Intratest oxygen isotope variability in planktonic foraminifera: Real vs. apparent vital effects by ion microprobe

R. Kozdon, T. Ushikubo, N. Kita, M. Spicuzza, J.W. Valley

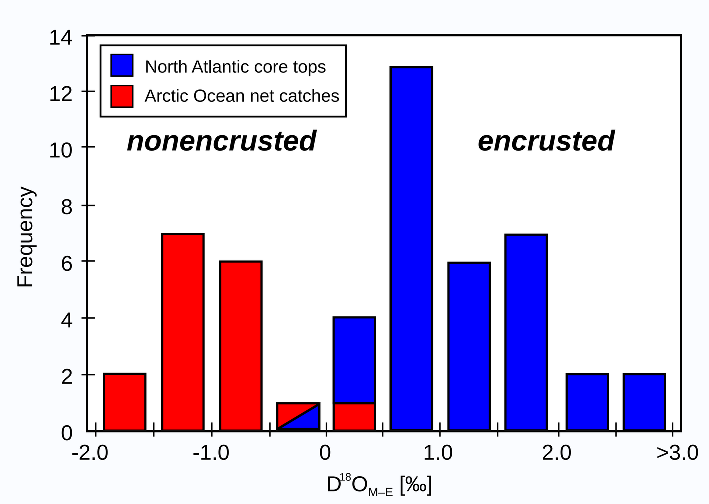
Department of Geology & Geophysics, University of Wisconsin - Madison

corresponding author: Reinhard Kozdon rkozdon@geology.wisc.edu

Abstract

Intratest oxygen isotope variations in the planktonic foraminifera *Neogloboquadrina pachyderma* sinistral (left coiling) from North Atlantic core top and multi-net samples were assessed by ion microprobe analysis from 2 to 6 µm spots with precision better than 0.7‰ in $d^{18}O$ (2 SD). Within a single foraminiferal test, $d^{18}O$ values vary from 0.5‰ to 3.7‰ [PDB], exceeding the range of equilibrium $d^{18}O$ in the specimens' habitat by a factor of three. The isotopic difference between the ontogenetic calcite and the crust averages 1.8‰. Neither of the two types of foraminiferal calcite precipitates in equilibrium with ambient seawater. The ontogenetic calcite exhibits a negative vital effect $D^{18}O_{(M-E)} = d^{18}O_{(measured)} - d^{18}O_{(equilibrium)}$ ranging from –0.5 to –1‰. The highest negative fractionation is associated with the inner walls of juvenile chambers. In contrast, a positive vital effect of about +0.8‰ was observed in the outer crust. Hence two vital effects which are different in sign are effective within a single foraminiferal test, indicating that 'whole test' values of this species are highly sensitive to the degree of encrustation and amplify or attenuate environmental signals.

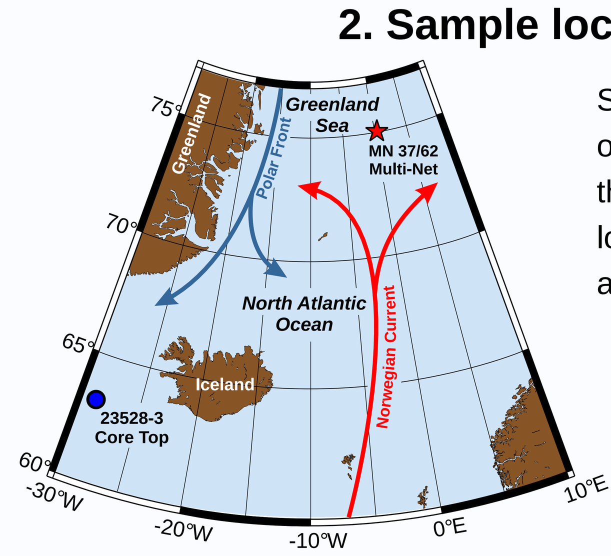
1. Single species vital effects



Histogram showing the range vital effects in *N. pachyderma* (sin.). Core top data are from Wu and Hillaire-Marcel (1994) and references therein; net catch $d^{18}O$ values are published in Bauch (1997).

Equilibrium values are calculated by the equation of O'Neil et al. (1969) using temperature and ambient seawater $d^{18}O$ values given in the publications.

2. Sample locations



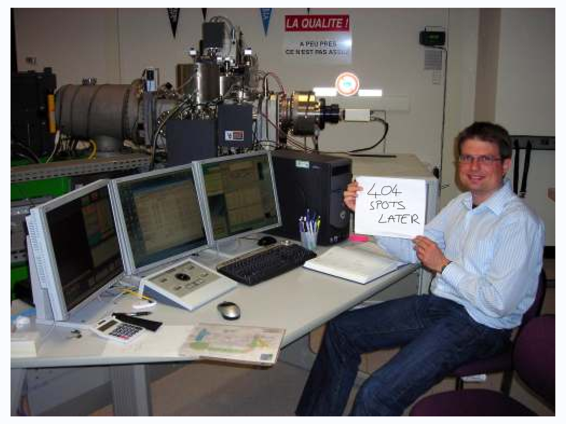
Simplified surface hydrography of the North Atlantic Ocean and the Greenland Sea and the locations of the multi-net station and sediment surface sample.

3. Analytical technique

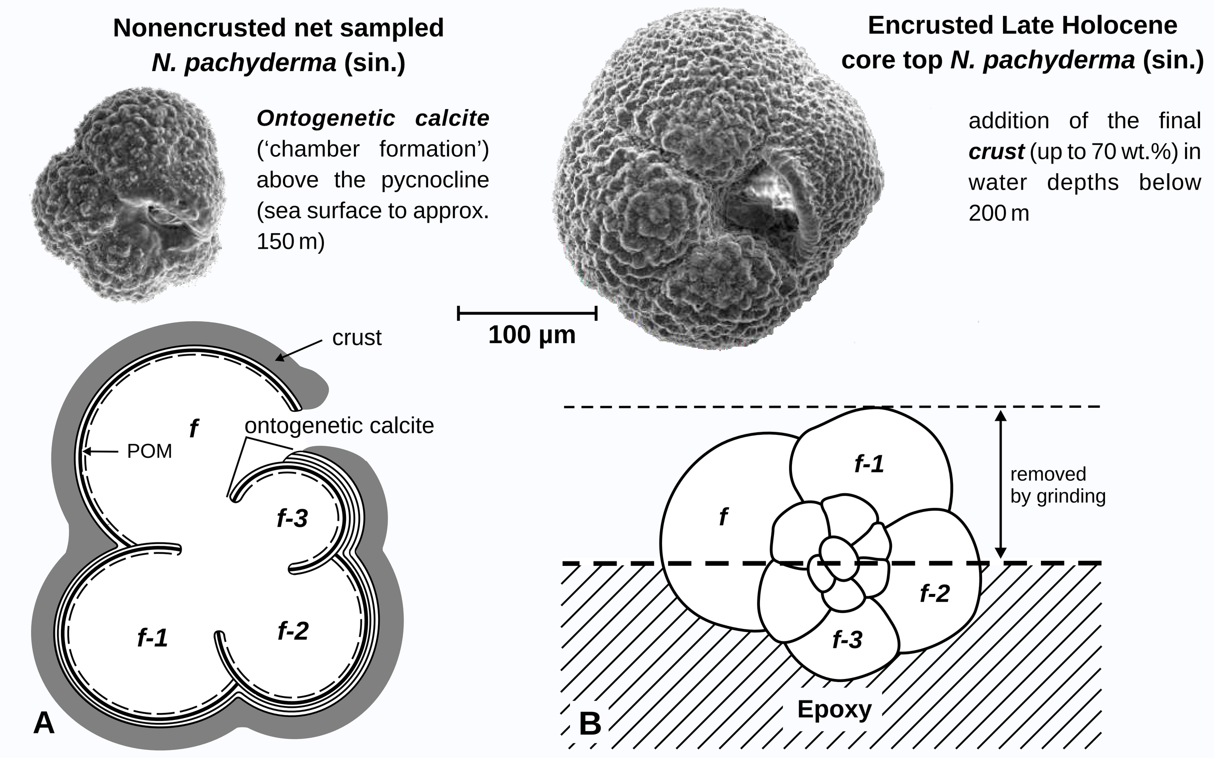
Wisc-SIMS (Cameca ims-1280 with multiple detectors)

General conditions of the analysis are similar to Page et al. (2007)

- **Primary:** $^{133}Cs^{+}$ with 15 to 18 pA, spot size typically 2 µm
- **Secondary:** –10 keV acceleration
  detection of ^{16}O in FC ($10^{11}\Omega$), intensity 1.3 to 2.1×10^{7} cps
  detection of ^{18}O in EM (Hamamatsu), intensity 2.7 to 4.6×10^{4} cps
  field aperture 4000 x 4000 µm
  entrance slit 122 µm
  energy slit 40 eV
  MRP = 2200
- total analytical time per spot 20 min. including pre-sputtering (5 min.)
- **Standard:** UWC-3 (in-house), diopside-bearing marble, Adirondack Mountains, New York (#95AK24, Edwards and Valley, 1998)
  $d^{18}O_{(SMOW)} = 12.49 \pm 0.03‰$



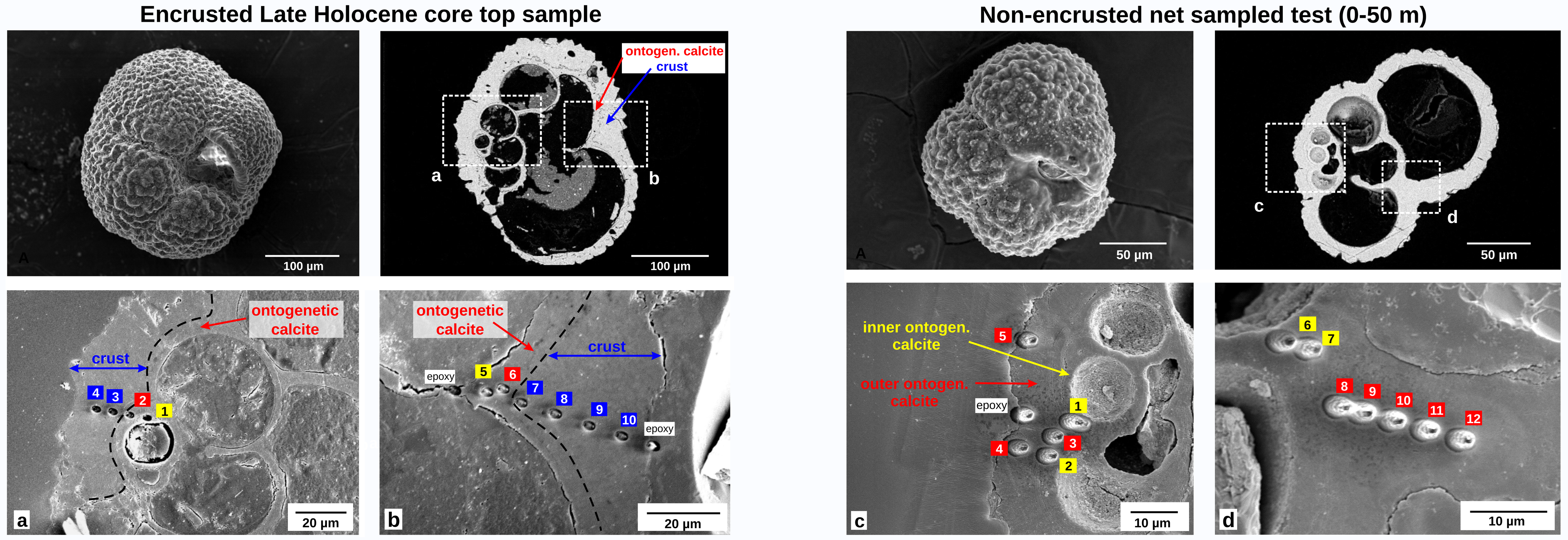
4. Foraminiferal chamber wall structure

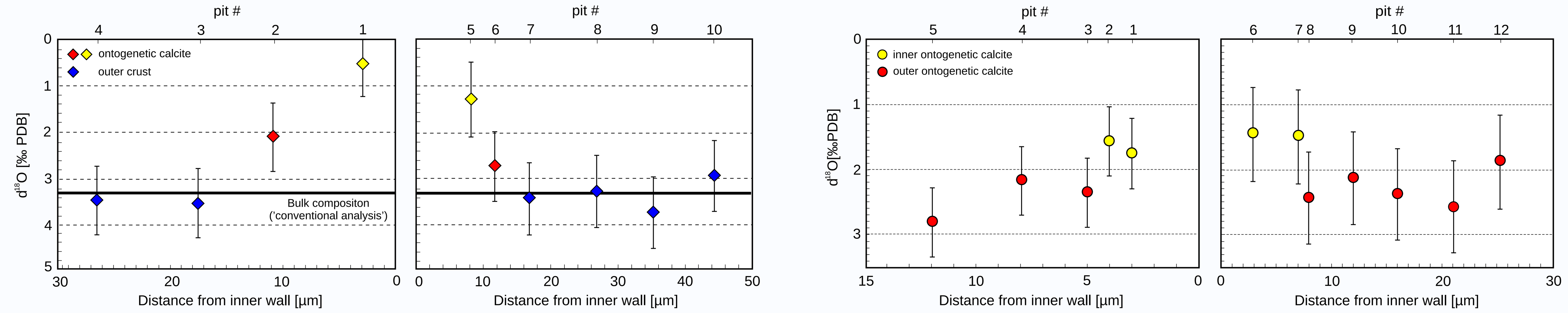


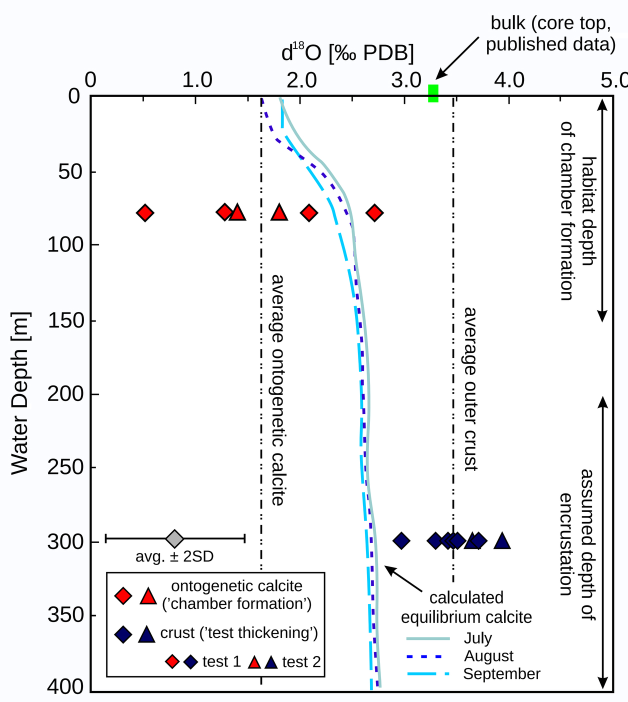
A) *N. pachyderma* (sin.) test microstructure of the final (f) and penultimate chambers (f-1 to f-3) of the last whorl. The average total number of chambers prior reproduction is 15. The primary organic membrane (POM) is the site of initial calcification and has two active surfaces, one calcifying on the outer and the other on the inner side. Every time these organisms form a new chamber, their whole pre-existing test is covered with a new layer of calcite. The crust, which may contribute more than 70% of the total test weight in this foraminiferal species (Kohfeld et al., 1996), is secreted at the end of their life cycle. **B)** Spiral view of *N. pachyderma* (sin.) embedded in epoxy. The illustrated polished surface corresponds to the analyzed cross sections .

5. Apparent vs. real vital effects

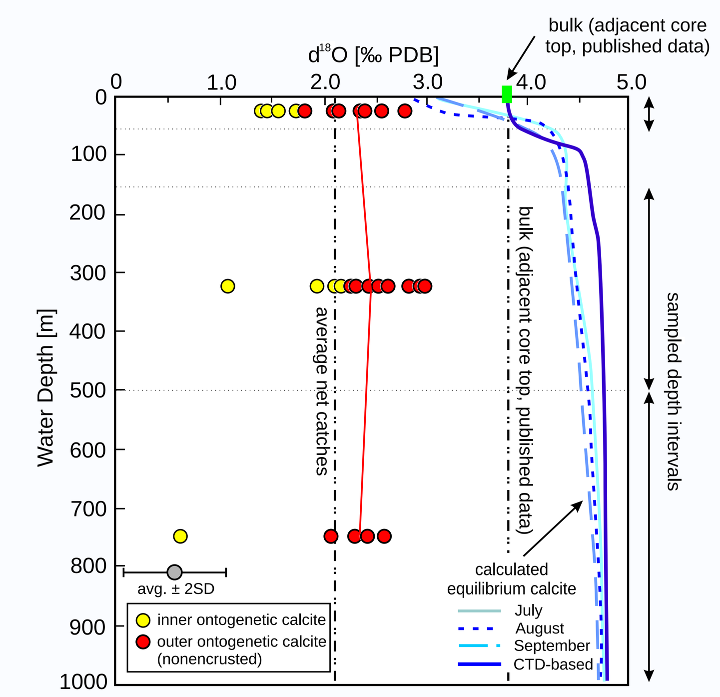
Encrusted Late Holocene core top sample | **Non-encrusted net sampled test (0-50 m)**





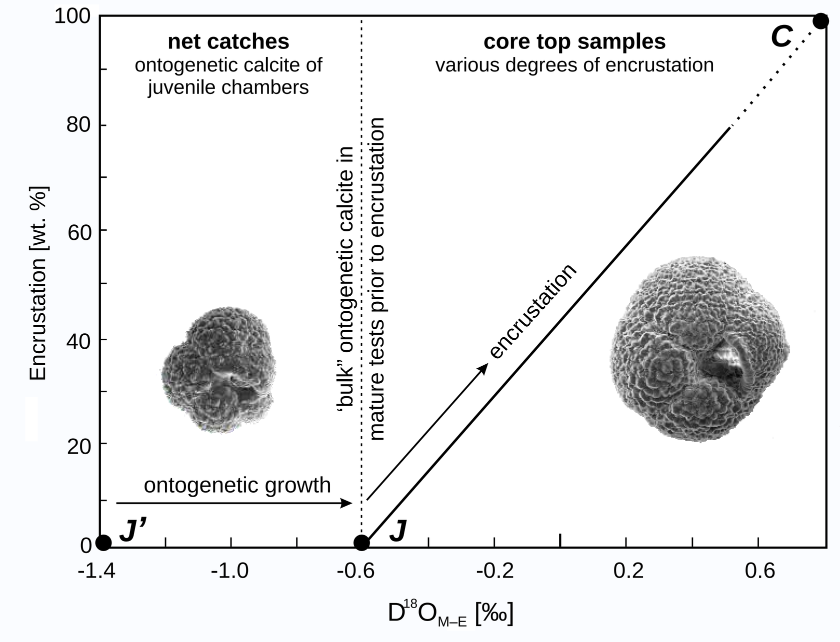


Oxygen isotope values of 2 to 6 µm spots in the ontogenetic calcite and the outer crust derived from two individual tests of core top *N. pachyderma* (sin.) plotted against calculated equilibrium calcite profiles from July to September (main planktonic bloom) at core location. The oxygen isotope ratios of the crust match published 'whole test' data from bulk foraminiferal analysis, indicating a high degree of test encrustation at core location.



Oxygen isotope values of 2x3 µm spots in four *N. pachyderma* (sin.) tests from the multi-net station MN37/62 plotted according to the sampled depth intervals. The equilibrium calcite profiles represent the months July to September, supplemented by (CTD) data. Published core top data from a nearby station are shown for comparison (core top PS2613; Simstich et al., 2003).

6. Relationship between 'apparent' vital effects and the degree of encrustation



The intermediate value ***J*** (juvenile) reflects no encrustation (100% ontogenetic calcite) with a $D^{18}O_{M-E}$ ($d^{18}O_{measured} - d^{18}O_{equilibrium}$) of –0.6‰. This is the average offset between the ontogenetic calcite layers of mature core top samples and the average equilibrium $d^{18}O_{calcite}$ in the euphotic zone. Endmember ***C*** (crust) reflects (hypothetical) 100 wt.% encrustation with a $D^{18}O_{M-E}$ of +0.8‰. The $D^{18}O_{M-E}$ of up to –1.4‰ in juvenile chambers and net catches is indicated by ***J'***. During ontogenetic growth, chamber $d^{18}O$ values increase and hence the vital effect decreases with chamber size, shifting the whole test $d^{18}O$ value from ***J'*** to ***J***.

7. Conclusions

- biomineralization can produce small-scale isotope zonation
- intratest $d^{18}O$ variations in the planktonic foraminifera *N. pachyderma* (sin.) are as high as 3.2‰ and exceed the range of the equilibrium $d^{18}O_{calcite}$ values in the specimens' habitat by a factor of three
- both the ontogenetic calcite and the crust precipitate in distinct disequilibrium with ambient seawater
- there are two vital effects that are opposite in sign
- small changes in the degree of encrustation shift whole test $d^{18}O$ values significantly and hence overprint environmental signals.

References

Bauch, D., 1997. Oxygen isotope composition of living *Neogloboquadrina pachyderma* (sin.) in the Arctic Ocean. Earth Planet. Sci. Lett. 146, 47–58.
Edwards, K.J. and Valley, J.W., 1998. Oxygen isotope diffusion and zoning in diopside: The importance of water fugacity during cooling. Geochim. Cosmochim. Acta, 62, 2265–2277.
Kohfeld, K.E., Fairbanks, R.G., 1996. *Neogloboquadrina pachyderma* (sinistral coiling) as paleoceanographic tracers in polar oceans: Evidence from Northeast Polynya plankton tows, sediment traps, and surface sediments. Paleoceanogr. 11 (6), 679–699.
O´Neil, J.R., Clayton, R.N. Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys., 15 (12), 5547–5558.
Page, F.Z., Ushikubo, T., Kita, N.T., Riciputi, L.R, Valley, J.W., 2007. High precision oxygen isotope analysis of picogram samples reveals 2-m gradients and slow diffusion in zircon. Am. Mineral. 92, 1772–1775.
Simstich, J., Sarnthein, M., Erlenkeuser, H., 2003. Paired $d^{18}O$ signals of *Neogloboquadrina pachyderma* (s) and *Turborotalita quinqueloba* show thermal stratification structure in Nordic Seas. Marine Micropal. 48, 107-125.
Wu, G. and Hillaire-Marcel, C., 1994. Oxygen isotope composition of sinistral *Neogloboquadrina pachyderma* tests in surface sediments: North Atlantic Ocean. Geochim. Cosmochim. Acta 58 (4), 1303–1312.