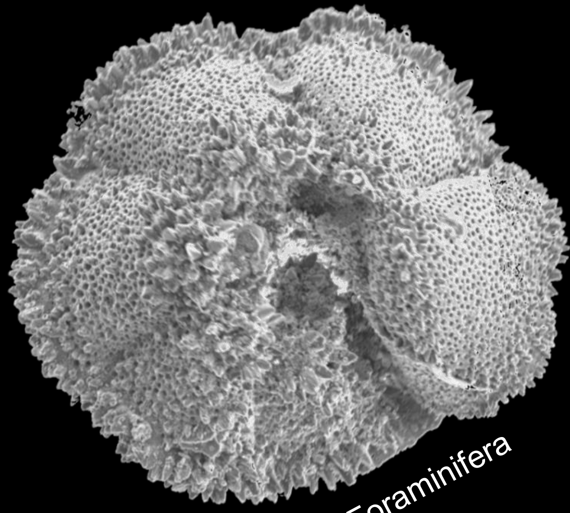
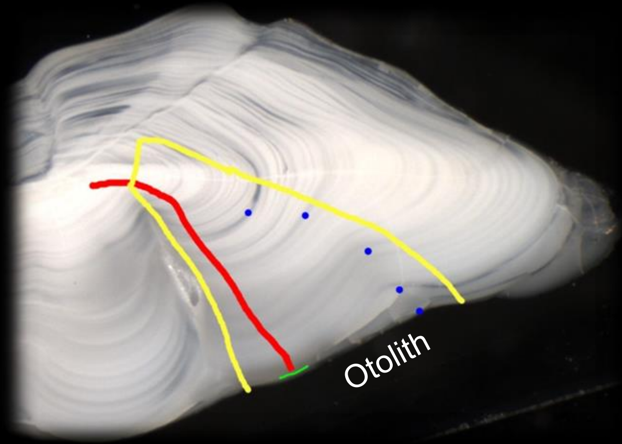
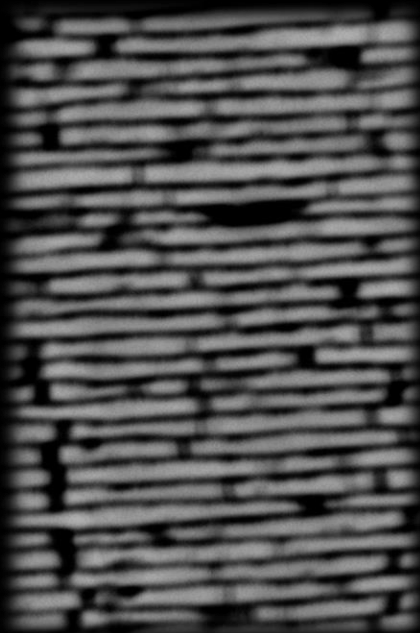
Carbon and Oxygen Isotope Analyses in Biocarbonates by SIMS

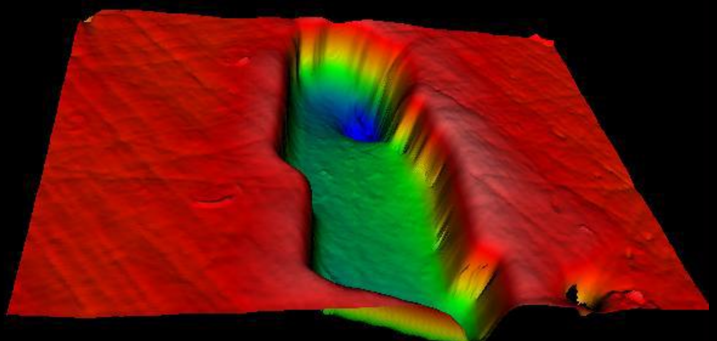




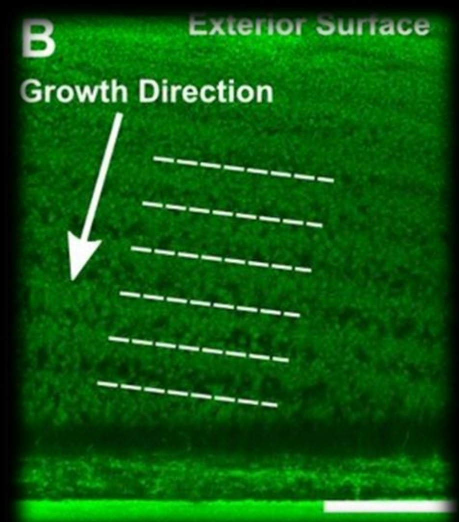
Nacre



5 µm



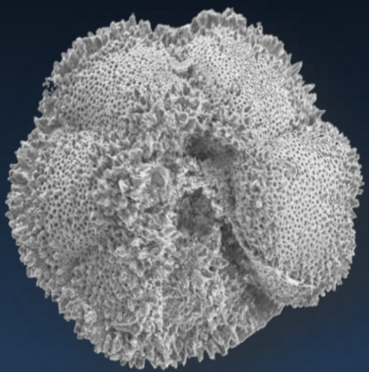
3D image of polished otolith



Confocal Laser Fluorescent Microscopy
Image of a Nautilus shell cross section

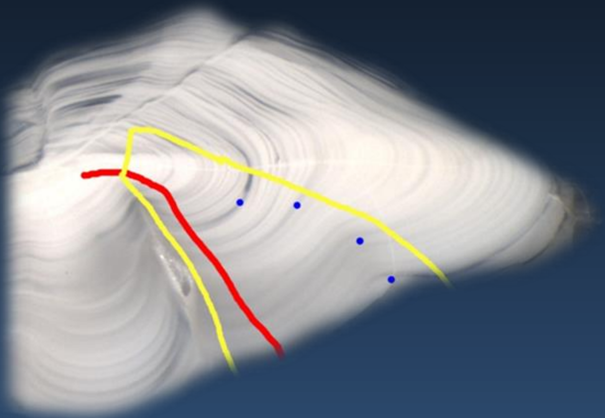
Reinhard Kozdon
Ian J. Orland, Noriko T. Kita, John W. Valley

$\delta^{18}O$ and $\delta^{13}C$ in biocarbonates by SIMS

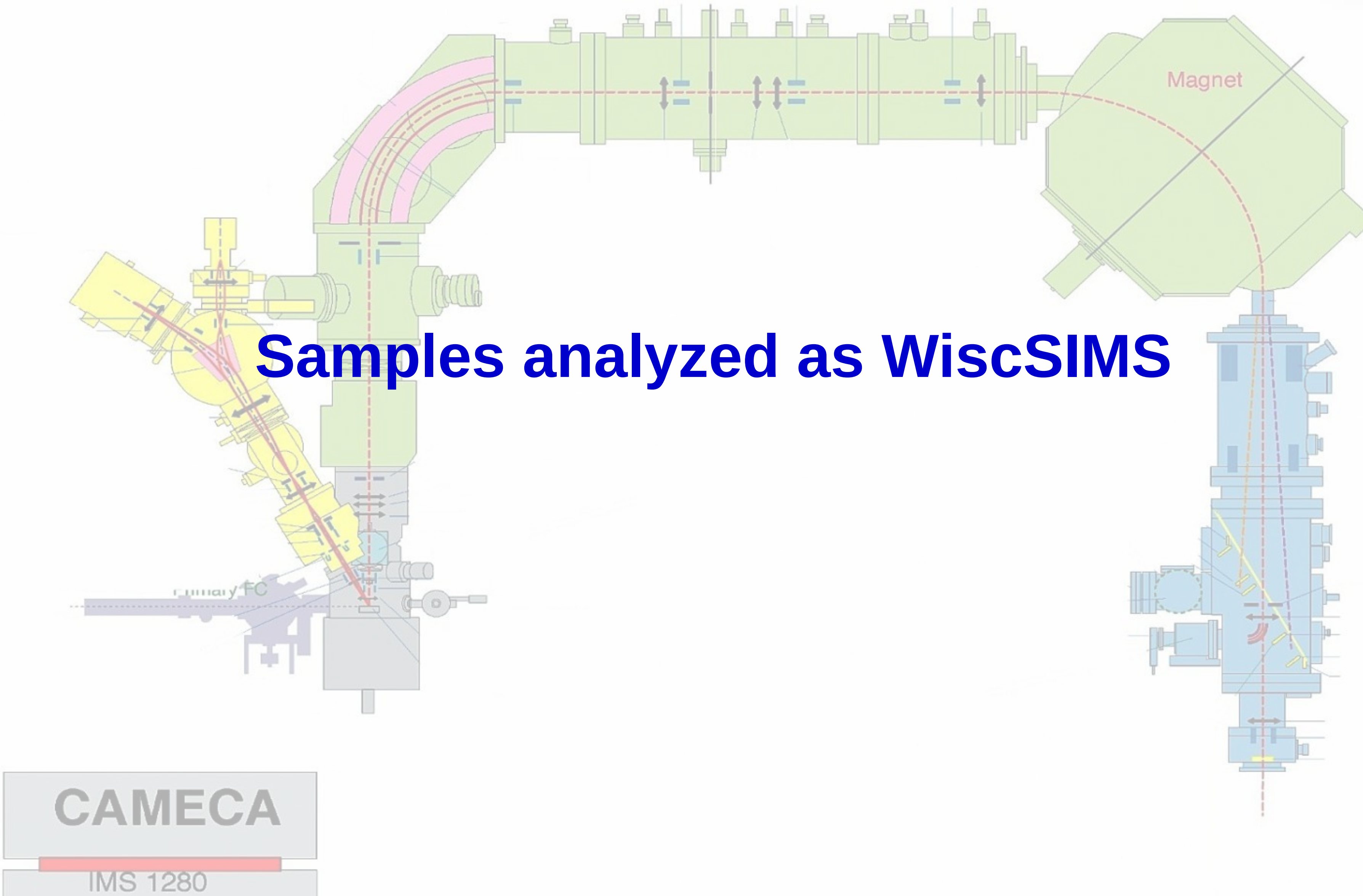


Carbonate samples analyzed at WiscSIMS:

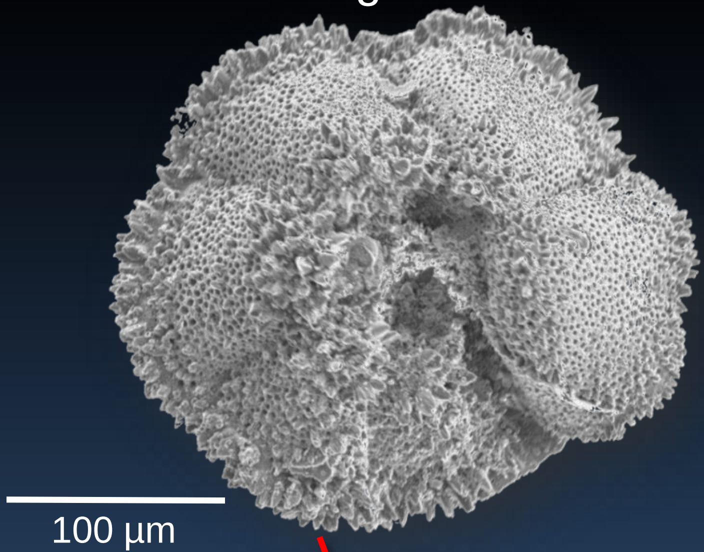
- foraminiferal shells
- speleothems
- nautilus shells
- mollusk shells
- fish otoliths
- corals

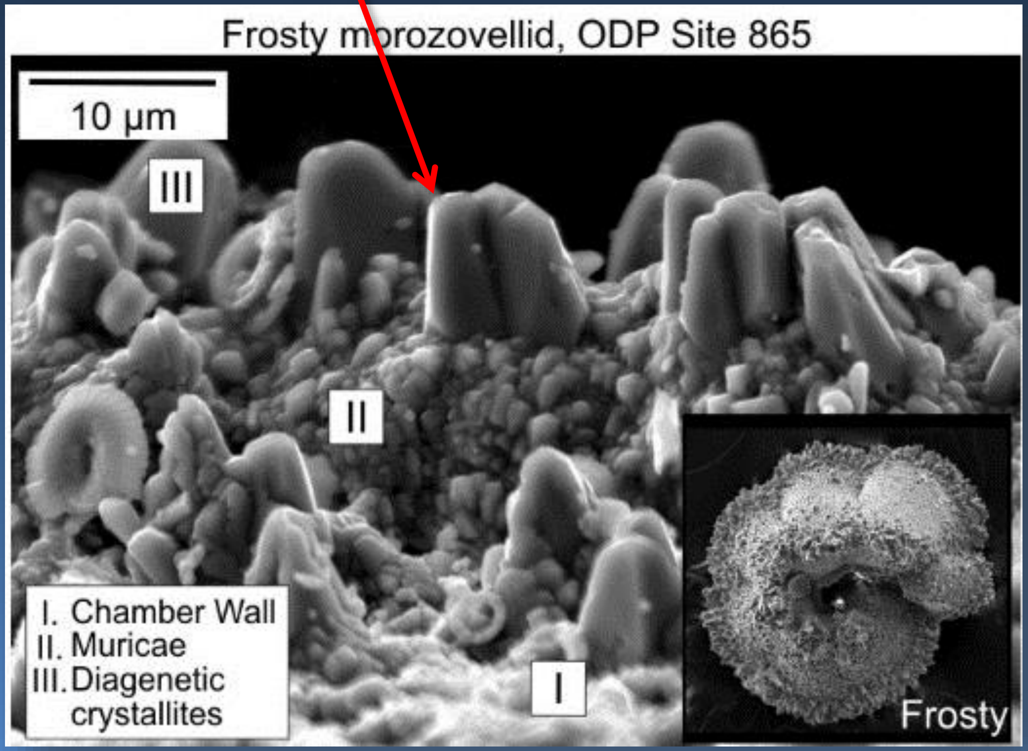


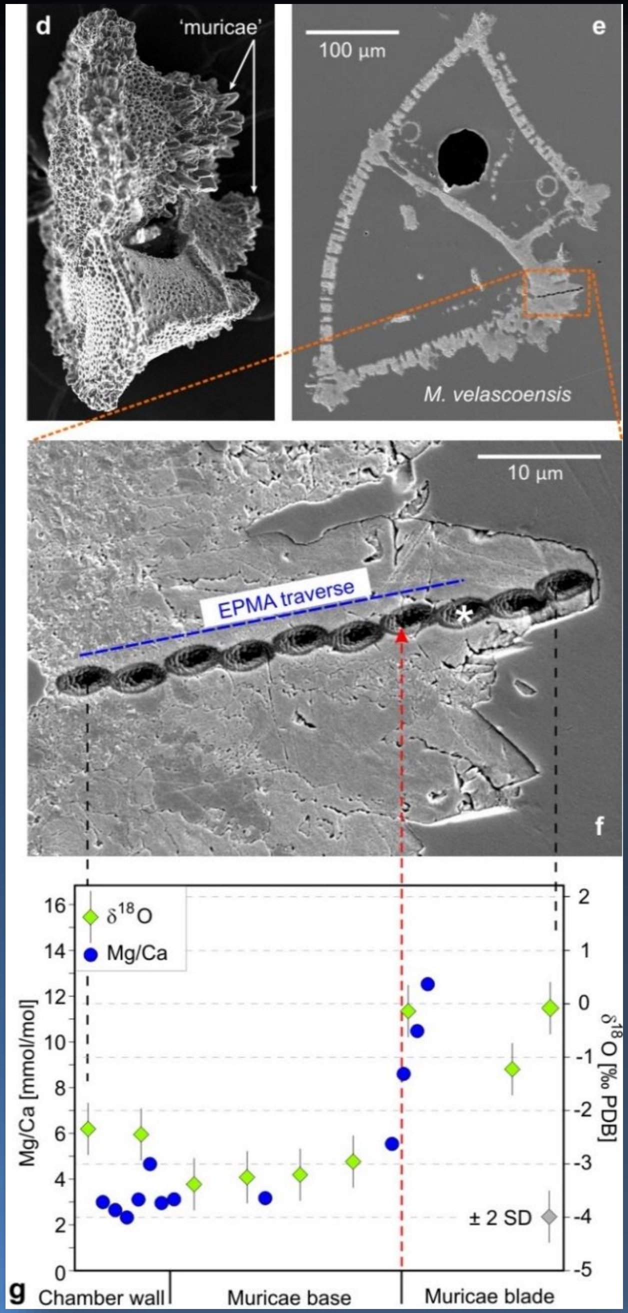
Samples analyzed as WiscSIMS



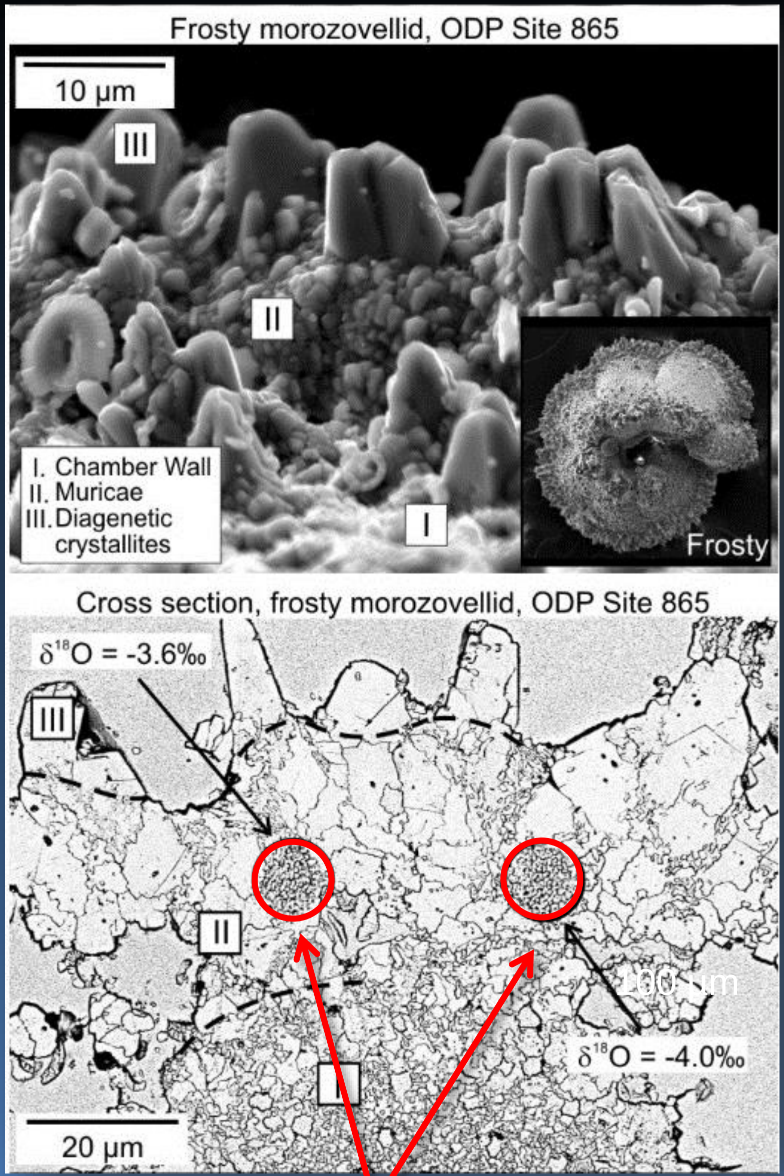
Identification of diagenetic calcite in foraminiferal shells – reassessment of paleorecords

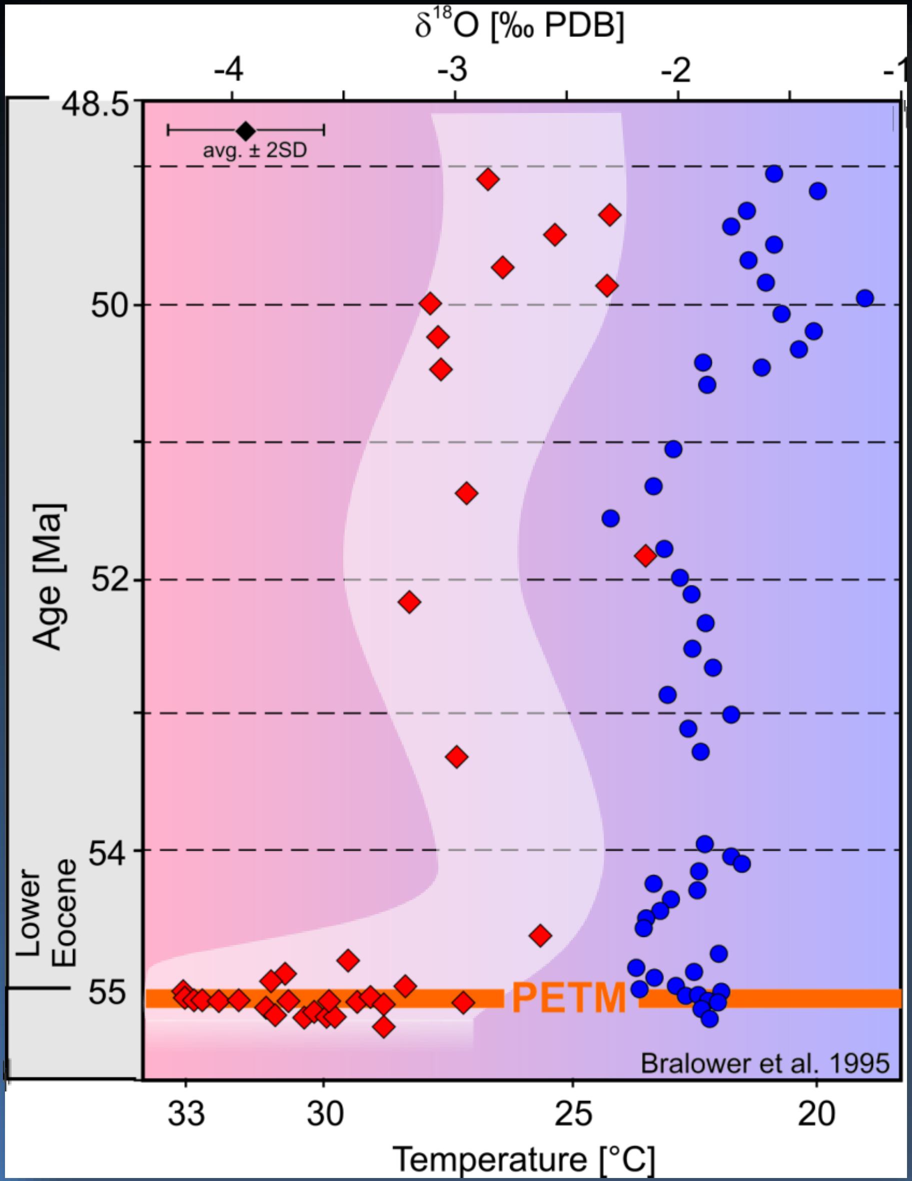






Identification of diagenetic calcite in foraminiferal shells – reassessment of paleorecords

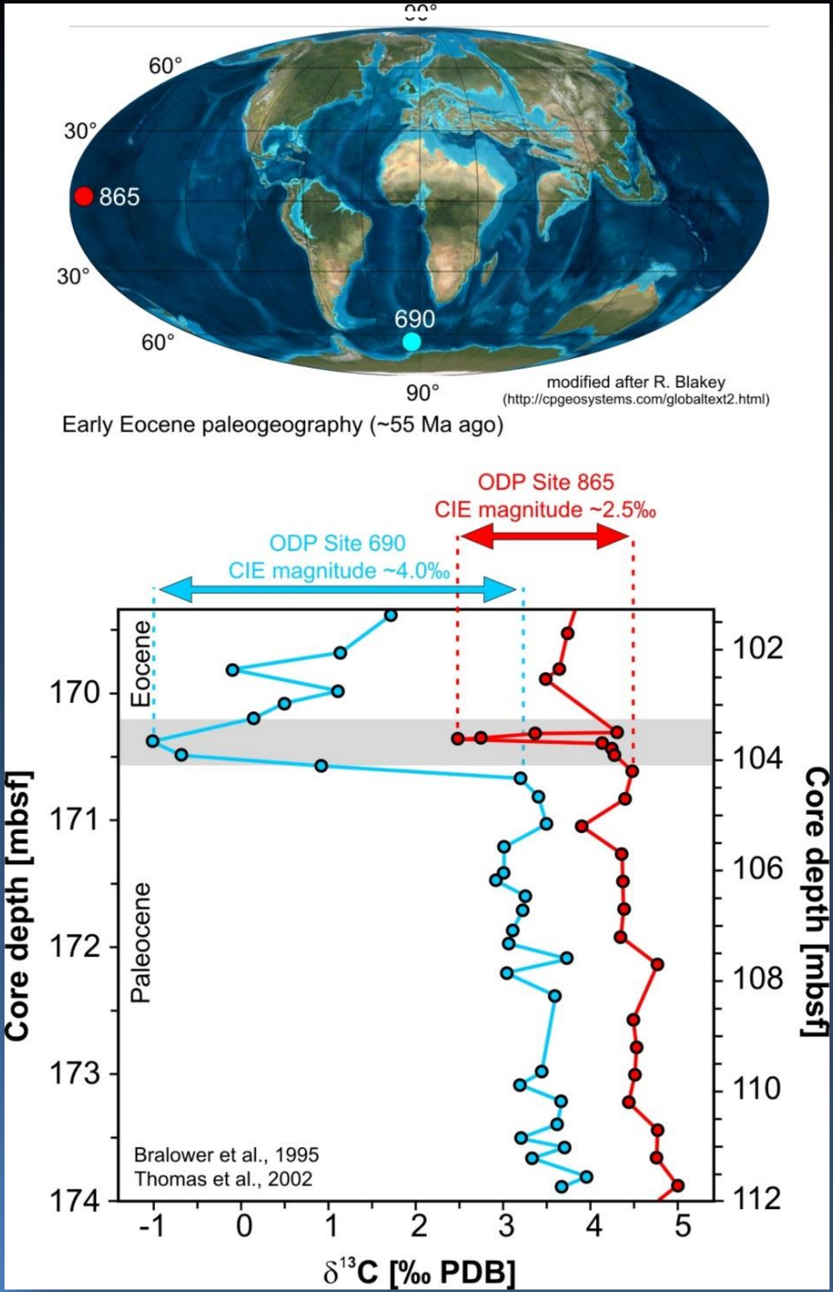


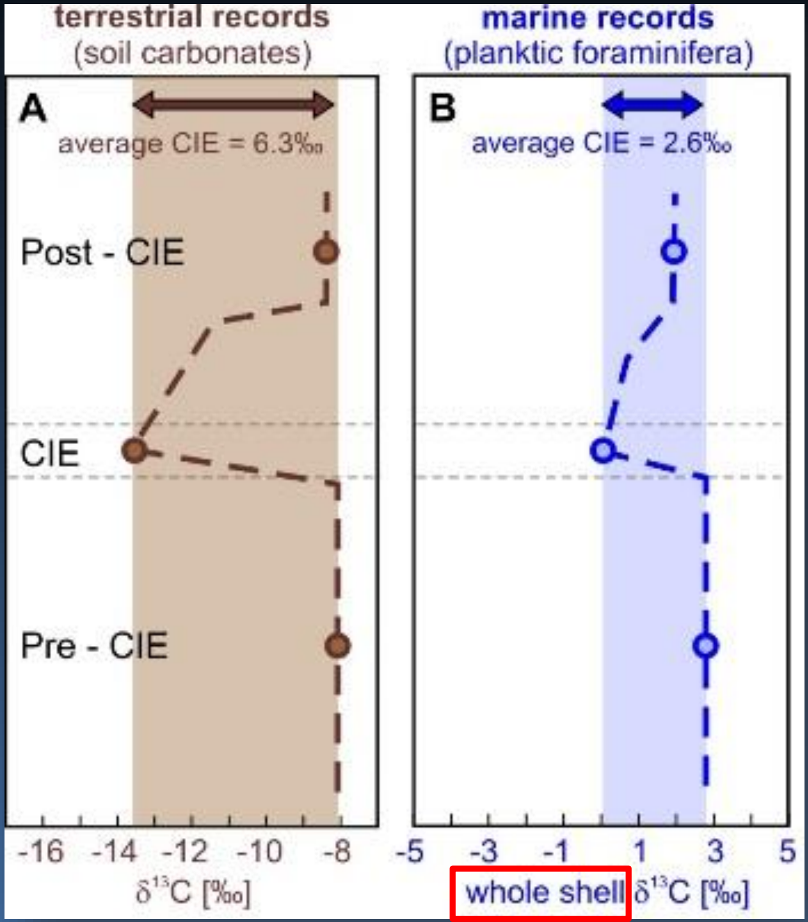


Kozdon et al. 2011

$\delta^{18}O$ measurements by SIMS in **alteration-resistant** domains

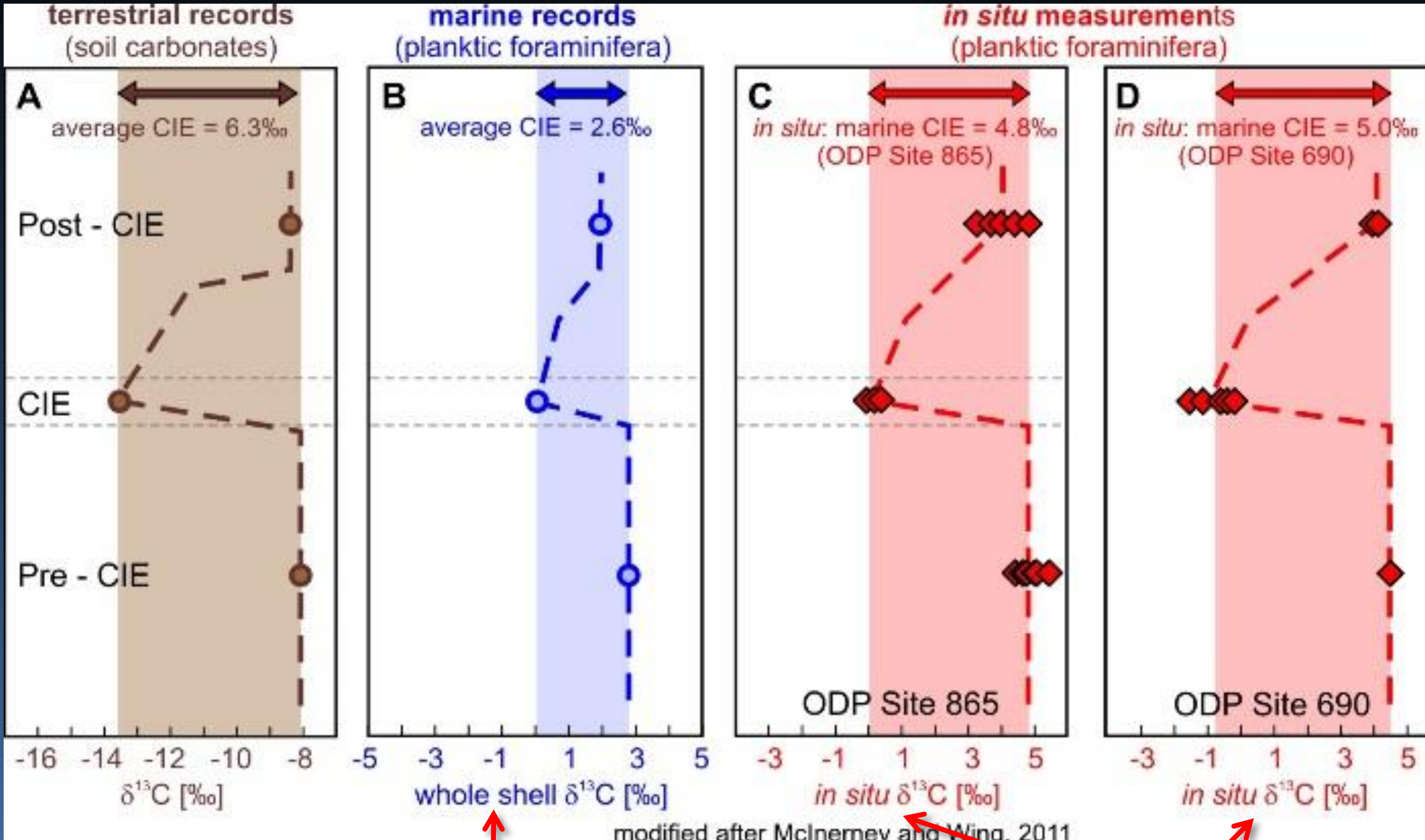
Magnitude of the Carbon Isotope Excursion (CIE) in the marine record





Modified after McInerney and Wing, 2012

Magnitude of the Carbon Isotope Excursion (CIE) in the marine record

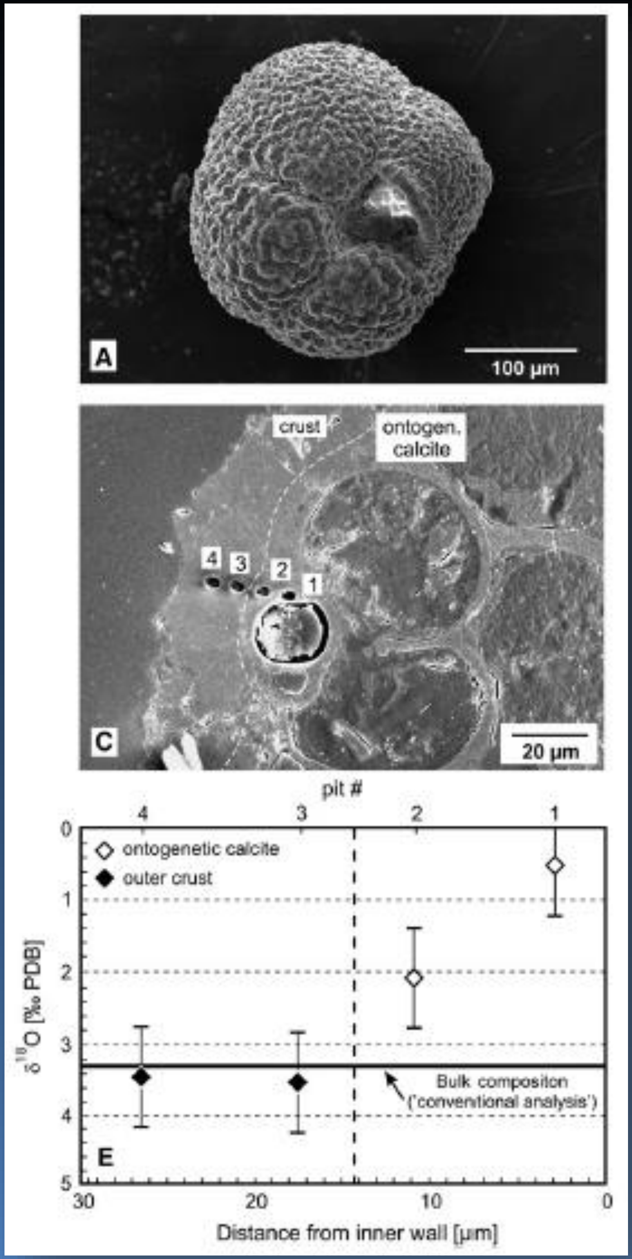


Kozdon et al., in prep.

whole shells

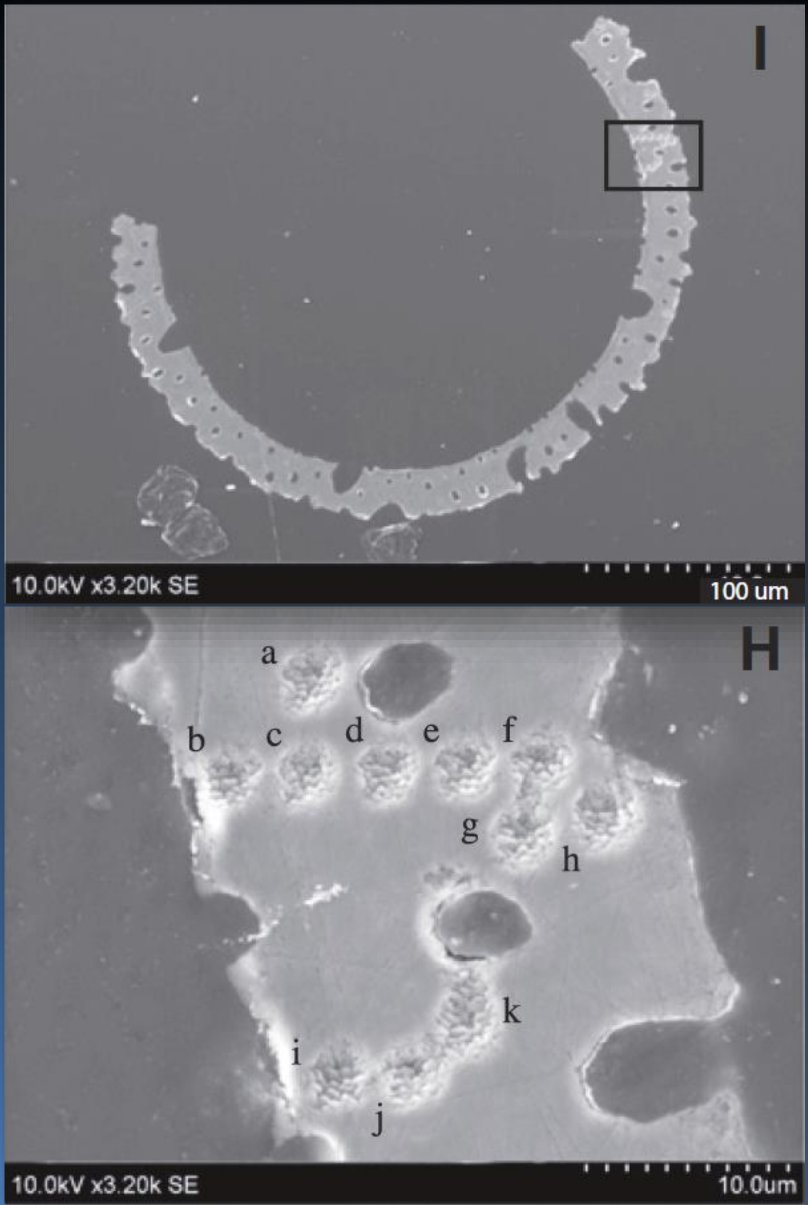
$\delta^{13}C$ measurements by SIMS in alteration-resistant domains

Intrashell $\delta^{18}O$ variability in foraminiferal shells

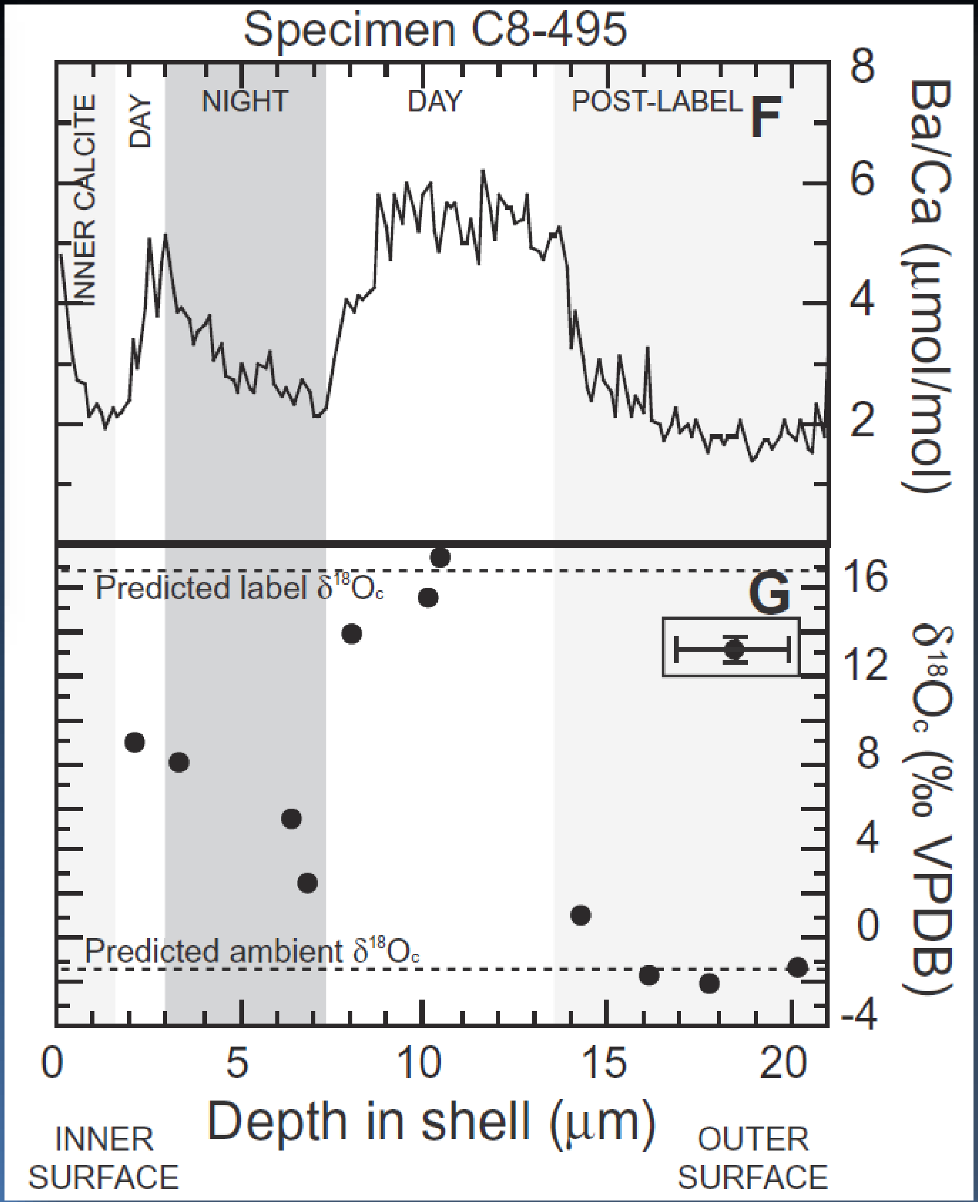


Kozdon et al., 2009

Measurements of **daily growth increments** in foraminiferal shells



Vetter et al. 2013

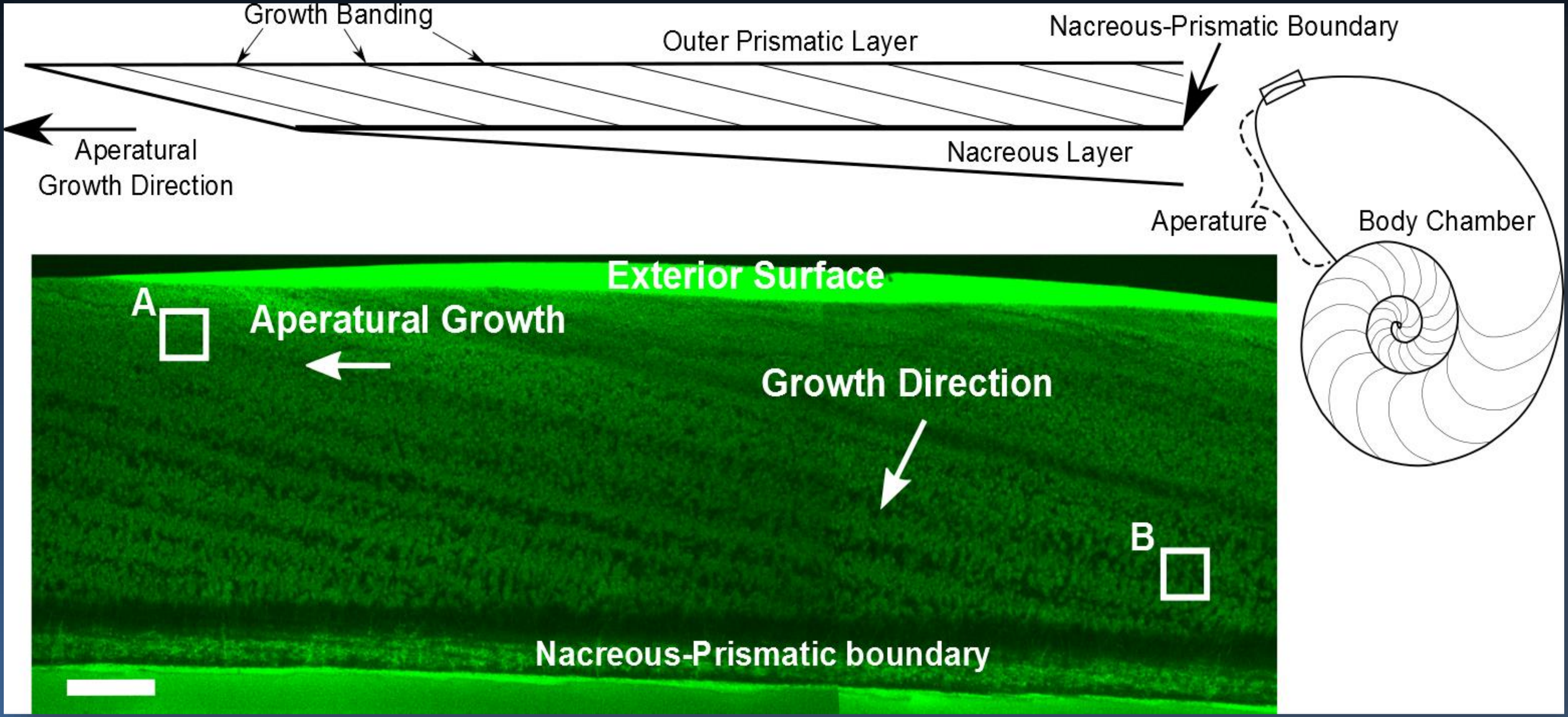


Vetter et al. 2013

Nautilus macromphalus

Wild-caught Nautilus macromphalus
from New Caledonia

Nautilus shell

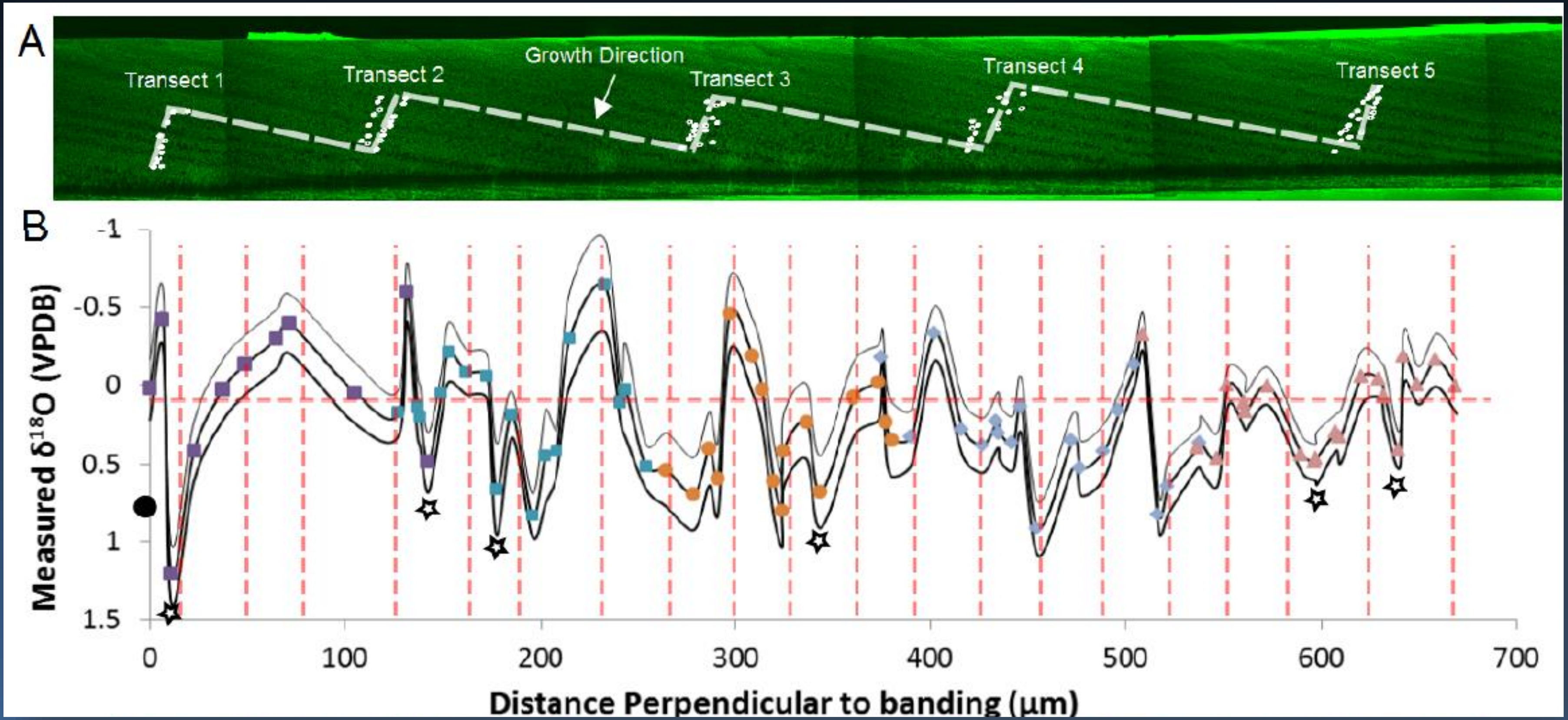


confocal laser fluorescence microscopy

Linzmeier et al., in prep.

Nautilus shell

One half centimeter (~20 days of growth) of Nautilus shell



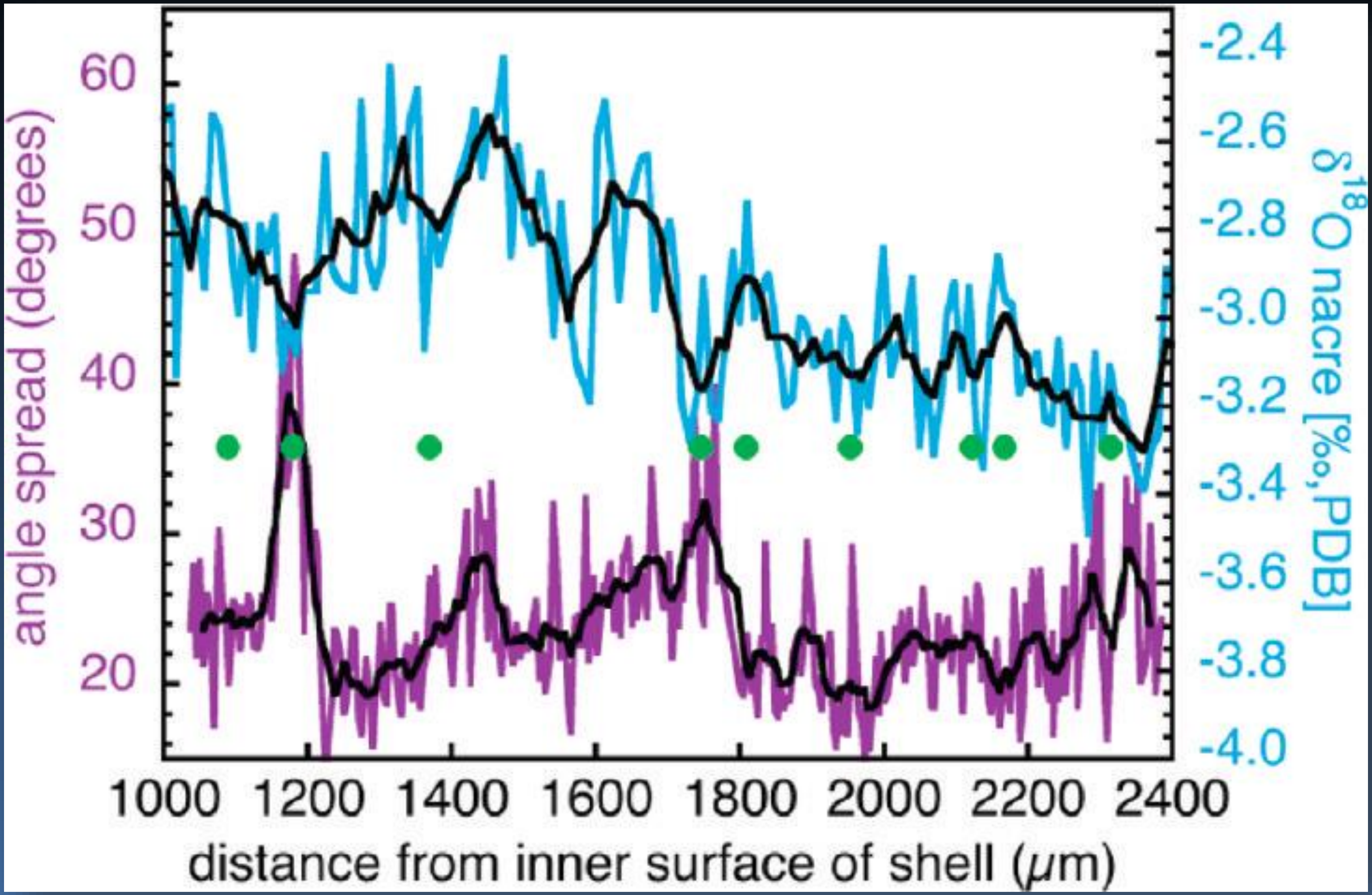
Linzmeier et al., in prep.

Mollusk shells

Tahitian black pearl oyster

Olson et al. 2012

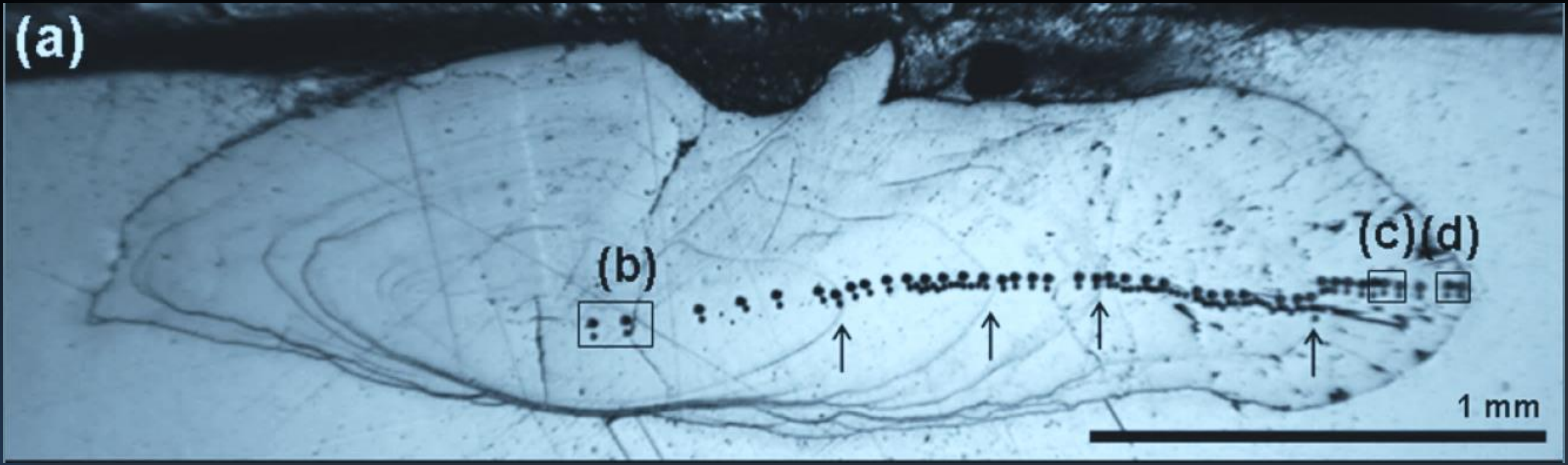
Mollusk shells

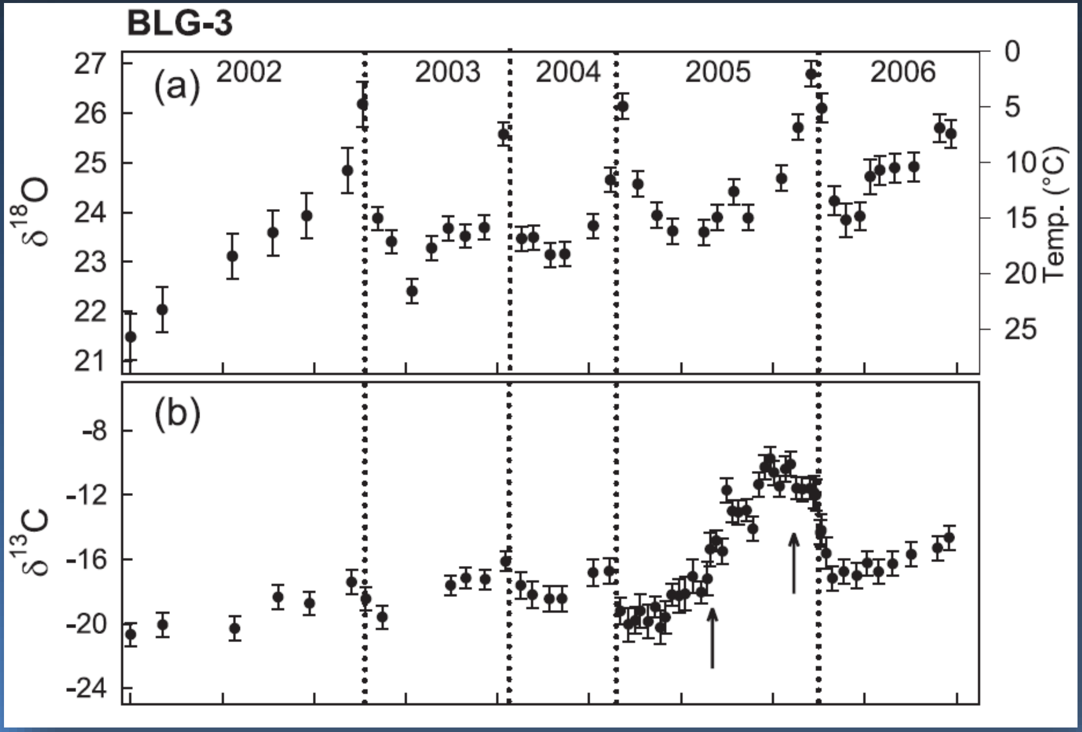


Olson et al. 2012

Otoliths

Otoliths (bluegill)

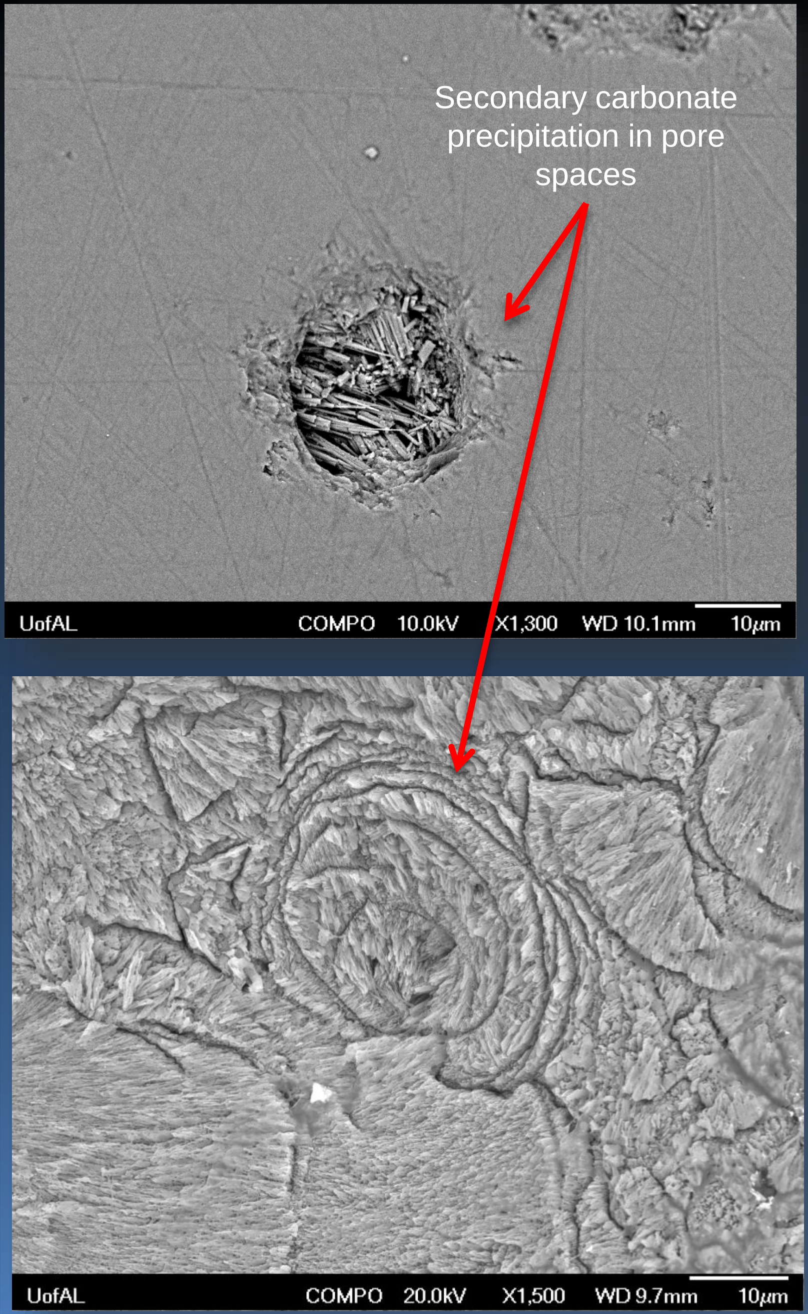




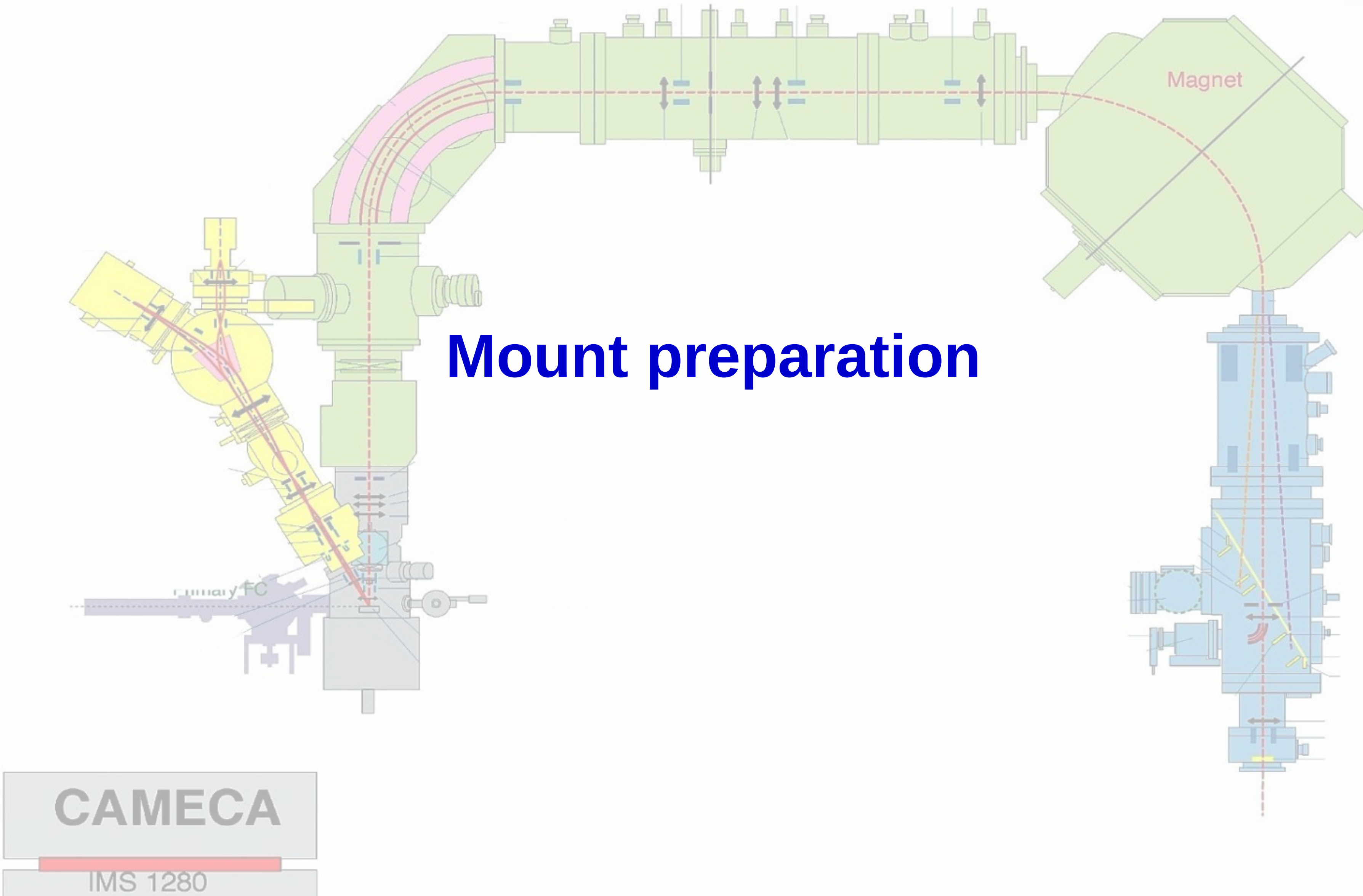
Weidel et al. 2007

Corals

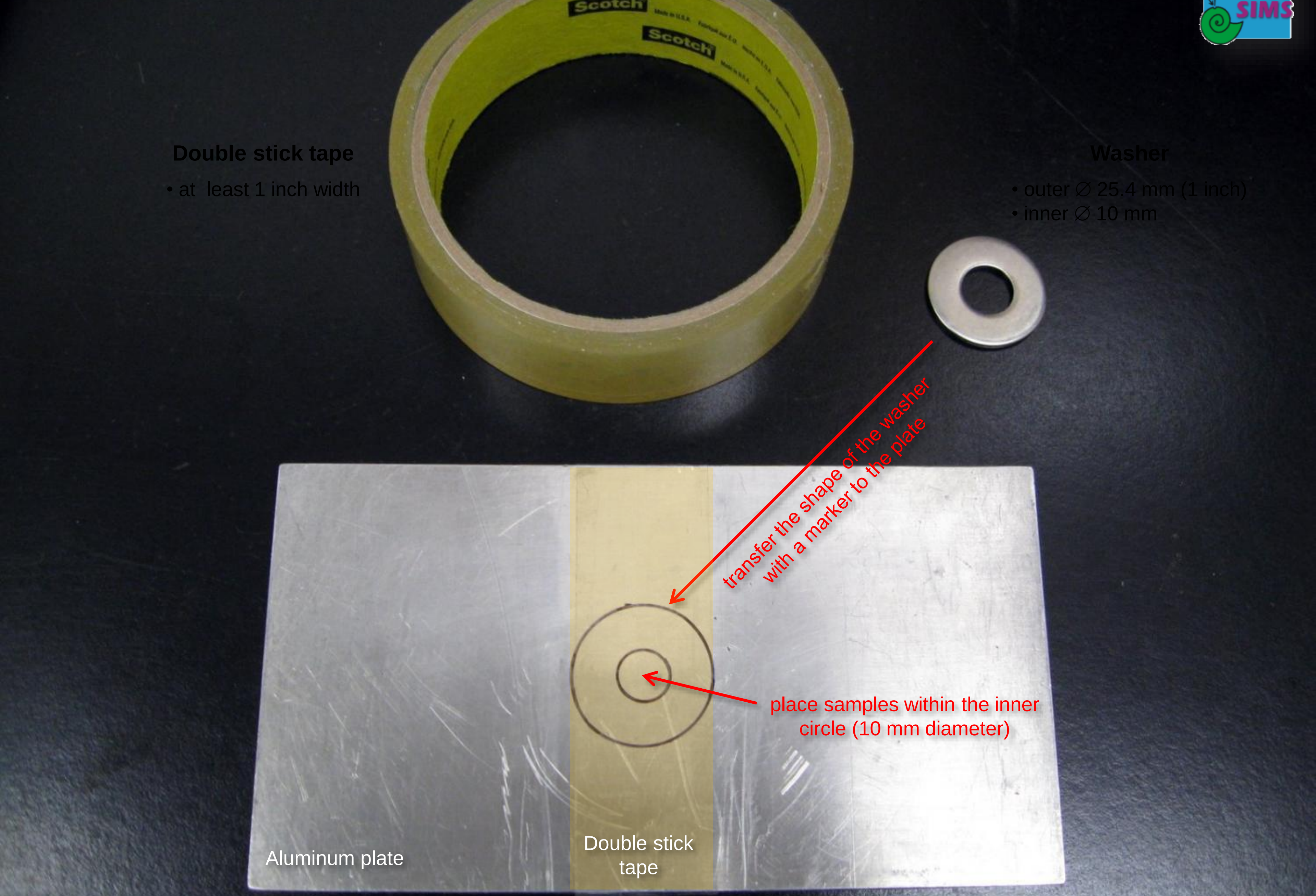

S. erubescens
F. Andrus, R. Cobb. University of Alabama

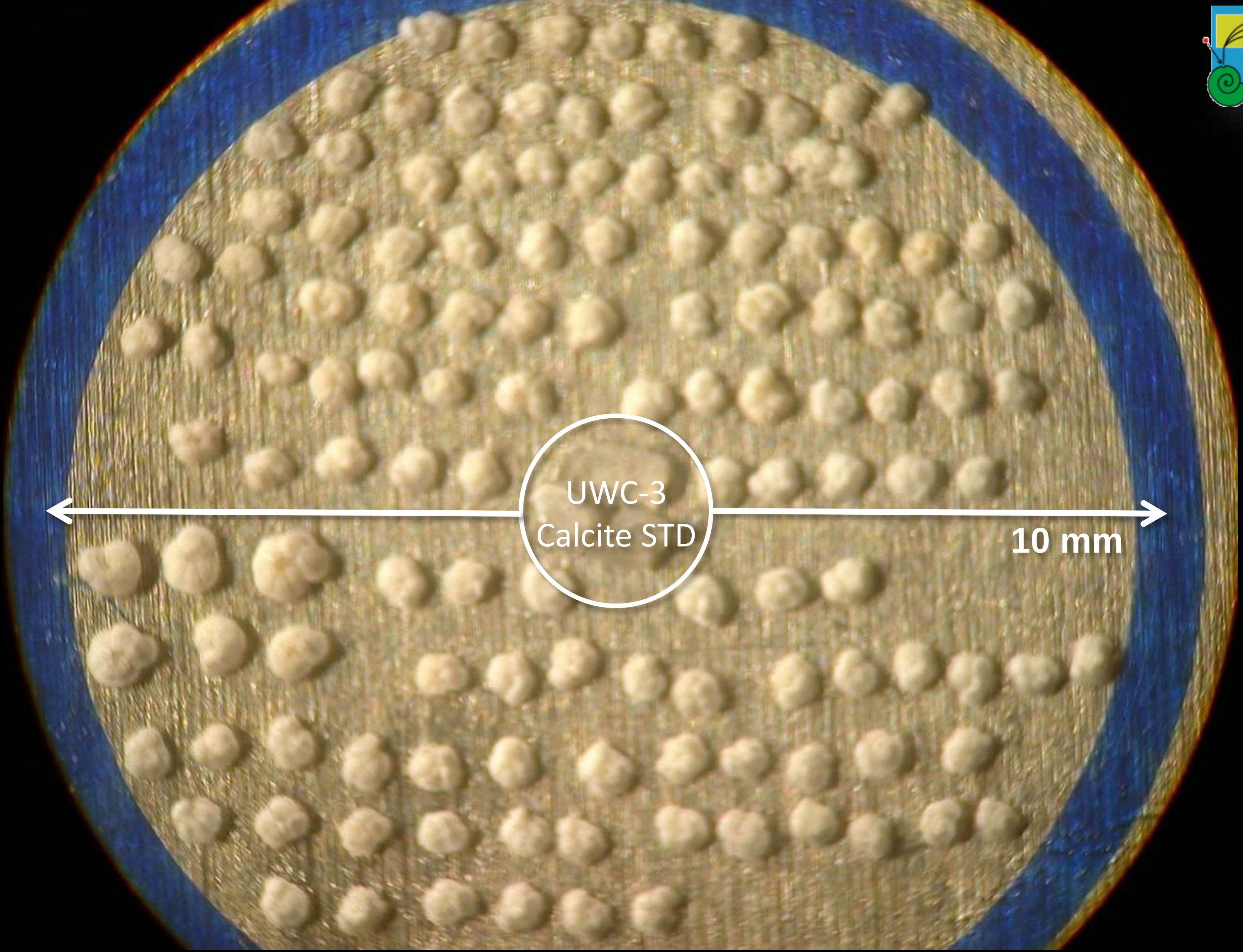

Secondary carbonate precipitation in pore spaces
UofAL COMPO 10.0kV X1,300 WD 10.1mm 10µm
UofAL COMPO 20.0kV X1,500 WD 9.7mm 10µm

Mount preparation



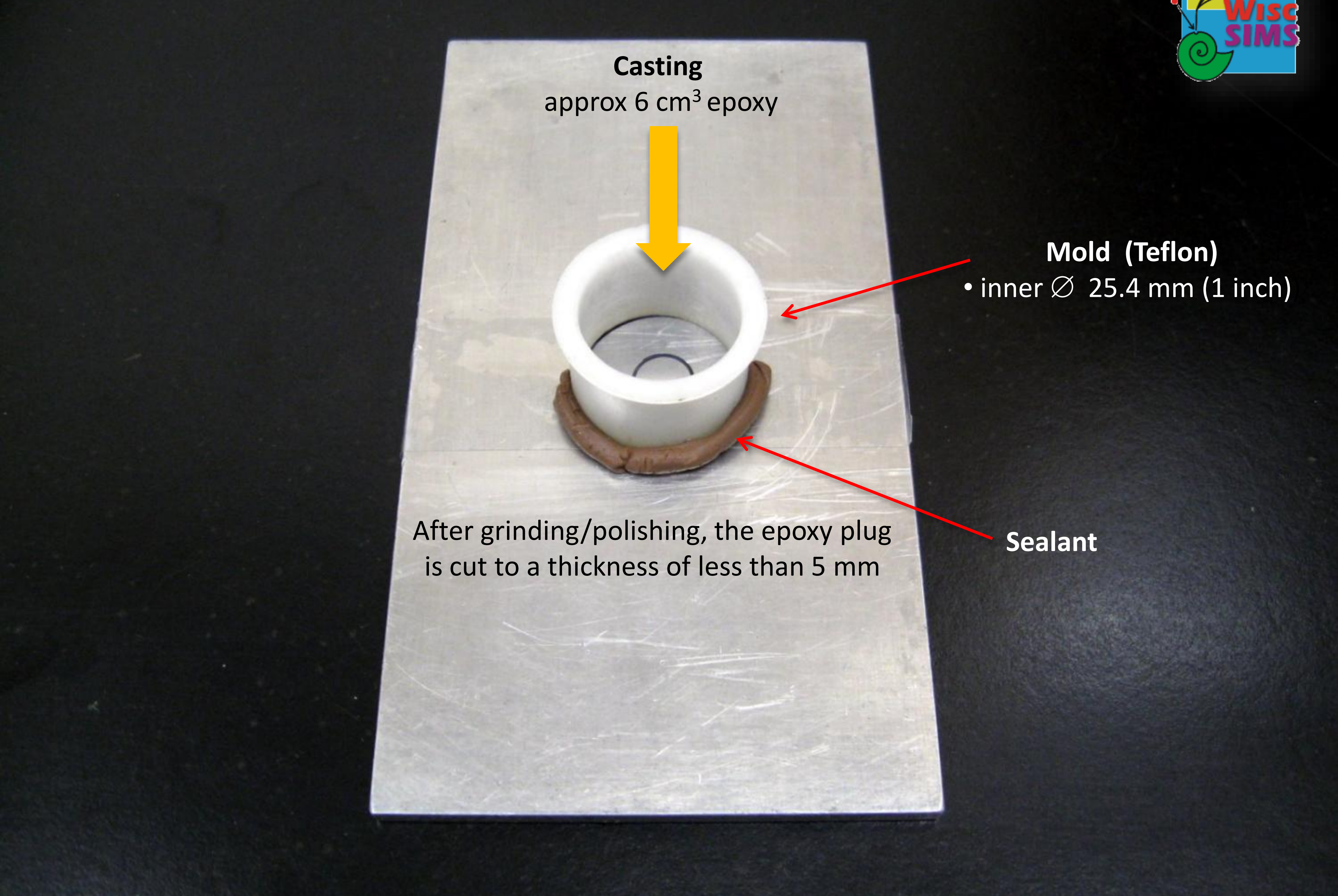
Epoxy mount for ion microprobe analysis of foraminiferal shells

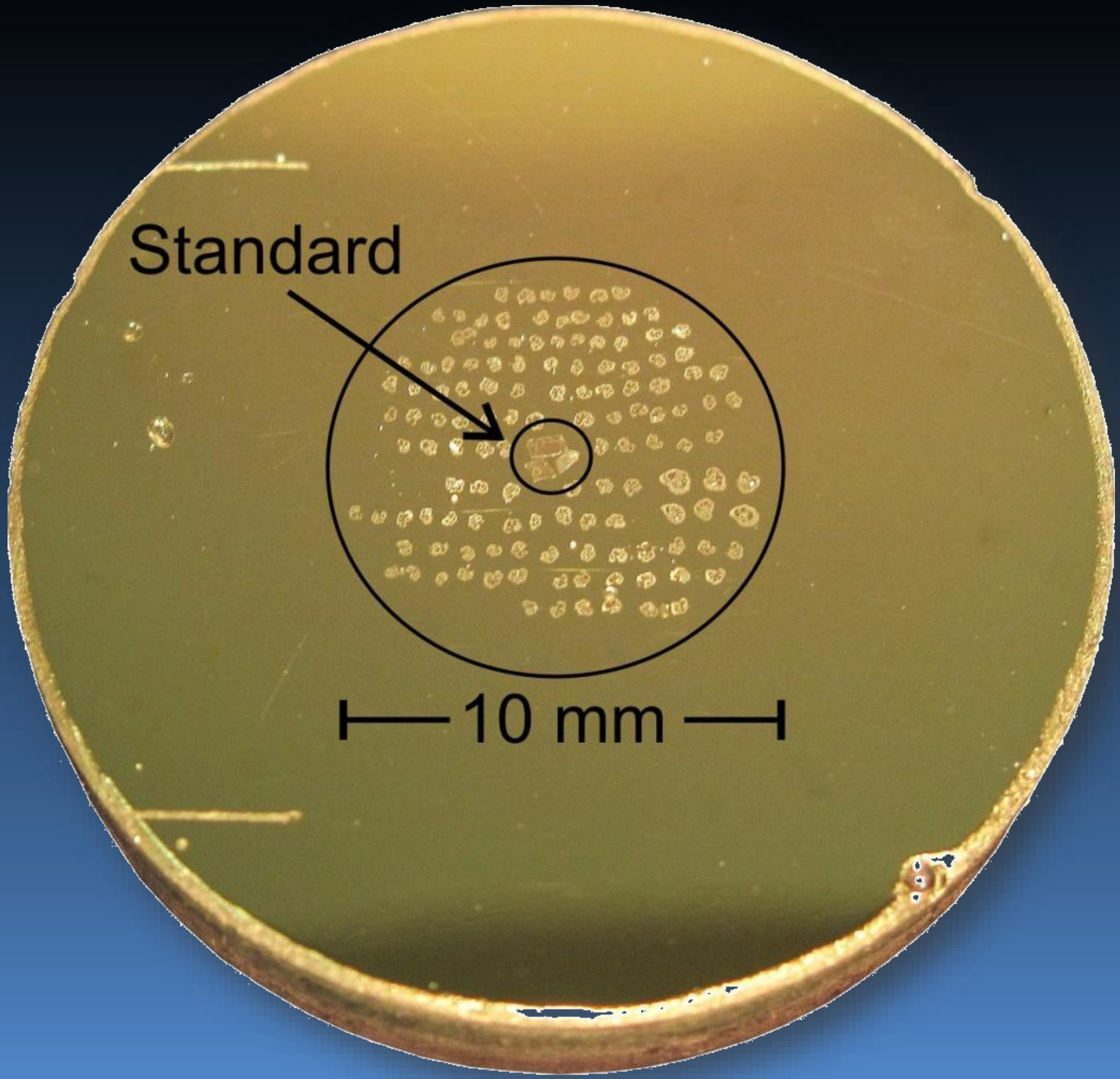




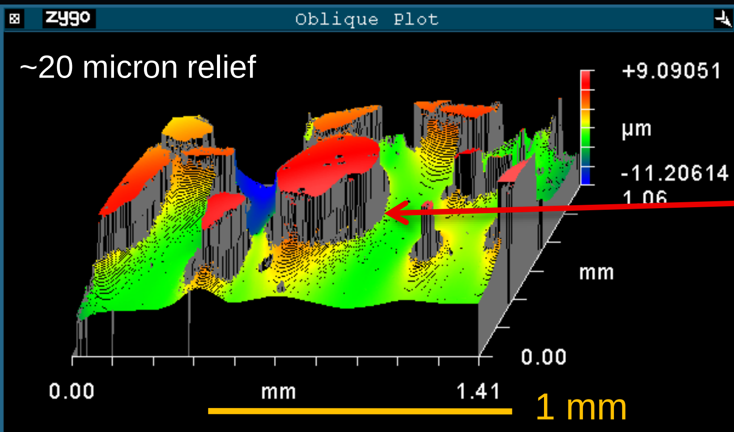
Example: Mounting of foraminiferal shells. Specimens are placed with the preferred orientation on the double stick tape (inner 10 mm of the washer marking). UWC-3 calcite standard (2 or 3 grains) are centered

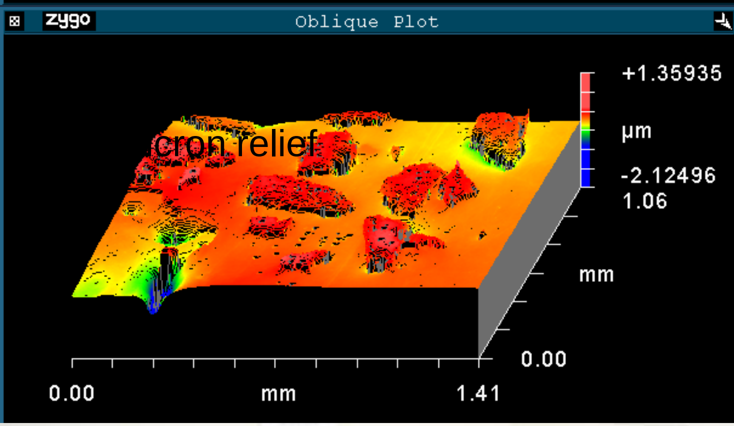
Sample casting




Standard
10 mm

Zircon grain mount – Evaluation of the polishing relief

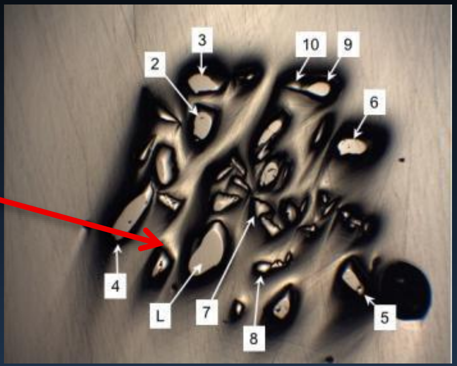


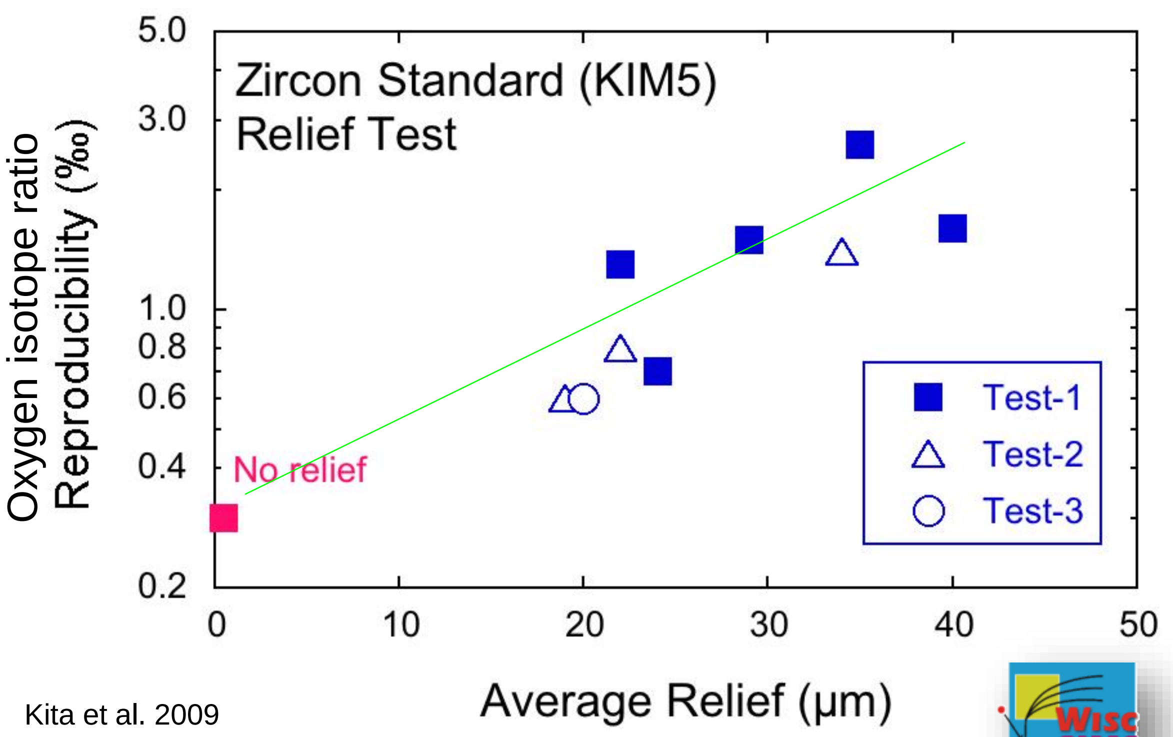


KIM-5

Zircon Standard

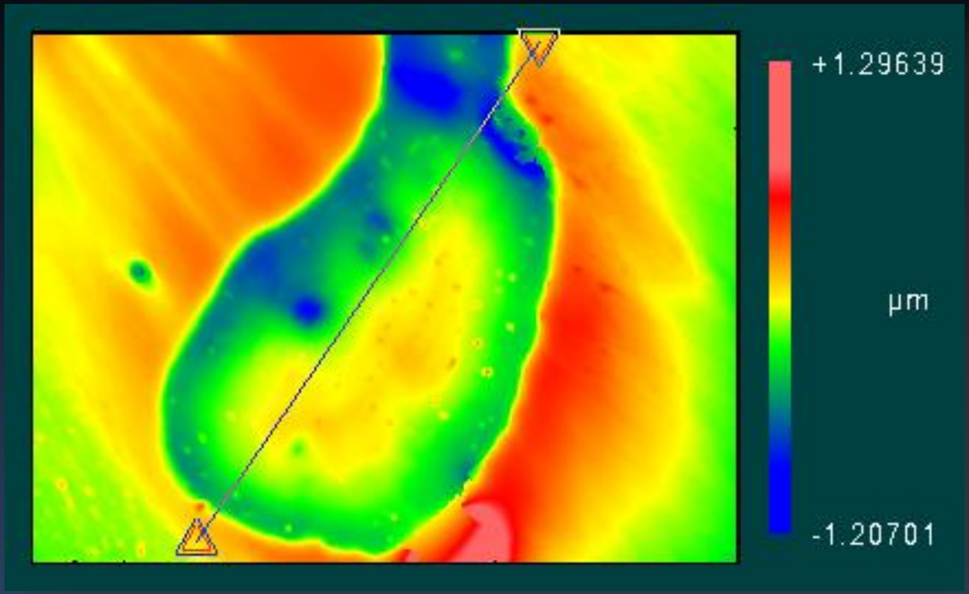
~20 micron relief





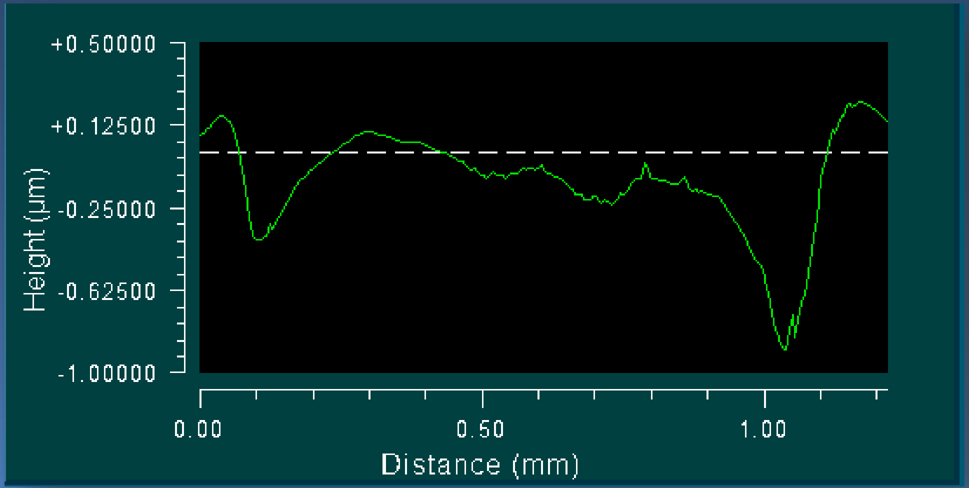
Example: Evaluation of the polishing relief of an otolith

Surface Map

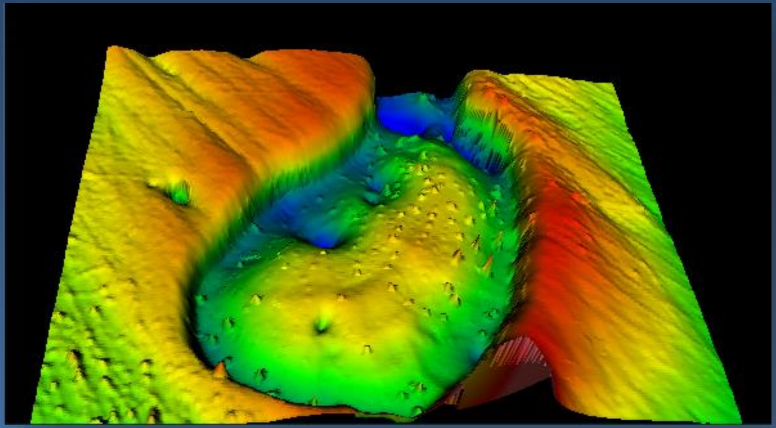


Reflected Light Image

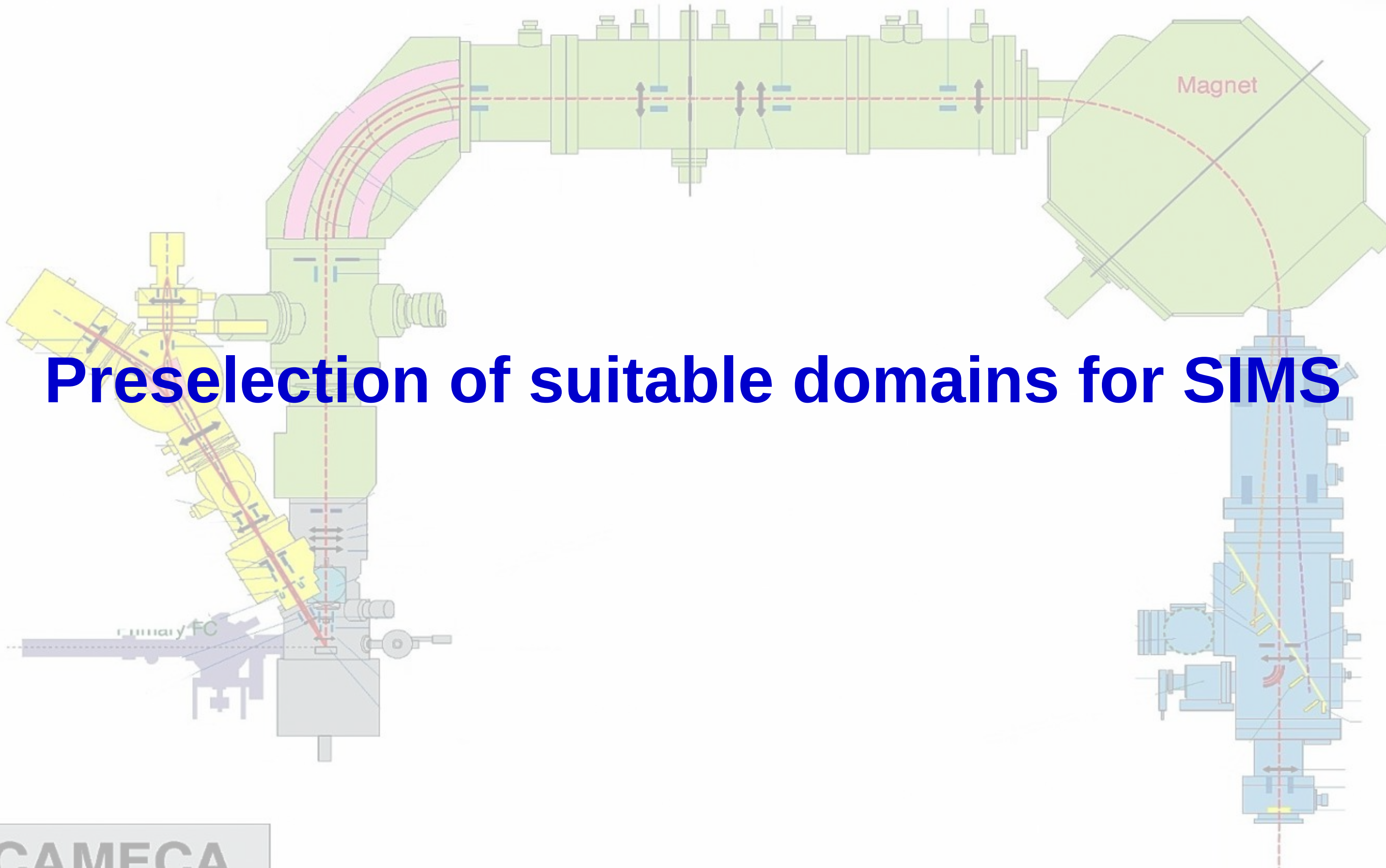
Surface Profile



3D-Model

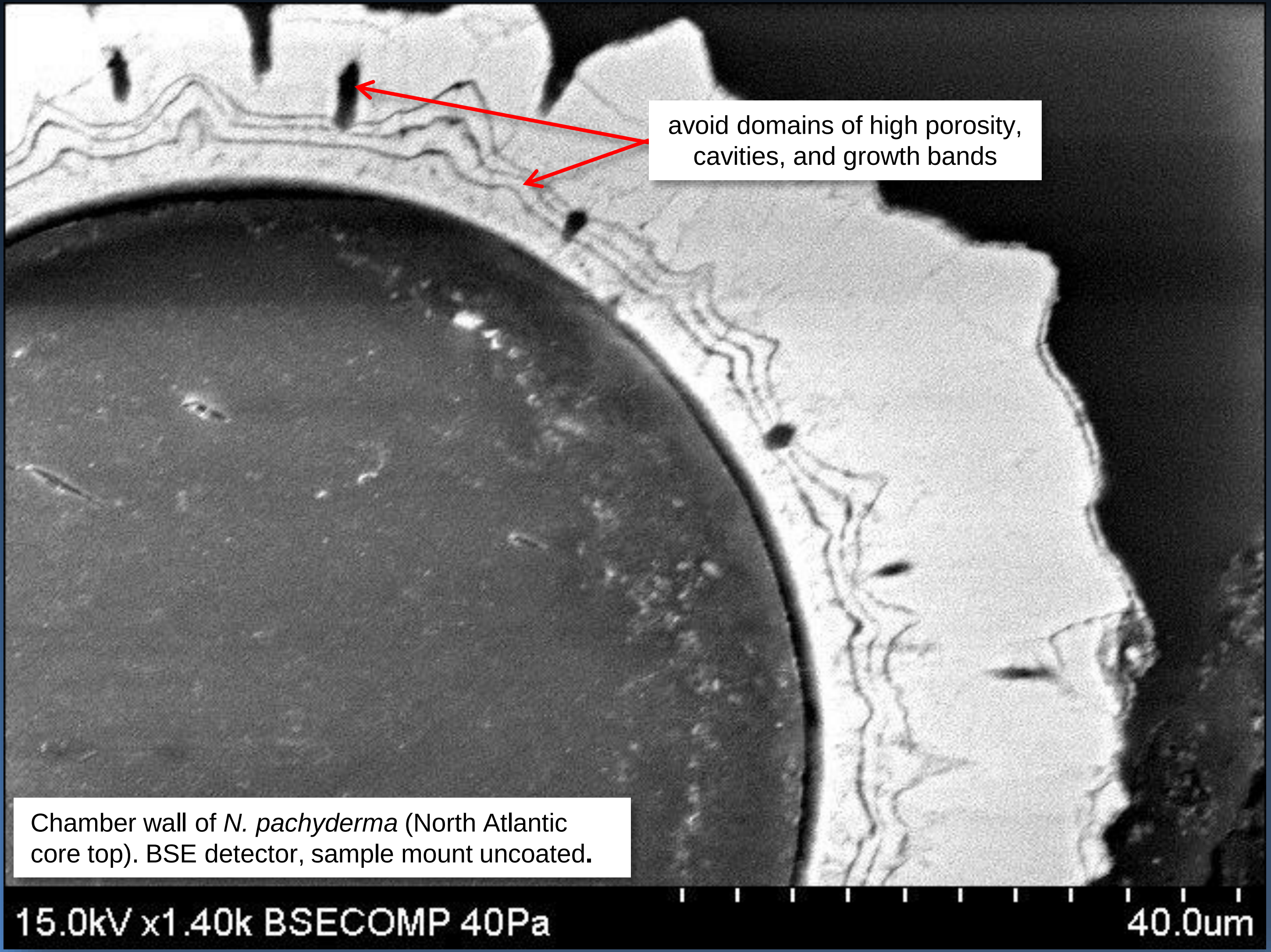


Preselection of suitable domains for SIMS



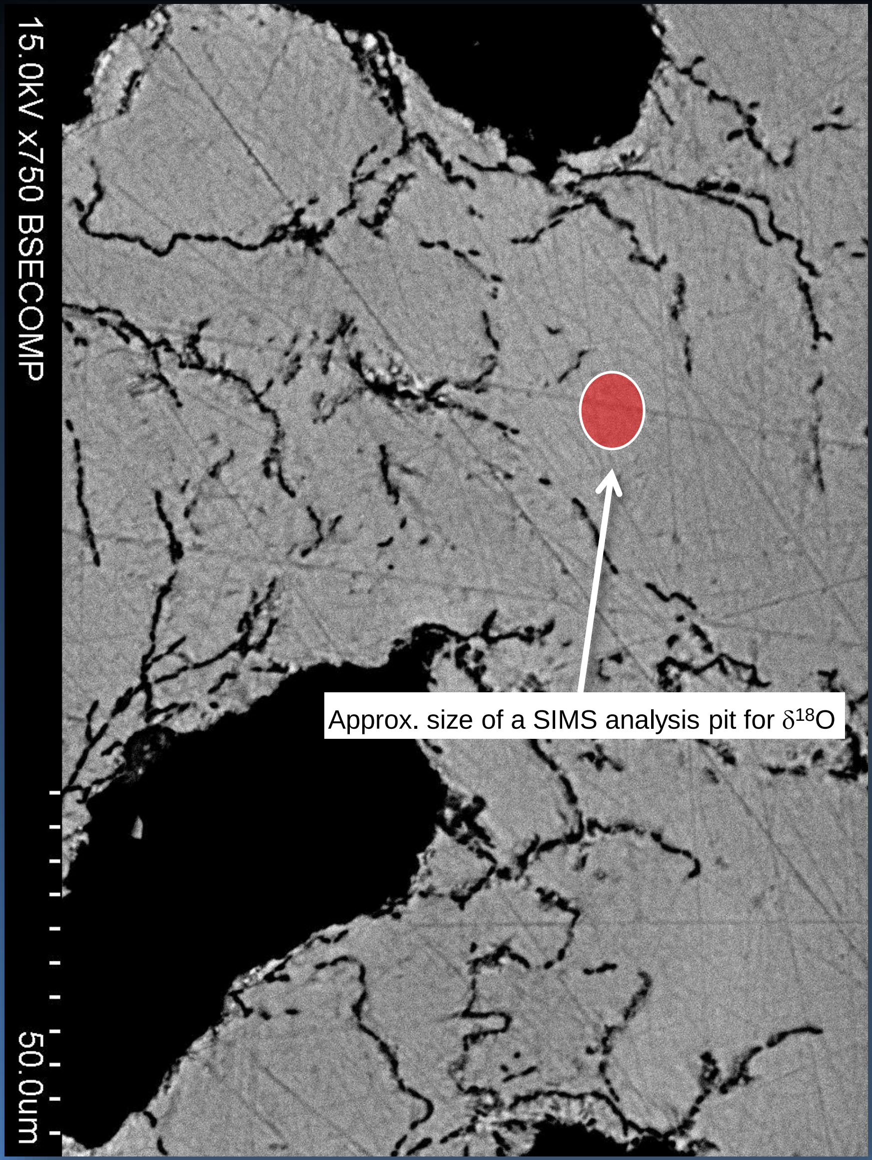
Example: Foraminiferal shells

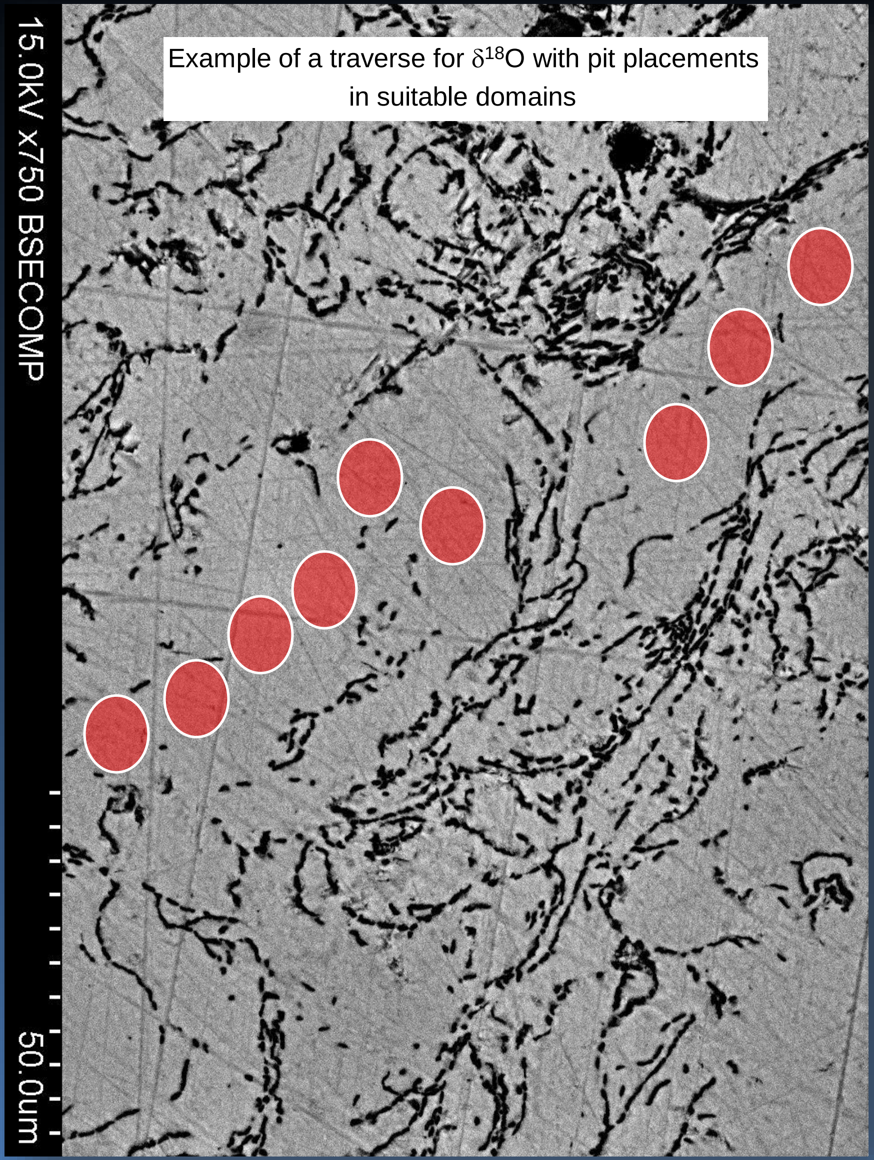
- imaging of **uncoated** samples by SEM in environmental mode using the backscattered electron detector (BSE) has shown to be a useful approach to locate growth bands and cavities that are filled by epoxy and/or organic material
- some of this features may not be clearly visible after coating. **Only non-porous areas can be safely analyzed with high precision and accuracy.**



Chamber wall of *N. pachyderma* (North Atlantic core top). BSE detector, sample mount uncoated.

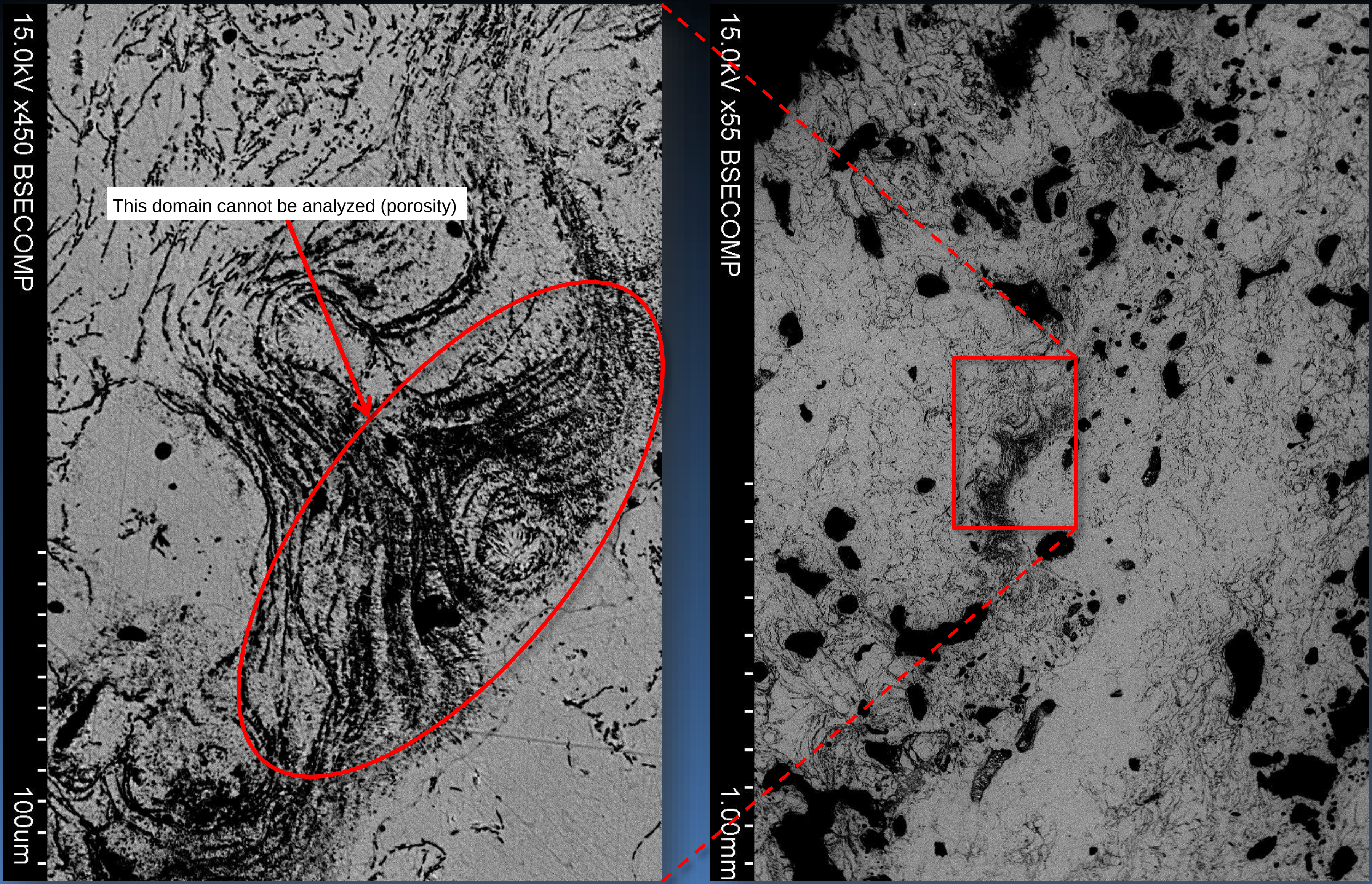
Example: Coral



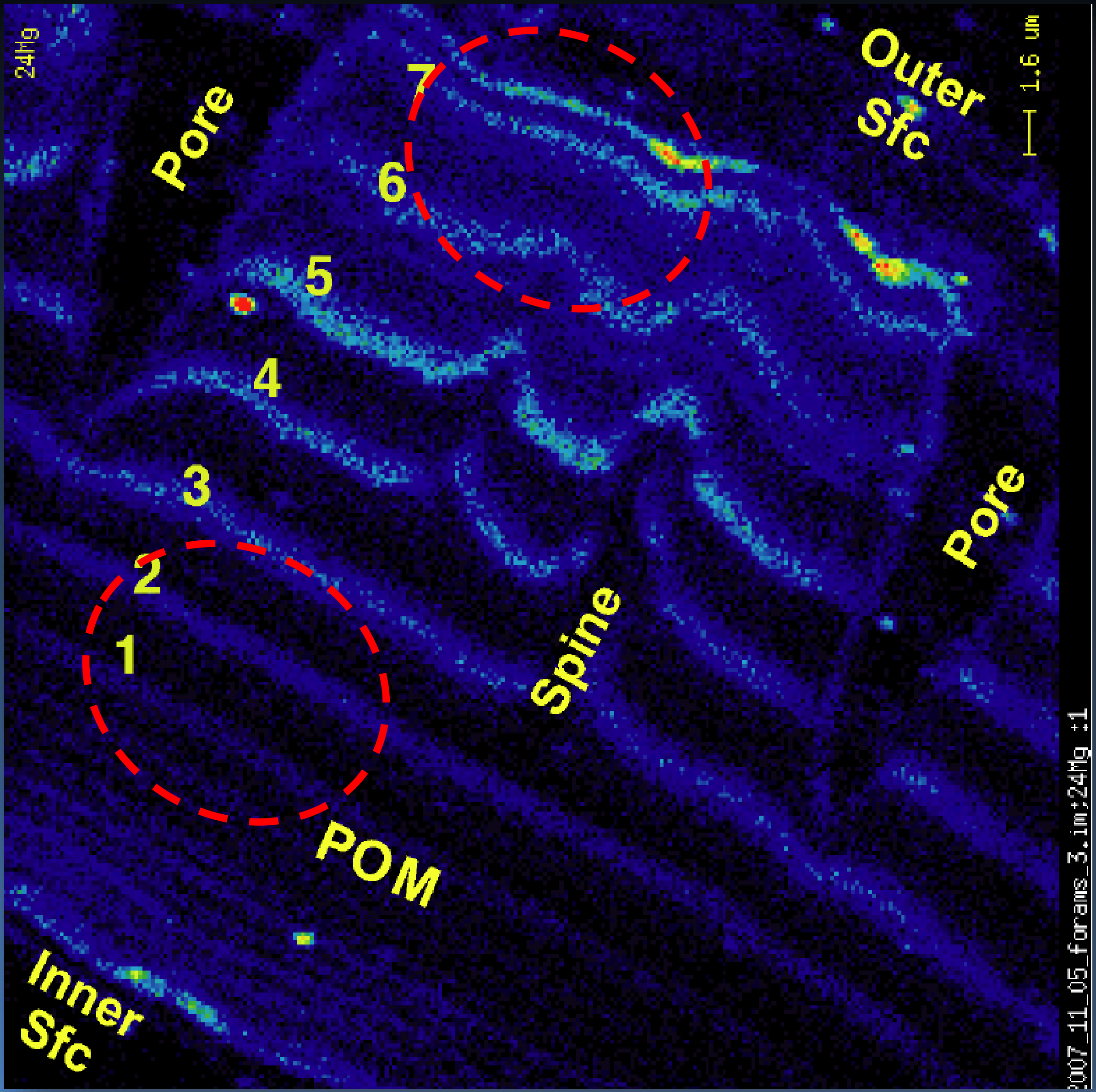


Analysis pits must be placed in nonporous domains. Data from pits overlapping epoxy or organic material may be compromised.

Example: Coral

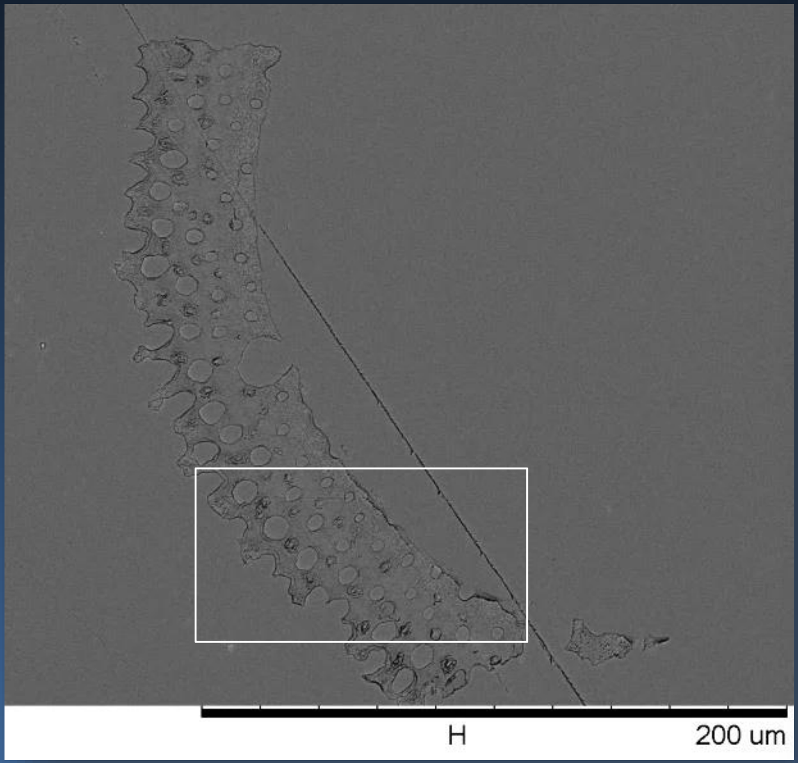


Example: Planning of $\delta^{13}C$ measurements in a foraminiferal shell.
The required spot size for $\delta^{13}C$ averages several growth bands.



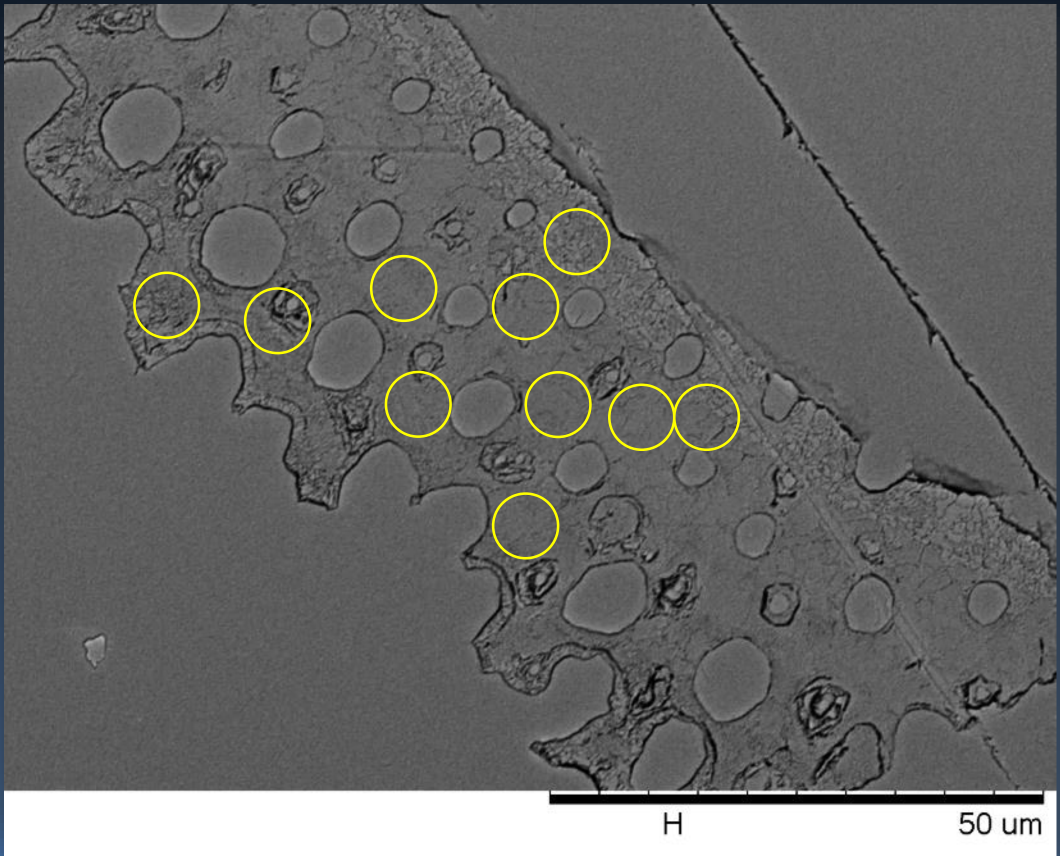
H. Spero

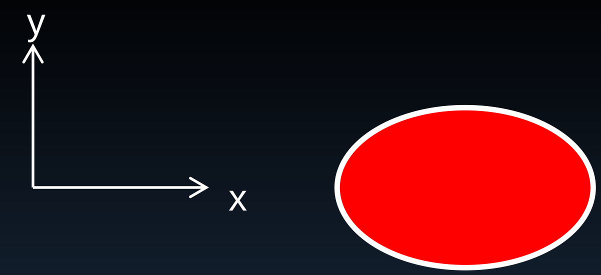
Example: Cultured Foraminifera



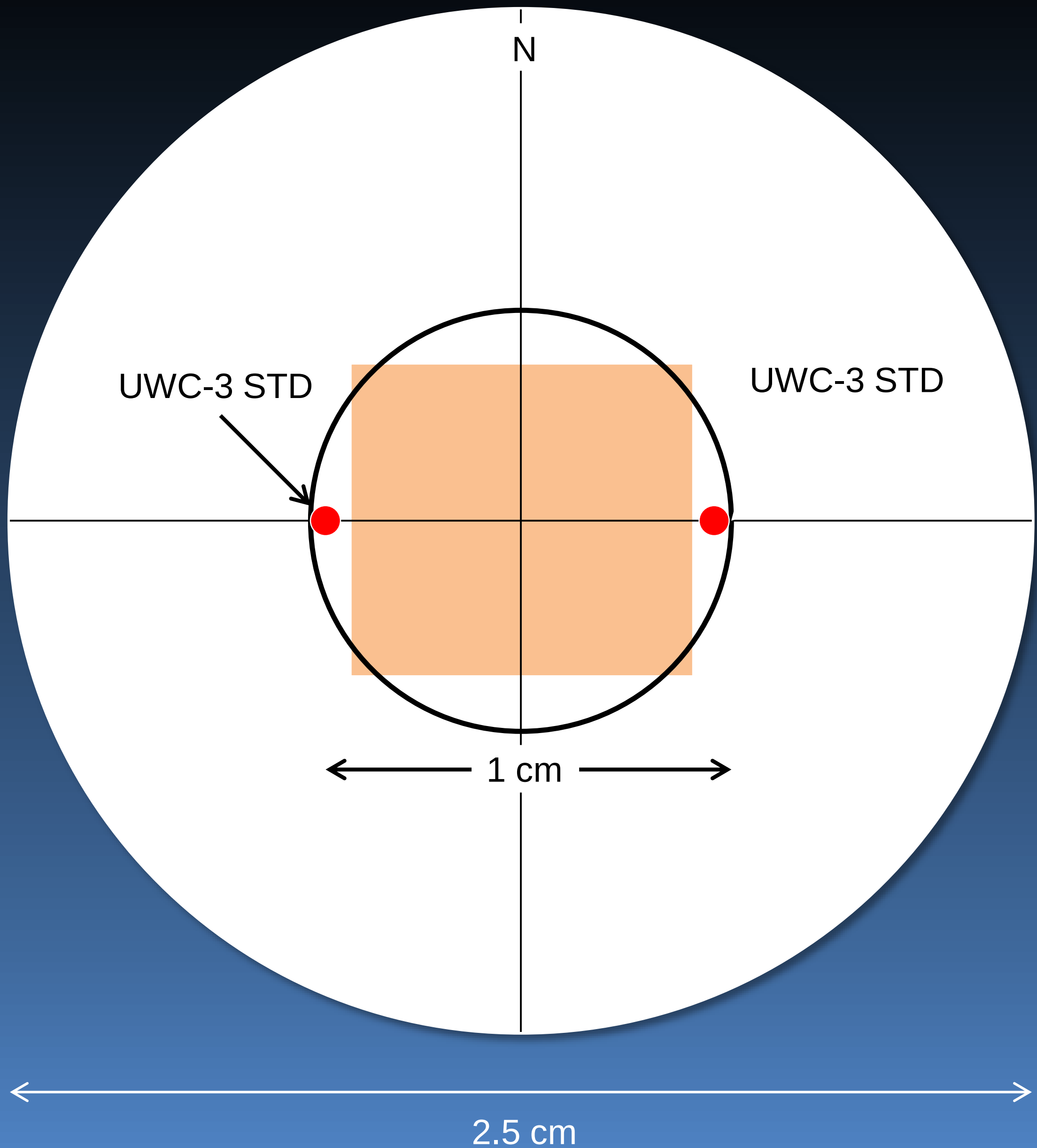
Vetter et al., in prep

Planned traverses for $\delta^{13}C$ measurements





typical shape of the SIMS beam spot

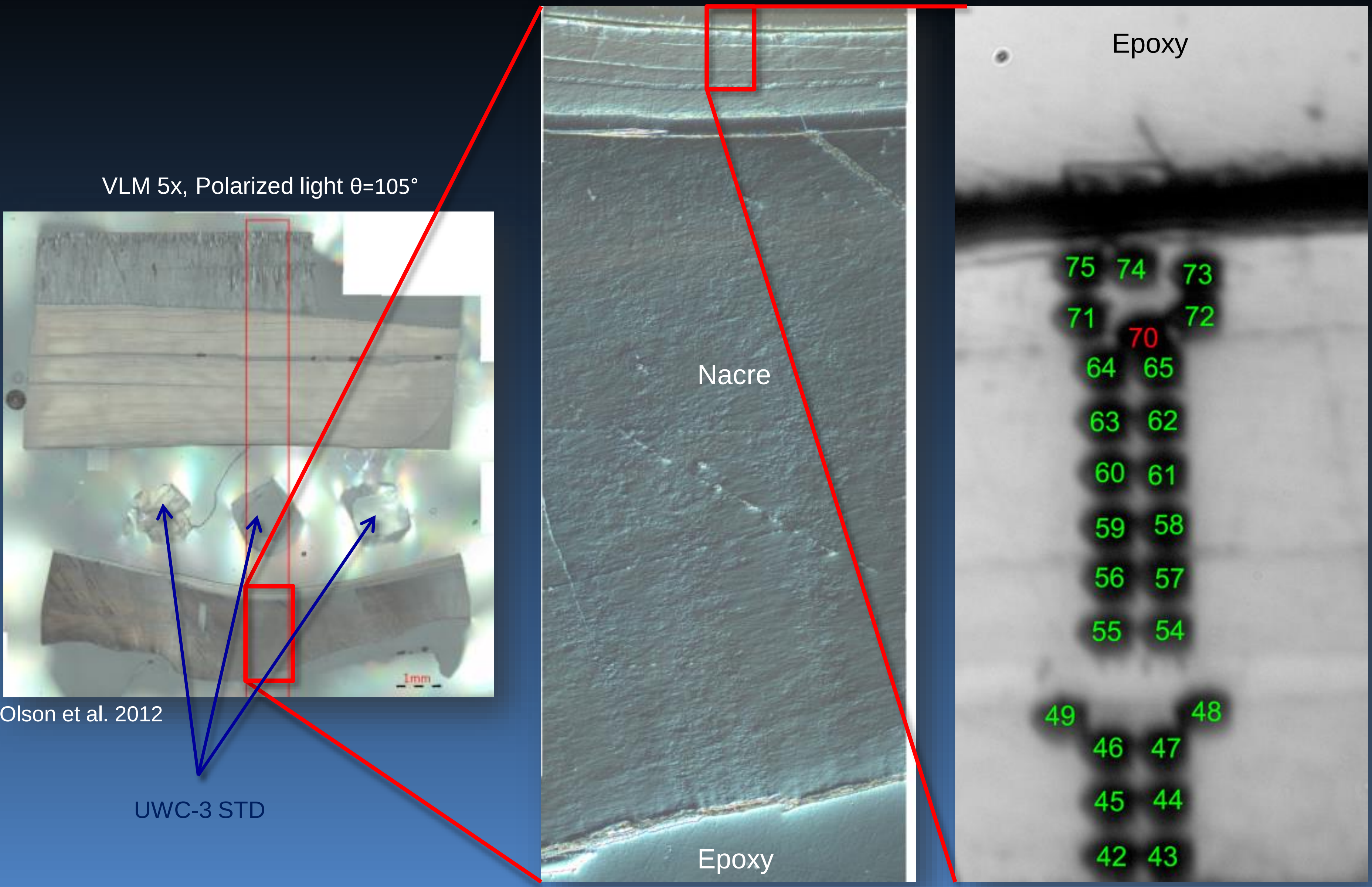


The SIMS beam spot is typically slightly elongated in x-direction.
Thus, traverses with high spatial resolution should be analyzed in y-direction (pits should not overlap!).

Example: Planning of $\delta^{18}O$ measurements in mollusk nacre

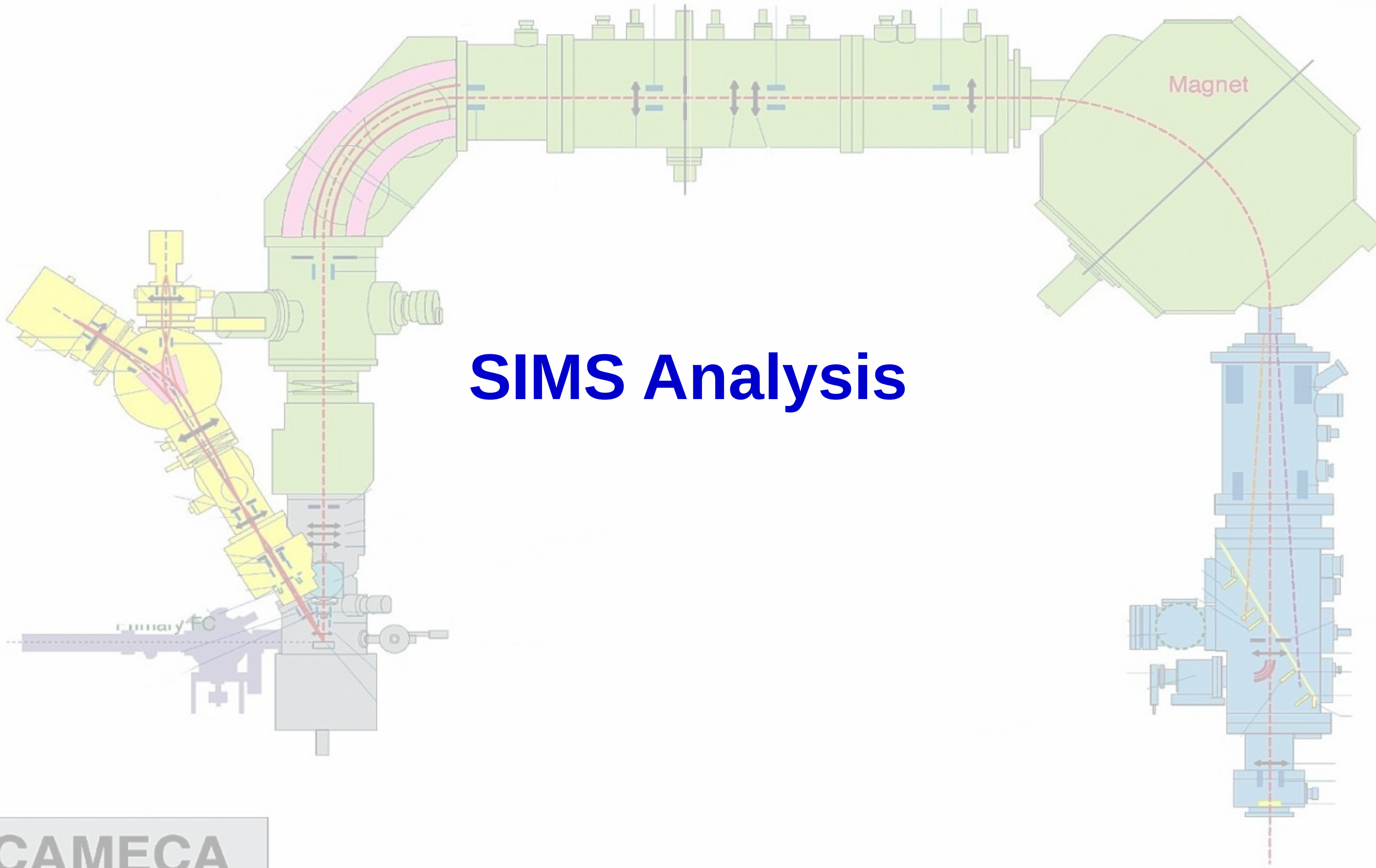
Tahitian black pearl oyster – cross section

VLM 5x, Polarized light θ=105°



Olson et al. 2012

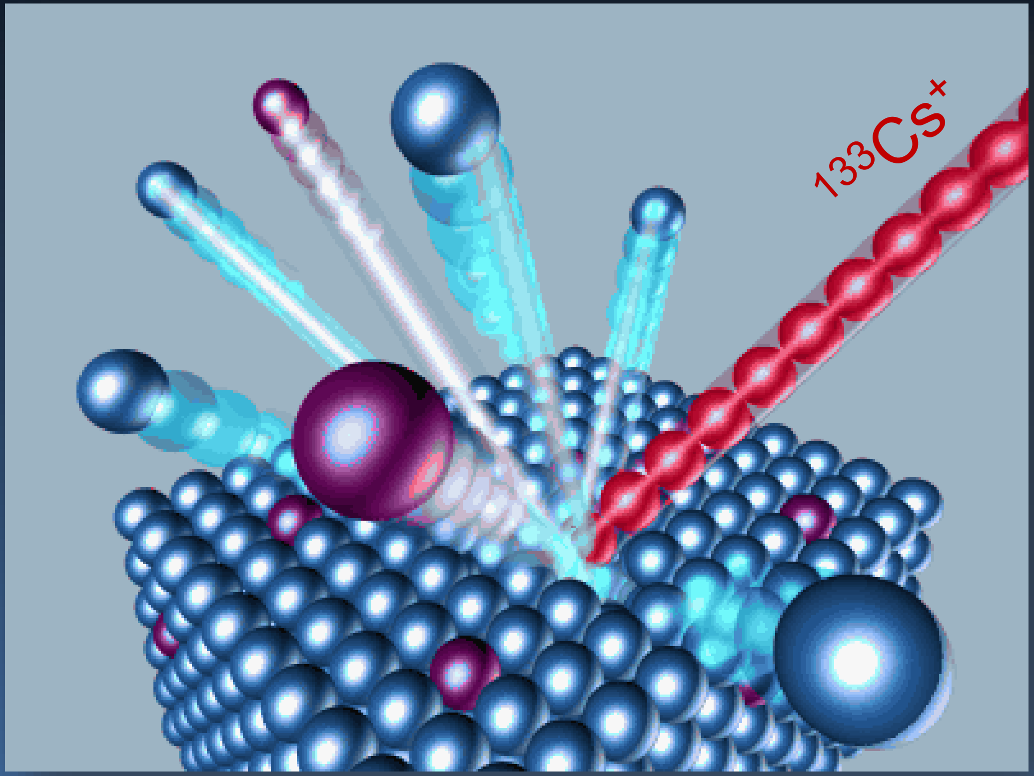
SIMS Analysis



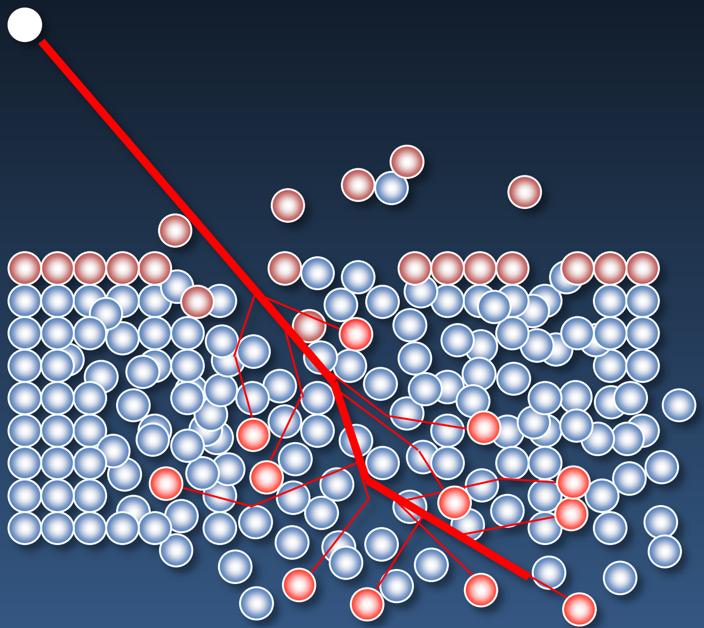
CAMECA

IMS 1280

Generation of secondary ions by sputtering

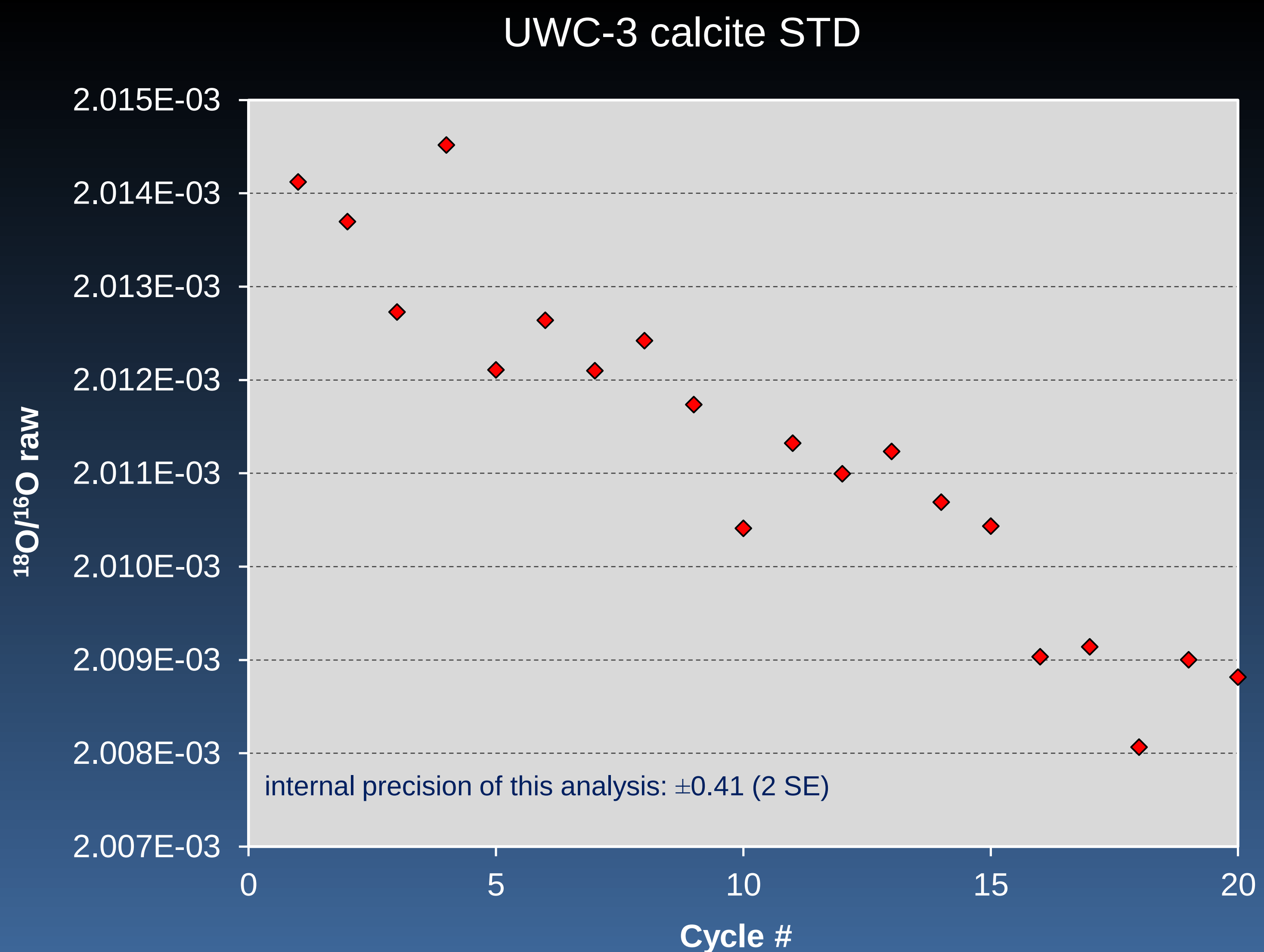


www.atomika.com



- Single atoms and clusters are ejected (collision cascade)
- A small fraction is ionized.

www.cameca.fr



The data for both ^{16}O and ^{18}O in a single spot are subdivided into a series of 20 cycles (for typical 10 µm-spot analytical conditions), and the internal precision is based on the SE of the 20 comparisons. The $^{18}O/^{16}O$ ratio in carbonate can vary significantly with depth during a single spot analysis, leading to a high internal error. However, this depth effect is reproducible from spot to spot and it is common to obtain external precision that is significantly better than would be predicted from the internal precision.

SIMS Data Table

Format Painter | Clipboard | Font | Merge & Center | Alignment | Number | Conditional Formatting | Format as Table | Styles

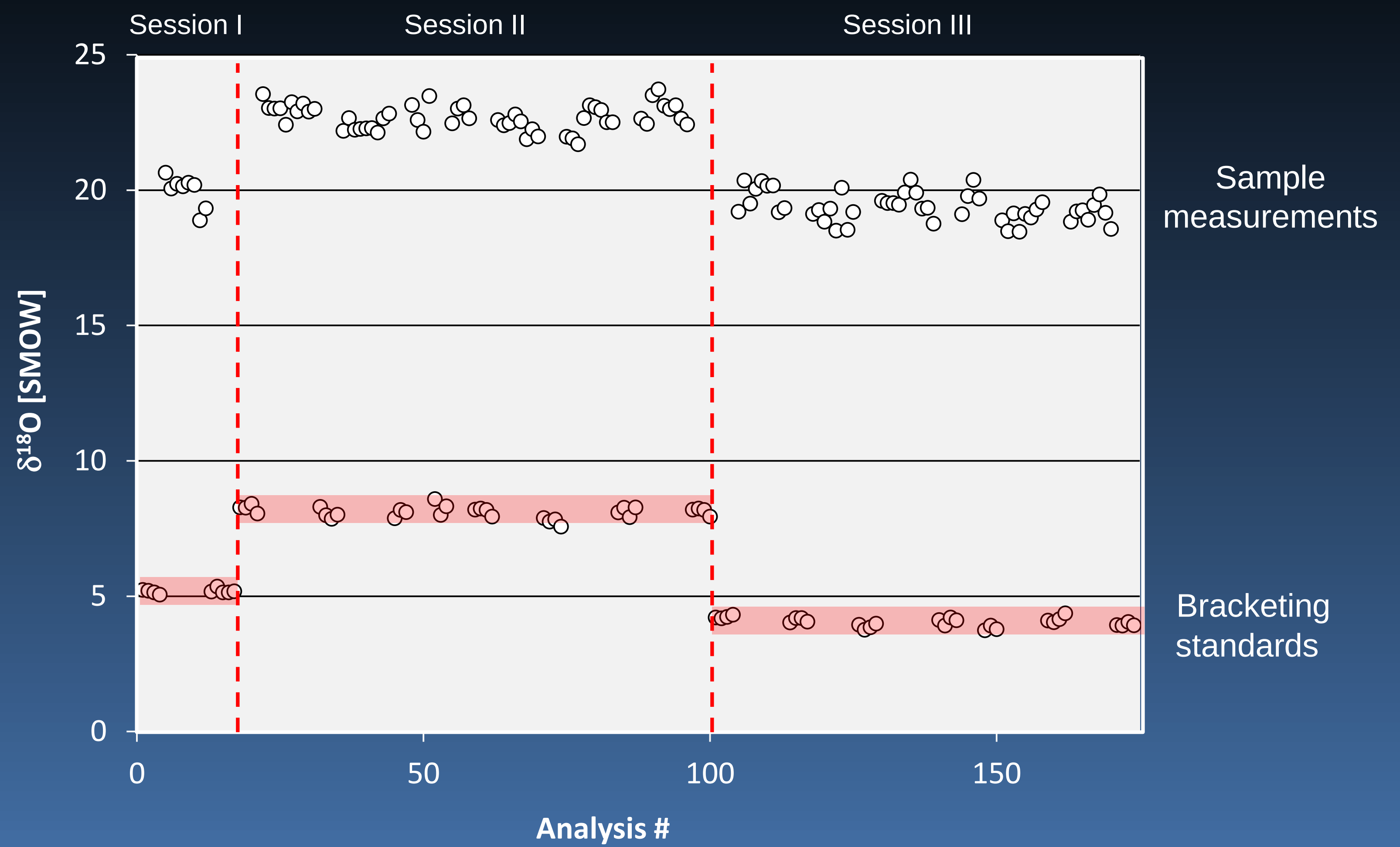
E81

	A	B	D	E	F	G	H	I	J	K	L
1	File	Comment	d18O[SMOW]	IMF	d18O_m	d18O-2SE	16O(E9 cps)	IP(nA)	Yield (E9cps/nA)	Yield (% of bracketing STD)	date
85	20130125@68.asc	UWC-3			2.711	0.534	1.962	0.668	2.939		1/25/20
86	20130125@69.asc	UWC-3, Cs = 154			2.841	0.374	2.053	0.703	2.921		1/25/20
87	20130125@70.asc	UWC-3			2.902	0.475	2.084	0.730	2.855		1/25/20
88	20130125@71.asc	UWC-3, Cs = 155			2.765	0.606	2.174	0.771	2.821		1/25/20
89		**bracket: average and 2 SD**		**0.99054**	**2.909**	**0.282**			**2.858**		
90											
91			**d18O[SMOW]**	**±2SD**							
92	20130125@72.asc	Shell 20 penult gam 72	28.13	0.24	18.388	0.540	2.135	0.811	2.632	92	1/25/20
93	20130125@73.asc	SHell 20 ult gam 73 (low yield)			17.510	0.631	2.009	0.810	2.479	87	1/25/20
94	20130125@74.asc	Shell 21 penult gam 74	28.18	0.24	18.429	0.569	2.078	0.809	2.568	90	1/25/20
95	20130125@75.asc	Shell 21 ult 75	27.90	0.24	18.160	0.445	2.038	0.794	2.566	90	1/25/20
96	20130125@76.asc	Shell 21 penult 76 (low yield)			14.828	0.828	1.801	0.795	2.265	79	1/25/20
97	20130125@77.asc	Shell 22 S 77	27.13	0.24	17.393	0.509	2.043	0.798	2.561	90	1/25/20
98	20130125@78.asc	Shell 22 S gam 78	27.84	0.24	18.094	0.468	2.126	0.798	2.665	93	1/25/20
99	20130125@79.asc	Shell 23 E gam 79	28.26	0.24	18.511	0.444	2.120	0.791	2.682	94	1/25/20
00	20130125@80.asc	Shell 23 NW 80	28.42	0.24	18.675	0.539	2.030	0.785	2.587	90	1/25/20
01	20130125@81.asc	Shell 24 N 81	28.75	0.24	18.998	0.501	2.083	0.770	2.705	95	1/25/20
02	20130125@82.asc	Shell 25 N 82	28.73	0.24	18.975	0.465	2.061	0.763	2.703	94	1/25/20
03	20130125@83.asc	Shell 25 N 83	28.12	0.24	18.370	0.403	1.953	0.753	2.593	91	1/25/20
04	20130125@84.asc	Shell 26 S 84 (low yield)			16.323	0.725	1.857	0.750	2.477	87	1/25/20
05	20130125@85.asc	Shell 26 S 85	29.00	0.24	19.243	0.585	2.027	0.742	2.733	96	1/25/20
06	20130125@86.asc	Shell 27 W 86 (low yield)			14.351	1.583	1.586	0.732	2.167	76	1/25/20
07											
08	20130125@87.asc	UWC-3			3.013	0.508	2.078	0.728	2.854		1/25/20
09	20130125@88.asc	UWC-3			2.882	0.507	2.071	0.720	2.878		1/25/20
10	20130125@89.asc	UWC-3, Cs-res. = 156			3.045	0.479	2.127	0.750	2.835		1/25/20
11	20130125@90.asc	UWC-3			2.976	0.415	2.149	0.773	2.780		1/25/20
12		**bracket: average and 2 SD**		**0.99052**	**2.892**	**0.235**			**2.860**		

average δ^{18}O[measured] of the eight bracketing STD analyses

± 2SD of the bracketing STD

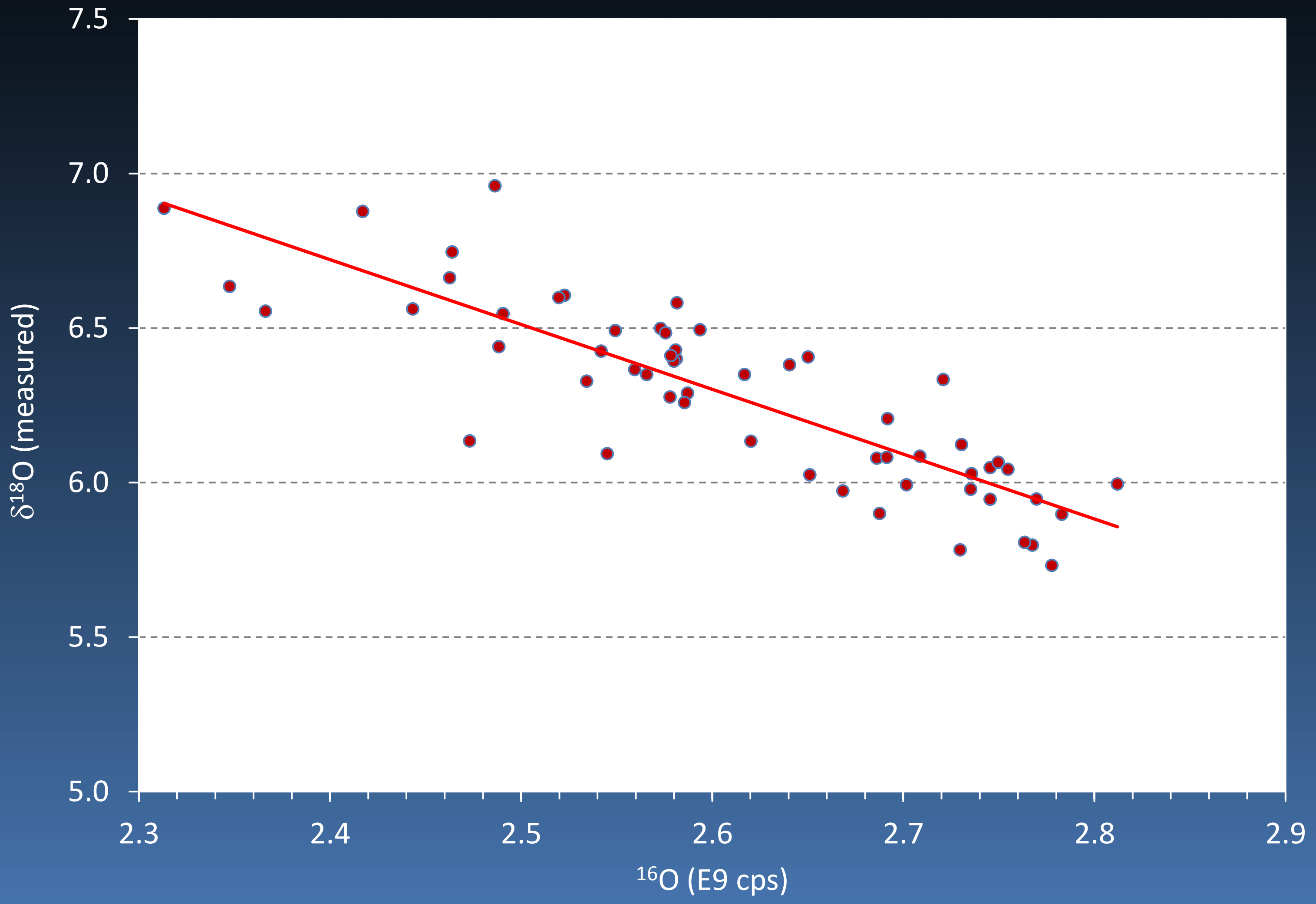
Spot-to-spot precision of ±0.3‰ (2SD) in $\delta^{18}O$ with 10 µm beam-spot



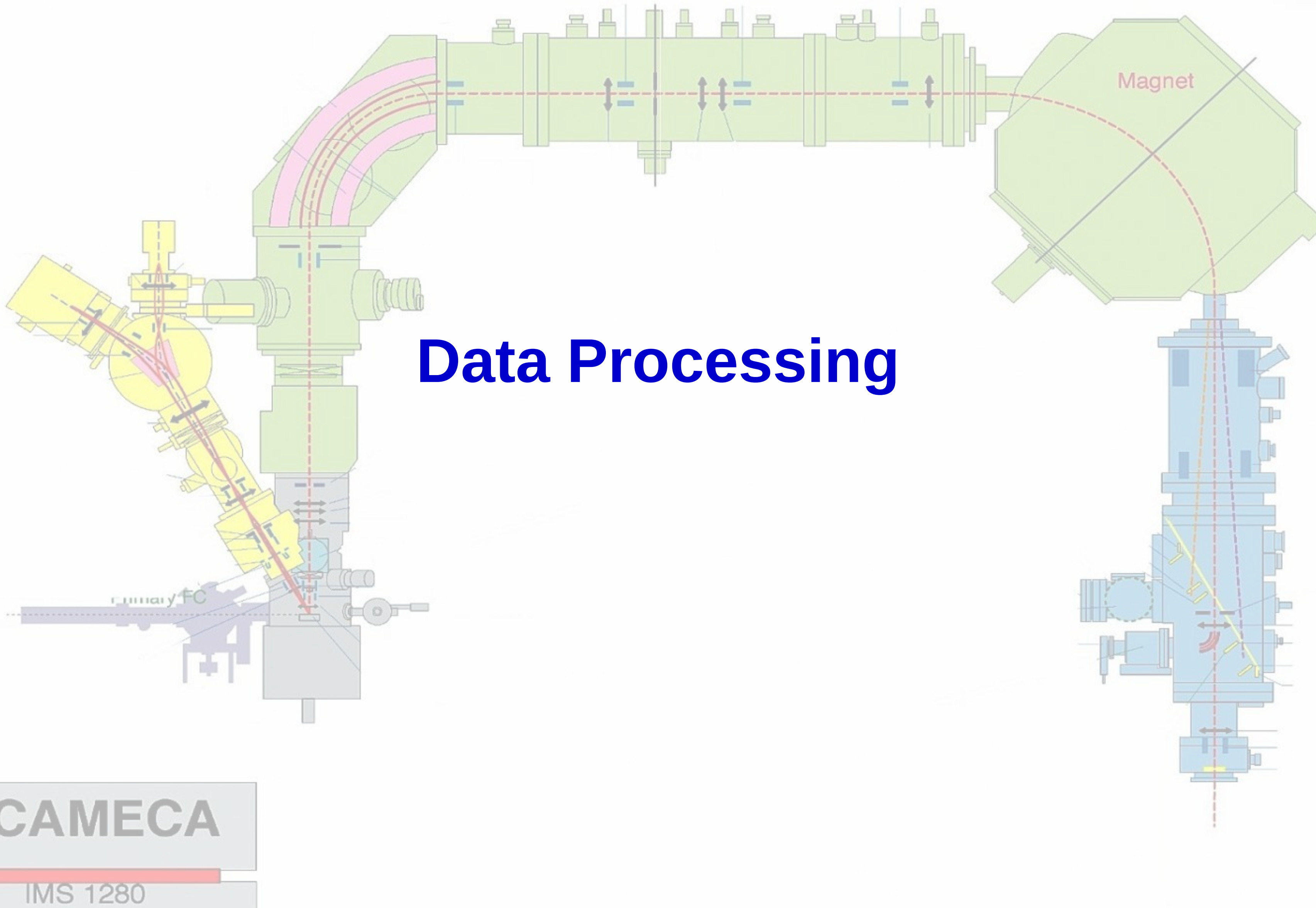
$^{16}O^-$ [cps] = ~$2*10^9$

$^{18}O^-$ [cps] = ~$4*10^6$ (FC-amplifier background: 1000 cps)

A consistent primary beam intensity is essential for carbonate analyses



Data Processing

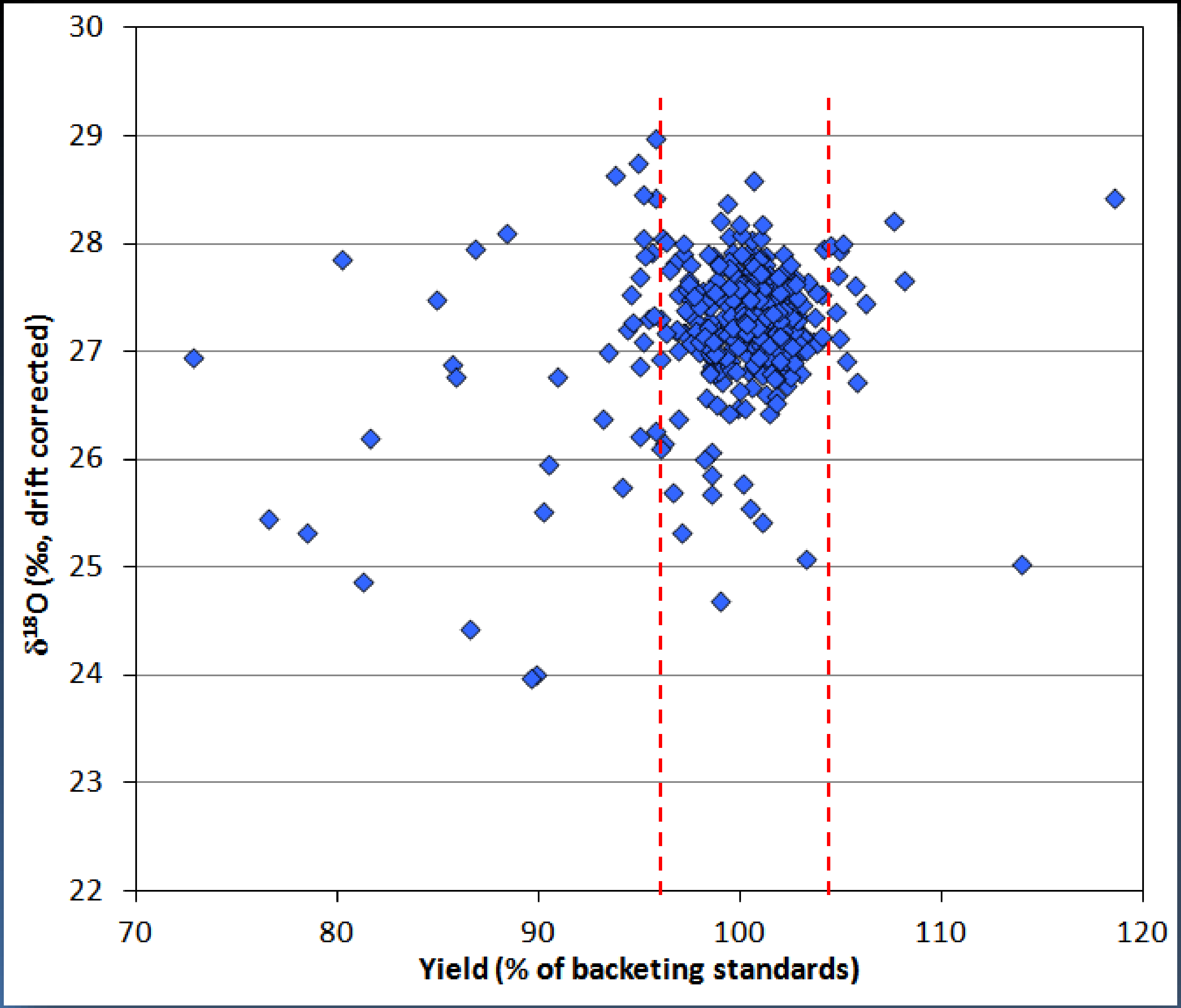


SIMS Data Table

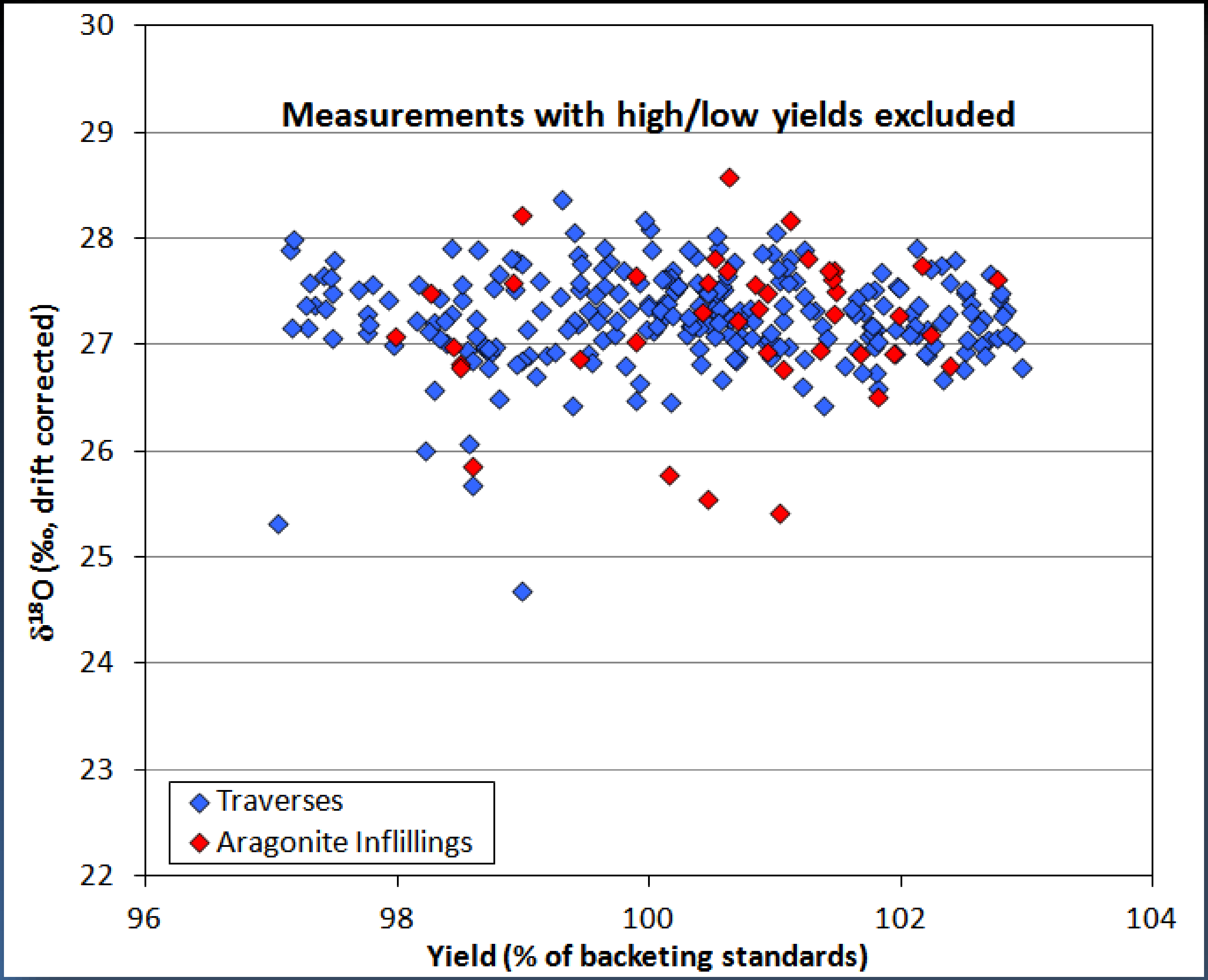
	A	B	D	E	F	G	H	I	J	K	L
1	File	Comment	d18O[SMOW]	IMF	d18O_m	d18O-2SE	16O(E9 cps)	IP(nA)	Yield (E9cps/nA)	Yield (% of bracketing STD)	date
85	20130125@68.asc	UWC-3			2.711	0.534	1.962	0.668	2.939		1/25/20
86	20130125@69.asc	UWC-3, Cs = 154			2.841	0.374	2.053	0.703	2.921		1/25/20
87	20130125@70.asc	UWC-3			2.902	0.475	2.084	0.730	2.855		1/25/20
88	20130125@71.asc	UWC-3, Cs = 155			2.765	0.606	2.174	0.771	2.821		1/25/20
89		**bracket: average and 2 SD**		**0.99054**	**2.909**	**0.282**			**2.858**		
90											
91			**d18O[SMOW]**	**±2SD**							
92	20130125@72.asc	Shell 20 penult gam 72	28.13	0.24	18.388	0.540	2.135	0.811	2.632	92	1/25/20
93	20130125@73.asc	SHell 20 ult gam 73 (low yield)			17.510	0.631	2.009	0.810	2.479	87	1/25/20
94	20130125@74.asc	Shell 21 penult gam 74	28.18	0.24	18.429	0.569	2.078	0.809	2.568	90	1/25/20
95	20130125@75.asc	Shell 21 ult 75	27.90	0.24	18.160	0.445	2.038	0.794	2.566	90	1/25/20
96	20130125@76.asc	Shell 21 penult 76 (low yield)			14.828	0.828	1.801	0.795	2.265	79	1/25/20
97	20130125@77.asc	Shell 22 S 77	27.13	0.24	17.393	0.509	2.043	0.798	2.561	90	1/25/20
98	20130125@78.asc	Shell 22 S gam 78	27.84	0.24	18.094	0.468	2.126	0.798	2.665	93	1/25/20
99	20130125@79.asc	Shell 23 E gam 79	28.26	0.24	18.511	0.444	2.120	0.791	2.682	94	1/25/20
100	20130125@80.asc	Shell 23 NW 80	28.42	0.24	18.675	0.539	2.030	0.785	2.587	90	1/25/20
101	20130125@81.asc	Shell 24 N 81	28.75	0.24	18.998	0.501	2.083	0.770	2.705	95	1/25/20
102	20130125@82.asc	Shell 25 N 82	28.73	0.24	18.975	0.465	2.061	0.763	2.703	94	1/25/20
103	20130125@83.asc	Shell 25 N 83	28.12	0.24	18.370	0.403	1.953	0.753	2.593	91	1/25/20
104	20130125@84.asc	Shell 26 S 84 (low yield)			16.323	0.725	1.857	0.750	2.477	87	1/25/20
105	20130125@85.asc	Shell 26 S 85	29.00	0.24	19.243	0.585	2.027	0.742	2.733	96	1/25/20
106	20130125@86.asc	Shell 27 W 86 (low yield)			14.351	1.583	1.586	0.732	2.167	76	1/25/20
107											
108	20130125@87.asc	UWC-3			3.013	0.508	2.078	0.728	2.854		1/25/20
109	20130125@88.asc	UWC-3			2.982	0.507	2.071	0.720	2.878		1/25/20
110	20130125@89.asc	UWC-3, Cs-res. = 156			3.045	0.479	2.127	0.750	2.835		1/25/20
111	20130125@90.asc	UWC-3			2.976	0.415	2.149	0.773	2.780		1/25/20
112		**bracket: average and 2 SD**		**0.99052**	**2.892**	**0.235**			**2.860**		

high internal 2SE (internal precision): pit crosscutting epoxy and/or secondary phase

low ^{16}O count rate, low yield: sample porosity, pit crosscutting epoxy

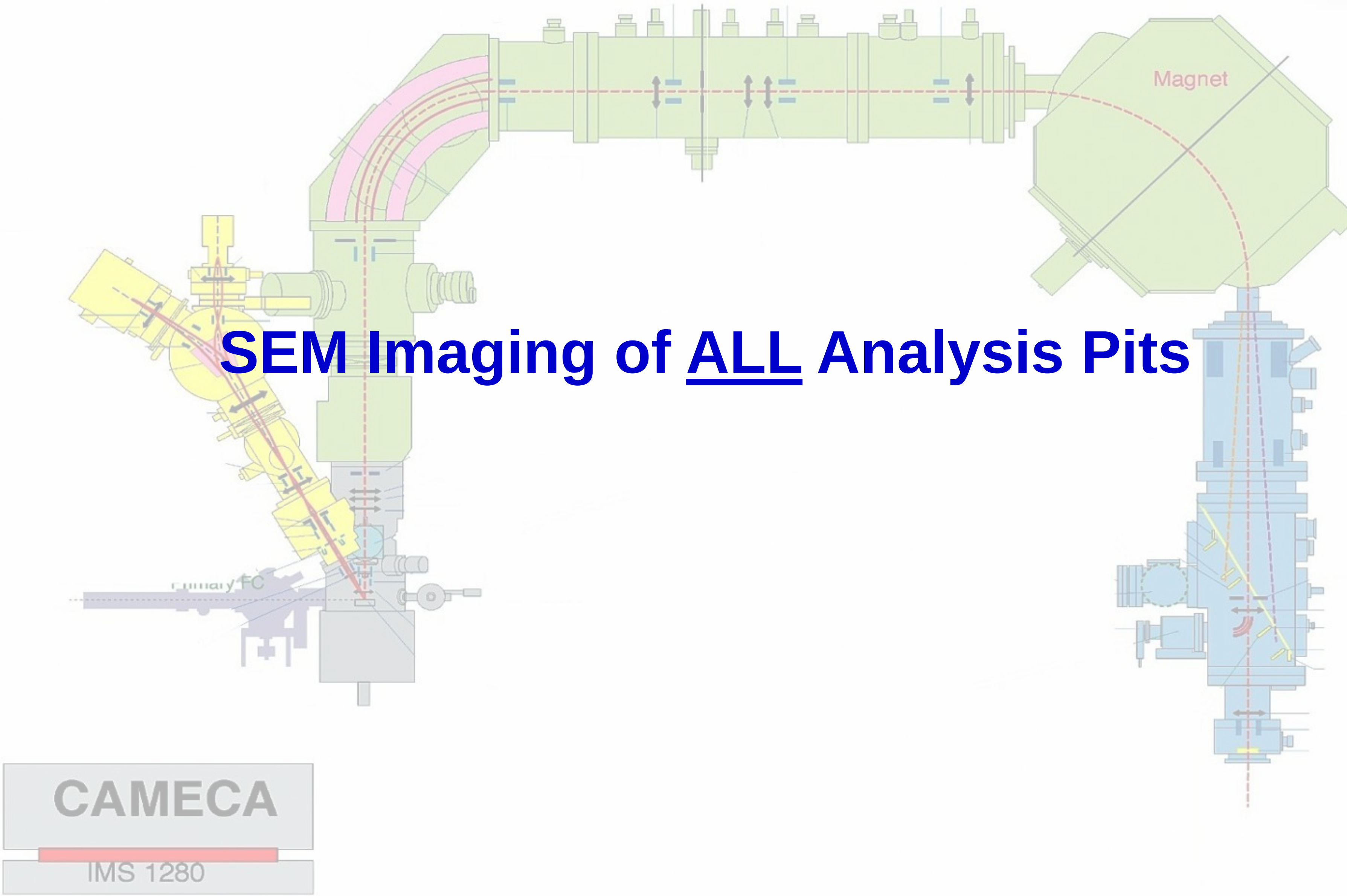


Data plotting outside the red dashed lines (yield <97% or >103% of the yield of the bracketing standards) were excluded, These pits likely contain a higher percentage of organics or are irregular (sample porosity, cavities, cracks, secondary phases).

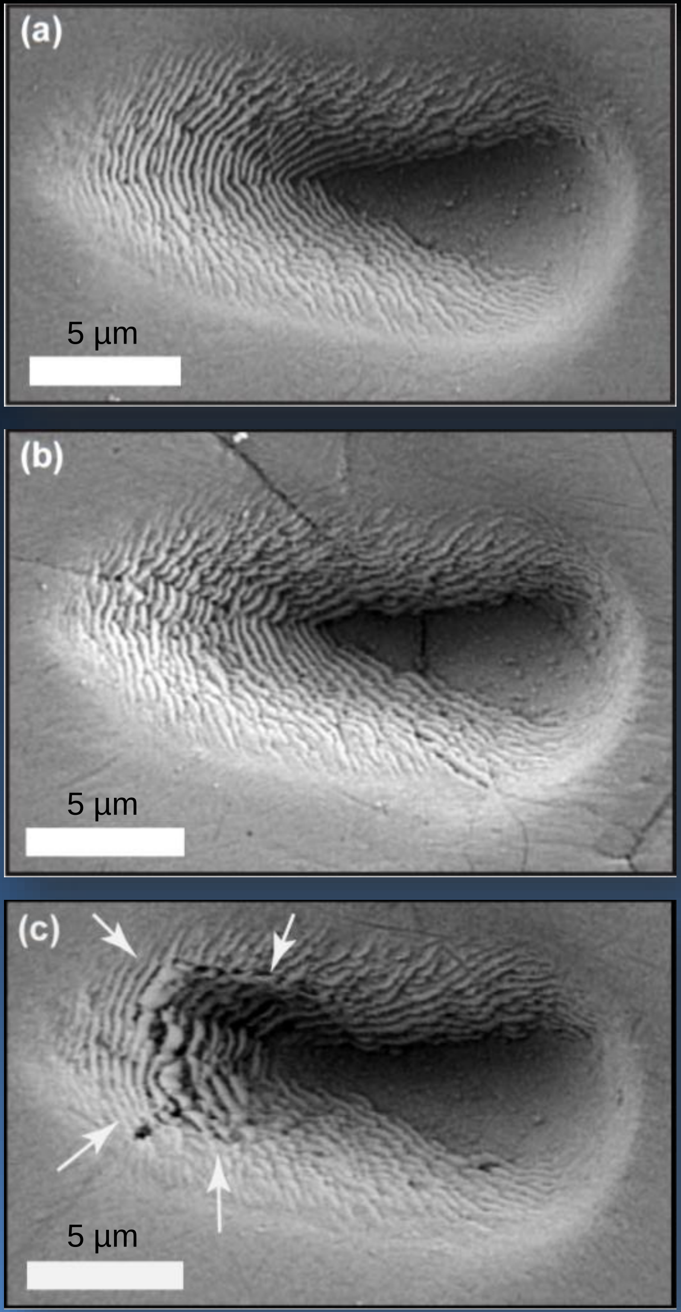


Data from pits with a yield of <97% or >103% of the yield in the bracketing standards were excluded. The remaining data show no correlation between yield and measured $\delta^{18}O$. The $\delta^{18}O$ values are corrected for instrumental drift, but not converted to the SMOW or PDB scale.

SEM Imaging of ALL Analysis Pits



Examples of ‘regular’ and ‘irregular’ ion microprobe pits in zircon following $\delta^{18}O$ analysis



Cavosie et al. 2005, EPSL

(a) ‘**Regular**’ pit, showing slight asymmetry due to inclination of primary beam

(b) ‘**Irregular**’ pit with through-going cracks, visible in the crater walls and floor

(c) ‘**Irregular**’ pit with a circular ‘cavity’ at the left side (defined by arrows). The analysis hit a mineral inclusion. Preferential sputtering of the inclusion is thought to have caused this feature. Pits are approximately 2-3 µm in depth.

It is tempting to accept data from ‘irregular’ pits. Such features often have no measurable affect on isotope ratio, however non-systematic and sometimes large shifts in measured $\delta^{18}O$ (up to +12‰ reported by Cavosie et al., 2005) demonstrate the importance to describe and evaluate ‘irregular’ pits.

Evaluation of SIMS analysis pits by SEM: Otolith

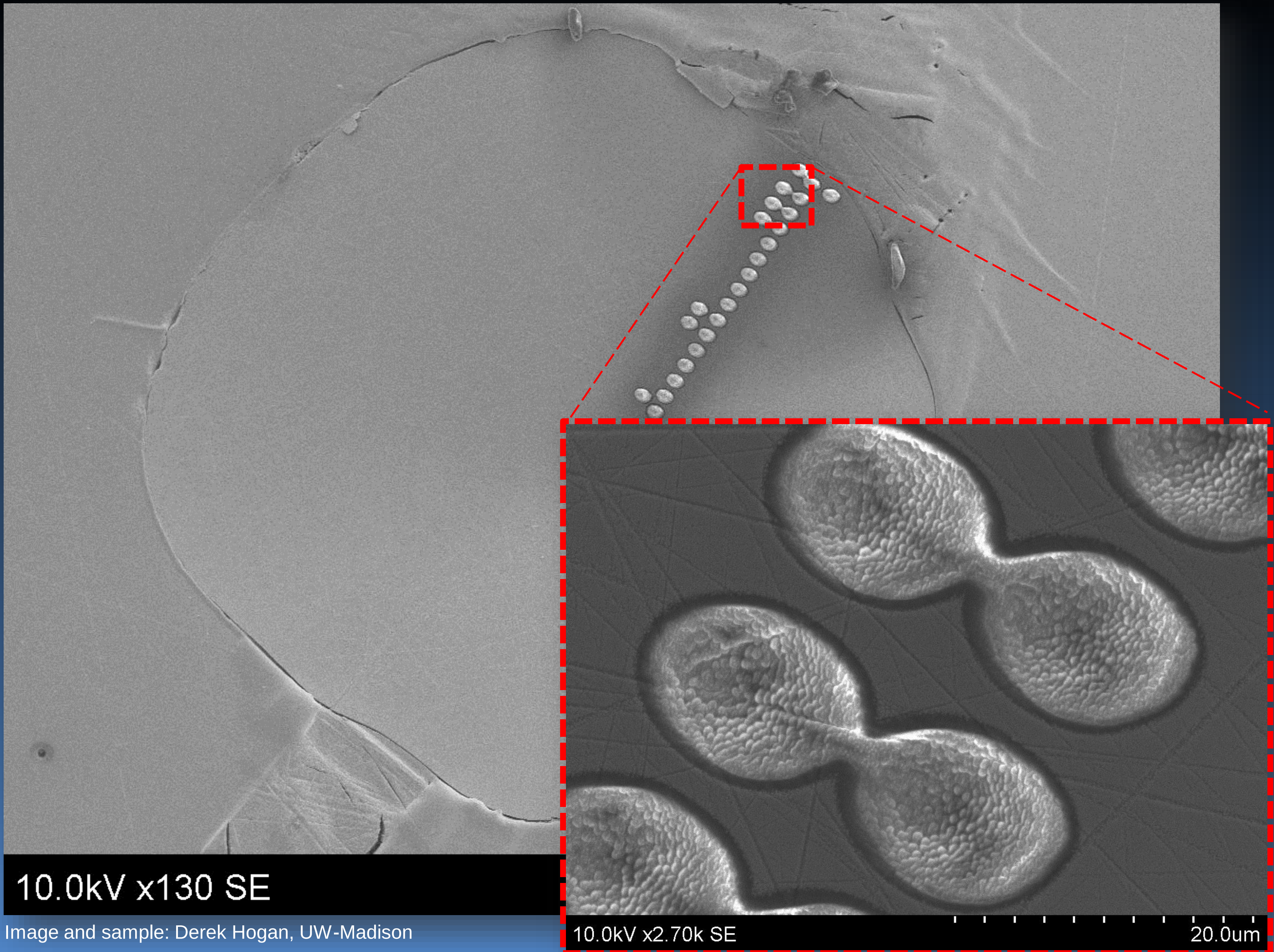
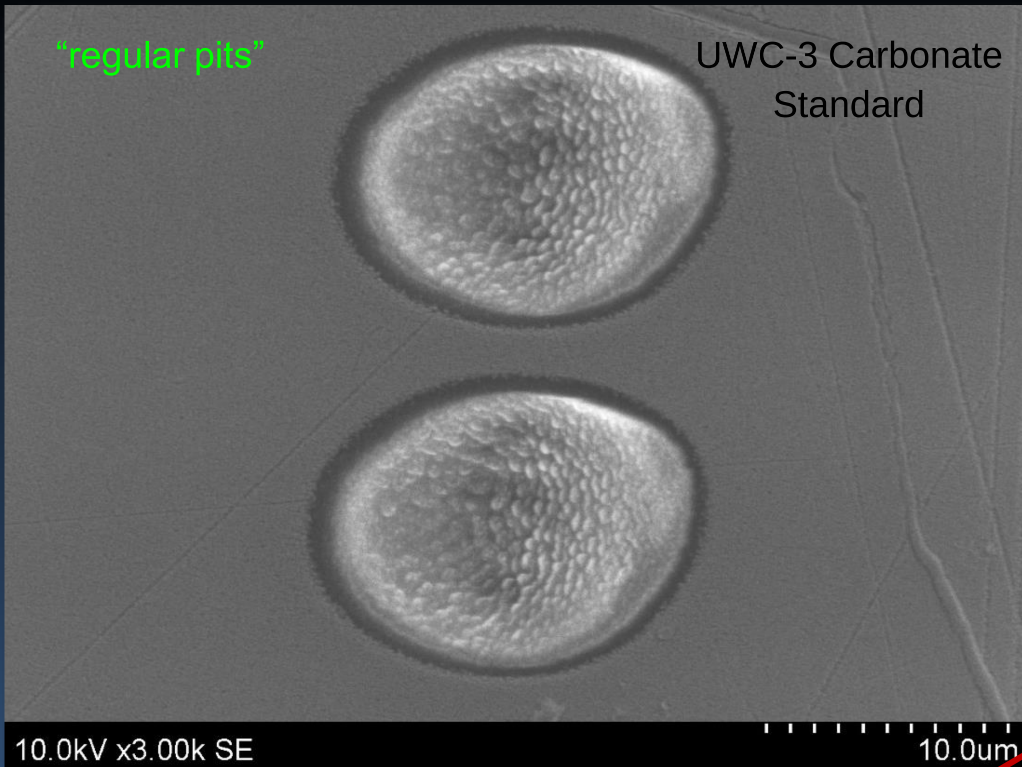
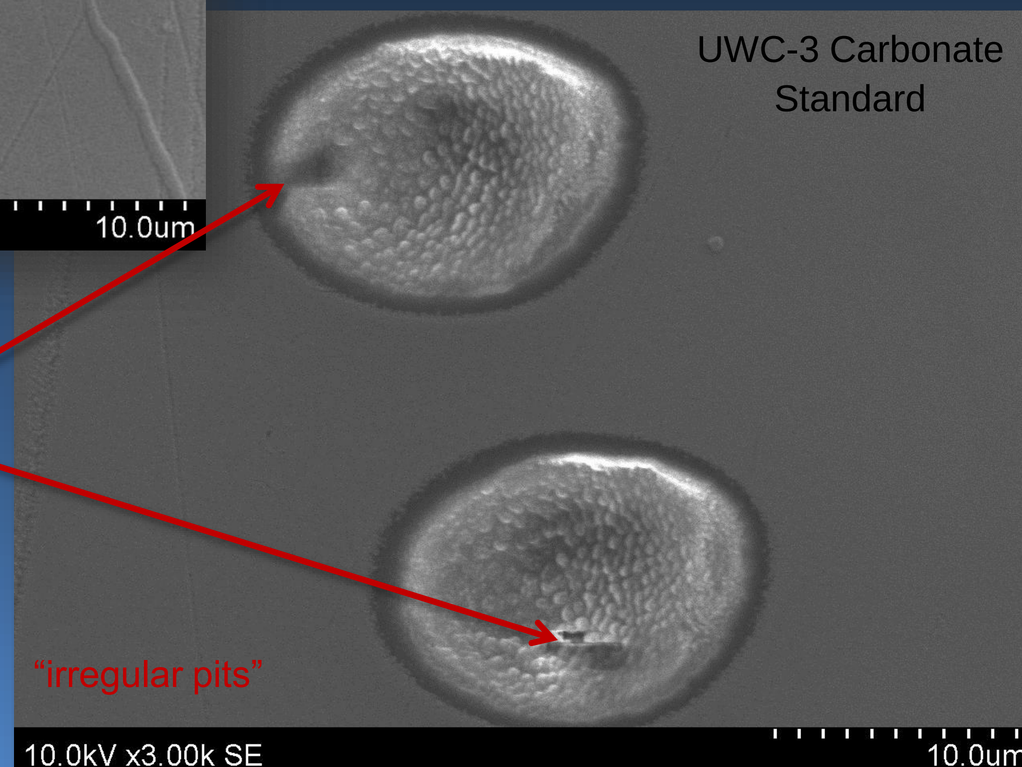


Image and sample: Derek Hogan, UW-Madison

Evaluation of SIMS analysis pits by SEM: UWC-3 carbonate STD

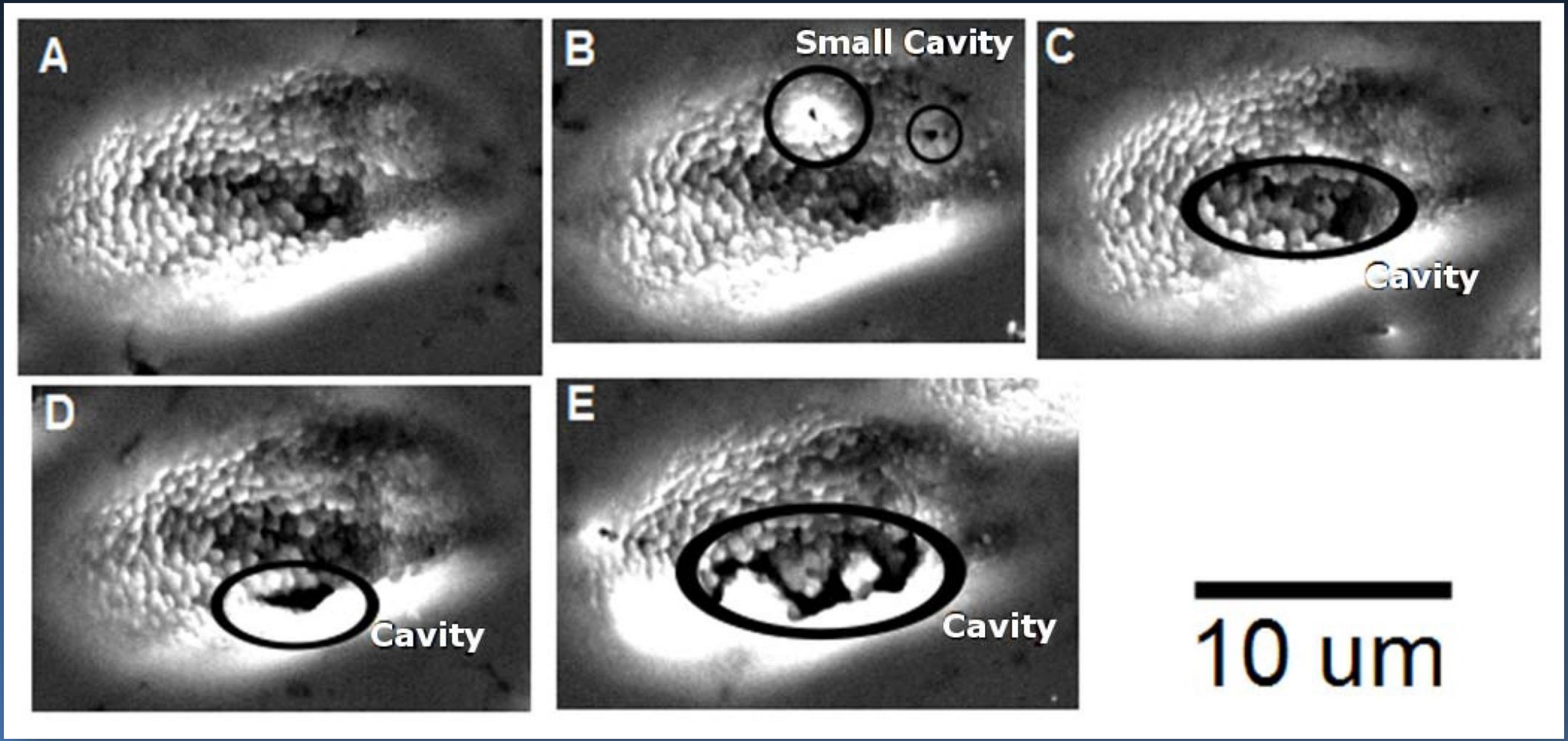




cavities and/or inclusions
data from these pits should not be used

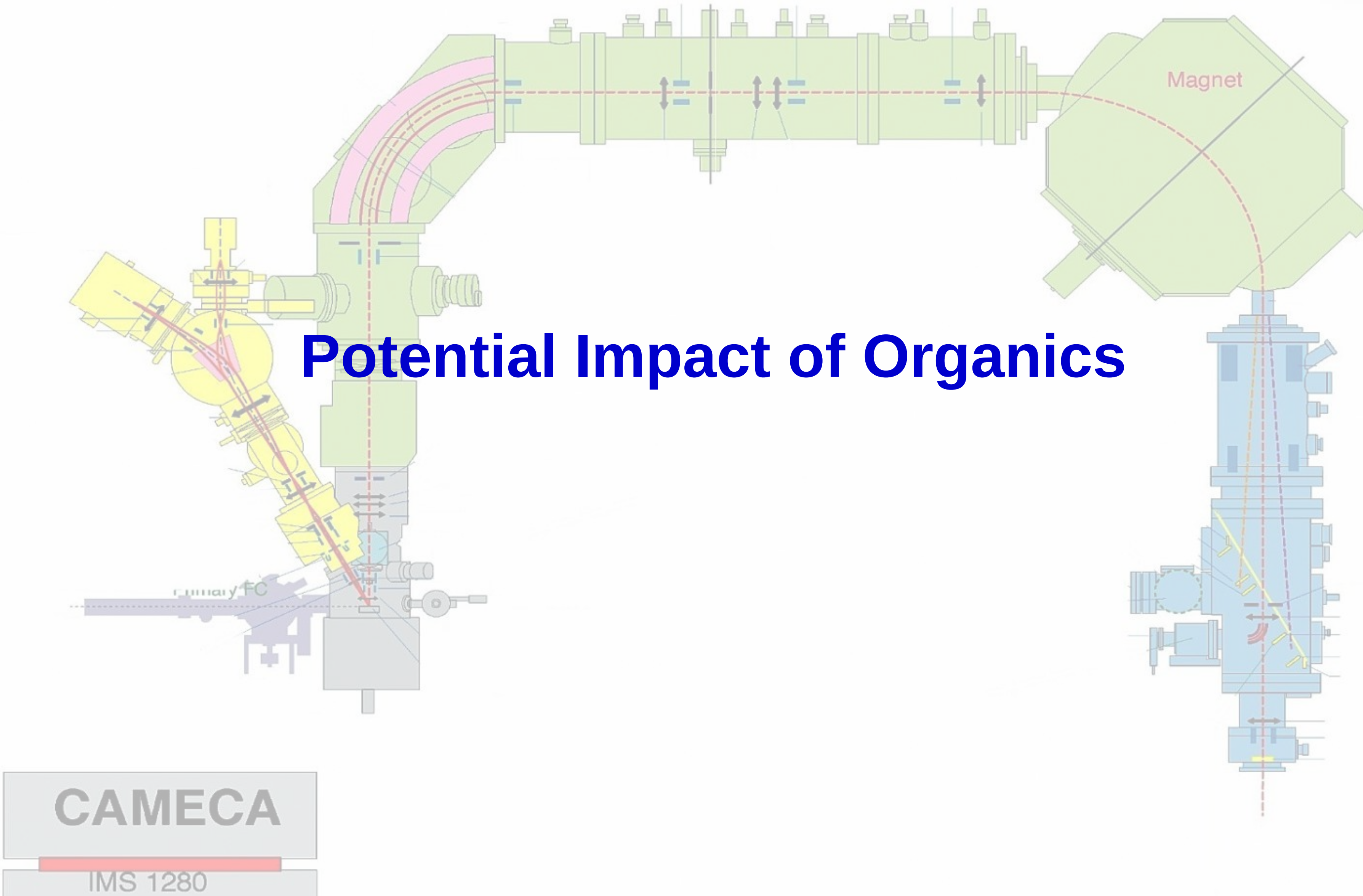
Evaluation of SIMS analysis pits by SEM: Nautilus shell (prismatic nacre)

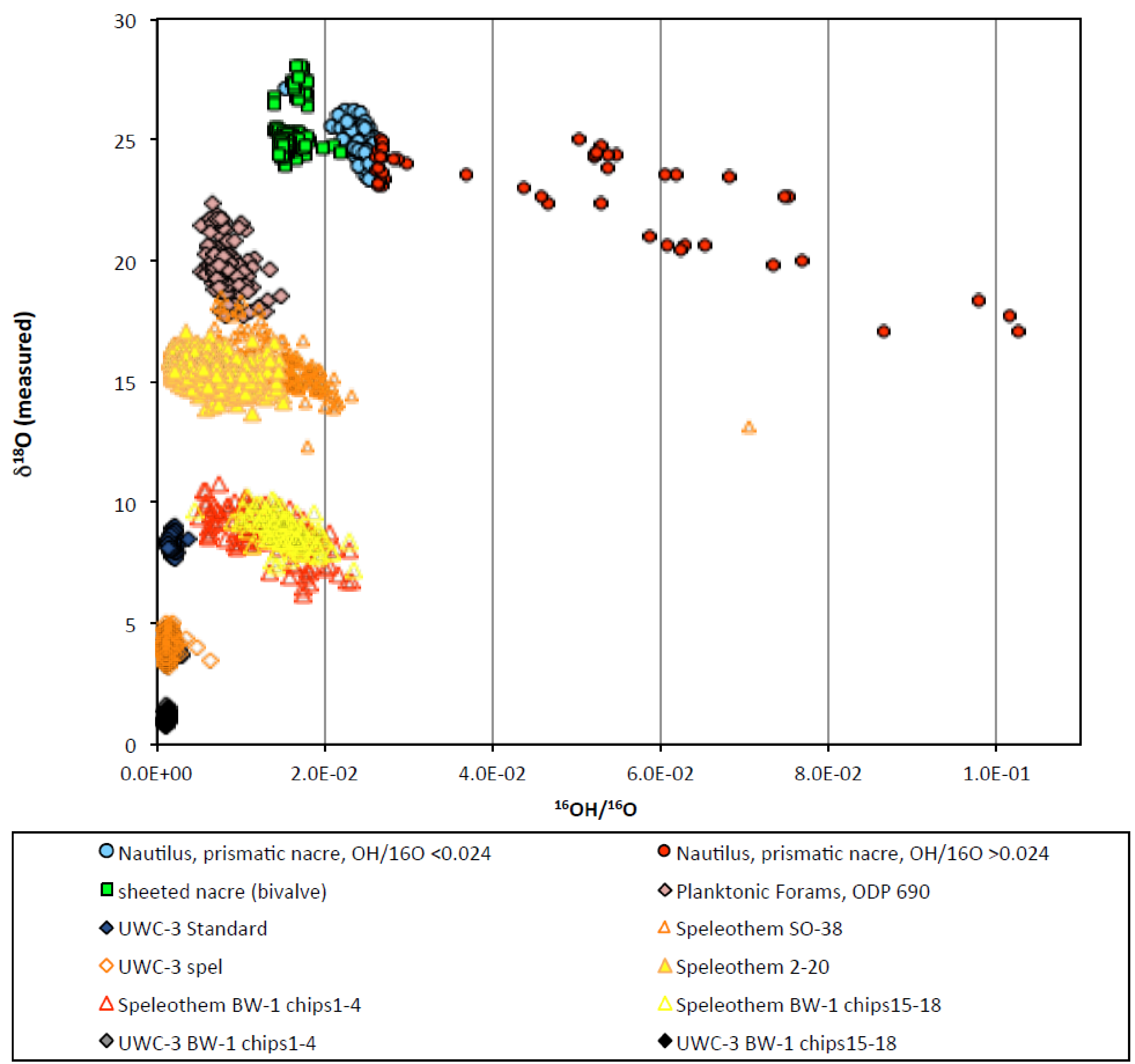
Regular and irregular pits in the prismatic aragonite shell



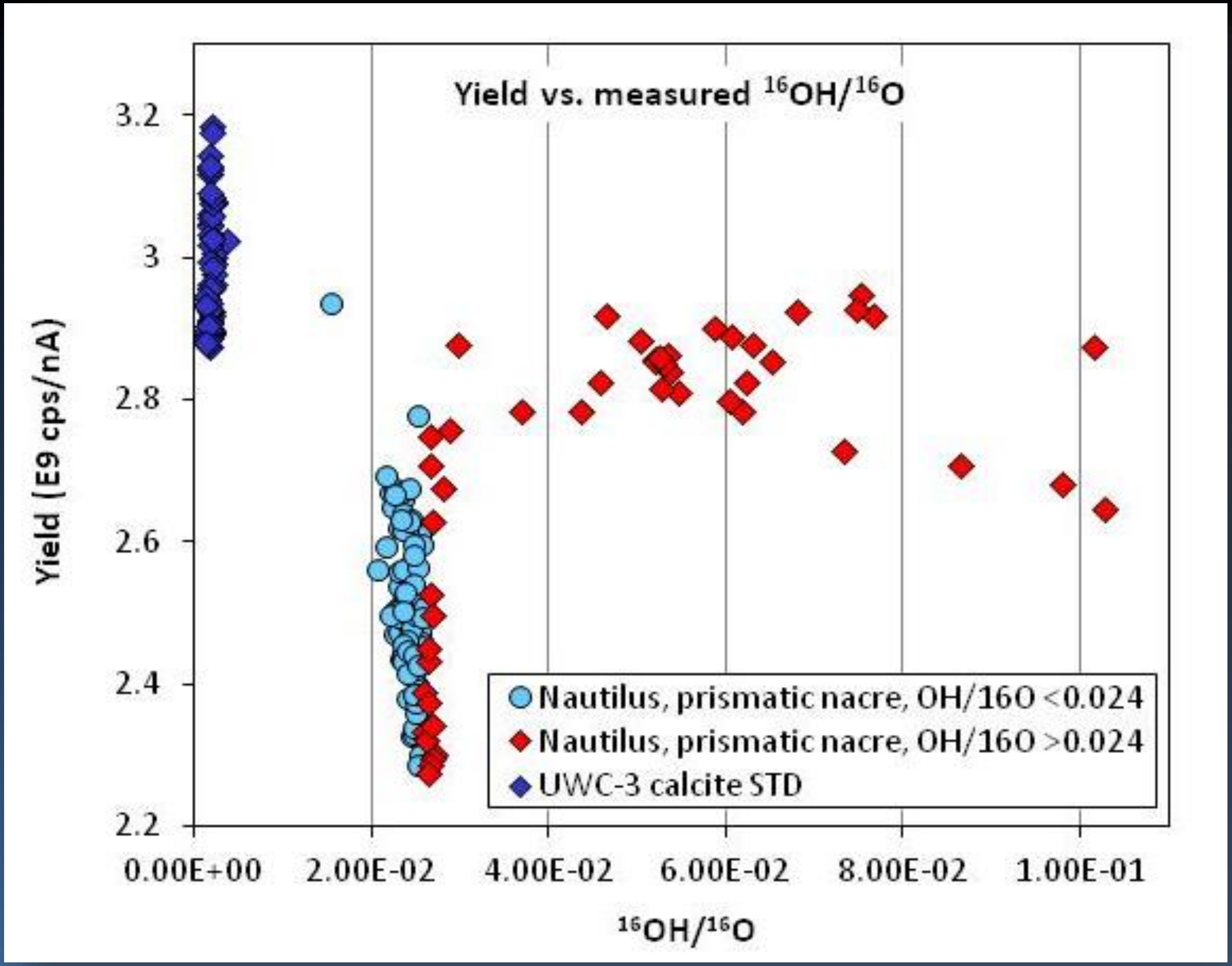
Linzmeier et al., in prep.

Potential Impact of Organics



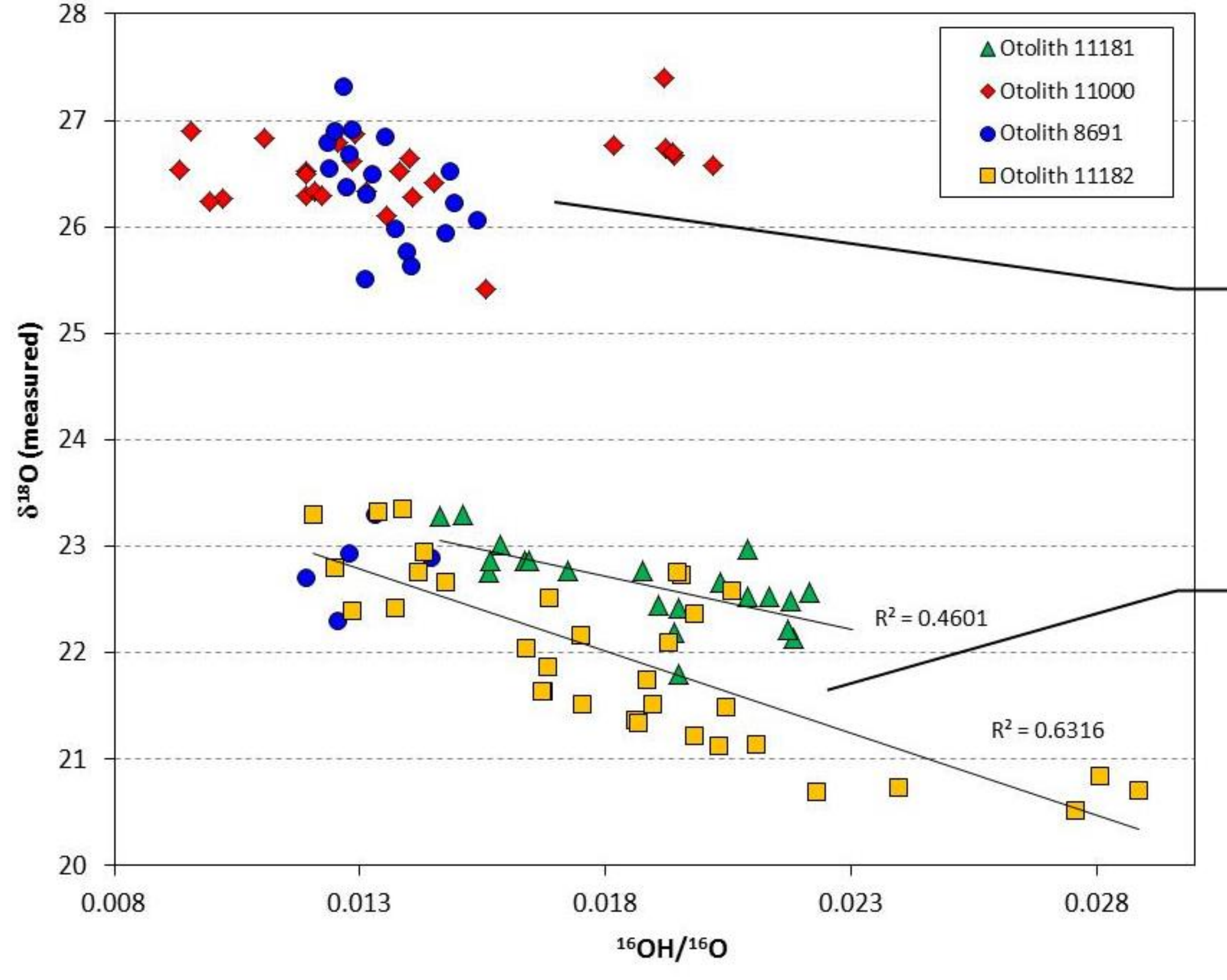


30
25
20
15
10
5
0
δ18O (measured)
0.0E+00
2.0E-02
4.0E-02
6.0E-02
8.0E-02
1.0E-01
16OH/16O
Nautilus, prismatic nacre, OH/16O <0.024
Nautilus, prismatic nacre, OH/16O >0.024
sheeted nacre (bivalve)
Planktonic Forams, ODP 690
UWC-3 Standard
Speleothem SO-38
UWC-3 spel
Speleothem 2-20
Speleothem BW-1 chips1-4
Speleothem BW-1 chips15-18
UWC-3 BW-1 chips1-4
UWC-3 BW-1 chips15-18



High $^{16}OH/^{16}O$ ratios indicate the presence of H, presumably organic material, in the analysis pit. The yield in the nonporous standard (UWC-3, coarse crystalline calcite) is about 10% higher than in the porous nautilus shell. Highest yields in the nautilus shell are observed in domains with a high $^{16}OH/^{16}O$ signal (or a high proportion of organics, respectively).

Removal of organics: Sample roasting (Example: Otoliths)

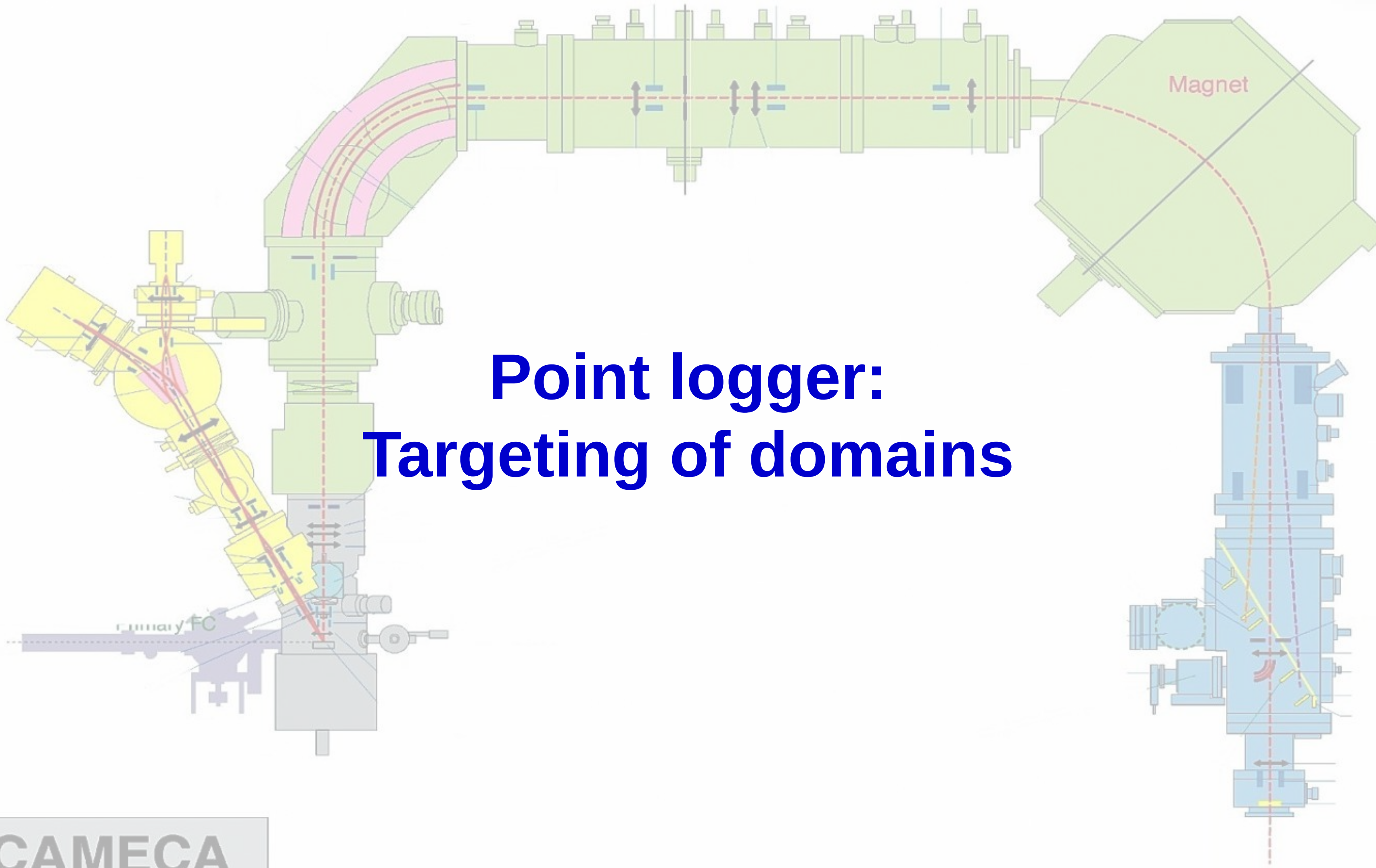


These otoliths represent two different rivers/water masses. They are smaller than the other two samples, however, they were roasted for a longer period of time (2 h at 262ºC).

These otoliths represent the same river/water mass. They are larger than the other two samples, however, they were roasted for a shorter period of time (30 min at 262ºC).

They may have disintegrated when roasted for a longer period. Chemical treatment?

Biocarbonates containing significant amount of organics (e.g. otoliths, bivalves, mollusks) should be roasted or chemically treated to remove organics. However, this may cause disintegration of the sample, therefore, “practice”- samples should be used to evaluate the best procedure.

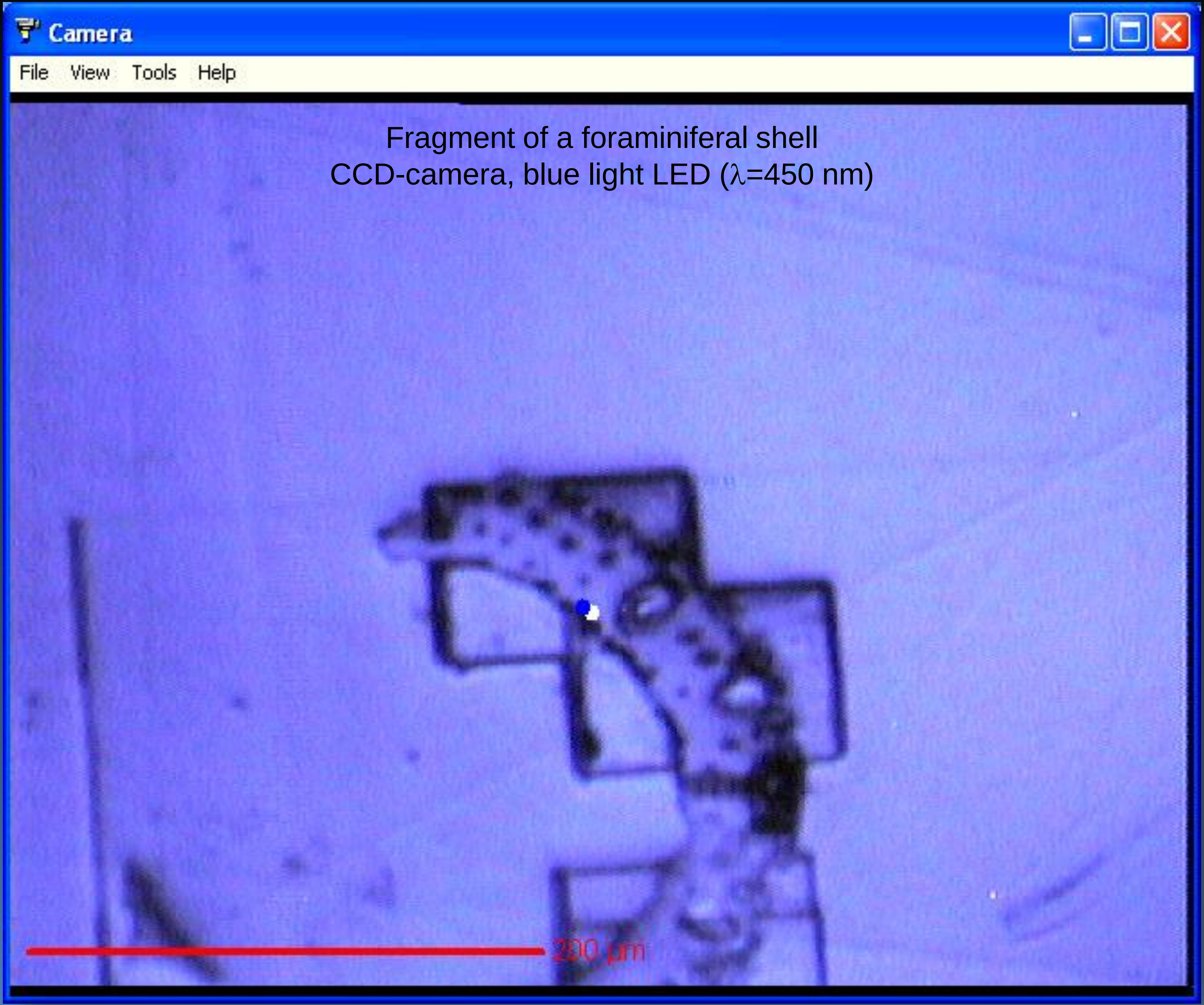


Point logger:
Targeting of domains

CAMECA

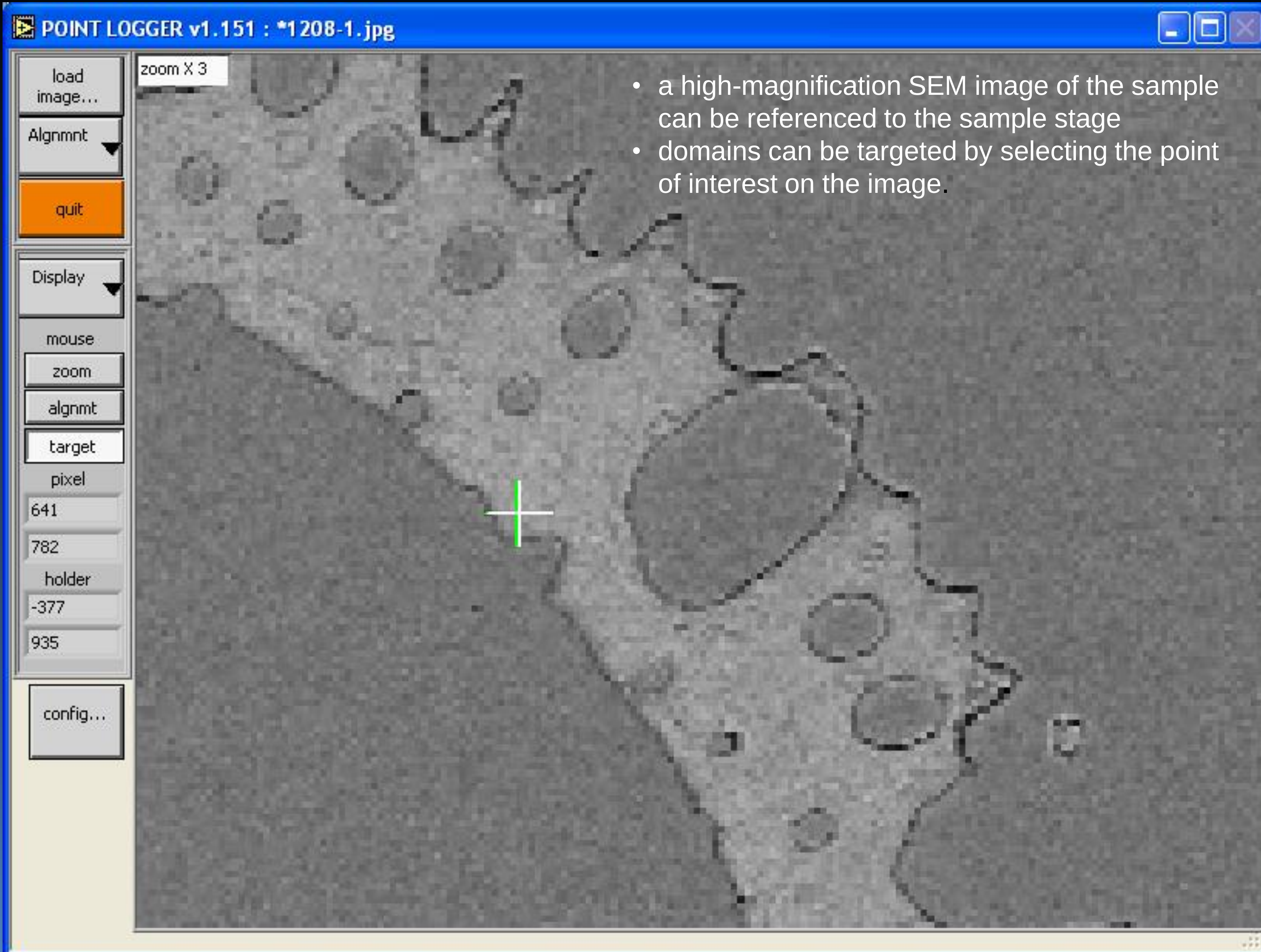
IMS 1280

Sample view by the built-in CCD camera



Vetter et al. 2013, GCA

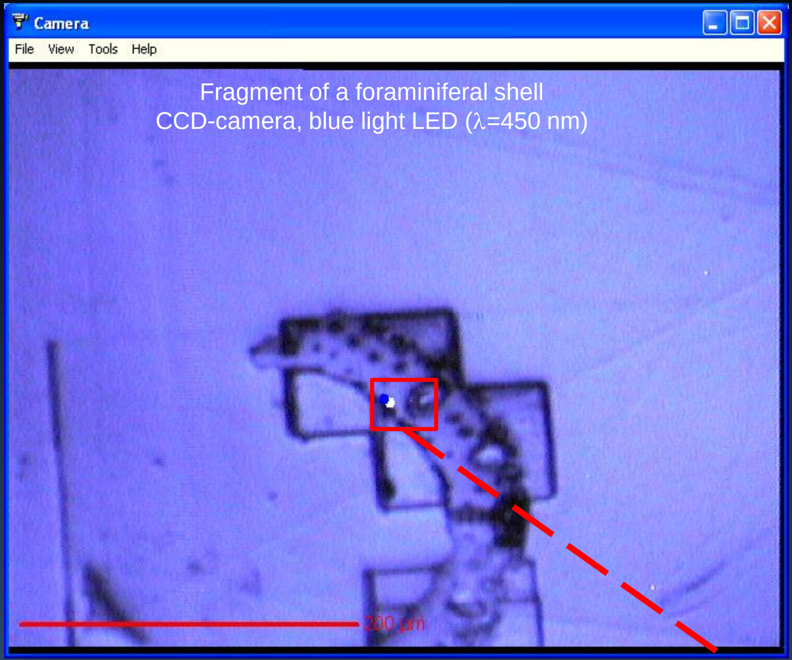
Point-Logger

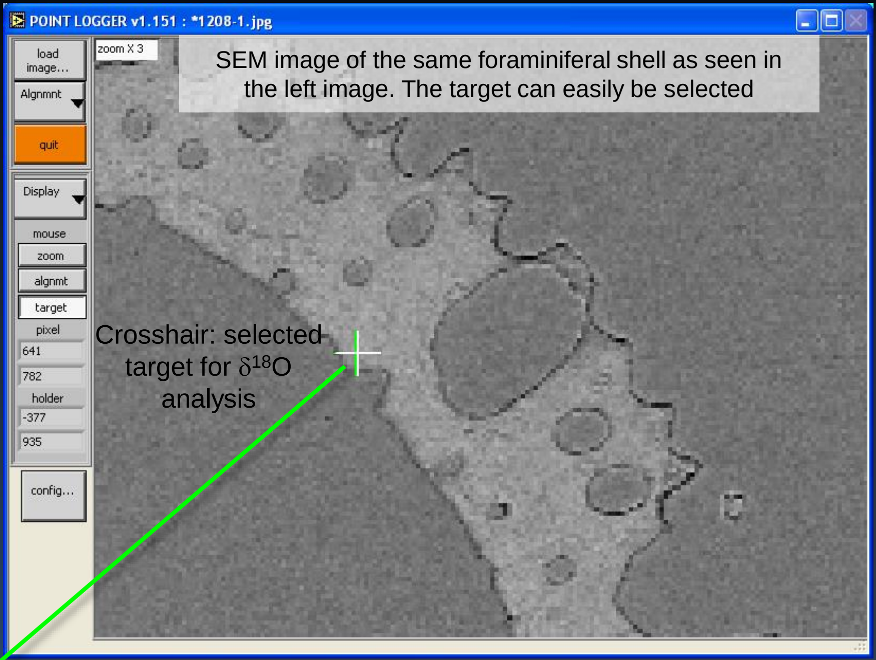


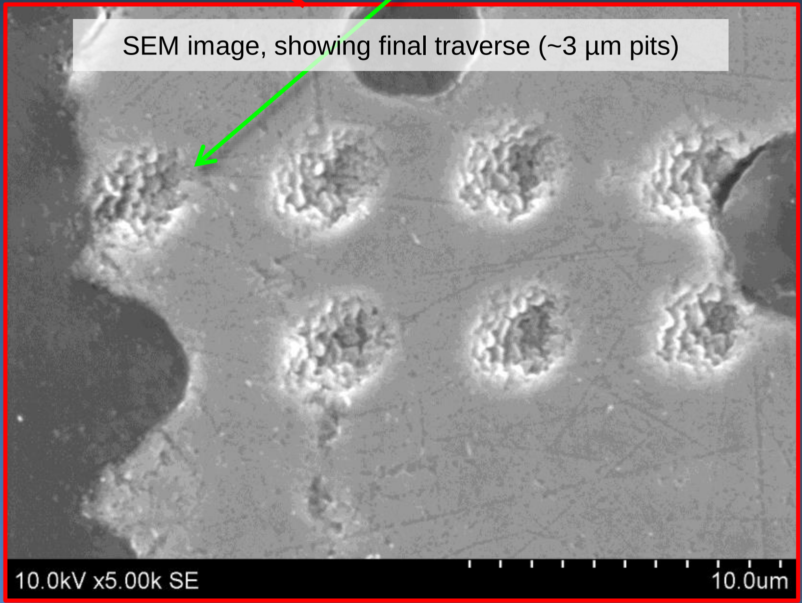
- a high-magnification SEM image of the sample can be referenced to the sample stage
- domains can be targeted by selecting the point of interest on the image.

During analysis, the sample can be seen by an optical microscope/CCD-camera. This representative image demonstrates the aiming-process (primary beam hits at blue marker). Typically this system is used for sample navigation and aiming.

For some types of samples, the resolution of the optical microscope (left image) is insufficient for precise aiming. We can upload SEM images (field of view ~500 µm) and align them to the sample stage. Subsequently, targets can be selected using the more detailed/higher resolution SEM image.





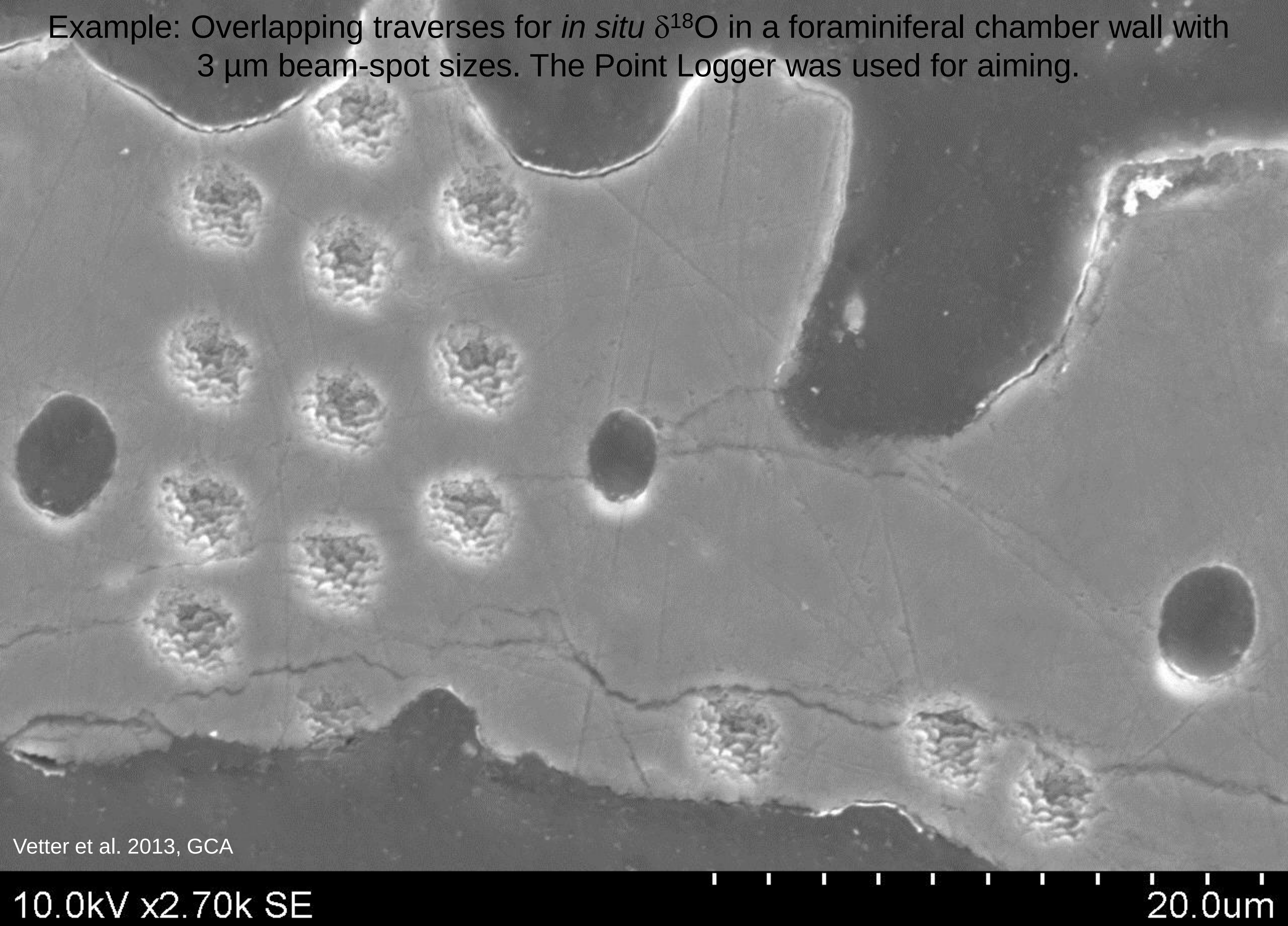


Point Logger

Using SEM images for precise aiming

Vetter et al. 2013, GCA
doi: http://dx.doi.org/10.1016/j.gca.2012.12.046

Example: Overlapping traverses for *in situ* δ^{18}O in a foraminiferal chamber wall with 3 µm beam-spot sizes. The Point Logger was used for aiming.



Vetter et al. 2013, GCA

Thank you!