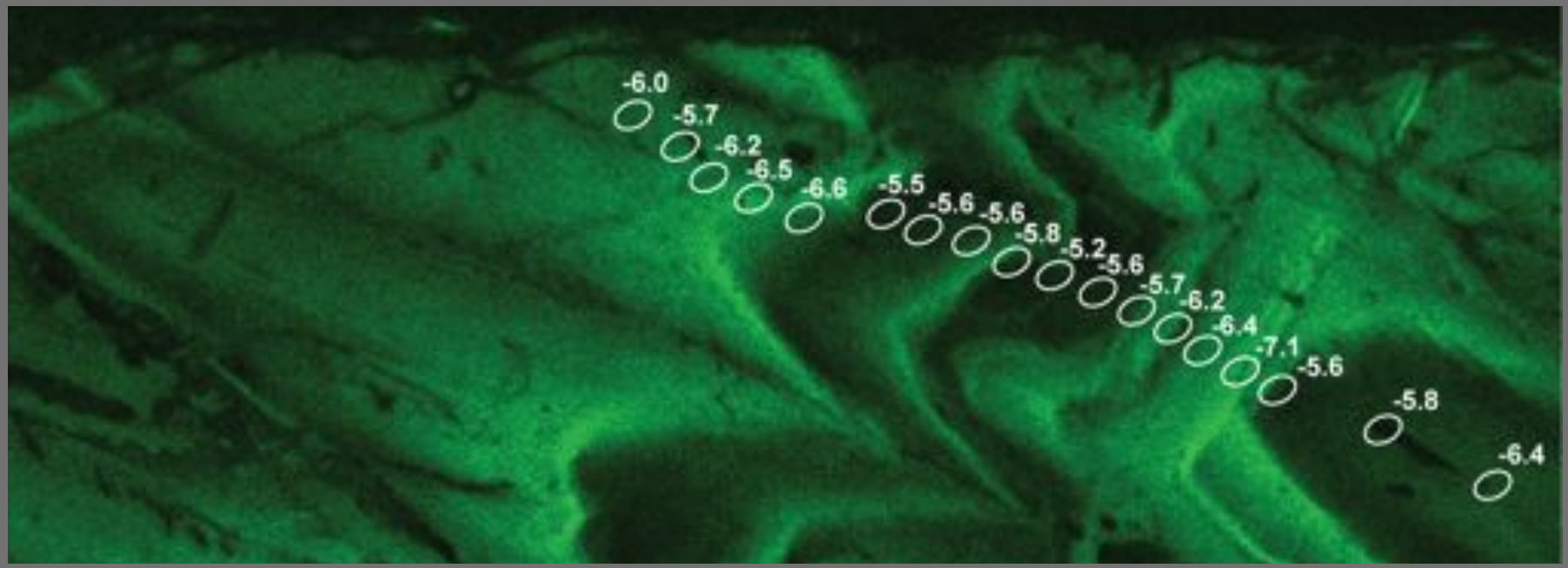
SpeleoSIMS

Developments and challenges in ion microprobe studies of speleothems at WiscSIMS



Ian J. Orland
NSF Postdoctoral Research Fellow
University of Minnesota – Twin Cities
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SpeleoSIMS

Developments and challenges in ion microprobe studies of speleothems at WiscSIMS

John W. Valley
Noriko T. Kita
Taka Ushikubo
Reinhard Kozdon
Kouki Kitajima
Ben Linzmeier
Mike Spicuzza
Brian Hess
Mira Bar-Matthews
Alan Matthews
Avner Ayalon
Yuval Burstyn

NSF, DOE, The Comer Foundation, Sigma Xi, BP, UW-Madison, and the Geological Survey of Israel

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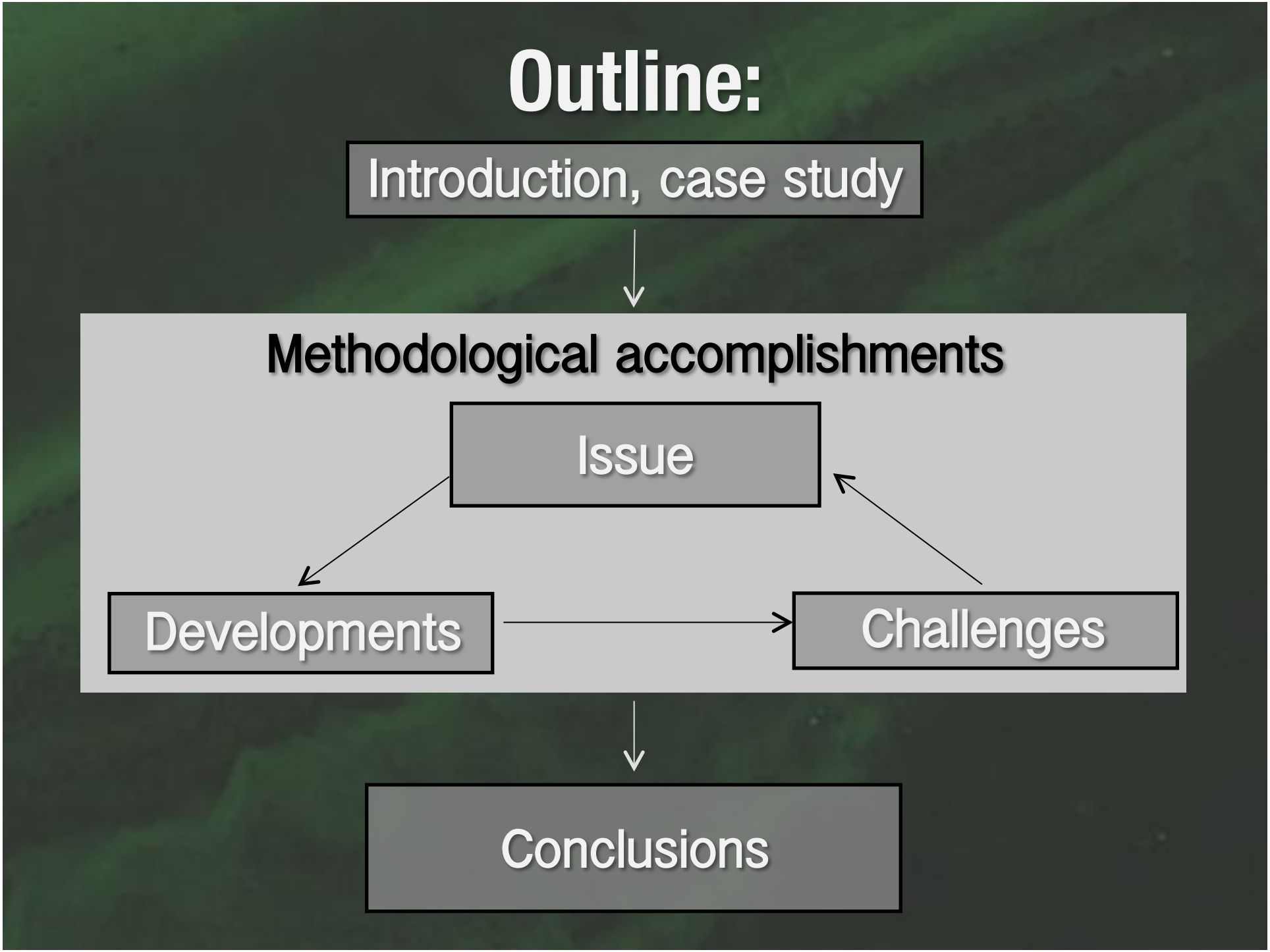
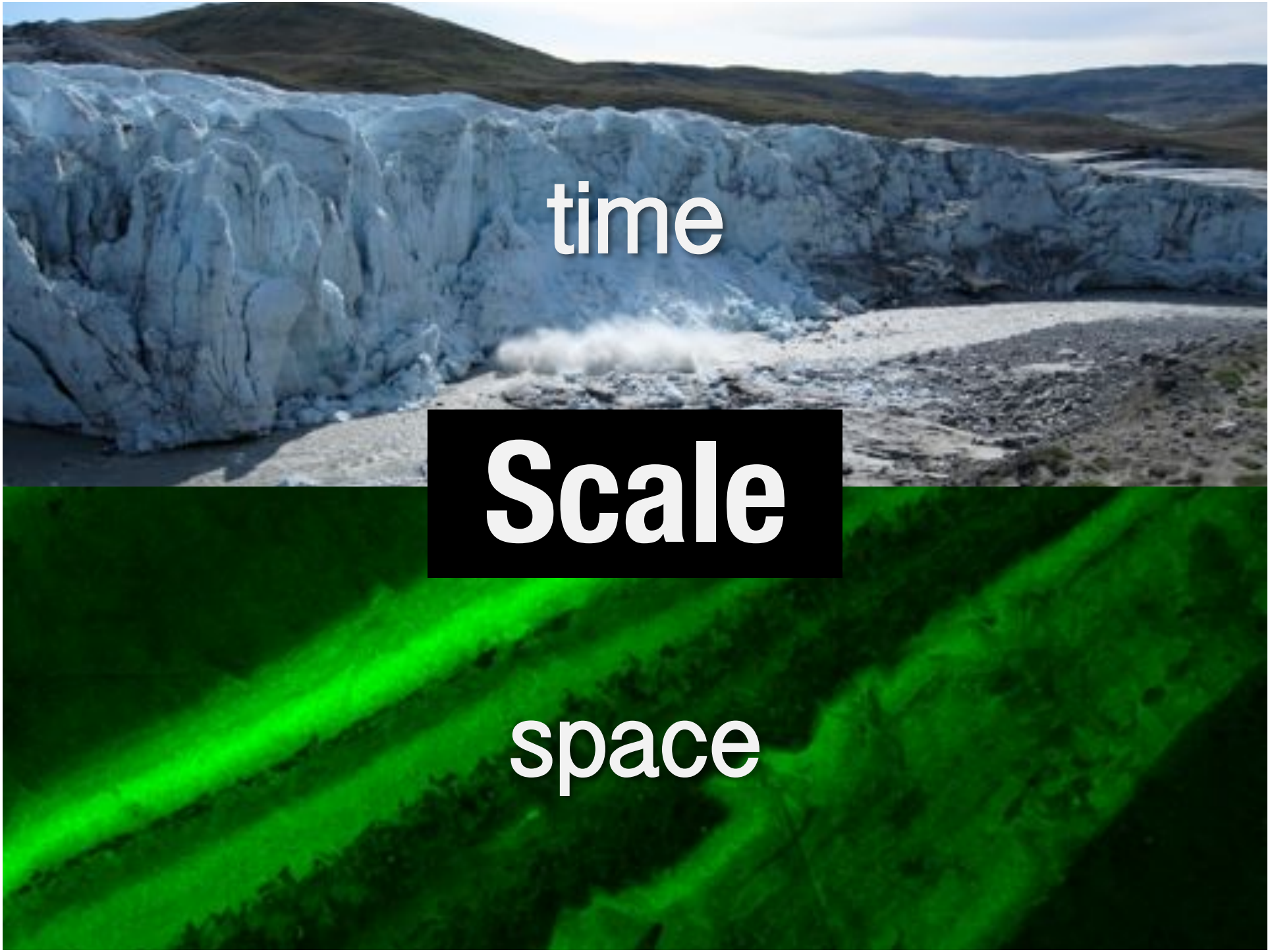
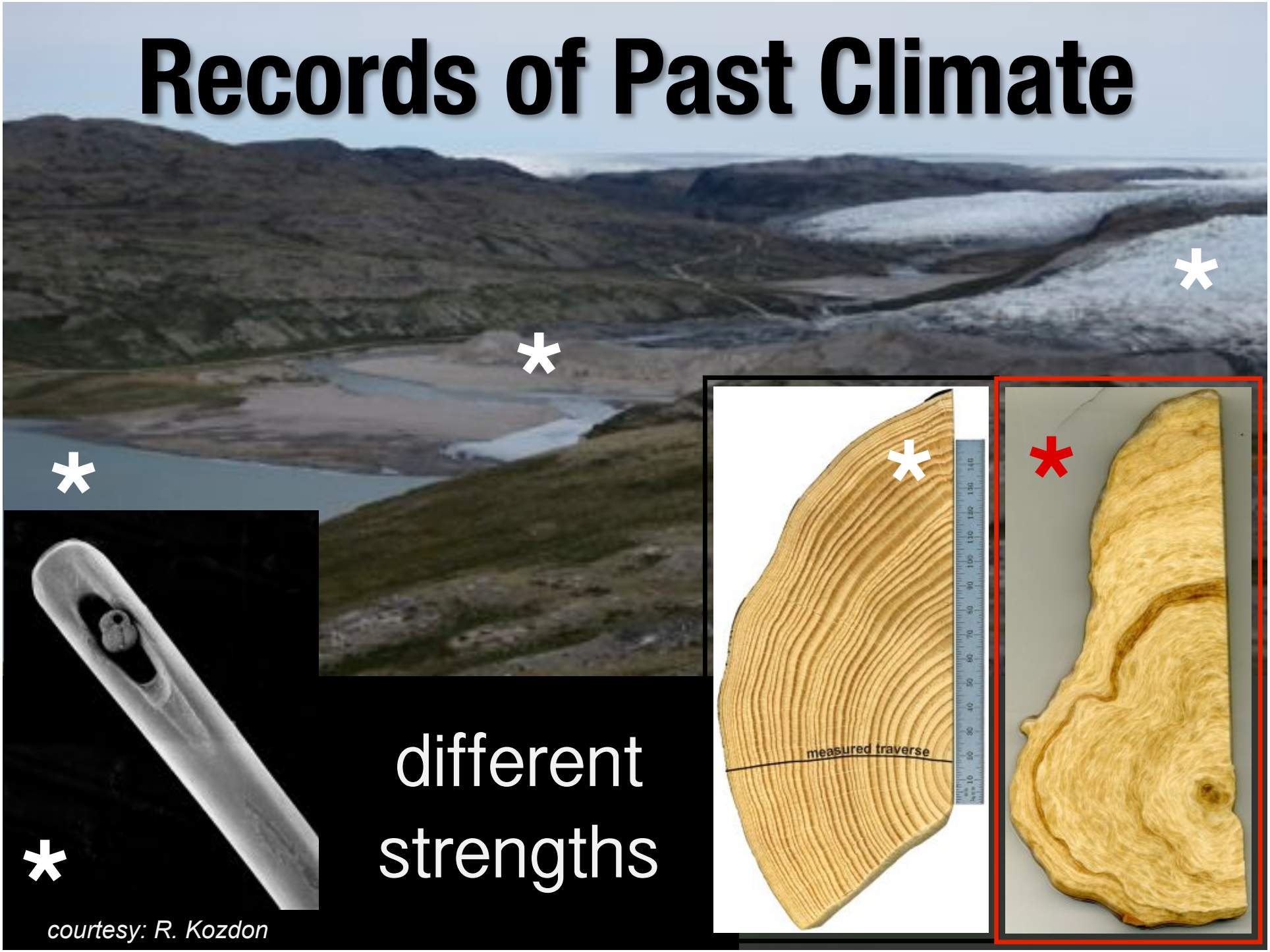
Outline:

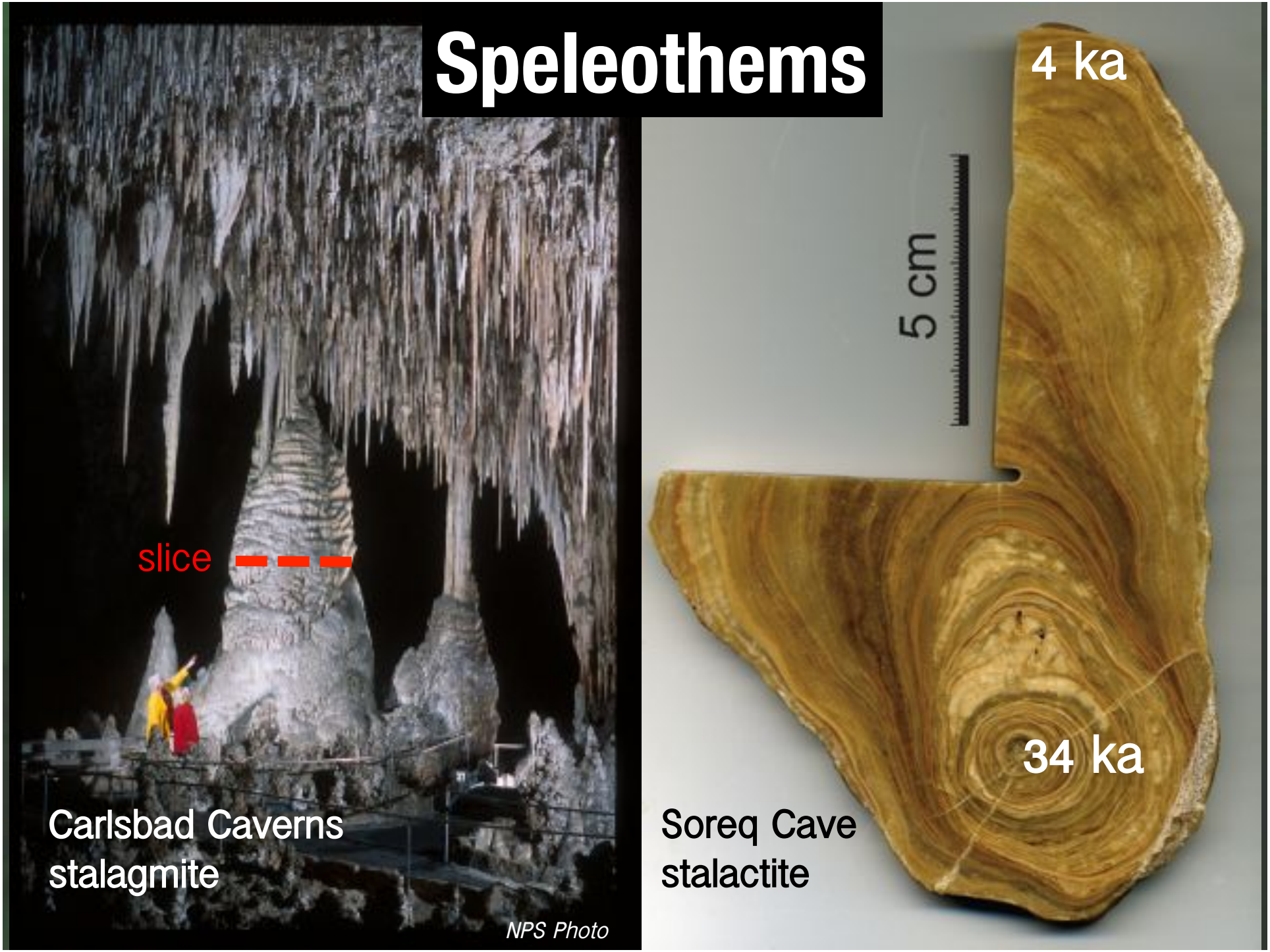

Introduction, case study
Methodological accomplishments
Issue
Developments
Challenges
Conclusions


time
Scale
space

Records of Past Climate

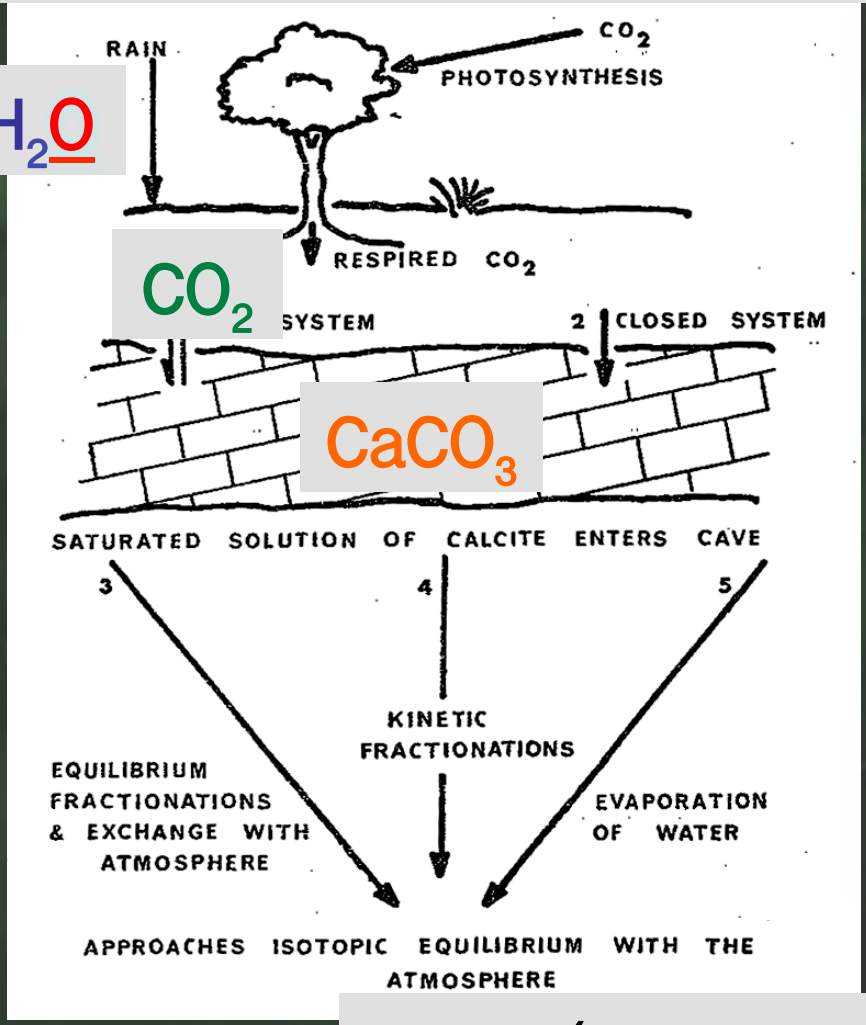


Speleothems



Speleothem formation

$$H_2O + CO_2 + CaCO_3 = Ca^{2+} + 2HCO_3^-$$



H_2O

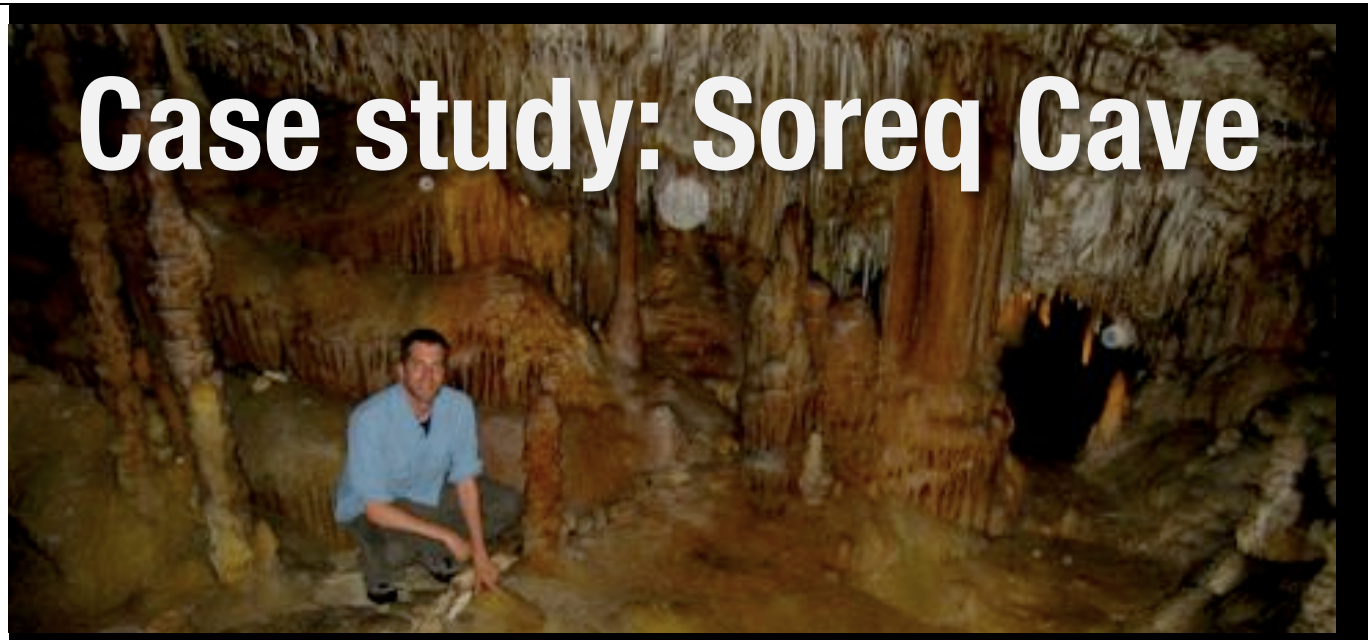
CO_2

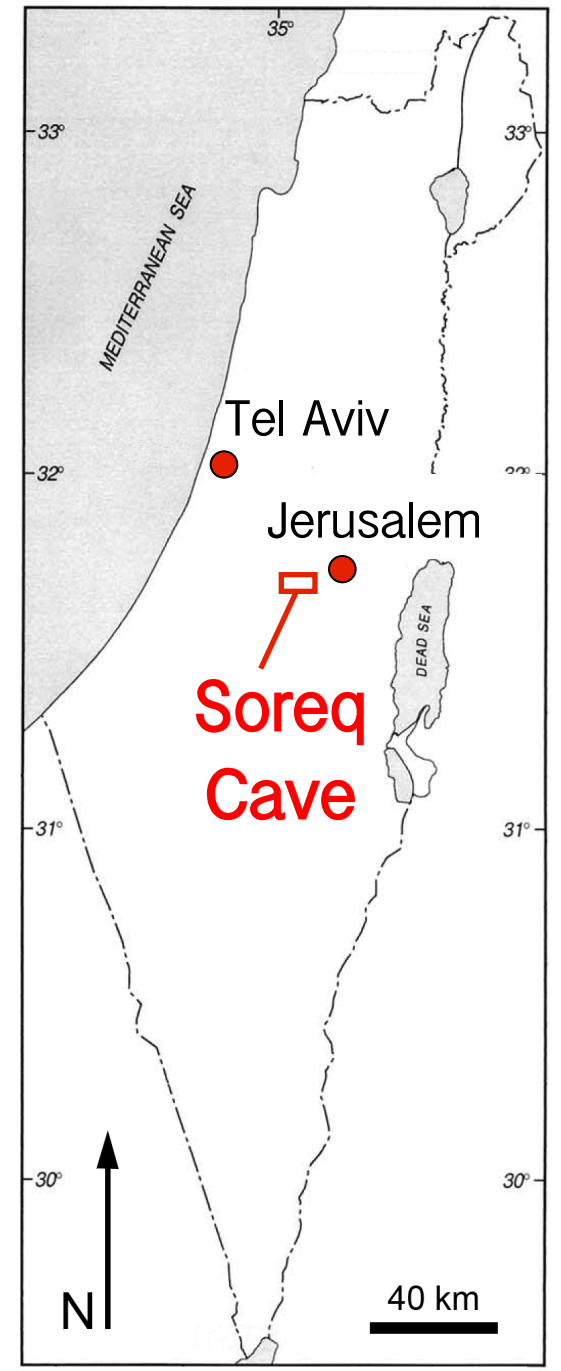
$CaCO_3$

adapted from Hendy, 1971

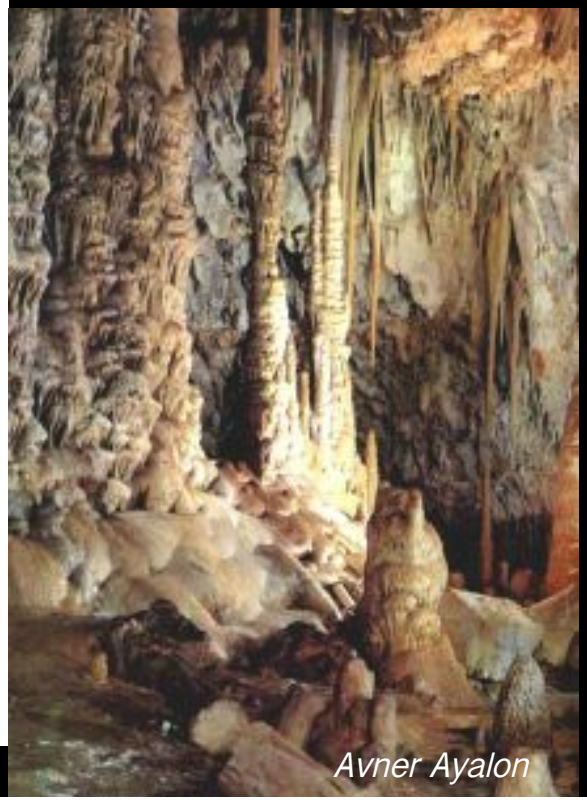
$CaCO_3$ (Stalagmite)

Case study: Soreq Cave

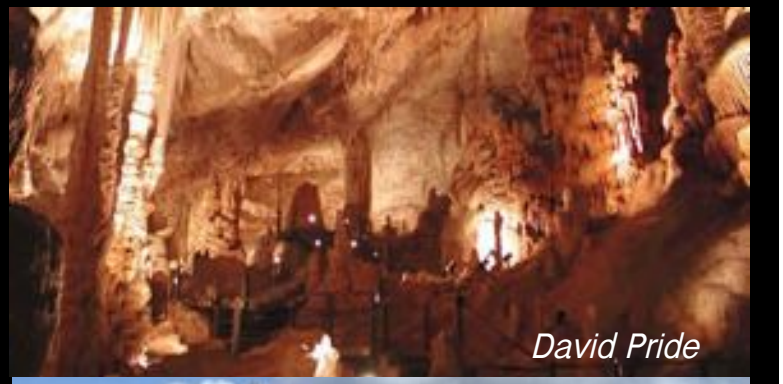




Ayalon et al., 1998



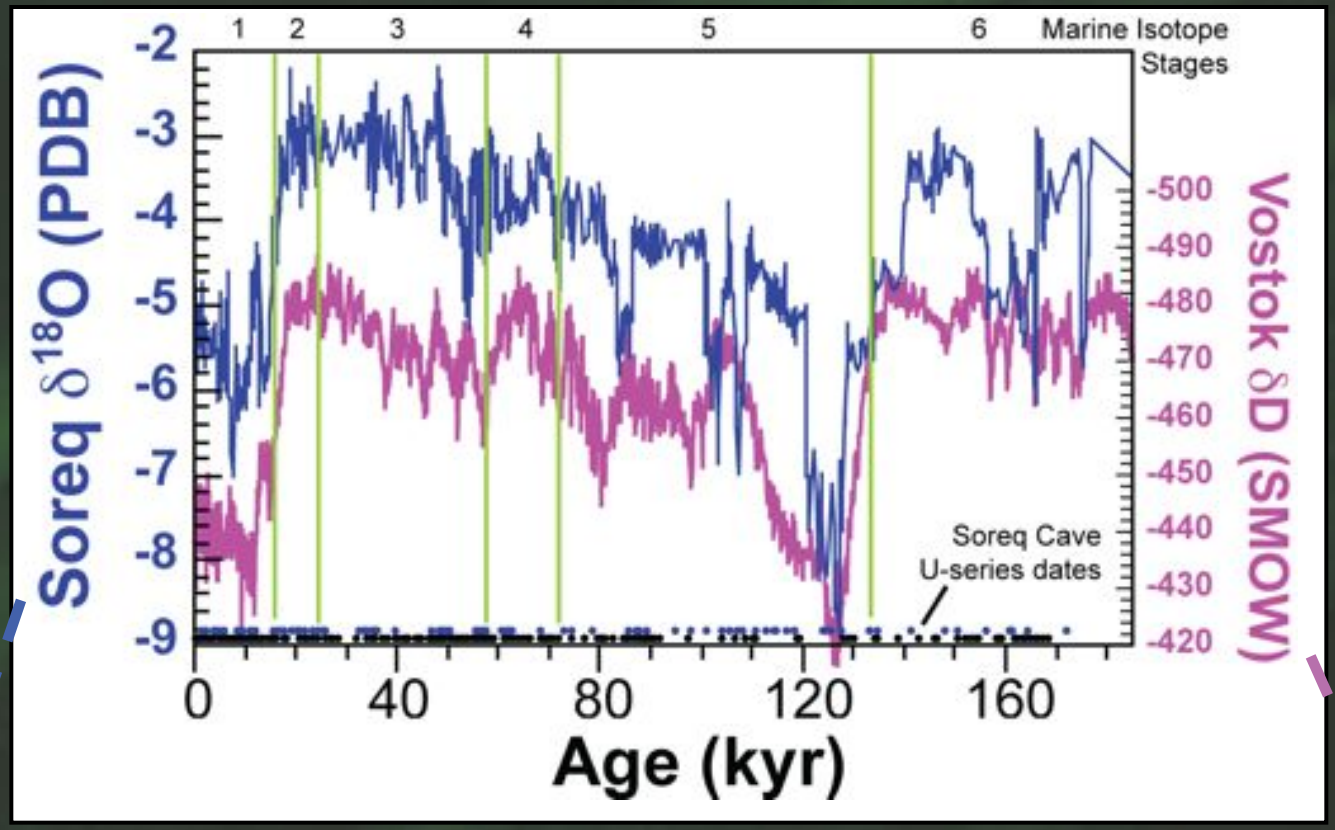
Avner Ayalon



David Pride

www.tripadvisor.com

Long-term record

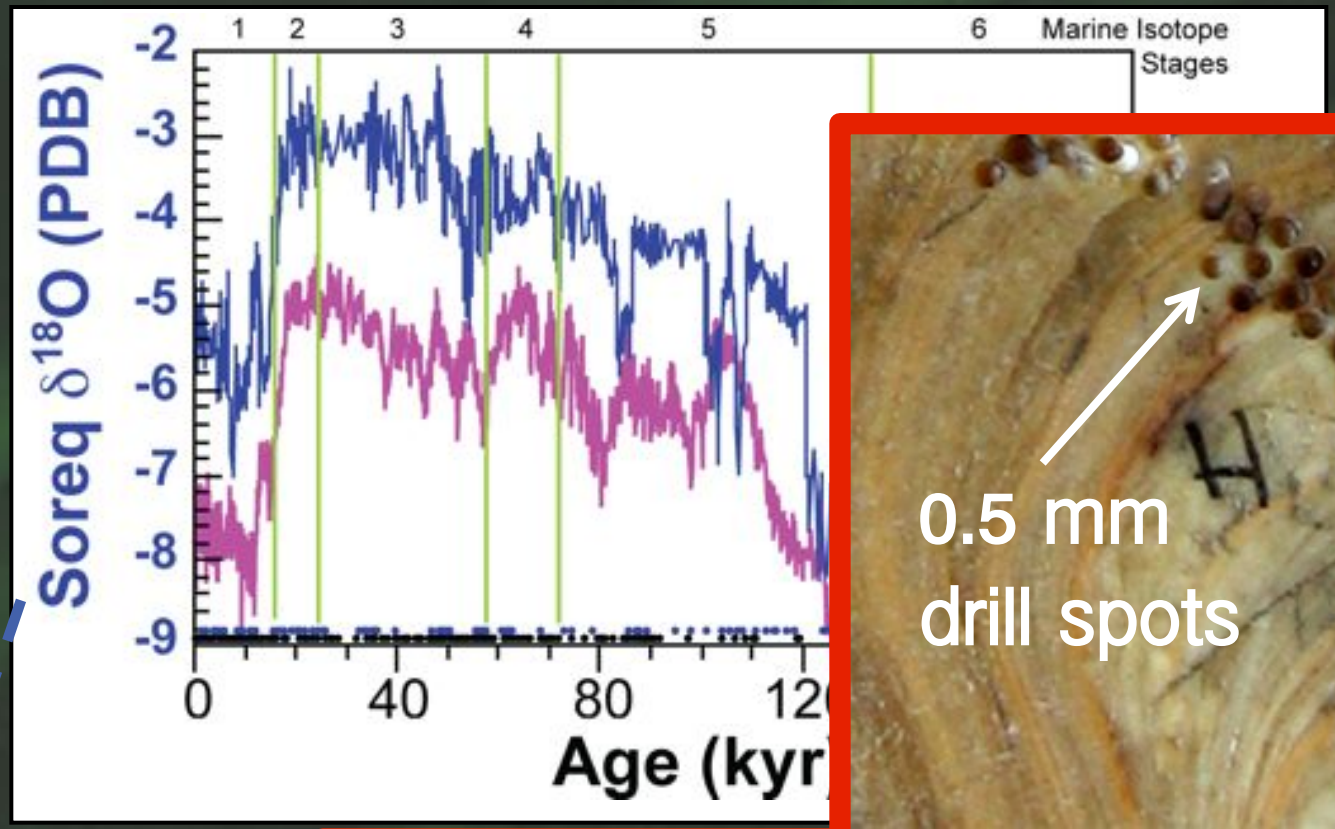


Soreq Cave

Antarctic Ice Core

from Bar-Matthews et al., 2003; Petit et al., 1999

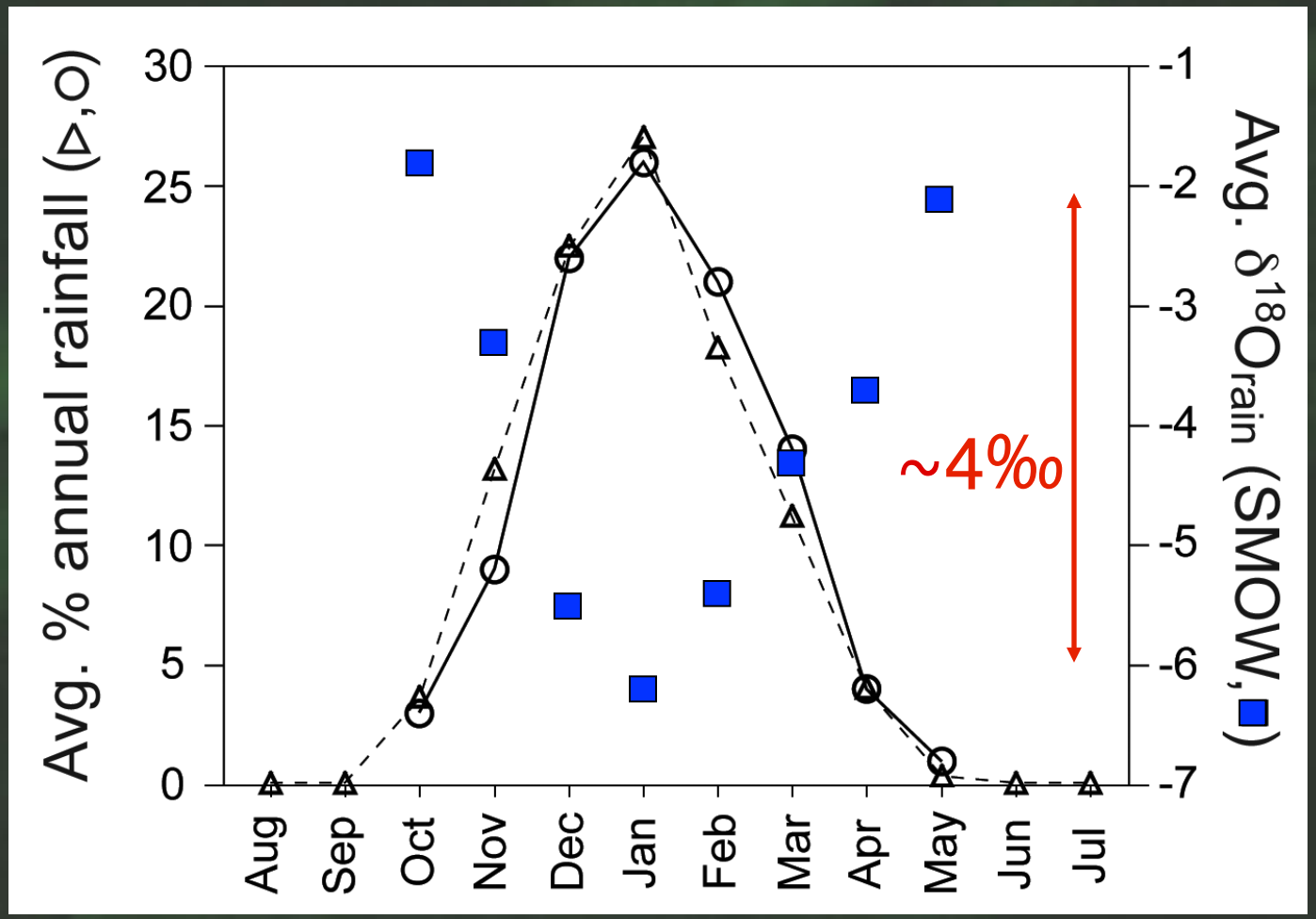
Long-term record



Soreq Cave

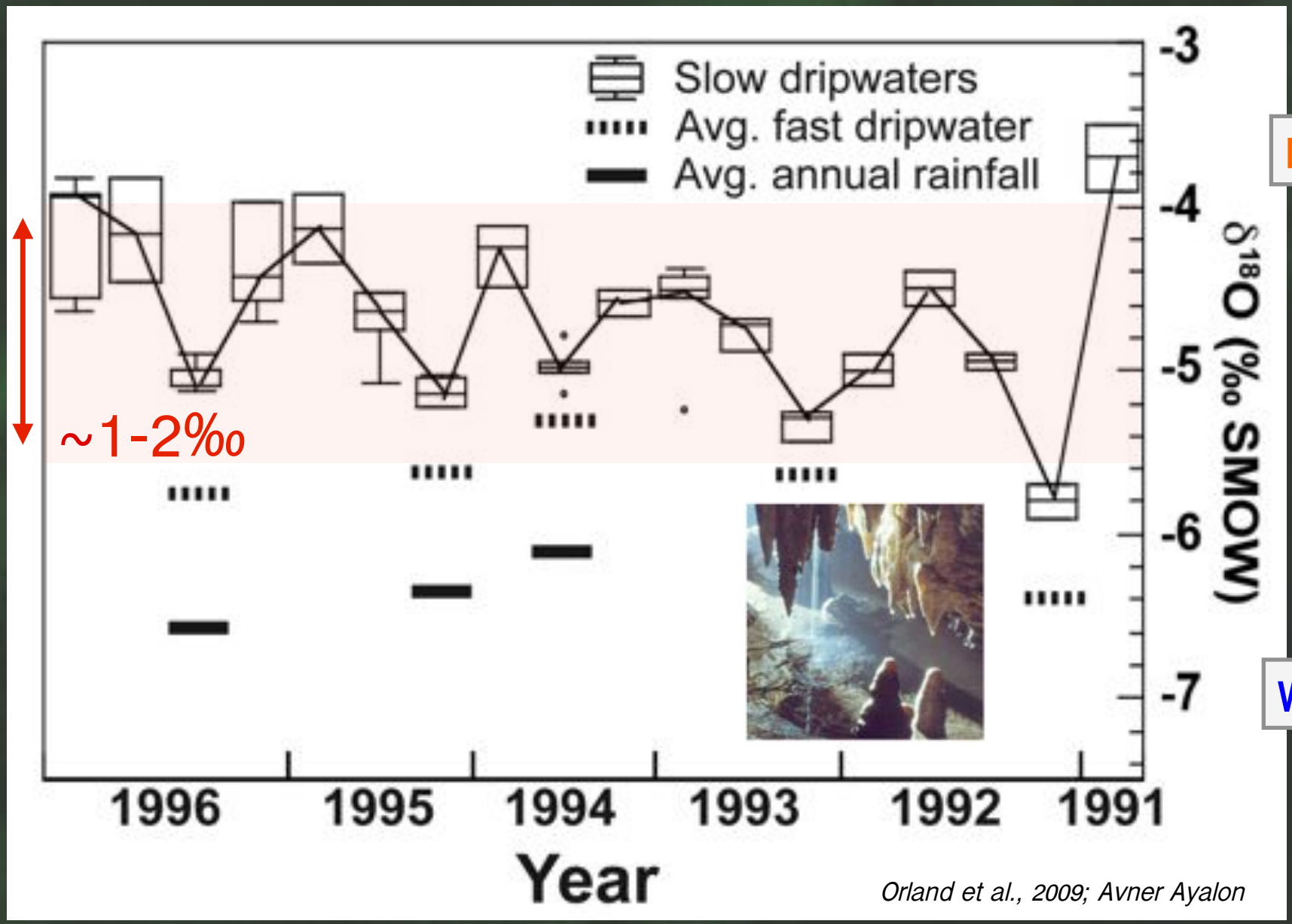
Is there a measurable signal of seasonality in Israel (& Soreq Cave speleothems)?

Modern observations: rainfall

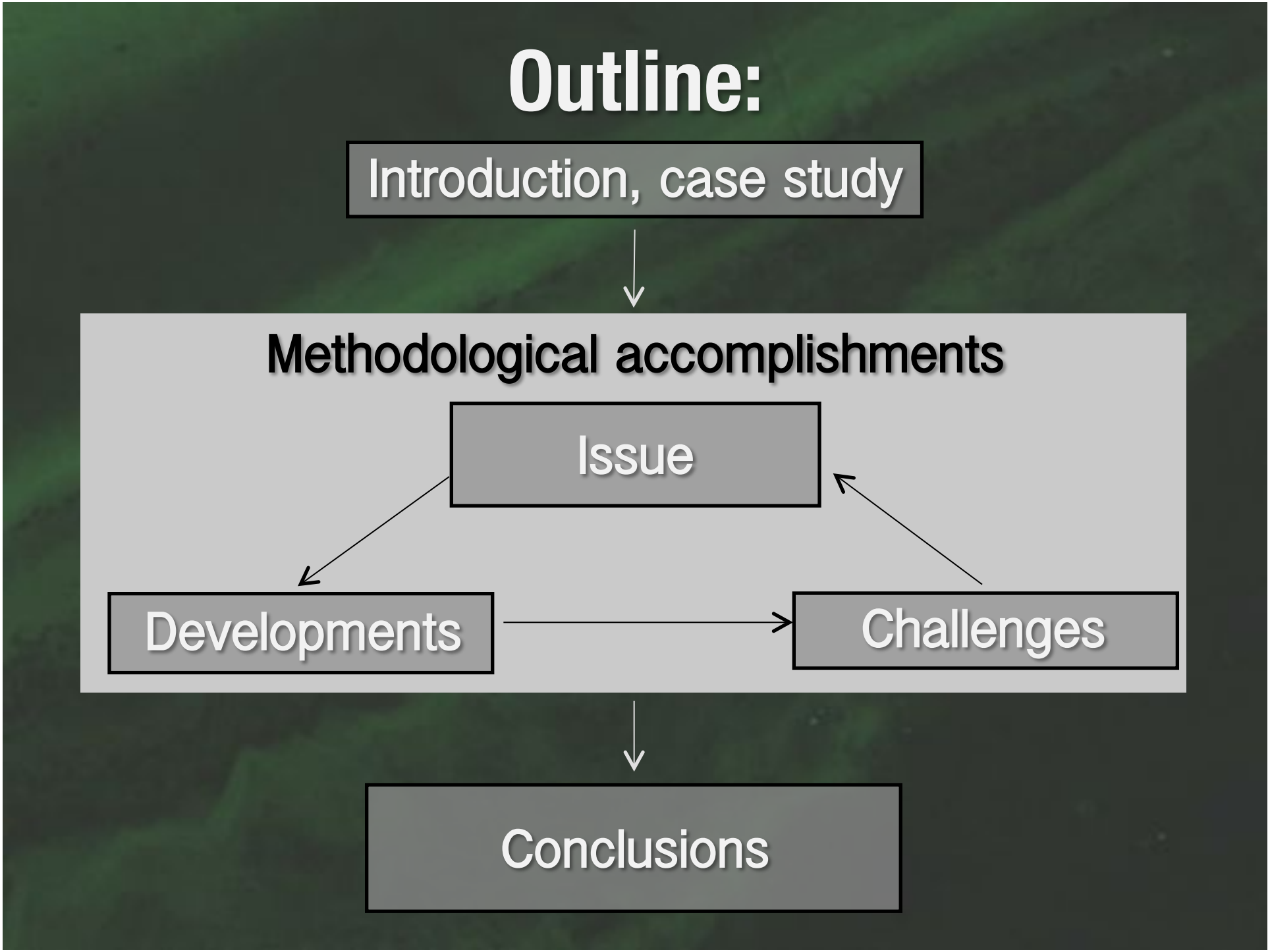


Orland et al., 2009

Modern observations: dripwater



Outline:


Introduction, case study
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Outline:

Introduction, case study

Dev es

Issues:

- WiscSIMS capabilities

- Imaging of fluorescent banding

- Sample preparation, registration

- Standardization, analytical output

- Comparison to conventional $\delta^{18}O$

- Trace element analyses

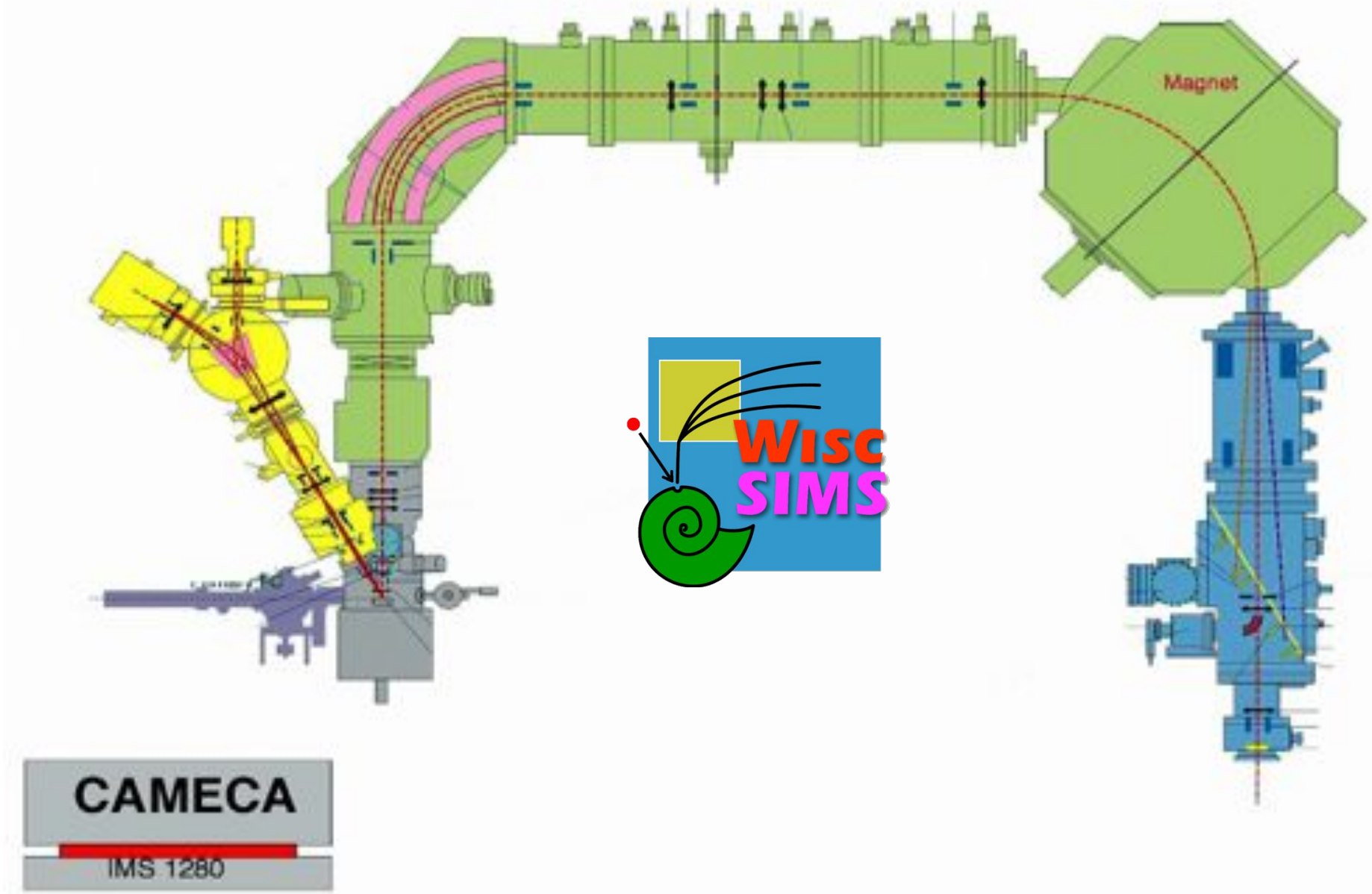
Conclusions

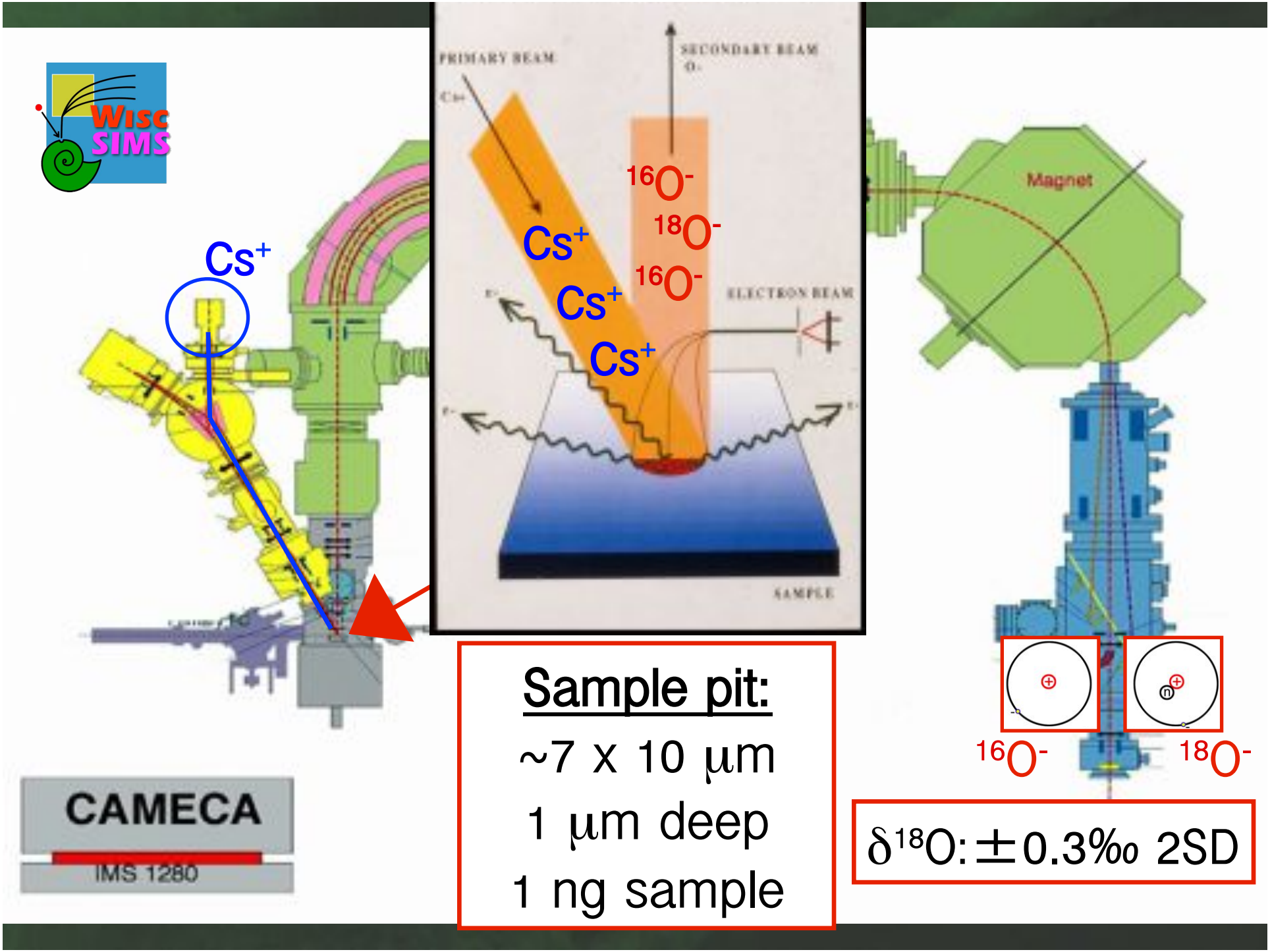
Method development

Objective is to obtain sub-annual resolution.

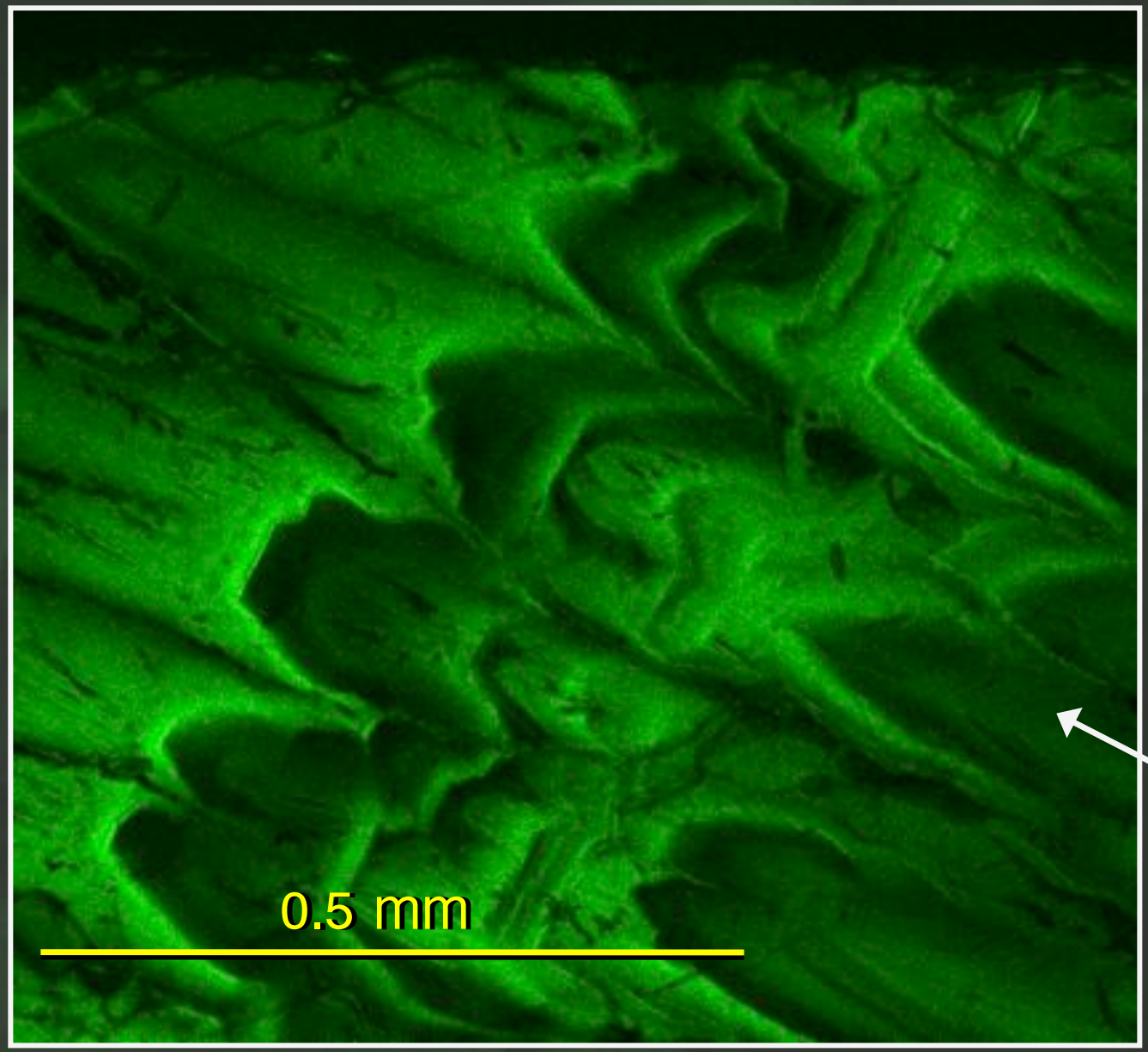
1) High-precision, high-spatial-resolution $\delta^{18}O$ analyses
   [Ion Microprobe]

2) Imaging of annual bands
   [Confocal Laser Fluorescent Microscope]

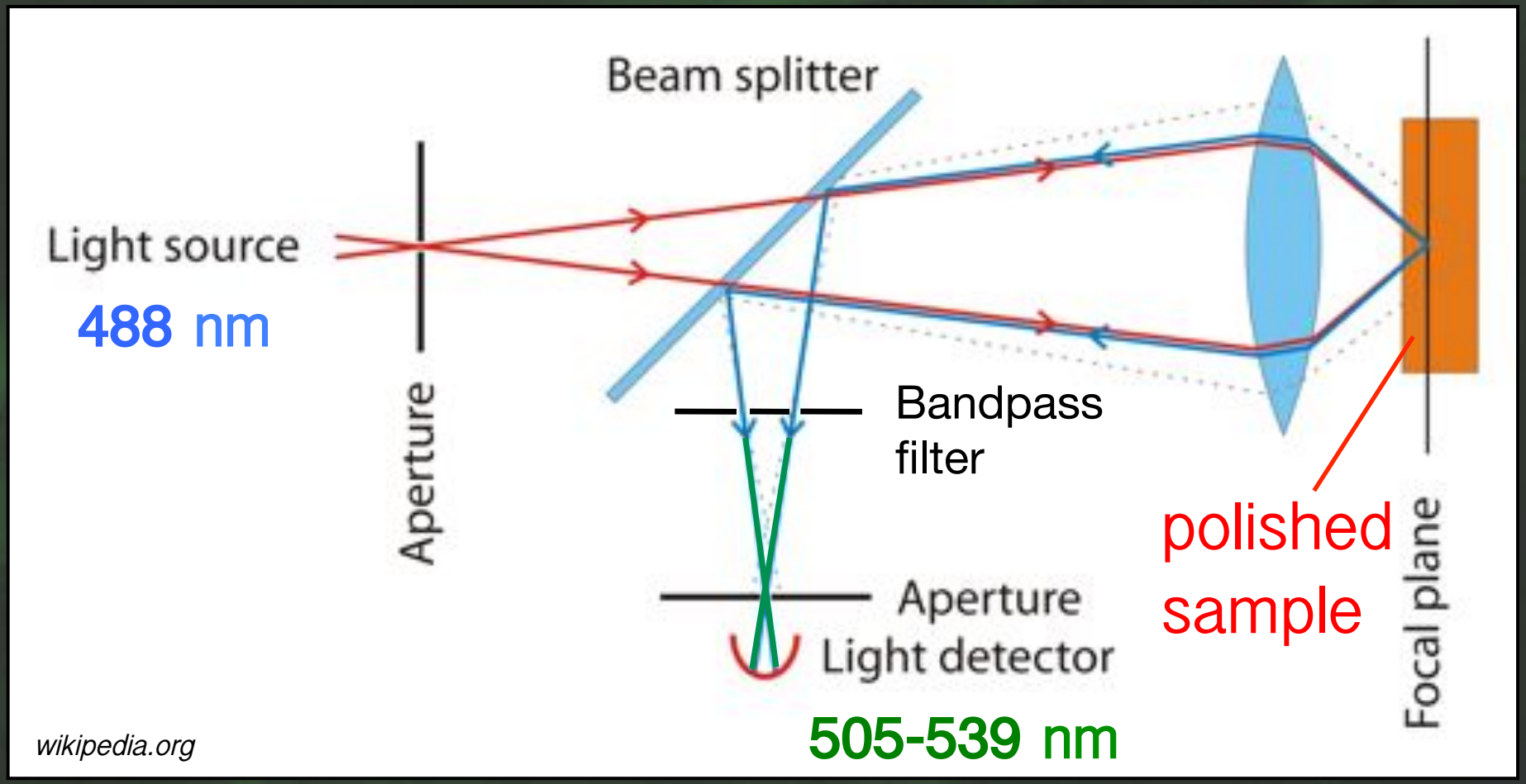

Magnet
WISC
SIMS
CAMECA
IMS 1280


Wisc SIMS
Cs+
PRIMARY BEAM
SECONDARY BEAM
16O-
18O-
16O-
Cs+
Cs+
Cs+
ELECTRON BEAM
SAMPLE
Magnet
16O-
18O-
CAMECA
IMS 1280
Sample pit:
~7 x 10 μm
1 μm deep
1 ng sample
δ18O: ±0.3‰ 2SD

Confocal Fluorescent Microscope

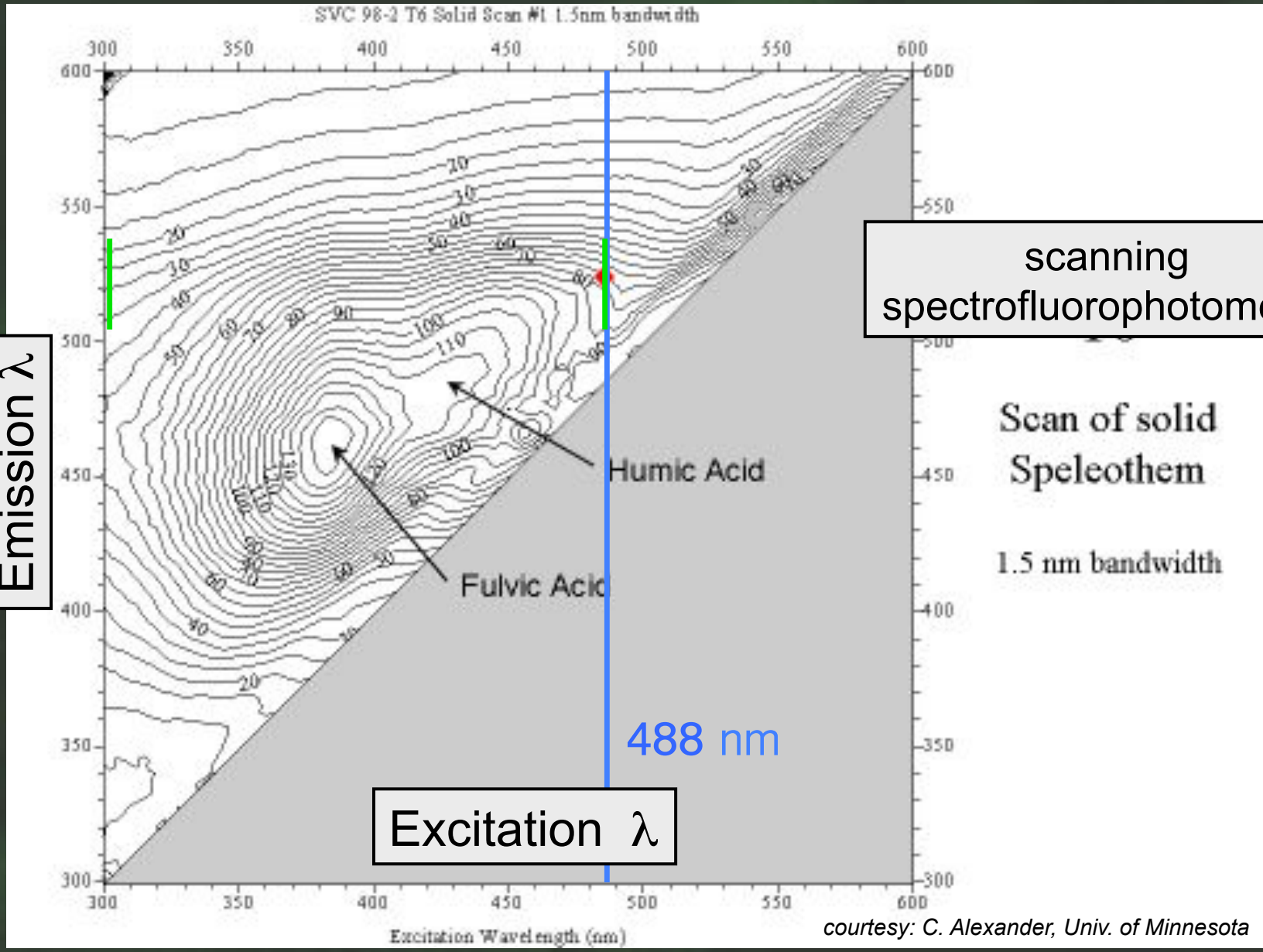


Confocal Fluorescent Microscope

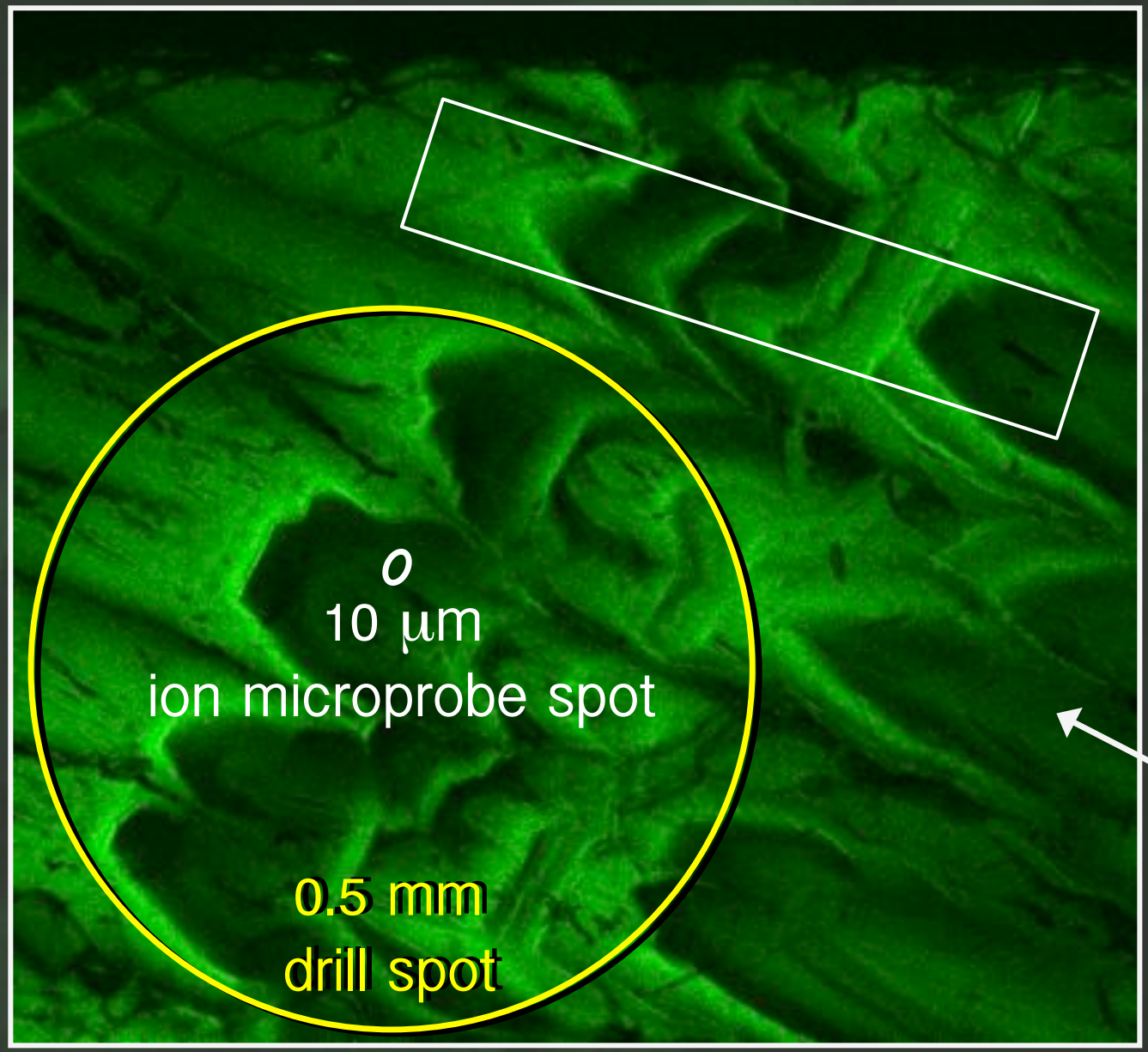


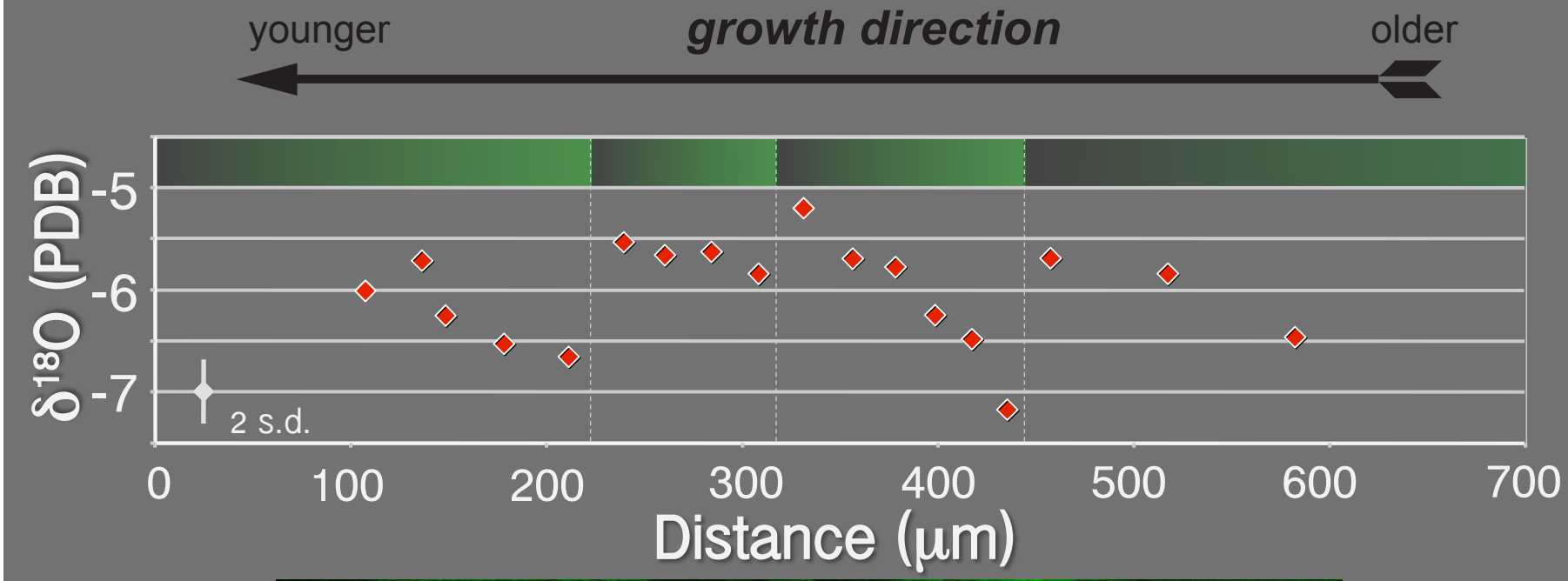
Organic molecules re-emit light with characteristic λ

Confocal Fluorescent Microscope



Confocal Fluorescent Microscope





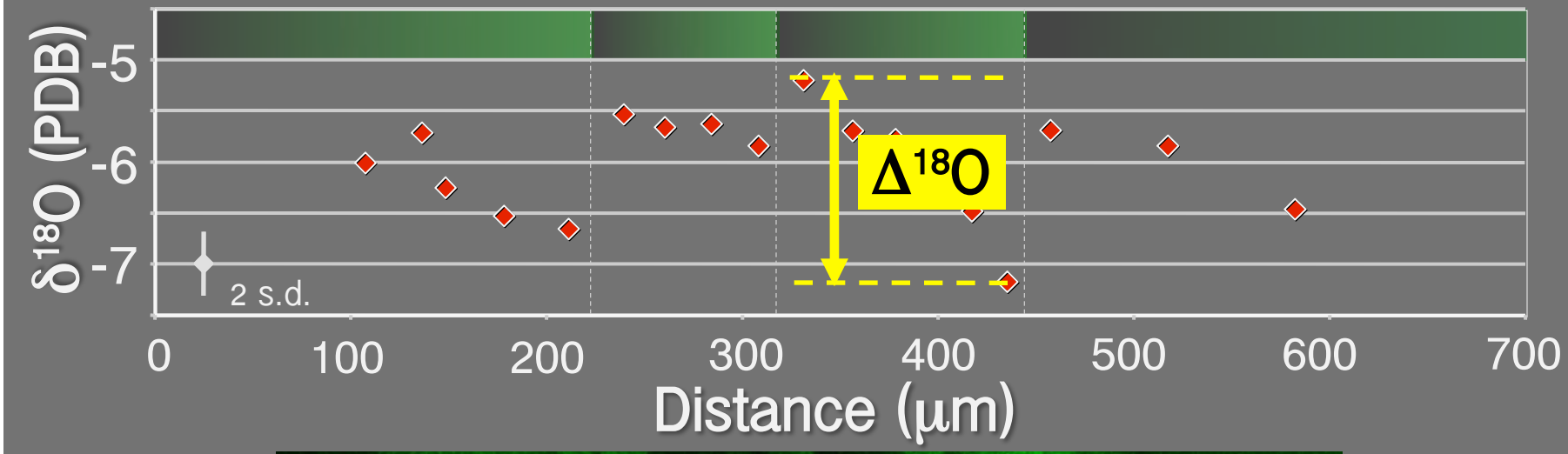
Dark zone: high $\delta^{18}O$ **Bright zone:** low $\delta^{18}O$

- organic poor
- dry season

- organic rich
- wet season

Orland et al., 2009

$$\Delta^{18}O = \delta^{18}O_{dark} - \delta^{18}O_{bright}$$



Dark zone: high $\delta^{18}O$ **Bright zone:** low $\delta^{18}O$

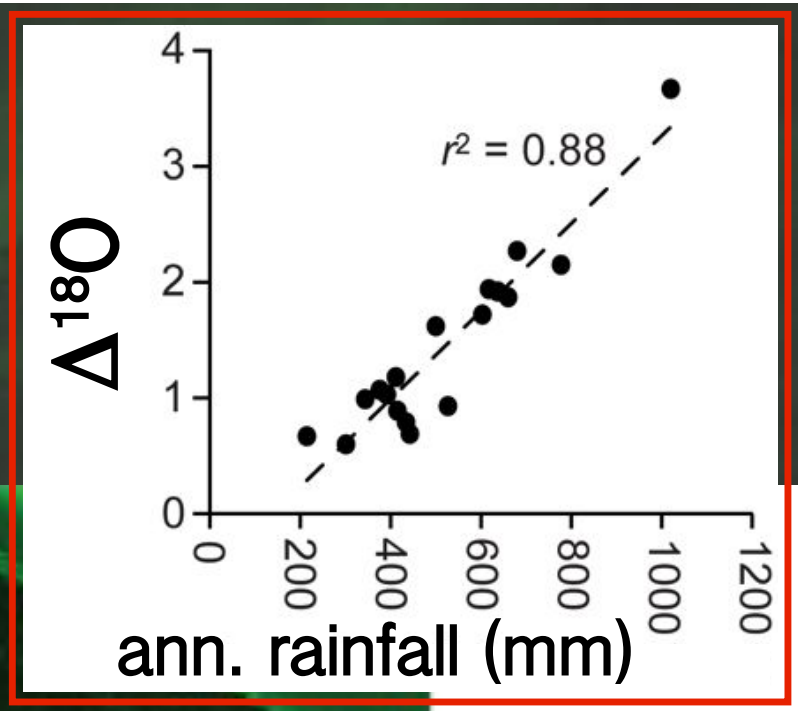
- organic poor
- dry season

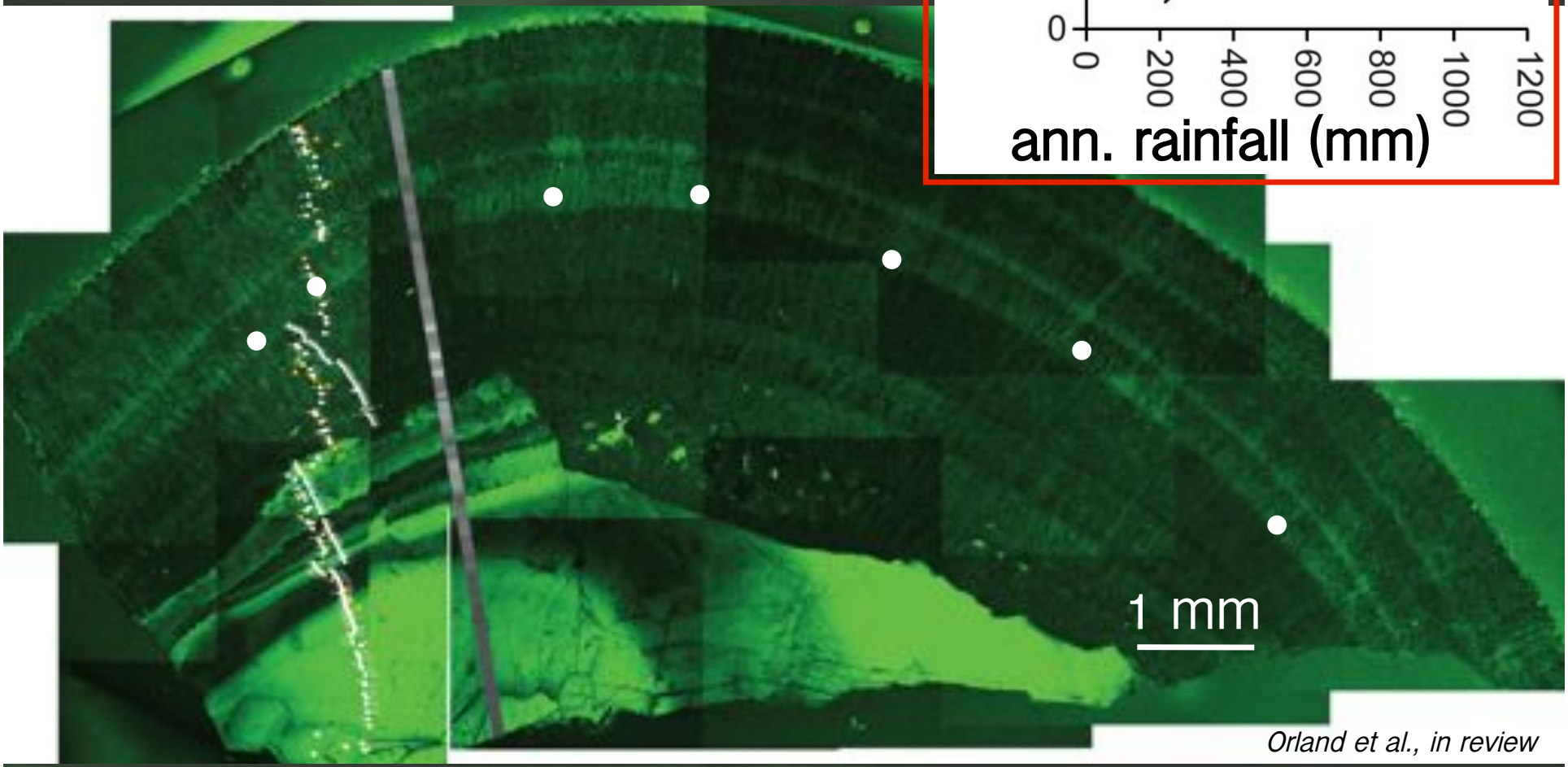
- organic rich
- wet season

Orland et al., 2009

Modern Samples:

- $\Delta^{18}O$ is a rain gauge
- mini-Hendy test (2SD = 0.31‰)



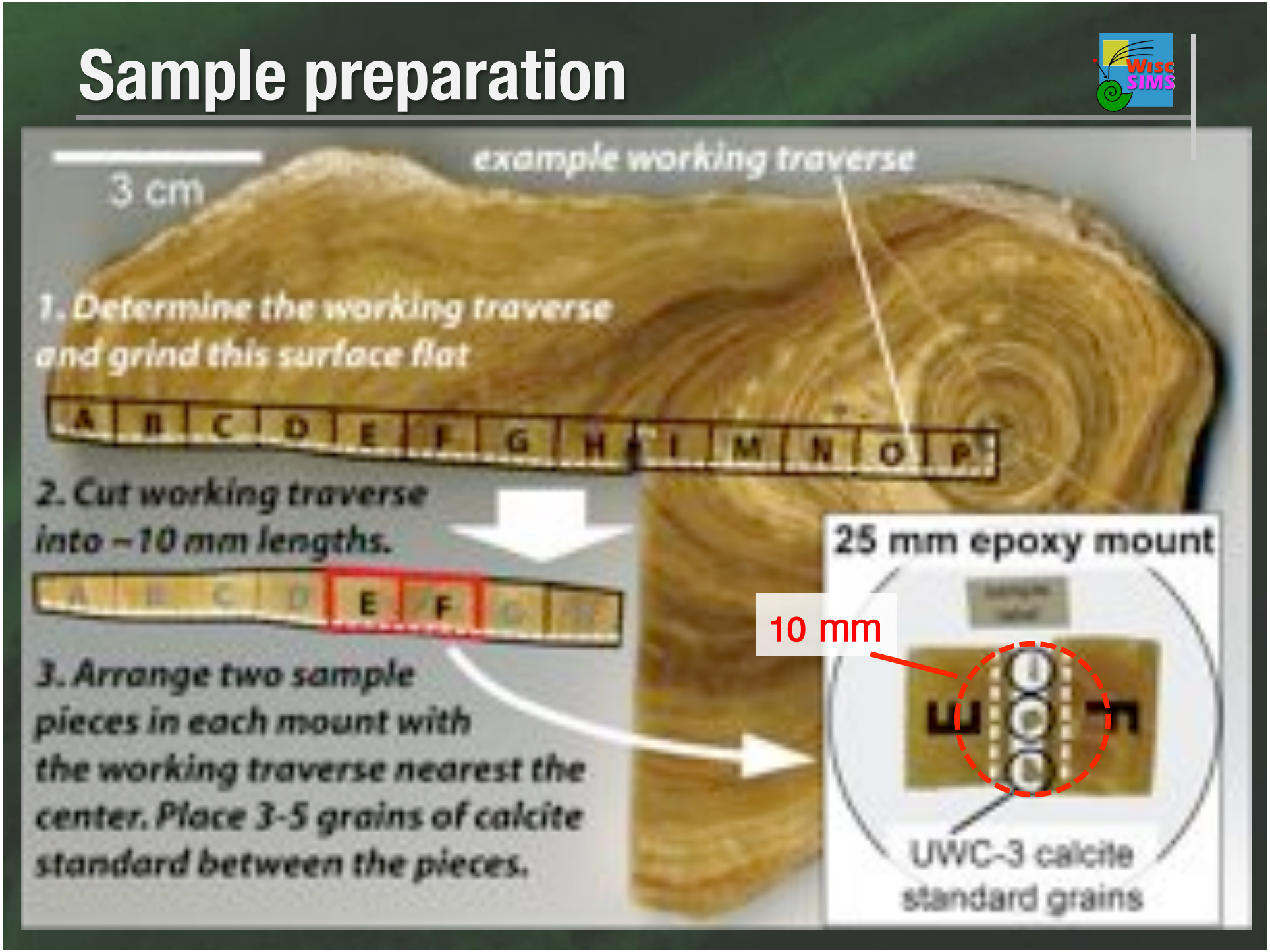


Orland et al., in review

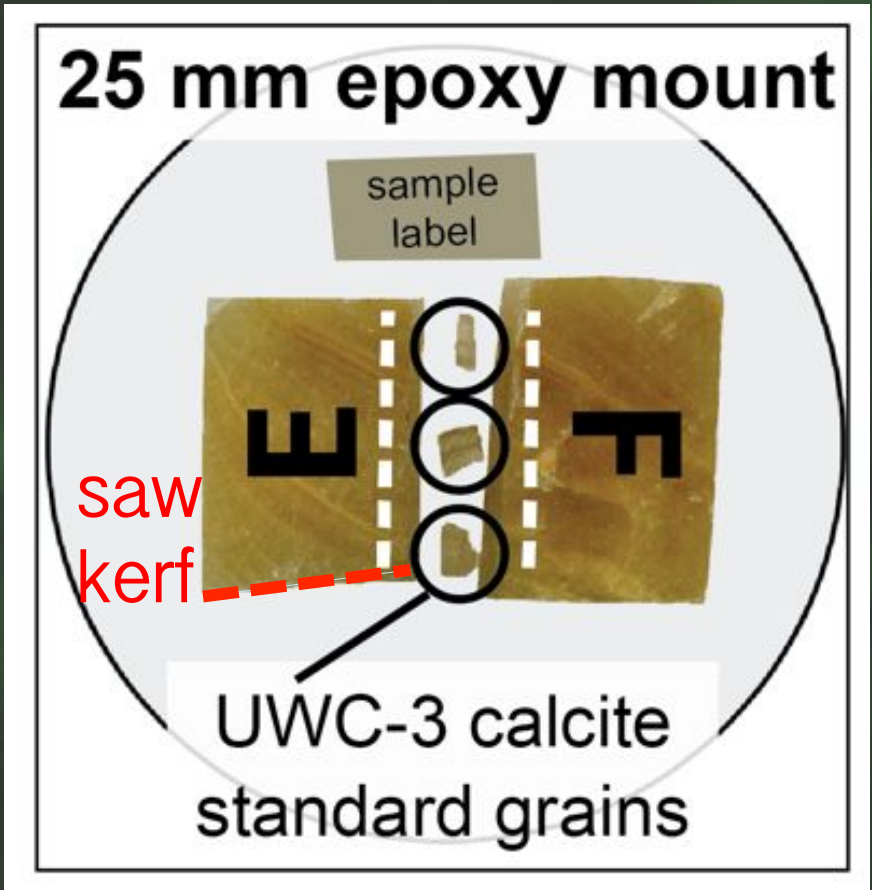
Paleo-Applications

1) Compare seasonality across broad time scales
2) Investigate rapid climate events at high resolution

Sample preparation



Sample registration

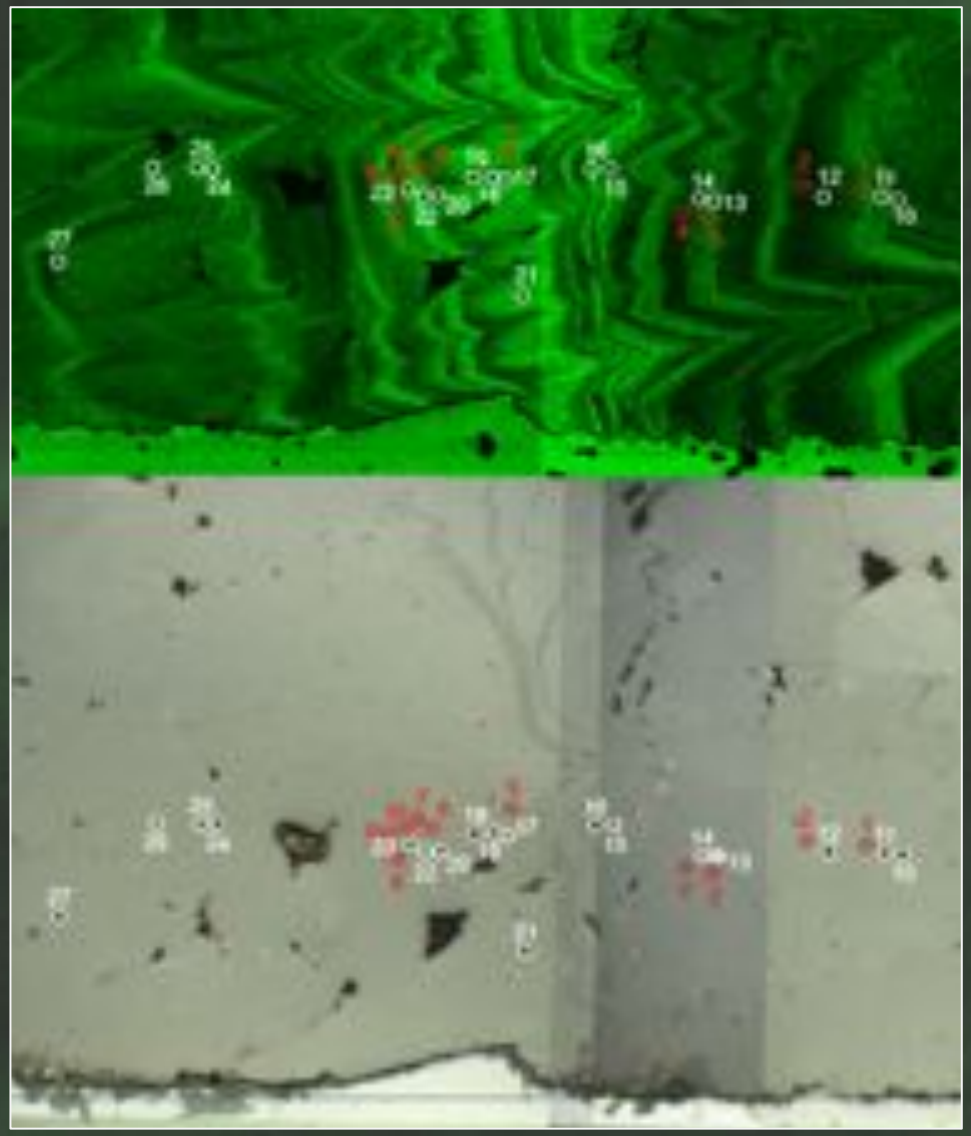


spot shape

3 issues:

1. Sample preparation and alignment
2. Image registration
   - for analysis
   - for mapping
3. Session registration

Sample registration

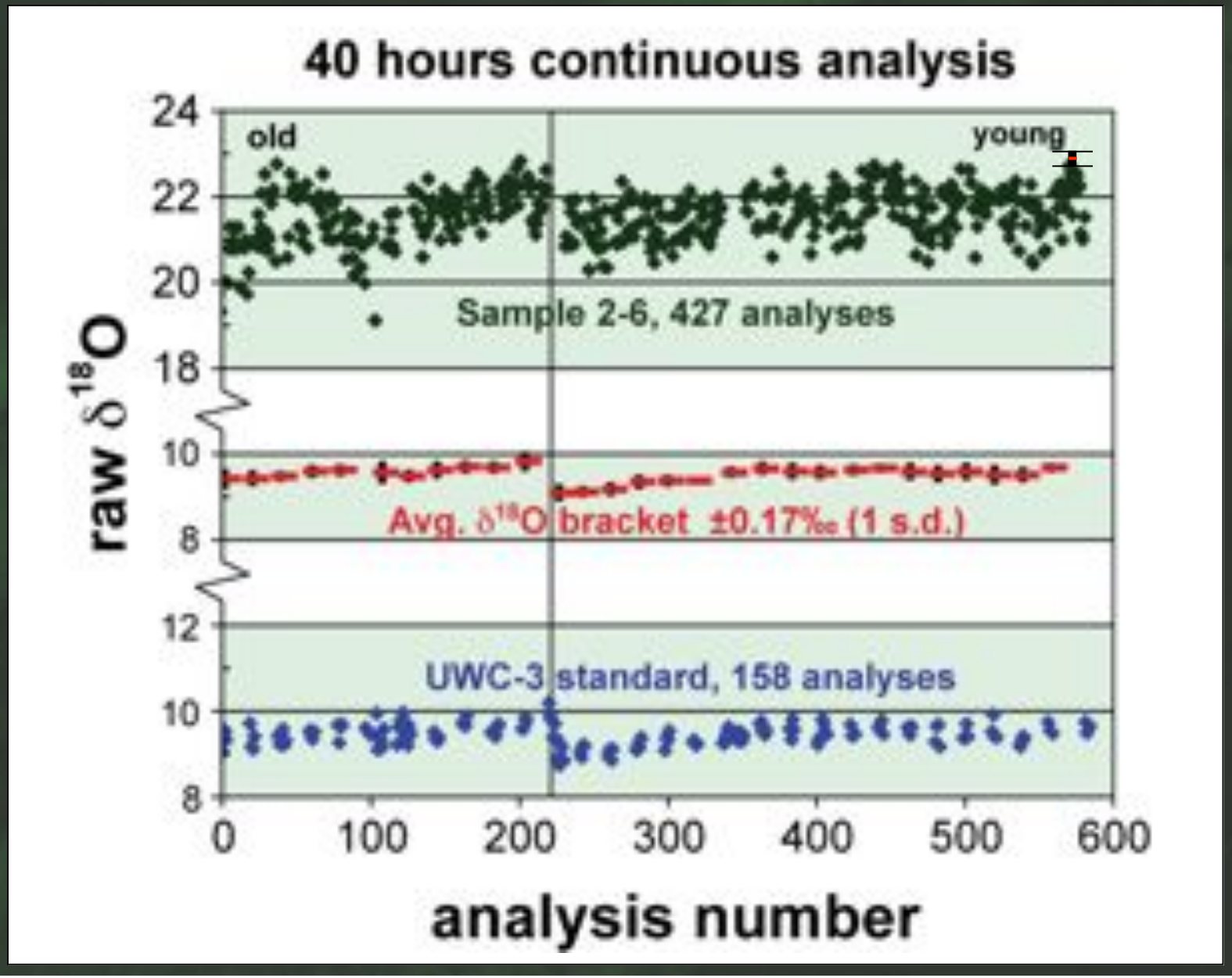


Orland et al., 2012

3 issues:

1. Sample preparation and alignment
2. Image registration
   - for analysis
   - for mapping
3. Session registration

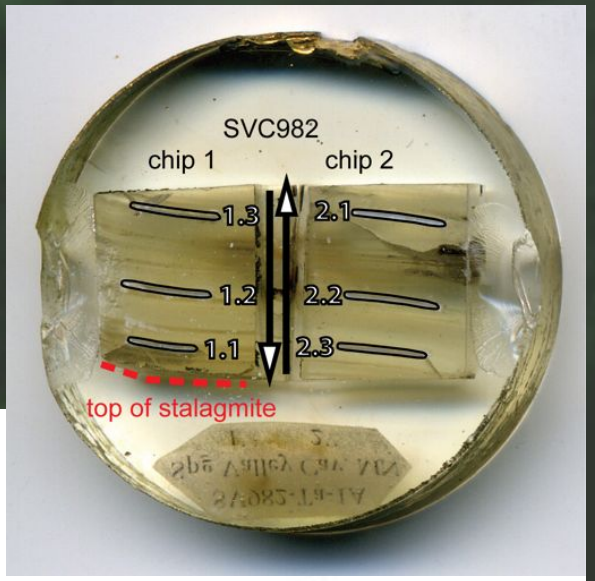
Standardization, rate of analysis

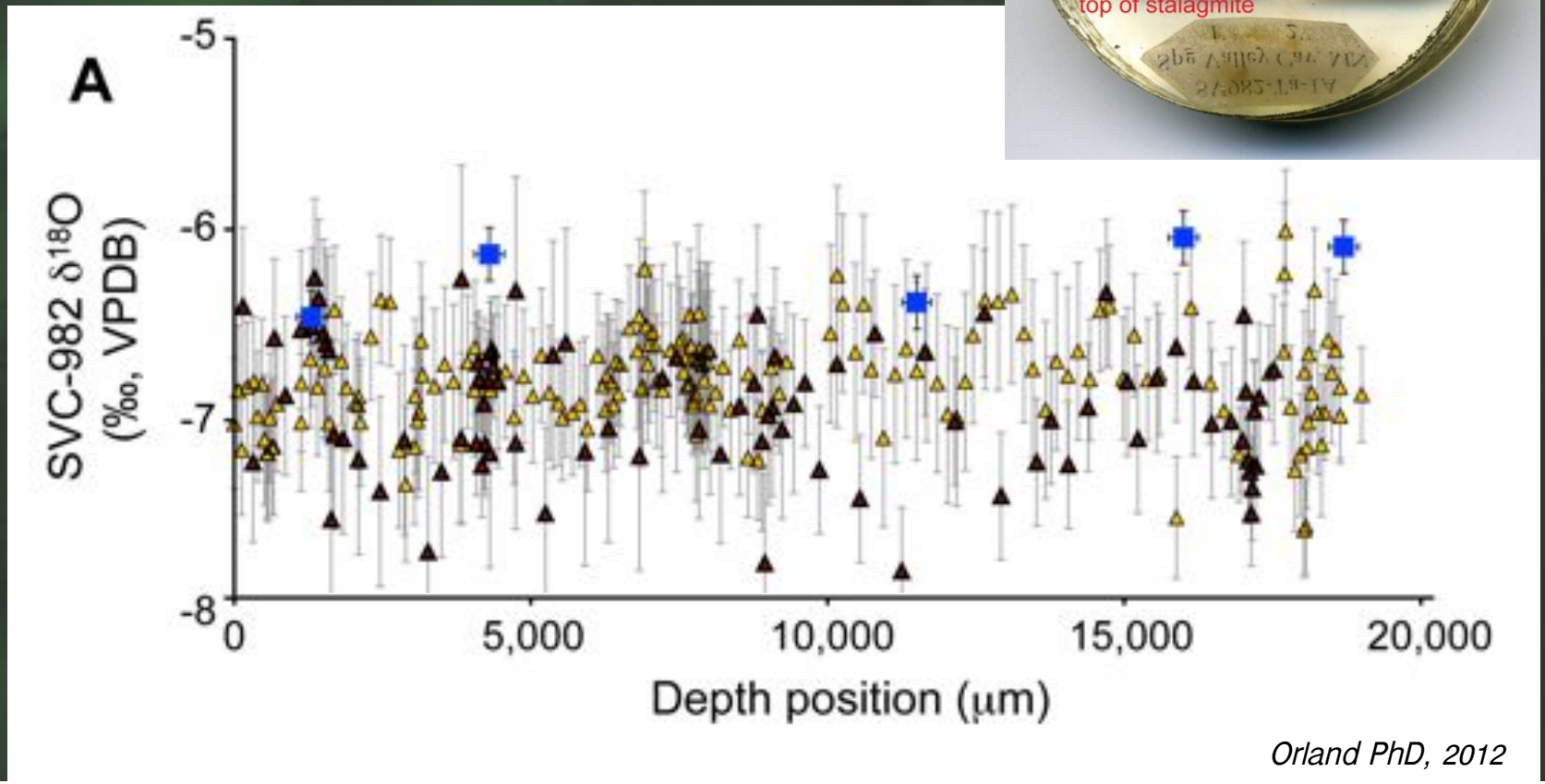


SIMS vs. conventional $\delta^{18}O$ data

Spring Valley Cavern, MN, USA

$\delta^{18}O$ offset: 0.57‰





Orland PhD, 2012

Tests to evaluate $\delta^{18}O$ offset

Roasting to remove organics

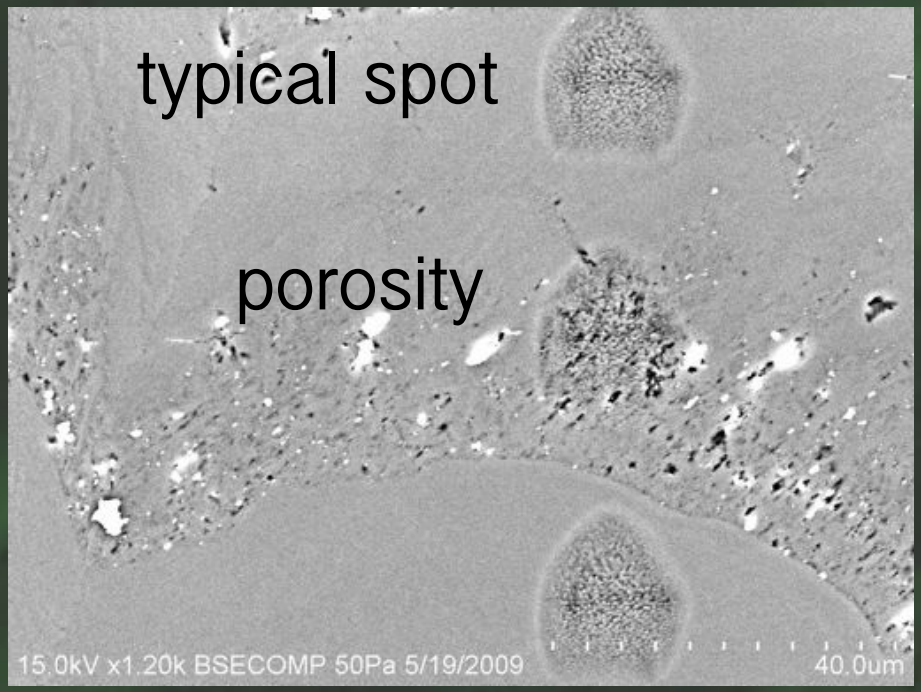
Test influence of sample porosity

Analysis of SIMS pit depths in sample vs. standard

Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

Influence of sample porosity



Orland et al., 2012

Porosity ~1-5%

Multiple analyses along single porous bands

Average 2SD of along-band analyses = 0.71‰

Tests to evaluate $\delta^{18}O$ offset

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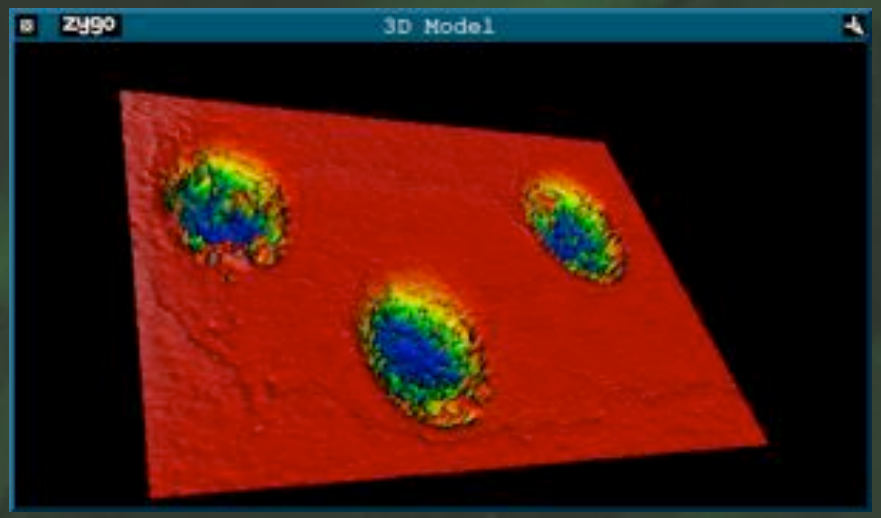
Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

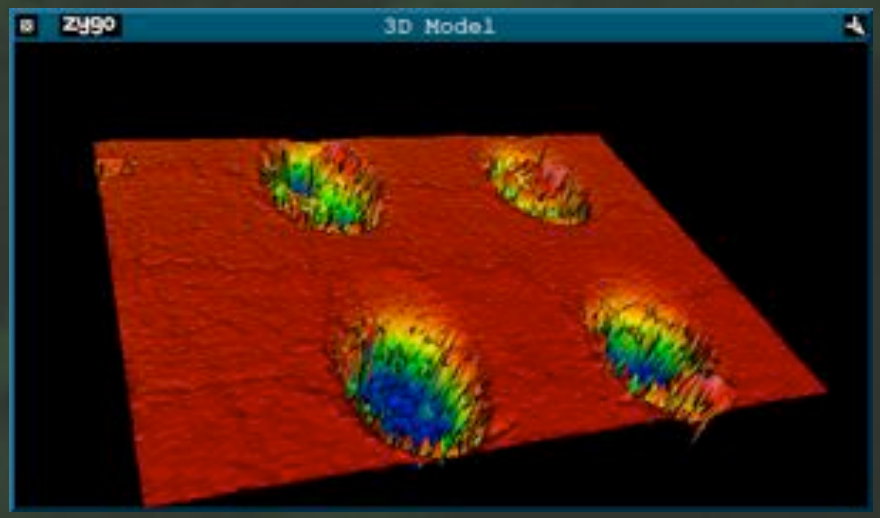
Pit depth comparison

Sample



average
pit depth =
1.5 μm

Standard



average
pit depth =
1.5 μm

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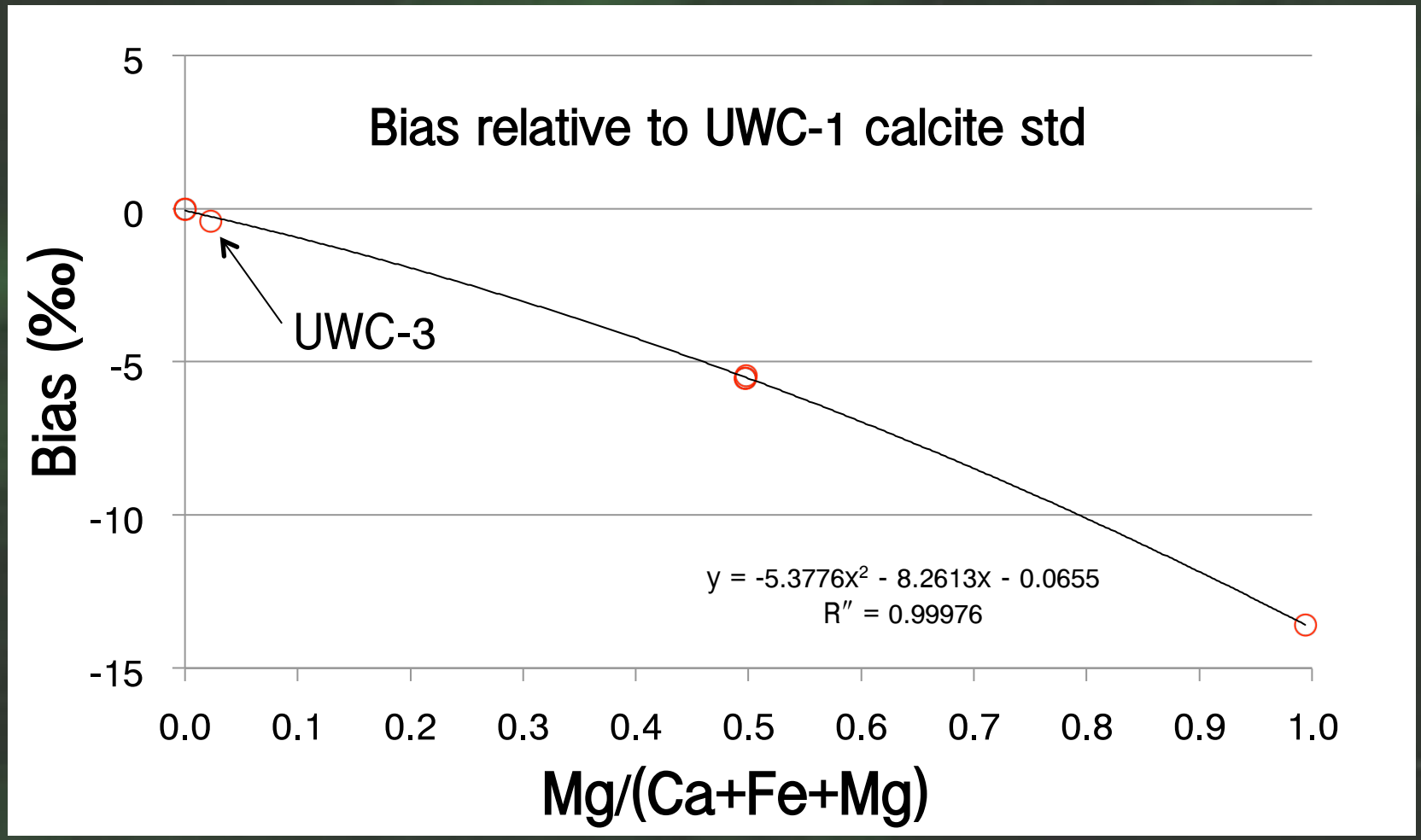
Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

Minor element composition

Influence of Mg content on instrumental bias?



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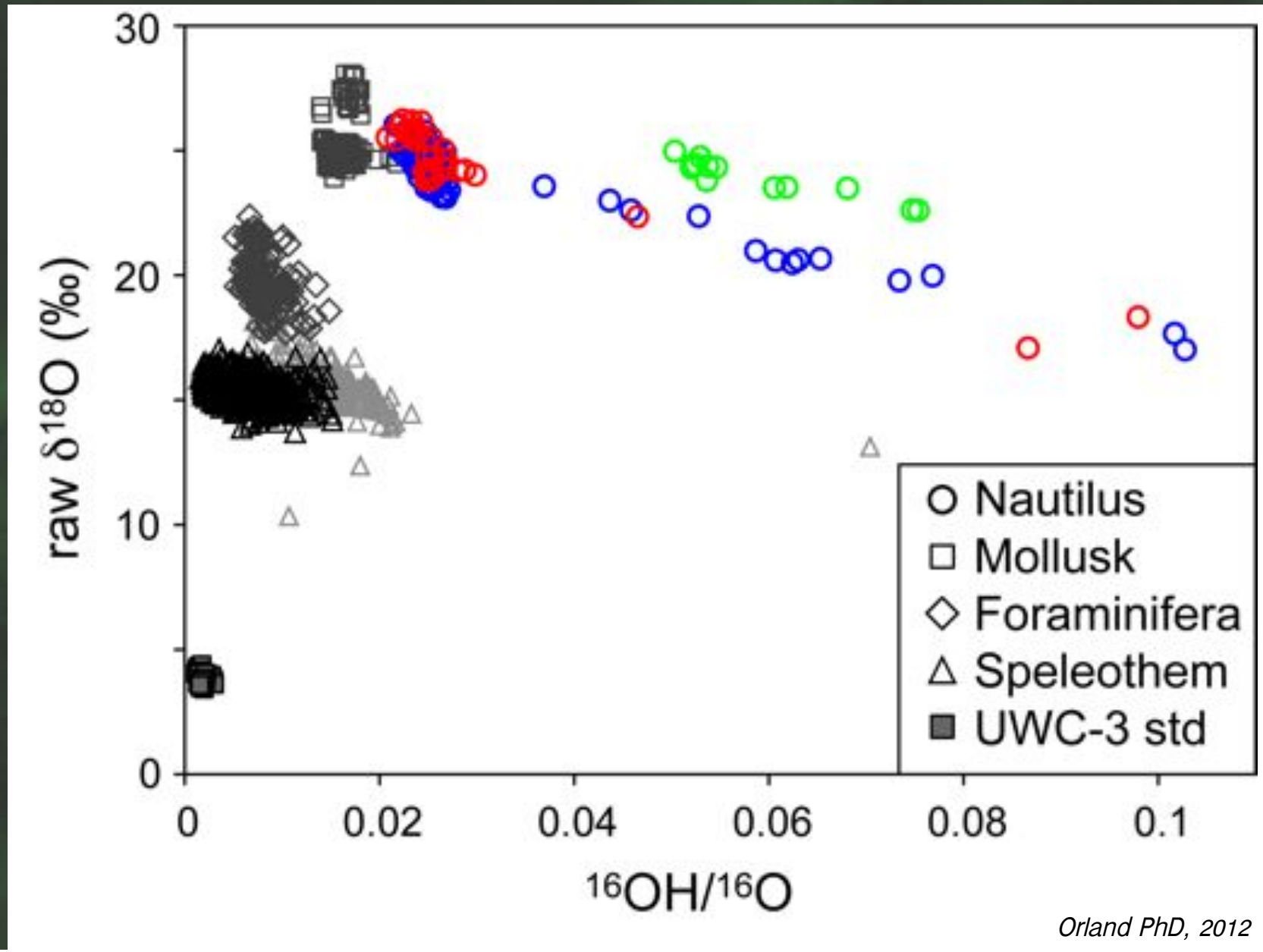
Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

OH/O peak height



Orland PhD, 2012

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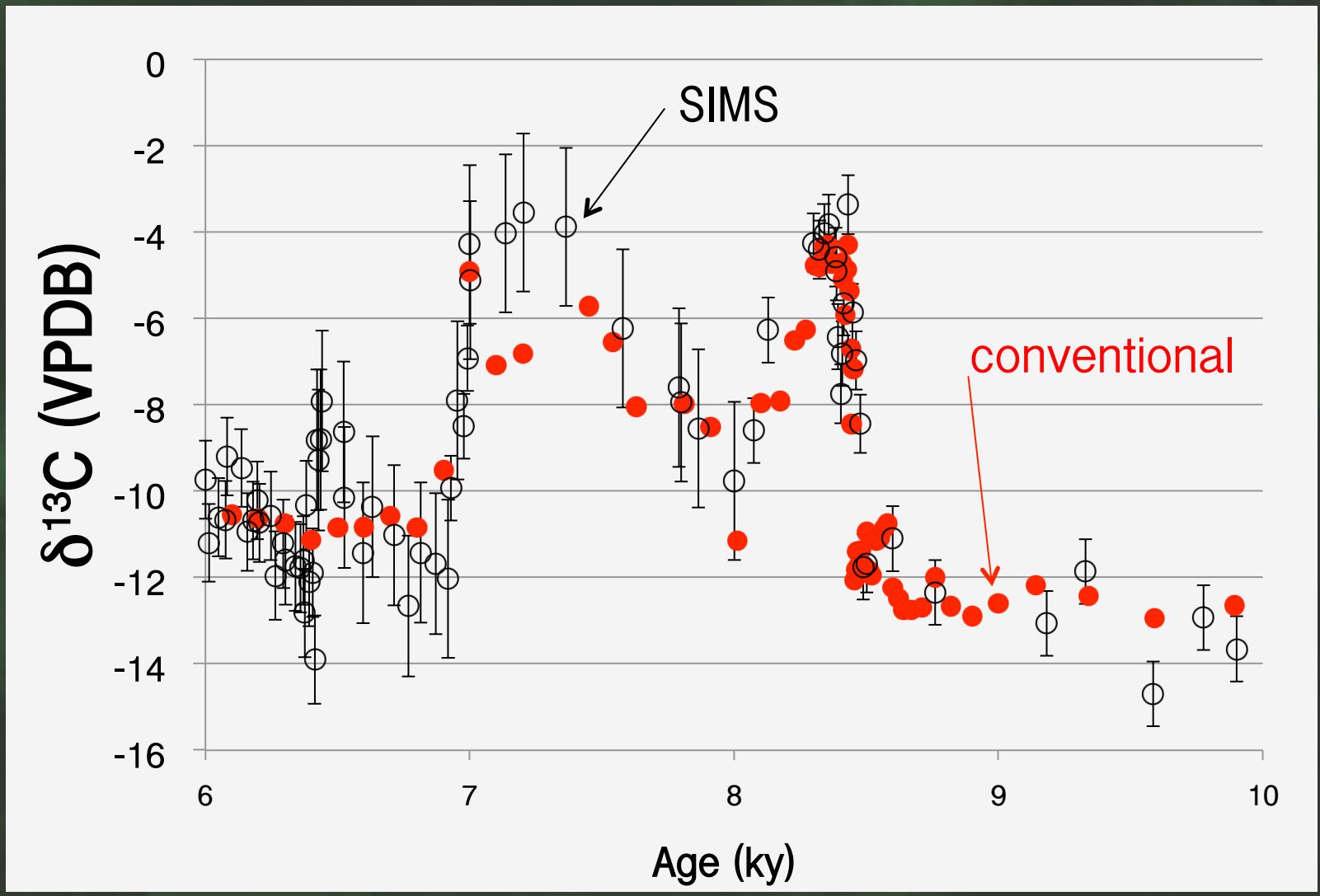
Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

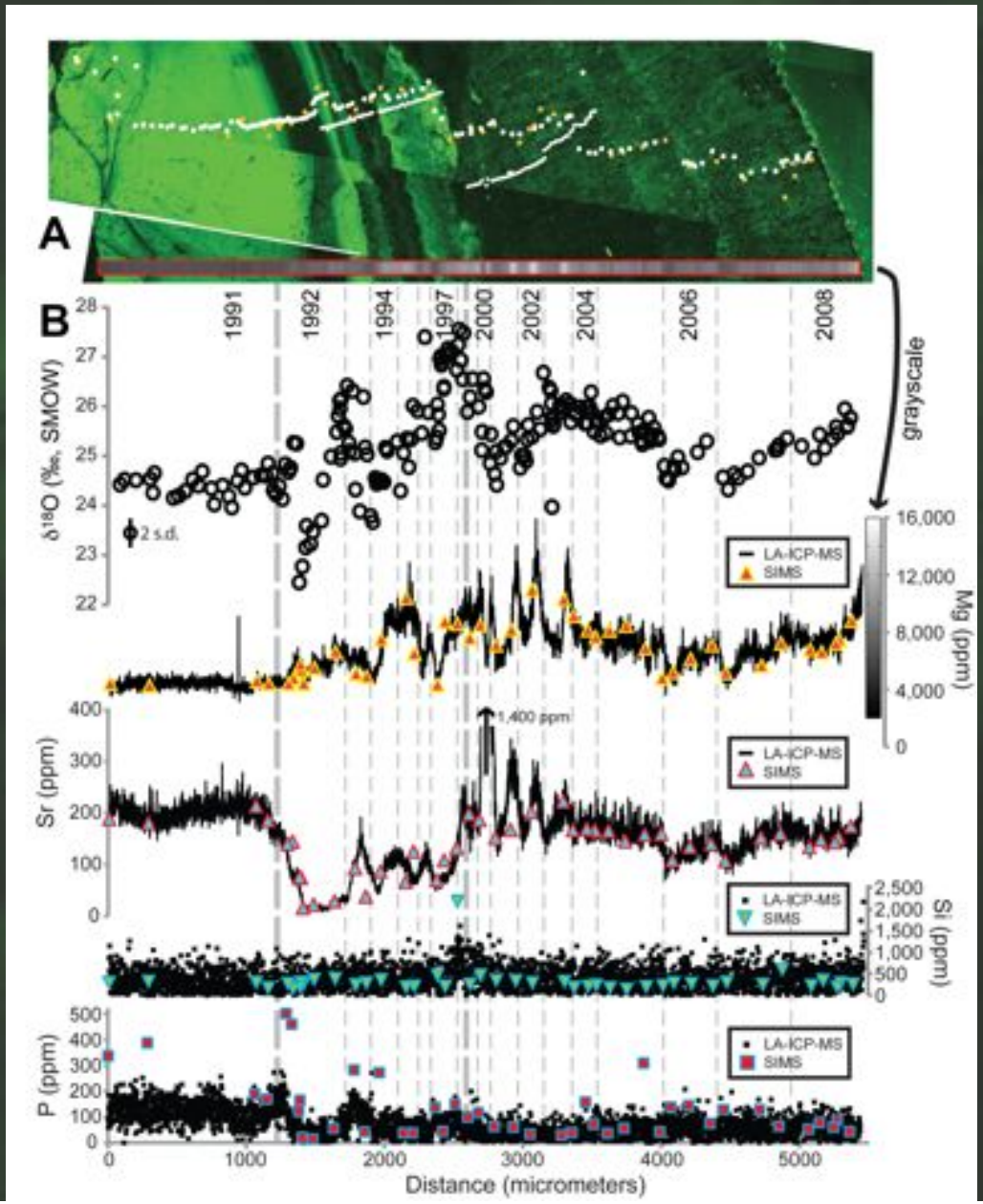
<u>Way forward:</u>

Lack of $\delta^{13}C$ offset points to H_2O as the source of $\delta^{18}O$ offset in SIMS vs. conventional analyses



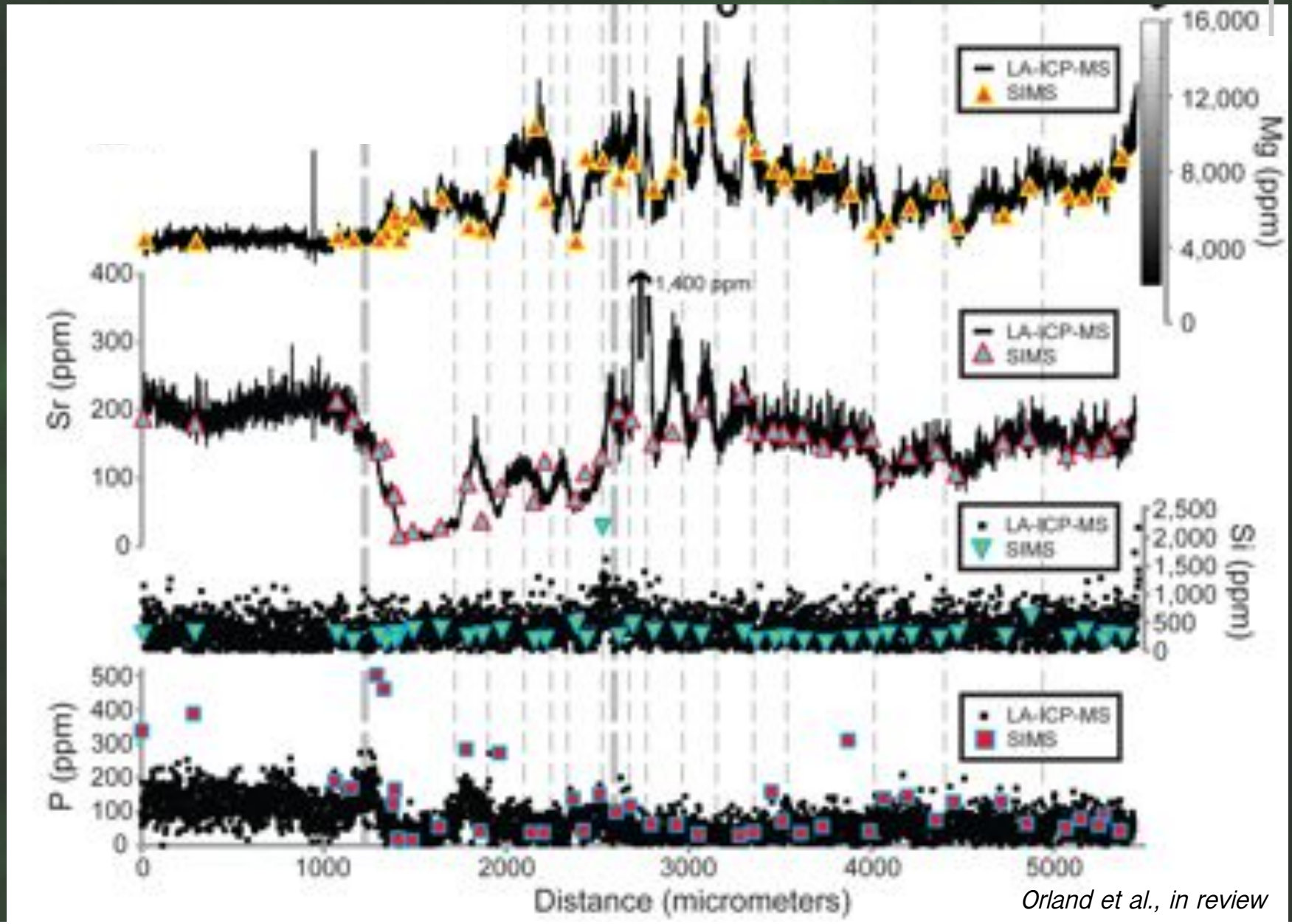
$\delta^{18}O$ offset in this same section is 0.9‰

Trace elements: SIMS & LA-ICP-MS



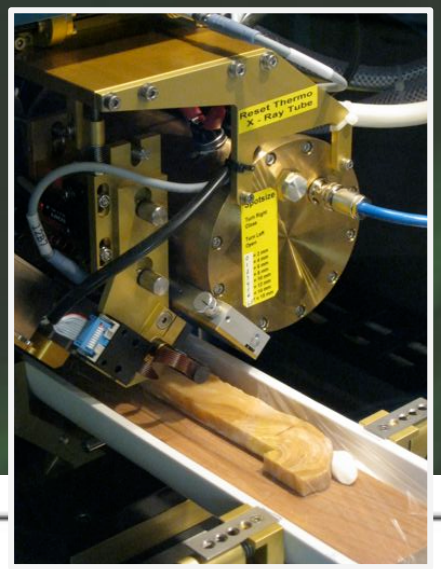
Orland et al., in review

Trace elements: SIMS & LA-ICP-MS

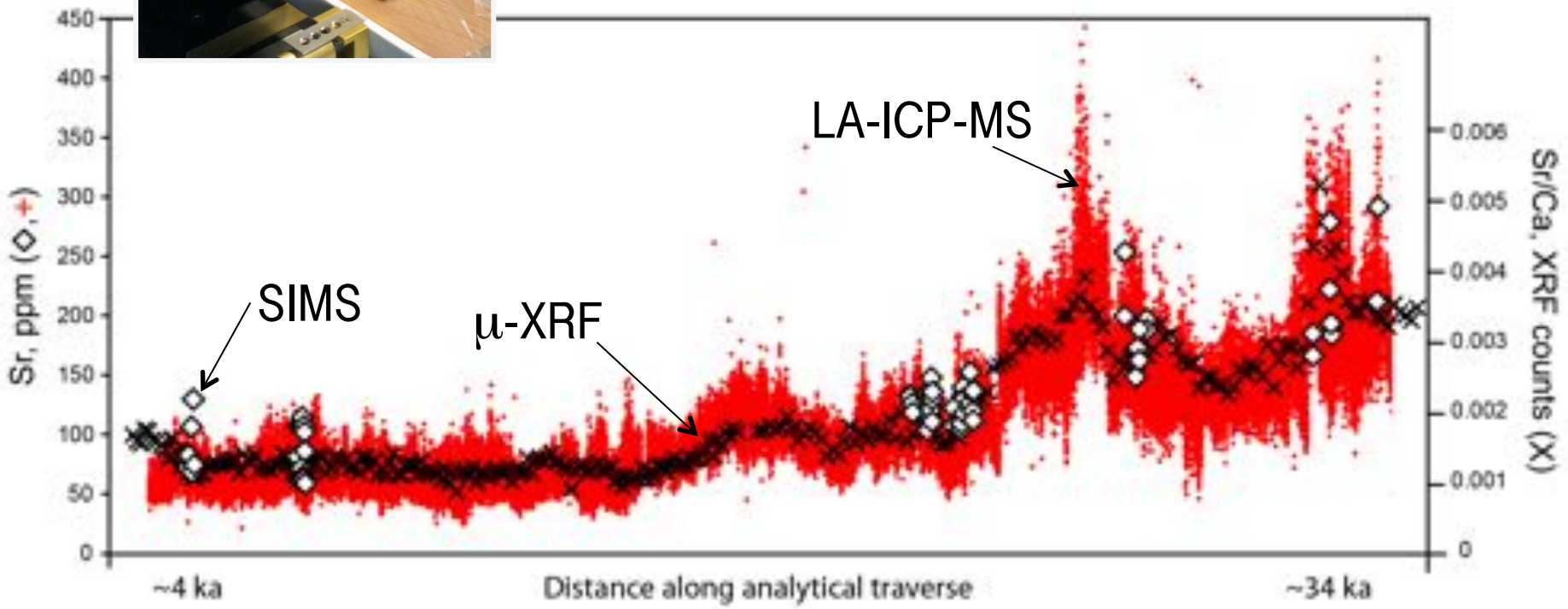


Orland et al., in review

Trace elements: SIMS & μ-XRF



100 μm resolution
Slit size = 2.0 x 0.1 mm



Conclusions

Promising progress so far, with room for more.

Jump in,
the ball pit's fine!