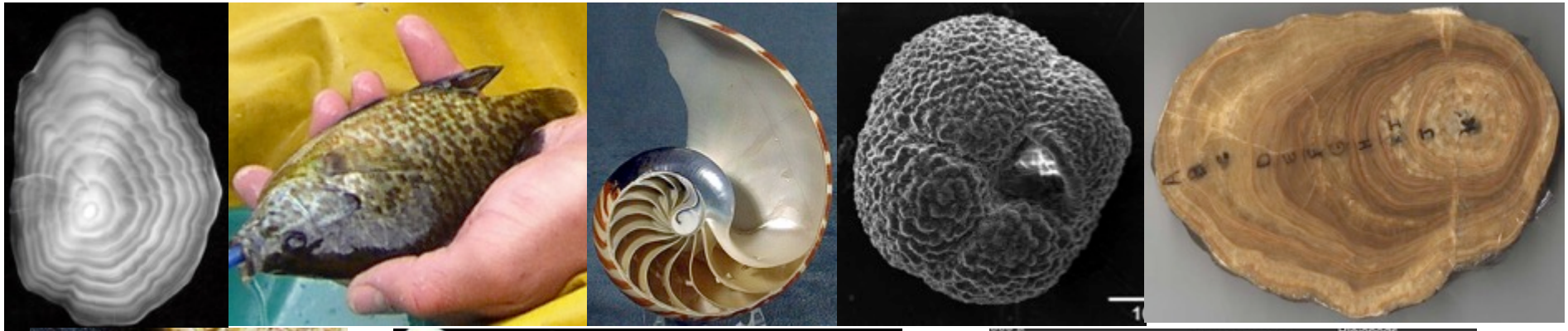
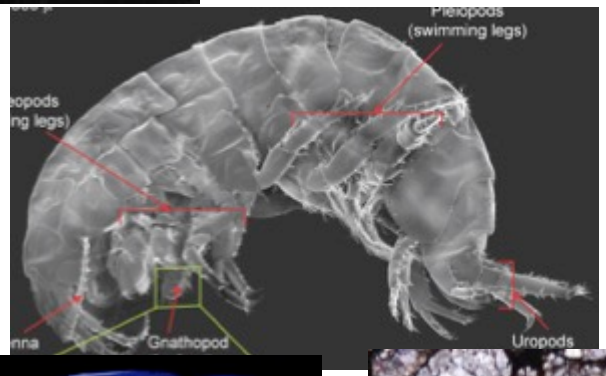
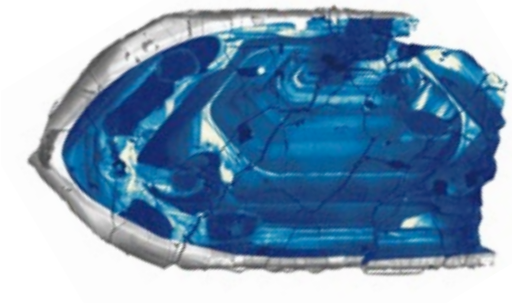
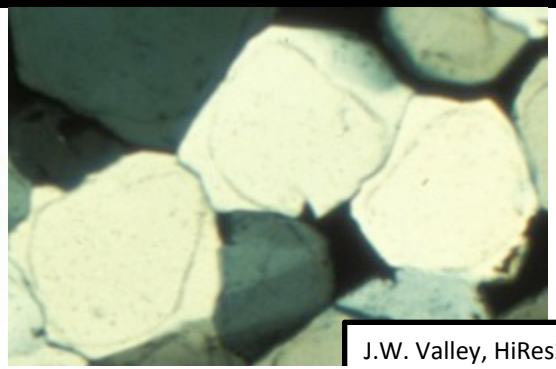
In Situ Isotope Geochemistry by Ion Microprobe: Accuracy vs. Precision

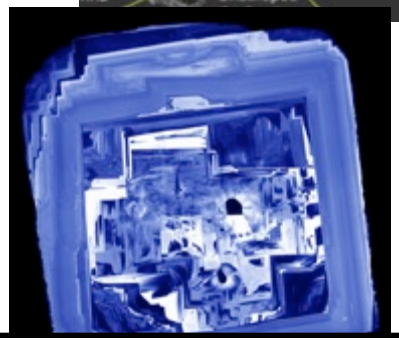
John Valley

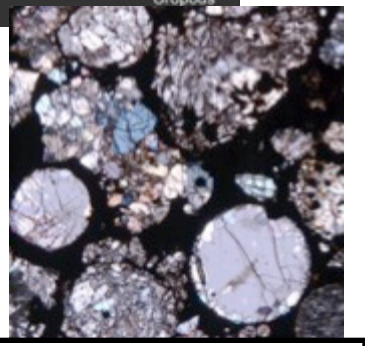












SIMS Measurement of stable isotope ratios

IMS-1280

Accuracy vs. Precision

SIMS vs. other techniques

Spot size vs. precision, FC vs. EM

X-Y effects

Polishing relief

Imaging: correlated analysis, targeting sample spots, pit evaluation

Regular vs. irregular pits

Standards: Bias, IMF

Crystallographic orientation effects

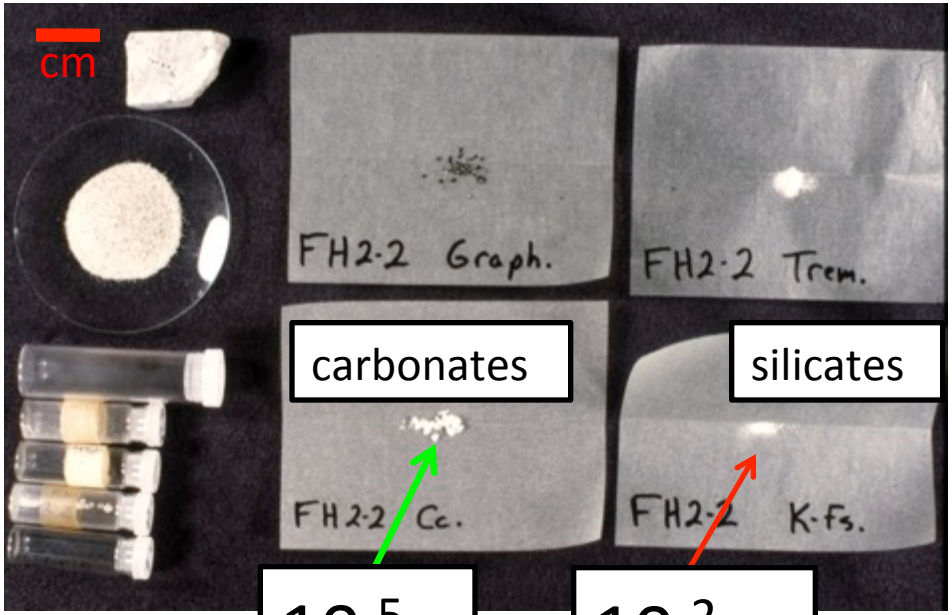
Applications: Otoliths, Tooth enamel, Diagenetic cements, Sulfides, Microfossils

Conventional (non-SIMS) Analysis of $\delta^{18}O$

Powders & chips

mm- to cm-scale

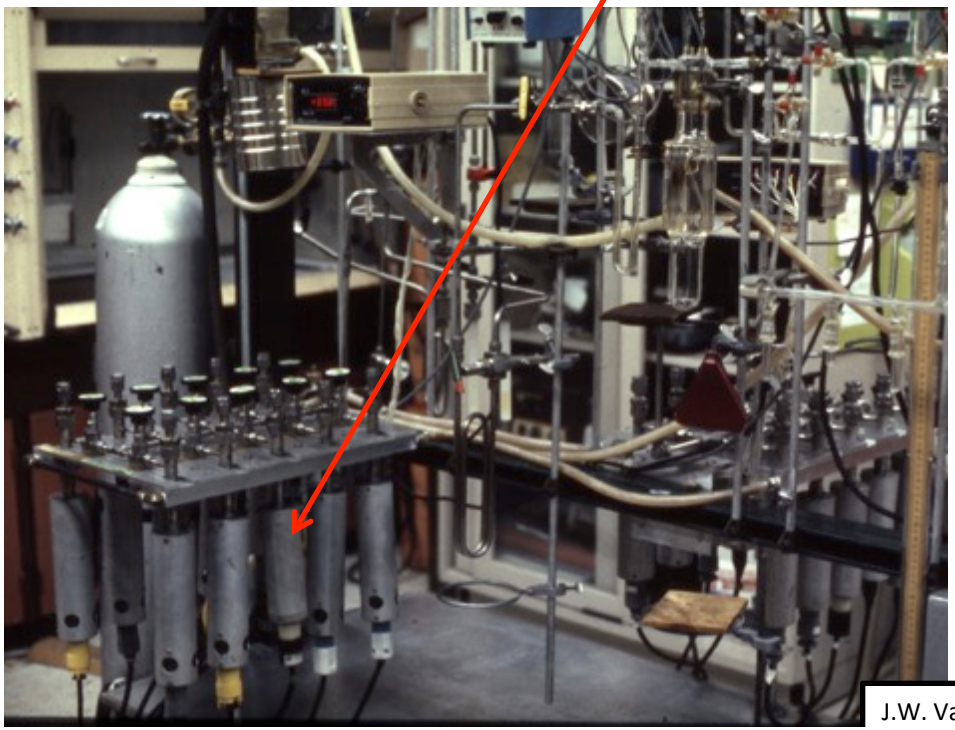
Gas-source mass spectrometer

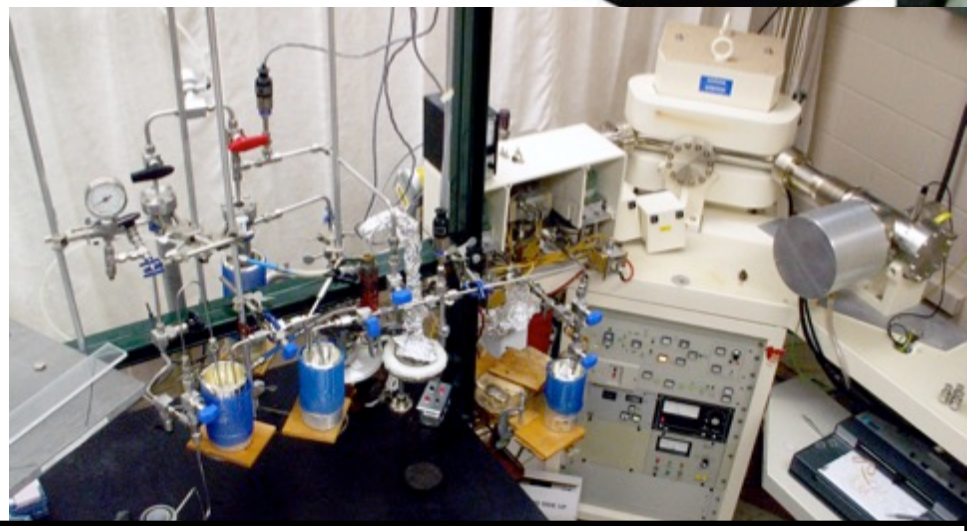


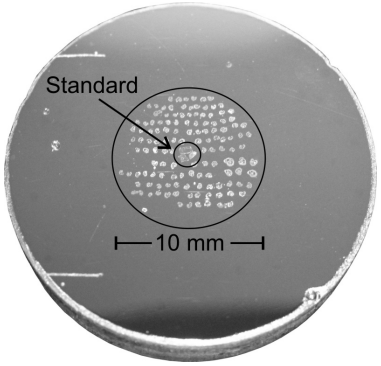
10^{-5} g

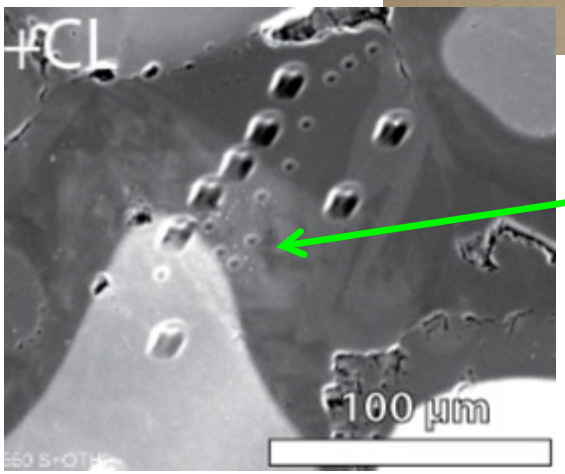
10^{-2} g

10^{-3}-10^{-4} g







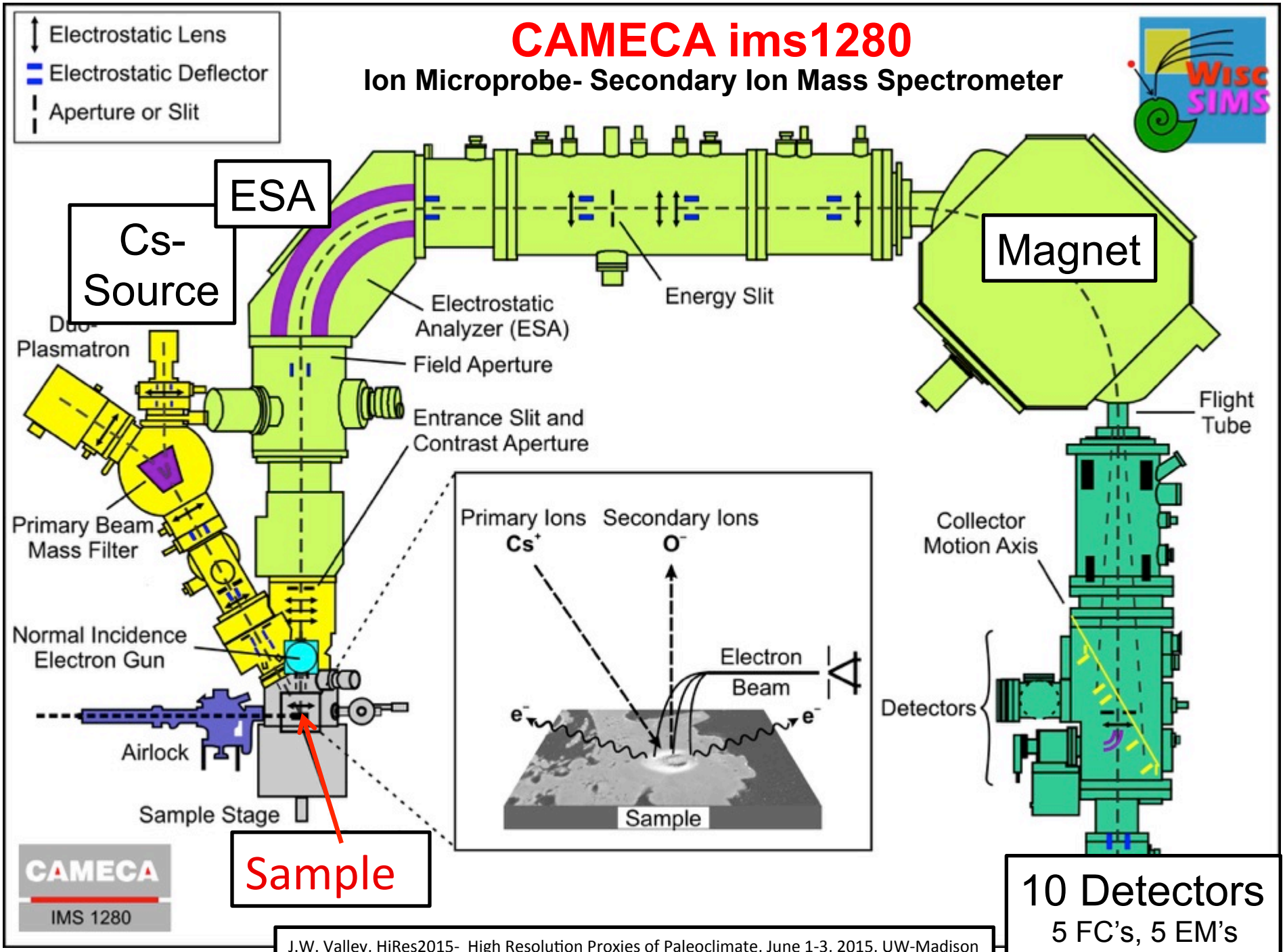


In situ analysis
1-10 micrometer spot
10^{-9} - 10^{-12} g Million to billion times smaller !

Isotope Ratios: H, Li, B, C, N, O, Mg, Si, S, Cl, Ca, Fe
Light & trace elements

CAMECA ims1280

Ion Microprobe- Secondary Ion Mass Spectrometer

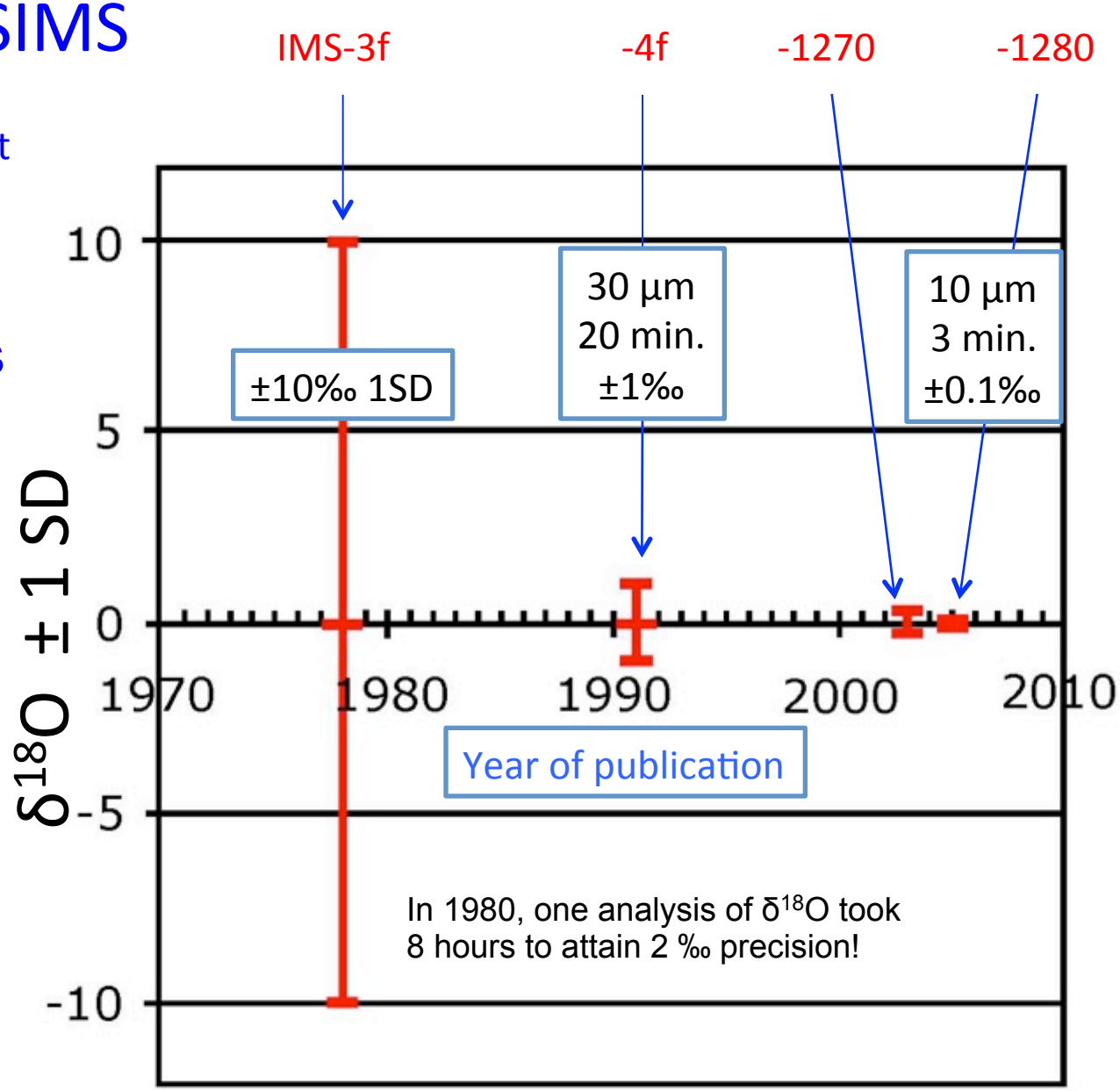


Ion Microprobe/ SIMS

Analytical Precision
30 years of Improvement

Oxygen Isotopes

IMS-1280
IMS-7f
nanoSIMS
SHRIMP II
Laser ablation

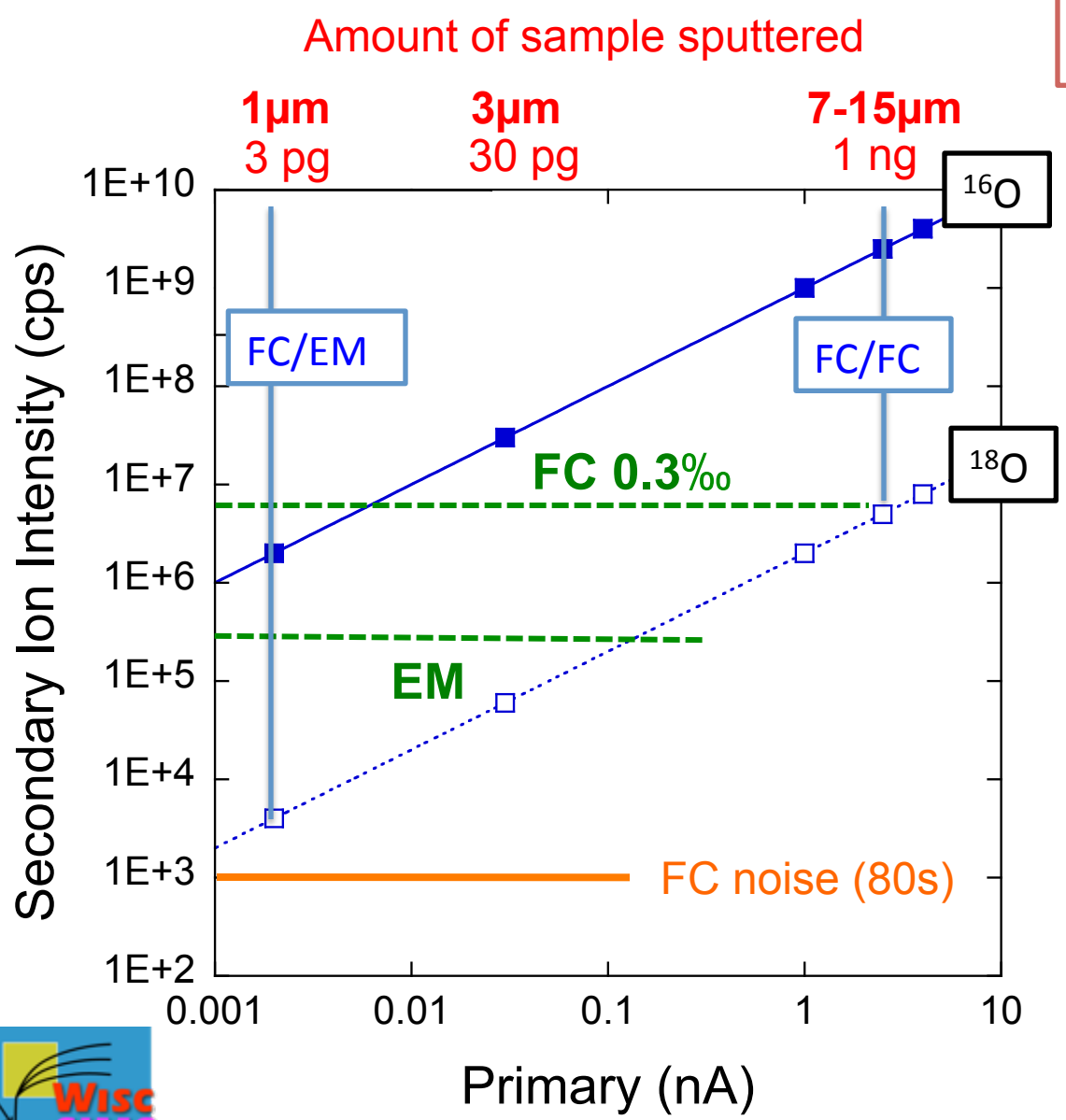


Valley & Kita 2009

Trade-Off

Precision vs. Spot Size

FC- Faraday Cup
EM- Electron Multiplier



($^{18}O/^{16}O$) Precision (‰)

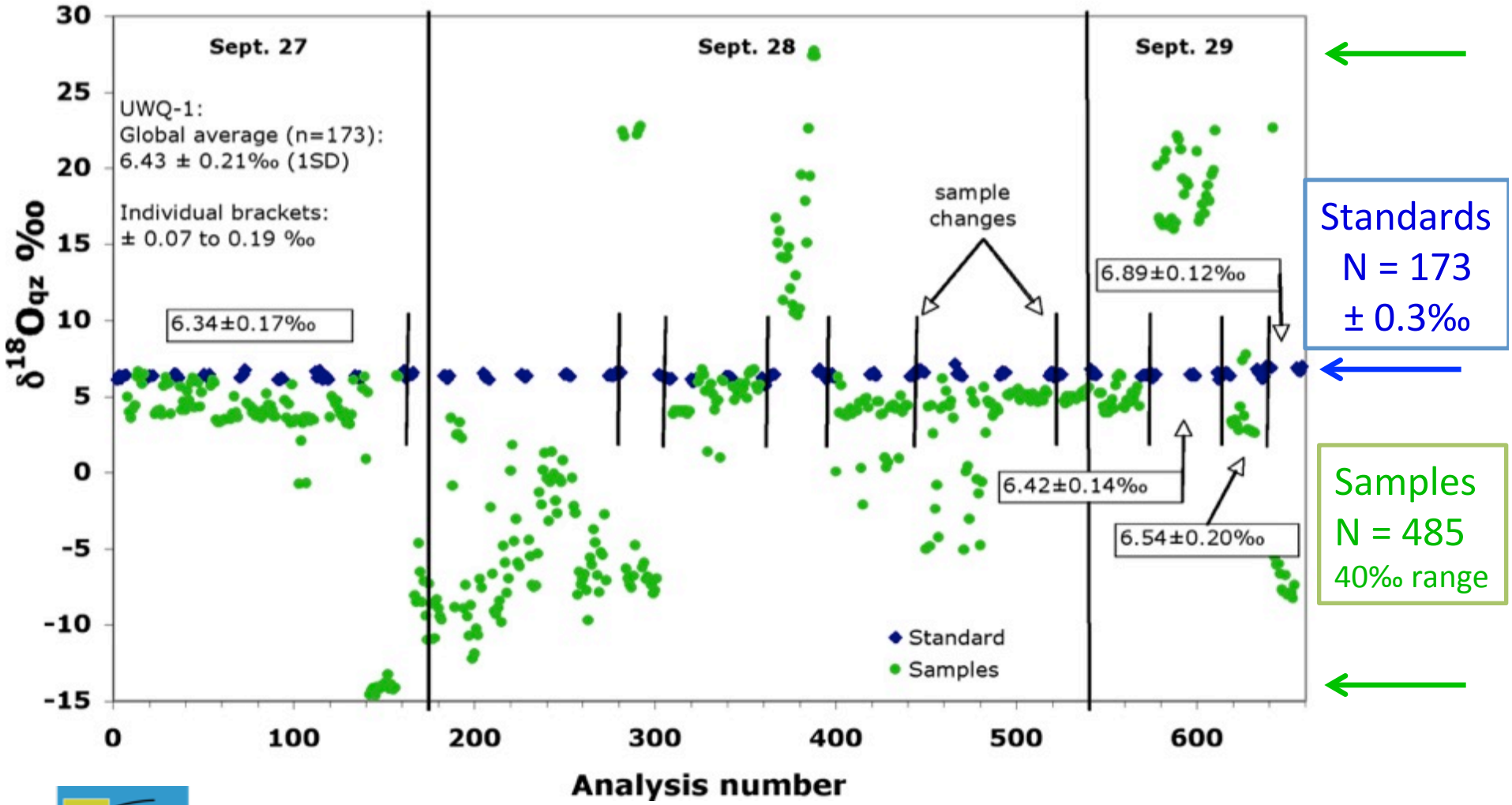
FC-FC Mode: ≤0.3‰
10-15µm (2-3nA)
3 min

FC-EM Mode: 0.5-1‰
1-3µm (2pA -30pA)
10-30 min

Kita, unpd

FC-FC: $\delta^{18}O$ 10 µm spot

Average Precision < 0.3‰ 2SD, 0.04‰ 2SE



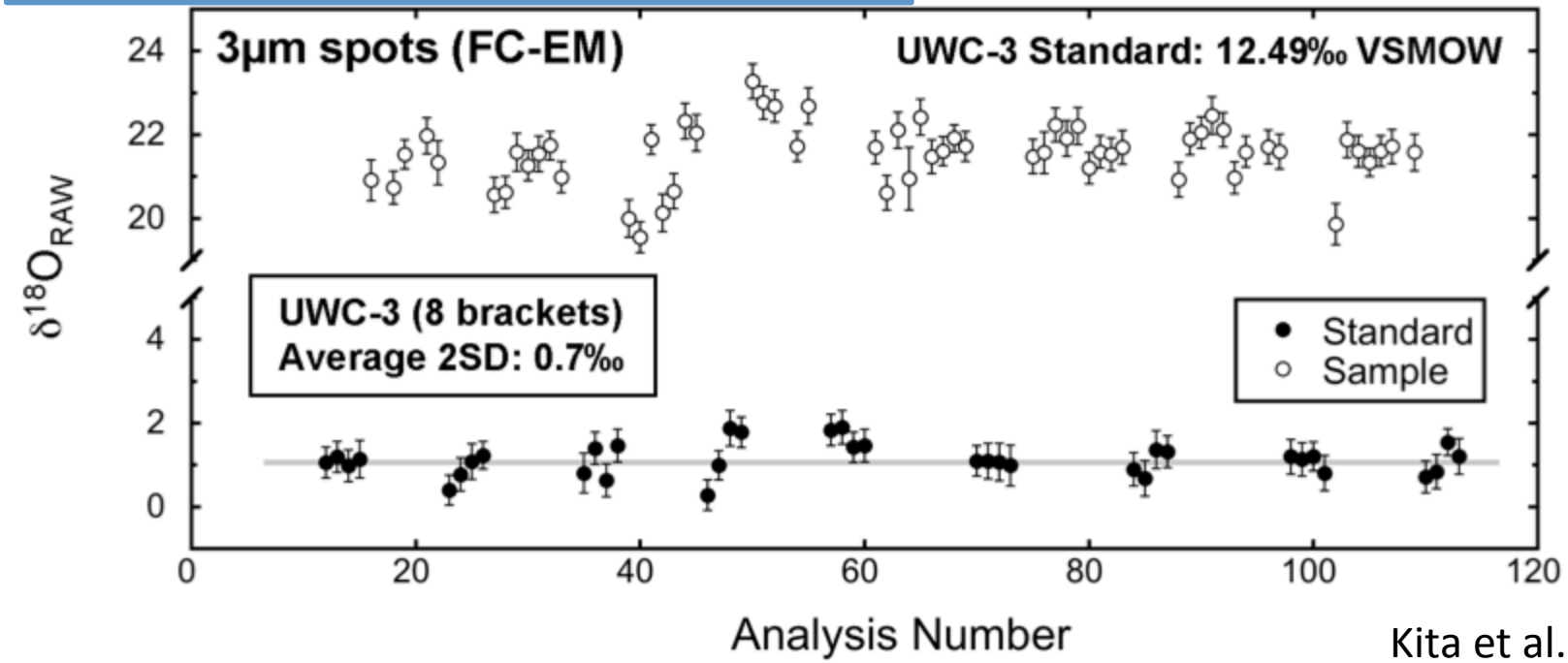
48 hrs, 658 analyses of quartz

Valley & Kita 2009

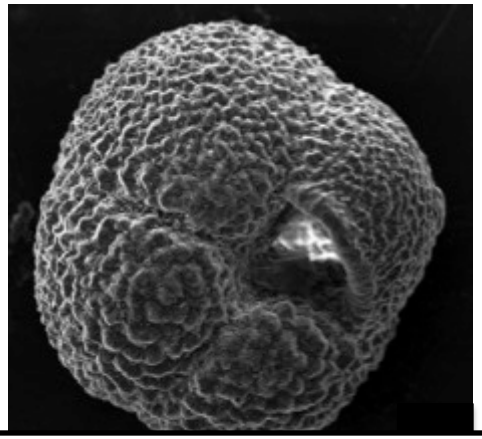
FC-EM: $\delta^{18}O$ 3 µm spot

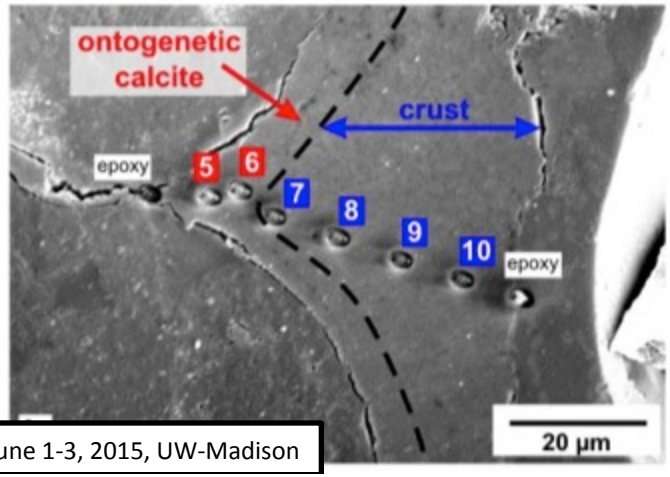
Calcite

2SD = 0.7 ‰



Kita et al. 2009

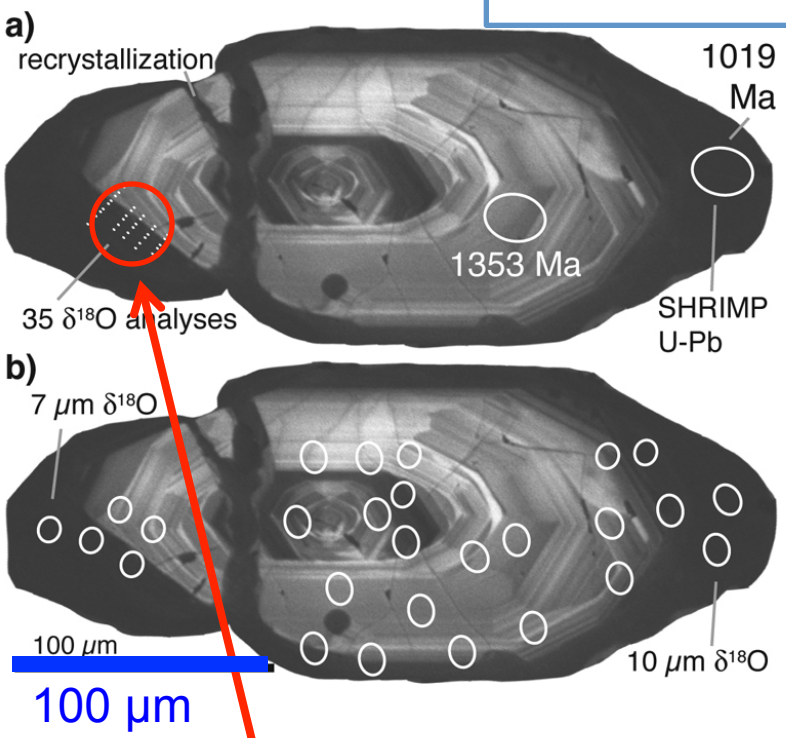


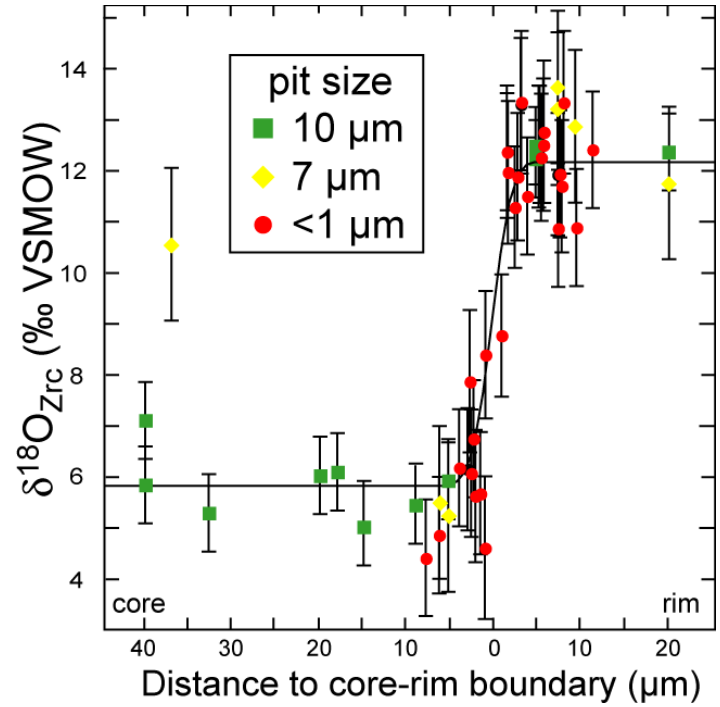


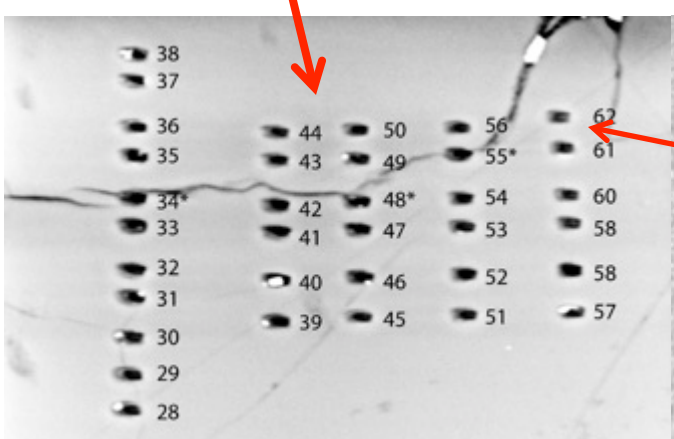
Kozdon et al. 2009

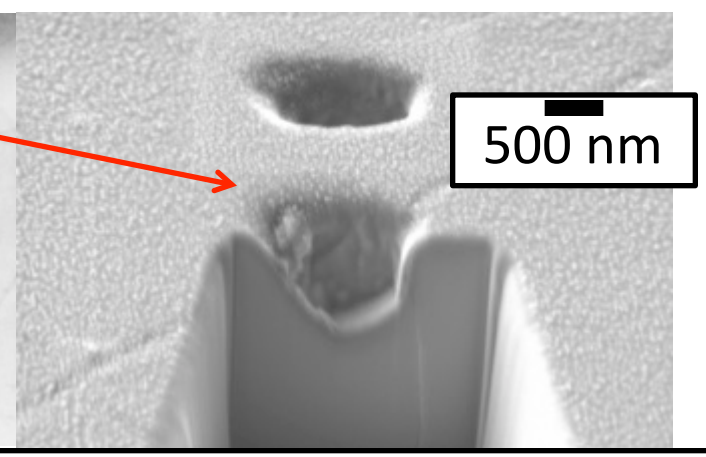
$\delta^{18}O$ sub 1-µm spot, ~ 1 pg

2 SD = 2 ‰





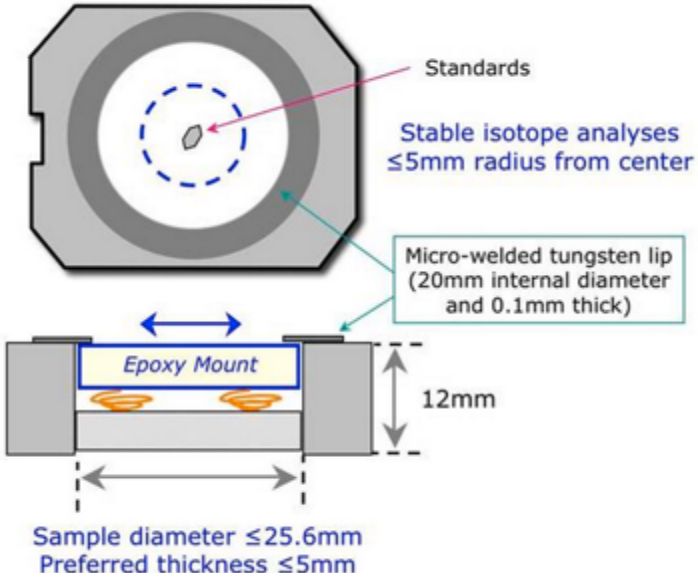


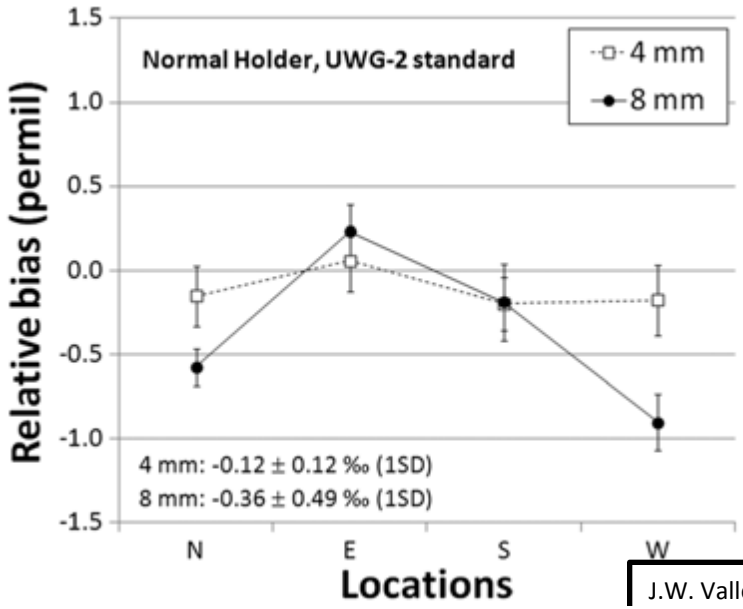


Page et al. 2007
Bowman et al. 2011

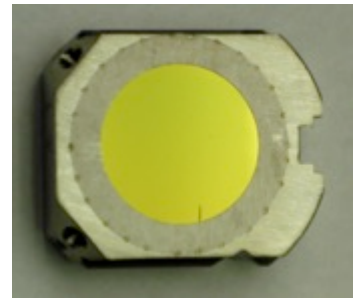
X-Y effect

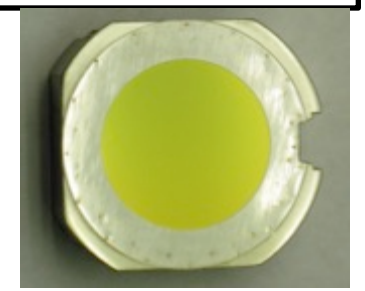
Larger holder minimizes X-Y effects

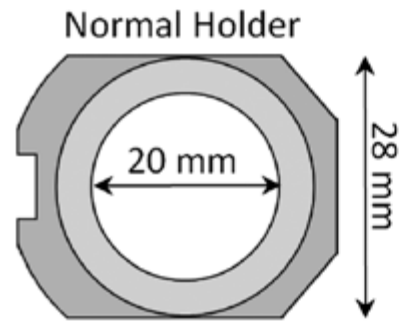


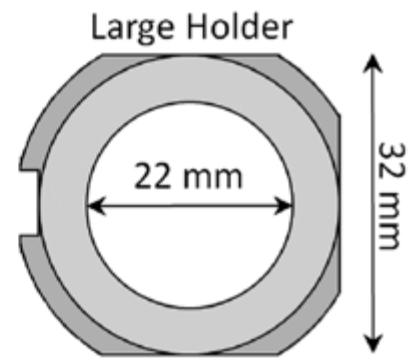


New larger holder



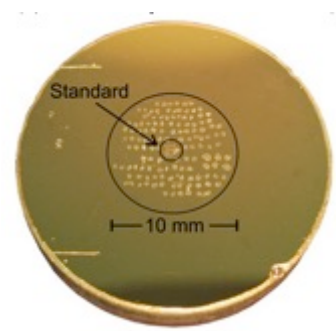


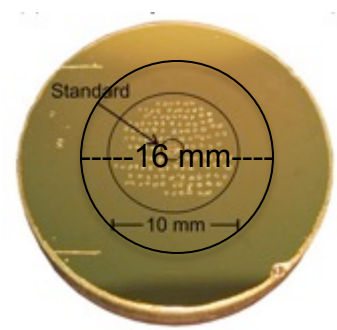




analysis zone:
10 mm diameter
78 mm^2

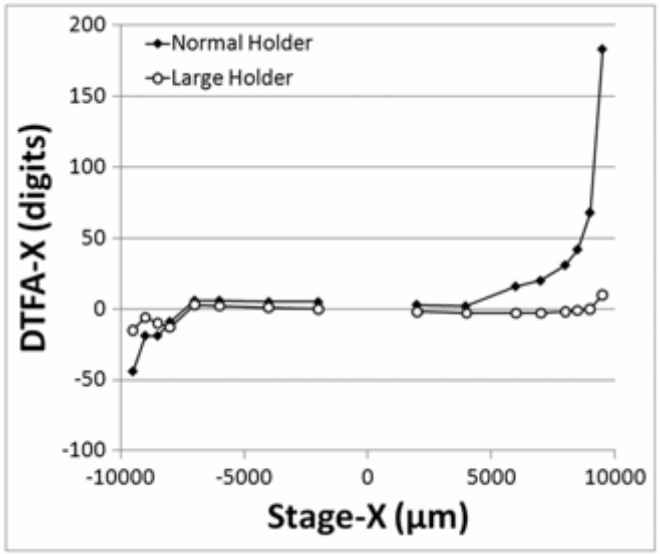
analysis zone:
16 mm diameter
201 mm^2

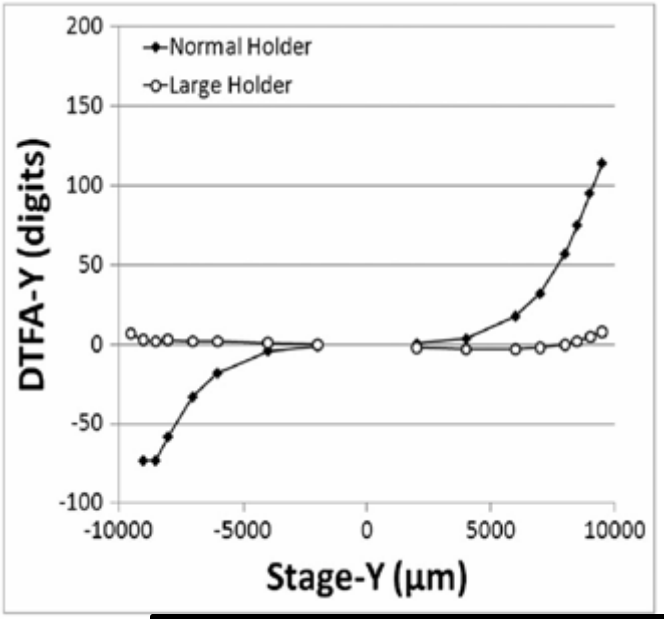




Peres et al. 2012

X-Y effect





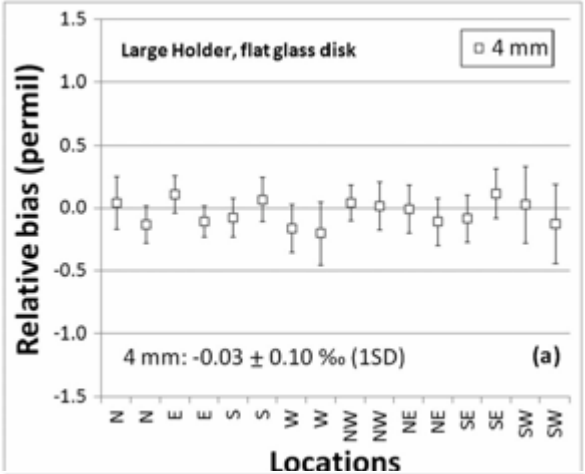
Flat glass disk

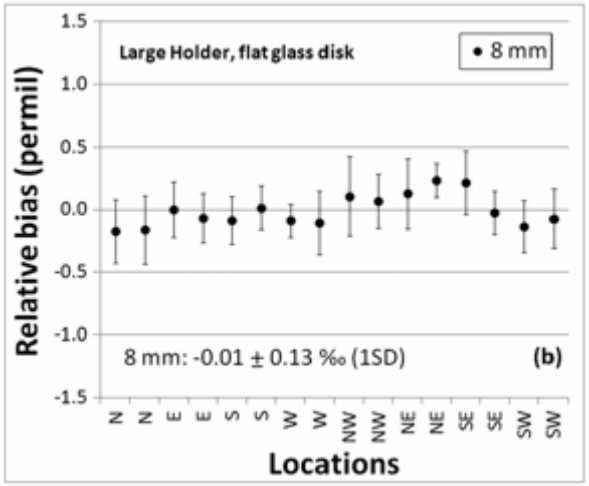
±0.10‰
Radius = 4mm

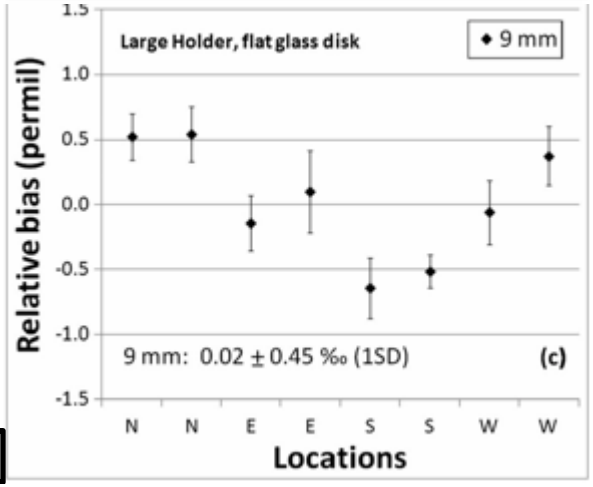
±0.13‰
Radius = 6mm

±0.45‰
Radius = 9mm

Peres et al. 2013
Surf. Interface. Anal.



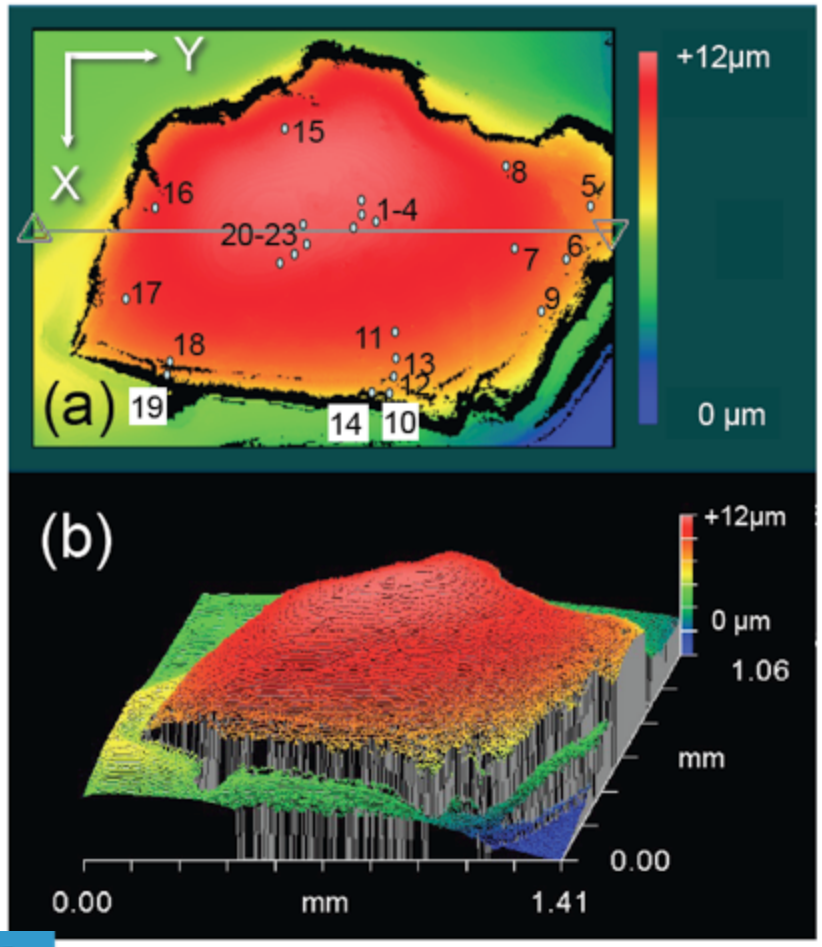




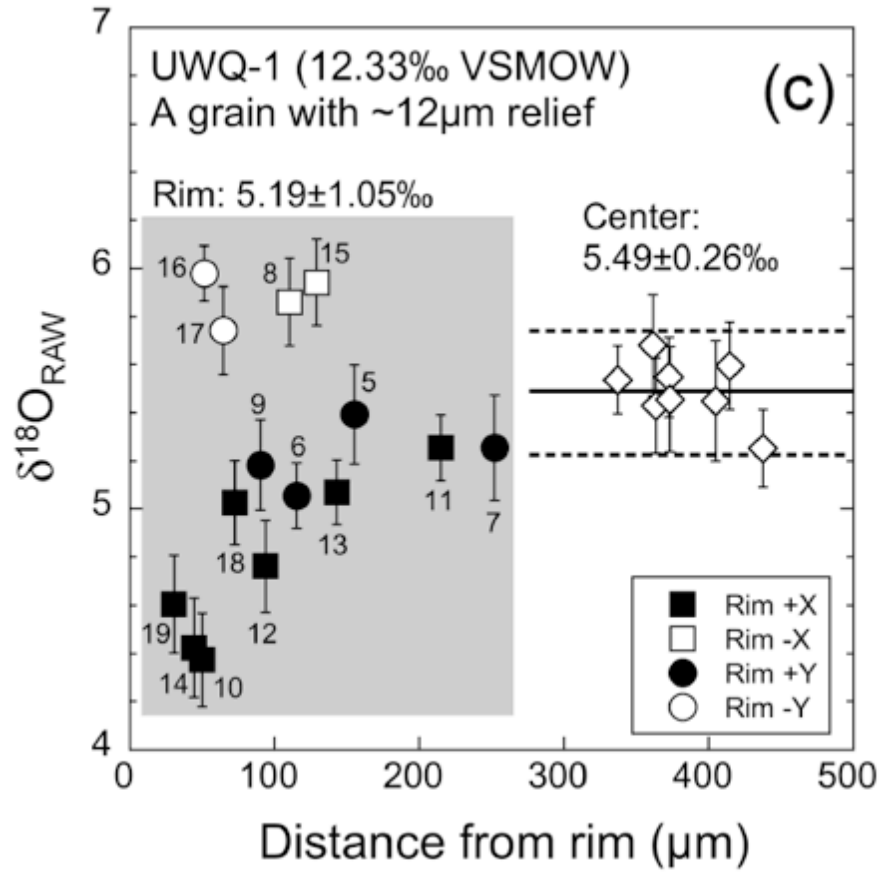
Polishing relief

Rounded or Inclined surface, Edges

Surface Profilometer ~10µm topography



Quartz



Kita et al. (2009)

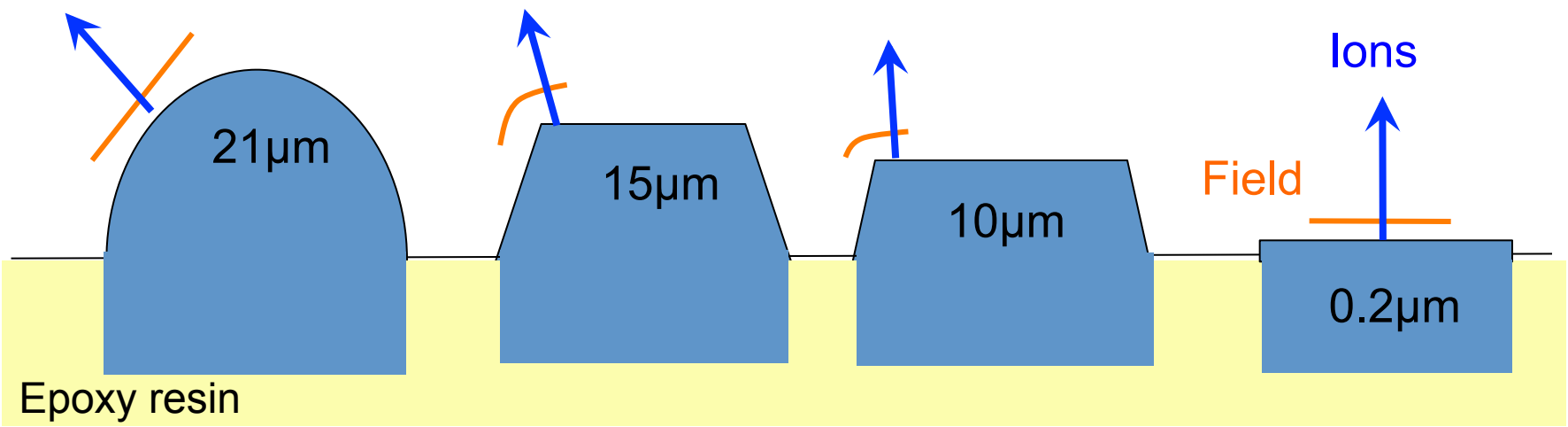
Polishing relief

Modification of surface electrostatic field

Zircon

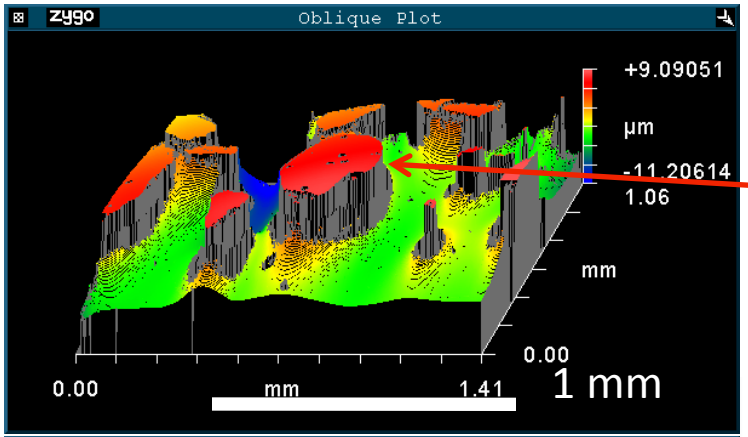
Request all the users to determine if polishing relief is less than a few µm

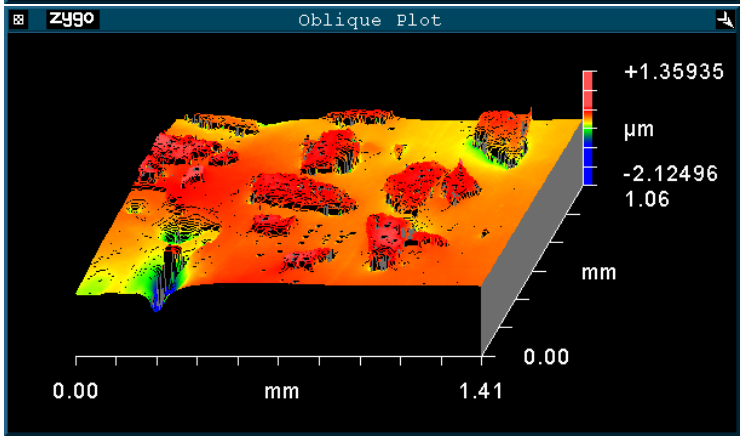
Changes the angle of secondary ions?



☹ Polishing Relief ☺

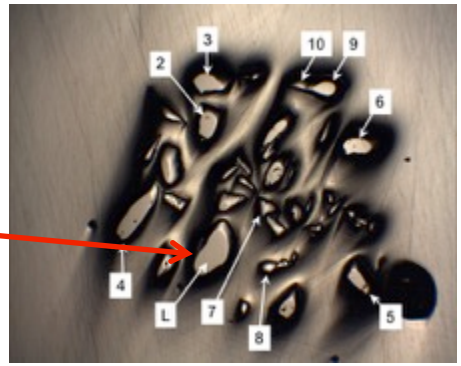
Polishing relief

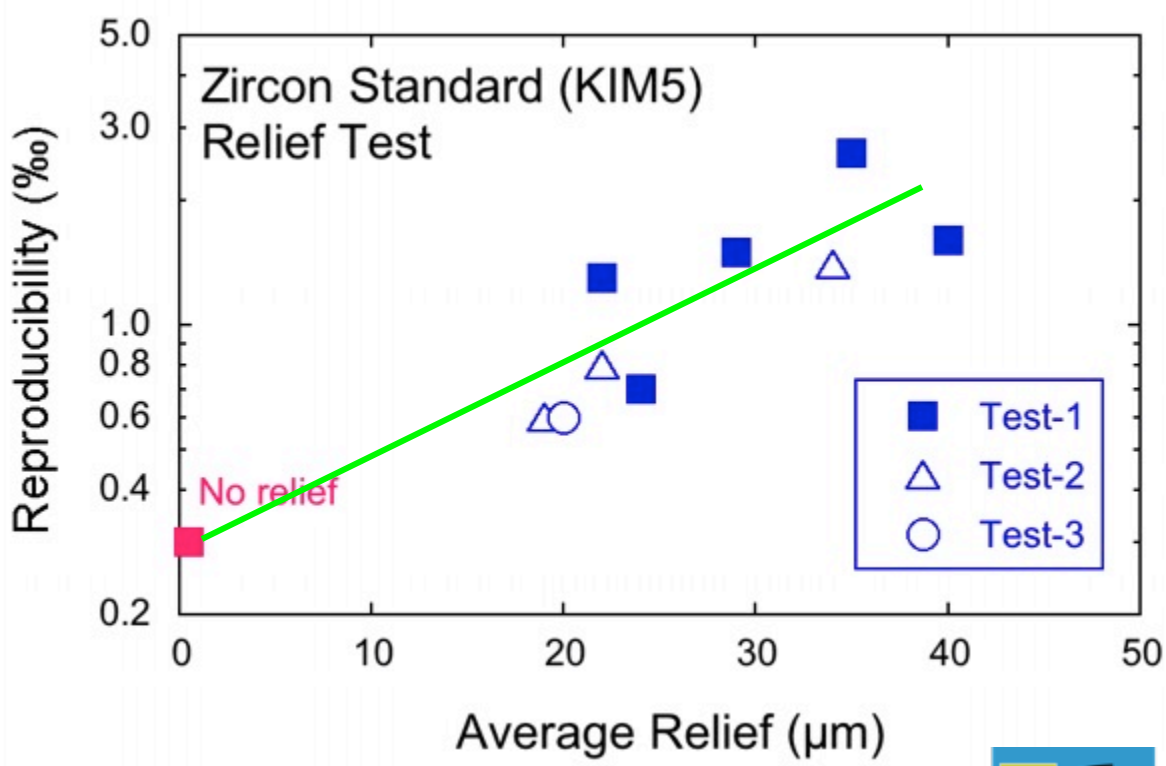




KIM-5

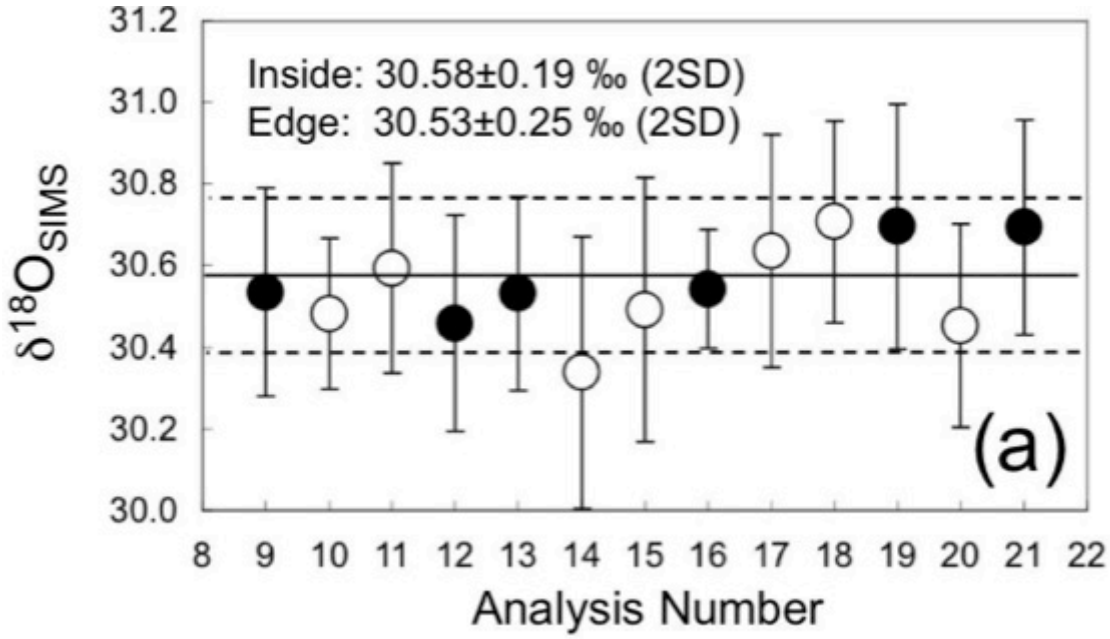
Zircon Standard





Kita et al. 2009

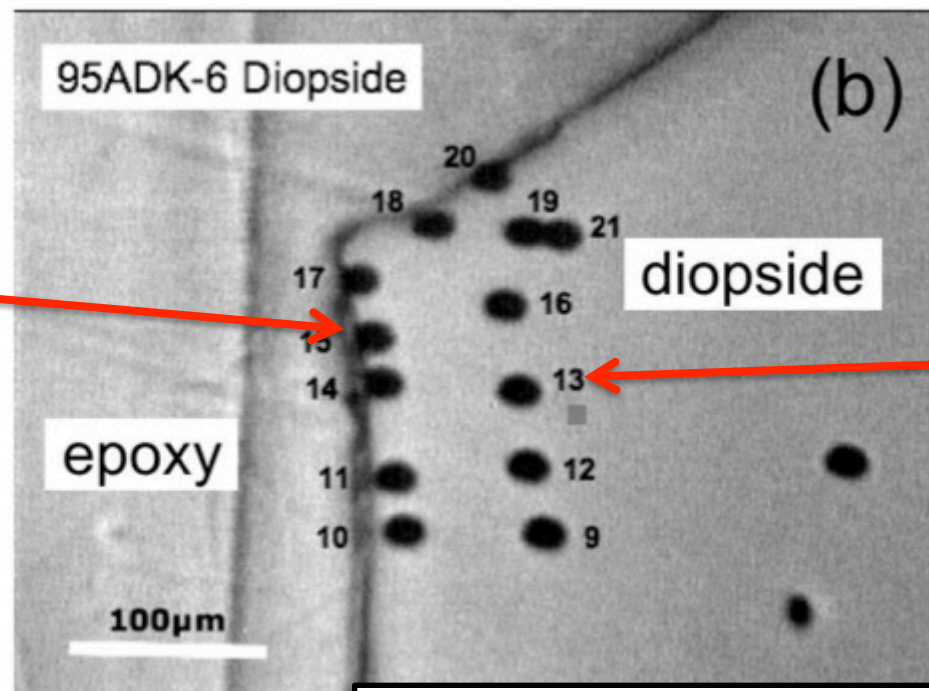
No Polishing relief



Well-Polished Sample Precise & Accurate

Grain boundary
Flat surface
Low relief

30.53‰
±0.09 2SE



30.58‰
±0.08 2SE

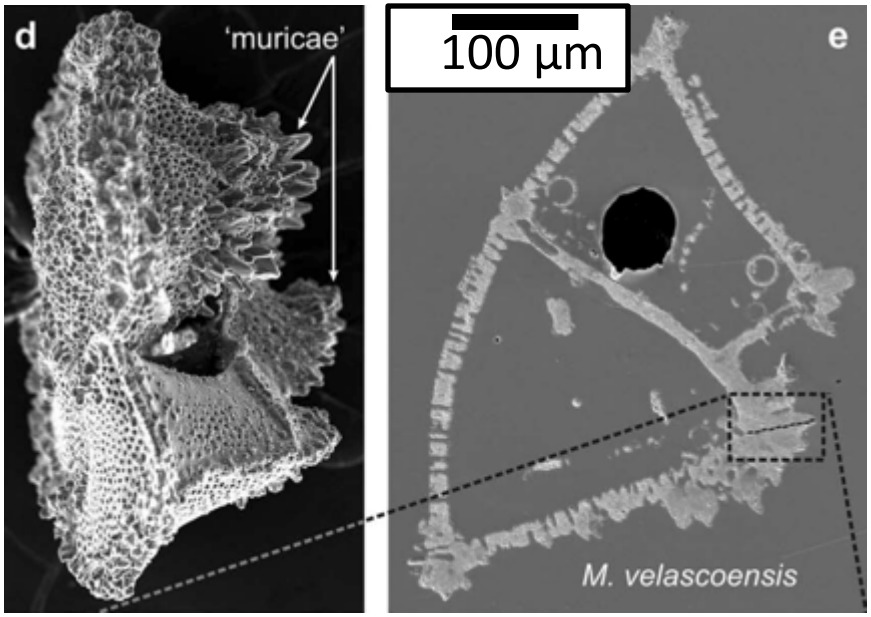
Kita et al. 2009

Correlated Analysis by SIMS

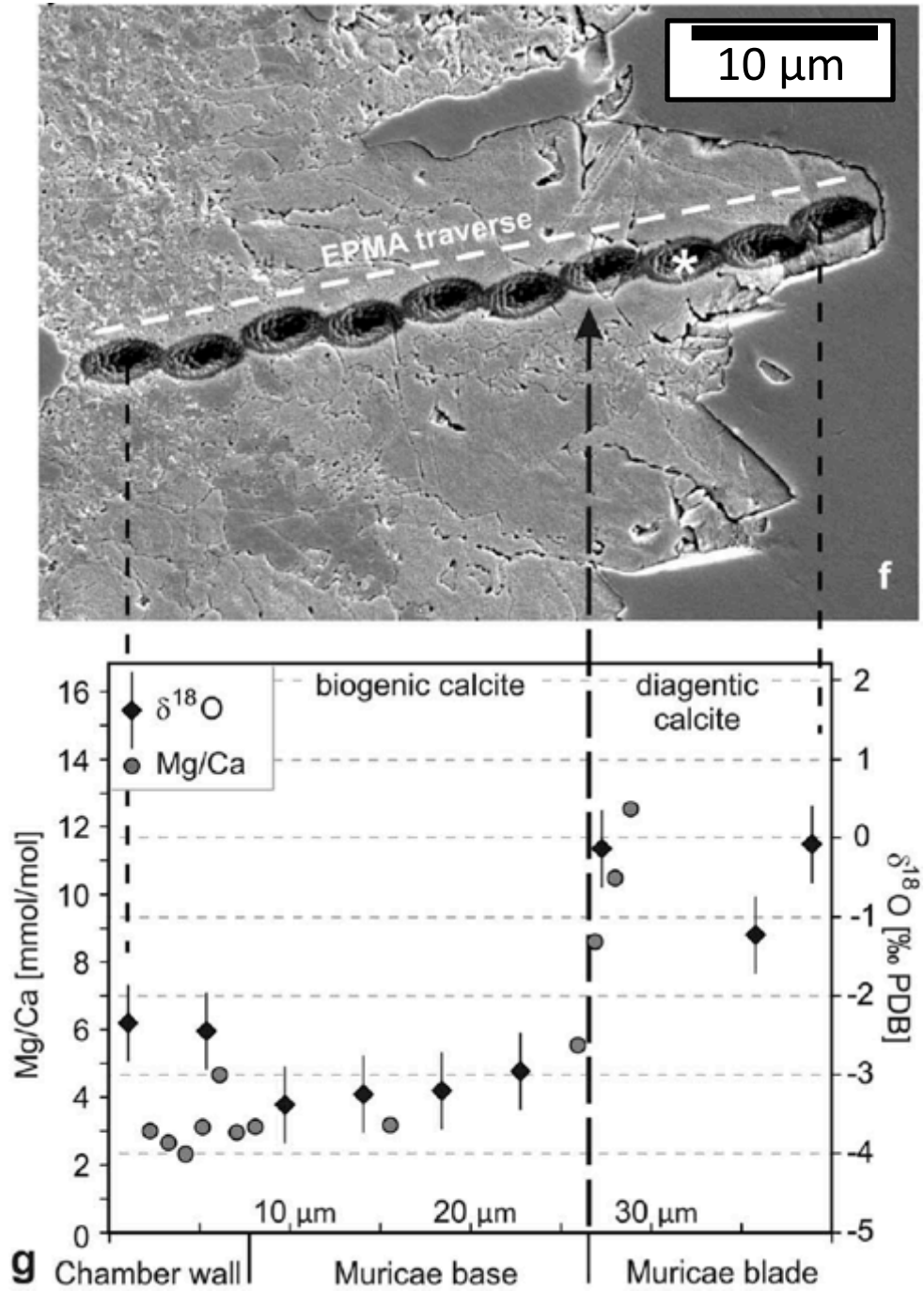
Foraminifera Calcite

$\delta^{18}O$ 3 µm spot SIMS

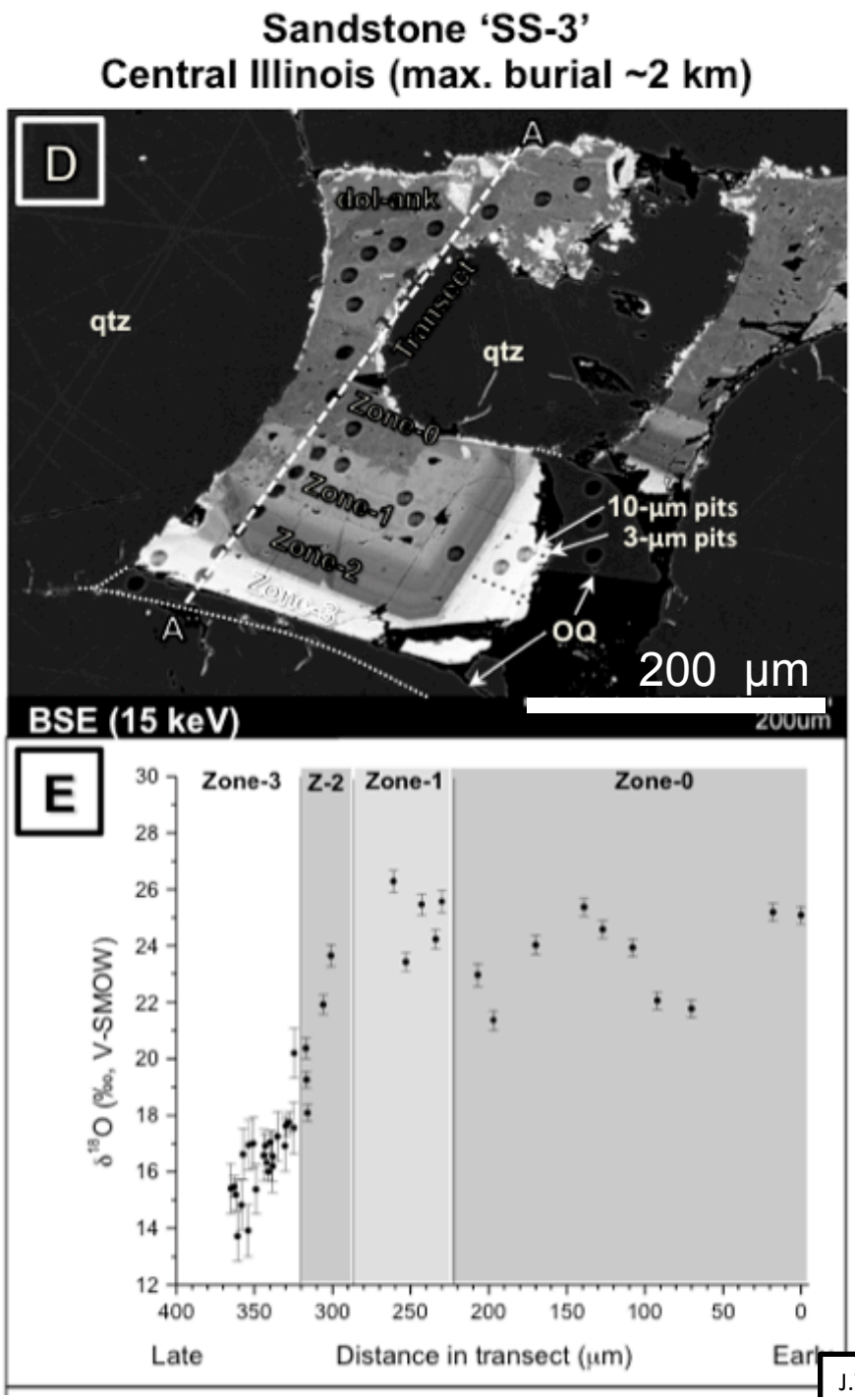
Mg/Ca EPMA



Kozdon et al. 2013



Correlated Analysis by SIMS



Carbonates

Imaging –
- Optics,
- SEM (BSE, CL),
- Confocal laser fluorescence

$\delta^{18}O$

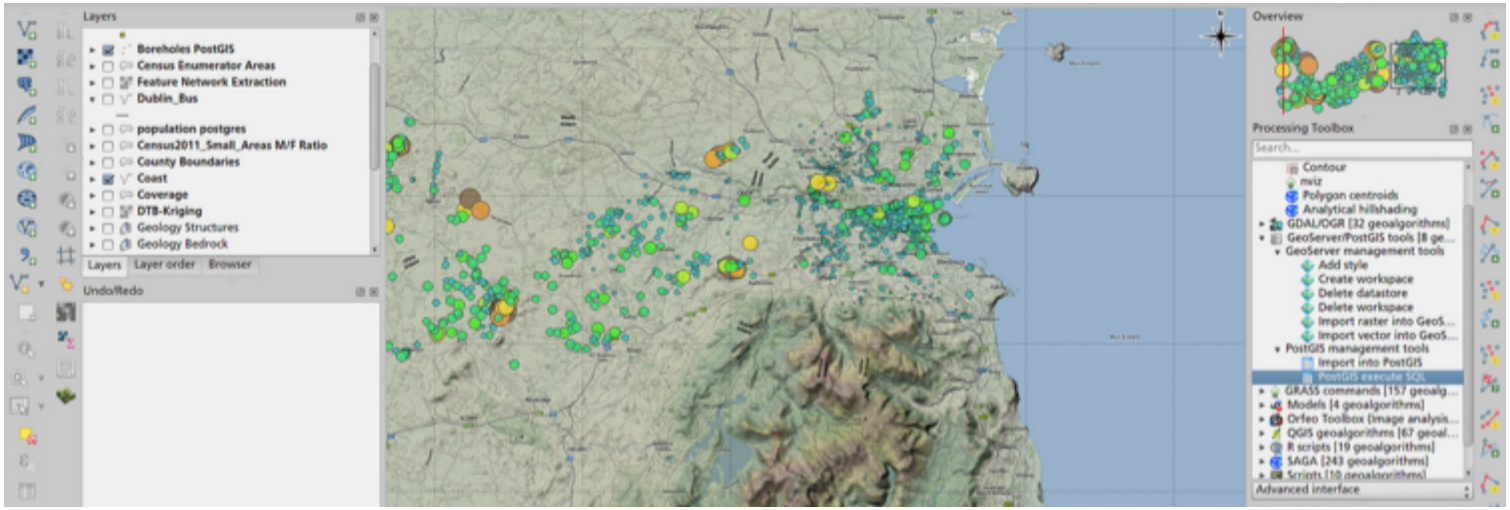
$\delta^{13}C$

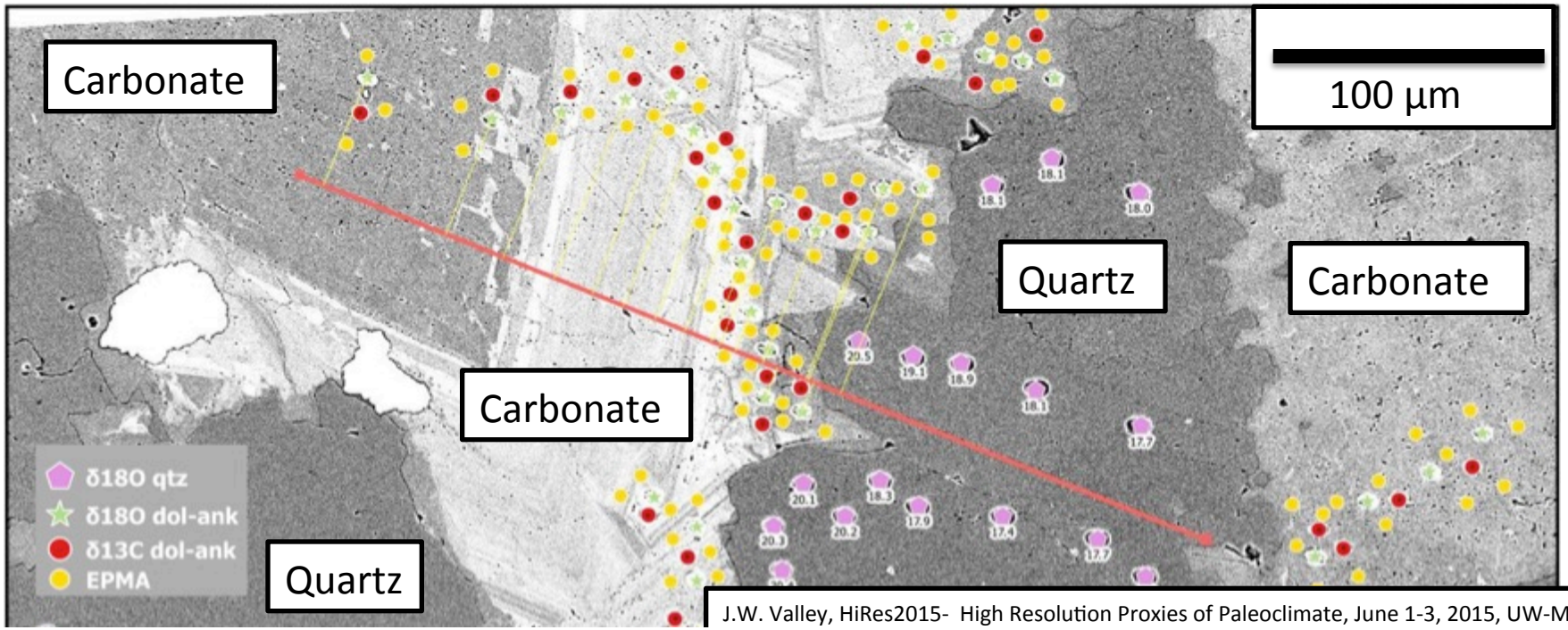
Major & Trace elements
- Fe/Mg
- Mg/Ca
- Sr/Ca

Sliwinski et al., HiRes2015Poster
Denny et al., HiRes2015Poster

QGIS Trademark

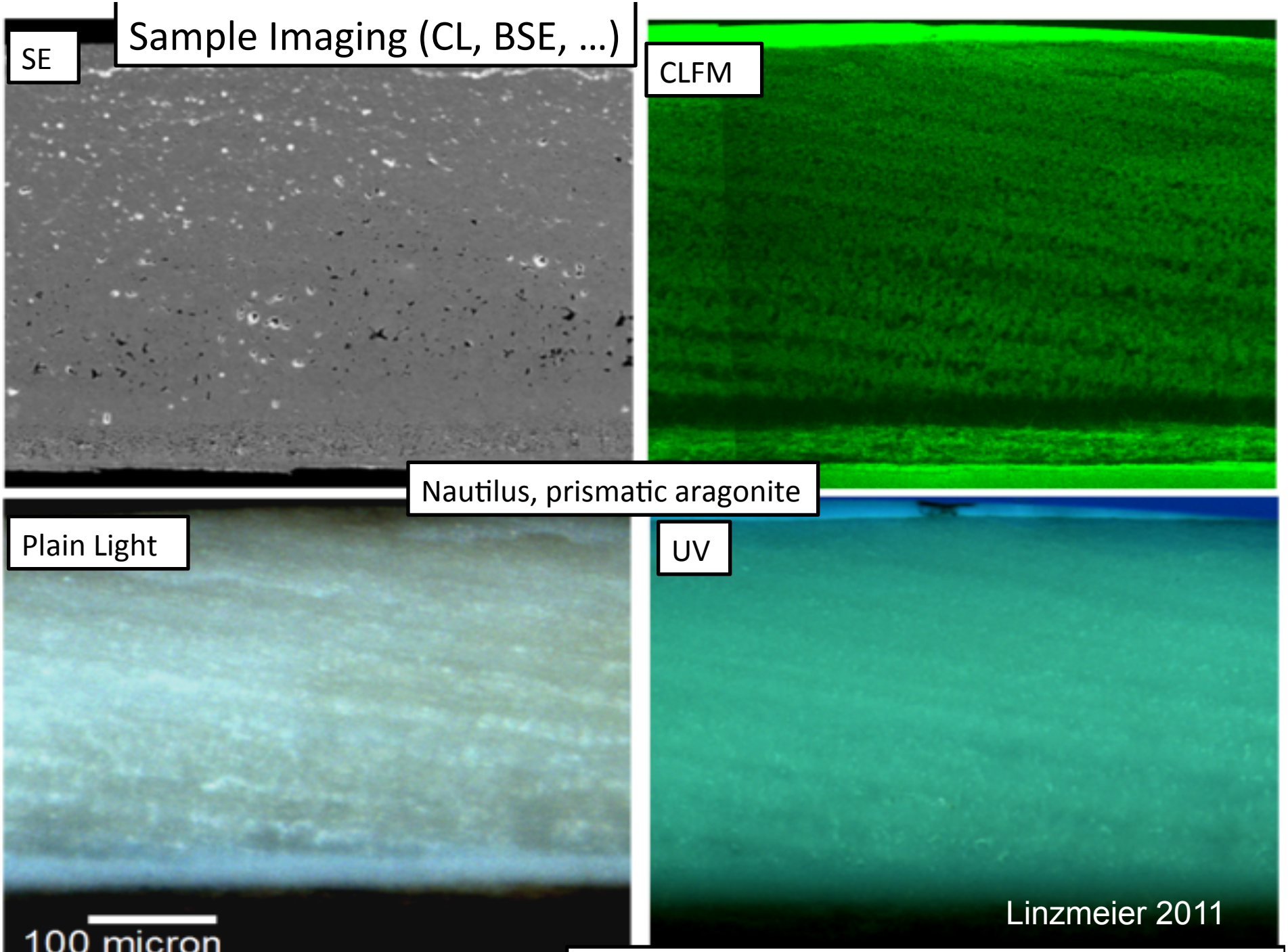
Cammack et al., 4:50 PM, Today





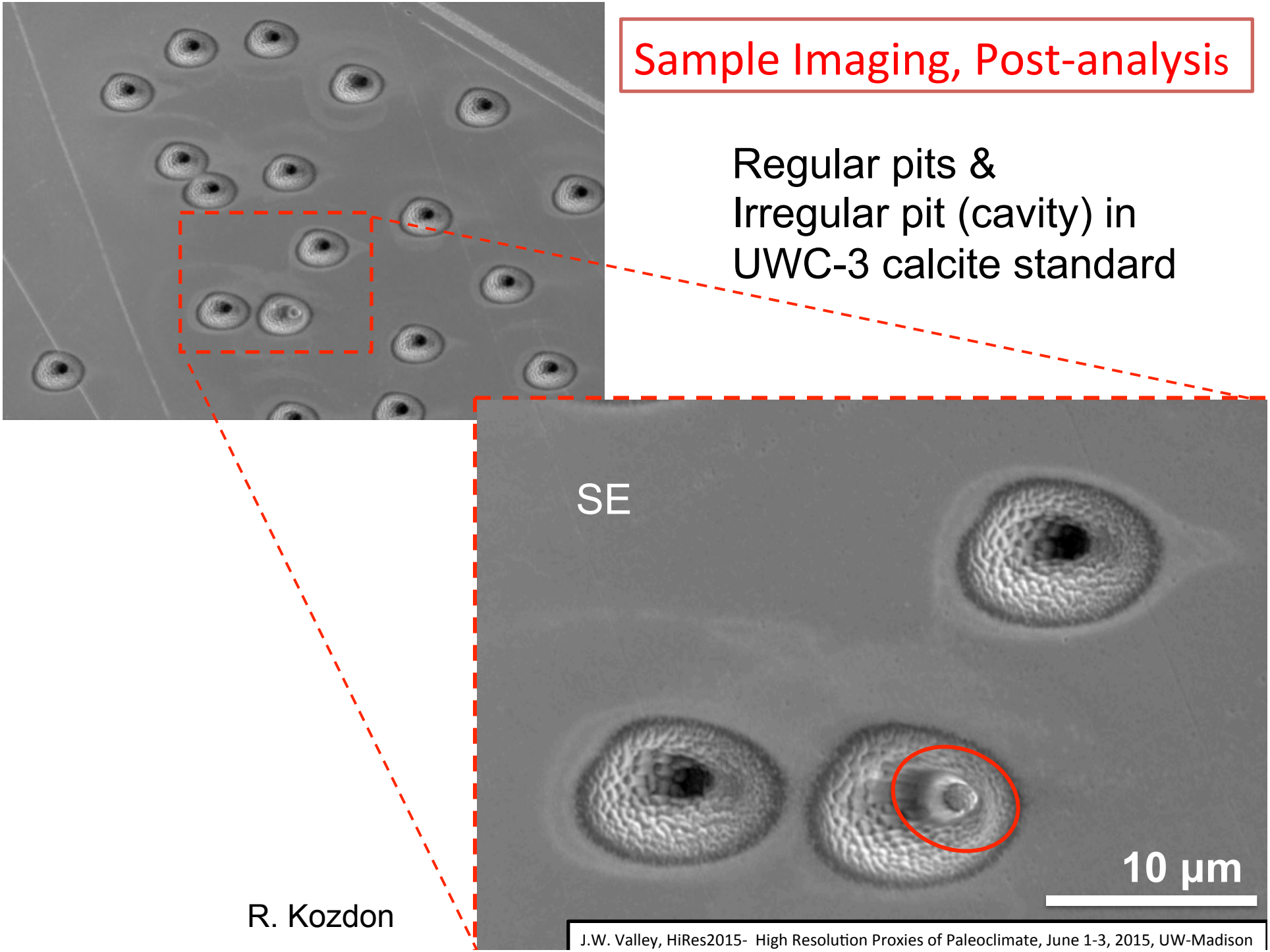
J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison

Sample Imaging (CL, BSE, …)

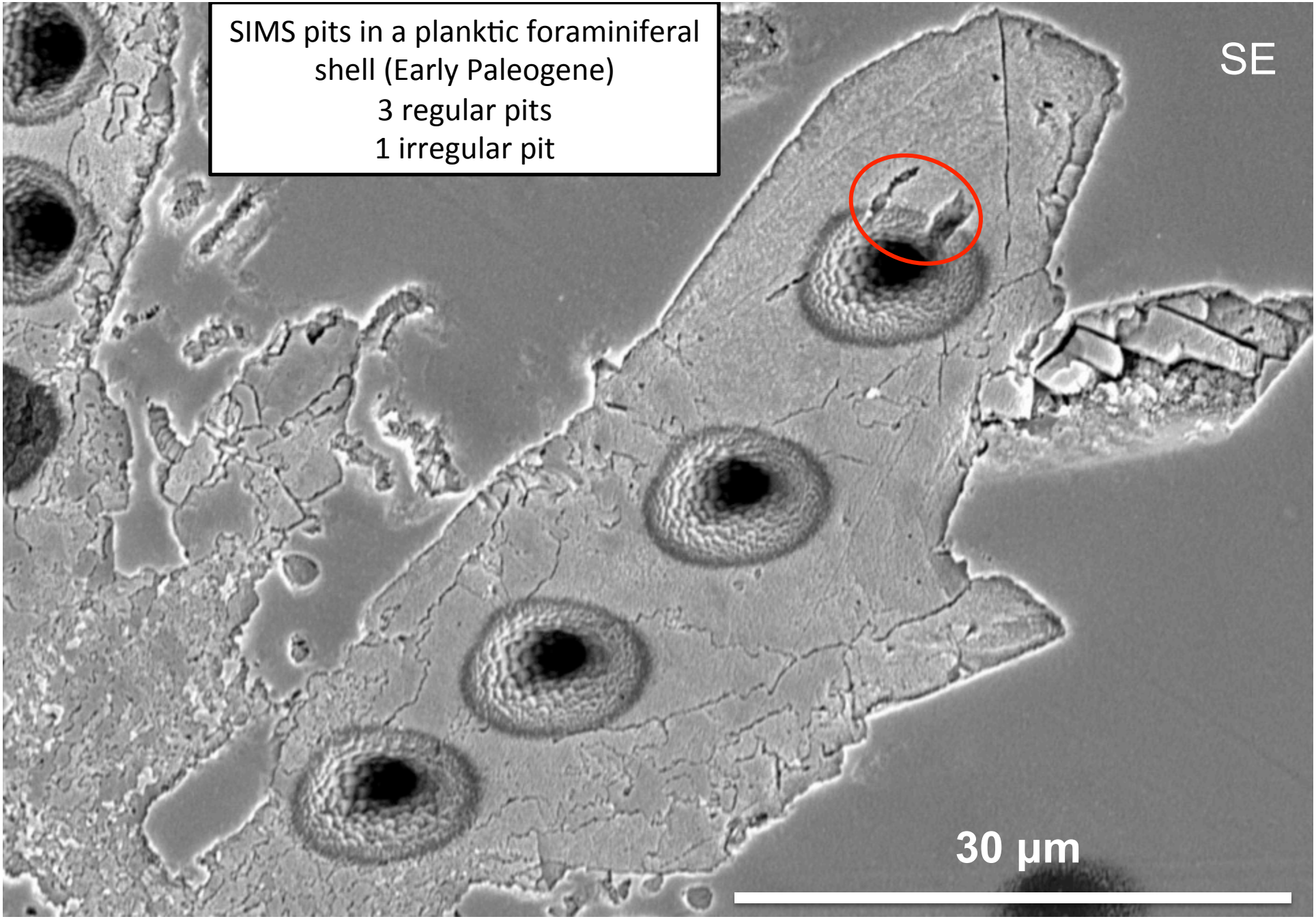


Sample Imaging, Post-analysis

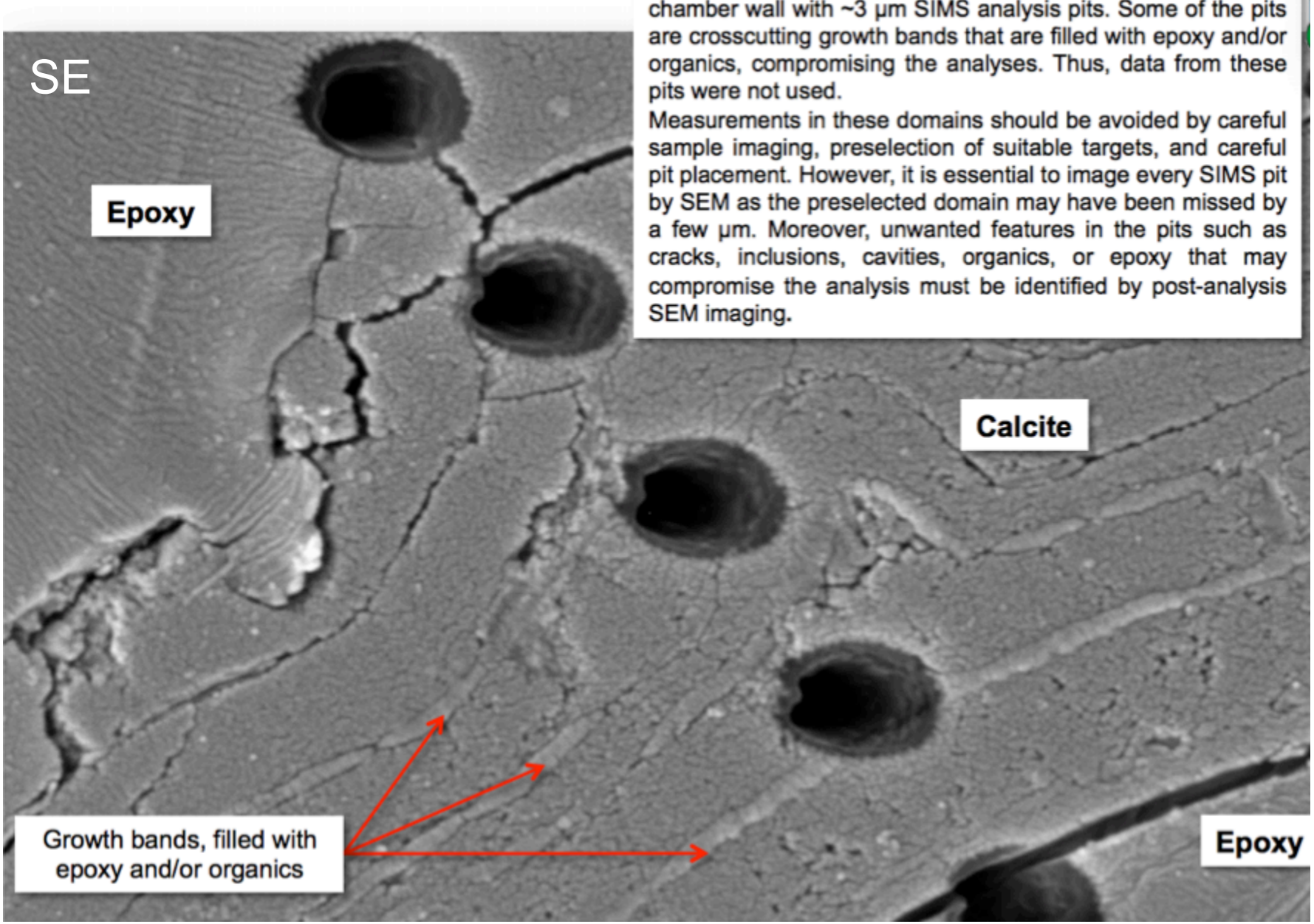
Regular pits &
Irregular pit (cavity) in
UWC-3 calcite standard



R. Kozdon


SIMS pits in a planktic foraminiferal shell (Early Paleogene)
3 regular pits
1 irregular pit
SE
30 µm

R. Kozdon



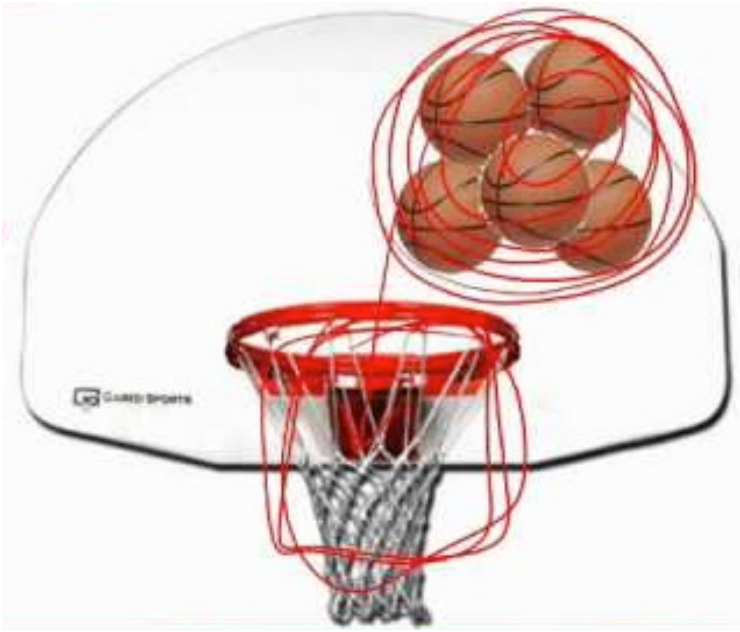
SE image of an Au-coated sample, showing a foraminiferal chamber wall with ~3 µm SIMS analysis pits. Some of the pits are crosscutting growth bands that are filled with epoxy and/or organics, compromising the analyses. Thus, data from these pits were not used.

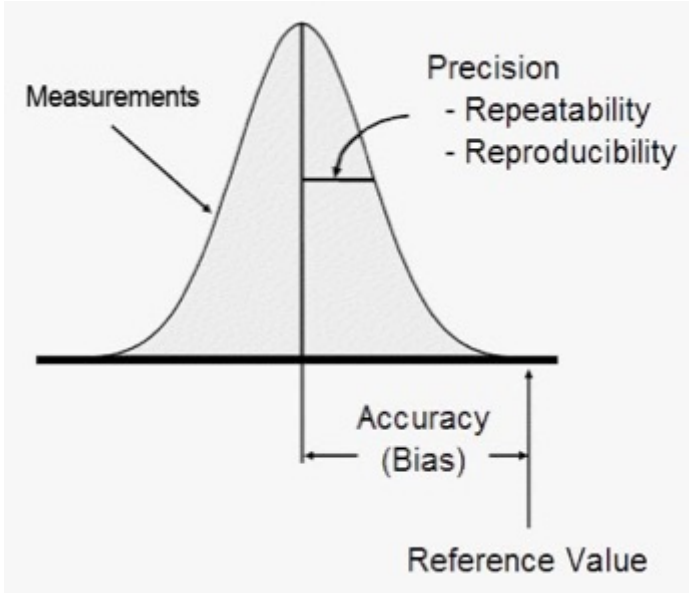
Measurements in these domains should be avoided by careful sample imaging, preselection of suitable targets, and careful pit placement. However, it is essential to image every SIMS pit by SEM as the preselected domain may have been missed by a few µm. Moreover, unwanted features in the pits such as cracks, inclusions, cavities, organics, or epoxy that may compromise the analysis must be identified by post-analysis SEM imaging.

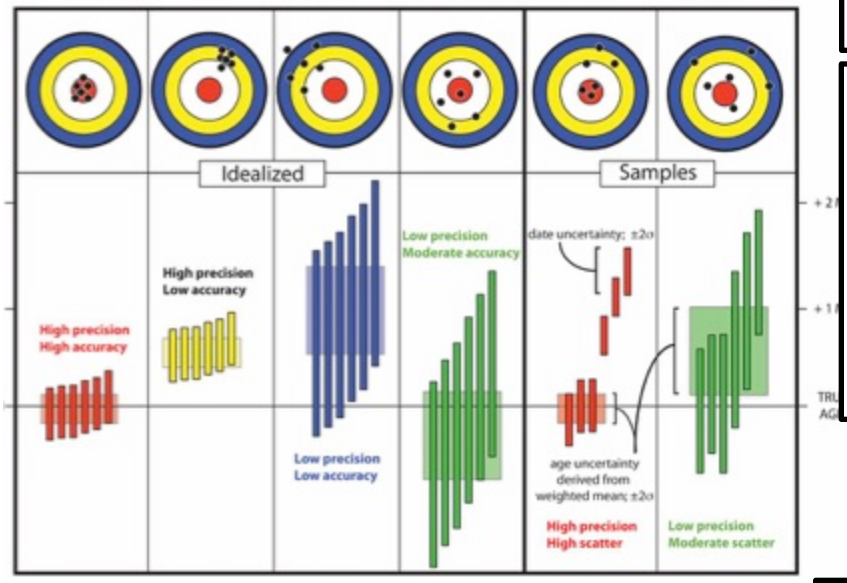
R. Kozdon

10 µm

Accuracy vs. Precision







Precision of SIMS measurements

σ, SD, SE

Standard deviation vs. Standard error

Accuracy of SIMS measurements

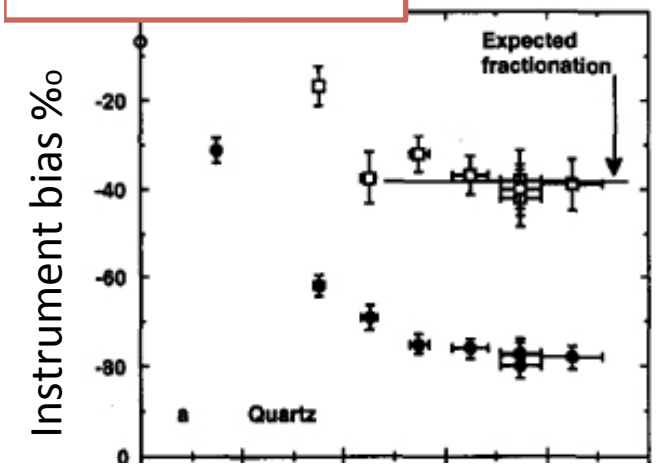
Bias (IMF): δ(measured) vs. δ(true)

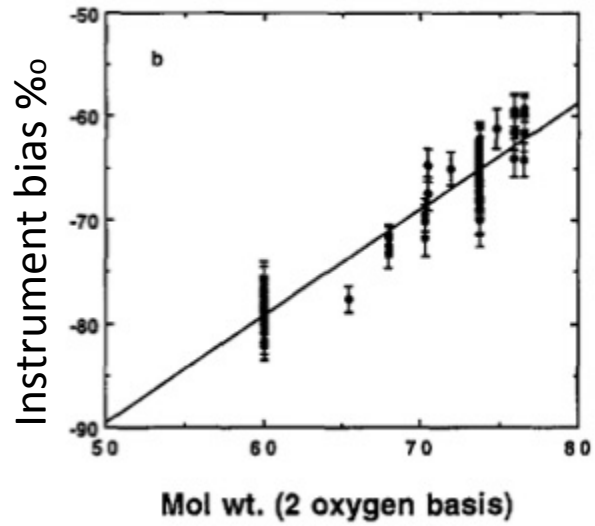
Reference standards

- chemical & structural match to samples
- calibrated & homogeneous

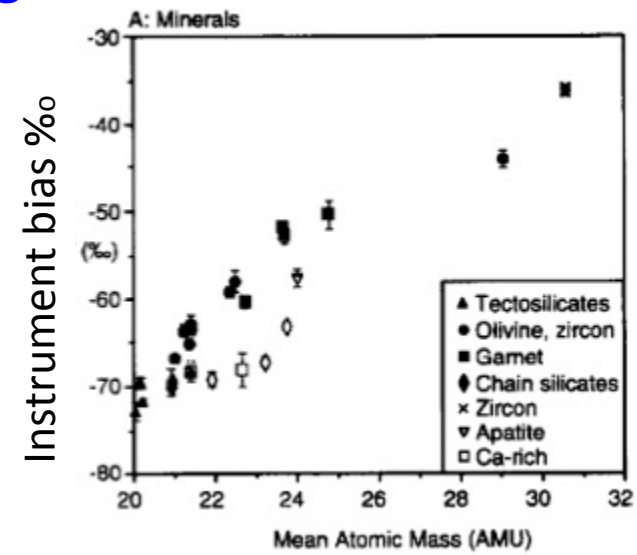
Bias- IMF

IMS-4f- High energy offset, Single EM Detector

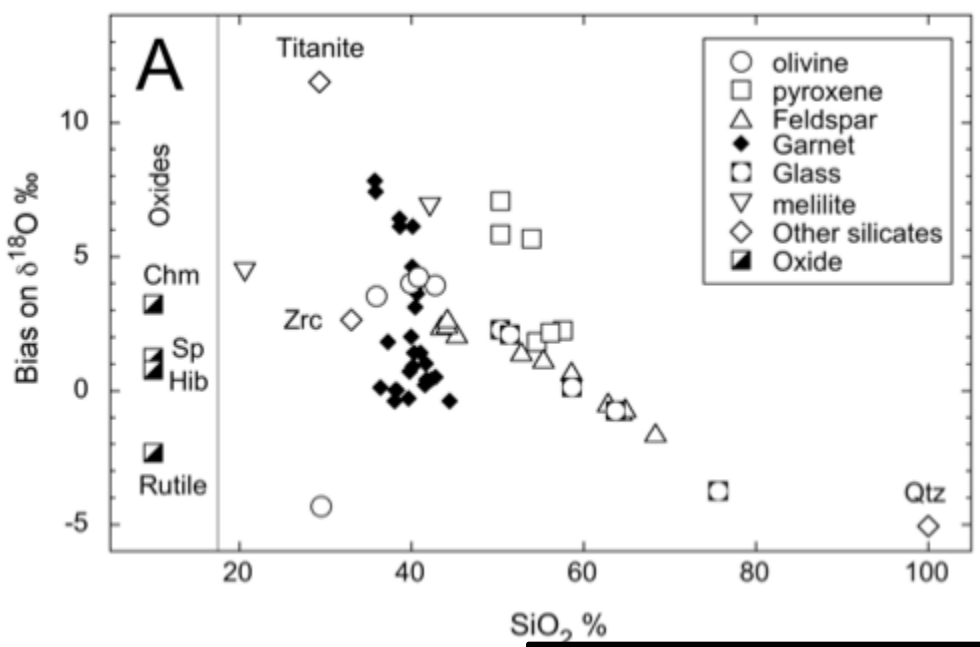




Hervig et al. 1992



Eiler et al. 1997

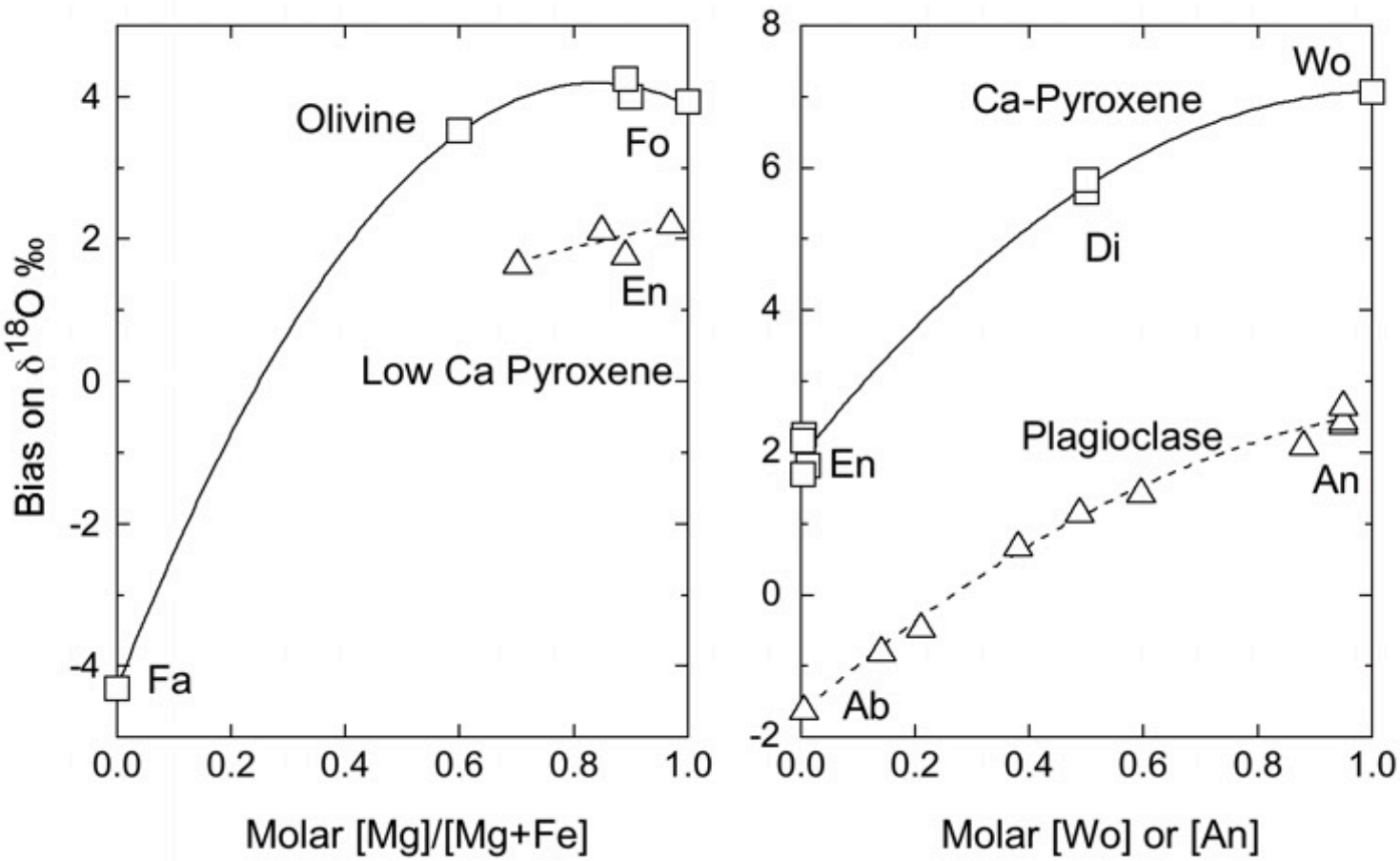


IMS-1280
Multiple FCs
MRP = 2500
Low E-offset

Valley and Kita 2009

Bias- IMF

Matrix effect of various minerals with solid solution

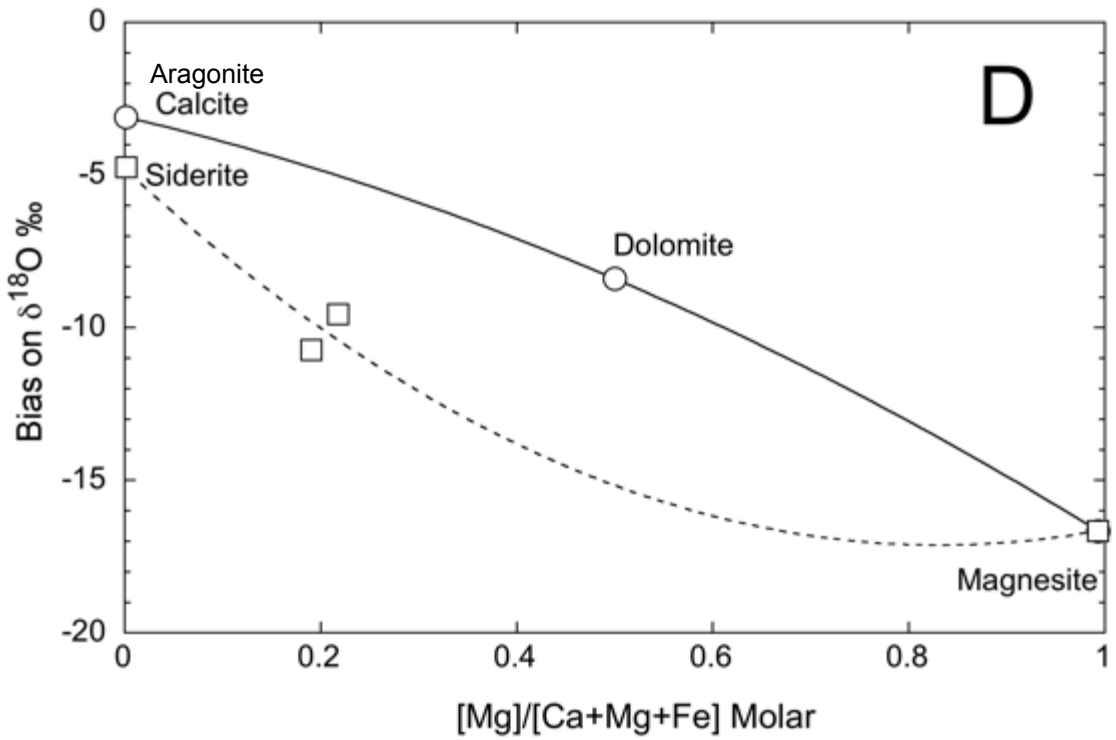


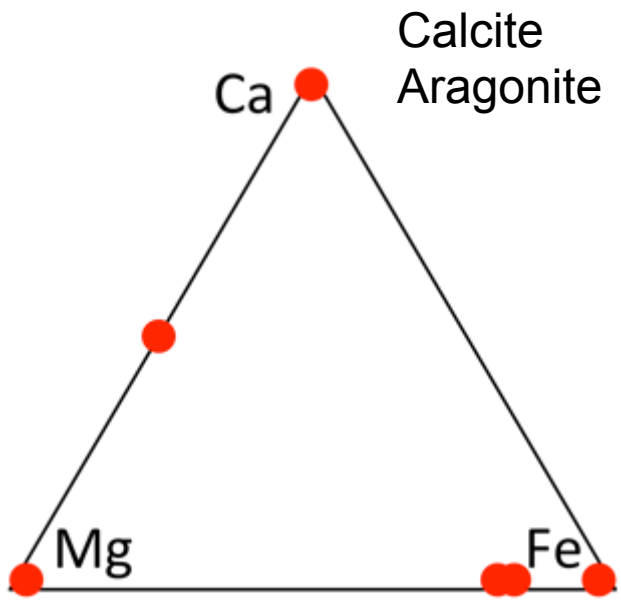
Valley and Kita (2009)

Bias- IMF

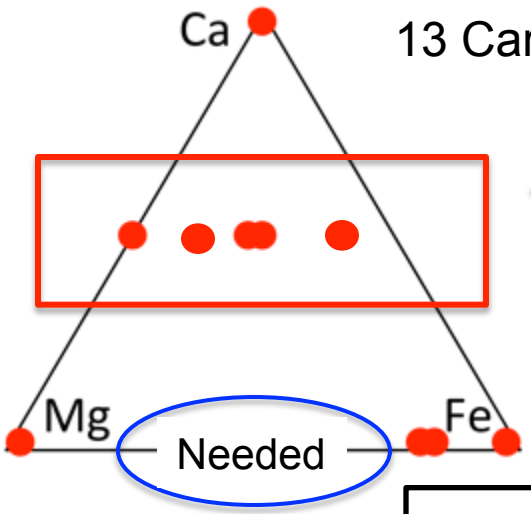
Carbonate standards-

$\delta^{18}O$ Instrument bias

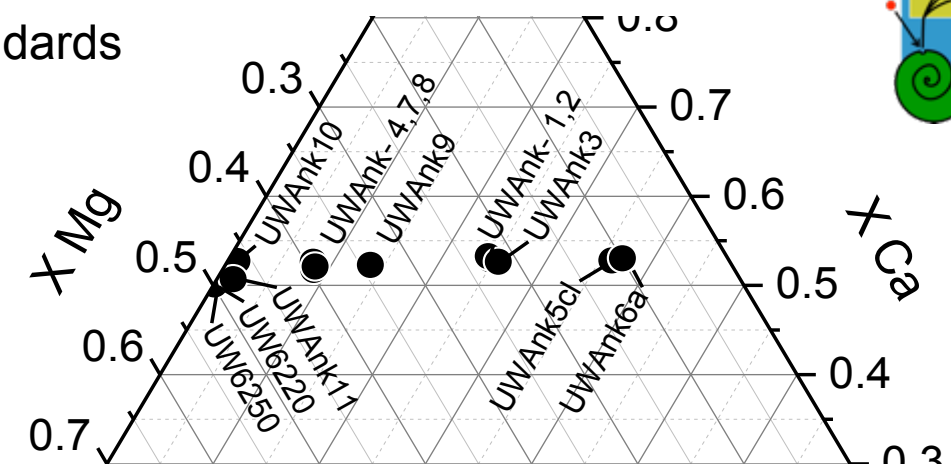




Valley & Kita 2009

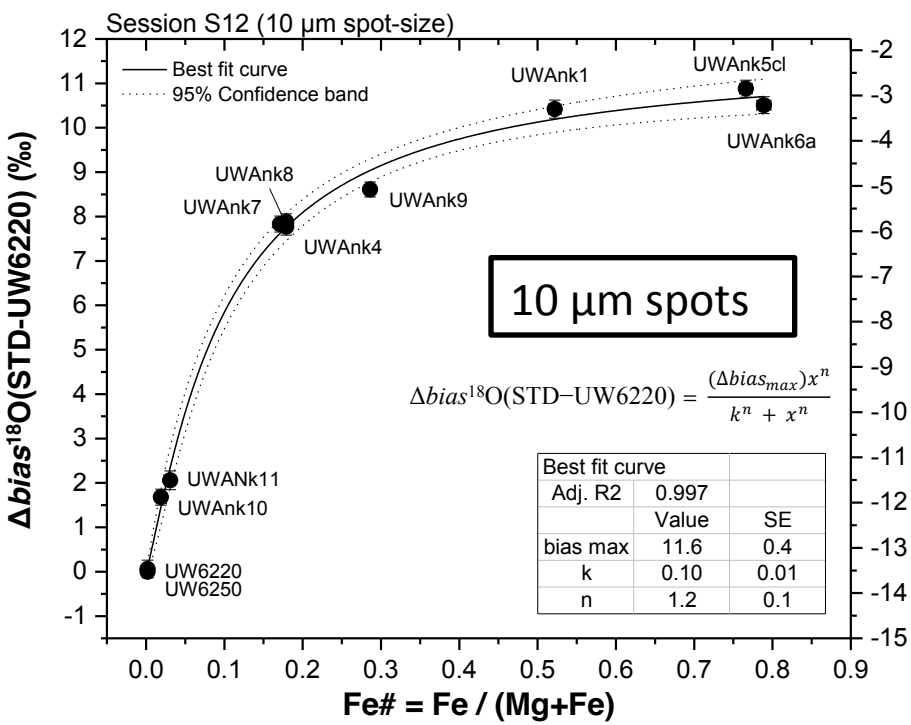


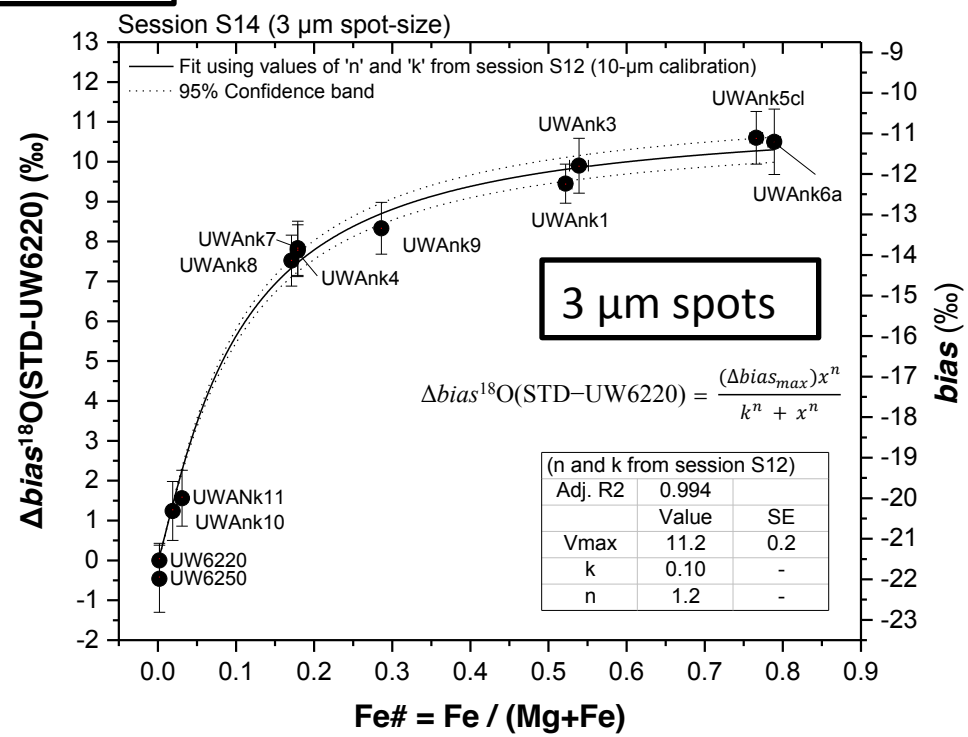
13 Carbonate Standards



Bias- Oxygen isotopes

Sliwinski et al. 2015a, HiRes2015Poster





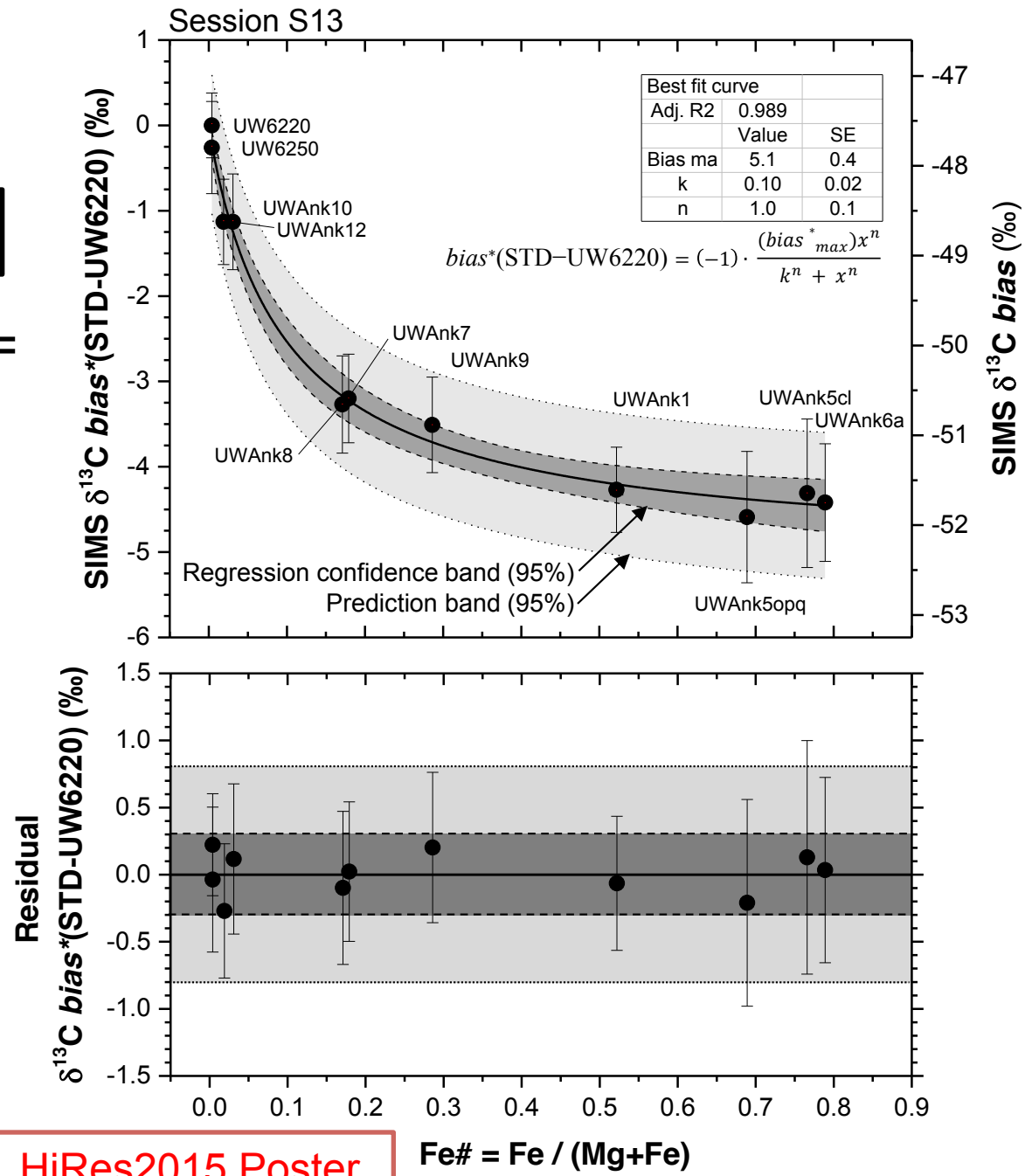
Bias- IMF

Carbon isotopes

$$\text{Bias*(Std-UW6220)} = -1\left(\frac{(\text{bias*}_{\text{max.}})X^n}{K^n + X^n}\right)$$

X =Fe#

K, n = constants



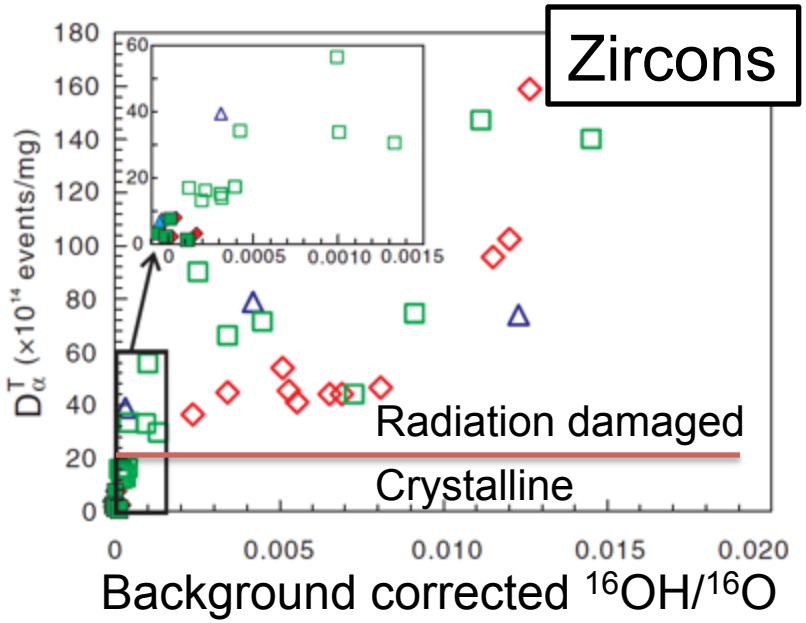
Sliwinski et al. 2015, HiRes2015 Poster

Biocarbonates

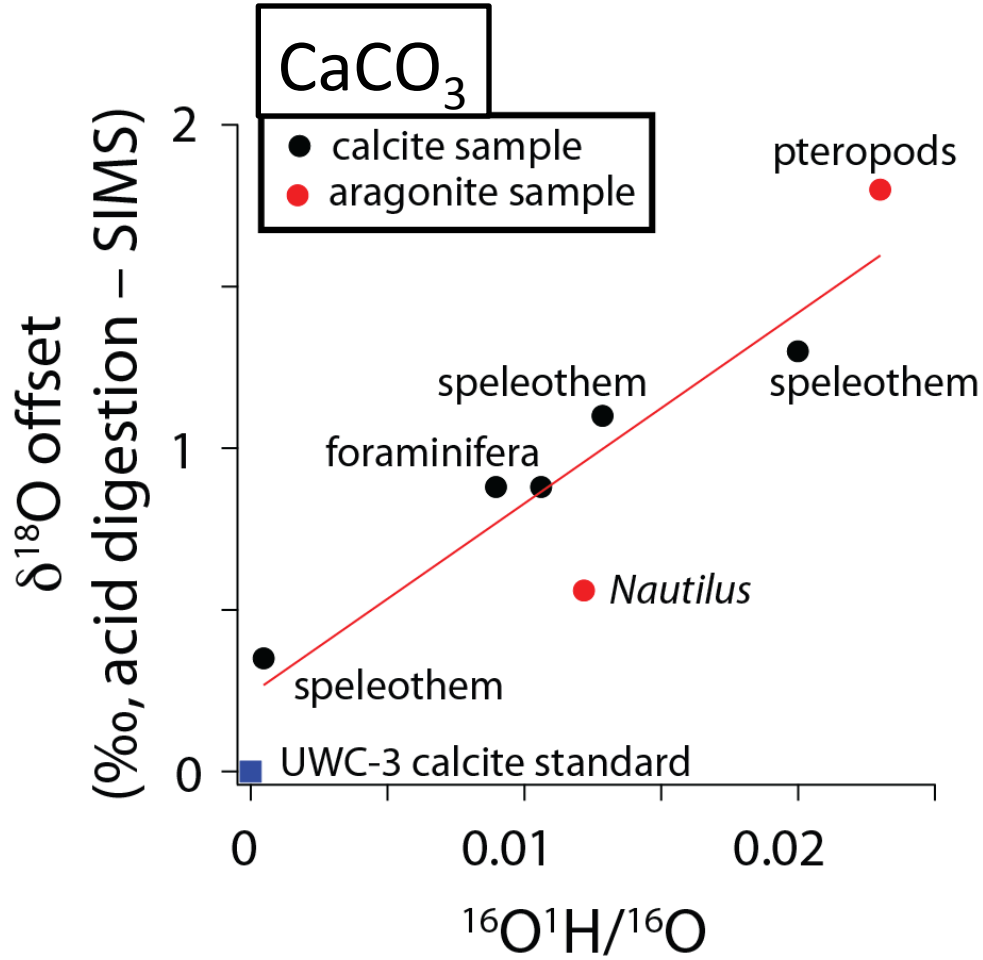
Orland, tutorial lecture, 9 AM, Tuesday

Monitor "water" on unused channel: H_2O, OH, Organic matter

^{16}O, ^{16}OH, ^{18}O	FC, FC, FC
^{12}C, ^{13}C, ^{13}CH	FC, EM, EM



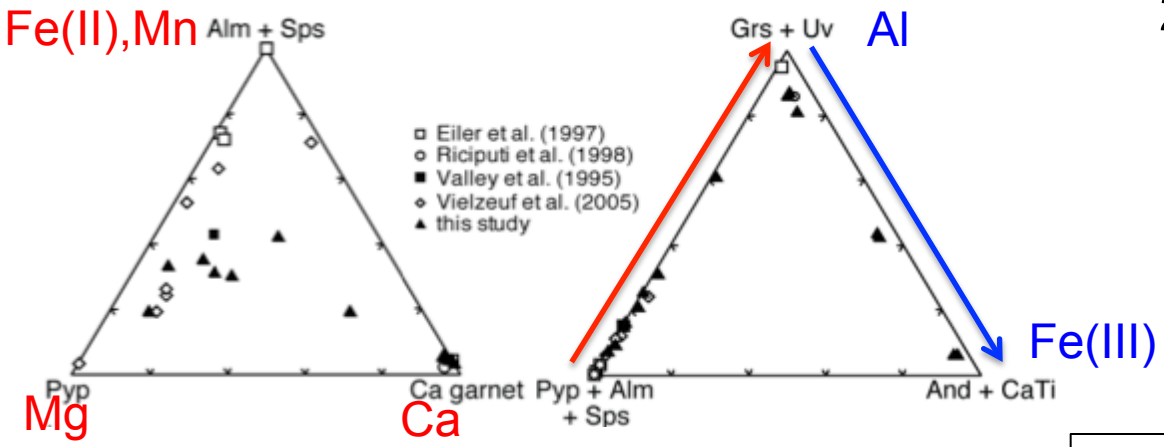
Wang et al. 2014



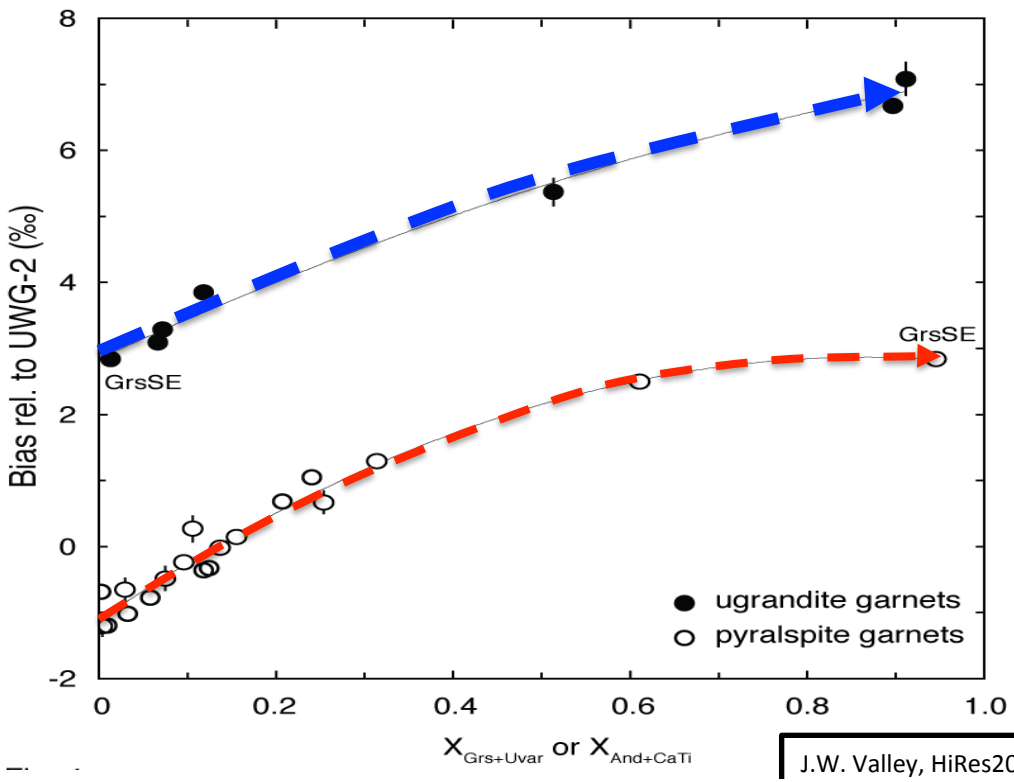
Orland et al. 2015

Bias- IMF

Garnet



25 garnet standards
Page et al. (2010)



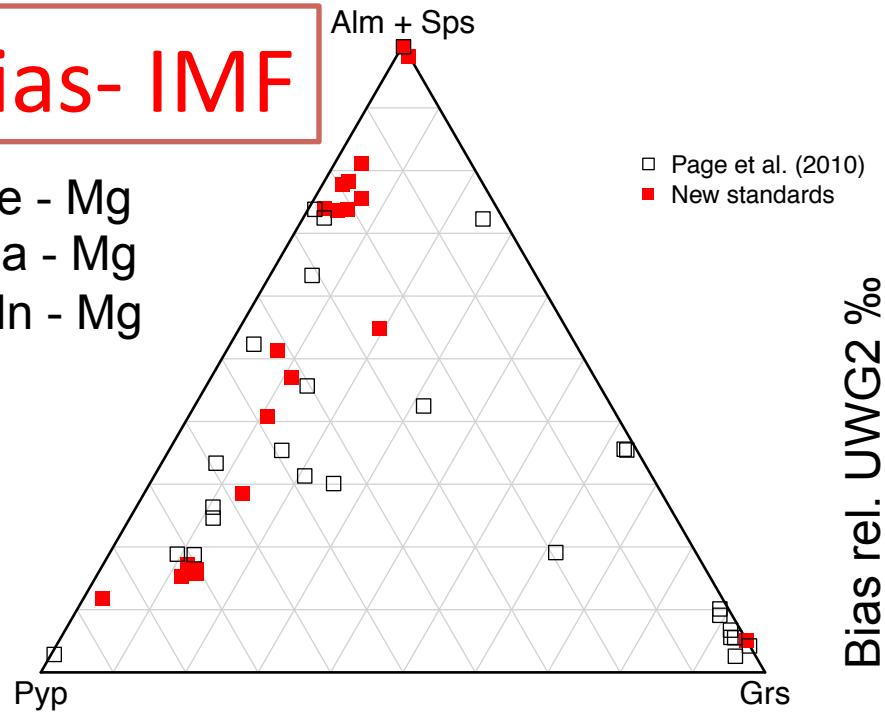
Pyrope:	$Mg_3Al_2Si_3O_{12}$
Almandine:	$Fe_3Al_2Si_3O_{12}$
Spessartine:	$Mn_3Al_2Si_3O_{12}$

Grossular:	$Ca_3Al_2Si_3O_{12}$

Andradite:	$Ca_3Fe_2Si_3O_{12}$

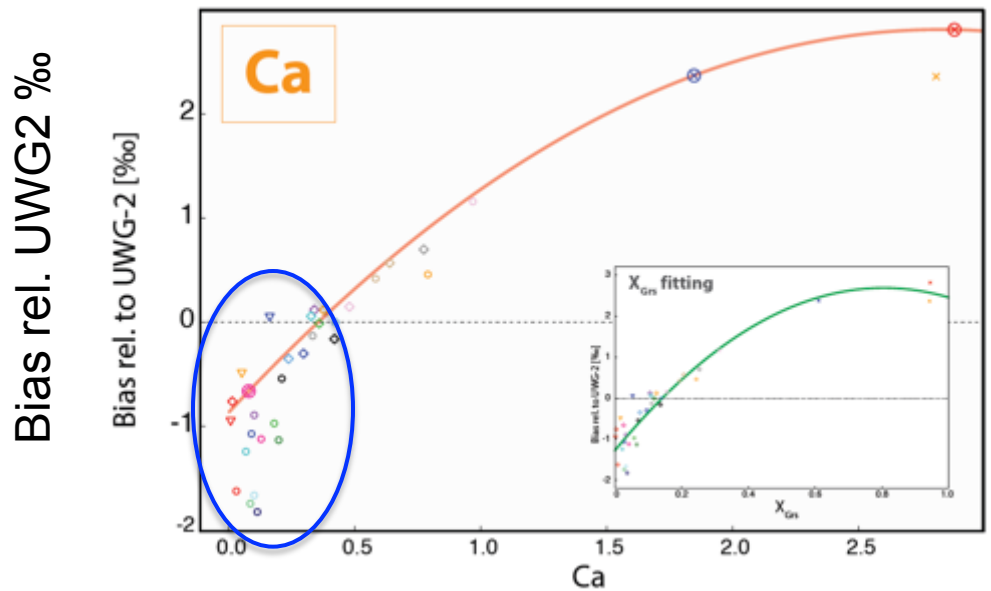
Bias- IMF

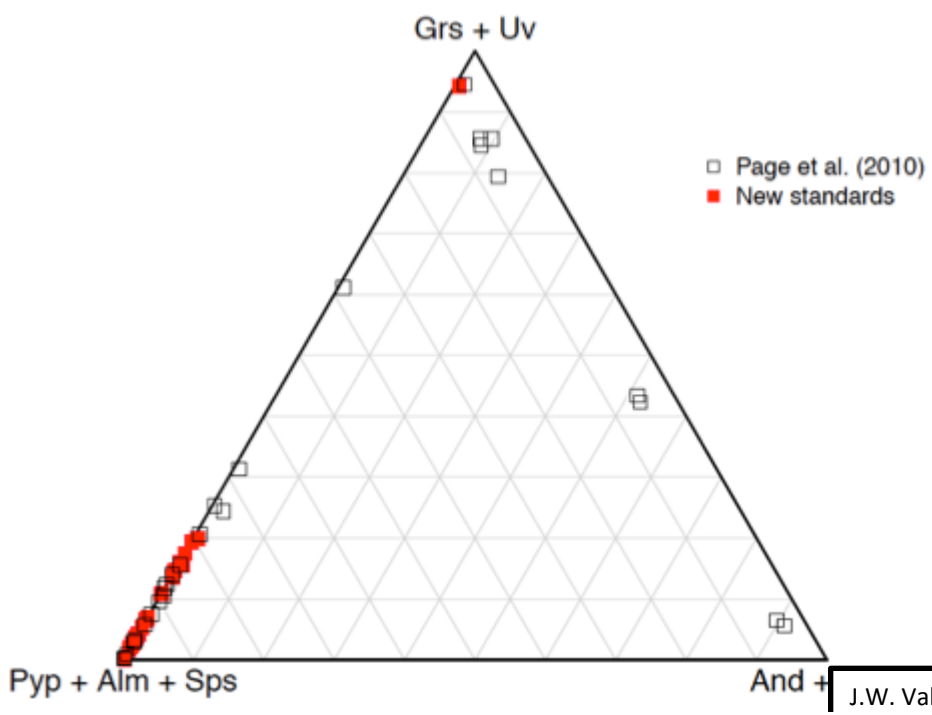
Fe - Mg
Ca - Mg
Mn - Mg

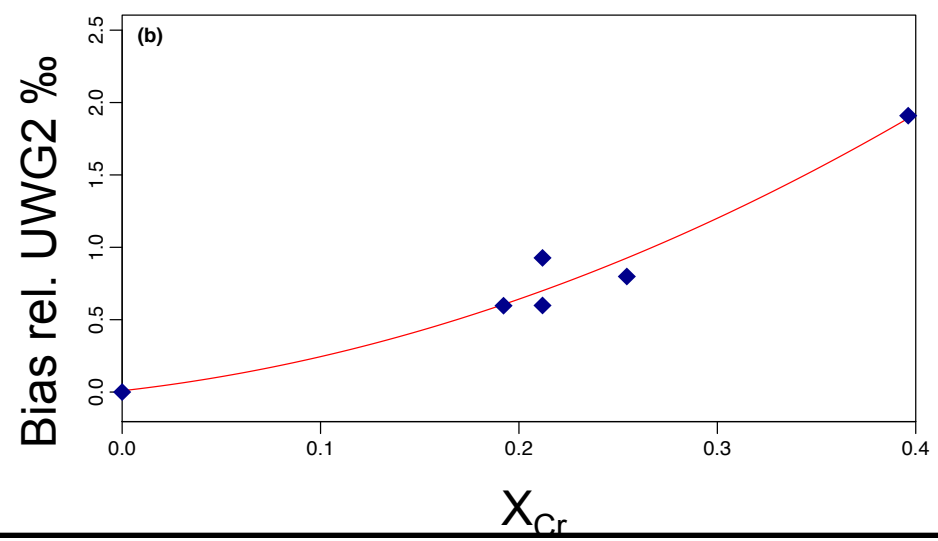


49 garnet standards

Kitajima et al., Poster, Tue.



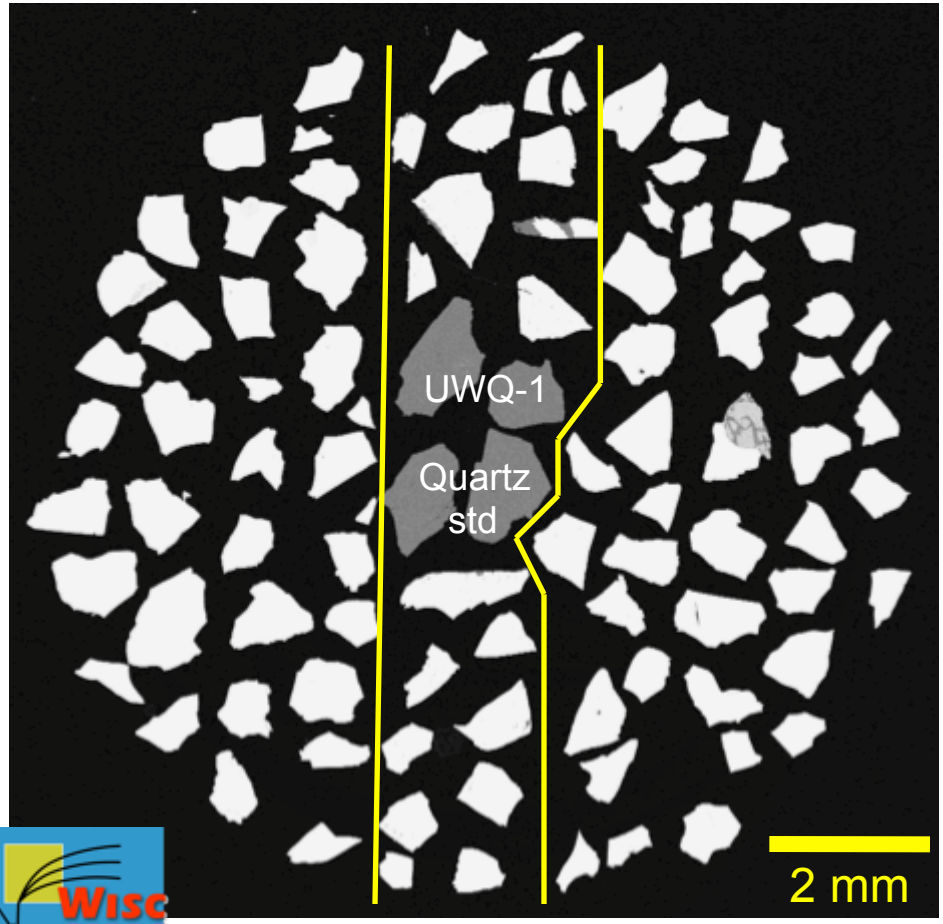




Crystal orientation

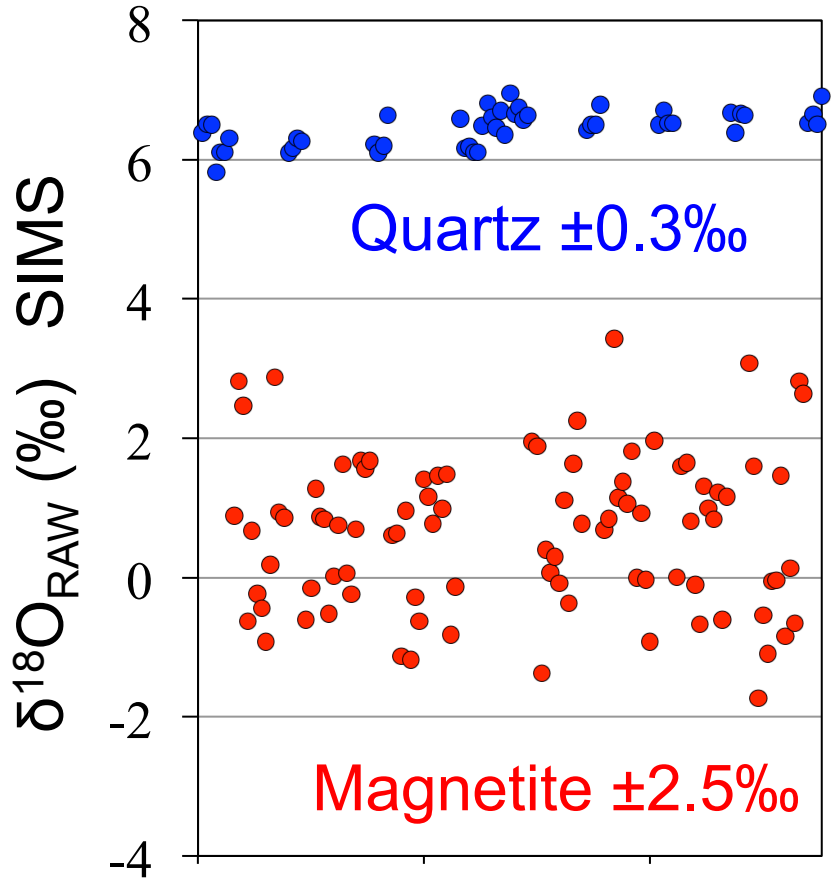
Magnetite

5830 M34572-A 5830



Poor reproducibility!

±2.5‰ (2SD)



Huberty et al. (2010)

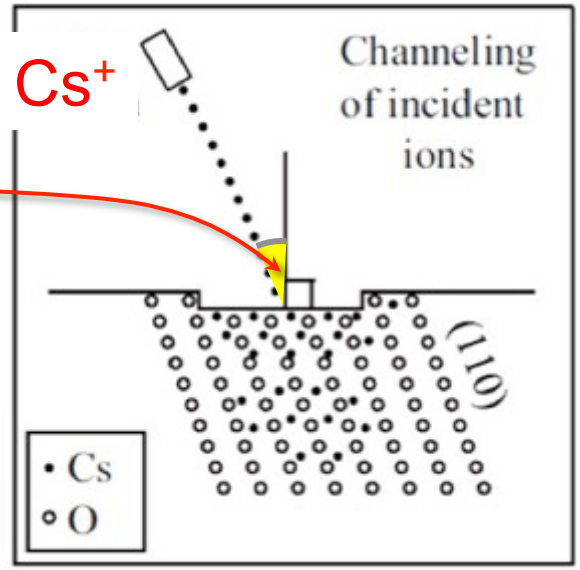
Crystal orientation

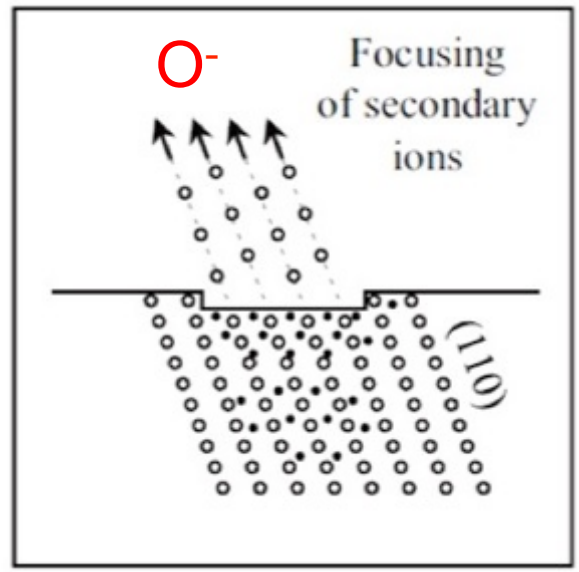
Ion Channeling and Focusing

Ion Channeling

Ion Focusing

θ=21°





Deeper Cs+ primary ion implantation

Preferential secondary ion ejection

Huberty et al. (2010)

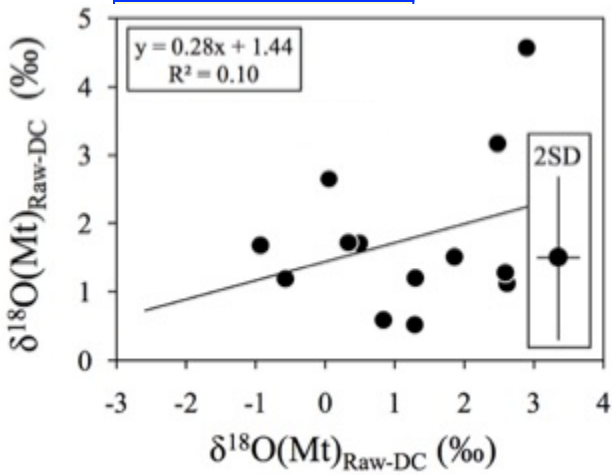
SIMS Raw $\delta^{18}O$ changes with Crystal Orientation

Crystal orientation

Low kV-Analyses of Multiple Grains

X-axis: Data obtained at the routine condition +10/-10kV (±3‰)

Y-axis: +10/-3kV 26˚

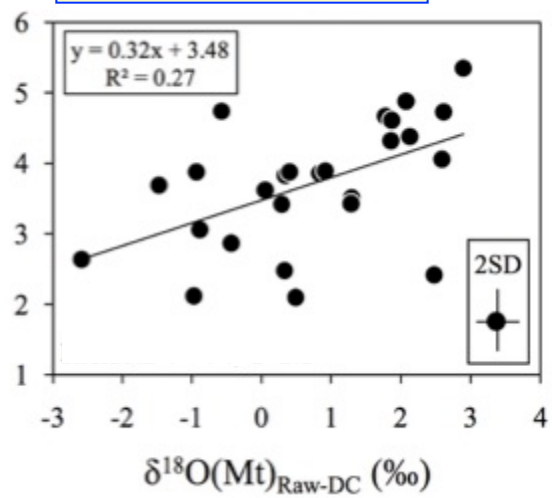


Quartz: ±1‰

Magnetite: ±2.2‰ ☹

*condition less stable

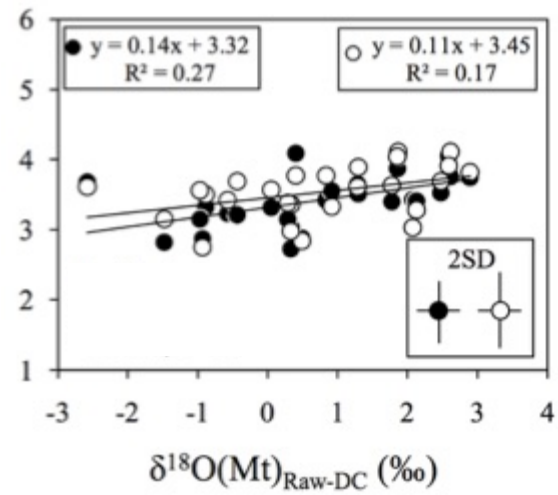
+6.5/-6.5kV 21˚



Quartz: ±0.4-0.5‰

Magnetite: ±1.8‰ ☹

+3/-10kV 14˚



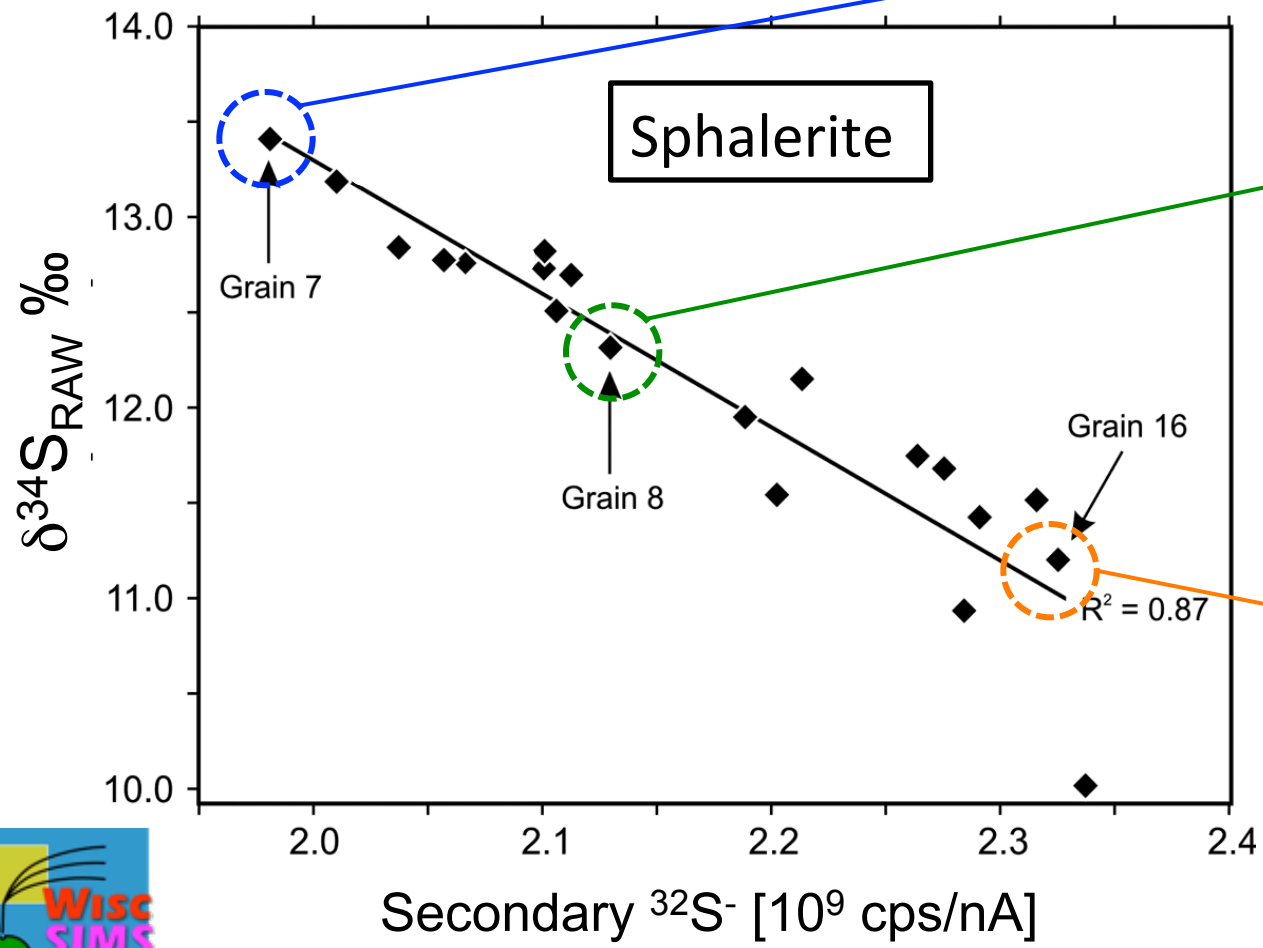
Quartz: ±0.4‰

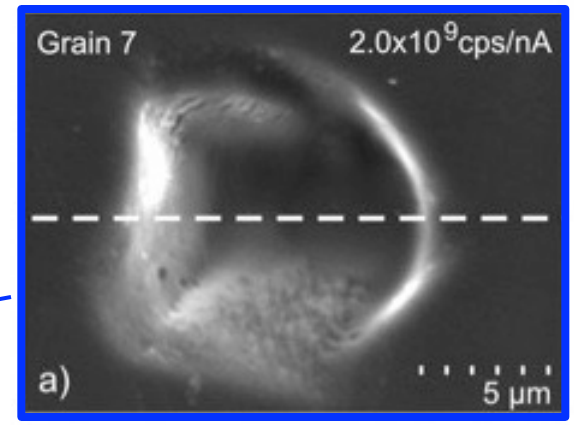
Magnetite: ±0.8‰ ☺

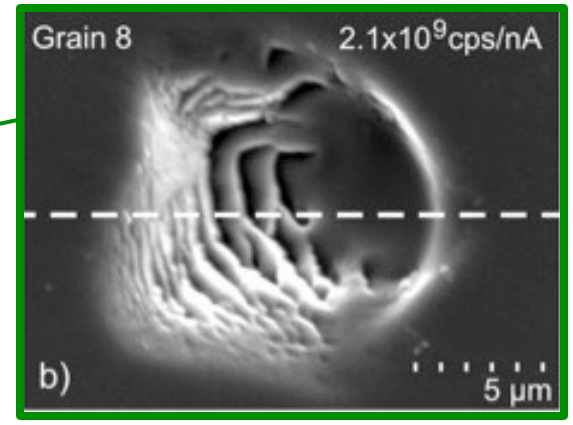
Huberty et al. (2010)
Kita et al. (2011)

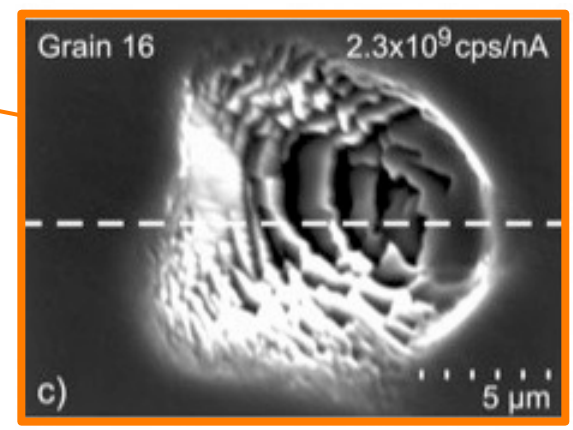
Crystal orientation

Morphology of SIMS pit shape
vs.
S Ion Yield and Isotope Ratio









Kozdon et al. 2010

Crystal orientation

Other Minerals, Isotopes?

Oxygen isotopes: Magnetite & Hematite: Huberty et al. (2010) ☹

Rutile: Gordon et al. 2012,

Sulfur isotopes: Sphalerite and Galena: Kozdon et al. (2010)

Fe isotopes: Magnetite: Kita et al. (2011)

C isotopes: graphite: Ushikubo (unpd)

+3kV/-10kV conditions minimize orientation effects.

Most minerals do **not** show crystal orientation effects ! ☺

carbonates, quartz, zircon, olivines, pyroxenes, feldspars, garnets, melilites, sphene, spinel, chromite for oxygen isotopes.

pyrite, chalcopyrite, pyrrhotite for sulfur isotopes.

Ion microprobe = SIMS

Isotopes, Trace elements, Light elements

$\delta^{18}O$ ±0.3‰, 10 µm spot, 3 minutes; ±1‰ < 1 µm spots
C, Si, O 3-isotopes, S 4-isotopes, Isotopes of a trace element (C- microfossils, bacteria)

Complements: Electron microprobe (Major and minor elements) & Other techniques

Petrology

Igneous & Metamorphic minerals,
Zircons
Diamonds & inclusions
Diagenetic cements

Meteorites

Materials Science

Thin films, depth profiles
Trace elements

Paleoclimate Proxies

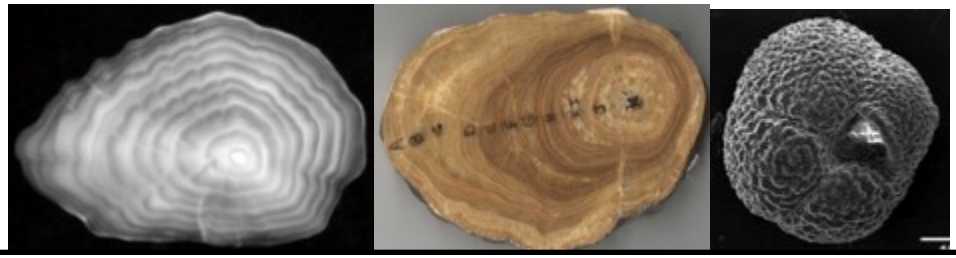
Foraminifera, Coral, Sponges,
Mollusks,
Speleothems
Fish otoliths
Tooth enamel
Finely layered sediments
Others: Diatoms, Pollen, ...

Biology

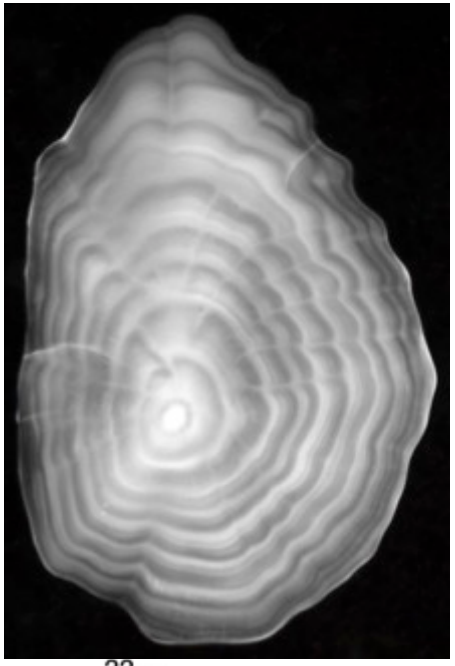
Anthropology & Archeology

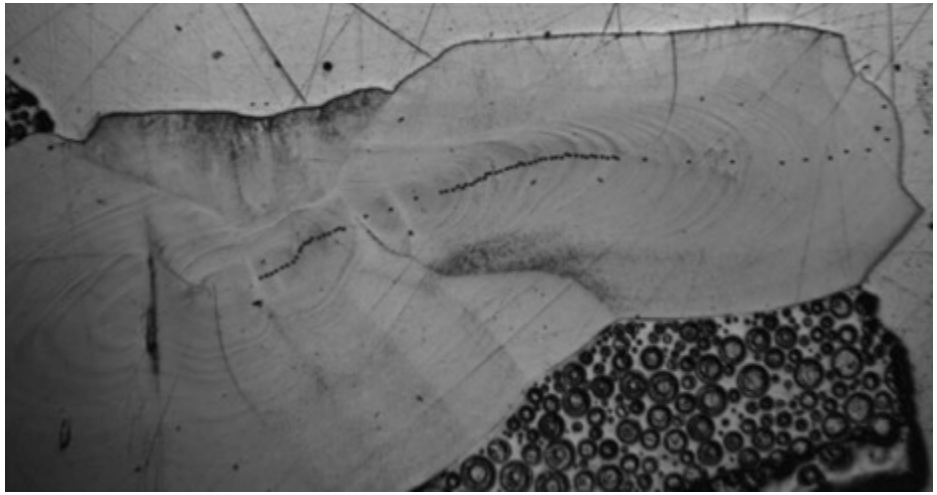
What are the opportunities for high resolution study of paleoclimate proxies?

Small, Precious or Zoned

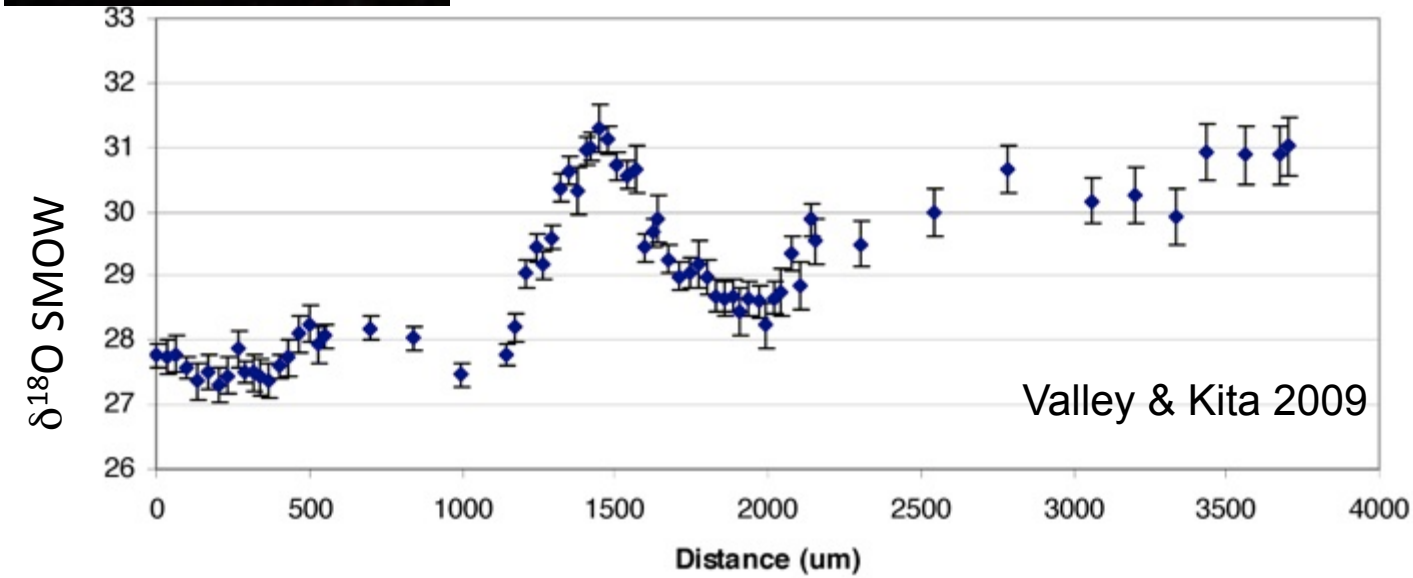


P. cod Otoliths, Aialik Bay, Alaska

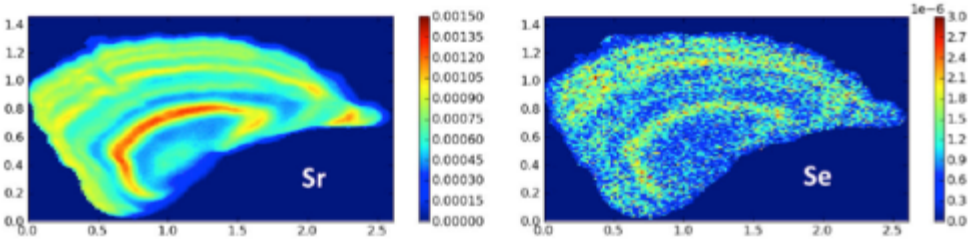




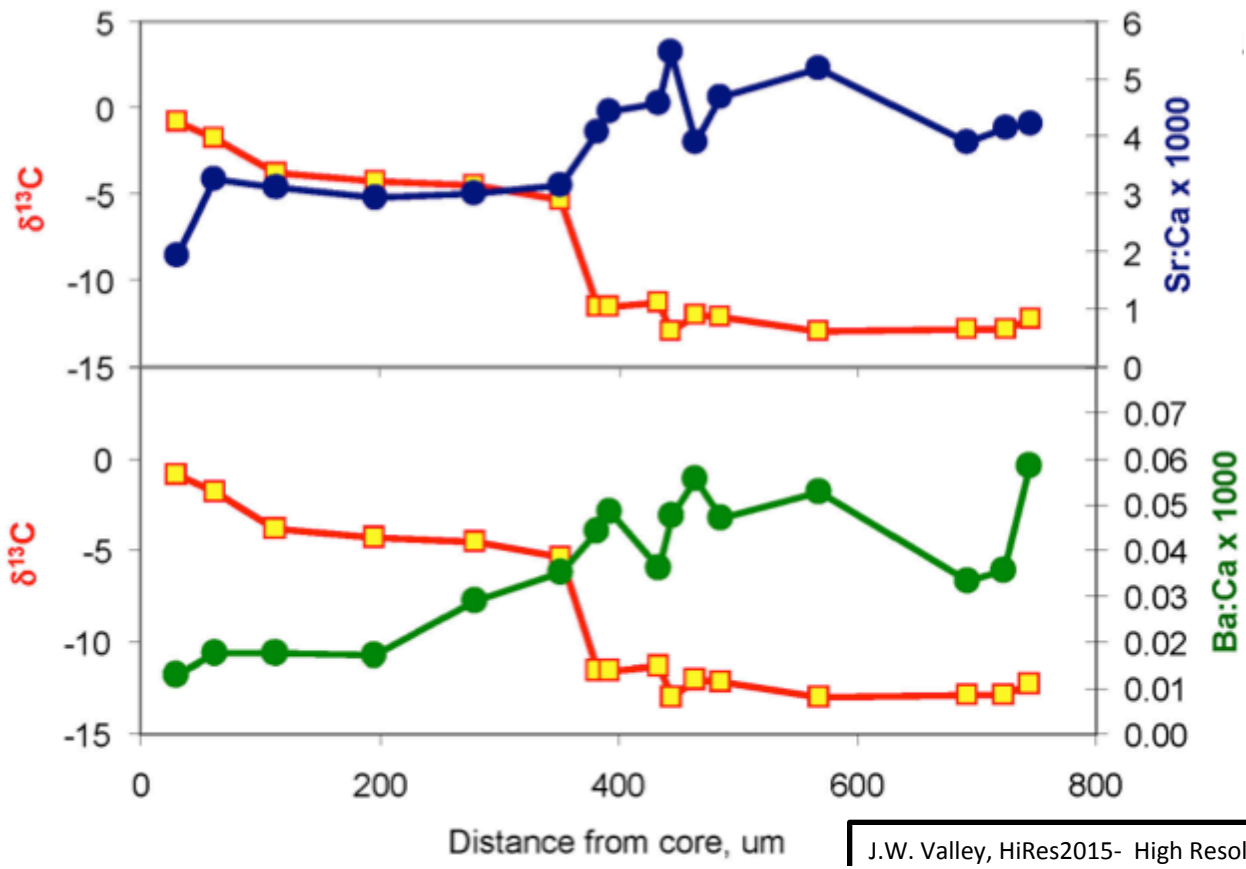
4 mm

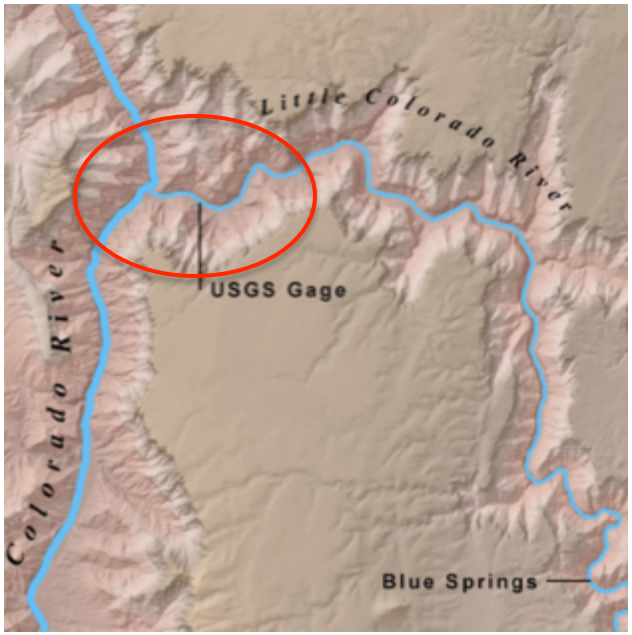


Otoliths – Humpback chub
Little Colorado River, Grand Canyon



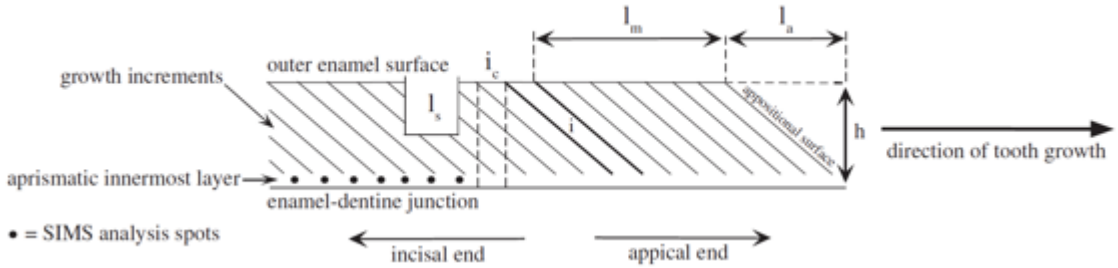
River	Ba:Ca x 10^{-3}	Se:Ca x 10^{-3}	Sr:Ca x 10^{-3}	$\delta^{13}C$, ‰
Little Colorado River	1.38 (0.36)	0.019 (0.002)	9.34 (0.92)	0.59 (1.24)
Colorado mainstem	1.43 (0.03)	0.024 (0.002)	10.80 (0.08)	-8.87 (0.49)

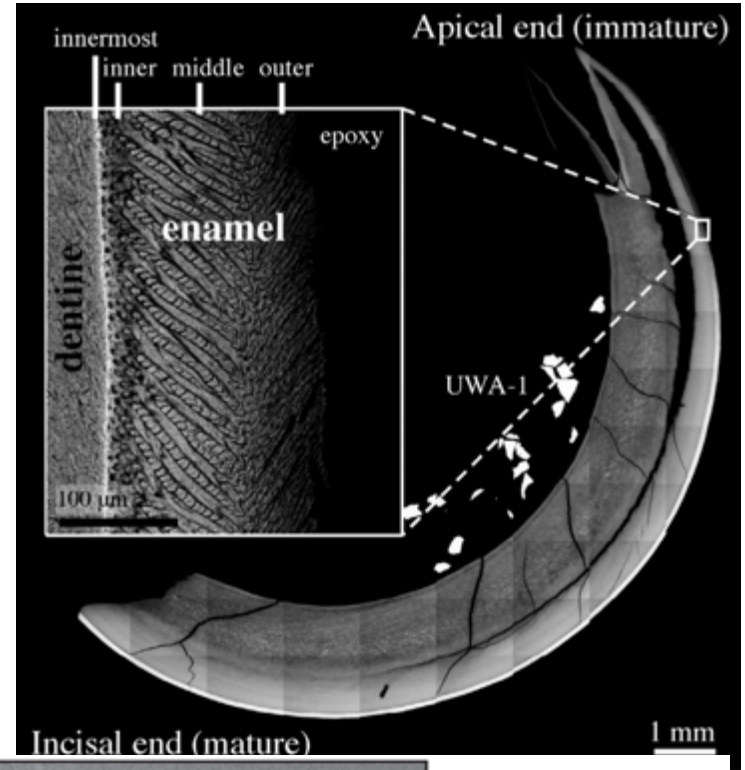


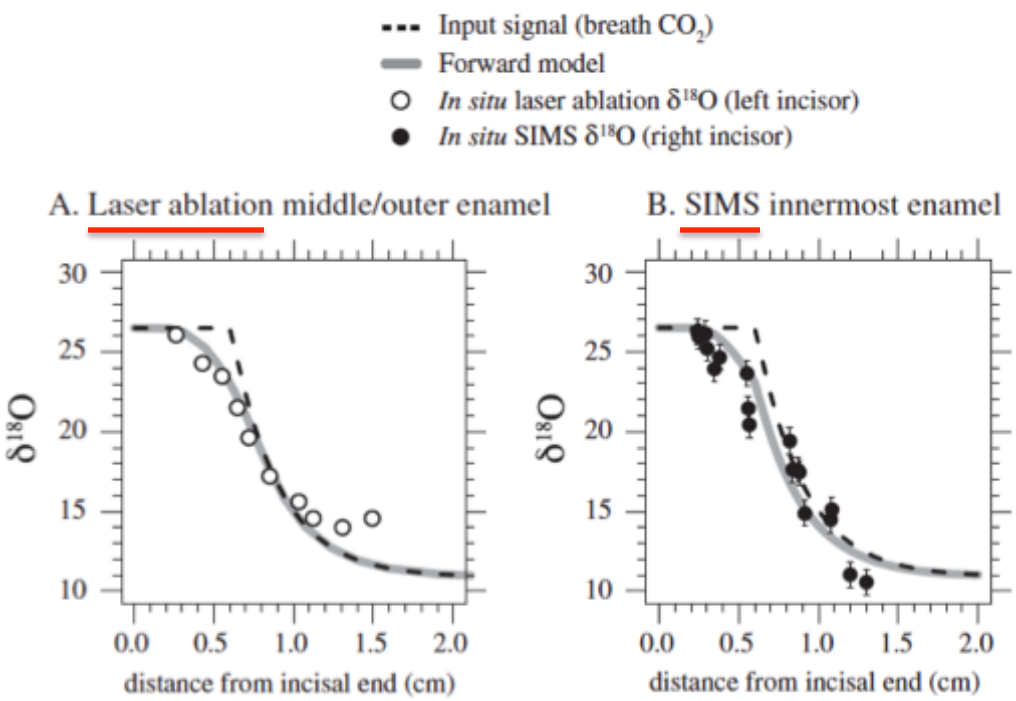


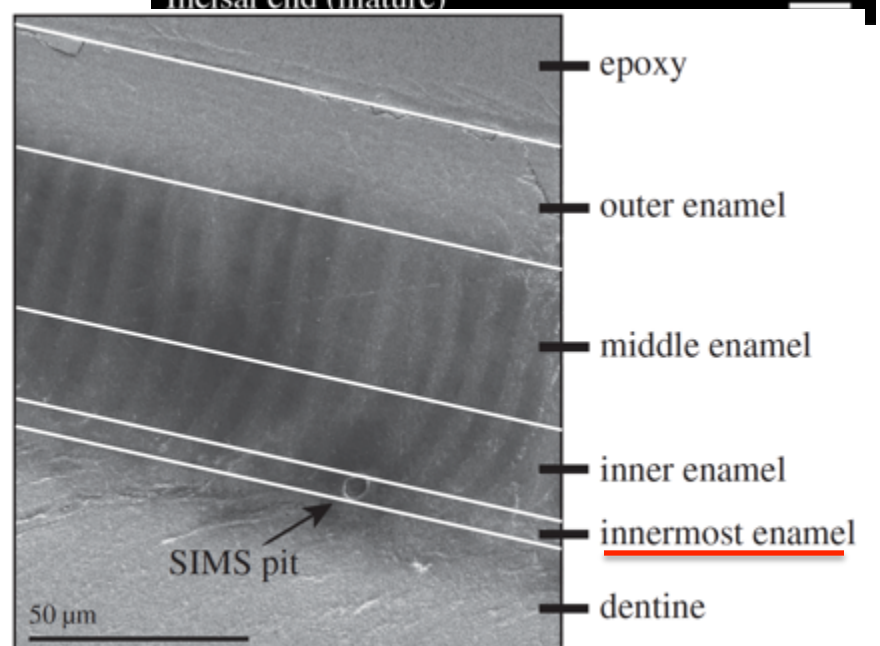
Limburg et al. 2013

Tooth enamel, wood rat



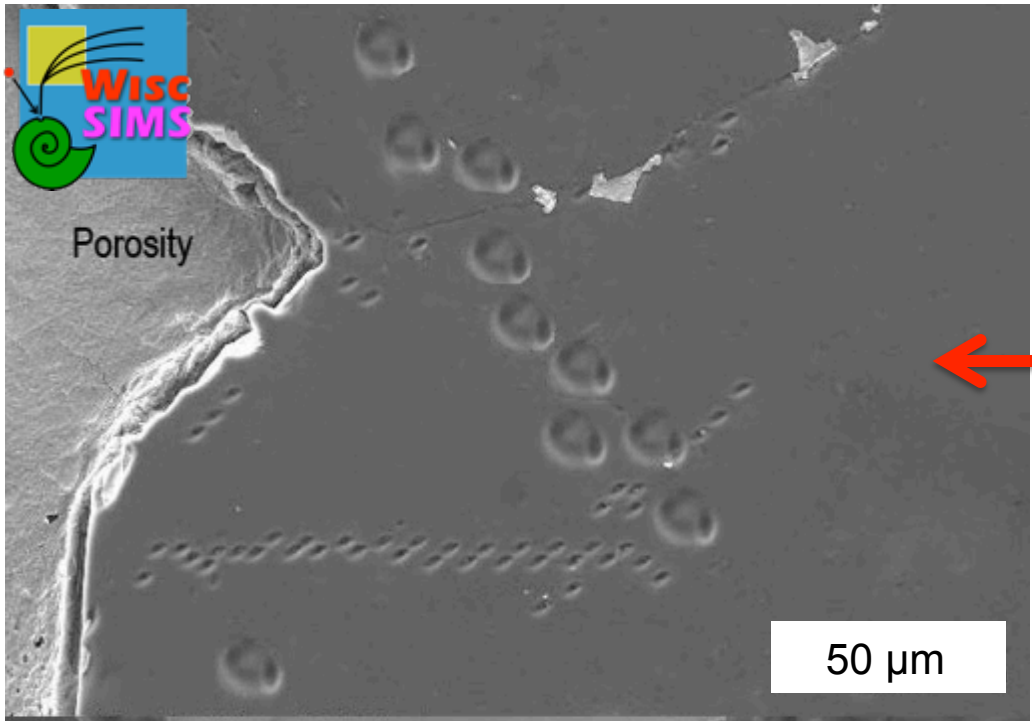


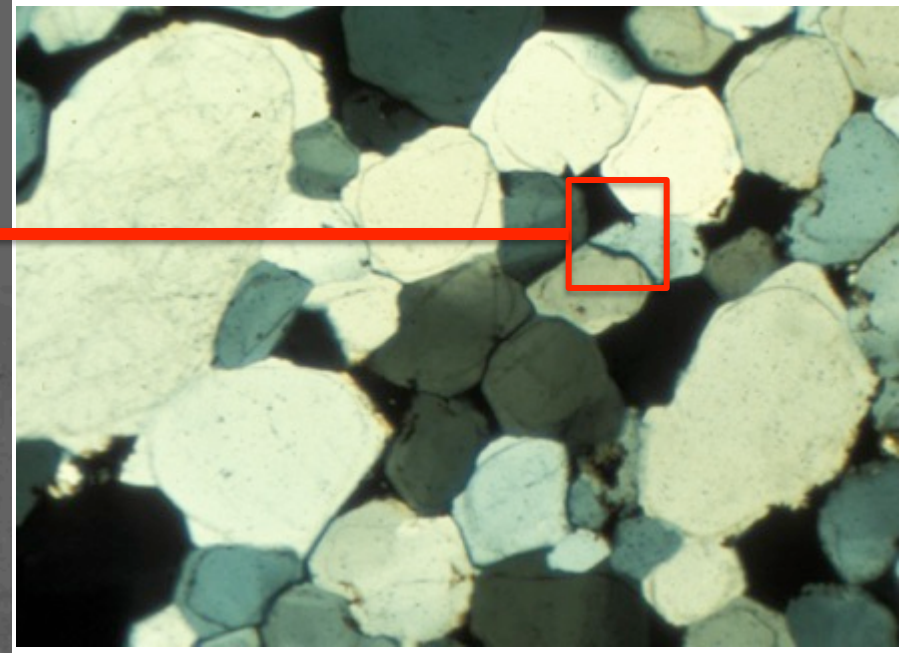


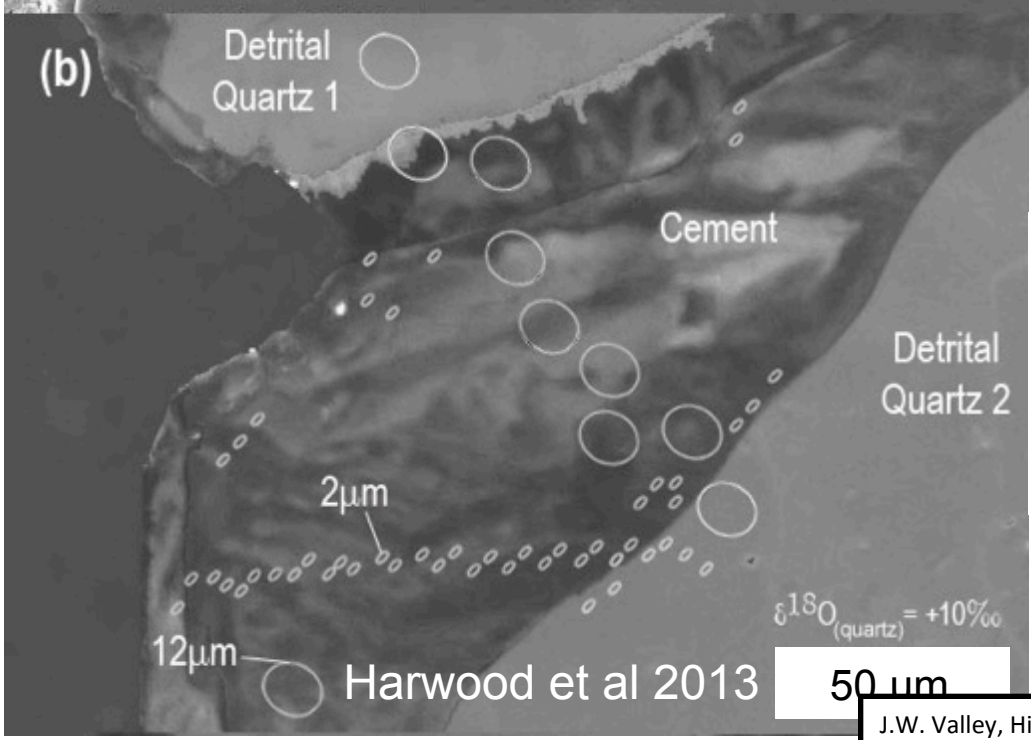


Blumenthal et al. 2014

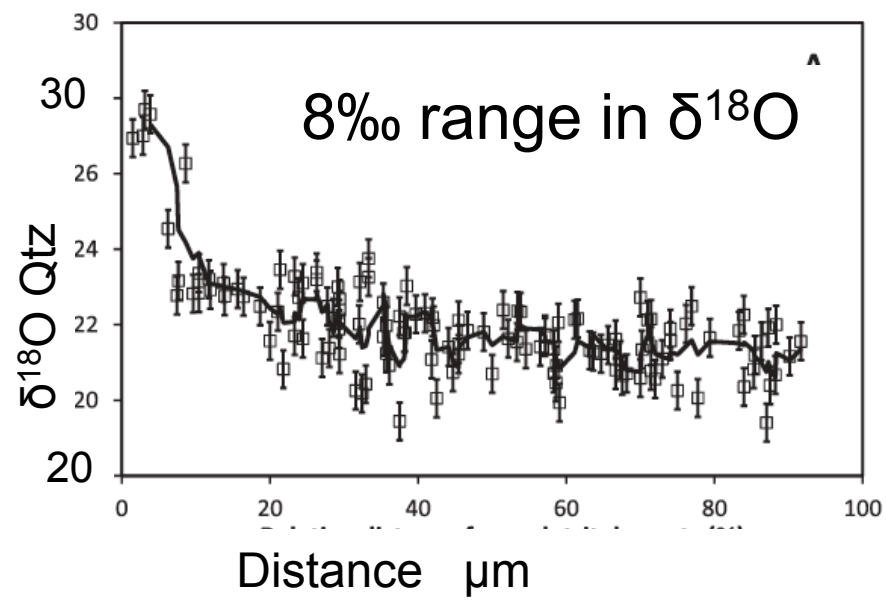
Quartz Overgrowths



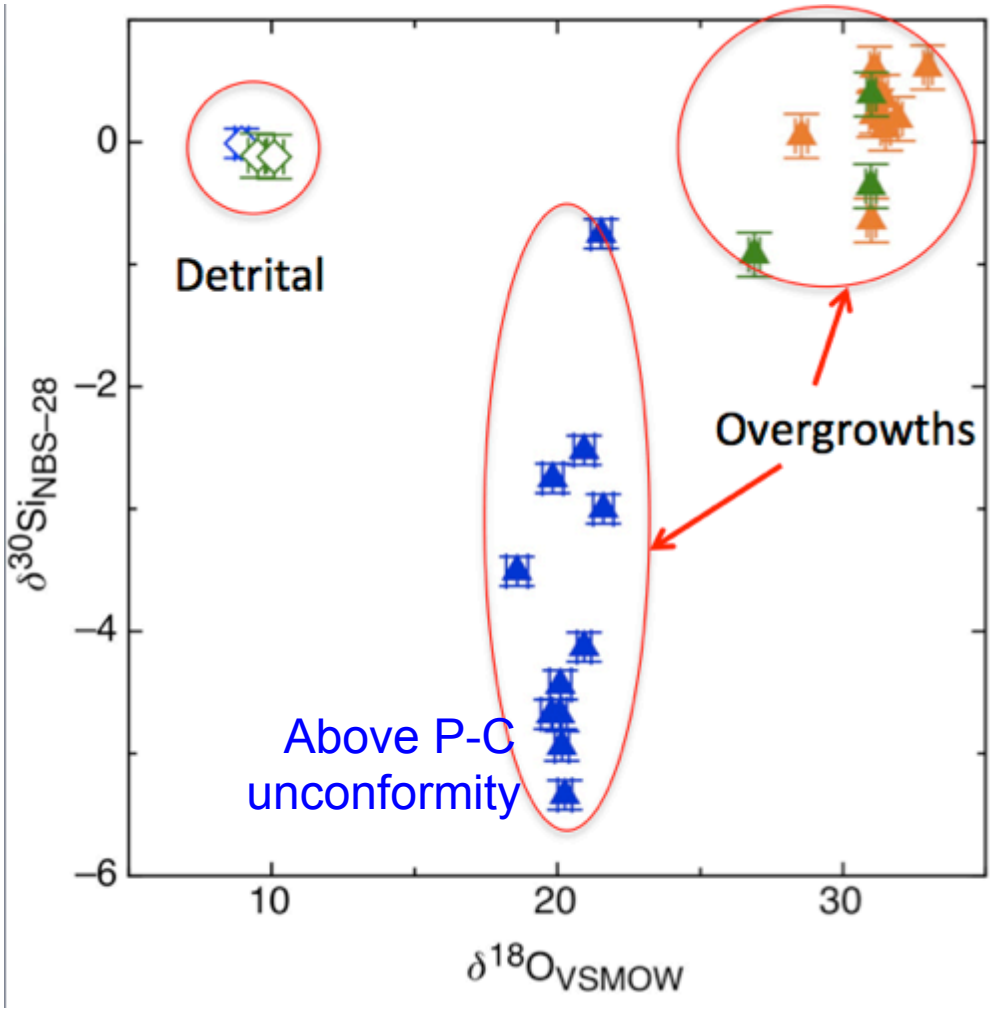


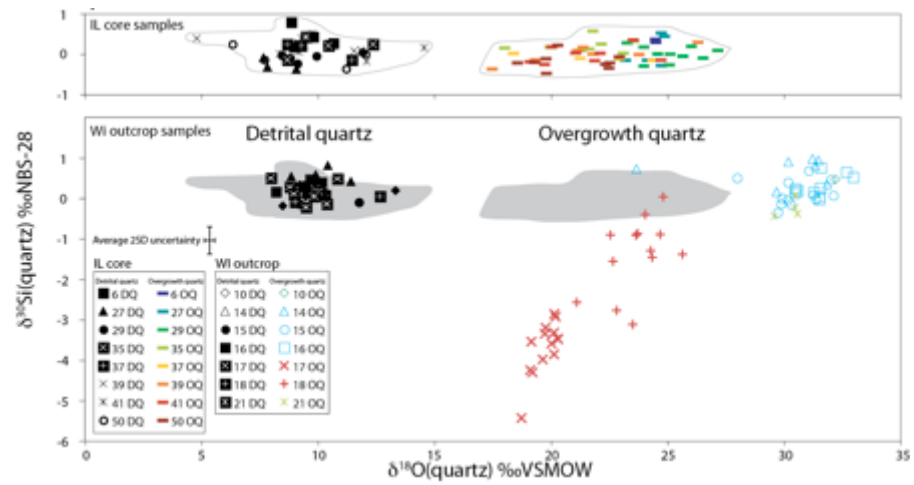


Harwood et al 2013



Mt. Simon sandstone, Wisconsin Arch

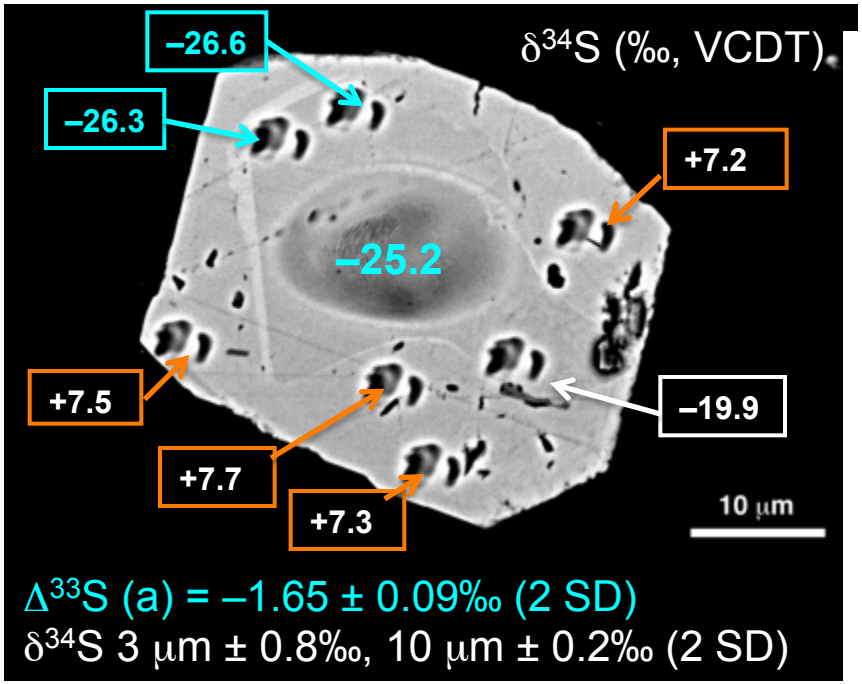


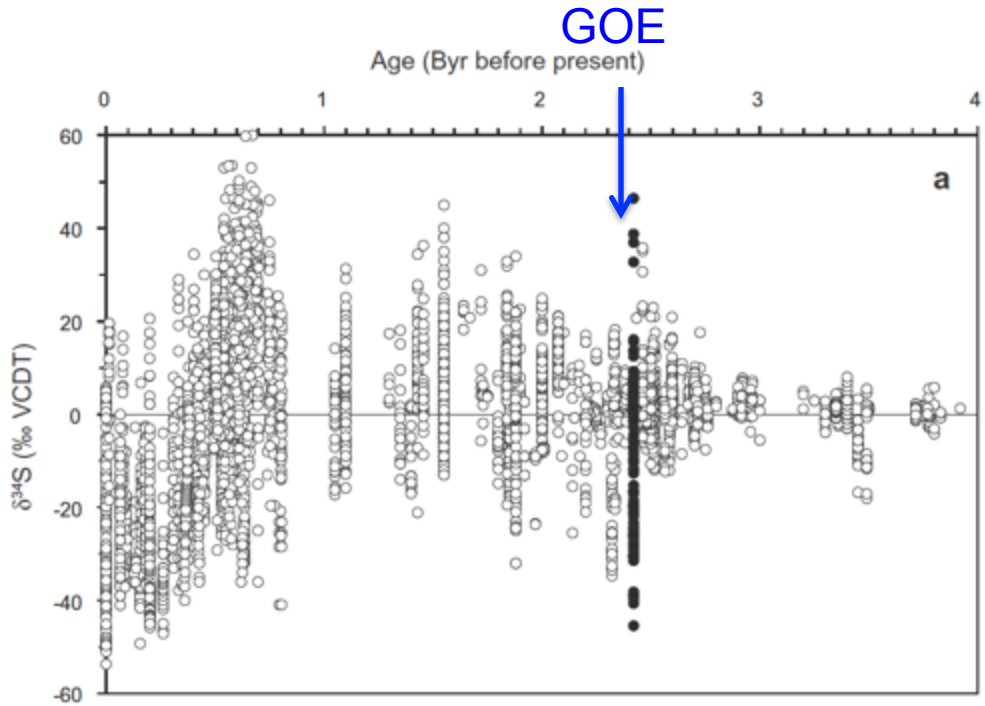


Pollington et al. unpbd.

Two analyses sessions
- 10 µm Sulfur 3 isotope (3 FCs)
- 3 µm Sulfur 2 isotope (2FCs)

Large negative $\delta^{34}S$ & non-zero $\Delta^{33}S$
- Microbial sulfate reduction
- ± 1 ‰ level resolvable $\Delta^{33}S$ MIF

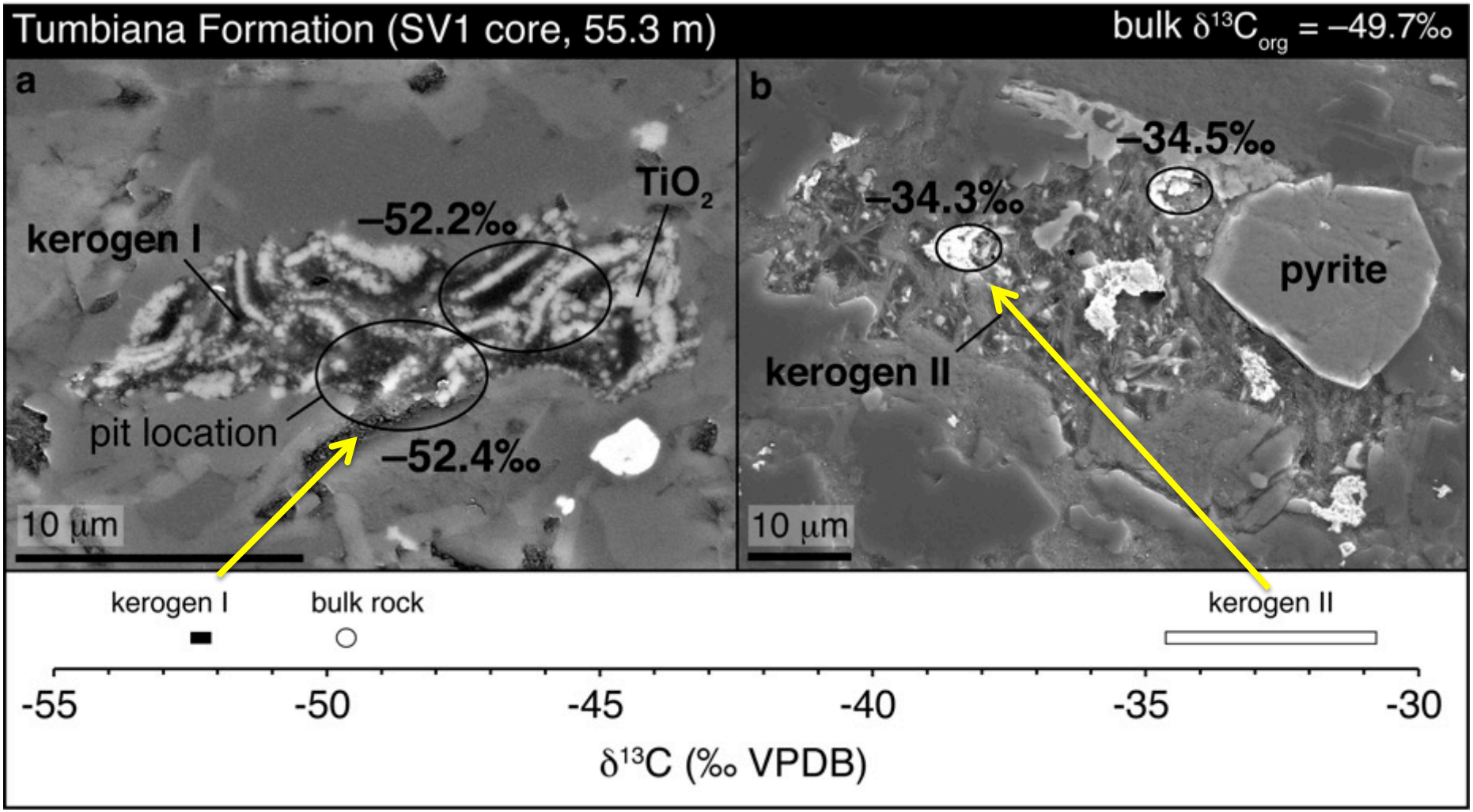




Turee Creek Group
2400 Ma
Sulfur Isotope ratios

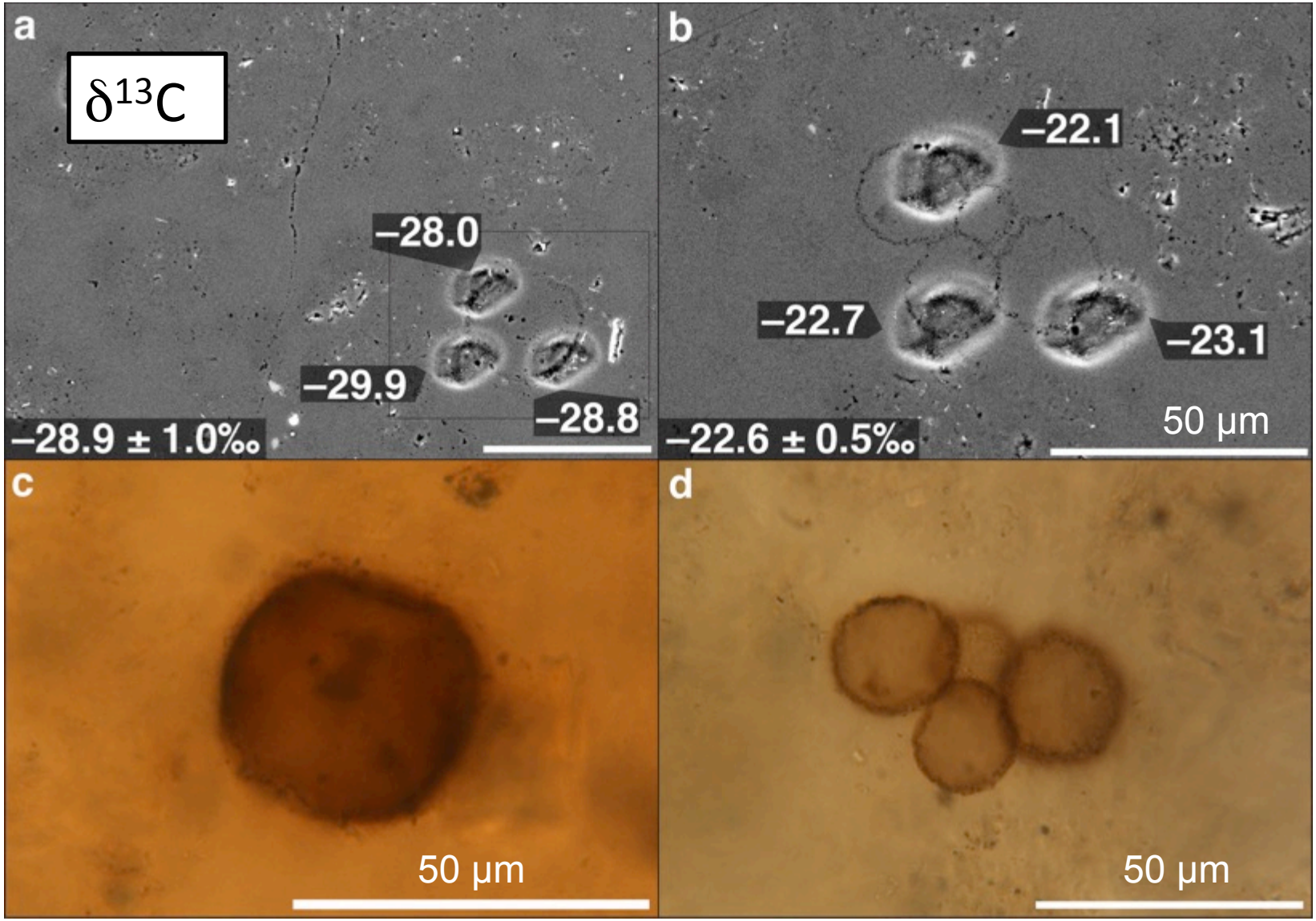
Williford et al. 2011

Kerogen bias varies with H ^{12}C, ^{13}C, ^{13}CH



$\delta^{13}C$ 2700 Ma Tumbiana Fm

Williford et al. 2013



Leiosphaerida crassa
eukaryote?

Myxococcoides sp.
cyanobacteria?

Williford et al. 2013

Chichkan Fm, Kazakhstan, 750 Ma

There are many opportunities for high resolution study of paleoclimate proxies

Small, Precious or Zoned