**Biogeosciences**

# Encrustation and trace element composition of *Neogloboquadrina dutertrei* assessed from single chamber analyses – implications for paleotemperature estimates

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**Abstract.** Crust formation is a common phenomenon in planktonic foraminifera. Because of their different formation mechanism and hence composition, crusts affect the overall test composition and therefore complicate the use of crust-bearing foraminifera in paleoceanography. Such species are often used to estimate subsurface paleotemperatures, and although the influence of encrustation on the trace element/Ca ratio is recognised, it has not been systematically explored between and within tests. Here we use laser ablation ICP-MS to assess the variability in trace element composition of the crust of *Neogloboquadrina dutertrei* within individual chambers, as well as the effect of compositional heterogeneity of the crust on whole test chemistry. Compositionally, the outer crust differs from inner layer by lower Mg/Ca and Mn/Ca, but is indistinguishable in Sr/Ca. Crust thickness decreases towards the younger chambers, and it may be entirely absent from the last chamber. In contrast to Mn/Ca and Sr/Ca, crustal Mg/Ca ratios show a tendency towards higher values on the younger chambers. These patterns in crust thickness and in crust Mg/Ca indicate that temperature is not the dominant factor controlling crust composition. Temperature estimates based on *N. dutertrei*, and presumably other crust-forming species too, are therefore biased towards too low values. Through comparison of modern and glacial tests, we show that this bias is not constant and that changes in crust thickness and/or in Mg/Ca values can spuriously suggest temperature changes.

## 1 Introduction

Many planktonic foraminifera form an outer crust that may account for a significant part of their total test mass (Bé, 1979, 1980; Duckworth, 1977; Hemleben et al., 1977). Such crusts are formed during the later stages of the foraminiferal life cycle. In some species crust formation is associated with gametogenesis, whereas in others it appears to be triggered by temperature decrease upon sinking of the test (Hemleben et al., 1989; Hemleben and Spindler, 1983). Crust formation occurs rapidly, in less than ∼ 20 h in culture conditions (Bé,
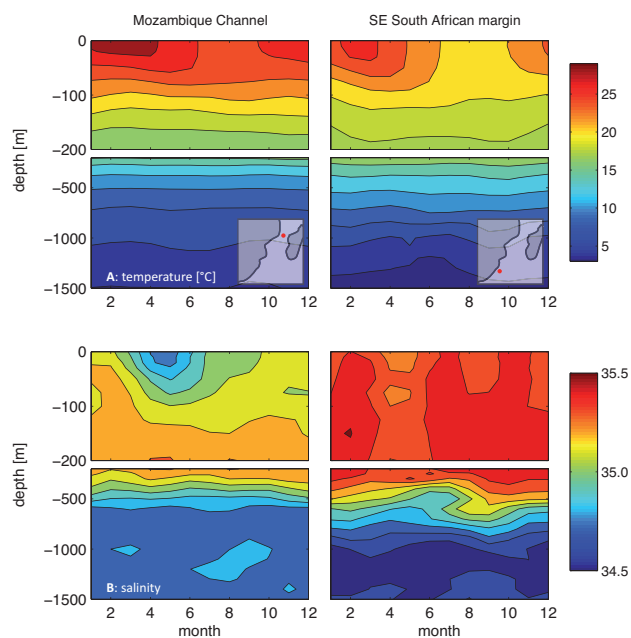
**Fig. 1.** Monthly averaged temperature **(A)** and salinity **(B)** for the Mozambique Channel and SE South African margin sites. Map insets show location of the sites (see also Table 1). Note the difference in scale for the upper 200 m. Data from World Ocean Atlas 2009 from the 1/4 degree grid cells closest to the sites; the SE South African Margin panels show averaged values for all sites (Antonov et al., 2010; Locarnini et al., 2010).

1980). Since the crust is known to be compositionally different from the inner test wall (e.g. Duckworth, 1977; Eggins et al., 2003), and its thickness varies within and between specimens, it is necessary to understand and quantify the effects of encrustation to reliably use whole test chemistry for paleoenvironmental reconstructions.

Here we assess the inter- and intra-test trace element variability of *Neogloboquadrina dutertrei* (*N. dutertrei*) from modern and glacial samples from the SW Indian Ocean to determine the effects of encrustation on the species' Mg/Ca, Mn/Ca and Sr/Ca ratios. *N. dutertrei* is a subtropical thermocline dweller (Bé and Tolderlund, 1971; Field, 2004), is non-spinose and bears symbionts (Gastrich, 1987). Intra-annual whole-test Mg/Ca and stable oxygen isotopes show considerable variability, but on average were suggested to reflect a depth habitat around 60 m depth, just below the surface mixed layer (Fallet et al., 2011; Bé and Hutson, 1977; Dekens et al., 2002). The species is often used to infer past thermocline conditions (Leduc et al., 2009; Kiefer et al., 2006). However, *N. dutertrei* often develops an outer calcite crust consisting of well-formed blocky calcite crystals (Sautter, 1998; Hemleben and Spindler, 1983). This crust has lower Mg/Ca values than the remaining part of the test and is known to significantly enrich the whole-test $\delta^{18}$O, both suggesting that the crust is formed at lower temperatures deeper

**Table 1.** Location of cores and moored sediment trap.

| Name | Lat (° S) | Lon (° E) | Depth (m) |
|---|---|---|---|
| CD154-01-01K | 29.29 | 33.14 | 1997 |
| CD154-02-03K[1] | 29.06 | 32.77 | 1626 |
| CD154-03-05K | 29.12 | 32.89 | 1747 |
| CD154-05-07K[1] | 29.93 | 33.82 | 1850 |
| CD154-10-10K/06P[1,2] | 31.17 | 32.15 | 3076 |
| MOZ-2 A-06/08[3] | 16.42 | 40.85 | 2000 |

[1] $^{210}$Pb excess;
[2] core top: 10K/LGM: 06P, other cores were used for both modern and LGM;
[3] sediment trap.

in the water column (Sautter, 1998; Fehrenbacher and Martin, 2010; Pena et al., 2005; Eggins et al., 2003; Sadekov et al., 2005). Anecdotal evidence suggests that crust formation in *N. dutertrei* occurs when temperatures drop below 15 °C, but very little remains known about crust formation in this species (Hemleben and Spindler, 1983). In order to quantify trace element variability within *N. dutertrei* tests and the influence of encrustation on bulk test composition, we present detailed test wall element/Ca profiles of a large number of tests from sediment samples of recent and glacial age from the SW Indian Ocean. This allows for a robust estimate of the effects of intra- and inter-test element/Ca variability in *N. dutertrei*.

## 2 Regional hydrography

Samples were taken from two locations in the SW Indian Ocean: the SE South African continental margin off Durban, and from the narrowest part of the Mozambique Channel. Both areas are characterised by large intra-annual variability in water mass properties due to meso-scale eddy activity and connected since most water that flows out of the Mozambique Channel ends up in the Agulhas current flowing along the SE South African margin (De Ruijter et al., 1999, 2002). Sea surface temperatures off Durban are lower than in the Mozambique Channel by on average ∼ 4 °C (Fig. 1a). The mean seasonal amplitude is ∼ 6, 1.5 °C more than in the Mozambique Channel (Fig. 1a). While the sea surface temperature variability shows a clear seasonal pattern, temperature below the seasonal thermocline shows higher frequency (70–90 days) eddy-related variability (Fallet et al., 2011), which is not resolved in the monthly averaged values (Fig. 1a).

Monthly mean sea surface salinity in the SE South African margin varies slightly around ∼ 35.6, and while average salinities in the Mozambique Channel are lower (35.0), they show a more pronounced influence of the seasonal variation in net precipitation (Fig. 1b). Both locations show a subsurface salinity maximum around 200 m depth, but values are considerably lower in the Mozambique Channel,

except below $\sim 750$ m (Fig. 1b). Subsurface intra-annual salinity variability is more pronounced in the SE South African margin area, particularly at $\sim 500$ m depth (Fig. 1b).

## 3   Materials and methods

Tests of *N. dutertrei* (355–500 µm) were picked from core-top and Last Glacial Maximum (LGM) age sediments from kasten cores from the SE South African margin (Table 1). Depth of the LGM in the cores was determined from the non-crust-forming *G. ruber* stable oxygen isotopes, magnetic susceptibility and lightness data. Modern ages for the core tops were inferred from the same planktonic $\delta^{18}O$ records and substantiated by high $^{210}Pb$ activities, indicative of $^{210}Pb$ excess and thus ages $< \sim 150$ yr. $^{210}Pb$ was analysed through its granddaughter $^{210}Po$ using $\alpha$-spectrometry (Table 1). In order to provide a statistically robust estimate of the TE/Ca variability in the Holocene and glacial populations, all sediment samples of the core top and LGM age have been lumped together. Comparison of the two populations is uncompromised since combining the samples affects both populations equally. In addition to the sediment samples, a limited number of tests from a sediment trap from the Mozambique Channel were analysed to provide a reference of diagenetically unaltered material (Table 1; for details on the moored trap, see Fallet et al., 2010).

All samples were repeatedly cleaned using short sonication with de-ionised water and methanol prior to analysis (cf. Eggins et al., 2003; Wit et al., 2010). Foraminiferal test minor element and trace element composition was determined using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) at Utrecht University. The system consists of a 193 nm laser (GeoLas 200Q Excimer) coupled to a sector field ICP-MS (Element 2, Thermo Scientific). Laser spots were 40–80 µm in diameter; repetition rate was set to 7 Hz and laser power density to 1 J cm$^{-2}$. The mass spectrometer was run in low-resolution mode, and masses monitored were $^{24}Mg$, $^{26}Mg$, $^{27}Al$, $^{43}Ca$, $^{44}Ca$, $^{55}Mn$ and $^{88}Sr$. Measurement routine took 0.34 s to cycle through the masses. Calibration was performed against a SRM NIST610 glass standard ablated at a higher energy density ($\sim 5$ J cm$^{-2}$) between every 12 foraminiferal samples. Simultaneous ablation of a calcite crystal (Iceland spar) at the lower energy density settings allowed for calculation of the analytical uncertainties of the ICP-MS, which are 0.06, 0.04 and 0.07 mmol mol$^{-1}$ (1$\sigma$) for Mg/Ca, Mn/Ca and Sr/Ca, respectively (Dueñas-Bohorquez et al., 2011).

Data reduction was done using the SILLS (Signal Integration for Laboratory Laser Systems) software package (Guillong et al., 2008). Raw counts of Mg, Mn, Sr and Ca were converted to concentrations using $^{43}Ca$ as an internal standard. Aluminium was taken as an indicator of detrital contamination. Measurements were performed on intact tests from the outside inwards. High counting rates at the start of

**Table 2.** Numbers of specimens analysed.

| | Analysed | Low Al/Ca | Double layered | % double layered |
|---|---|---|---|---|
| Core top | 205 | 121 | 87 | 72 |
| LGM | 218 | 178 | 152 | 85 |

the ablations profiles are not included in the integrated the ablation profile (Eggins et al., 2003; Hathorne et al., 2009). To provide an indication of the effect of intra-test Mg/Ca variability, calcification temperature estimates were obtained using the following equation: $T(°C) = 11.11 \times \ln(Mg/Ca \times 2.92)$ (Anand et al., 2003). Applicability of a whole test calibration to single chamber data presented here is discussed in Sect. 5.1.

To assess intra-test variability (multiple), measurements were conducted per chamber on a limited number of specimens ($n = 9$, 97 profiles) from the SE South African margin. Previous work has shown that antepenultimate chamber (F-2) may yield valuable information on the compositional variability of the whole test (Eggins et al., 2003). The inter-test variability was therefore obtained from measurements of this chamber of $> 100$ individual tests from both core-top and LGM samples (Table 2). The sediment trap specimens ($n = 15$) were analysed on F-2 only. Since ablation time and pit depth have been shown to be linearly related (Hathorne et al., 2003), test wall thickness was estimated from ablation time.

## 4   Results

### 4.1   Crust and trace element/Ca layering

The presence or absence of a crust consisting of blocky calcite crystals is not readily visible by conventional binocular light microscopy. However, scanning electron microscope (SEM) pictures clearly show the rough crystalline texture of the crust (Fig. 2). The size of the crystals and/or the presence of the crust vary between the chambers, with the final and penultimate chambers (F0 and F-1) often having a relatively thin crust or lacking one at all (Fig. 2a). The distribution and thickness of the crust over the chambers is heterogeneous. Sediment trap samples from the Mozambique Channel show a crust consisting of smaller crystals than those from the SE South African margin (Fig. 2c).

The ablation profiles of many tests show a pronounced two-layered structure of the test wall in most chambers (Fig. 3). Mg/Ca and Mn/Ca are often lower in the outer layer (in F-2 the mean difference between the two layers in core-top samples is 1.6 mmol mol$^{-1}$ and 7.5 µmol mol$^{-1}$, respectively), whereas Sr/Ca is relatively constant throughout the chamber wall (Fig. 3). The changes from low to high Mg/Ca and Mn/Ca coincide with each other. This layering
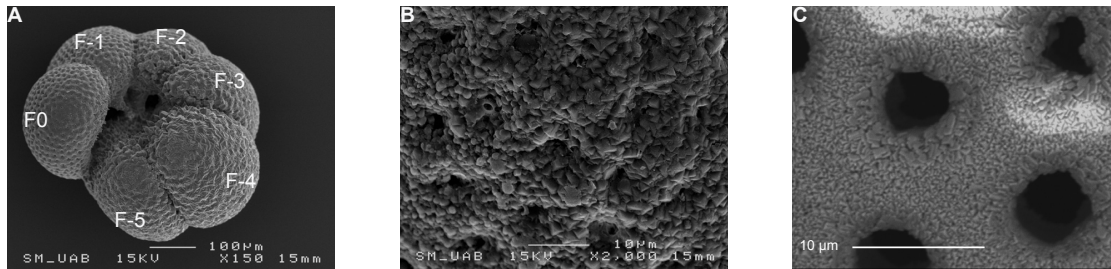
**Fig. 2.** SEM pictures of *N. dutertrei*. (**A**) Overview of entire test from LGM sediment with the naming of the chambers indicated. Note the large crystals on F-2 to F-5. (**B**) Close-up of the crust morphology of a LGM test. (**C**) Close-up of the crust morphology of a test from the sediment trap. No cleaning was applied prior to SEM photography.
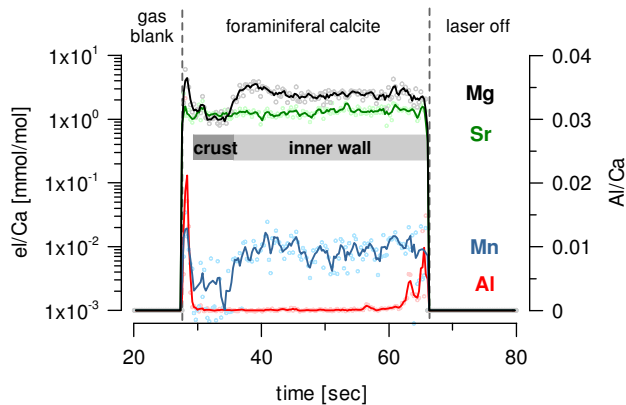


**Fig. 3.** Element/Ca ratios through chamber F-2 of *N. dutertrei* from the Mozambique Channel sediment trap. Thick lines represent 3-point running means. The double layering is highlighted with grey bars. The high values at the beginning of the ablation profiles are ignored in the analyses. The Al/Ca shows presence of a sediment infill of the test; this part of the profile is therefore not taken into account when calculating the average values (despite the limited effect of the infill on other element/Ca ratios). As Al cannot be quantified absolutely, Al/Ca ratios are expressed as raw counts and therefore unit less.

is observed in the F-2 chambers of 81 % of the sediment trap specimens, 72 % of the core top and 85 % of the LGM tests.

## 4.2 Intra-test variability

The thickness of both the inner and outer layer shows a consistent pattern over the chambers. Typical shells have walls that are thickest on F-4 and thin progressively towards younger (F-3 to F0) and older (F-5) chambers (Fig. 4). The outer layer is always thinner than the inner one, but the thinning pattern in both layers is similar (Fig. 4). Double layering is not observed on all chambers; it is often absent from F0 and F-1 and occasionally also from F-2.

In the outer layer Mg/Ca values show an increase towards F0 that is clearest in the last two to three chambers (Figs. 5a and 6). This pattern is not always present in the inner layer
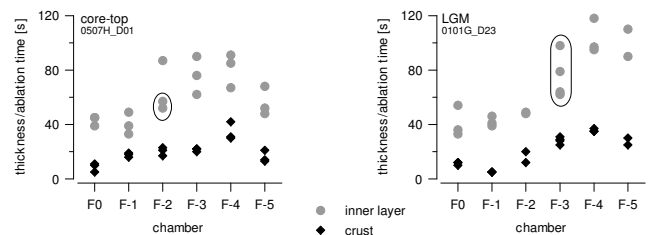


**Fig. 4.** Intra-test layers thickness pattern in *N. dutertrei*, examples from a core top (left) and an LGM (right) specimen from sediments from the SE South African margin. Each pair of a grey dot and a black diamond represents a single measurement. Encircled dots are minimum values only, in cases where the wall was not completely ablated. For chamber coding see Fig. 2.

(Fig. 5a). Mn/Ca ratios in the outer layer are always lower than in the inner layer (Fig. 5b). Although Mn/Ca values are variable in both layers, no systematic inter-chamber trend is detectable. Sr/Ca shows very little variability throughout the test wall and between different chambers (Fig. 5c).

## 4.3 Inter-test variability and Holocene–LGM changes

### 4.3.1 Composition

Mg/Ca in the inner layer of core top specimens varies between 1.2 and 5.0 mmol mol$^{-1}$ around a mean value of 2.7 mmol mol$^{-1}$ (Fig. 7a). The median Mg/Ca in this layer does not differ from those of specimens from the LGM, but the variability increases considerably (interquartile range, IQR, increase: 0.6 mmol mol$^{-1}$; Fig. 7a). Core top mean Mg/Ca in the outer layer is 1.1 mmol mol$^{-1}$ and shows less variability (IQR: 0.4 mmol mol$^{-1}$) than the inner layer (Fig. 7a). In contrast to the inner layer, the outer layer shows a 0.3 mmol mol$^{-1}$ lower mean and median Mg/Ca in the LGM, while variability in Mg/Ca of the outer layer is similar in recent and the LGM specimens (Fig. 7a).

Core top Mn/Ca mean values of the inner and outer layers are 12.7 and 5.2 µmol mol$^{-1}$, respectively (Fig. 7b). Both variability and mean values in the inner layer were higher
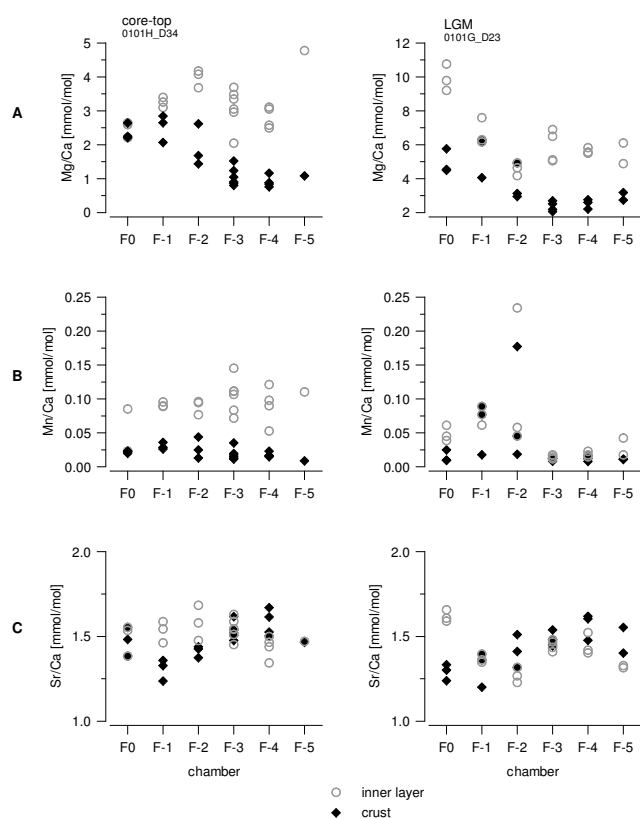
**Fig. 5.** Intra-test trace element variability in *N. dutertrei*, examples from a core top (left) and an LGM (right) specimen from sediments from the SE South African margin. **(A)** Mg/Ca; **(B)** Mn/Ca and **(C)** Sr/Ca ratios for individual chambers. Symbols as in Fig. 4.

during the LGM, but this pattern is less clear in the outer layer (Fig. 7b).

The Sr/Ca in both layers in the core tops differs very little, and both layers have higher Sr/Ca in the LGM samples (Fig. 7c). However, the increase in Sr/Ca in the LGM samples is slightly larger in the outer layer (0.07 mmol mol$^{-1}$ on average; Fig. 7c).

### 4.3.2 Outer layer thickness

Core top average outer layer ablation time (∼ wall thickness) varies between 20 and 25 s. In only very few tests (∼ 1 %), the outer layer makes up more than 55 % of the test wall thickness (Fig. 8a). LGM tests have thicker outer layers that make up a small, but significantly higher proportion of the test walls (Student's t-test on the means, 99 % confidence level; Fig. 8b).

## 5 Discussion

SEM pictures of *N. dutertrei* from the SW Indian Ocean show that many tests are (partly) covered by blocky calcite
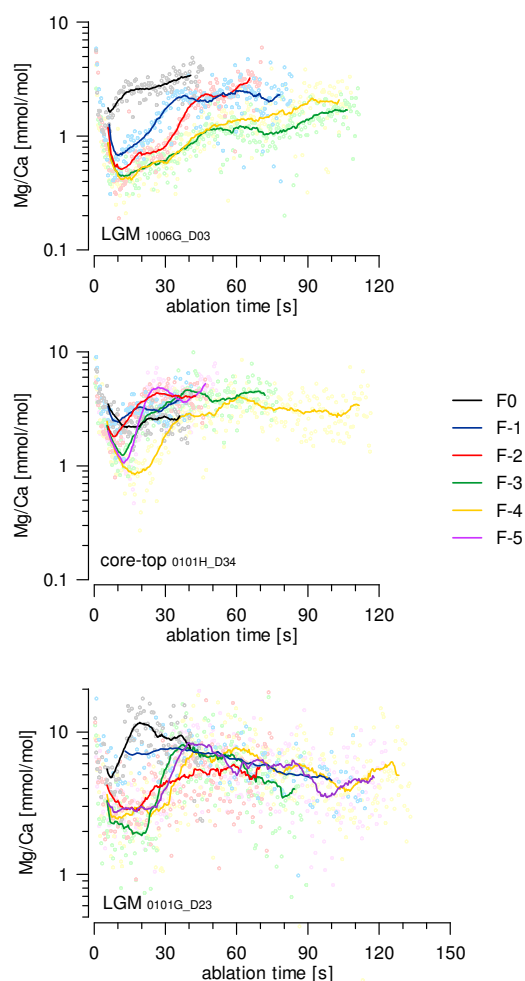


**Fig. 6.** Mg/Ca profiles through individual *N. dutertrei* chambers from SE South African margin sediments, both core-top and LGM age. Dots represent raw data, thick lines 25-point smoothed averages that highlight the double-layered structure of the test walls. Note differences in the scale of the y-axes. The difference between the layers is statistically robust at the 95 % confidence interval (Student's t-test on means).

crystals, and Mg/Ca and Mn/Ca profiles through these tests with a blocky calcite surface reveal a pronounced double-layered structure of the shell walls (Figs. 2, 3 and 6). The outer layer is characterised by lower Mg/Ca and Mn/Ca ratios when compared to the inner layer. This outer low Mg and Mn layer is not distributed uniformly over the chambers, and several profiles show variability in the composition of both layers. The heterogeneous distribution of the low Mg/Ca and Mn/Ca on the individual chambers is similar to the presence of blocky crystals observed on the outside of the test (Fig. 2).

The transition between the inner and outer layer in the LA-ICP-MS profiles may not be razor sharp due to (a) surface structures on the inner layer and (b) bottom of the laser pit being not exactly perpendicular to the surface of the chamber

(and the plane of the layer boundary), both leading to a slight mixing of Mg- and Mn signals between the layers. Also, whether the intra-layer variability (Fig. 6) reflects finer-scale additional layering remains to be investigated, but it does not affect the net compositional difference between the two layers.

The rough crystalline texture of the outer layer is characteristic for crustal calcite in a number of planktonic foraminiferal species (e.g. Bé, 1980; Hemleben et al., 1977), and various authors have shown compositional differences between crustal and lamellar calcite (e.g. Duckworth, 1977; Sautter, 1998). In *N. dutertrei*, the presence of a crust has been extensively documented using various analytical methods (Sautter, 1998; Eggins et al., 2003; Hemleben et al., 1985). Here we use this correlation between crystal morphology and differences in Mg/Ca and Mn/Ca in the profiles to distinguish between the two layers (cf. Sautter, 1998; Fehrenbacher and Martin, 2010; Kozdon et al., 2009; Sadekov et al., 2005). Others have described the layering in foraminiferal test walls as primary or lamellar ontogenetic calcite on the inside and a gametogenic calcite layer, including a crust, on the outside (e.g. Erez, 2003; Hemleben et al., 1977). Here we define the layers based on compositional differences, and to avoid alluding to their formation process we refer to the outer, low Mg and Mn layer as the crust.

Recognition of encrusted specimens using normal light microscopy is not straightforward, although Sautter (1998) mentions that presence of clearly visible micropores is a good criterion to distinguish non-encrusted specimens. However, light microscopy (and SEM imagery) only offers information on the presence, but not on the degree of encrustation. Micro-scale analysis thus remains the most reliable way to determine the extent of, and correcting for encrustation.

The laser ablation results presented here are indistinguishable from conventional ICP-MS data on the same sediment trap sample (Fallet et al., 2011). For the same collecting cup, Fallet et al. (2011) report a Mg/Ca value of $3.09\,\text{mmol}\,\text{mol}^{-1}$; we determine a whole-wall mean of $2.88 \pm 0.72\,\text{mmol}\,\text{mol}^{-1}$ and crust and inner layer Mg/Ca values of $1.45 \pm 0.48$ and $3.48 \pm 1.06\,\text{mmol}\,\text{mol}^{-1}$, respectively. This presence of double-layered tests in samples from the sediment trap excludes the possibility that the element patterns in the test walls are caused by diagenesis (Pena et al., 2005). Moreover, similar variability in crust Mg/Ca and in crust thickness between chambers has been observed in specimens of *N. dutertrei* from the SE Indian and Atlantic oceans (Eggins et al., 2003; Fehrenbacher and Martin, 2010), but also in other deep-dwelling species such as *G. truncatulinoides* and *G. inflata* (Duckworth, 1977; Hathorne et al., 2009), indicating that the observed pattern is not exclusive to our samples nor to *N. dutertrei* alone.

The decrease in thickness of the inner layer with younger chambers (Fig. 4) agrees well with typical lamellar calcification in which a layer of calcite is precipitated onto existing chambers with every chamber added (Erez, 2003 and
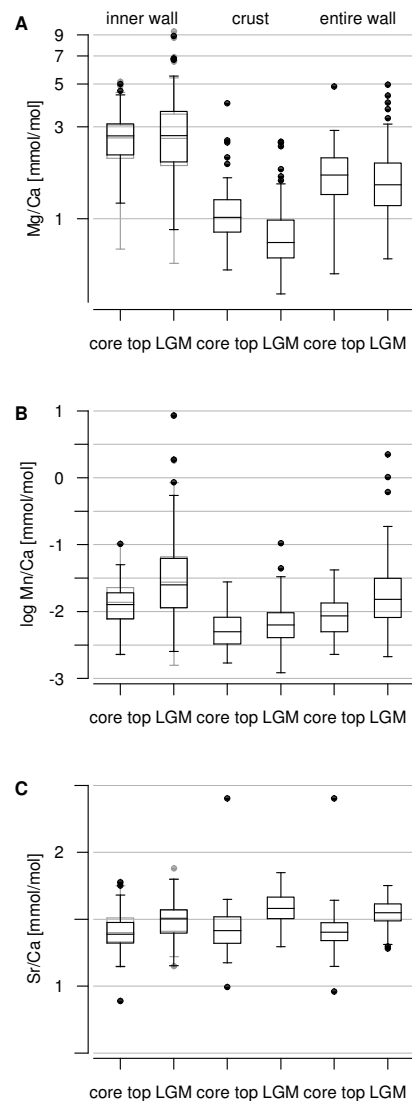


**Fig. 7.** Core top-LGM element/Ca changes in F-2 of *N. dutertrei* in crust and non-crust calcite. **(A)** Mg/Ca, **(B)** Mn/Ca and **(C)** Sr/Ca. Horizontal lines show median values, boxes interquartile ranges and bars the interquartile ranges multiplied by 1.5. Values outside these ranges are considered as outliers (dots). The grey boxes in the inner wall panel show the dispersion in all samples, i.e. including those without double layering.

references therein). Surprisingly, crust thickness follows a similar pattern, being thinnest on chambers formed later (Fig. 4), thereby resembling variability in wall thickness due to lamellar calcite growth. The observed increase in Mg/Ca of the crust towards the younger chambers would then suggest upward migration of this species during crust formation. This suggestion of gradual crust formation is in contradiction with laboratory studies that showed that crust formation occurs rapidly and simultaneously on all chambers (where crust formation takes place) when the foraminifer descends to colder waters near the end of its life cycle (Bé et al., 1979;
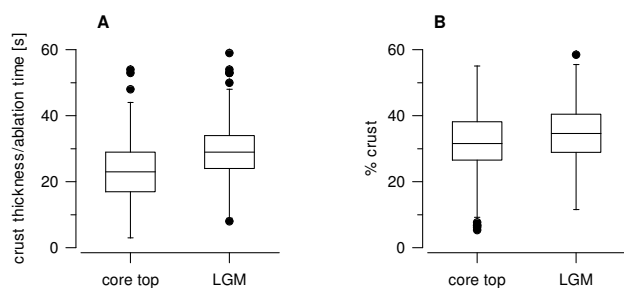
**Fig. 8.** Core top-LGM crust thickness (**A**) and crust proportion (**B**) changes in F-2 of *N. dutertrei*. Symbols as in Fig. 7.



**Fig. 9.** Illustration of the influence of crust heterogeneity on temperature estimates. Calculated Mg/Ca-temperatures through the walls of two tests from the same sediment trap bottle (colours denote different tests). Thick lines show average crust and inner layer values and arrows the whole wall mean. Mn/Ca profiles through the two tests are close to the detection limit, but appear different.

Hemleben and Spindler, 1983; Hemleben et al., 1985). Furthermore, *N. dutertrei* is thought to descend in the water column as it ages (e.g. Hemleben et al., 1989), and therefore the inter-chamber increase in crust Mg/Ca towards the final chamber is unlikely to be related to decreasing seawater temperatures under which those chambers form. This has important implications for the application of the species' Mg/Ca to reconstruct past seawater temperature.

Although limited data are available, seawater manganese concentrations in the Indian Ocean, distant from the oxygen minimum zones in the Arabian Sea, generally show a maximum in the upper $\sim 200$ m and very little change below these depths (Morley et al., 1993). The low Mn/Ca in the crust therefore confirms its precipitation deeper in the water column than the inner layer. The relatively uniform Mn/Ca of the crust across chambers indicates that crust formation took place entirely below the surface Mn maximum. This too renders it unlikely that variability in crust Mg/Ca reflects upward migration through the water column.

### 5.1 Implication for paleotemperature estimates

Since the crust makes up a considerable part of the total calcite mass, temperature reconstructions based on whole test Mg/Ca values of crust-forming foraminifera only partly reflect temperature. The potential error associated with this variability in Mg/Ca may be enhanced through preferential preservation of the low Mg/Ca crust in the sediments, but importantly also during conventional reductive cleaning. Additionally, when Mg/Ca values are converted to temperature, the bias towards low temperature will be enhanced by the logarithmic nature of the calibrations.

Several Mg/Ca-temperature calibrations exist for *N. dutertrei* (Anand et al., 2003; Von Langen et al., 2005; Dekens et al., 2002). All are based on whole test measurements and have overlapping exponential constants, i.e. an equal sensitivity to temperature. Whether these calibrations can be applied to single layers from individual chambers has not been tested, but some evidence suggests that this is unlikely to be the case. Primiarily, the nearly identical range in Mg/Ca in both layers (Fig. 7a) suggests that both layers were
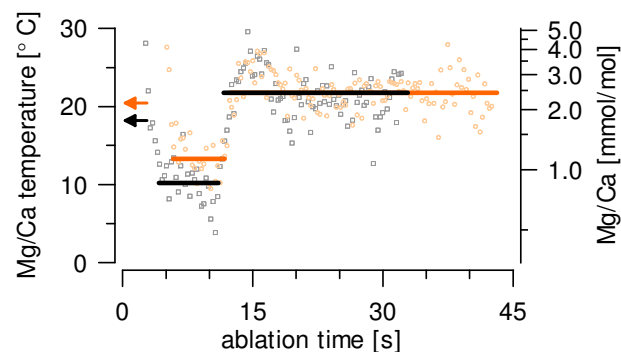
formed under a similar temperature variability regime. This is unlikely if the crust is formed deeper in the water column where temperature variability is lower than in the thermocline (Fig. 1). A crust-only calibration may therefore have a steeper slope. If, on the other hand, the crust were formed at a depth similar to the inner layer, the different composition of the crust would require a calibration with a higher pre-exponential constant to account for the difference in Mg/Ca values. In both cases a different calibration is needed to convert individual layer Mg/Ca to temperature. Additionally, Bolton et al. (2011) have shown that for *G. ruber* Mg/Ca temperature calibrations differ for individual chambers. The choice of a particular calibration can thus not be justified in the absence of independent determination of the depth of formation of both layers. For this reason we refrain from comparing inferred temperatures to seawater values; although the inferred temperature differences may be more robust than absolute temperatures, the values presented here should be taken as indicative only.

Both thickness and Mg/Ca of the crust influence whole shell Mg/Ca value and consequently bias temperature estimates from whole-test measurements. Figure 9 depicts the Mg/Ca values converted to temperature through the test wall of two specimens from the same sediment trap sample that clearly show both effects. Both tests settled within the same 3-week period and therefore calcified under nearly identical conditions. This is reflected in the identical Mg/Ca values of the inner layer. The Mg/Ca of the crust and the ratio of crust to inner layer calcite are however very different for both tests, causing the temperature estimates based on the entire profile to differ by over $2\,°C$ (Fig. 9). If the temperature sensitivity of the calibration(s) holds for the individual layers, the Mg/Ca contrast between the crust and the inner layer would amount to $> 10\,°C$, indicating a formation depth difference of several hundreds of meters.

The effect of encrustation on whole-test Mg/Ca is also clear in the sediment samples from the SE South African margin. The crust is considerably lower in Mg/Ca, the equivalent of > 3 °C, in LGM specimens (Fig. 7a). Together with the slight increase in the relative proportion of the crust (Fig. 8b), this lowers the average composition of the entire wall and – by extension – of the whole test (Fig. 7a). The lower LGM whole-test Mg/Ca ratios suggest a lowering of thermocline temperatures, but only through detailed (LA-ICP-MS) analysis it becomes obvious that this cooling is entirely due to a Mg/Ca decrease of a slightly thicker crust and hence is unrelated to actual changes in temperature.

## 5.2 Potential controls on crust heterogeneity

The pattern of progressive increase in thickness and Mg/Ca ratios of the crust of *N. dutertrei* could suggest that crust formation occurs gradually and over a prolonged period. It appears that thicker crusts have lower Mg/Ca, perhaps as a result of formation deeper in the water column (Figs. 4 and 5). Laboratory studies have shown that species of the genus *Neogloboquadrina* are capable of adopting a benthic life style and surviving for a prolonged period in cold and dark conditions (Hemleben et al., 1985). Hemleben et al. (1977) also mention gradual crust formation in *G. menardii*, but information on the duration of the crust formation process is not available. The thicker crusts with larger crystals on chambers F-4 to F-2 would indeed be consistent with continued growth deeper in the water column and potentially at the sea floor. Yet the Mg/Ca data do not show a simultaneous Mg/Ca increase through the crust that one would expect from continued growth during descent through the water column. On the contrary, crustal Mg/Ca is often lowest at the boundary between the outer and inner layer (Fig. 6).

The difference in crystal size of the crust of samples collected in the Mozambique Channel and those on the SE South African margin could suggest that there are regional differences and thus environmental parameters influencing crust formation (Fig. 2b and c). Temperature is lower and salinity higher in the upper 100 m of the water column in SE South African margin area, but it is not clear if and how this could account for the different crust morphology. Importantly, samples from both locations show the same layering in Mg/Ca and Mn/Ca, so while there may be hydrographic controls on the crust morphology, the composition appears independent of water column conditions.

## 5.3 Holocene–LGM changes

The inner and outer layer median Mg/Ca in modern *N. dutertrei* tests differ by ∼ 1.7 mmol mol$^{-1}$ (Fig. 7a), which translates into a temperature difference of ∼ 10 °C. However, to obtain a reasonable estimate of paleotemperature based on the Mg/Ca of the inner layer of *N. dutertrei*, a new calibration is needed. Such an inner wall Mg/Ca calibration,

perhaps chamber-specific, will have to take into account the significant (and apparently random) intra-test variability. Future studies should preferably target the older chambers, as these appear to integrate most of the (life) history of the test. However, rigorous (re)calibration of the species' Mg/Ca–temperature relationship would be the only way to avoid the bias from encrustation.

The Mg/Ca of the inner layer likely provides a more reliable paleothermometer than whole-test Mg/Ca. The similarity between the core top and LGM inner wall Mg/Ca (Fig. 7a) is striking since nearby temperature records based on surface dwelling foraminifera and alkenones do show lower LGM temperatures, particularly in winter (Levi et al., 2007; Bard and Rickaby, 2009). An explanation for the near constant Mg/Ca ratios is that (sub)thermocline temperatures did not change or that *N. dutertrei* adjusted its depth or seasonal habitat to remain in a certain temperature range.

Both crust and inner layer show elevated Mn/Ca ratios in the LGM samples; the inner layer supposedly formed higher in the water column, more so than the crust (Fig. 7b). These Mn/Ca may be used to infer changes in seawater Mn concentration due to variable terrigenous input (Klinkhammer et al., 2009). Culture studies with benthic foraminifera have shown that Mn uptake linearly relates to Mn concentration in the seawater (Munsel et al., 2010). Therefore, the observed (near) doubling in the median Mn/Ca in the inner layer thus may suggest a twofold increase in Mn concentration in the ambient seawater, likely related to enhanced terrigenous input via dust or lower sea level. The smaller increase in crustal Mn/Ca indicates that the dissolved Mn increase during the LGM was most pronounced in the surface waters (Fig. 7b).

The nearly constant Sr/Ca through the entire test walls contrasts with Mn/Ca and Mg/Ca. Hathorne et al. (2009) and Eggins et al. (2003) report similar behaviour of strontium, also in other crust-bearing species. The similarity of the Sr/Ca in both layers, which are precipitated under different environmental (temperature, salinity, pH etc.) conditions, suggests that Sr uptake in *N. dutertrei* does not depend on those factors and is biomineralised in a unique way (Lea et al., 1999). The approximately 10 % increase in Sr/Ca in the LGM shells (Fig. 7c) is in accordance with other reconstructions based on the genus *Neogloboquadrina*, and probably too large to be caused by an increase in the oceans' Sr inventory alone (Stoll et al., 1999; Elderfield et al., 2000).

## 6 Conclusions

Detailed trace element profiling using LA-ICP-MS of tests of *N. dutertrei* demonstrated that the outer crust of blocky calcite crystals is compositionally different from the inner test wall. In the antepenultimate chamber of core top and LGM samples, median Mg/Ca and Mn/Ca are 1.7–2.0 mmol mol$^{-1}$ and 8–19 µmol mol$^{-1}$ lower in the crust than in the inner layer. Sr/Ca ratios are invariant through the entire wall.

Over 70 % of the analysed tests have such a crust on chamber F-2, but the crust is not homogeneously distributed over the individual chambers. There is a clear thinning of the crust towards younger chambers, and a crust is often absent from the ultimate and penultimate chambers. Mg/Ca ratios also show a pattern over the different chambers and increase in the last formed chambers. Both patterns in thickness and composition point at biological control on crust formation and composition, impacting the use of the species' Mg/Ca to reconstruct past seawater temperature.

We have illustrated this temperature bias using modern and LGM samples. Modern tests grown under very similar conditions show clearly different crust composition and crust to inner layer ratio, causing considerable whole test Mg/Ca differences. Tests from LGM samples tend to have more and slightly thicker crusts, enlarging the Mg/Ca bias due to encrustation. In the SW Indian Ocean, decreased bulk test Mg/Ca in LGM age samples is caused by changes in the crust alone. This highlights the need for detailed analyses, where it is possible to separate the crustal from the inner layer and calls for better understanding of the mechanisms of crust formation in order to improve paleotemperature estimates based on the Mg/Ca of encrusted foraminifera.

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