Quantifying Isotopic and Elemental Variations in Planktic Foraminifera at the Micron Scale

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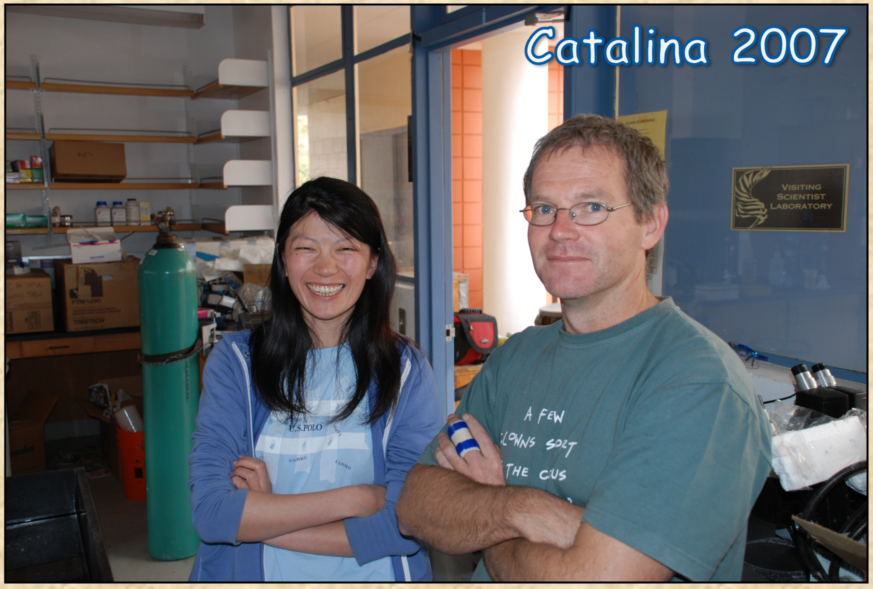
Thank you to many collaborators

- Ann Russell, Jenn Fehrenbacher and Oscar Branson (UC Davis)
- Lael 'Spider' Vetter (Tulane)
- 2007/11 foram culturing team
- Steve Eggins (ANU)
- Claudia Mora (LANL)
- Alex Gagnon (U. Washington)
- Reinhard Kozdon (Rutgers/LDEO)
- John Valley (WiscSIMS)



The field of modern Paleoceanography began in 1955

J. Geology 1955

PLEISTOCENE TEMPERATURES[1]

CESARE EMILIANI
University of Chicago

ABSTRACT

Oxygen isotopic analyses of pelagic Foraminifera from Atlantic, Caribbean, and Pacific deep-sea cores indicate that the temperature of superficial waters in the equatorial Atlantic and Caribbean underwent periodic oscillations during the Pleistocene with an amplitude of about 6° C. The temperature record of the Pacific cores was much affected by local oceanographic conditions.

Seven complete temperature cycles are shown by a Caribbean core. By extrapolating rates of sedimentation based on radiocarbon data, an age of about 280,000 years is obtained for the earliest temperature minimum. Correlation with continental events suggests that the earliest temperature minimum corresponds to the first major glaciation.

The chronology of Pacific cores proposed by Arrhenius (1952) must be modified if correspondence with the chronology of Atlantic and Caribbean cores is desired.

In one Pacific core which extends to the Pliocene, the 610-cm. level below top is believed to represent the Plio-Pleistocene boundary. About fifteen complete temperature cycles occur above this level, and the length of Pleistocene time is estimated at about 600,000 years. The so-called pre-Günzian stages appear to span a time interval about as long as the Günz and post-Günzian stages. A glacial lowering of sea-level of about 100 m. is indicated.

Closely spaced samples from short pilot cores furnish a detailed temperature record for postglacial times. A continuous temperature increase from about 16,500 to about 6,000 years ago is indicated, followed by a small temperature decrease. The temperature maximum at about 6,000 years ago is correlated with the "Climatic Optimum."

Isotopic analyses of calcareous benthonic Foraminifera show that the temperature of bottom water in the equatorial Pacific during glacial ages was similar to the present, but in the eastern equatorial Atlantic it was about 2.1° C. lower. This difference resulted from the large amount of marine ice present in the North Atlantic. Interglacial bottom temperature in the equatorial Pacific was not more than about 0.8° C. higher than glacial temperatures; interglacial data for the equatorial Atlantic are inconclusive with respect to temperature but indicate an influx of ice meltwater along the bottom larger than at present.

Correspondence in time between temperature variations in the low latitudes, as shown by the cores, and glacial events in the high northern latitudes indicates close correspondence between glacial or interglacial phases and wet or dry phases, respectively.

Good correlation exists between times of temperature minima as indicated by extrapolated rates of sedimentation and times of insolation minima in high northern latitudes. Control of world climate during the Pleistocene by insolation in the high northern latitudes is indicated. A retardation of about 5,000 years occurred between temperature and insolation cycles.

Complete revision of current correlations between the insolation curve and continental events is necessary.

The glacial epoch and its ages may be explained by a theory combining topographical and insolation effects.

Conditions may be suitable for the beginning of a new ice age in about 10,000 years.

INTRODUCTION

The idea of using as a thermometer the variations with temperature of the fractionation factors in isotopic exchange equilibria was first formulated by Urey (1947), in particular relation to the oxygen isotopes in the system CO_2-H_2O-$CaCO_3$.

Three important problems required solution before even preliminary testing of the method could be attempted:

1. The precision attainable at that time in the mass spectrometric measurements of oxygen isotope ratios had to be increased about ten times: an improved six-inch 60° deflection mass spectrometer, based on Nier's design (Nier, 1940, 1947), was constructed by McKinney, McCrea, Epstein, Allen, and Urey (1950); this instrument has now made some 12,000 analyses in Urey's laboratory without subsequent modification.

2. A method of extracting CO_2 from

[1] Manuscript received August 11, 1955.

Caribbean core A180-73

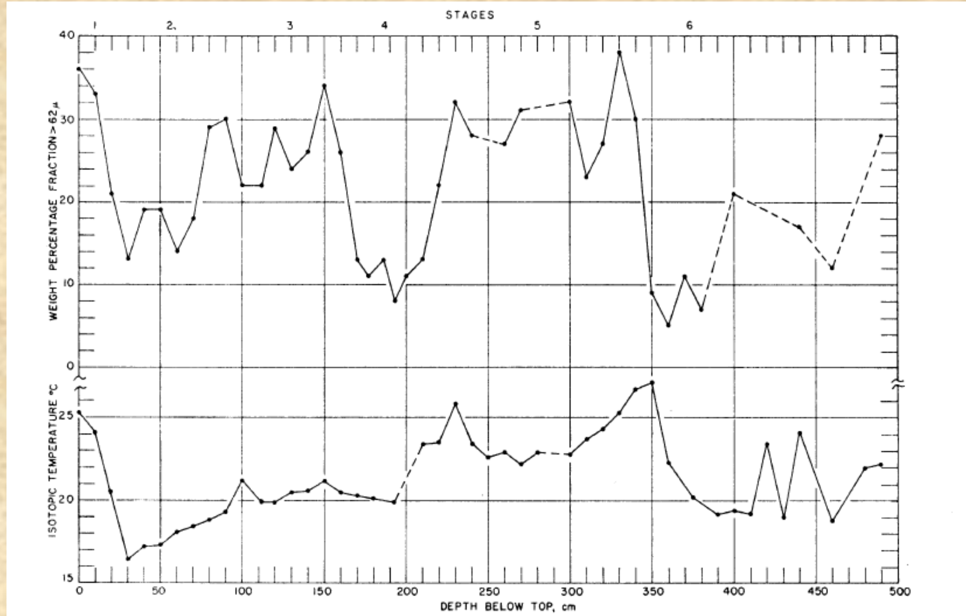


FIG. 4.—Core A180-73: percentages of the fraction larger than 74 μ and isotopic temperatures obtained from *Globigerinoides sacculifera*.

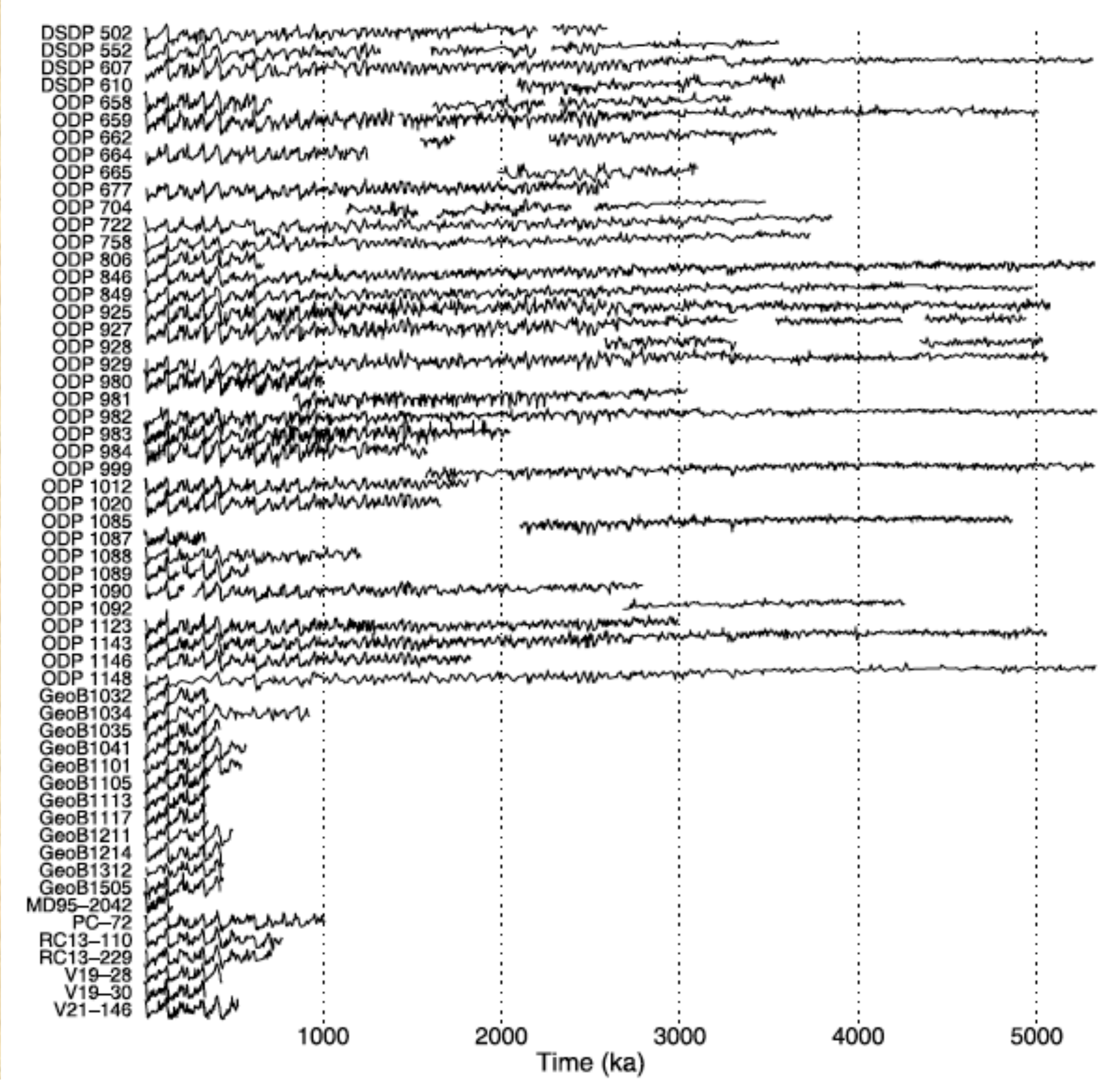
sionally also from the smallest fraction). Depending upon their size, about 100–400 tests are required to make up the 5 mg. of calcium carbonate necessary for each isotopic analysis.

A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records

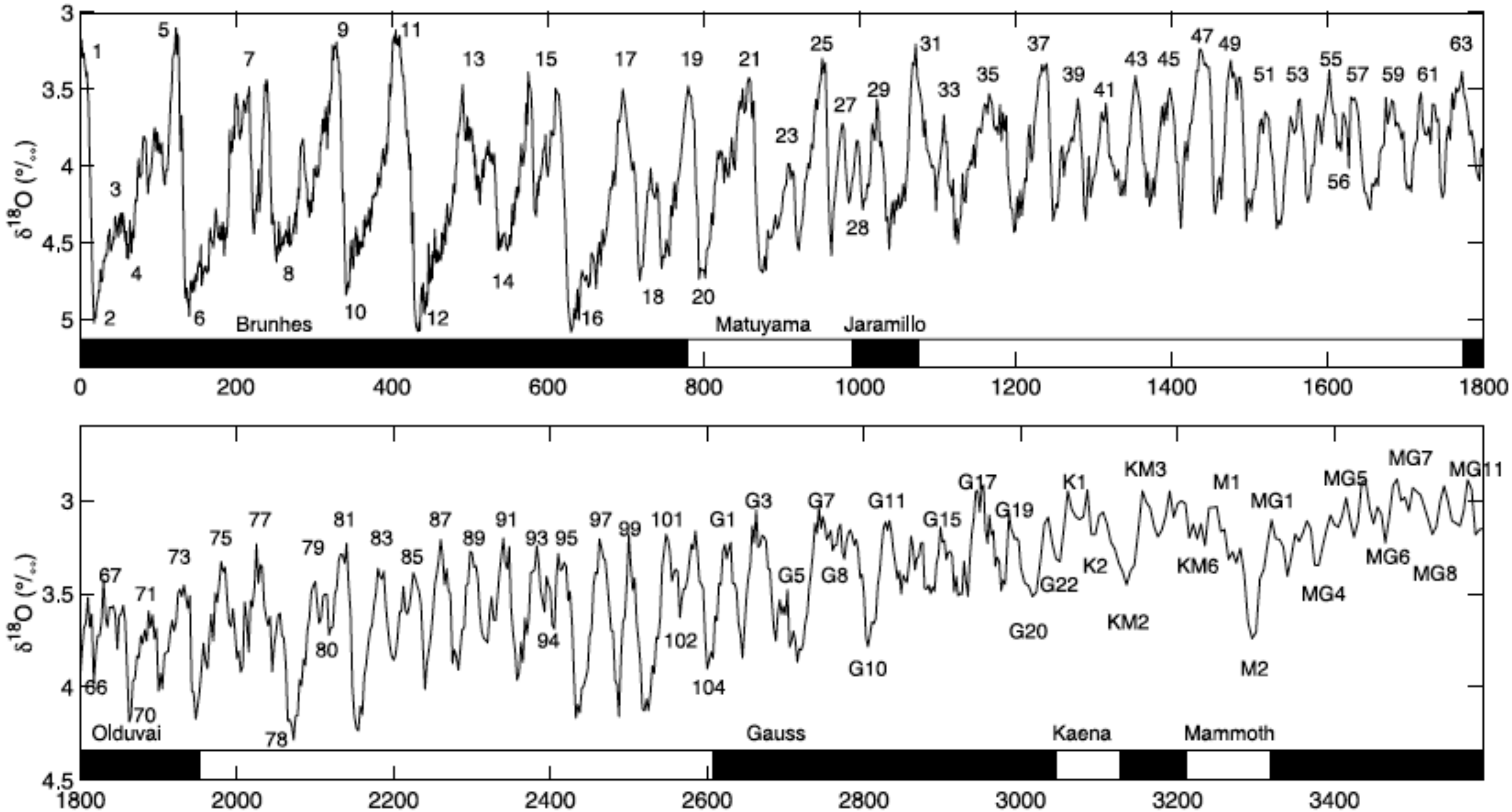
PALEOCEANOGRAPHY, VOL. 20, PA1003, doi:10.1029/2004PA001071, 2005

Lorraine E. Lisiecki
Department of Geological Sciences, Brown University, Providence, Rhode Island, USA

Maureen E. Raymo
Department of Earth Sciences, Boston University, Boston, Massachusetts, USA



LR05 stack – most citations in journal *Paleoceanography*……..ever



Lisiecki and Raymo, 2005

Most cores do not have the decadal or century temporal resolution to directly address societally relevant questions about the climate system.

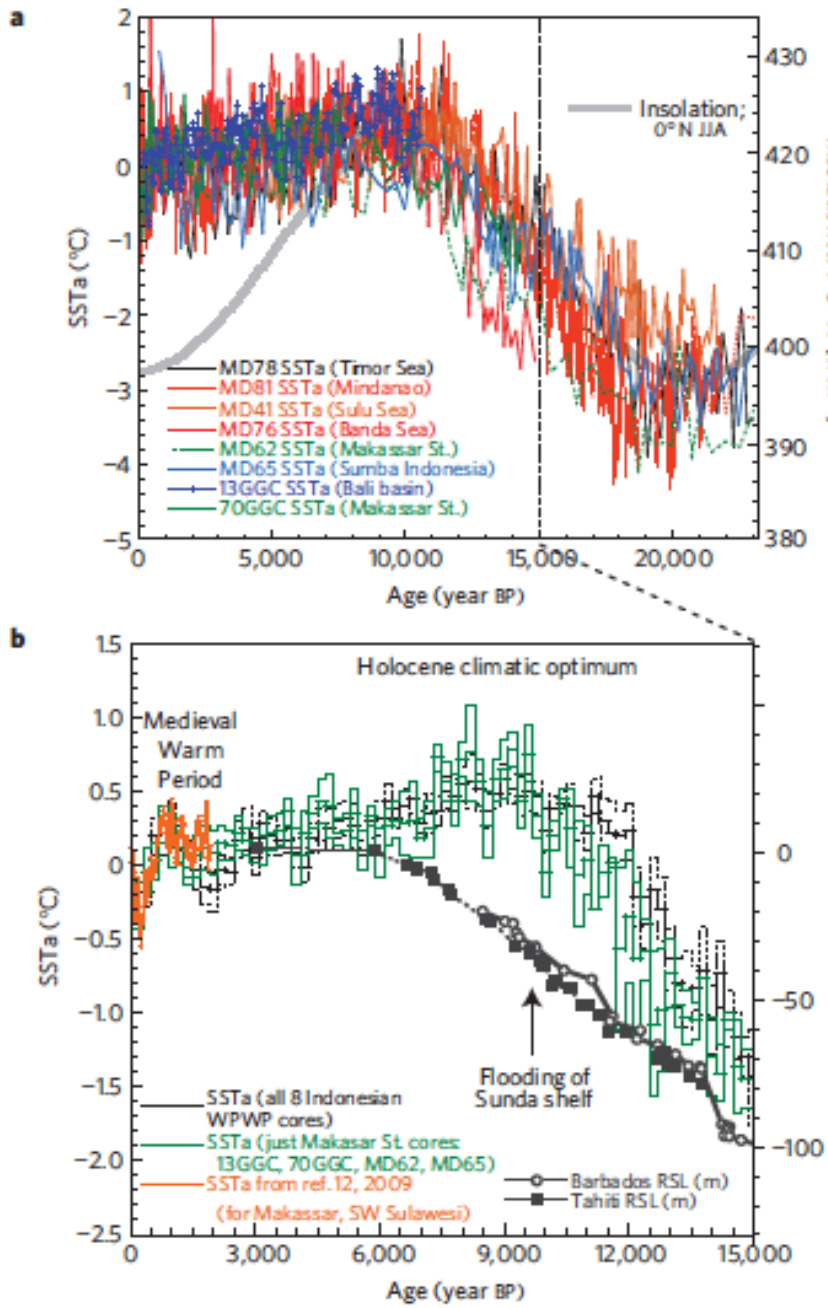
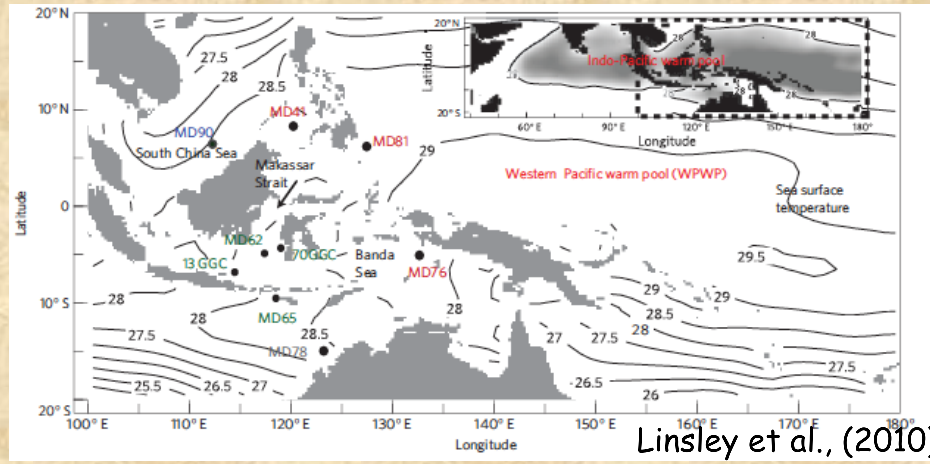


Figure 2 | Planktonic foraminifera Mg/Ca records of mixed-layer temperatures in the WPWP. a, Comparison of Indonesian and WPWP



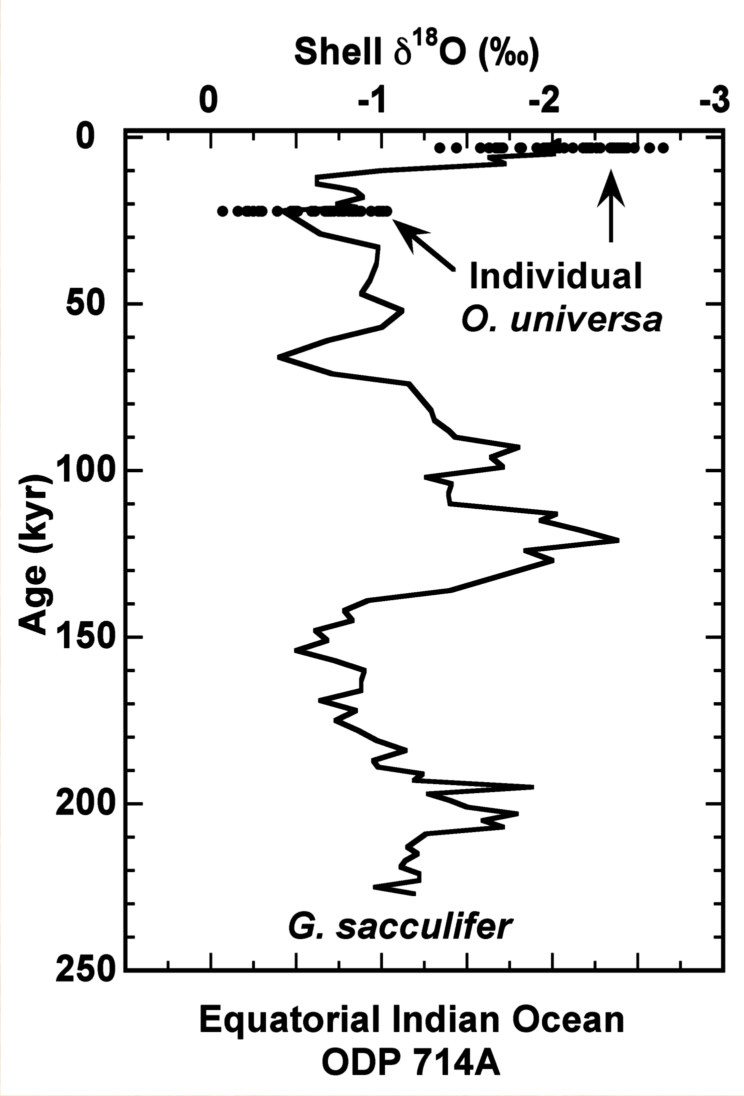
Linsley et al., (2010)

http://www.microscopy-uk.org.uk/micropolitan/marine/foram/Globigerina_ooze.jpg

Late Pleistocene oxygen isotope stratigraphy; equatorial Indian Ocean (Maldives)

Novel questions

- Paleoecology
- Seasonality
- Water column hydrography
- Bioturbation
- Diagenesis
- Selective dissolution
- Water column light variation



Outline

- Experimental organism - *Orbulina universa*
- LA-ICPMS and NanoSIMS reveal the timing of Mg banding in O. universa
- Combining SIMS and LA-ICPMS to resolve intrashell $\delta^{18}O$ and $\delta^{13}C$ variations at the micron scale
- Tracing carbon flow in a symbiont system by combining NanoSIMS and TEM
- Exploring the chemistry of a calcite bio-mineral interface with APT (atom probe tomography)

One of the most important climate archives - the $CaCO_3$ shells of planktonic foraminifera

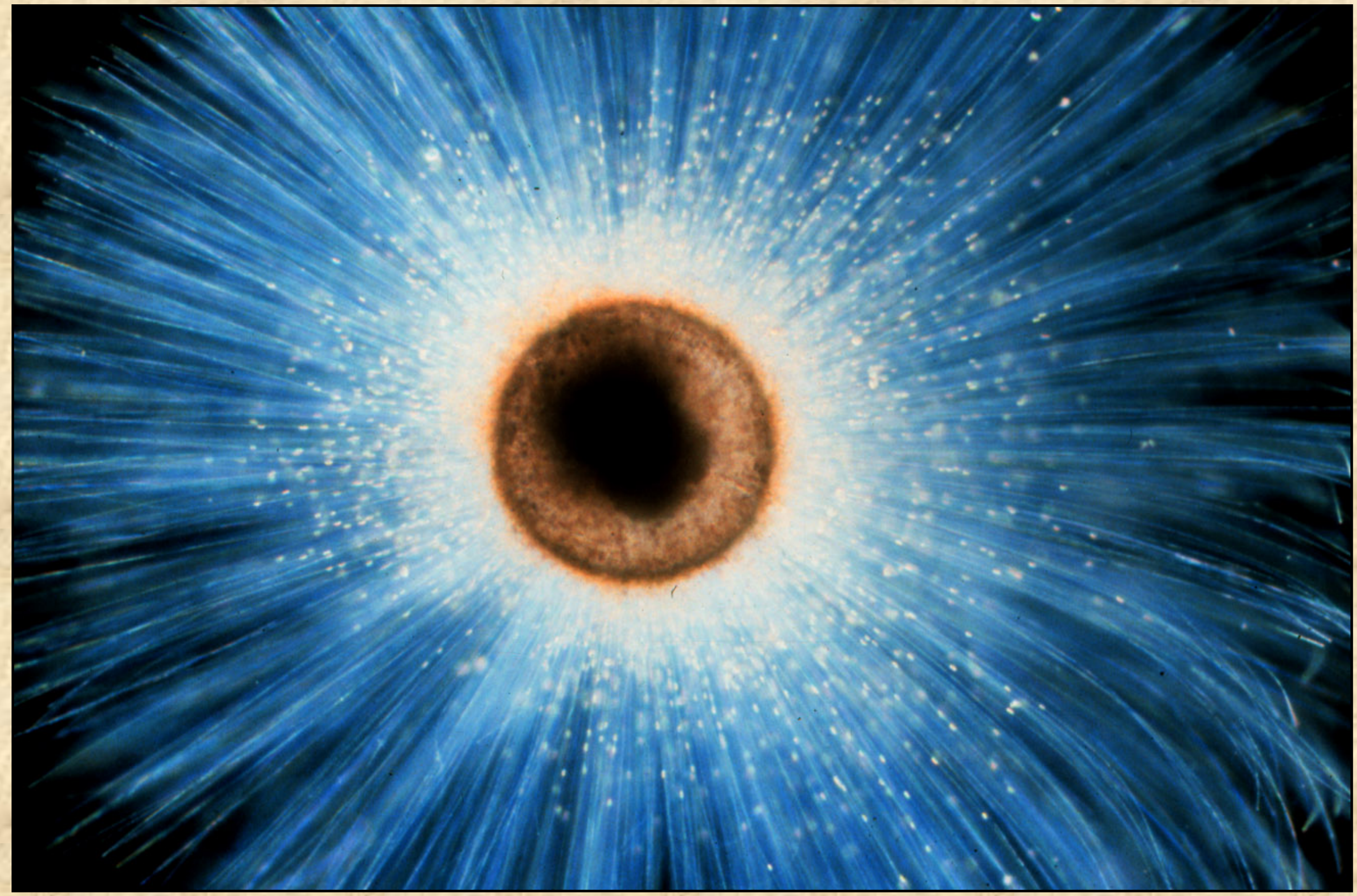
Sphere diameter ~500 µm

O. universa

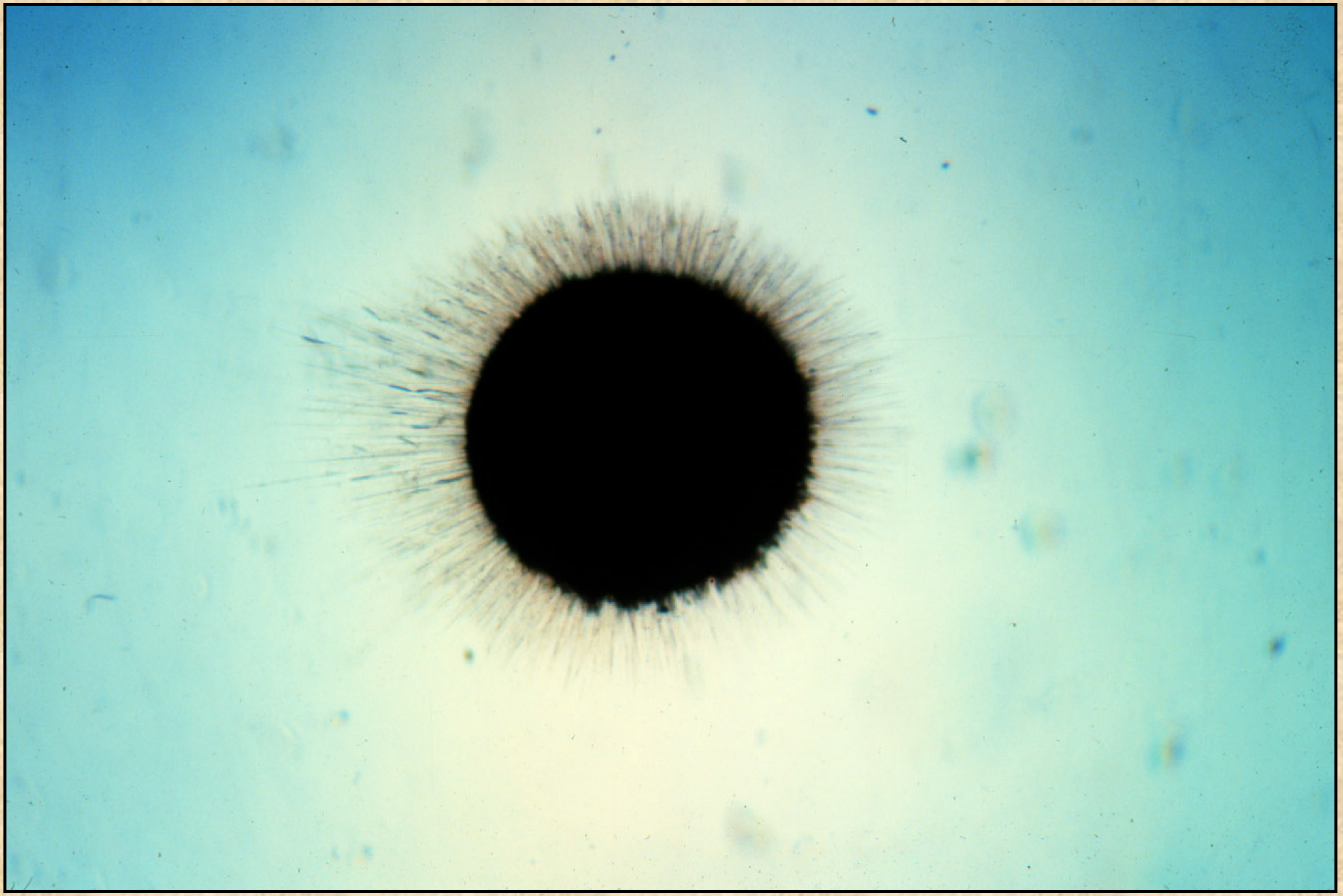
Pre-sphere, trochospiral shell form of *O. universa*; note symbionts on spines

O. universa (with sphere) - feeding on brine shrimp nauplius

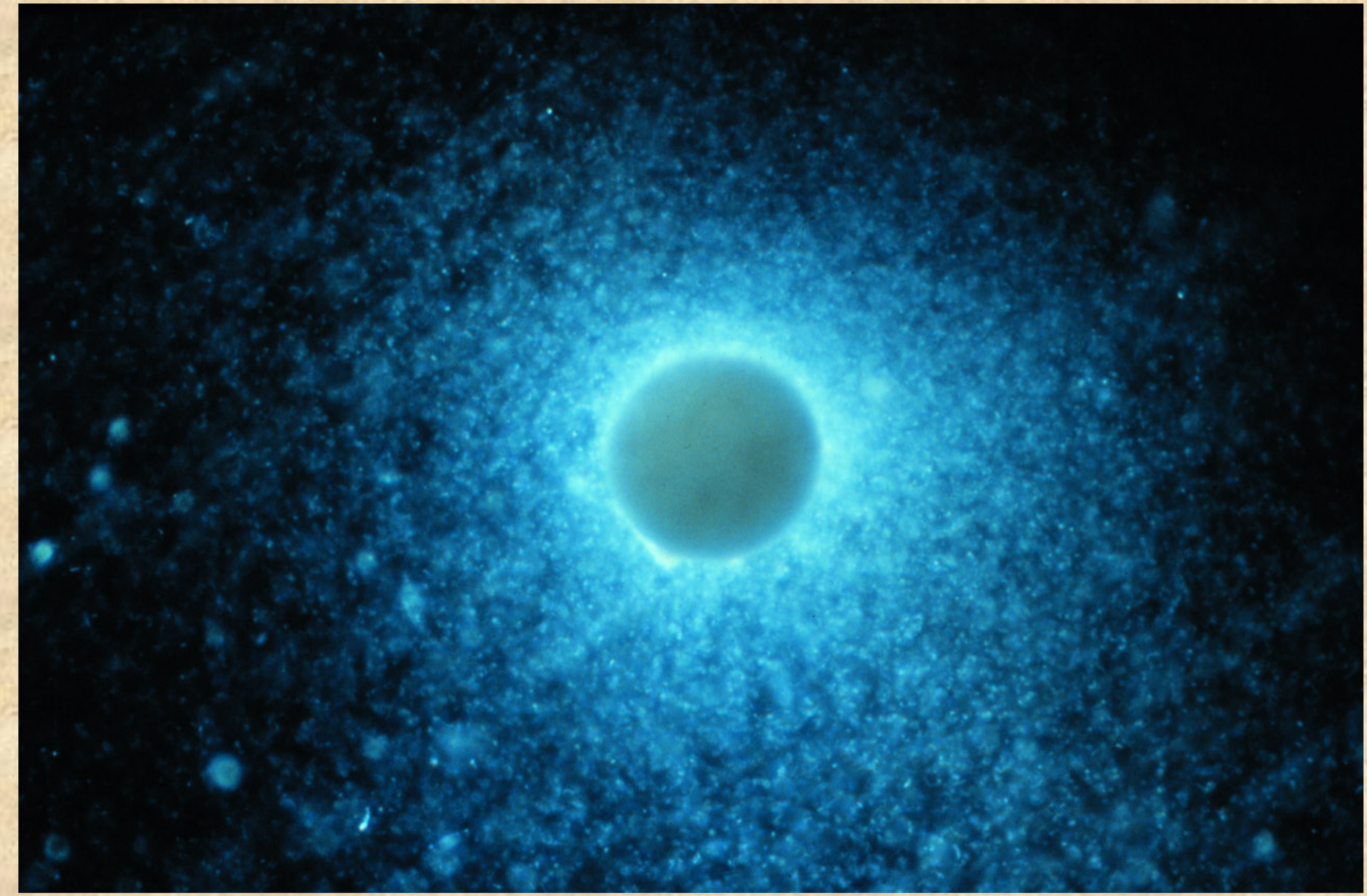
Most planktic foraminifera complete their lifecycles in 2-4 weeks. *O. universa* secretes and thickens its spherical chamber over the final 3-7 days of its lifecycle



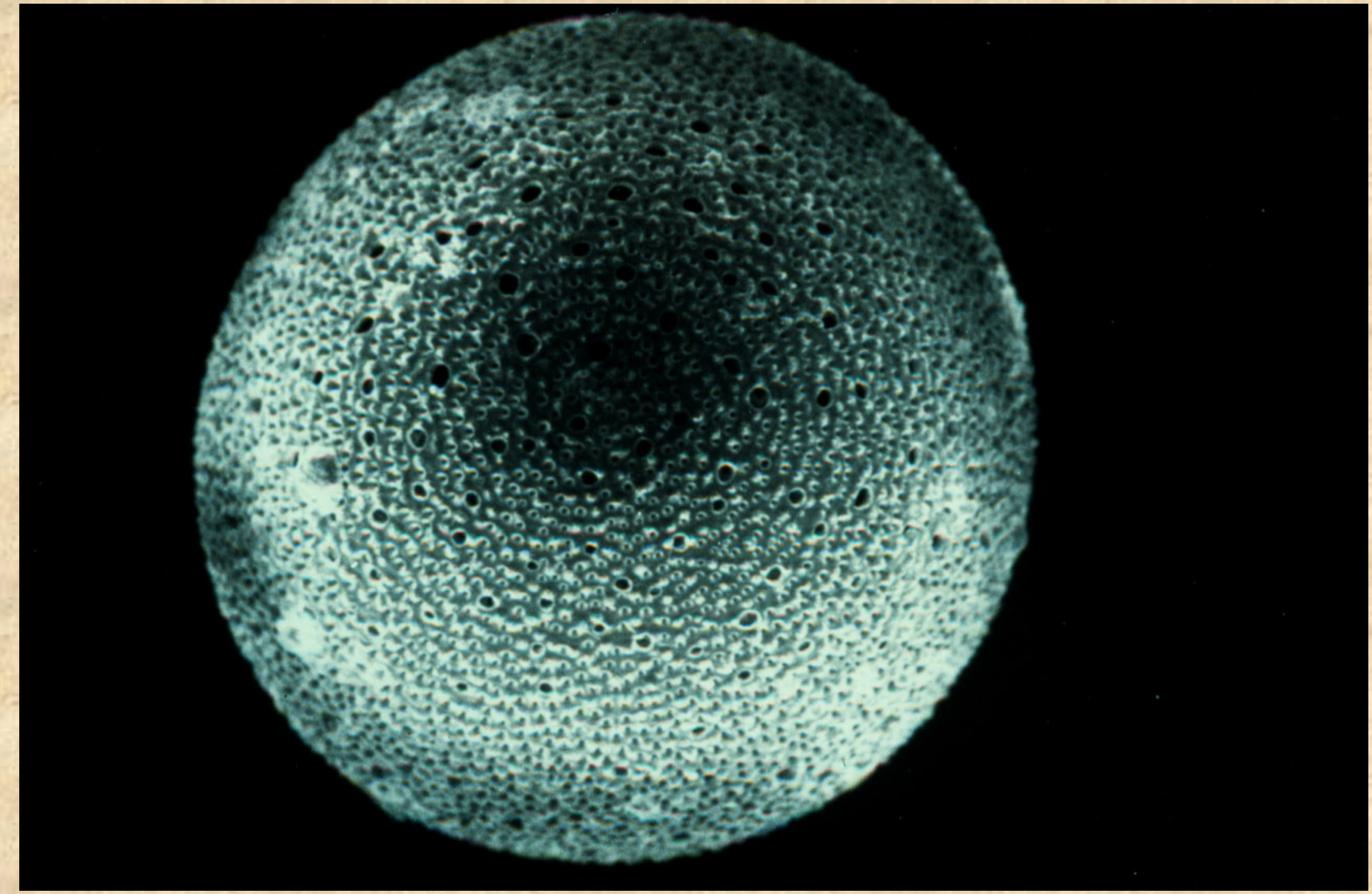
After sphere thickening, *O. universa* sheds its spines over a 12h period

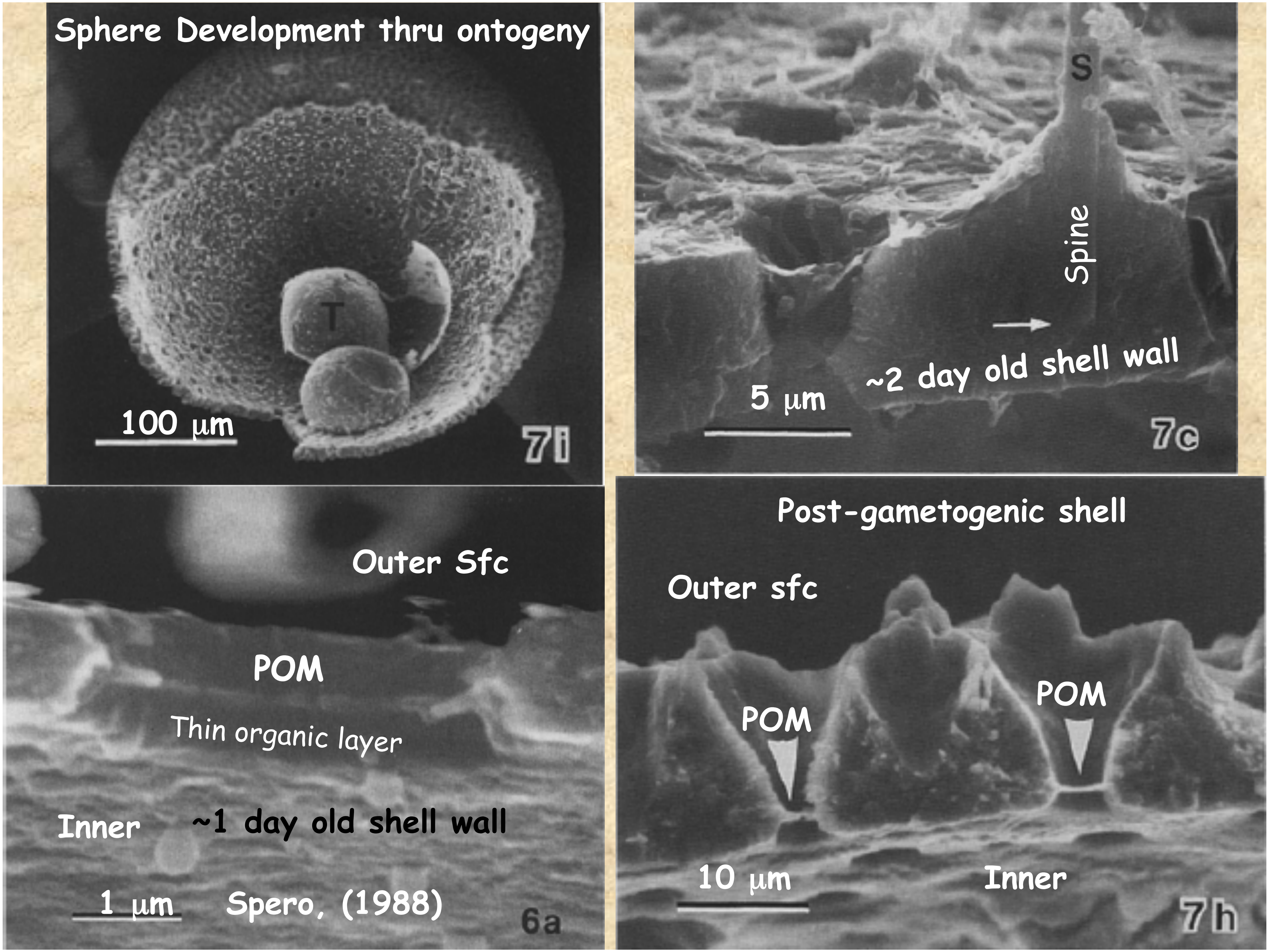


Gametes are released within 24 hours of spine shortening, ending the life of the individual

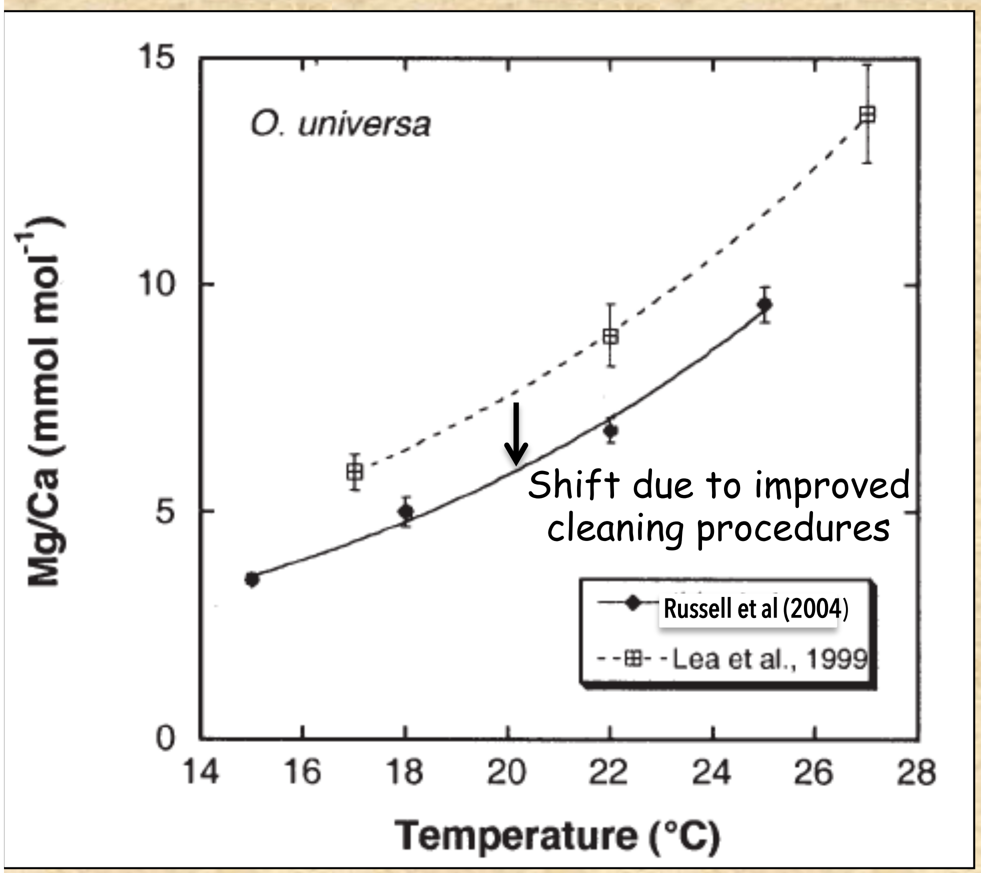


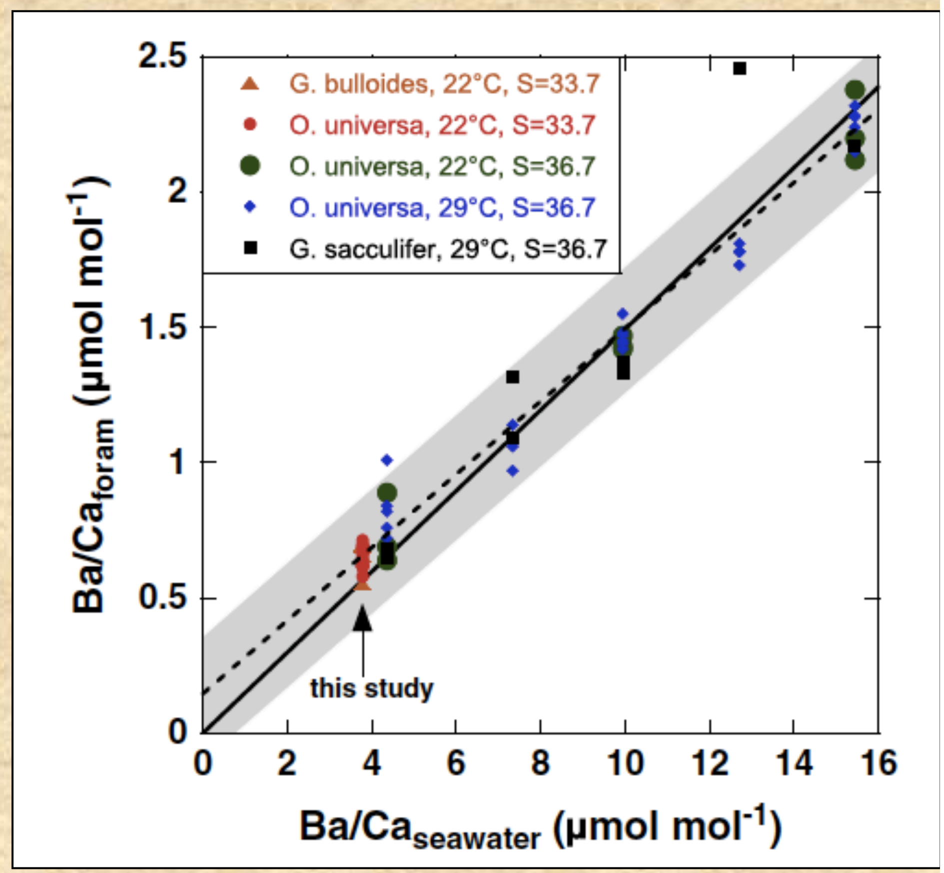
Post-gametogenic *O. universa* from the laboratory is identical to a million year old fossil.




Sphere Development thru ontogeny
T
100 µm
7i
S
Spine
~2 day old shell wall
5 µm
7c
Outer Sfc
POM
Thin organic layer
Inner
~1 day old shell wall
1 µm
Spero, (1988)
6a
Post-gametogenic shell
Outer sfc
POM
POM
10 µm
Inner
7h

Orbulina universa experiments yield robust calibrations for Me/Ca ratios; Shell Mg/Ca covaries with temperature and Shell Ba/Ca is proportional to [Ba_{sw}]



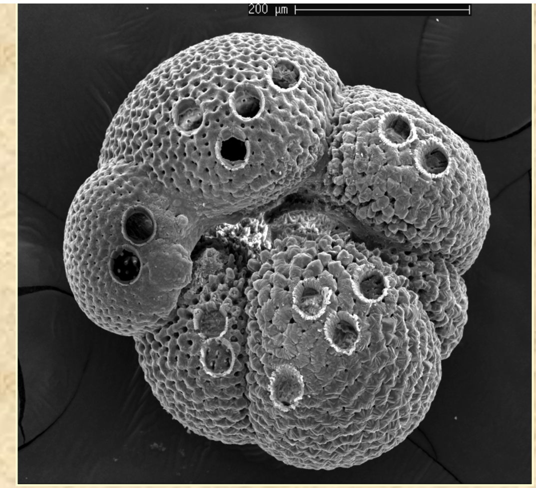


Lea & Spero (1992, 94)
Hönisch et al (2011)

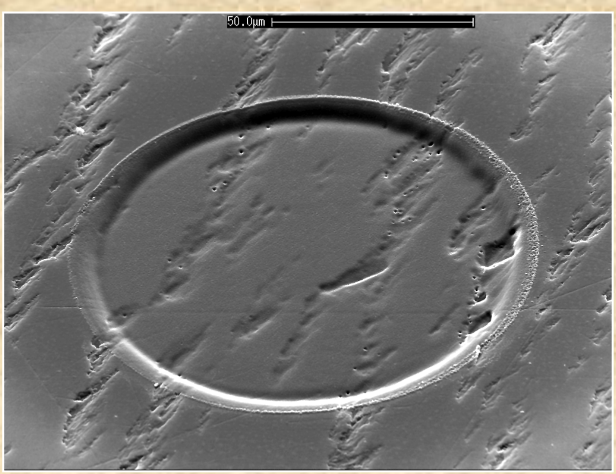
LA-ICPMS depth profiling

Deep UV laser (193 nm) and low pulse energy ($\sim$0.1-0.2 GW/cm^2)

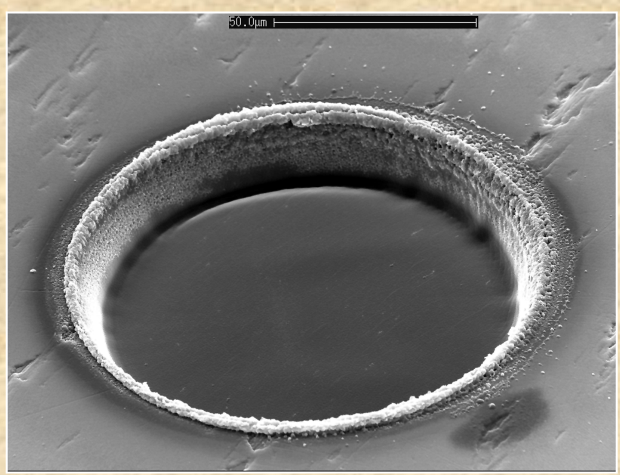
Each laser pulse shaves ~100 nm layer from test surface



Neogloboquadrina dutertrei

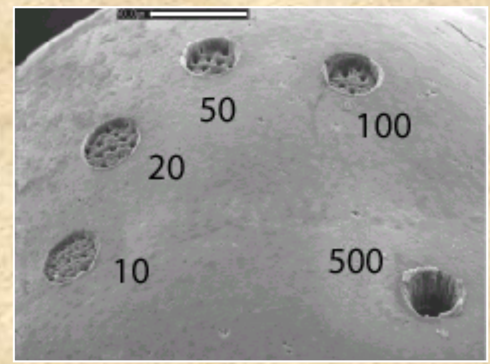


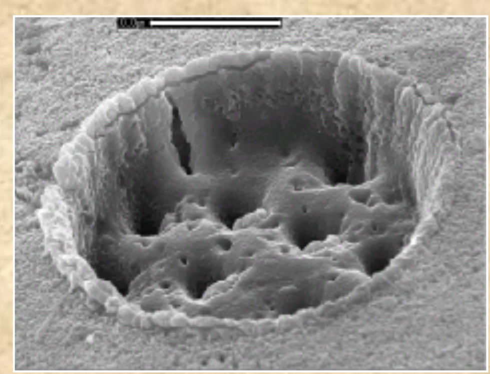
10 laser pulses



100 laser pulses

Gem quality Iceland spar

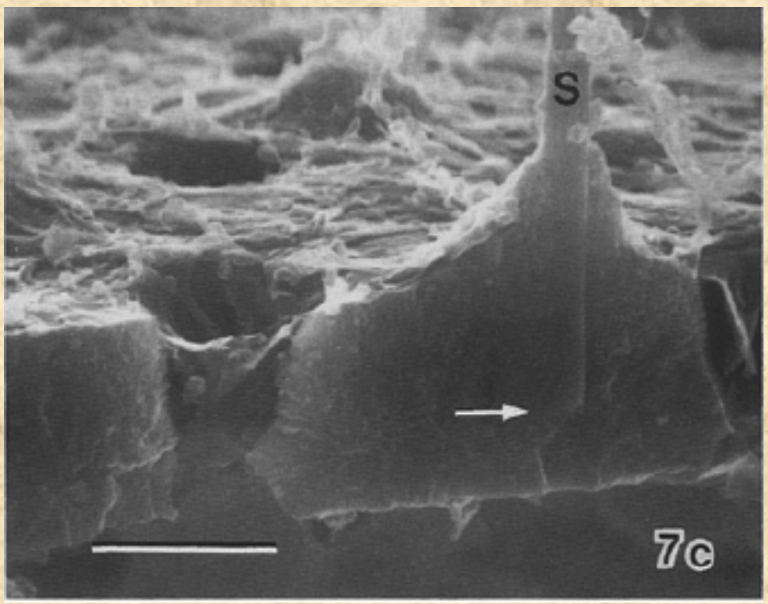




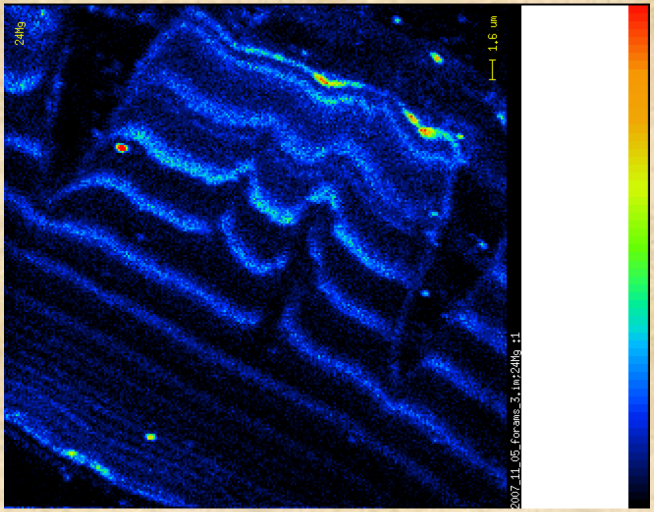
Pulleniatina obliquiloculata

Eggins et al (2004)

Orbulina sphere wall

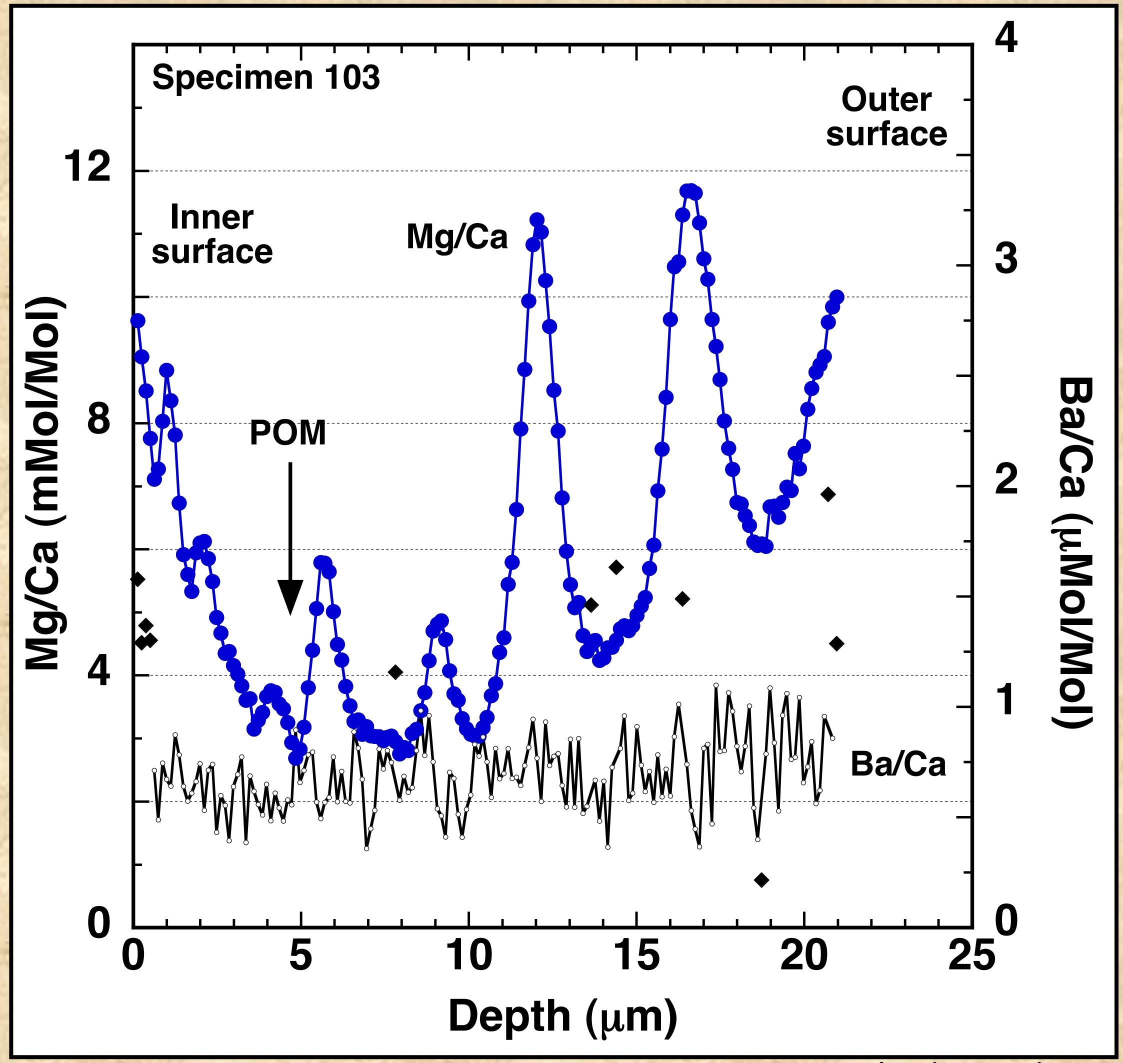


NanoSIMS image of
Orbulina wall [Mg]



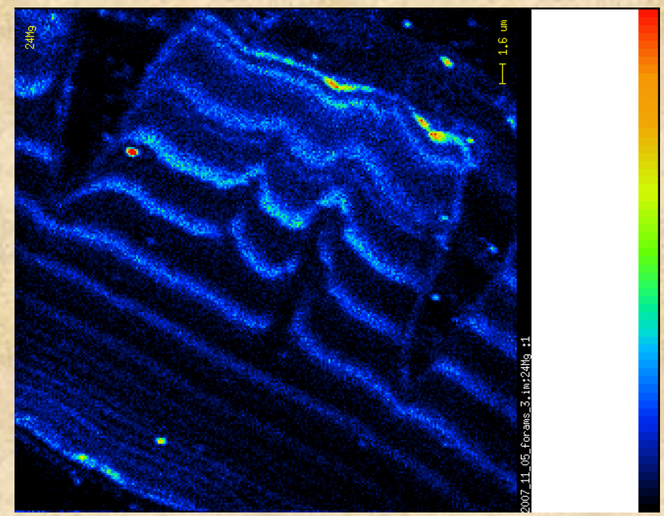
Aleksy Sadekov (unpub image)

LA-ICPMS profile of *O. universa* grown on 12h:12h L:D cycle @ 20C in seawater
One days growth adds ~4-5 μm to the shell wall



Spero et al., (2015)

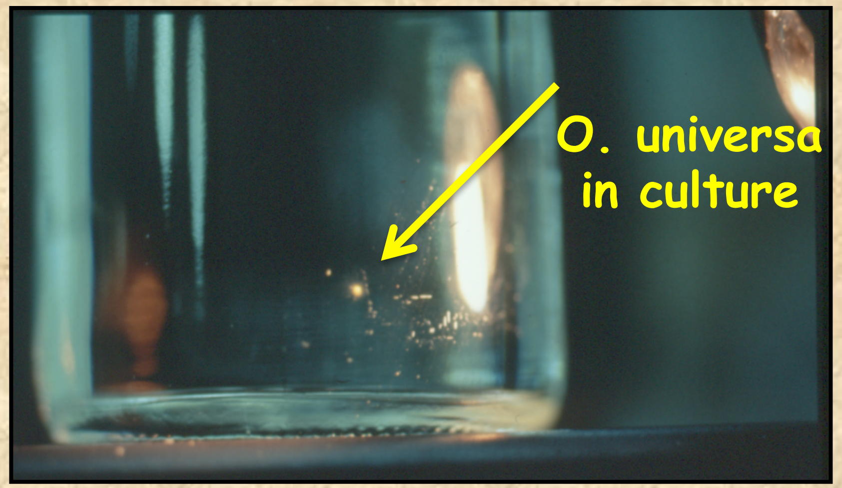
NanoSIMS image of Orbulina wall [Mg]

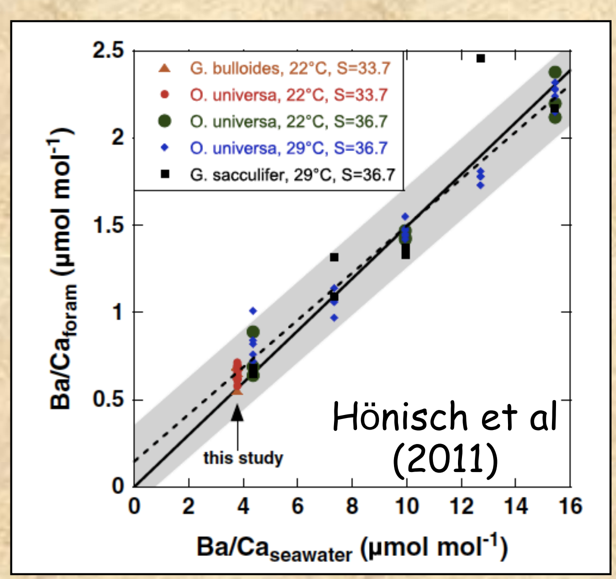


Aleksy Sadekov (unpub image)

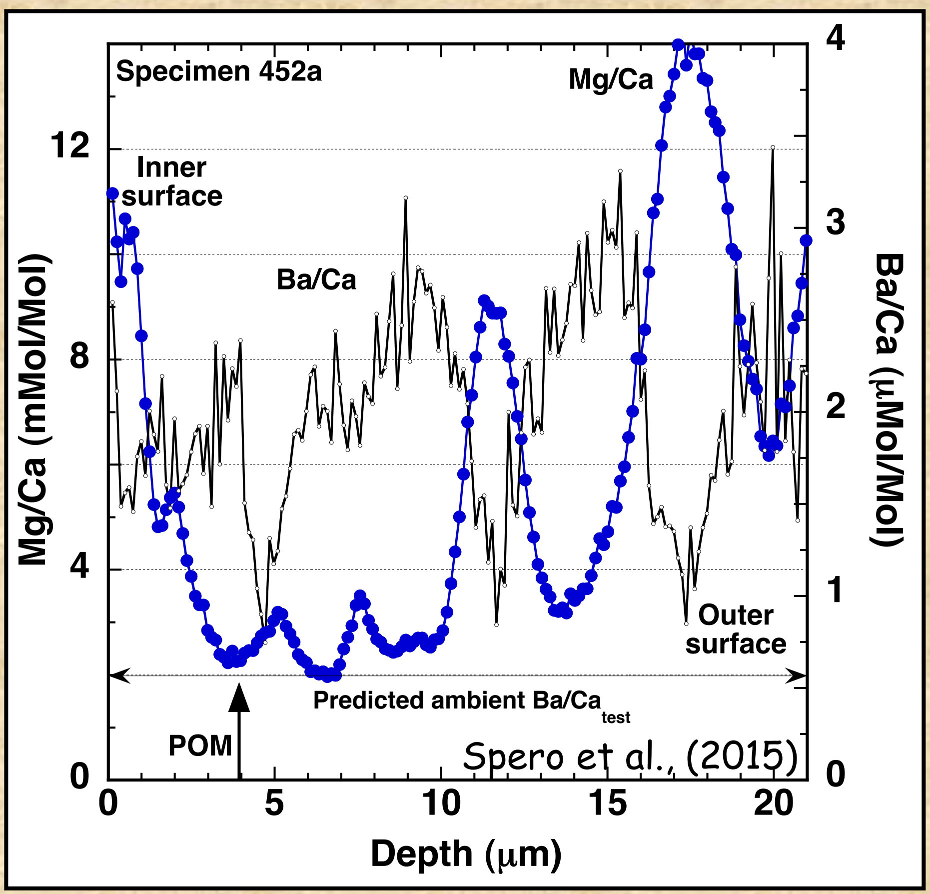
Ba/Ca is constant thru shell

Orbulina universa can be transferred between different culture jars that have normal or geochemically modified seawater to label calcite





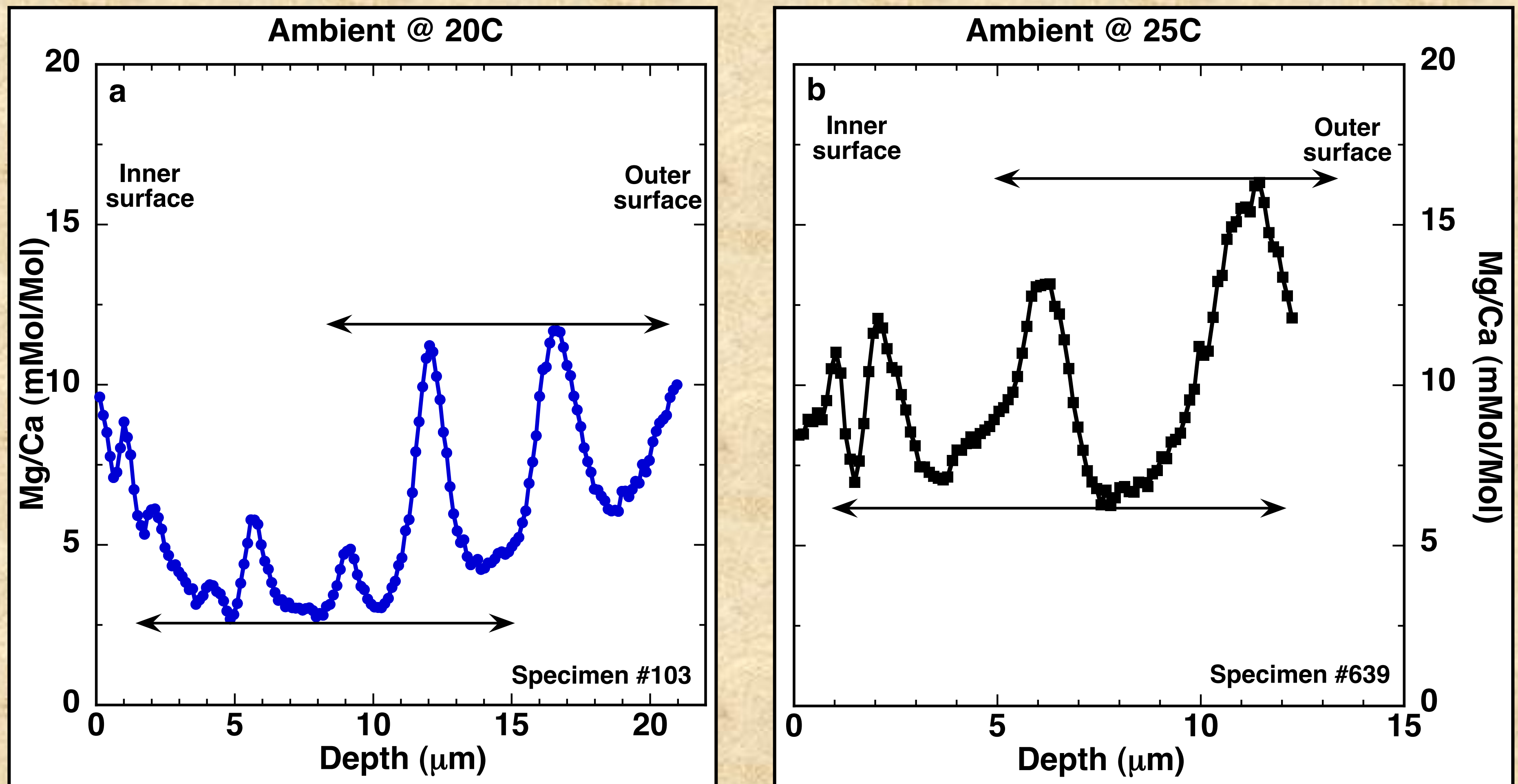
12h Day Ba - Spike



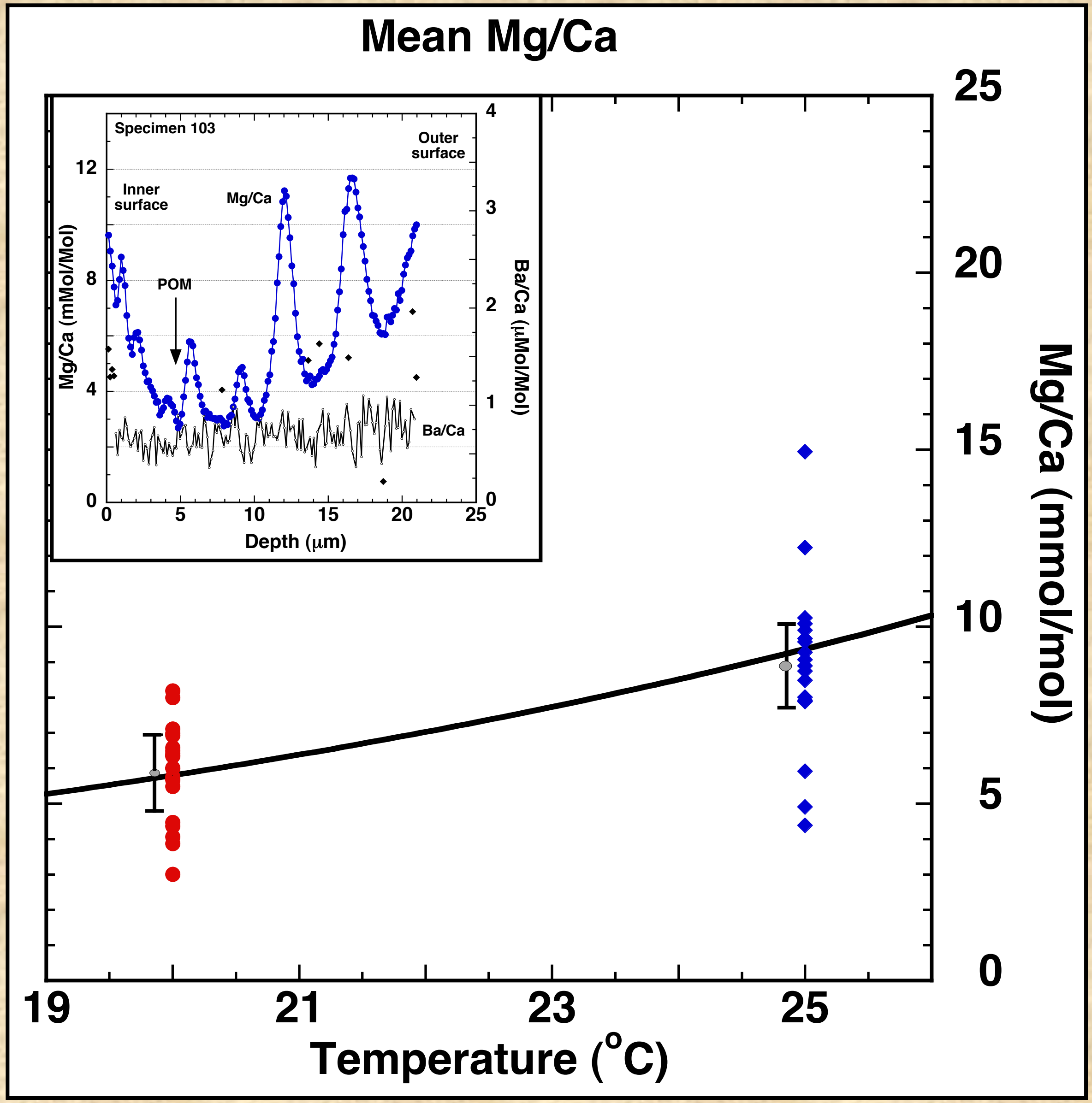
Low Mg/Ca bands are added during the day

Comparison of Mg/Ca ratios between 20C and 25C groups - T affects both day and night calcite

O. universa @ 20C　　　　O. universa @ 25C



Spero et al., (2015)



Calibration relationship of Russell et al (2004) with laser data

The really good news - Mg/Ca paleothermometry works well

Mg/Ca vs T based on LA -ICPMS and solution ICPMS agree well

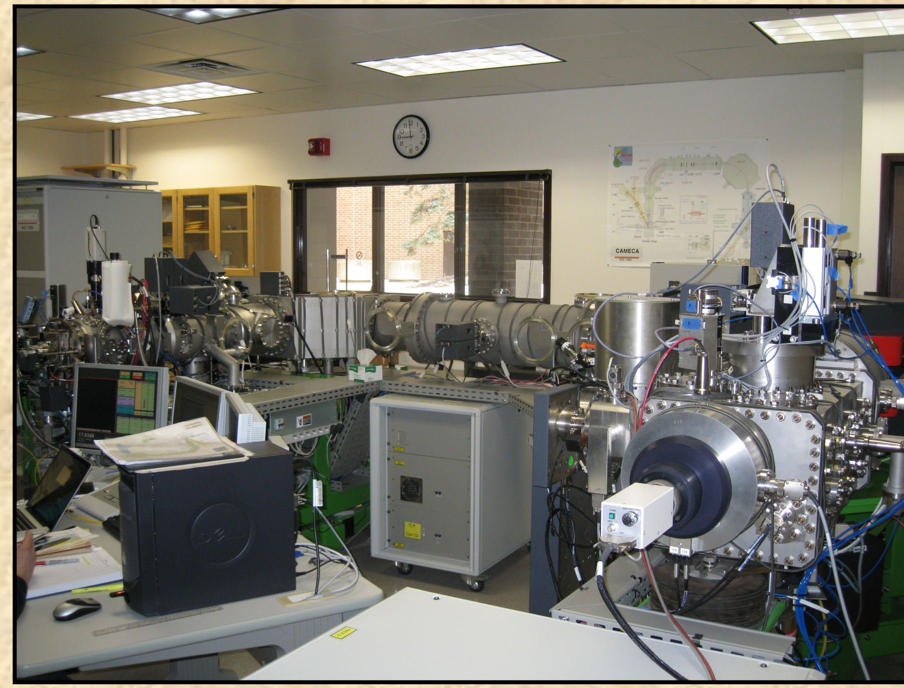
Intershell variability likely reflects # days shells calcified

Spero et al., (2015)

Combining SIMS and LA-ICPMS; pulse chase experiments with *Orbulina universa*

Resolving 12/24 hr intrashell calcite bands in an *O. universa* shell

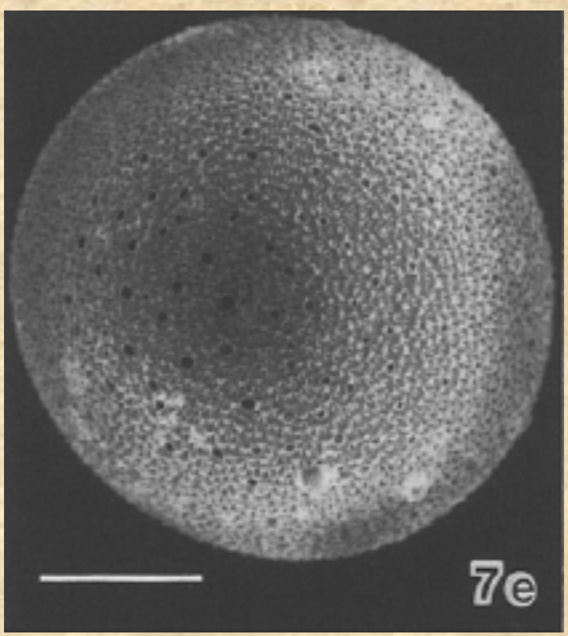
Spider Vetter, Claudia Mora and Reinhard Kozdon analyzing cultured foraminifera



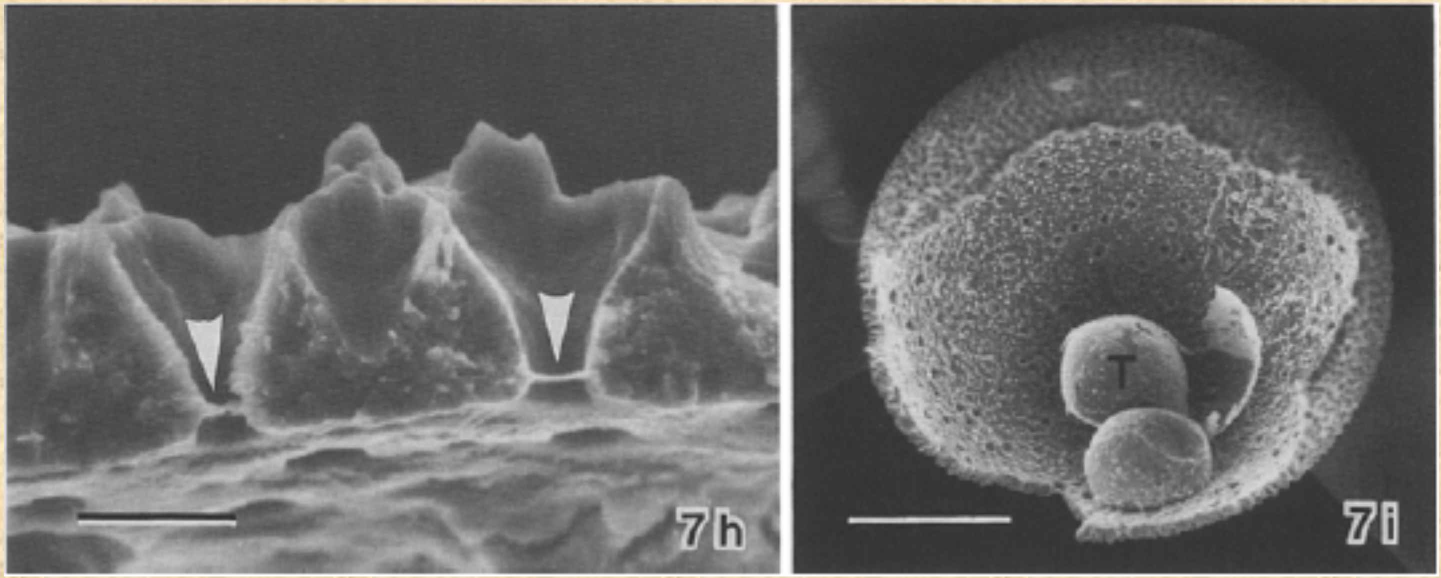
U. Wisconsin SIMS – Cameca 1280

Combining SIMS and LA-ICPMS; pulse chase experiments with *Orbulina universa*

- Culture *O. universa* in ambient & then labeled (Ba/Ca, ^{87}Sr, ^{13}C or ^{18}O-enriched) seawater
- Crack post-gam shells into fragments
- Analyze one fragment with LA-ICPMS, another using SIMS



Cross-section through *Orbulina universa* shell



(Spero 1988)

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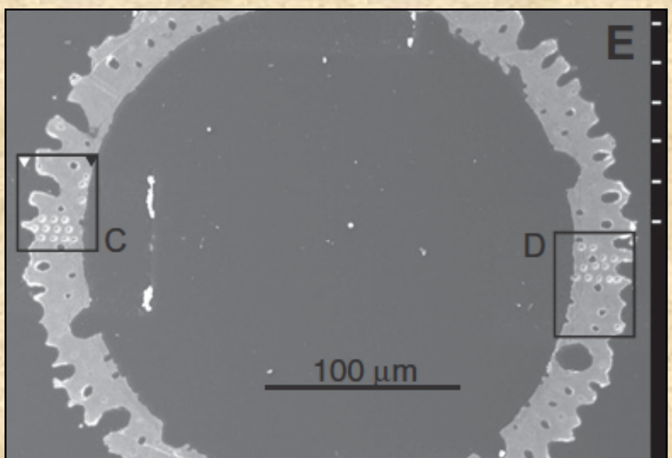
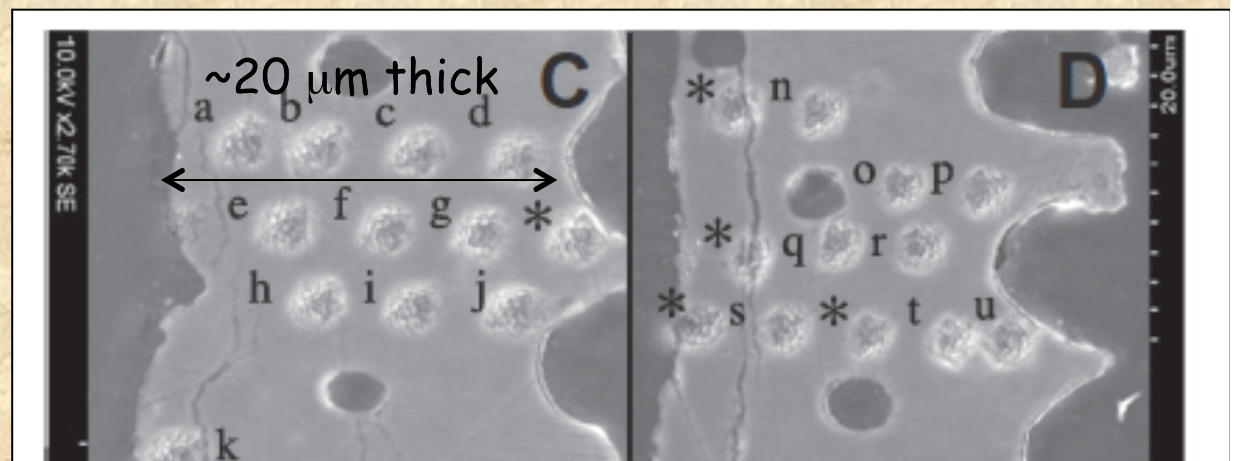
SciVerse ScienceDirect
Geochimica et Cosmochimica Acta 107 (2013) 267–278
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Micron-scale intrashell oxygen isotope variation in cultured planktic foraminifers

Lael Vetter[a,*], Reinhard Kozdon[b], Claudia I. Mora[c], Stephen M. Eggins[d], John W. Valley[b], Bärbel Hönisch[e], Howard J. Spero[a]

SIMS spots across *O. universa* chamber;
2x3 μm for $\delta^{18}O$



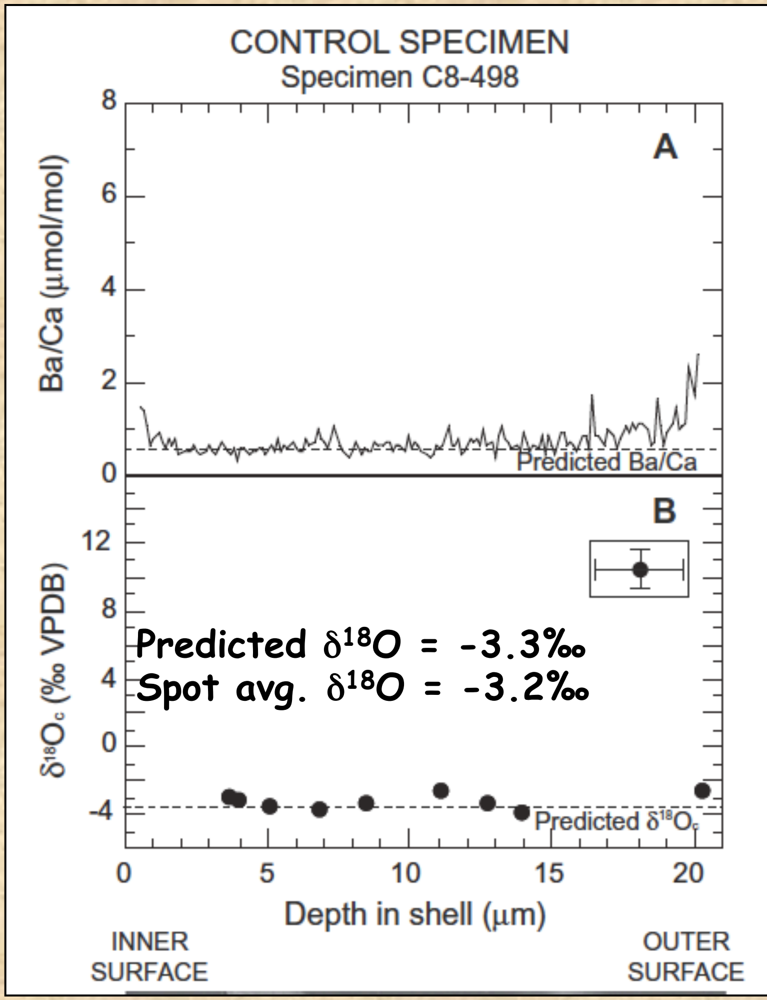


•2σ individual spot s.d. (all runs) ranges between ±0.3-1.1‰

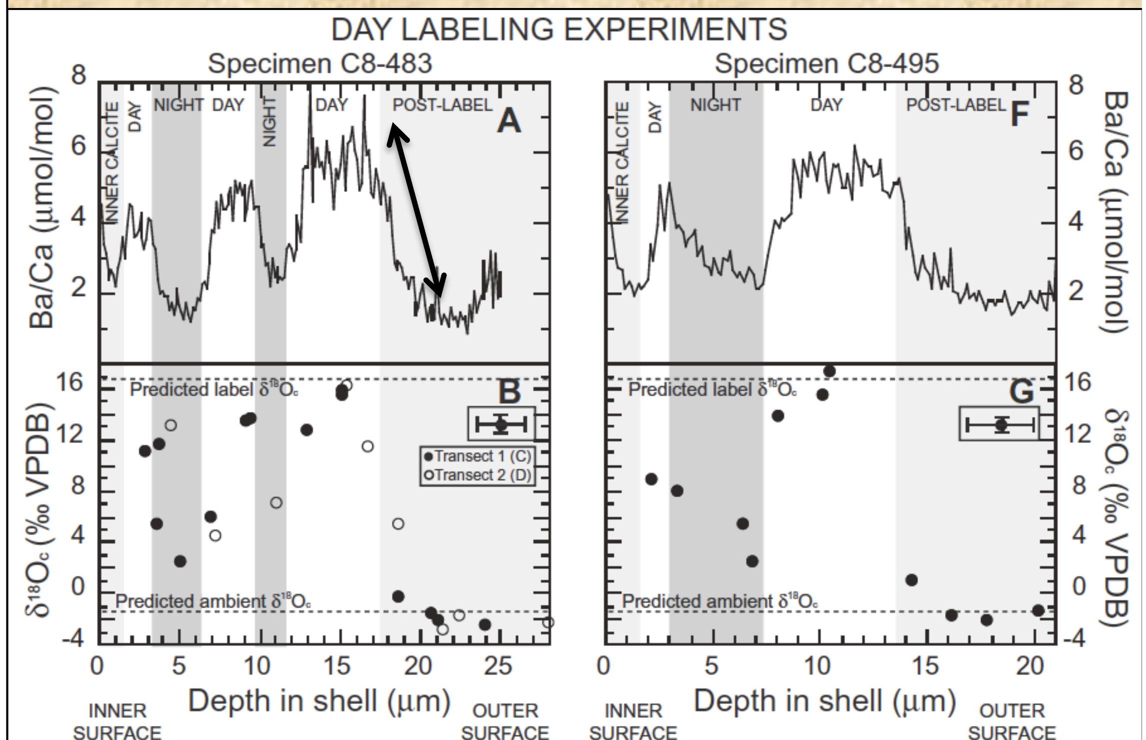
•2σ experiment s.e. = ±0.4‰ (n=9)

Full $\delta^{18}O_c$ shift is recorded across 2-3 μm of calcite!

Multiple spots are needed to obtain statistically relevant averages



Predicted $\delta^{18}O$ = -3.3‰
Spot avg. $\delta^{18}O$ = -3.2‰



(Vetter et al., 2013)

Available online at www.sciencedirect.com
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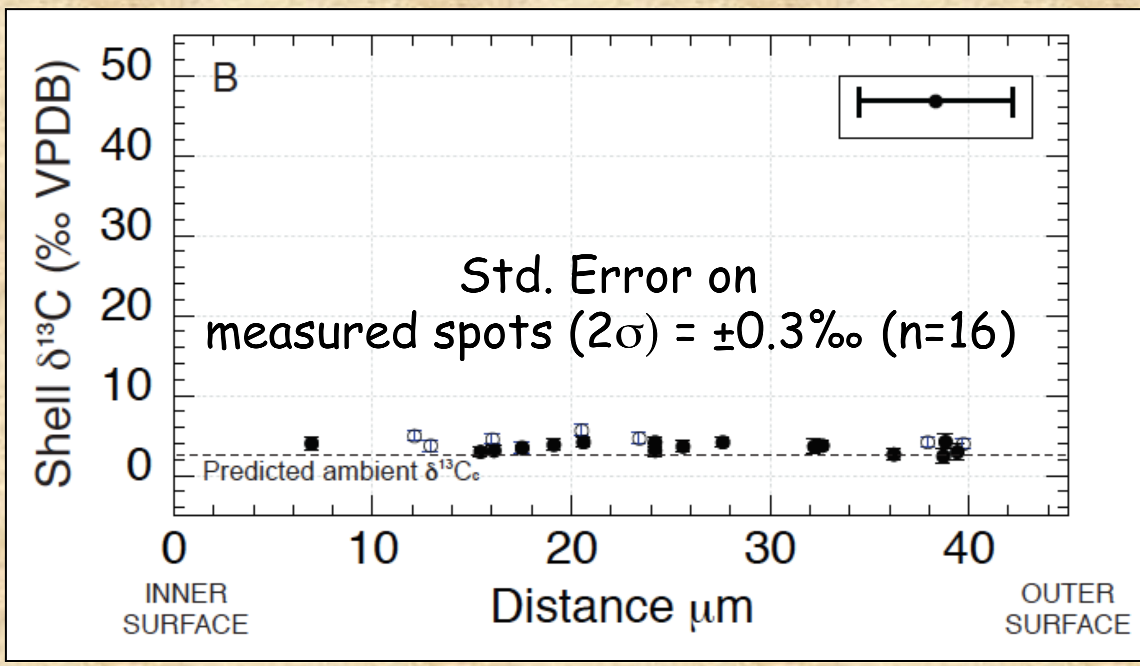
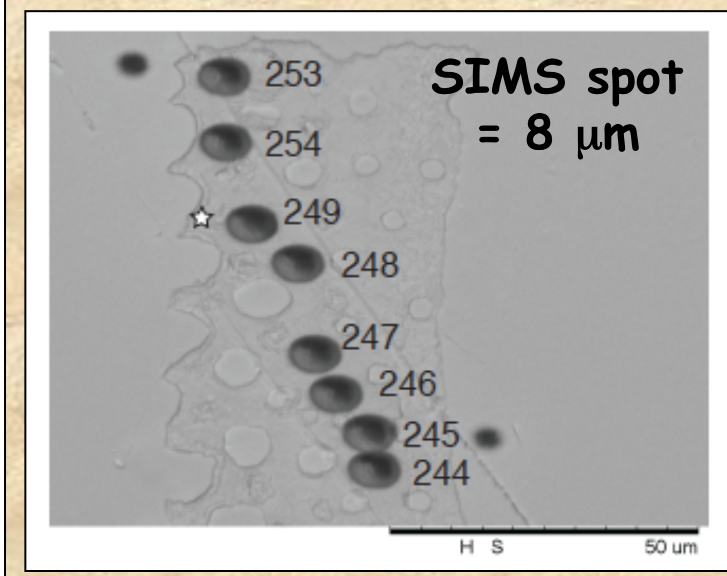
Geochimica et Cosmochimica Acta 139 (2014) 527–539
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

SIMS measurements of intrashell $\delta^{13}C$ in the cultured planktic foraminifer *Orbulina universa*

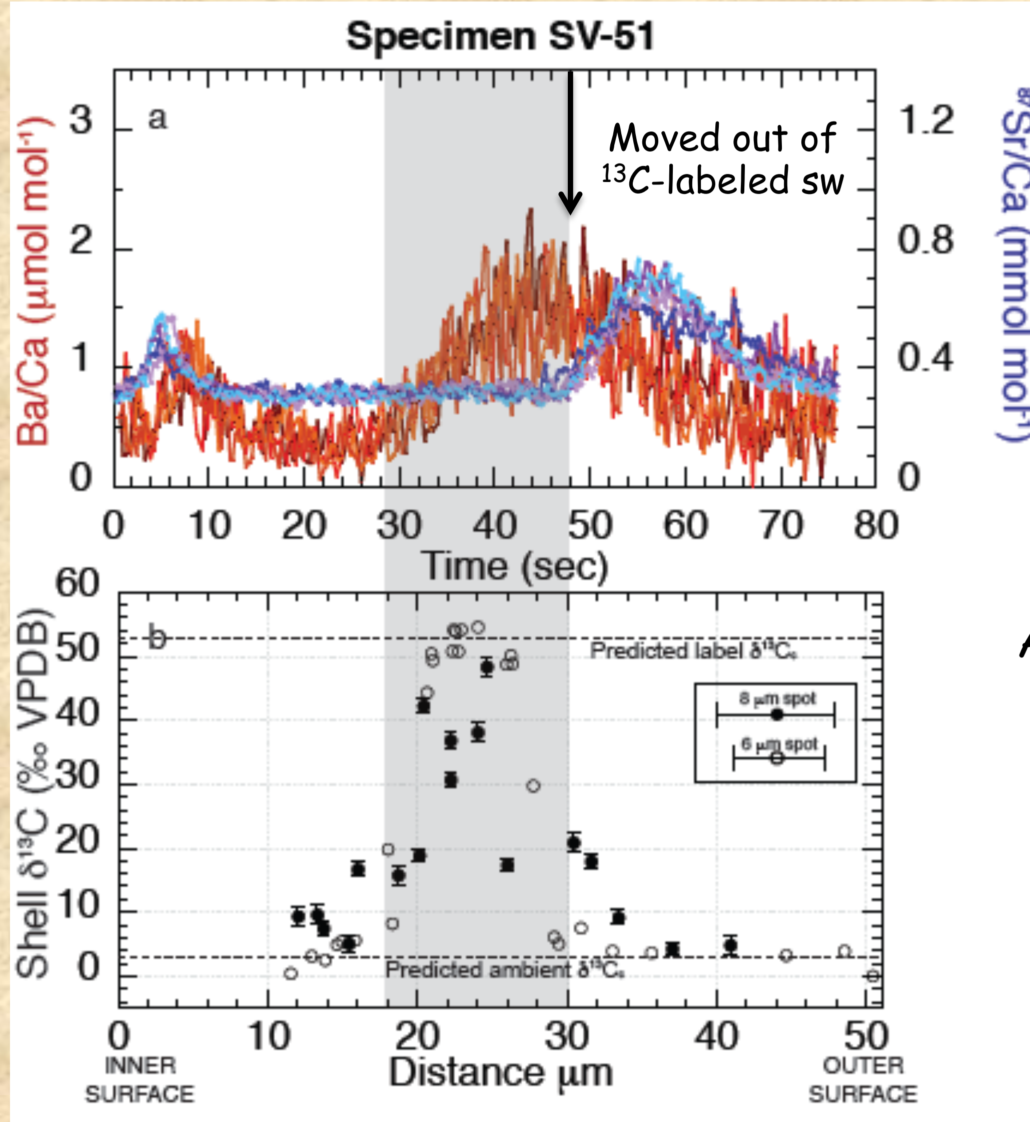
Lael Vetter [a,*], Reinhard Kozdon [b], John W. Valley [b], Claudia I. Mora [c], Howard J. Spero [a]





Vetter et al (2014)

6 μm SIMS spot recovers the predicted range (+3.2 to +51.8‰) of $\delta^{13}C$ values. 24 hr band width estimated to be 4-5 μm.



Vetter et al. (2014)

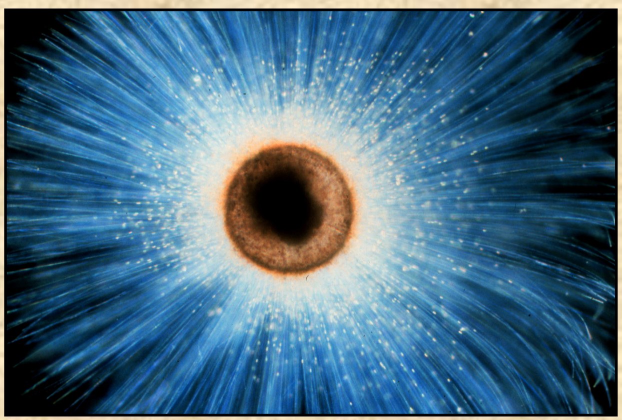
LA-ICPMS used to identify Ba and ^{87}Sr tracers added to seawater to constrain calcite with ^{13}C spike

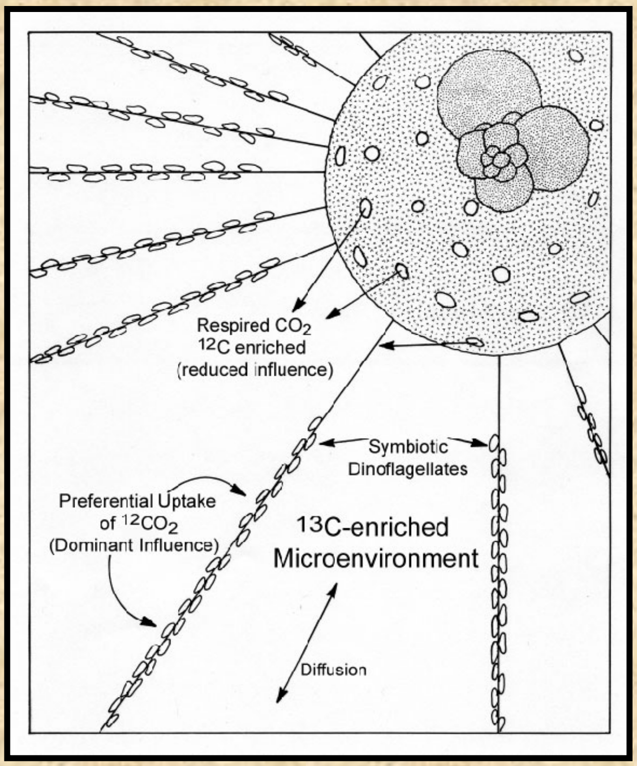
Avg $\delta^{13}C$ = 51.5‰ ±1.4‰ 2σ s.e. (n=11)

Closed symbols – 8 μm spot
Open symbols – 6 μm spot

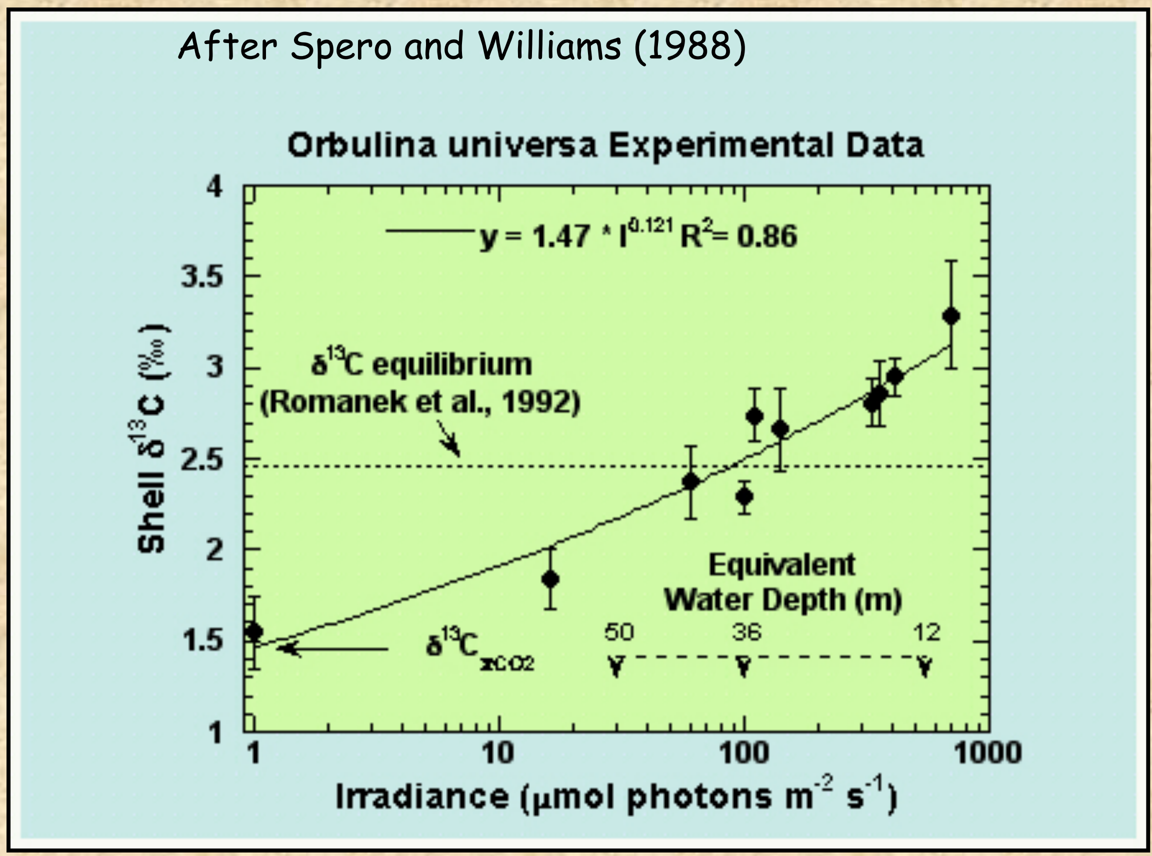
Avg $\delta^{13}C$ = 3.7‰ ±0.2‰ 2σ s.e. (n=4)

The symbiotic system plays a major role in controlling shell geochemistry - effect of light on shell $\delta^{13}C$





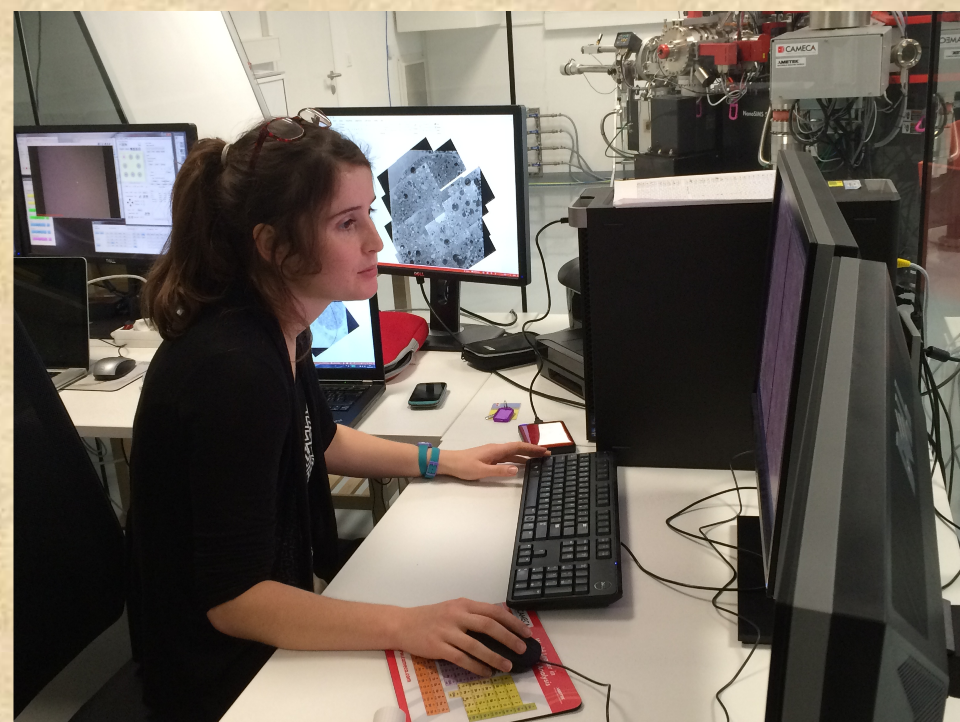
Spero and DeNiro, 1987



Exploring carbon flow through a symbiont system using ^{13}C and TEM/ NanoSIMS

Charlotte LeKieffre and Anders Meibom
Univ. Lausanne, Switzerland

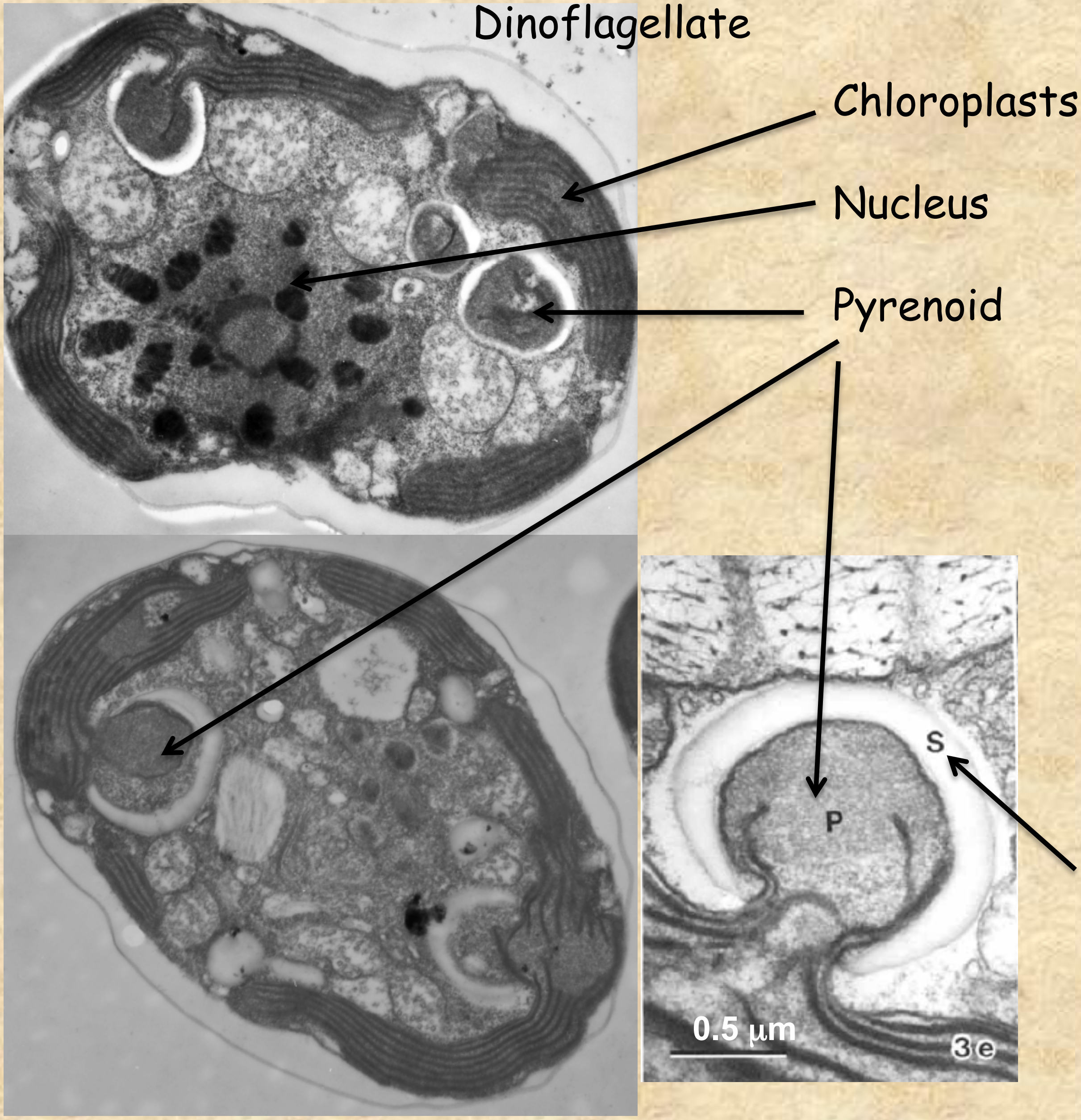
Charlotte LeKieffre on NanoSIMS 50L



Diurnal rhythm in a symbiotic planktonic foraminifera

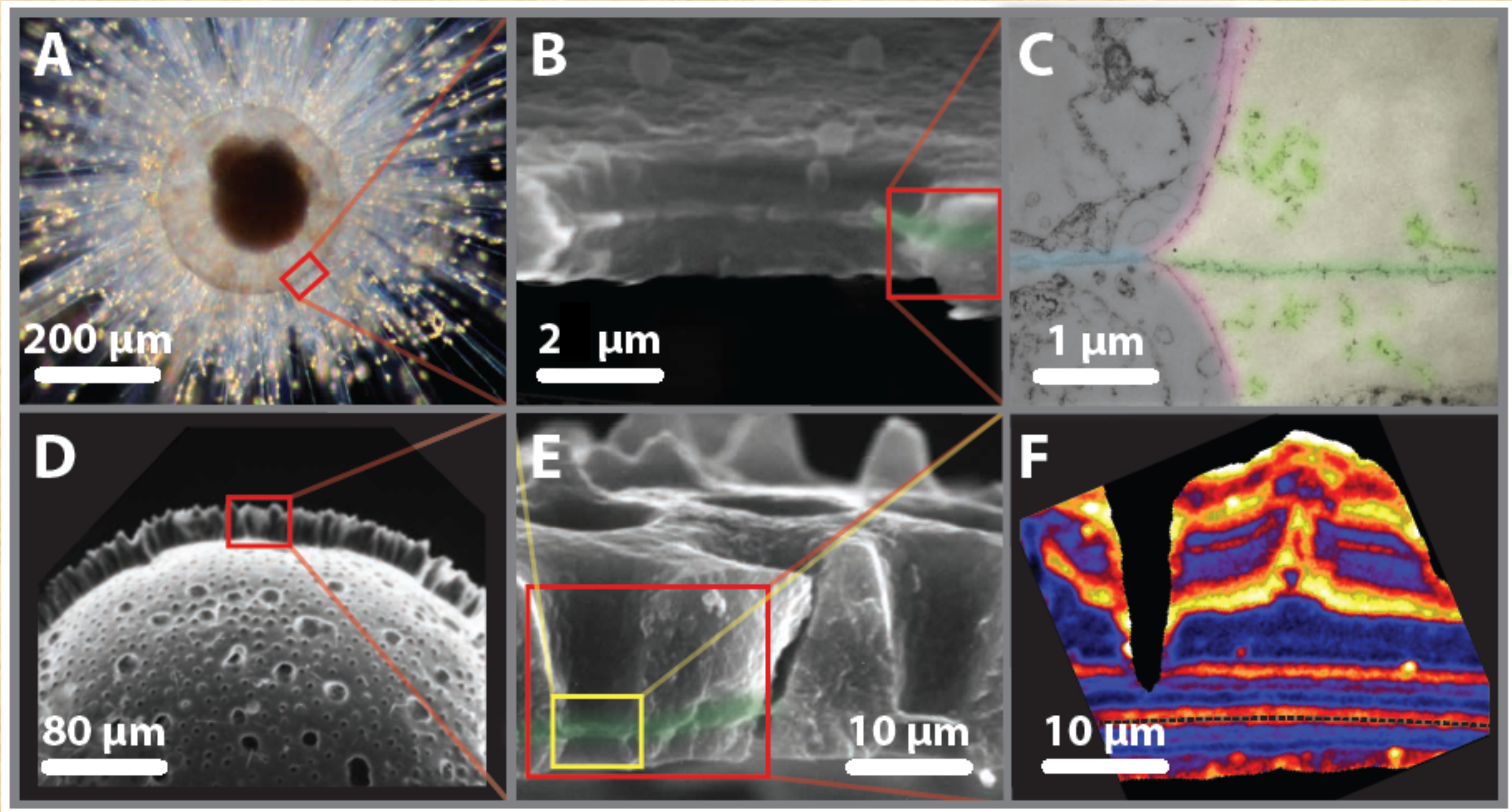
Symbionts migrate into vacuoles in foraminifera at night and move on to spines during the day

Combining TEM and NanoSIMS to explore symbiont to host carbon update and translocation

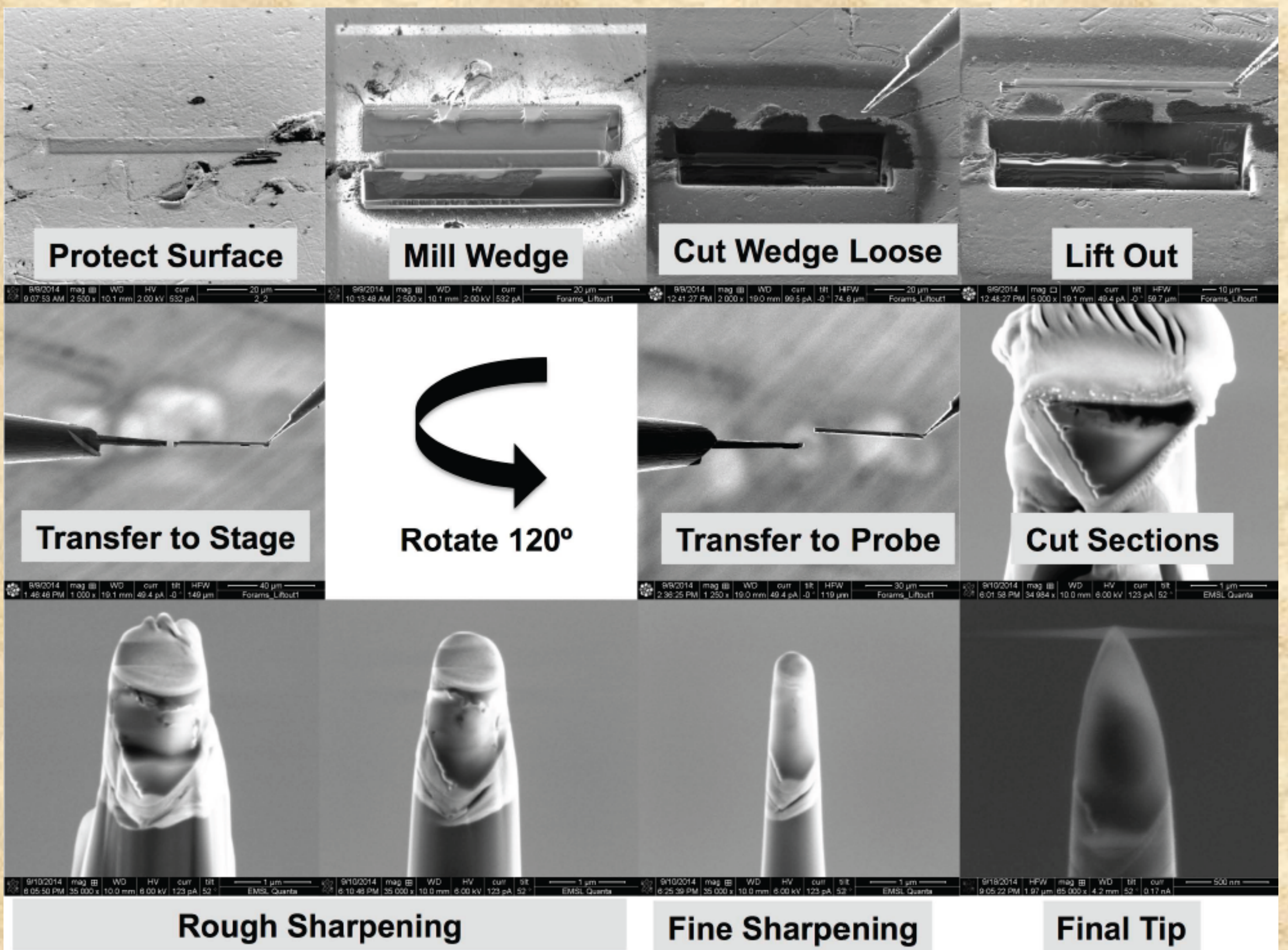


Exploring The Chemistry of a Bio-Mineral Interface with Atom Probe Tomography

Oscar Branson, Daniel Perea, Howard J Spero, Maria Winters, Alexander C Gagnon



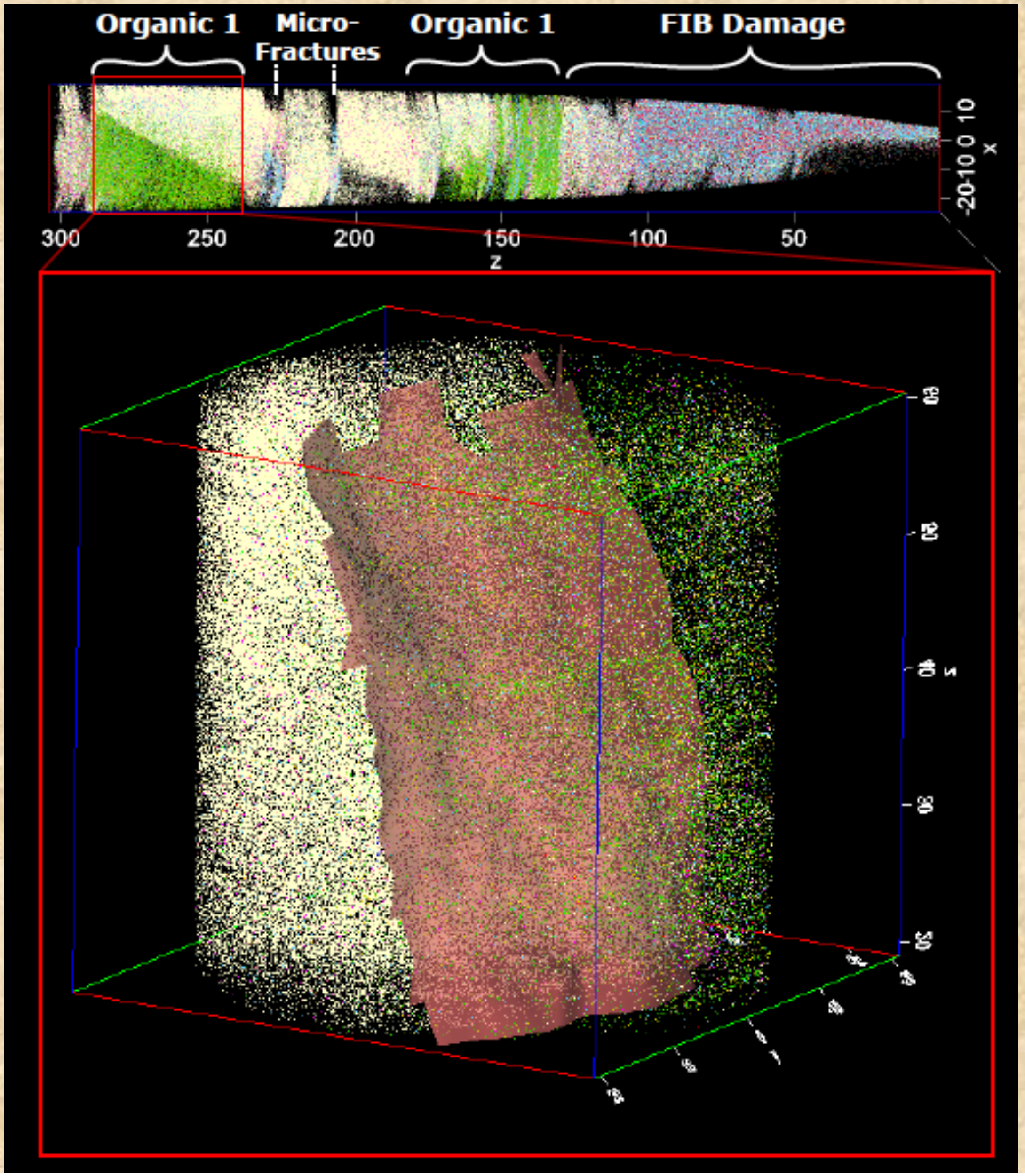
Extracting a shell wall sample with a focused ion beam (FIB)



Branson, et al. (manuscript in prep)

Point cloud data using a Cameca Local Electron Atom Probe (LEAP) 4000

Organic/mineral interface



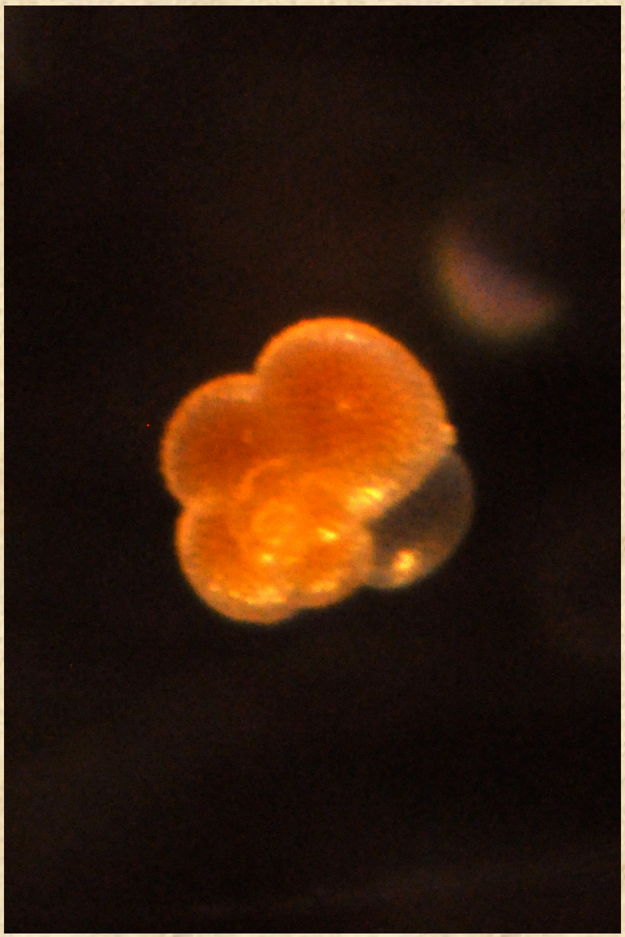
Choosing the right chamber/shell region for analysis is important for paleoceangraphic reconstructions

Intratest oxygen isotope variability in the planktonic foraminifer *N. pachyderma*: Real vs. apparent vital effects by ion microprobe

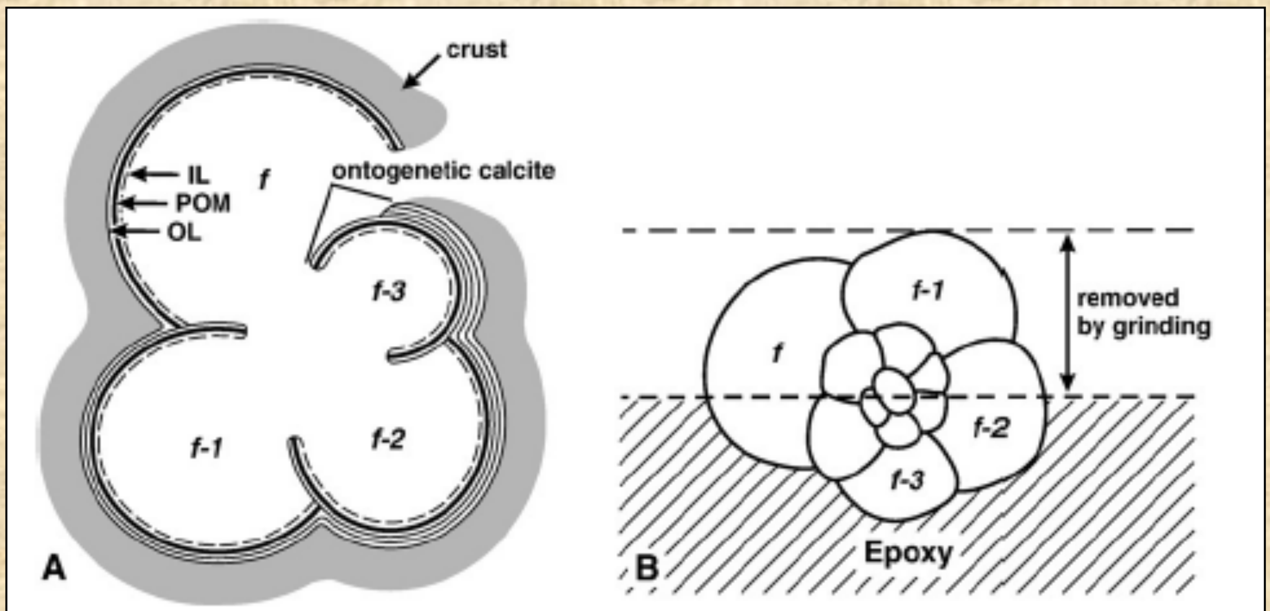
Chemical Geology 258 (2009) 327–337

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

Department of Geology & Geophysics, University of Wisconsin-Madison, 1215 W Dayton St., Madison, WI 53706, USA



N. pachyderma – non-spinose & adds calcite crust at end of its lifecycle



The Paleoclimate Frontier…..

- New instrumentation/applications are ushering in the next growth phase in paleoceanography and paleoclimatology
- Techniques such as LA-ICP-MS, SIMS and NanoSIMS, TEM, APT are mutually compatible and offer a view of spatial variation in materials that has not been previously possible.
- **BUT**….. SIMS, NanoSIMS, LA-ICP-MS are the *wrong* tools for >90% of our questions!
- **HOWEVER**……they are the tools that will likely yield many of the breakthrough discoveries over the next decade. *So pick your problems and tools carefully.*