCO$_3$)	ORNL Batch 169191	83.93% ^{43}Ca	30%
^{87}Sr (as SrCO$_3$)	NIDC LH-136990	91.26% ^{87}Sr	20%
Sr (as SrCl$_2$*6H$_2$O)	Sigma Aldrich ACS Lot MKB0071V	99% cations as Sr ($<$0.05% Ba, $<$0.05% Ca)	15%

2. Methods

2.1. Live-Collected Specimens and Preparation for Culture

Culture experiments were conducted at the UC Davis Bodega Marine Laboratory (BML) and followed procedures outlined by von Langen et al. (2005). *Neogloboquadrina incompta* and *N. pachyderma* were collected between 1 and 35 km offshore of Bodega Head, CA, using vertically integrated 155 μm mesh net tows deployed to a maximum depth of 200 m. Most specimens were recovered ~35 km offshore (38°11.6 0N, 123°23.9 0W), and tow material was returned within 2–12 h to BML to be sorted. Samples were allowed to warm to ambient air temperature (10–18°C) during transit, because chilling material during the return trip was found to inhibit foraminifera recovery, potentially due to thermal shock.

2.2. Culture Methods

Individual foraminifera were picked from plankton tows based on suitability for culture, assessed by the presence of colored cytoplasm and absence of crusting. Specimens selected for culture were rinsed once in filtered seawater, transferred via pipette into individual 75 mL polystyrene Falcon© flasks of filtered seawater (0.6 μm), and allowed to recover for ~16 h at treatment temperature. Recovery was indicated by the extension of a rhizopodial network and visible movement or streaming of rhizopods. An aliquot of a concentrated single-spike solution was added by volume to filtered seawater to achieve an isotopic or elemental enrichment to label calcite formed in culture (Table 1). Individuals that recovered were transferred into filtered seawater containing one of these labels.

Foraminifera were held at constant temperature (±0.15°C) in recirculating baths in individual Falcon© Flasks with nearly consistent salinity (33 ± 0.5 on the practical salinity unit (psu) scale). Illumination was provided on a 12 h light-dark cycle at 55 ± 15 μmol photons m^{-2} s^{-2} by CREE XP-E 72 Watt LED lights (full spectrum). Once in labeled seawater, each specimen was photographed and measured. Each individual was observed daily and fed a 1 day old, freeze-killed *Artemia* nauplius every other day until gametogenesis or death. Gametogenesis was defined as the release of gametes, always preceded by pregametogenic characteristics including retraction of rhizopodia and loss of cytoplasm color. In contrast, a nongametogenic death was defined as the cessation of feeding and rhizopodial activity without pregametogenic features or the release of gametes. Culture solutions were replenished after feedings with spiked seawater from the same batch. After completion of their life cycle, specimens were rinsed in deionized water and archived for analysis.

2.3. Spike and Seawater Preparation

Foraminifera were kept in filtered seawater obtained from an offshore seawater intake system. Seawater was labeled geochemically with one label, either elemental Sr, ^{43}Ca, or ^{87}Sr, to identify culture-grown calcite using LA-ICP-MS to profile through the shell wall. Stock solutions were made by dissolving powdered materials into ~4% Fisher Optima HCl in Millipore water (Table 1). All labels produced signals identifiable by LA-ICP-MS; however, we found isotopic labels to be preferable to elemental Sr, due to high natural Sr variability found in ocean-grown calcite.

After adding a label, seawater for temperature treatments (6, 9, and 12°C) was returned to the measured ambient pH of incoming seawater by adding small aliquots of 0.1 N NaOH. For pH experiments with *N. incompta*, carried out only at 12°C, seawater pH was adjusted further to achieve a target pH$_T$ (total scale) between 7.4 and 8.2 by adding 0.1 N HCl or 0.1 N NaOH to labeled seawater. Due to a paucity of *N. pachyderma* in the net tows, we did not conduct pH experiments on this species and all *N. pachyderma* were held at ambient pH by the above method.

Table 2
Average Mg/Ca Ratios of Whole Shells, Crusted Calcite, and Ontogenetic Calcite in N. incompta *From Santa Barbara Basin (MV0811-15JC and SPR0901) and* N. pachyderma *From the Bering Sea (U1340), Along With the Number of Individual Foraminifera Analyzed*

Core	Core depth (cm)	Age (ka)	Species	Whole shell Mg/Ca (mmol/mol)	Crust Mg/Ca (mmol/mol)	Ontogenic Mg/Ca (mmol/mol)	n
SPR0901-10BC	~	Modern	*N. incompta*	1.3 ± 0.4	0.9 ± 0.3	2.0 ± 0.4	10
MV0811-15JC	301–303	7.4	*N. incompta*	1.4 ± 0.5	1.0 ± 0.4	1.8 ± 0.7	6
MV0811-15JC	751–731	14.7	*N. incompta*	1.4 ± 0.5	1.1 ± 0.4	1.7 ± 0.6	5
U1340 (1H-1A)	1–2	14.5	*N. pachyderma*	1.0 ± 0.4	0.8 ± 0.3	1.5 ± 0.9	5
U1340 (1H-3A)	45–47	17.8	*N. pachyderma*	0.7 ± 0.4	0.6 ± 0.6	0.9 ± 0.5	13

2.4. Culture Water Sampling

Culture water was sampled at the start (from batches of labeled filtered seawater) and end (from several individual flasks) of each experiment and analyzed for pH_T and total alkalinity. The pH_T was measured spectrophotometrically with *m*-cresol purple dye, using an Ocean Optics Jaz Spectrophotometer EL200 (SD ± 0.003). Total alkalinity was determined via automated Gran titration on a Metrohm 809 Titrando (SD ± 2.809 μmol/kg) using 0.1 N HCl with acid concentrations standardized using Dickson certified reference materials. All carbonate system calculations were performed using CO2Calc (Robbins et al., 2010) with CO_2 constants K_1, K_2 from Millero (2010).

2.5. Fossil Specimens

To compare Mg/Ca temperatures based on our experimental Mg/Ca:temperature relationships for *N. incompta* and *N. pachyderma* with those from other paleothermometers, fossil specimens were selected from two Santa Barbara Basin cores and a Bering Sea core. Specimens of *N. incompta* were selected from early Holocene (7.4 ka) and Bølling-Allerød (14.7 ka) intervals from Santa Barbara Basin piston core MV0811-15JC (34.37°N, 120.13°W; 418 m water depth) (Table 2). An age model (radiocarbon) for these samples was previously published (Moffitt et al., 2014). The $\delta^{18}O$ of *G. bulloides* (Moffitt et al., 2014) from these down-core sediment intervals provided an independent temperature estimate for comparison with *N. incompta* Mg/Ca temperatures and were based on a species-specific culture-derived relationship (Bemis et al., 1998) and published $\delta^{18}O_{seawater}$ (Bemis et al., 2002). *Neogloboquadrina incompta* specimens were also picked from a nearby box core (SPR0901-10BC, 34.28°N, 120.04°W; 596 m water depth) to obtain an estimate of modern oceanographic conditions (≪250 years) (D. Pak, unpublished data). Since *G. bulloides* specimens were not available from these sediments to provide a modern $\delta^{18}O$-based temperature, we compared calculated Mg/Ca temperatures with modern average instrumental late-summer temperature at 50 m from WOA13 (1955–2013) (Locarnini et al., 2013). This depth and time period was chosen as being comparable to paleotemperatures from *G. bulloides*, which is most abundant in the Southern California Bight during July–September, at 40–80 m depth (Kincaid et al., 2000; Field, 2004). In Bering Sea core U1340 (53.4°N, 179.52°W; 1,294 m water depth), fossil *N. pachyderma* were picked from Bølling-Allerød (14.5 ka) and early deglacial (17.8 ka) intervals. The age model for U1340 is based on radiocarbon, and alkenone-derived paleotemperature estimates are available from Schlung et al. (2013).

2.6. Sample Preparation and Analysis
2.6.1. Sample Cleaning

Cultured planktic foraminifera were cleaned prior to LA-ICP-MS analysis to remove organics by immersion in a 1:1 mixture of 0.1 N NaOH and 30% H_2O_2 at 65°C for 30 min during which they were ultrasonicated for four 10 s periods (Mashiotta et al., 1999). All down-core and sediment surface shells were cleaned by immersion in a 1:300 mixture of 0.1 N NaOH and 30% H_2O_2 for 30 min while being periodically sonicated as for cultured shells. Fossil shells were, however, subjected to more extensive sonication than cultured shells (sonicated five to ten times for 10 s intervals) to remove any authigenic material not present in cultured specimens.

2.6.2. LA-ICP-MS Methods

All shells were ablated using a Photon Machines 193 nm ArF laser with an ANU HelEx dual-volume laser ablation cell coupled to an Agilent 7700x quadrupole-ICP-MS, in the Department of Earth and Planetary Sciences, University of California Davis. A 30 μm circular or 44 μm square spot was used to analyze each adult chamber

from the outside-in with up to four repeat ablations per chamber. Analysis followed the methodology described in Fehrenbacher et al. (2015). Individual chambers were ablated at 5 Hz with a fluence of 0.58 J cm^{-2}, and ablated material was transported in a He-Ar gas mixture. All ratios were standardized to NIST SRM 610, which was analyzed periodically between foraminifera to correct for drift. Al/Ca and Mn/Ca were monitored in fossil foraminifera, and two shells showing low (<30 μmol/mol) but variable Al/Ca profiles were excluded from our results. No specimen had elevated Mn/Ca > 60 μmol/mol.

2.6.3. Electron Microprobe Methods

Based on observation and LA-ICP-MS analyses, two *N. incompta* shells, determined to have grown both a new chamber and added a crust while in culture at 12°C, were selected for elemental image mapping by electron microprobe. Shells were embedded in epoxy (EpoFix), sectioned to expose a cross-sectional area of the chamber, and carbon coated. Foraminifera were analyzed with a Cameca SX-100 electron microprobe in the Department of Earth and Planetary Sciences, University of California, Davis, for Mg and Ca, using a 0.5 μm spot size with a dwell time of 0.5 s, 15 keV voltage, and a 15 nA beam current. Ca counts below 3,500 count(s) per second were filtered to minimize edge effects.

2.6.4. Development of Mg/Ca:Temperature Relationships

Our results include chambers which were entirely grown in culture or that calcified extensively enough in culture that ocean-grown (unlabeled) calcite was too thin to be analytically resolved by laser and thus made up a negligible proportion of total calcite. A Mann-Whitney test comparing Mg/Ca ratios in chambers grown entirely in culture and those with an analytically negligible ocean-grown portion showed no significant difference in Mg/Ca ratios at 12°C ($p = 0.645$) or 9°C ($p = 0.095$). Each point in the resulting Mg/Ca:temperature relationship is composed of the average across all included chambers from a single individual. Error on temperatures is reported based upon the average standard error around mean Mg/Ca at each treatment temperature.

2.7. Statistical Treatment of Data

All data analyses were done using the stats and "nlme" packages in R (https://R-project.org/) (R Core Team, 2013). For statistical tests in which an assumption of normality was required, an angular transformation was applied to Mg/Ca ratio data and a Shapiro-Wilks test was used to confirm normal distribution of data. For the purposes of this analysis, data from this study (single shells) were weighted equally with those from von Langen et al. (2005) (pooled chambers) for *N. incompta*. As a result, Mg/Ca:temperature relationships are weighted toward our data set at temperatures represented in both data sets.

3. Results

3.1. Culture Observations

Chamber addition and ontogenetic changes were observed in *N. pachyderma* and *N. incompta*, culminating in gametogenesis. Chambers formed as previously described in these and other nonspinose species (Bé et al., 1979; Hemleben et al., 1989; von Langen, 2001), beginning with colored cytoplasm enclosing all or most of the shell and forming the outline of a new chamber. The eventual retreat of cytoplasm into the shell then revealed a translucent new chamber, which filled with red (for most *N. pachyderma*) or red-orange (for most *N. incompta*) cytoplasm and gradually thickened, as indicated by a decrease in translucence over the course of 1–3 days. Prior to gametogenesis, the rhizopodial network was "sticky," allowing foraminifera to adhere to flask walls and to aggregate food particles and available debris or detritus around the shell.

After calcifying the ultimate (F) chamber, individuals signaled the beginning of gametogenesis by a decrease in "stickiness" and a gradual lightening of cytoplasm color followed by a retraction of the rhizopodial network and a cessation of feeding. By the end of this process, foraminifera were opaque, white, and lacked rhizopodia. This "pregametogenic" phase was accompanied in some *N. incompta* individuals, by the addition of a crusted texture. During gametogenesis, the individual expels gametes, leaving behind a nearly empty shell. Some individuals appeared to release small spheres of cytoplasm with independent rhizopodia some days prior to, or without the appearance of, pregametogenic characteristics. Similar structures were previously observed and thought to be potentially indicative of an asexual reproductive phase by von Langen (2001). We were unable to confirm this interpretation, as maturation into proloculi was not observed in association with the release of either cytoplasm spheres or gametes.
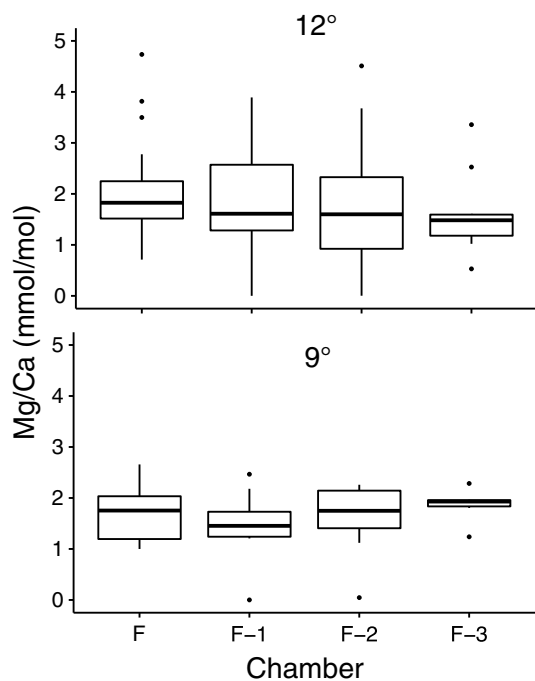
Figure 1. Mg/Ca ratio averages from sequential chambers of *N. incompta* at 12°C (top) and 9°C (bottom). Boxes encompass the 1st and 3rd quartiles, with horizontal black bars denoting the mean. No significant differences were found between successive chambers at either temperature. All calcite (both crust and ontogenetic) is included, although crusting was found in only 13% of *N. incompta*.

3.2. Influence of Crusting on Shell Mg/Ca Ratios

The Mg/Ca ratios derived from LA-ICP-MS profiles of labeled, laboratory-grown calcite of *N. incompta* were compared across culture-grown (see section 2.6.4) calcite in the four chambers of the adult whorl. Although *N. incompta* were also cultured at 6°C, no analytically discernable calcite was added at this treatment. Where multiple ablation profiles through a single chamber were possible, they were averaged to produce a single chamber Mg/Ca ratio. A repeated measures analysis of variance was used to identify significant differences across chambers within a single individual. No significant difference was found in Mg/Ca ratios across sequential chambers in the adult whorl (F, F-1, F-2, and F-3) within a temperature treatment at either 9°C ($p = 0.825$) or 12°C ($p = 0.950$) (Figure 1). The same was true of *N. pachyderma* at 6°C ($p = 0.419$), and 12°C ($p = 0.216$). The culture-grown portions from all chambers were therefore combined into a single-shell average Mg/Ca ratio.

Overall, the incidence of geochemical crusts forming in culture was extremely low, occurring in only 13% of *N. incompta* ($n = 6$), and in no *N. pachyderma* (Table 3). In the 12°C treatment, two *N. incompta* added a new chamber followed by a crust. In these chambers, the texturally crusted portion of the shell had substantially lower Mg/Ca ratios (1.7 and 1.0 mmol/mol) than the ontogenetic calcite (3.2 and 2.5 mmol/mol) (Figure 2). Whole shell Mg/Ca ratios, integrating both portions of the shell (2.2 mmol/mol and 1.8 mmol/mol) would thus reflect a mixture of ontogenetic and crust calcite Mg/Ca ratios. A two end-member (binary) mixing model indicates that the Mg/Ca ratio of crusted calcite contributed a 60% and 40% proportion of the whole shell Mg/Ca ratio in these shells.

Bands of high- and low-Mg/Ca ratios were observed in several *N. incompta* shells, grown both in the laboratory and in the ocean, but were confined to the inner, ontogenetic layer of the shell. Crust Mg/Ca ratios, in contrast, were relatively homogenous (Figure 3).

3.3. Mg/Ca Temperature Relationships in Ontogenetic Calcite

Combining data from *N. incompta* shell Mg/Ca ratios grown at 9°C and 12°C (Table 4) with those from von Langen et al. (2005) produces equation (1) for *N. incompta* where *T* is temperature:

$$Mg/Ca \ (mmol/mol) = 0.71(\pm0.14)^* e^{(0.08(\pm0.01)^* T)} \tag{1}$$

An exponential model is applied, as the Mg/Ca ratio of planktic foraminifera shells has been shown to increase exponentially with temperature (e.g., Barker et al., 2005; Jonkers et al., 2013; Lea et al., 1999; Mashiotta et al., 1999; Nürnberg, 1995; Rosenthal et al., 1997; Vázquez Riveiros et al., 2016). LA-ICP-MS analyses of *N. incompta* grown in culture revealed high interindividual Mg/Ca ratio variability (Figure 4), which was not accounted for by temperature or pH. This variability cannot be attributed to salinity ($\pm$<1 psu), nor ontogeny as there were no significant differences between chambers. Although still unexplained, such interspecimen variability has also been observed in the foraminifers *Orbulina universa* and *Globigerinoides sacculifer* grown under constant conditions (Dueñas-Bohórquez et al., 2011; Spero et al., 2015).

In the Mg/Ca:temperature relationship derived from *N. pachyderma* cultured at 6, 9, and 12°C, Mg/Ca ratios were higher than those estimated from previously published *N. pachyderma* Mg/Ca:temperature relationships from core tops and sediment traps (Hendry et al., 2009; Jonkers et al., 2013; Kozdon, Eisenhauer, et al., 2009; Nürnberg, 1995; Vázquez Riveiros et al., 2016), and different from those in *N. incompta* (Figure S1 in the supporting information). Our results, using individual shell LA-ICP-MS profiles, yield the following relationship (Figure 4) where *T* is temperature:

$$Mg/Ca \ (mmol/mol) = 0.71 \ (\pm0.2)^* T - 2.49(\pm1.5) \tag{2}$$

Table 3
Seawater Parameters and Mg/Ca in Cultured Foraminifera, Including Mg/Ca Ratios for Each Chamber and a Chamber Average for Each Individual Shell

Species	Culture conditions Temperature (°C)	pH (total)	$[CO_3^{2-}]$ (µmol/kg)	Alkalinity (µmol/kg)	Mg/Ca (mmol/mol) F	F-1	F-2	F-3	F-4	F-5	Shell average	Life history New chamber in culture?	Crust?	Gametogenic?	Longest dimension (µm) Initial	Final
N. incompta	9	7.8			1	1.25	1.5	1.93			1.42	y	y	y	168	149
N. incompta	9	7.8			1.83						1.83	y	n	y	192	204
N. incompta	9	8.13	117.14	2040	2.1	2.47	2.26	1.97			2.20	n	n	y	242	256
N. incompta	9	8.13	117.14	2040	2.66	1.58	2.2				2.12	n	n	y	242	283
N. incompta	9	8.13	117.14	2040		2.18	1.78	2.28			2.19	n	n	y	185	210
N. incompta	9	8.13	117.14	2040		1.45	2.12	1.93			1.84	n	n	y	219	239
N. incompta	9	8.13	117.14	2040							2.03	y	n	y	199	207
N. incompta	9	8.05	142	1781	1.68	1.46	1.72	1.8			1.67	n	y	y	150	201
N. incompta	9	8.05	142	1781	1.04	1.21	1.12	1.24			1.15	y	n	y	178	199
N. incompta	12	7.8			2.13						2.13	y	n	y	110	206
N. incompta	12	7.8			2.39						2.39	y	n	y	211	233
N. incompta	12	7.8			2.78						2.81	y	n	y		
N. incompta	12	7.8			2.38	2.33	3.33	1.59			2.38	y	n	y		
N. incompta	12	8	127.31	2366	1.49	1.62	1.73				1.61	y	n	y	151	168
N. incompta	12	8	127.31	2366	2.25	1.56	2.42				2.08	y	y	y	86	100
N. incompta	12	8	127.31	2366	1.54	1.71	1.6				1.62	y	n	n	93	102
N. incompta	12	8	127.31	2366	1.8	1.98	1.22	2.55			1.89	y	n	y	108	113
N. incompta	12	8	127.31	2366	1.83	1.6	1.7				1.7	y	n	n	92	97
N. incompta	12	8.14	172.55	2417.92	2.21	2.31	2.33				2.28	y	n	y	111	133
N. incompta	12	8.14	172.55	2417.92	1.47	1.83	1.46	1.48			1.56	y	n	y	102	113
N. incompta	12	8.14	172.55	2417.92	1.67	1.4					1.54	y	y	y	102	106
N. incompta	12	8.14	172.55	2417.92	1.55	1.24					1.40	y	n	n	90	94
N. incompta	12	8.14	172.55	2417.92	2.25	2.72	2.82				2.60	y	n	n	75	84
N. incompta	12	8.14	172.55	2417.92	1.8	1.53					1.67	y	n	y	102	108
N. incompta	12	8.14	172.55	2417.92	2.43	3.19					2.81	y	n	n		
N. incompta	12	8.05	132.42	2092	3.5	2.65	1.82	2.53			2.66	n	n	n	356	381
N. incompta	12	8.05	132.42	2092	2.61	2.81	2.32	1.59			2.57	n	n	y	320	345
N. incompta	12	8.05	132.42	2092		1.4	0.64				1.21	n	n	y	254	269
N. incompta	12	8.05	132.42	2092	1.32						1.32	n	n	y		
N. incompta	12	8.05	132.42	2092	3.82	3.58	3.68				3.69	n	n	y		
N. incompta	12	7.41	31.67	1927							1.38	n	n	n	261	277
N. incompta	12	7.41	31.67	1927	2.06						2.06	n	n	y	179	190
N. incompta	12	7.41	31.67	1927	2.12		2.01				2.07	n	n	y	138	149
N. incompta	12	7.41	31.67	1927	1.89	3.4	3.42	3.36			3.02	n	n	n	202	206
N. incompta	12	7.41	31.67	1927	4.74	3.89	4.51	5.49			4.66	n	n	y	171	181
N. incompta	12	7.41	31.67	1927	1.57						1.57	n	n	y		
N. incompta	12	8	115.94	2029	0.57	0.56	0.6	1.02			0.69	n	n	n	346	362
N. incompta	12	8	115.94	2029	1.04						1.04	y	n	y	268	300
N. incompta	12	8	115.94	2029	1.51	1.24	0.92	1.28			1.24	y	y	y	280	293
N. incompta	12	8	115.94	2029	0.84	0.7	0.66	0.53			0.68	y	n	y	233	235
N. incompta	12	8	115.94	2029	0.71	0.73	0.7				0.71	n	n	n	286	311
N. incompta	12	8	115.94	2029	0.99	1	1.2				1.06	n	n	y	262	320
N. incompta	12	8	115.94	2029	1.52						1.52	n	y	y	206	238
N. incompta	12	8	115.94	2029	1.52						1.52	y	n	n	289	318
N. incompta	12	8	115.94	2029	2.02	1.61	2.33				1.99	y	n	y		

Table 3. *(continued)*

Species	Culture conditions				Mg/Ca (mmol/mol)							Life history			Longest dimension (μm)	
	Temperature (°C)	pH (total)	[CO$_3^{2-}$] (μmol/kg)	Alkalinity (μmol/kg)	F	F-1	F-2	F-3	F-4	F-5	Shell average	New chamber in culture?	Crust?	Gametogenic?	Initial	Final
N. pachyderma	6	7.8			1.44						1.44	n	n	n	69	79
N. pachyderma	6	7.8			1.48	1.51					1.50	n	n	n		117
N. pachyderma	6	7.8			1.36	1.08	2.97				1.80	n	y	n	71	194
N. pachyderma	6	7.8			2.68	1.09	1.27				1.68	n	n	n	184	213
N. pachyderma	9	7.8			4.9	4.11					4.90	y	n	y	194	194
N. pachyderma	9	7.8			4.77		2.35				4.44	y	n	n	175	184
N. pachyderma	12	7.8			4.29	4.07	5.26				3.32	y	y	y	172	
N. pachyderma	12	7.8			6.42						5.25	n	n	n		282
N. pachyderma	12	8.05	132.42	2099	7.29	6.79					6.79	n	y	y	262	
N. pachyderma	12	8.05	132.42	2099		8.39		8.9			8.19	y	n	y	248	296

Note. Blank cells indicate data that were not collected and have not been included in any analyses. Life history information is also noted including whether crusting or gametogenesis occurred in culture and the longest dimension of the shell as measured at the beginning and end of culture experiments.

The resulting Mg/Ca:temperature relationship cannot be constrained beyond linear, as has been published for other limited temperature ranges studied in *N. pachyderma* (Hendry et al., 2009; Kozdon, Eisenhauer, et al., 2009). However, an exponential fit, as reported elsewhere (Jonkers et al., 2013; Mashiotta et al., 1999; Nürnberg, 1995; Vázquez Riveiros et al., 2016), may be more appropriate over a larger range of temperature.

3.4. Impact of Crust Formation on Mg/Ca Ratios in Fossil Specimens

Neogloboquadrina incompta and *N. pachyderma* analyzed from intervals in Santa Barbara Basin cores SPRO901-10BC and MV0811-15JC, and Bering Sea core U1340 contained inner ontogenetic calcite and outer crusts (identified by texture and relatively low-Mg/Ca ratios compared to ontogenetic calcite) (Figures S2 and S3). These observations are similar to the texture and geochemistry observed in cultured *N. incompta* (Figures 2, 3, and S3), and other fossil shells (Hathorne et al., 2003; (*N. incompta* and *N. dutertrei*) Bolton & Marr, 2013; de Nooijer et al., 2014; (*N. dutertrei*) Steinhardt et al., 2015). *Neogloboquadrina pachyderma* was more heavily crusted than *N. incompta*, with crust contributing between 30 and 90% of total calcite, as determined by the fraction of the total ablation time required to pass through each portion of the shell. This is as compared to 20–70% in *N. incompta* fossils. In some areas, the inner chamber calcite had been lost, potentially due to vigorous cleaning or dissolution. The loss of this shell portion is clear by both Scanning Electron Microscopy (SEM) and LA-ICP-MS analyses (Figure S3).

3.5. Applying the Mg/Ca:Temperature Relationships to Fossil Specimens

Whole shell Mg/Ca ratios in all adult chambers of *N. incompta* sampled from intervals in Santa Barbara Basin cores SPR0901-10BC and MV0811-15JC (modern, 7.4 ka, and 14.7 ka intervals) were intermediate between the low-Mg/Ca ratio of crust and high-Mg/Ca ratio of ontogenetic calcite for the same specimens (Table 5 and Figure 5). The temperature calculated from the von Langen et al. (2005) Mg/Ca:temperature relationship for Santa Barbara Basin fossil *N. incompta* from the three time slices differed depending on whether they were based on whole shell Mg/Ca ratios or only the ontogenetic portions of the shell (Table 5). When based only on ontogenetic calcite, Mg/Ca-based temperatures from the 7.4, 14.7 ka and modern intervals were 12°C, 11°C, and 10°C, respectively, as compared to δ^{18}O-derived temperatures from *G. bulloides* (12°C during both down-core intervals) and modern average seasonal temperatures of 11°C at 60 m water depth (Table 5).

In Bering Sea core U1340, the Mg/Ca:temperature relationship (equation (2)) was applied to Mg/Ca ratios in ontogenetic calcite from *N. pachyderma*, to obtain calculated temperatures of 6°C (at 14.5 ka) and 5°C (at 17.8 ka). These temperatures are consistently lower than $U_{37}^{k'}$ temperatures from the samples nearest in age (10°C at 14.5 ka and 9°C at 17.8 ka) (Schlung et al., 2013; Figure 6; Table 6). The von Langen et al. (2005) Mg/Ca:temperature relationship applied to whole shell Mg/Ca ratios from these time intervals yielded temperatures of 2°C (14.5 ka) and 7°C (17.8 ka), with other published equations producing a range of results from 0 to 10°C at 14.5 ka and $-7°$ to 4°C at 17.8 ka (Figure 6 and Table 6).

3.6. pH

For *N. incompta* at 12°C, the treatment at which pH experiments were carried out, there was no significant trend ($p = 0.123$) between Mg/Ca ratios and pH_T (7.4 < pH_T < 8.1; 31.7 μmol kg^{-1} < [CO$_3^{2-}$] < 172.6 μmol kg^{-1}) (Figure 7 and Table S1). Moreover, a general linear mixed effects model, taking into account experimental temperature as well as measured pH within treatments, found no significant effect of pH ($p = 0.188$).
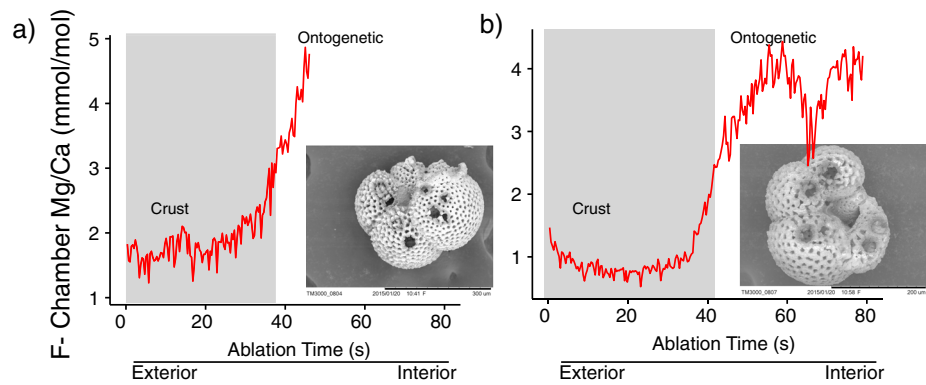
Figure 2. Representative LA-ICP-MS profiles through two *N. incompta* specimens (a) #278 and (b) #198 that grew both a new chamber and a crust in the laboratory, along with SEM images of the external shell. LA-ICP-MS profiles begin with the outer, crusted surface of the shell (0 s) and continue through the inner ontogenetic calcite layer. The crust has lower, more homogeneous Mg/Ca ratios than the inner ontogenetic calcite.

4. Discussion

4.1. Intershell and Intrashell Mg/Ca Ratio Variability in Cultured Foraminifera

The average Mg/Ca ratios from individual foraminifera in each treatment agree well with results from pooled chambers in previous experiments (von Langen et al., 2005). However, the range of Mg/Ca ratios documented in individual chambers at a single temperature is greater than in pooled chambers, a result similar to previous findings in *G. sacculifer* (Dueñas-Bohórquez et al., 2011). The observation of this high interindividual variability in cultured shells demonstrates that whereas either pooled chambers or multiple shell average Mg/Ca ratios may correlate with temperature, other physiologic factors, not directly related to hydrography, exert partial control over individual chamber Mg/Ca ratios. This finding indicates the need for caution in interpreting environmental conditions using single-shell or single-chamber analyses in these two neogloboquadrinid species.

Observed Mg/Ca ratio banding in *N. incompta* appeared similar to that reported in *N. dutertrei* (Fehrenbacher & Martin, 2010), *N. pachyderma* (Jonkers et al., 2016), and other species of planktic foraminifera (e.g., Eggins et al., 2004; Sadekov et al., 2005; Spero et al., 2015). As it occurred in culture-grown calcite, banding cannot be the product of migration within the water column with vertical changes in temperature and/or pH (Jonkers et al., 2016; Spero et al., 2015). Nor can banding be attributed to symbiont activity or alteration of the
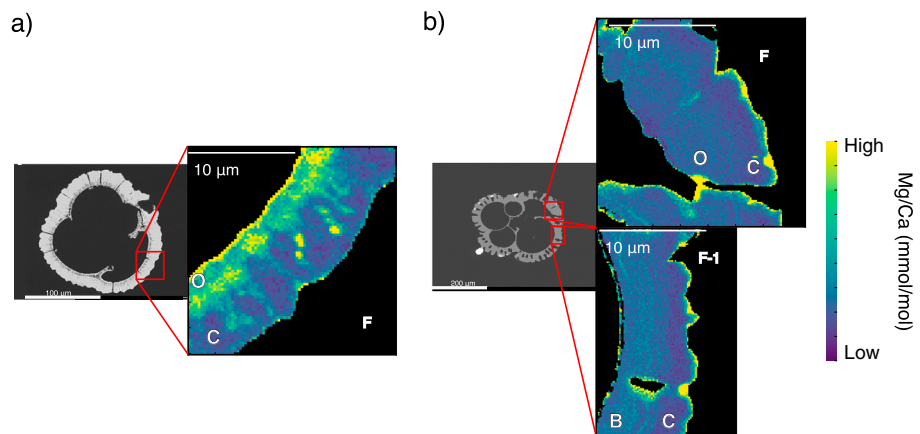

Figure 3. Backscatter images and Electron Microprobe maps of cultured *N. incompta* Mg/Ca ratios. Both F chambers were grown entirely in culture at constant temperature (12 ± 0.15°C). Foram #278 (a) has ontogenetic calcite (O) with a relatively high-Mg/Ca ratio and a crust (C) with a homogenous, low-Mg/Ca ratio. Some heterogeneity may be present in the ontogenetic calcite, but banding is not resolvable. Foraminifer #298 (b) shows a similar pattern in the culture-grown F chamber, although the Mg/Ca ratio difference between crust and ontogenetic calcite is less than in #176. Both F chamber and F-1 chamber (partially ocean grown) show Mg/Ca ratio banding (B) toward the interior portion of the shell.

Table 4

Average and Standard Deviation of Mg/Ca Ratios in N. incompta *and* N. pachyderma *at Each Temperature Treatment, Number of Individual Foraminifera Analyzed, and the Resulting Mg/Ca:Temperature Relationships*

Species	Culture temperature (°C)	N	Average Mg/Ca (mmol/mol)	Mg/Ca:temperature relationship
N. incompta	9	9	1.7 ± 0.5	Mg/Ca (mmol/mol) = 0.71($\pm$0.14)*exp$^{(0.08(\pm0.01)*T)}$
	12	36	1.9 ± 0.8	Equation (1)
N. pachyderma	6	4	1.6 ± 0.2	Mg/Ca (mmol/mol) = 0.71 ($\pm$0.2)*T − 2.49($\pm$1.5)
	9	2	4.7 ± 0.3	Equation (3)
	12	4	5.9 ± 2.1	

Note. The relationship for *N. incompta* has been combined with species-specific data from von Langen et al. (2005).

microenvironment, as *N. incompta* and *N. pachyderma* lack photosymbionts. In *O. universa* and *N. dutertrei* Mg/Ca ratio banding varies on a diurnal time scale, possibly mediated by mitochondrial processes (Fehrenbacher et al., 2017; Spero et al., 2015). This may also be the case for *N. incompta*.

4.2. Mg/Ca:Temperature Relationships in Ontogenetic Calcite

Despite high interindividual variability in *N. incompta* specimens cultured at a given temperature, the averages of all single-shell Mg/Ca ratios at one temperature from this study are consistent with the temperatures predicted by the von Langen et al. (2005) relationship, obtained using a solution-based methodology. This supports the observation that foraminifera analyzed by LA-ICP-MS can give results comparable to those achieved from solution measurements (Hathorne et al., 2003). All cultured neogloboquadrinids were primarily composed of ontogenetic calcite, and we suspect from descriptions of ontogeny that the previous culture-based Mg/Ca:temperature relationships for these species may hold the same inherent bias toward ontogenetic calcite (von Langen, 2001). Thus, both the Mg/Ca:temperature relationships presented here (based explicitly on ontogenetic calcite) as well as the von Langen et al. (2005) relationship may produce unrealistically cold temperatures when applied to whole shells with crusts. More robust temperature reconstructions utilizing these *N. incompta* Mg/Ca:temperature relationships may be achieved if crust calcite is excluded from analyses. In *N. pachyderma*, cultured between 6 and 12°C, Mg/Ca is higher and more sensitive to temperature than previously published relationships based on solution analyses of core tops or sediment traps (Figure 4). We hypothesize that the absence of low-Mg/Ca ratio crusts accounts for the higher Mg/Ca ratios and higher temperature sensitivity in cultured neogloboquadrinids as compared to core tops and sediment traps. Thus, the Mg/Ca:temperature relationship presented here should be applied only to the ontogenetic portion of the shell and may only be valid over the range of culture temperatures.
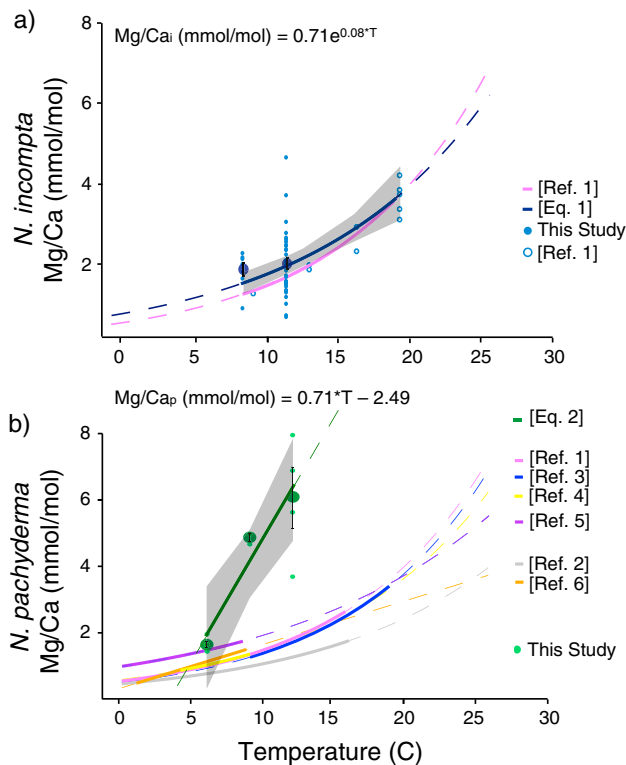
4.3. Application of Mg/Ca:Temperature Relationships in Ontogenetic Calcite to Fossil Neogloboquadrinids

Application of Mg/Ca:temperature relationships specific to ontogenetic calcite in fossil *N. incompta* from the Santa Barbara Basin resulted in temperatures slightly closer to those from *G. bulloides* δ^{18}O and modern comparisons, than those from whole shell Mg/Ca ratios utilizing the von Langen et al. (2005) relationship (Table 5). The degree of crusting in *N. incompta* may be low enough in Santa Barbara Basin that application of Mg/Ca:temperature relationships based on ontogenetic calcite rather than whole shells makes little difference. However, using a Mg/Ca:temperature relationship specific to ontogenetic calcite in *N. incompta* should be considered in environments with extensive or temporally variable

Figure 4. Neogloboquadrinid shell Mg/Ca ratios versus seawater temperature from this study, compared to published relationships. Individual specimen Mg/Ca ratios from this study are shown in small closed circles. (a) Mg/Ca ratios in *N. incompta* (9 and 12°C) from this study and from von Langen et al. (2005) (small open circles) are compared. In the latter, each point represents an analysis of 10–30 pooled chambers grown in culture. To facilitate comparison, the average (±1 standard error) of individual specimen Mg/Ca ratios at each temperature from this study are also shown (large closed circles), along with the 95% confidence interval based on the standard error of predicted values of each equation; (b) Mg/Ca ratios in *N. pachyderma* at 6, 9, and 12°C (this study) compared with published relationships for this species and one for *N. incompta* and *N. dutertrei* (von Langen et al., 2005). Key to references in legend: Ref. 1, von Langen et al. (2005); Ref. 2, Nürnberg (1995); Ref. 3, Jonkers et al. (2013); Ref. 4, Vázquez Riveiros et al. (2016); and Ref. 5, Kozdon, Eisenhauer, et al. (2009).

Table 5
Comparison Between Average Late-Summer Temperatures at 50 m, δ^{18}O-Derived Temperatures and Mg/Ca-Derived Temperatures From N. incompta *Obtained From Santa Barbara Basin Cores SPRO901-10BC and MV0811-15JC*

Core	Age (ka)	Temperature estimates (°C)	δ^{18}O	von Langen whole Shell (°C)	von Langen crust only (°C)	Ontogenetic only	
						von Langen (°C)	Equation (2) (°C)
SPR0901-10BC	Modern	11 (60 m Summer)	-	10	6	12	10
MV0811-15JC	7.4	12	−0.13	10	6	13	12
MV0811-15JC	14.7	12	−0.60	10	8	12	11

Note. Mg/Ca-temperature calibrations use the von Langen et al. (2005) relationship and equation (1). Oxygen isotope data are from Moffitt et al. (2014). Error on temperatures calculated using equation (1) are ±0.6°C, based upon standard error around mean Mg/Ca at each treatment, averaging ±0.4 Mg/Ca mmol/mol.

encrustation, or for analyses in which the differences between individual foraminifera (potentially with differing degrees of encrustation) could be highly significant.

Comparison of *N. pachyderma* Mg/Ca temperatures to alkenone temperatures in the Bering Sea requires an adjustment for depth and seasonality. Alkenone temperatures are assumed to reflect annual mean SST based on their calibration to this parameter. However, in the Bering Sea, high-amplitude seasonality and a short coccolithophore growing season result in alkenone-derived temperatures that are biased toward summer-fall SST (Caissie et al., 2010; Schlung et al., 2013). In the North Pacific, *N. pachyderma* records a similar late-summer seasonal signal (Jonkers & Kučera, 2015; Thunell & Honjo, 1987) but calcifies deeper in the water column (Bauch et al., 2002). The difference between the depth habitat of *N. pachyderma* and coccolithophorids is a likely cause of apparent temperature differences in the two records (Laepple & Huybers, 2013; Leduc et al., 2010; Nürnberg et al., 2000). In the Sea of Okhotsk, the maximum abundances of uncrusted *N. pachyderma* are found at 50 m (Bauch et al., 2002), while crusted forms are observed from 50 to 150 m depth on the Japan Margin (Arikawa et al., 1983). Thus, we similarly interpret crusting as beginning at around 50 m in the Bering Sea, and ontogenetic calcite in *N. pachyderma* as forming at this or slightly shallower depths. August-September average temperatures at the core location in the modern Bering Sea range from 7–9°C at the surface to 4–5°C at 50 m, a difference of ~4°C (Locarnini et al., 2013). Under the assumption that the shallow temperature profile of the Bering Sea and the depth at which ontogenetic and crust calcite formed during the deglacial were comparable to those in the modern ocean, then the calcification temperature of *N. pachyderma* ontogenetic calcite would be ~SST($U^{k'}_{37}$) −4°C.

a)

Santa Barbara Basin

b)

Bering Sea

Crust
Uncrusted
Whole

Figure 5. Mg/Ca of crusted (black) and ontogenetic (white) calcite, compared with whole shell average Mg/Ca (gray) for (a) *N. incompta* from Santa Barbara Basin cores SPRO901-10BC (modern) and MV0811-15JC (7.4 and 14.7 ka) and (b) *N. pachyderma* from Bering Sea core U1340 (14.5 and 17.8 ka). Boxes encompass the 1st and 3rd quartiles, and horizontal bars represent average Mg/Ca. *N* refers to the number of individual foraminifera analyzed.

Our ontogenetic calcite-specific Mg/Ca:temperature relationship yields temperatures indistinguishable from those at the presumed calcification depth for both Bering Sea intervals (6°C at 14.5 ka and 5°C at 17.8 ka). By contrast, while several previously published Mg/Ca:temperature relationships produce temperatures within 2°C of assumed 50 m temperature at 14.5 ka (6°C) (Jonkers et al., 2013; Nürnberg, 1995; von Langen et al., 2005), all result in lower temperatures at 17.8 ka (5°C) by 1–11°C (Figure 6) (Jonkers et al., 2013; Kozdon, Eisenhauer, et al., 2009; Nürnberg, 1995; Vázquez Riveiros et al., 2016; von Langen et al., 2005). This could be partly the result of a 10% increase in crust calcite in this interval, as described above. It is also important to note that not all Mg/Ca:temperature relationships were developed based on a North Pacific population of *N. pachyderma*, a distinction which may be important given the genetic diversity within *N. pachyderma* (Darling & Wade, 2008) and the potential for genetic influences on Mg/Ca ratios (Sadekov et al., 2016;
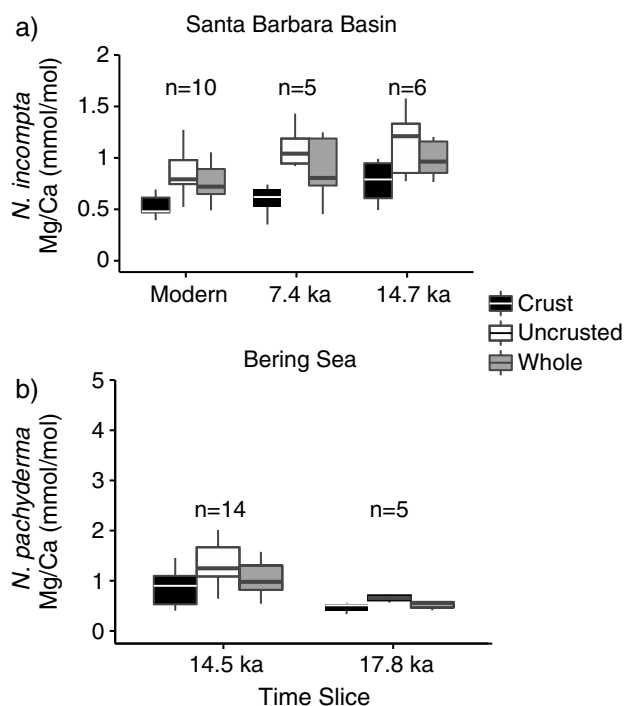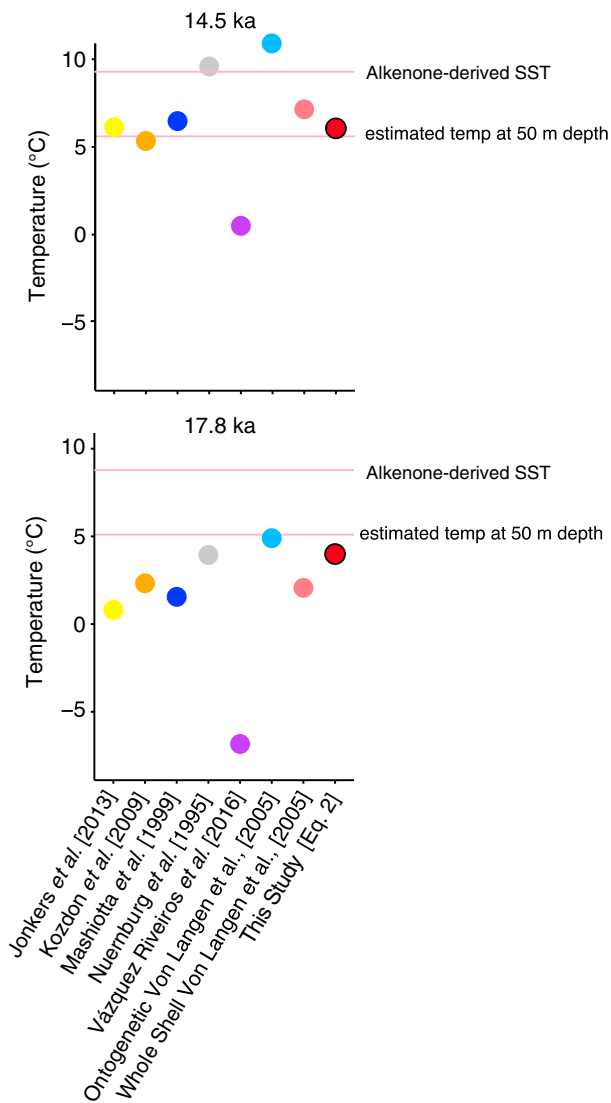
Figure 6. Temperatures calculated from the Mg/Ca:temperature relationship presented in this study (ontogenetic calcite only) and from previously published relationships (whole shells), applied to *N. pachyderma* from the Bering Sea. The von Langen et al. (2005) relationship is shown applied to both whole shell and ontogenic calcite. The pink lines designate the alkenone-derived temperatures, and an estimated temperature at 50 m depth.

Vázquez Riveiros et al., 2016). Only the Mg/Ca:temperature relationship presented here based on ontogenetic calcite gives temperatures within 1°C of 50 m calcification temperatures and reproduces the (small) relative temperature difference between time periods (Table 6 and Figure 6). Thus, for *N. pachyderma*, application of a Mg/Ca:temperature relationship developed specifically for ontogenetic calcite may represent an important tool for some down-core temperature reconstructions.

Estimating the relative proportion of crust to ontogenetic calcite from Mg/Ca ratios is not possible by whole shell solution analyses, although crusts are detectable using SEM imaging and often light microscopy. Avoiding heavily encrusted neogloboquadrinids when selecting shells for paleothermometry and then applying a Mg/Ca:temperature relationship based on ontogenetic calcite may offer a partial solution, especially if analyses are confined to final chambers, which are often less encrusted (Steinhardt et al., 2015). Alternatively, distinguishing between crust and ontogenetic calcite using LA-ICP-MS analyses and a Mg/Ca:temperature relationship specific to calcite type is a potentially effective approach for improving Mg/Ca paleo-temperature reconstructions from neogloboquadrinid foraminifera.

4.4. Crusting in the Laboratory

LA-ICP-MS analyses of *N. incompta* specimens cultured under controlled conditions show that crust calcite has relatively low-Mg/Ca ratios compared to ontogenetic calcite at constant conditions (Figures 2 and 3). This finding is consistent with recent observations from a sediment trap showing that *N. pachyderma* crust calcite has a low-Mg/Ca ratio, absent any environmental changes in the water column in which they grew (Jonkers et al., 2016). Thus, the low-Mg/Ca ratio signature of crust calcite observed in fossil neogloboqua-drinids cannot be purely a temperature signal from deepwater cal-cification. Rather, there must be a difference in Mg/Ca:temperature sensitivity between the two calcite types (assuming that the Mg/Ca ratio in crust calcite is indeed temperature sensitive). This implies that crust thickness and its relative contribution to the whole shell Mg/Ca ratio is an important source of variability in traditional solu-tion Mg/Ca paleothermometry using neogloboquadrinids. We note that crust growth in culture was rare and that culture calibrations tend to be biased toward the youngest chambers, which are both more likely to grow in culture and are found to be less crusted in

Table 6

Comparison Between $U_{37}^{k'}$ Temperatures From the Bering Sea (Mean Summer SST) (Schlung et al., 2013), $U_{37}^{k'}$ Temperatures Adjusted for 50 m Depth (4°C Offset; See Text) (Locarnini et al., 2013), and Mg/Ca-Derived Temperatures Obtained Using the Relationship Developed in This Study for Ontogenetic Calcite From N. pachyderma *Ontogenetic Calcite Equation (2) and Temperatures Obtained by Applying Published Core Top Relationships to Whole Shell Average Mg/Ca*

Core	Age (ka)	$U_{37}^{k'}$ temp estimates (°C)	Adjusted $U_{37}^{k'}$ temp estimates (°C)	This study (°C)	Maximum temperature from previously published equations (°C)	Minimum temperature from previously published equations (°C)
U1340	14.5	10	6	6	10 (Ref. 1)	0 (Ref. 2)
U1340	17.8	9	5	5	4 (Ref. 1)	−7 (Ref. 1)

Note. Ref. 1, Nürnberg et al. (1996); Ref. 2, Vázquez Riveiros et al. (2016). Error on temperatures calculated using equation (2) are ±1.6°C, based upon standard error around mean Mg/Ca at each treatment, averaging ±0.2 Mg/Ca mmol/mol.
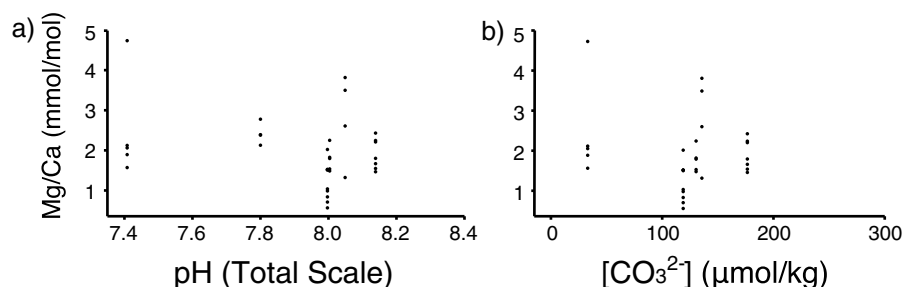
Figure 7. Mg/Ca ratios (mmol/mol) from individual specimens of *N. incompta* relative to (a) pH and (b) $[CO_3^{2-}]$ for laboratory-grown *N. incompta* calcite at 12°C. No relationship was detected between pH or $[CO_3^{2-}]$ and Mg/Ca at either temperature treatment ($p = 0.078$ and $p = 0.057$, respectively).

fossil foraminifera (Jonkers et al., 2012; Steinhardt et al., 2015). Thus, neogloboquadrinid encrustation is rare or absent for most cultured foraminifera and variable and difficult to constrain by solution analyses in core tops. This variability in the degree of encrustation present in foraminifera used for calibration will inevitably result in bias toward either warmer or colder computed temperatures when applied to shells with differing degrees of crusting.

Moreover, the rarity of crust growth in culture suggests a trigger for crusting that is not replicated in our laboratory experiments. Low temperature has been proposed as one possible trigger for some nonspinose tropical species (Hemleben et al., 1989), although argued against for *N. pachyderma* by Jonkers et al. (2016). We used a range of temperatures (6–12°C), including those typical of the cold extreme at our collection site (6°C) and observed no temperature dependence in the rare incidences of crust occurrence and therefore exclude temperature as a trigger in these species. Crusting has also been associated with reproduction in neogloboquadrinids (Arikawa, 1983), an association supported by the observation of crust addition shortly prior to gametogenesis in cultured specimens. Although all crusted foraminifera in this study did undergo gametogenesis, not all foraminifera that underwent gametogenesis formed a crust (Table 3), indicating that crusting is not obligatory for reproduction.

4.5. Ontogeny and Chamber-to-Chamber Mg/Ca Variability in Neogloboquadrinid Foraminifera

Previous studies of *G. sacculifer* (Dueñas-Bohórquez et al., 2011) and *N. dutertrei* (Jonkers et al., 2012) have identified Mg/Ca ratio shifts in successive chambers, with Mg/Ca ratios decreasing in *G. sacculifer* and increasing in *N. dutertrei* through the chamber whorl. In the current study, however, no significant Mg/Ca ratio difference was found between successive chambers grown at a single temperature (Figure 1). Thus, ontogenetic processes cannot explain the observation in fossil neogloboquadrinids of Mg/Ca ratio trends in successive chambers where reported changes in ocean-grown individual chamber Mg/Ca ratios are not explained by differential crusting and thus differing crust/ontogenetic calcite ratios across chambers.

4.6. Effect of pH or $[CO_3^{2-}]$ on Mg/Ca

Our results suggest that seawater pH or $[CO_3^{2-}]$ have a negligible effect on Mg/Ca ratios of ontogenetic calcite in neogloboquadrinid foraminifers, although we are unable to distinguish between the two parameters, as they covary in our treatments. This contrasts with the response of spinose planktic foraminifers *O. universa* and *G. bulloides* (Lea et al., 1999; Russell et al., 2004). This means that pH is not likely to be the cause of temperature bias associated with high latitudes and upwelling environments. It is possible that physiologic differences in calcification between spinose and nonspinose foraminifera control the presence or magnitude of pH effects on Mg incorporation, a hypothesis bolstered by the range of results for inorganic carbon system-dependent Mg/Ca incorporation reported across benthic foraminifera species (Dissard et al., 2010; Elderfield et al., 2006; Raitzsch et al., 2010; Rathmann & Kuhnert, 2008; Rosenthal et al., 1997; Yu & Elderfield, 2008). It is also possible that a Mg/Ca:pH relationship may exist across all planktic foraminifera but that this influence is only significant at higher temperatures than those at our collection site (8–14°C) and experiments (12°C) which were markedly lower than for previous experiments with spinose species (22°C) (Lea et al., 1999; Russell et al., 2004). In either case, our results indicate that pH and $[CO_3^{2-}]$ are not significant controls over neogloboquadrinid Mg/Ca ratios over our experimental temperature range.

5. Conclusions

We determined the relationship between temperature and Mg/Ca ratios in cultured planktic foraminifers *N. pachyderma* and *N. incompta* and found an influence of temperature in the ontogenetic calcite of both species but no relationship between Mg/Ca ratios and pH and/or [CO_3^{2-}]. Mg/Ca-derived temperatures based on *N. incompta* agree well with the previous culture-based Mg/Ca:temperature relationship (von Langen et al., 2005), which has been used in concert with new results to produce a species-specific relationship for *N. incompta*. The Mg/Ca ratios in ontogenetic calcite of cultured *N. pachyderma* are more sensitive to temperature than implied by published relationships based on sediment traps or core tops, due to the presence of crust calcite. We developed a new approach, applying our culture-based Mg/Ca:temperature relationships (based on ontogenetic calcite only) to the ontogenetic portion of fossil shells, identified and analyzed by LA-ICP-MS. Initial tests of this approach in fossil *N. incompta* are in agreement with δ^{18}O-temperatures derived from *G. bulloides* and with instrumental temperatures. A marked improvement is made in reconstructions using *N. pachyderma* when crust calcite is excluded, and temperature is derived from Mg/Ca ratios in ontogenetic calcite alone, using our culture-based relationships. This approach provides a potentially useful strategy for improved temperature reconstructions, with particular relevance for high-latitude regions where temperature changes reconstructed using *N. pachyderma* have previously appeared muted.

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Paleoceanography

Supporting Information for
Relationships between Temperature, pH, and Crusting on Mg/Ca Ratios in Laboratory-Grown *Neogloboquadrina* Foraminifera

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Contents of this file

Additional Supporting Information (Files uploaded separately)

Table S1. Seawater parameters and Mg/Ca in cultured foraminifera, including Mg/Ca ratios for each chamber and a chamber average for each individual shell. Blank cells indicate data, which was not collected or did meet standards of quality control and has not been included in any analyses. This table has been included as a separate file due to size.

Table S2. Average Mg/Ca and standard deviation of *N. incompta* at multiple pH at a single temperature.

Species	pH	Average Mg/Ca (mmol/mol)	N
N. incompta (12 °C)	7.4	2.5±1.2	6
	7.8	2.4±0.3	4
	8.0	1.4±0.5	14
	8.1	2.3±1.0	5
	8.1	2.0±0.6	7

Figure S1. Relationships found in this study between temperature and Mg/Ca for *N. pachyderma* and *N. incompta* shown with solid lines (confidence interval envelope = 95%) over the temperatures at which these were calibrated, as well as average Mg/Ca at each calibration temperature and standard error. In the case of *N. incompta*, the relationship is derived from a combination of new results from this study (shown) as well as species-specific data from von Langen et al., [2005].
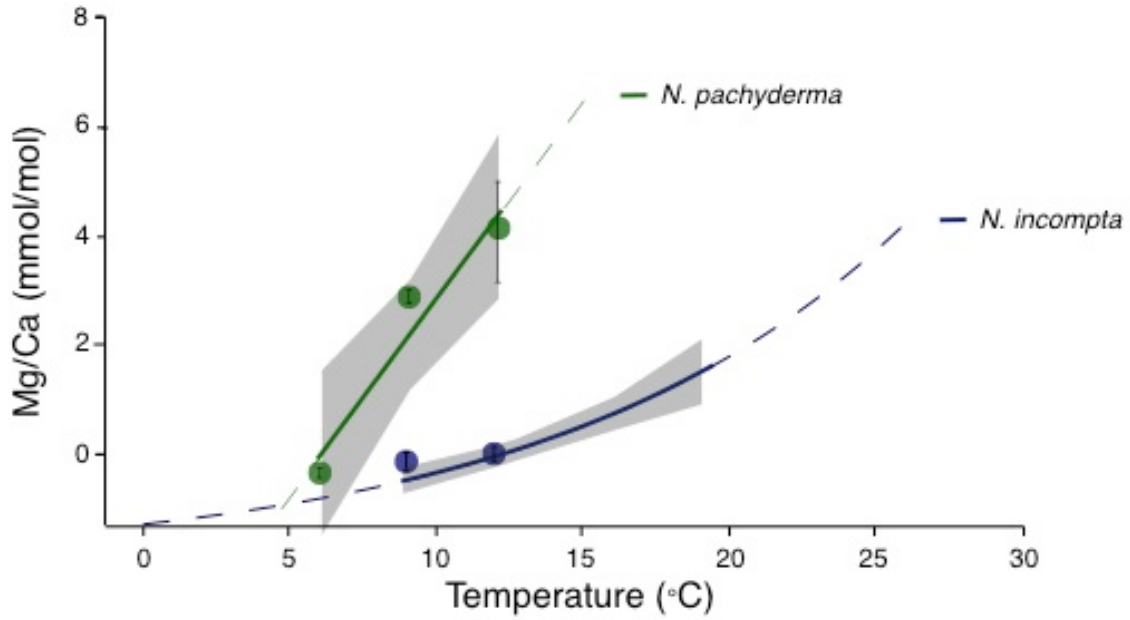
Figure S2 SEMs of fossil *N. pachyderma* from the Bering Sea showing a) a representative *N. pachyderma* shell from these samples and b) a shell fragment containing a section in which ontogenic calcite has been stripped away. Such areas were identifiable by LA-ICP-MS as well as by SEM and light microscopy when shells were broken.
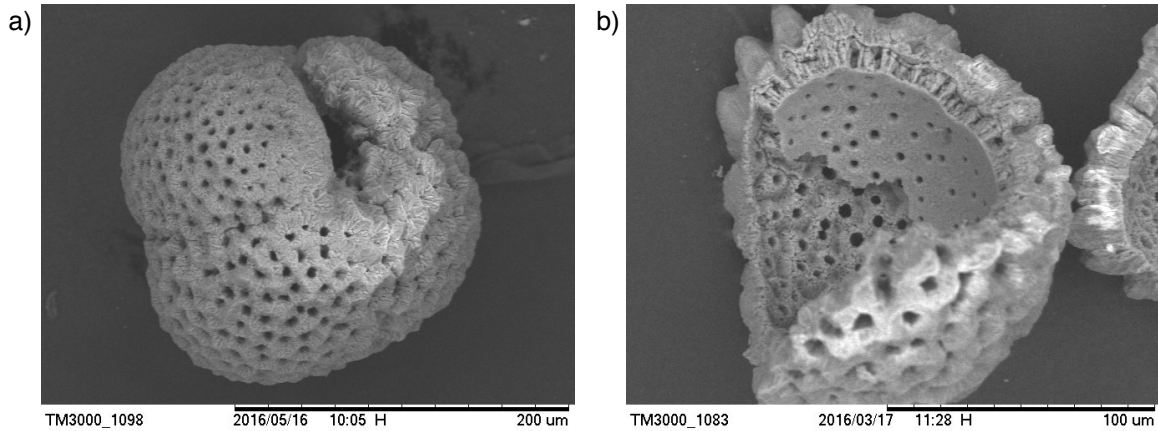
a)

TM3000_1098   2016/05/16   10:05 H   200 um

b)

TM3000_1083   2016/03/17   11:28 H   100 um

Figure S3. SEMs of a) and b) *N. incompta* which added a new chamber and a crust at 12 °C in culture and c) and d) fossil *N. incompta* from Santa Barbara Basin which grew all chambers and a crust in the field.