

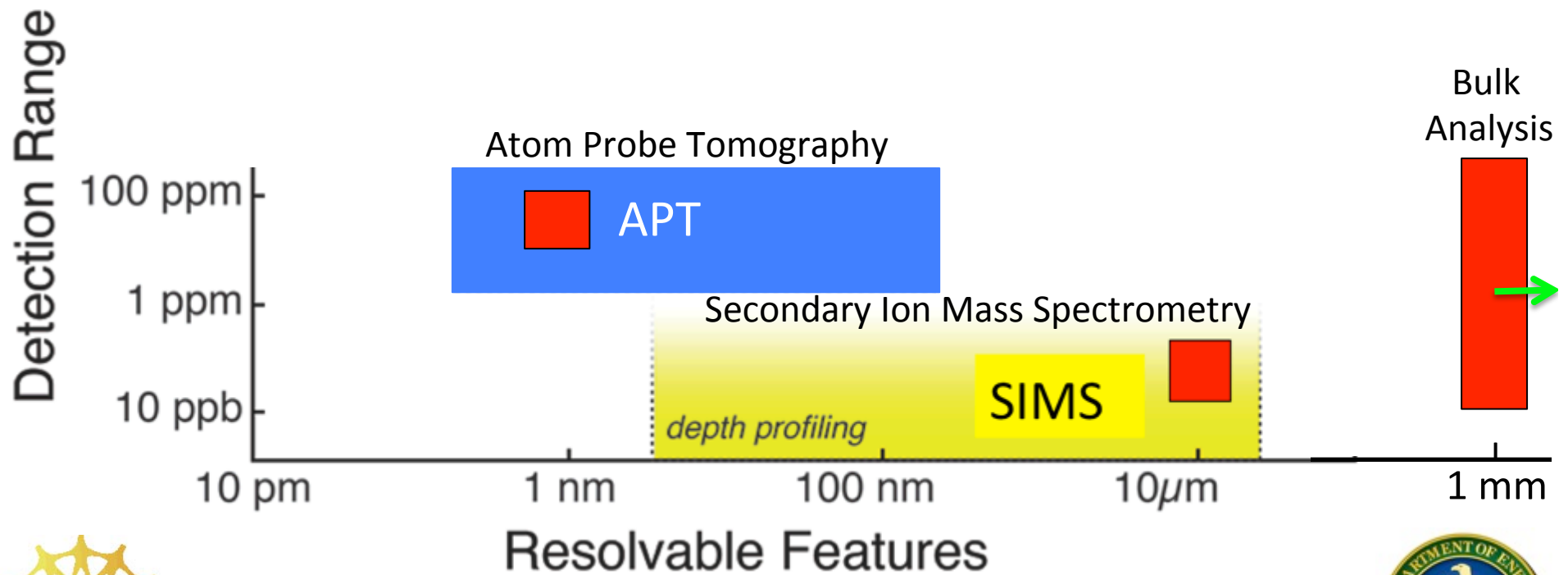
Go Small or Go Home

How Small is Too Small for Isotope Ratio Analysis?

John Valley

UW - Madison

Tyler Blum, David Reinhard

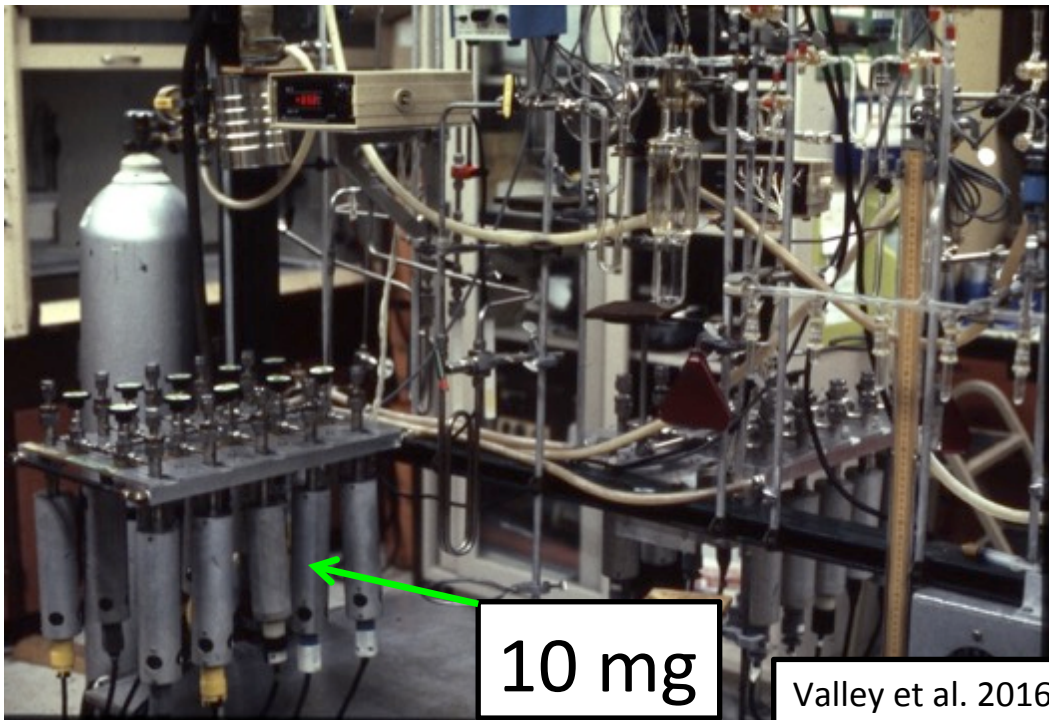
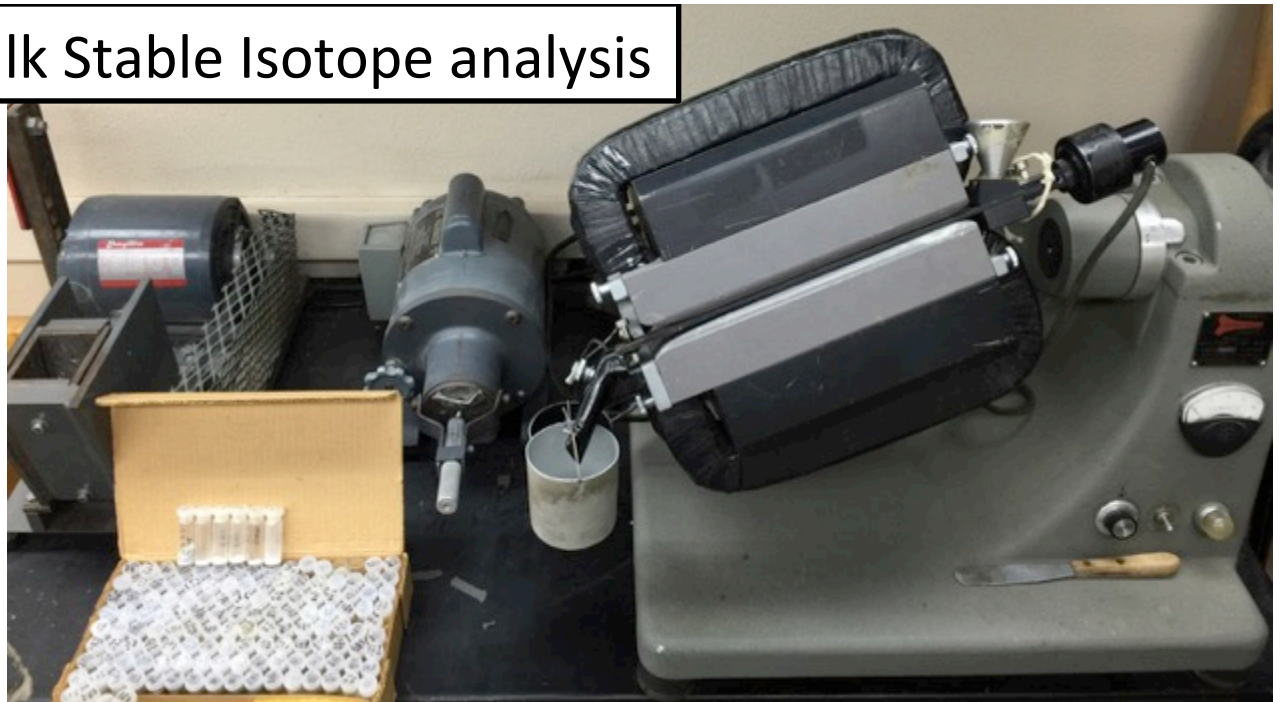


Valley et al. 2016, GSA, Denver



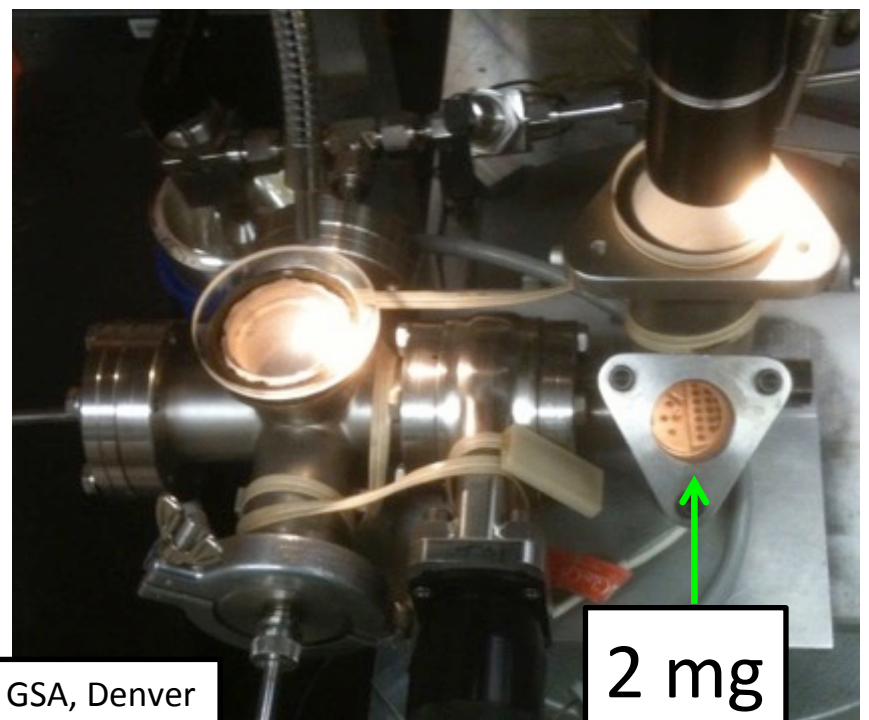


Bulk Stable Isotope analysis



10 mg

Valley et al. 2016, GSA, Denver

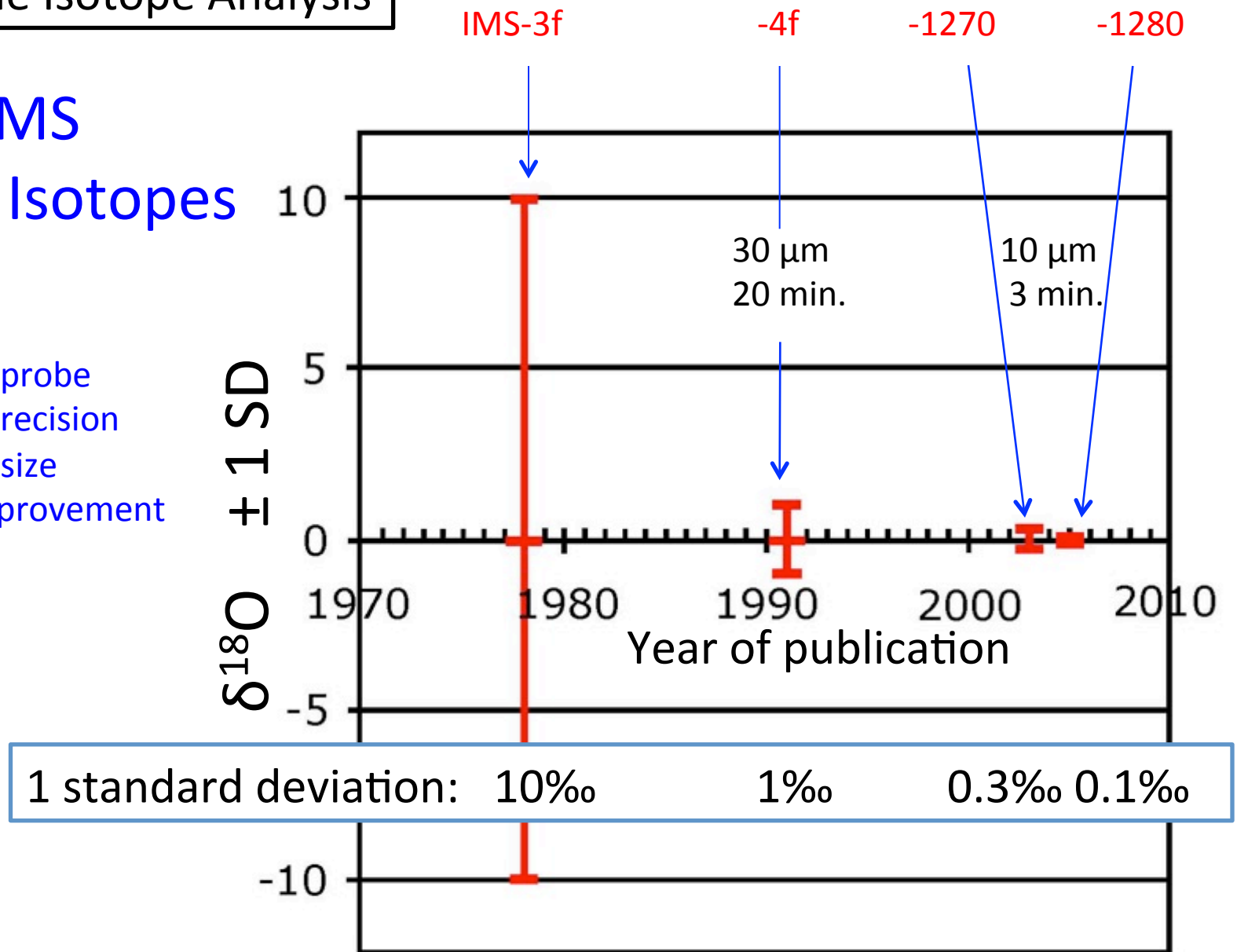


2 mg

In situ Stable Isotope Analysis

SIMS Oxygen Isotopes

Ion Microprobe
Analytical Precision
& Spot size
30 years of Improvement



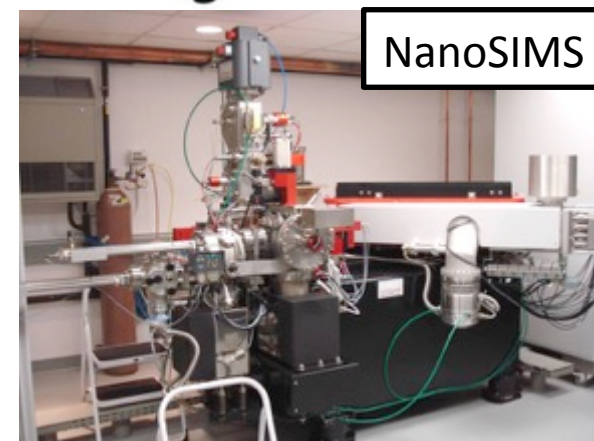
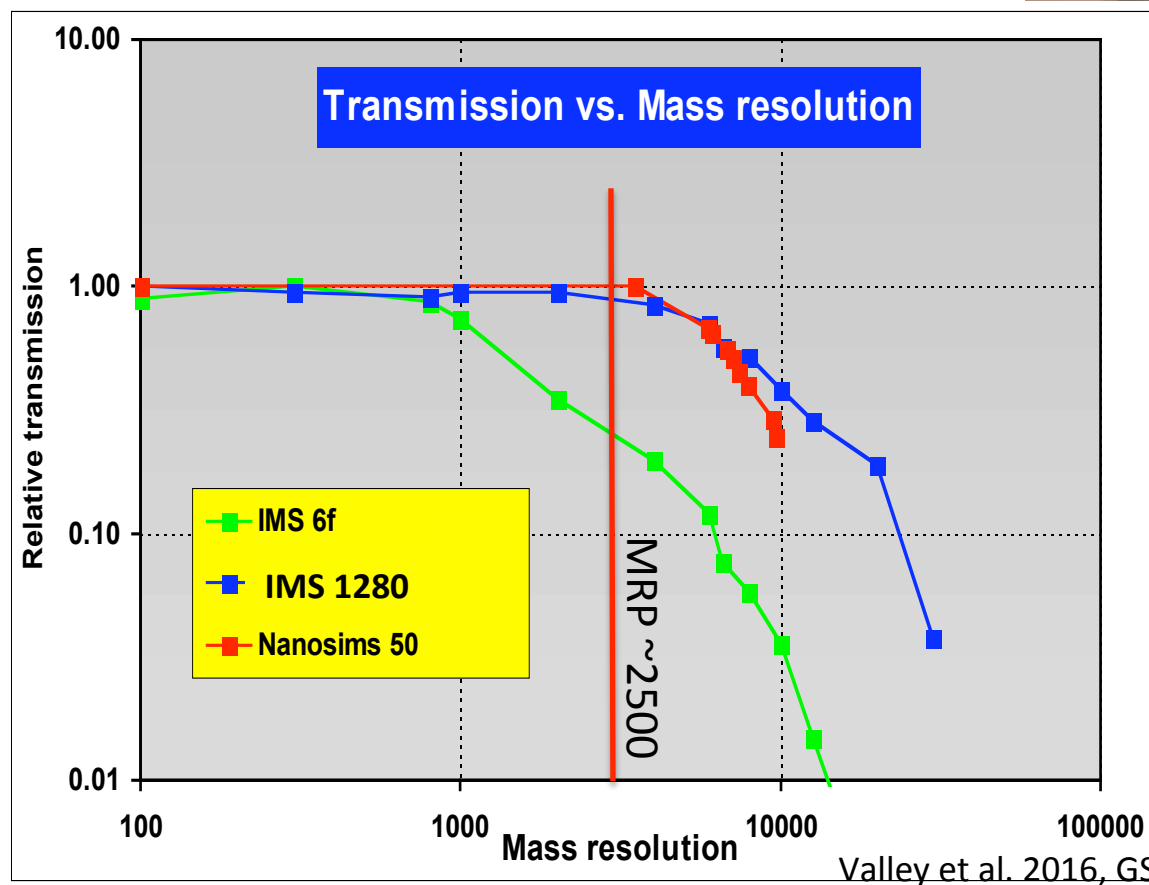
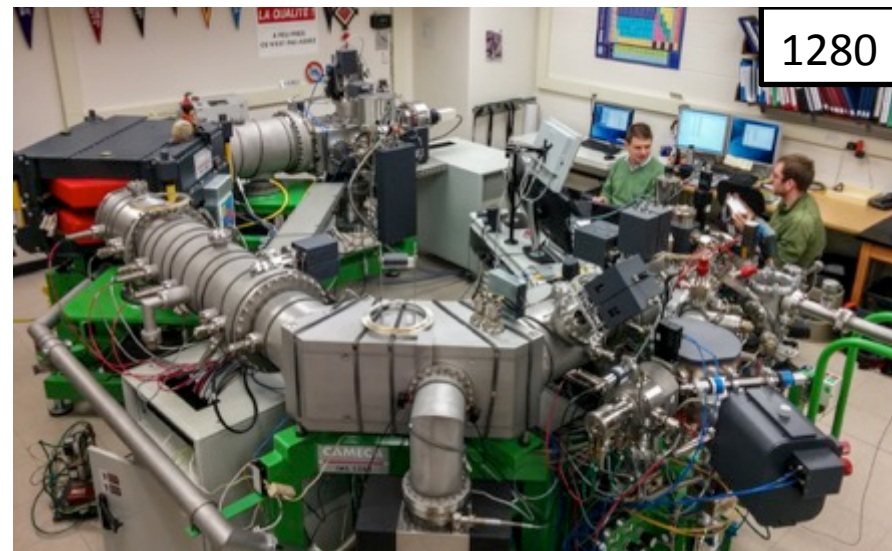
CAMECA

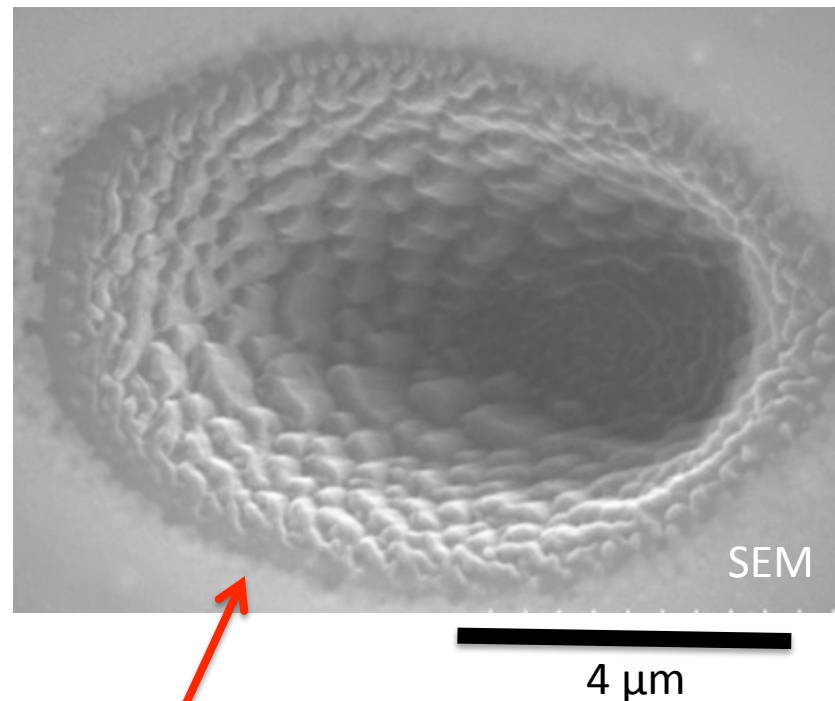
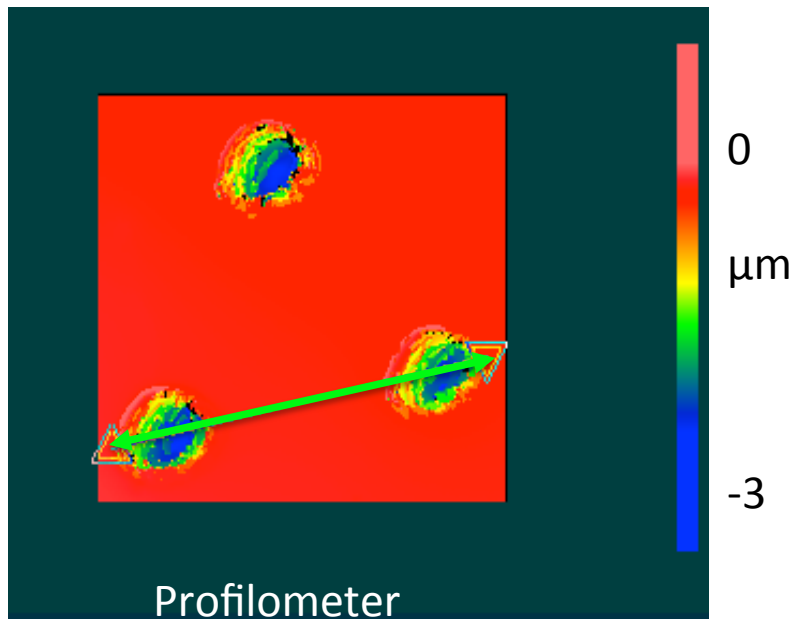
IMS- 3f, -7f

* IMS- 1270, -1300

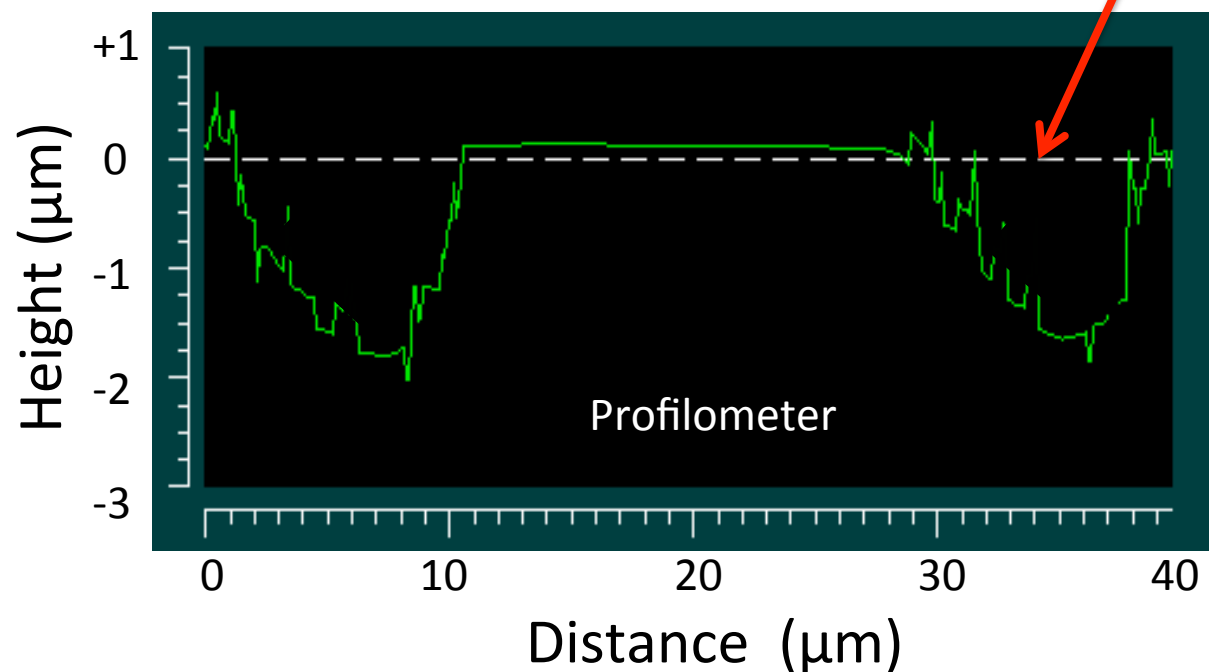
NanoSIMS

SHRIMP



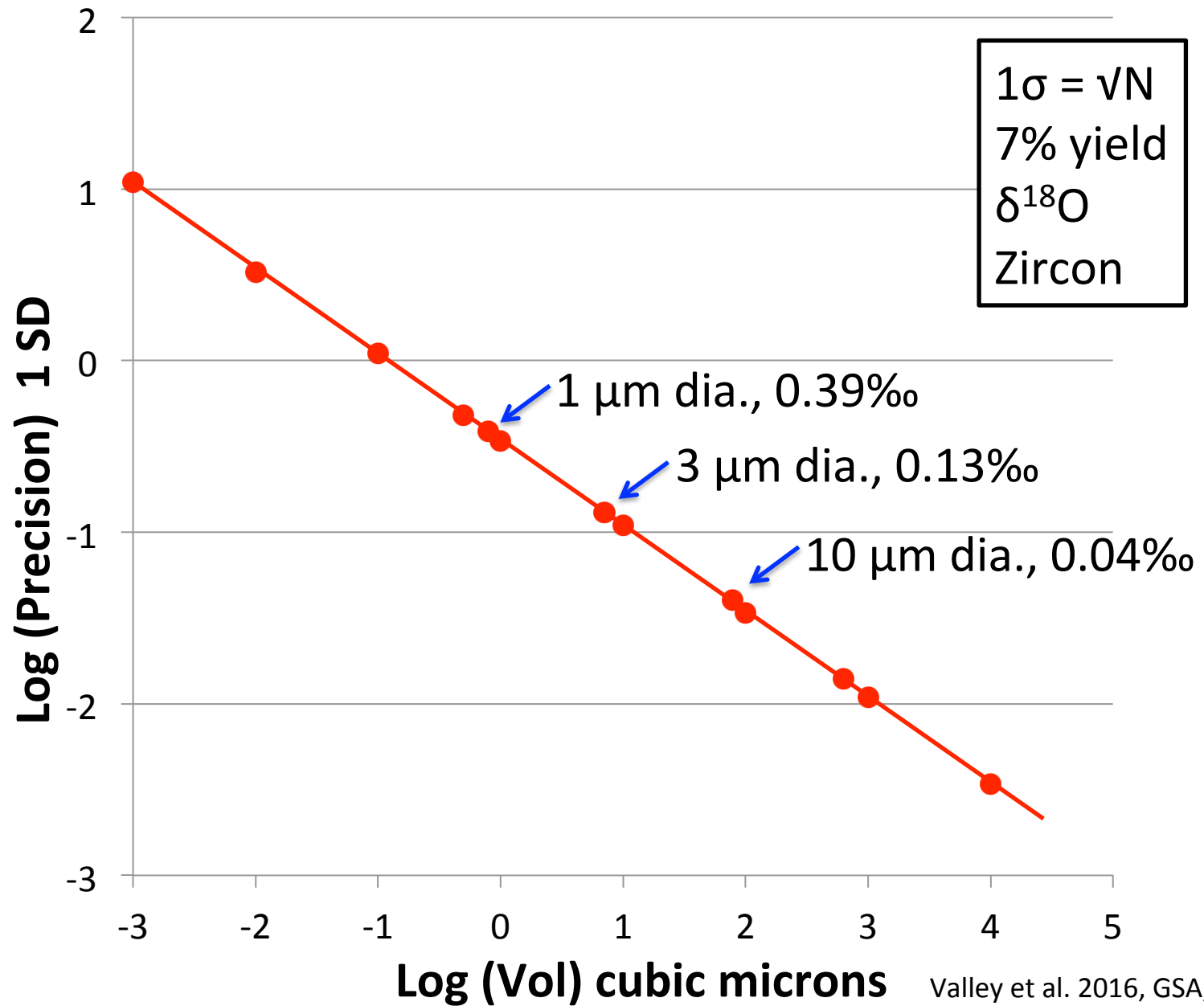


Volume = $75 \mu\text{m}^2$

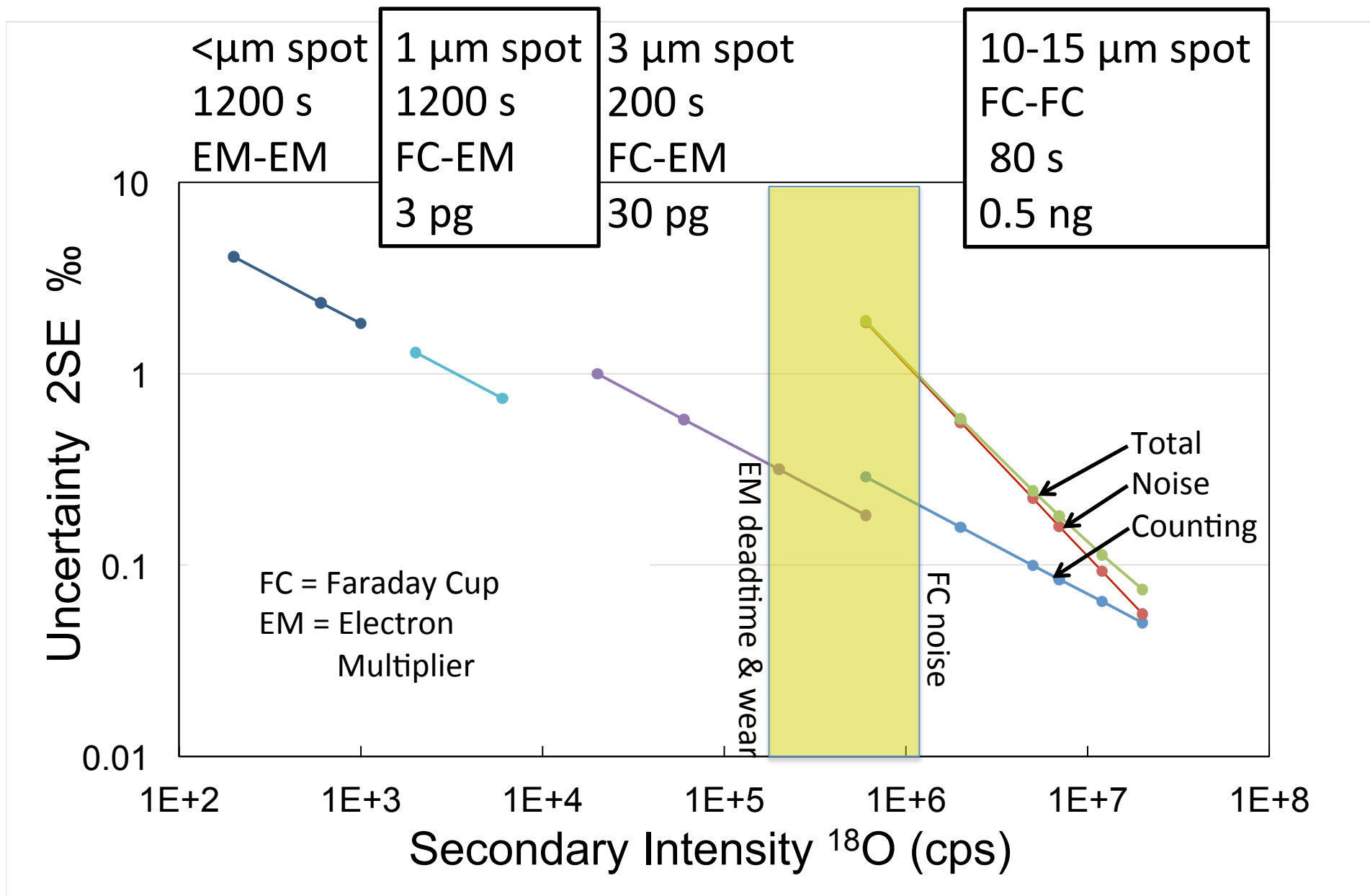


Useful ion yield
~7% for $\delta^{18}\text{O}$
IMS-1280
at WiscSIMS

Theoretical Limit: Precision vs. Pit Volume



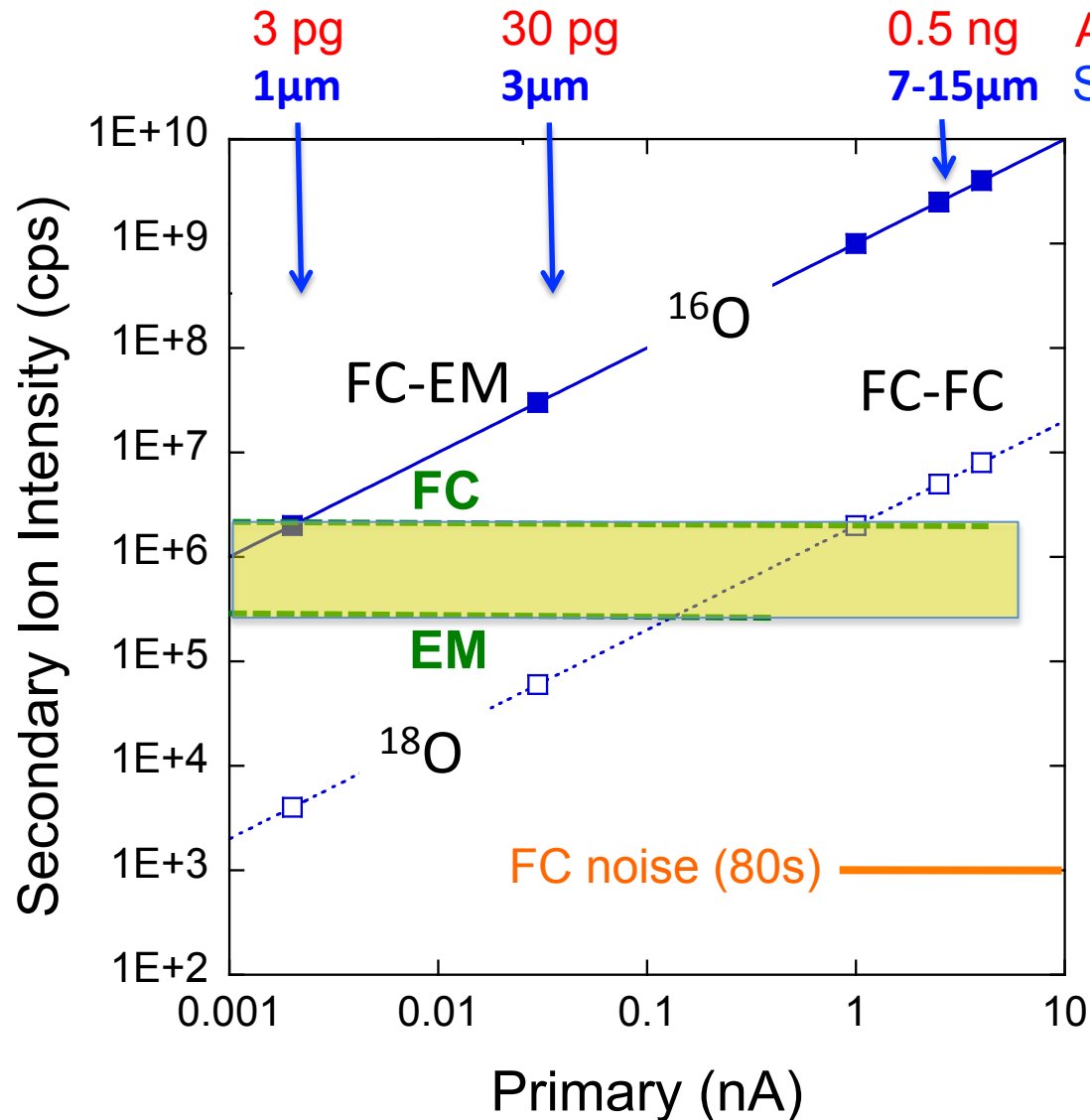
SIMS Uncertainty $^{18}\text{O}/^{16}\text{O}$



Additional factors: Deadtime, QSA, IMF

Valley et al. 2016, GSA, Denver

Precision of Analyses vs. Primary Beam Current



$^{18}\text{O}/^{16}\text{O}$ Precision
2 SD ‰

FC-FC Mode:

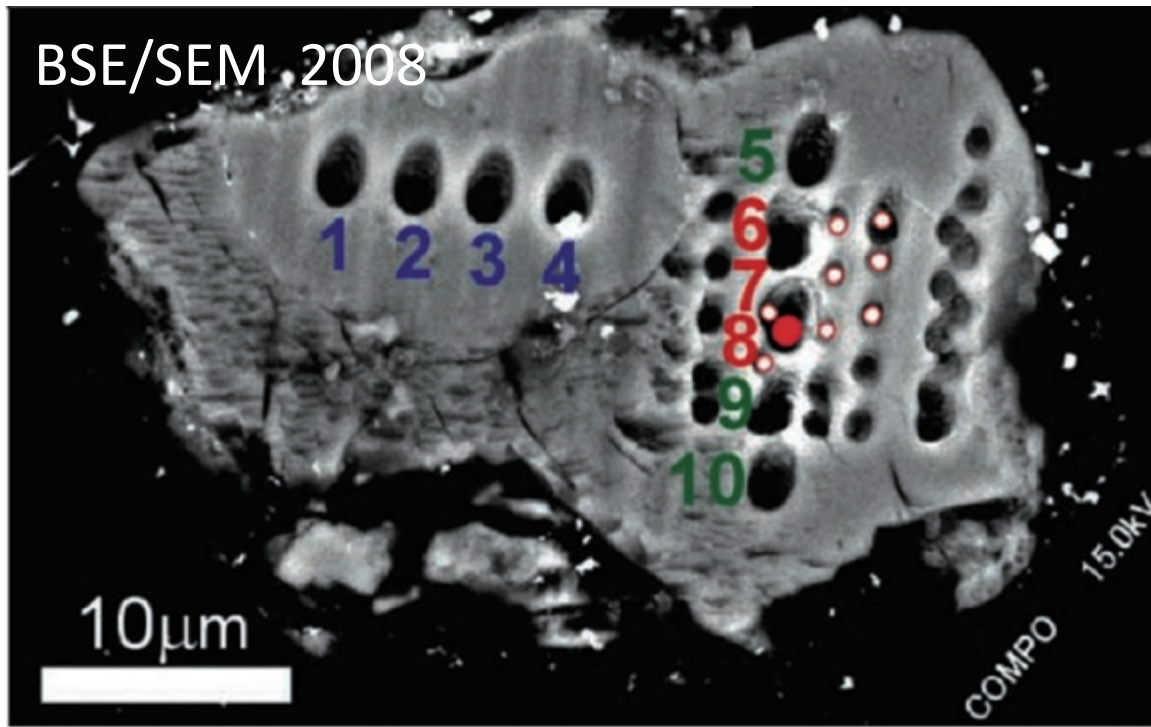
10-15 μ m (2-3nA)
 $\leq 0.3\text{‰}$ 3 min

FC-EM Mode:

1-3 μ m (2pA -30pA)
0.5-1‰ 10-30 min

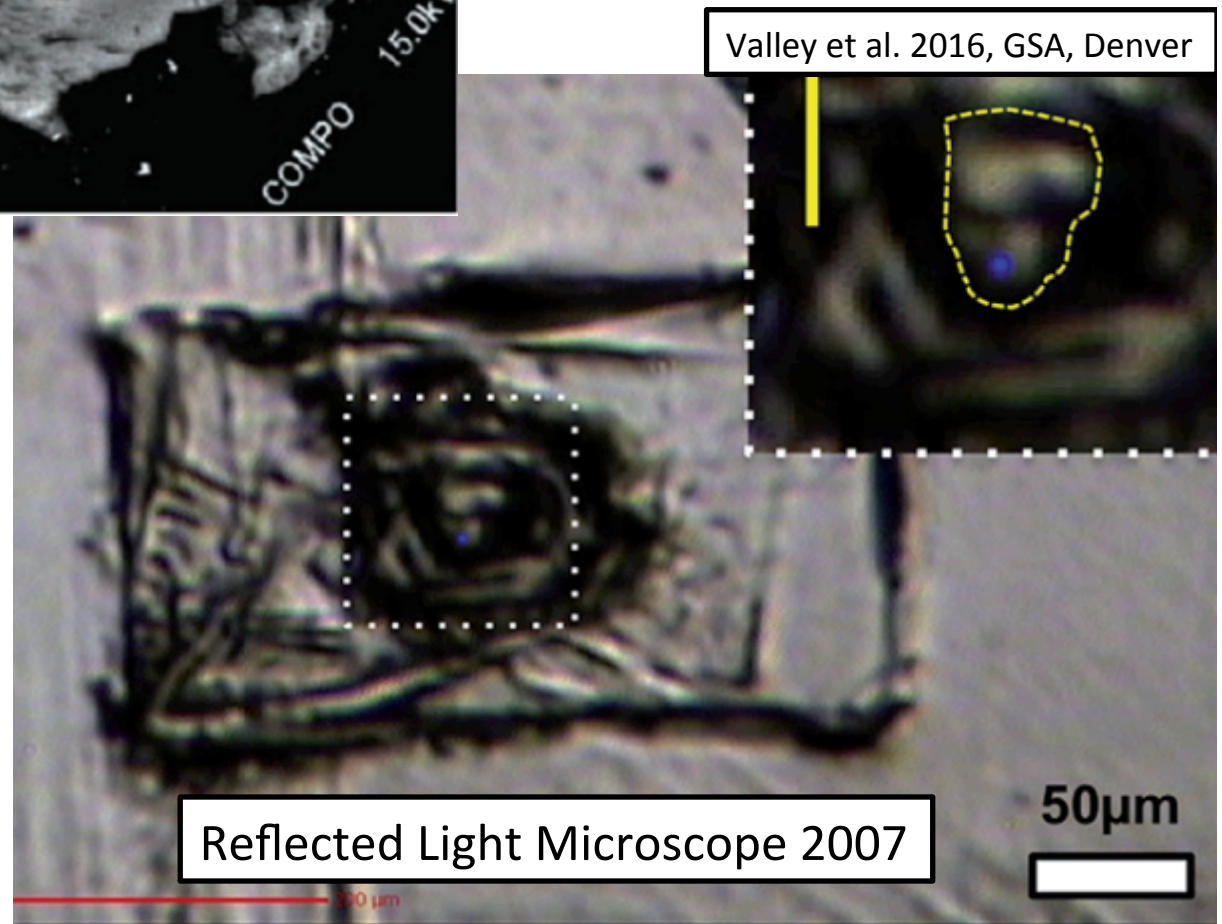
Kita 2011 BGSW

BSE/SEM, 2008

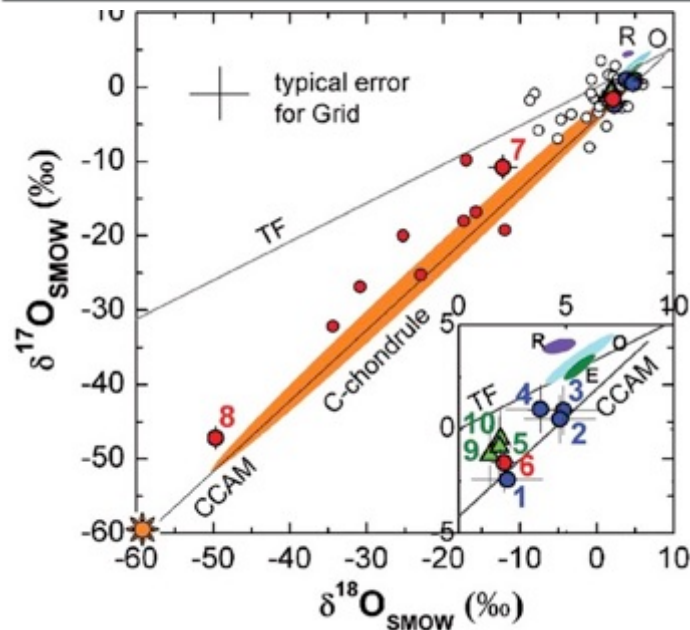


Comet Wild 2

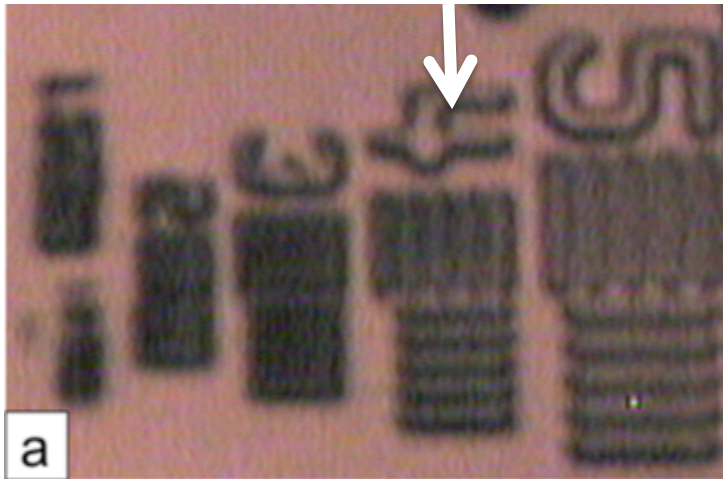
Valley et al. 2016, GSA, Denver



Reflected Light Microscope 2007



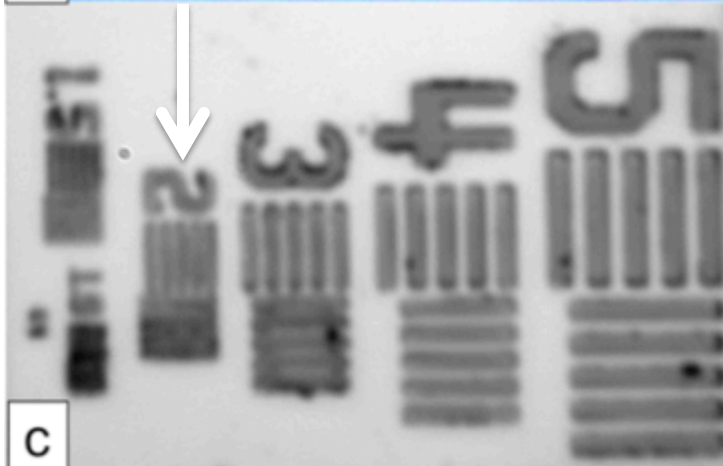
Nakamura et al. 2008, Science



White Light
 $\lambda = 400-700 \text{ nm}$
 $3.5 \mu\text{m}$

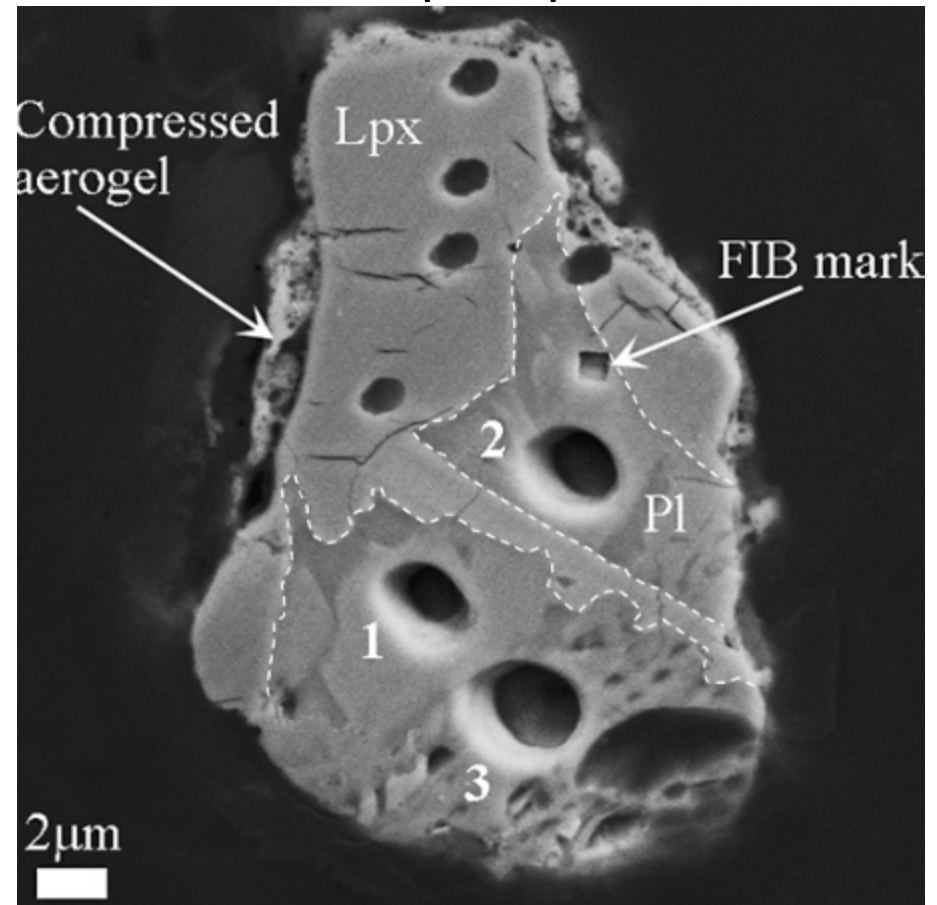


Blue LED
 $\lambda = 455 \text{ nm}$
 $2.2 \mu\text{m}$



UV LED
 $\lambda = 365 \text{ nm}$
 $1.3 \mu\text{m}$

1 & 2 μm spots, 2015



Nakashima et al. 2015

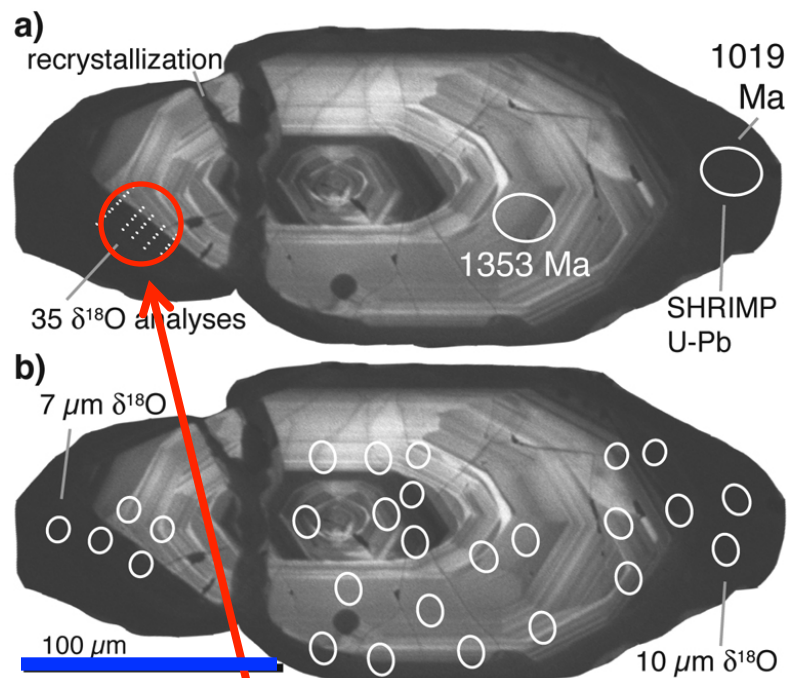
Badgerscope software

Kita et al. 2015

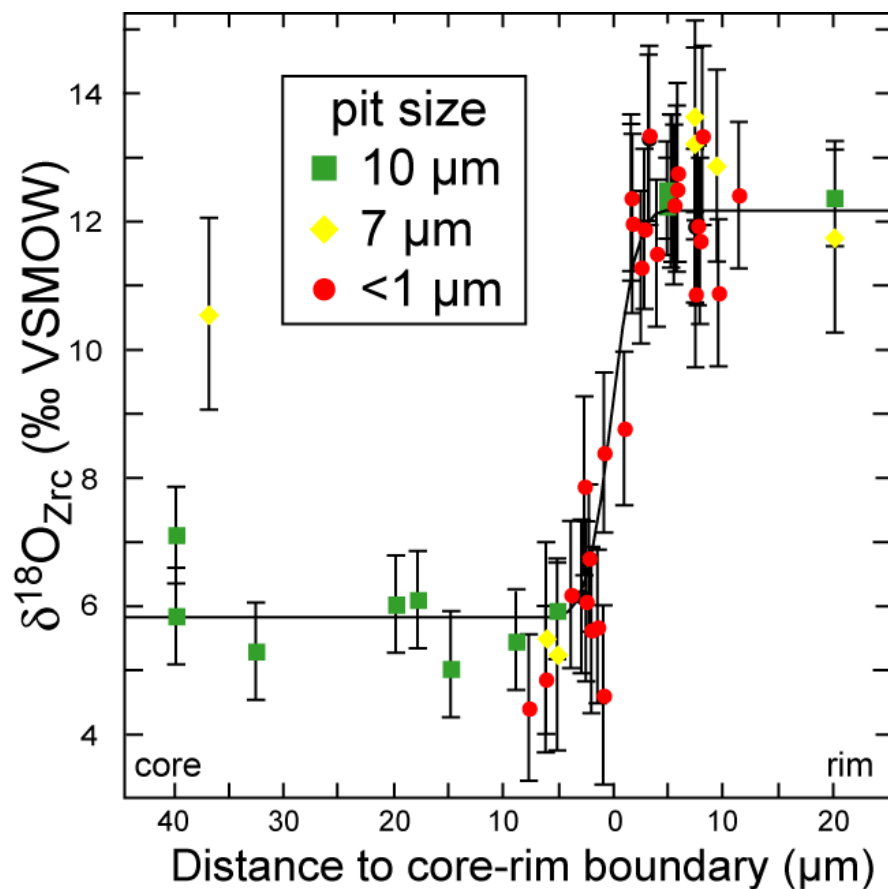
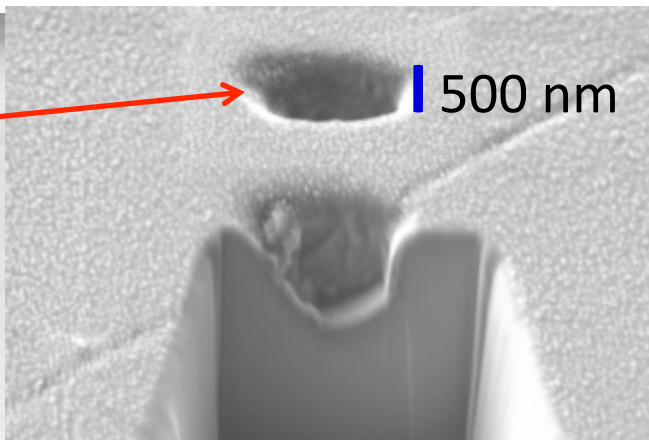
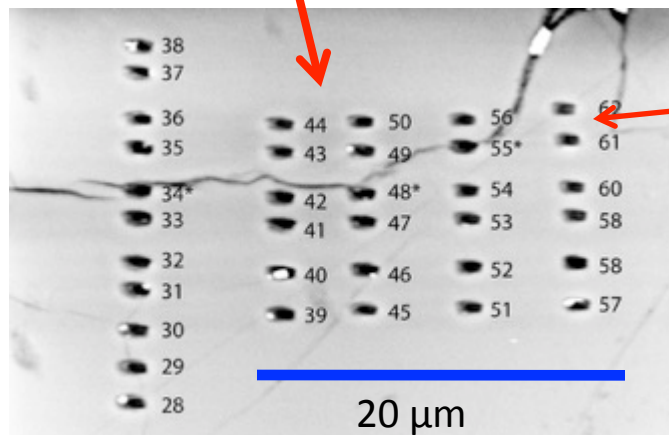


Valley et al. 2016, GSA, Denver

Oxygen diffusion in Zircon



Sub-micron spot - $\delta^{18}\text{O}$



Page et al. 2007

Bowman et al. 2011

Valley et al. 2016, GSA, Denver



Atom Probe Tomography

Quantitative

Spatially resolved, sub-nm

Single-atom scale

Mass-spectrometry

Nano-Geochronology

Evaluate Pb mobility

in zircon

LEAP 3000

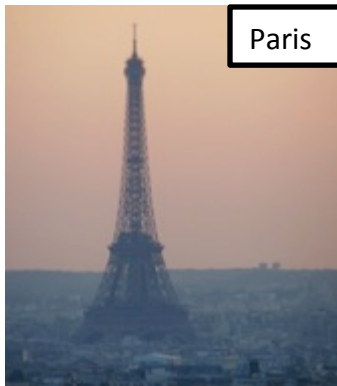
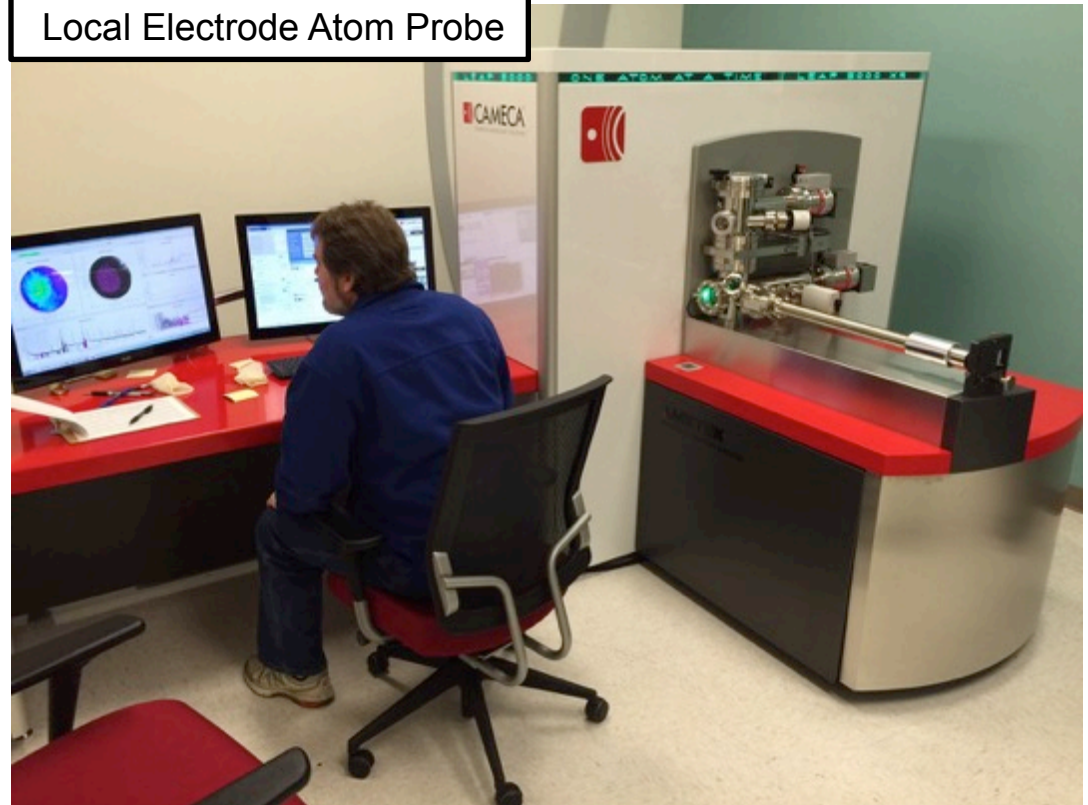
LEAP 4000

LEAP 5000

LEAP 5000

Local Electrode Atom Probe

Valley et al. 2016, GSA, Denver



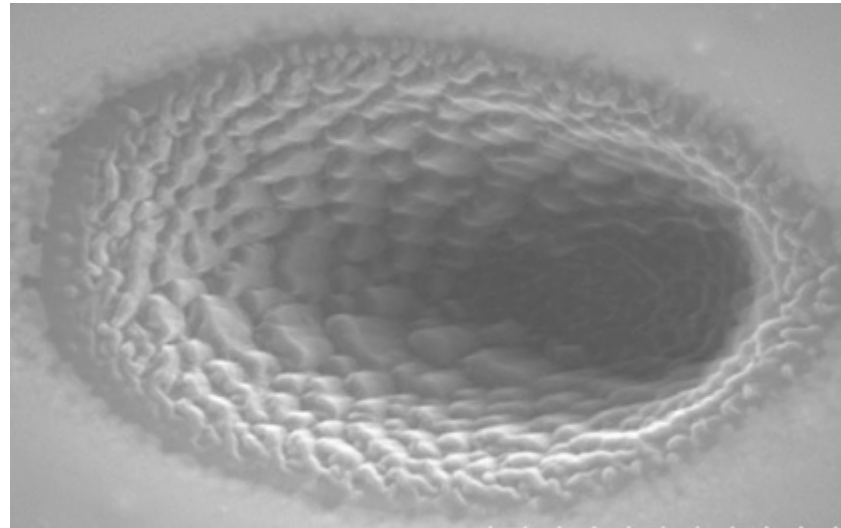
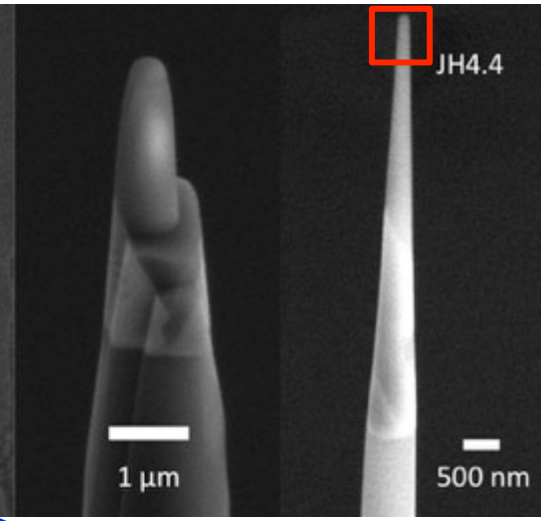
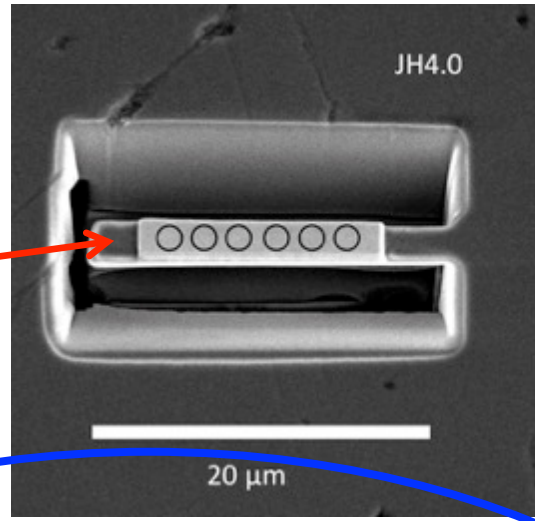
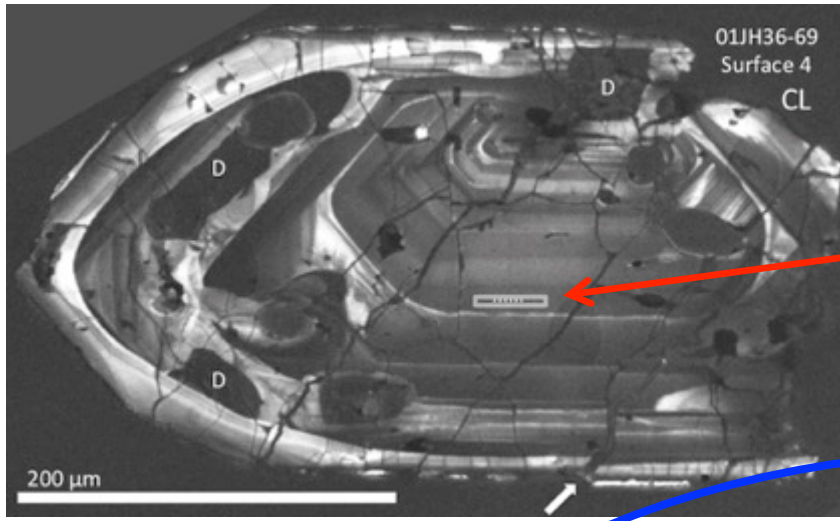
Paris



Madison

CAMECA Instruments
Factory, Madison, WI

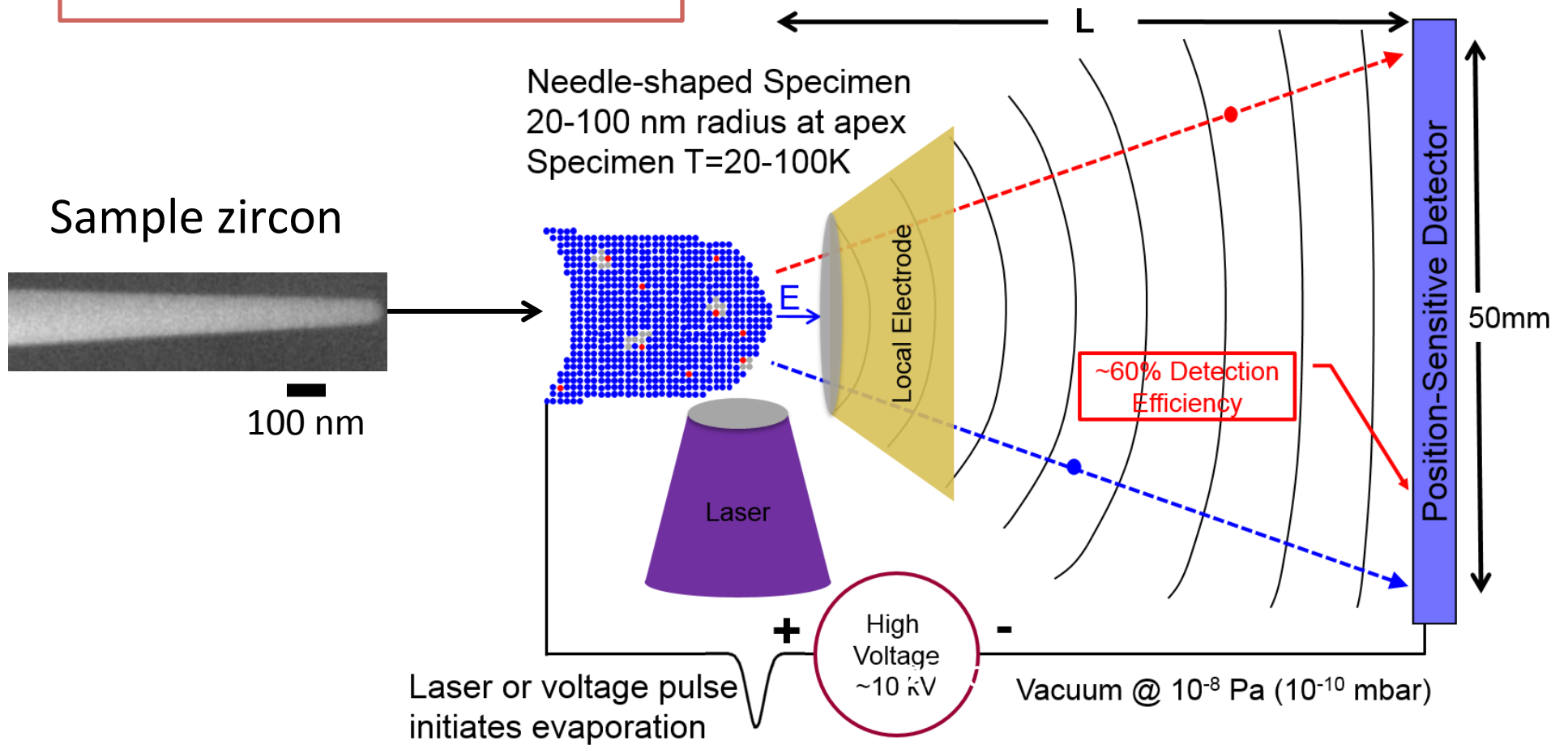




SIMS pit

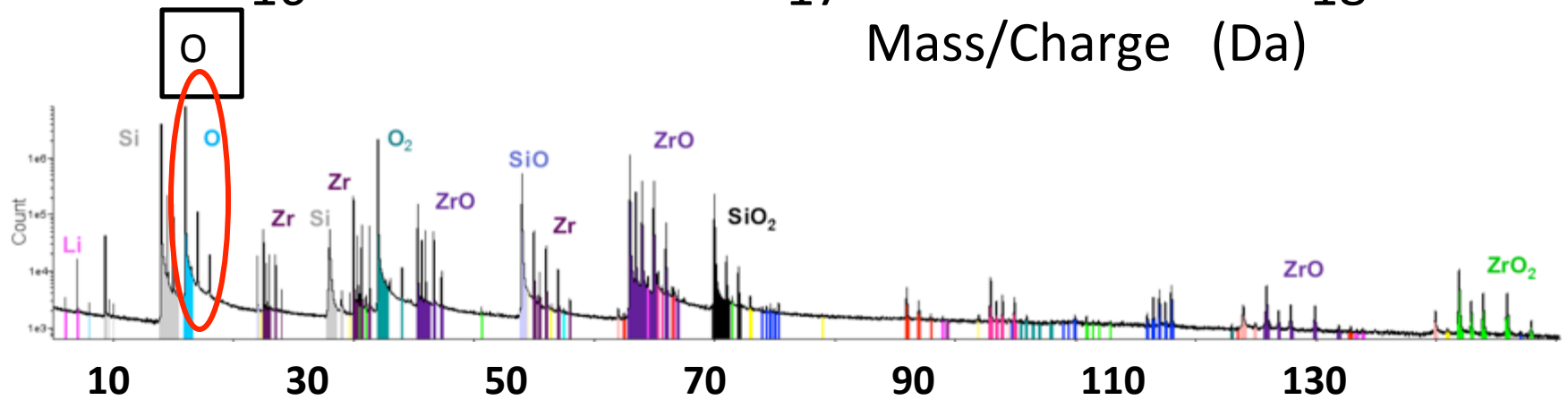
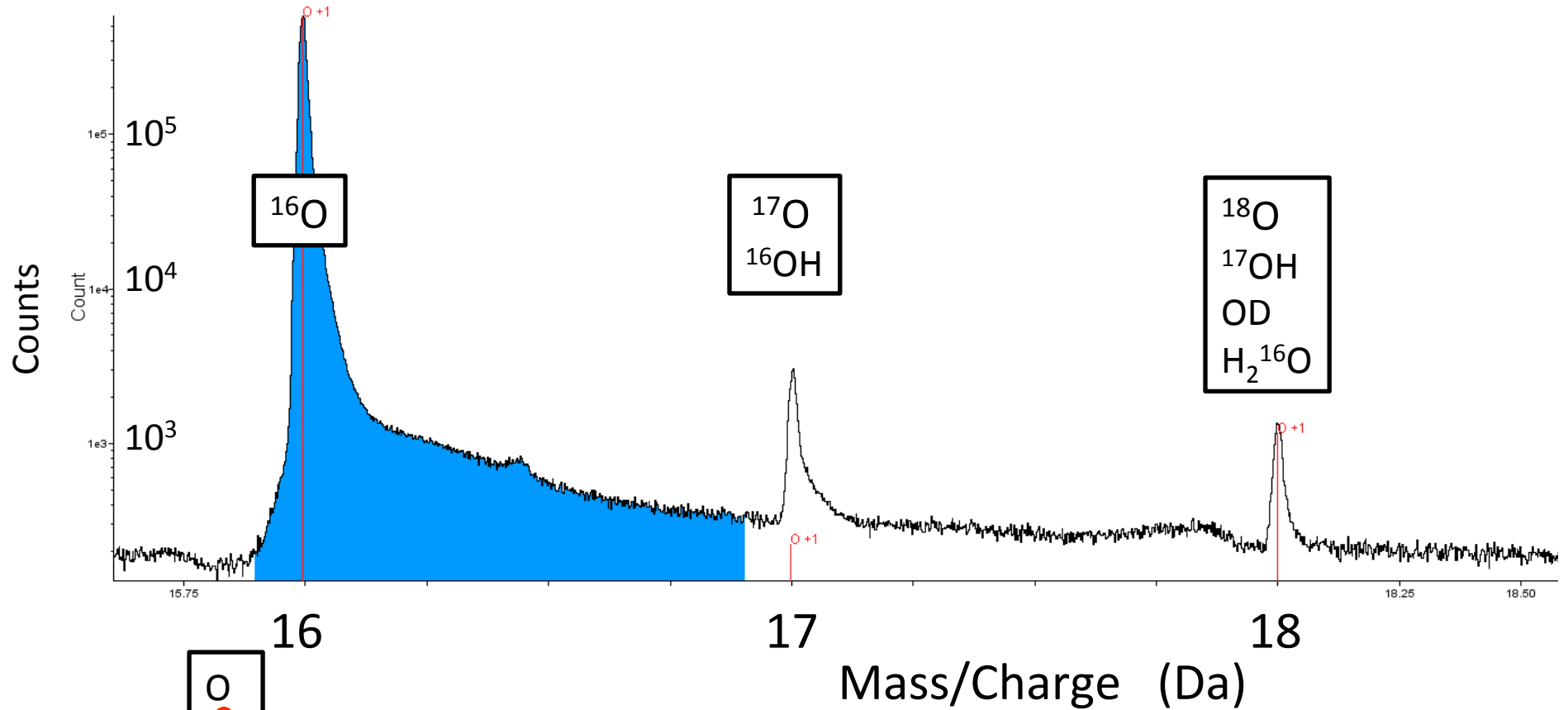
APT Specimen → 
 10^5 - 10^6 smaller than SIMS

Atom Probe Tomography APT



Valley et al. 2015 Am Min

APT spectra on zircon



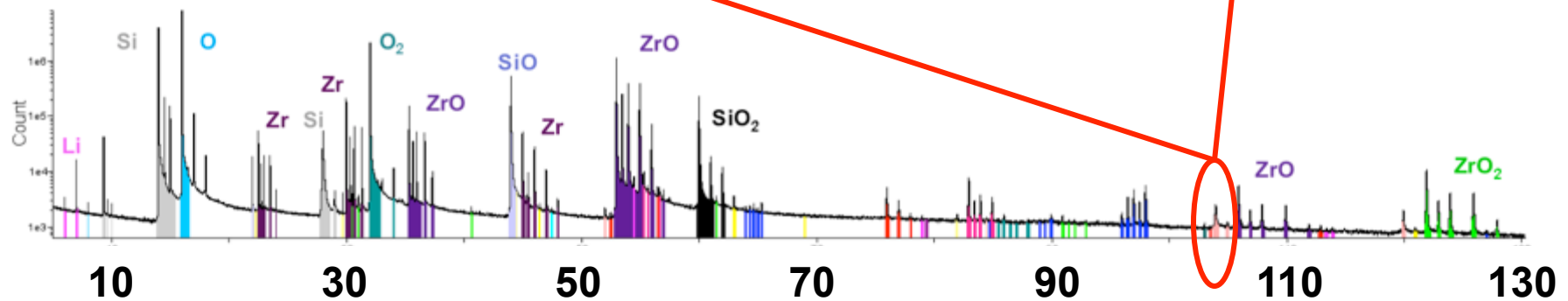
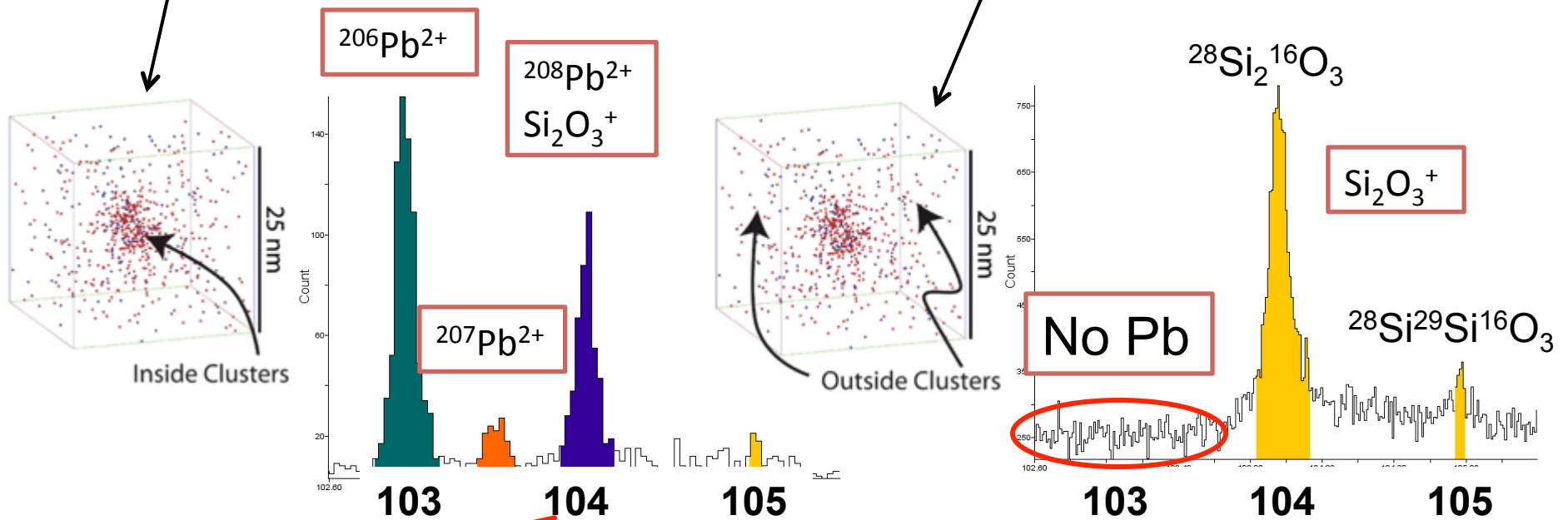
Valley et al. 2015 Am. Min.

(Da)  CAMECA® Valley et al. 2016, GSA, Denver

Inside Y-rich clusters

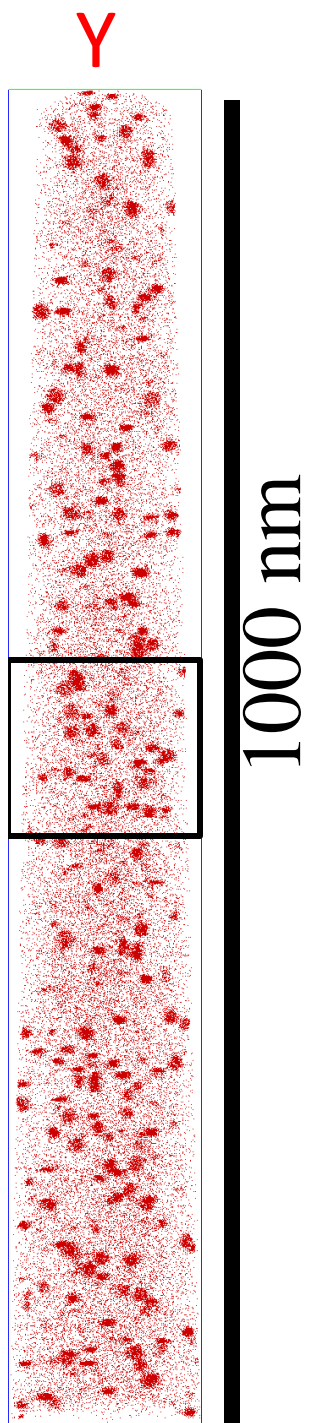
ARG 2.5 Ga

Outside clusters



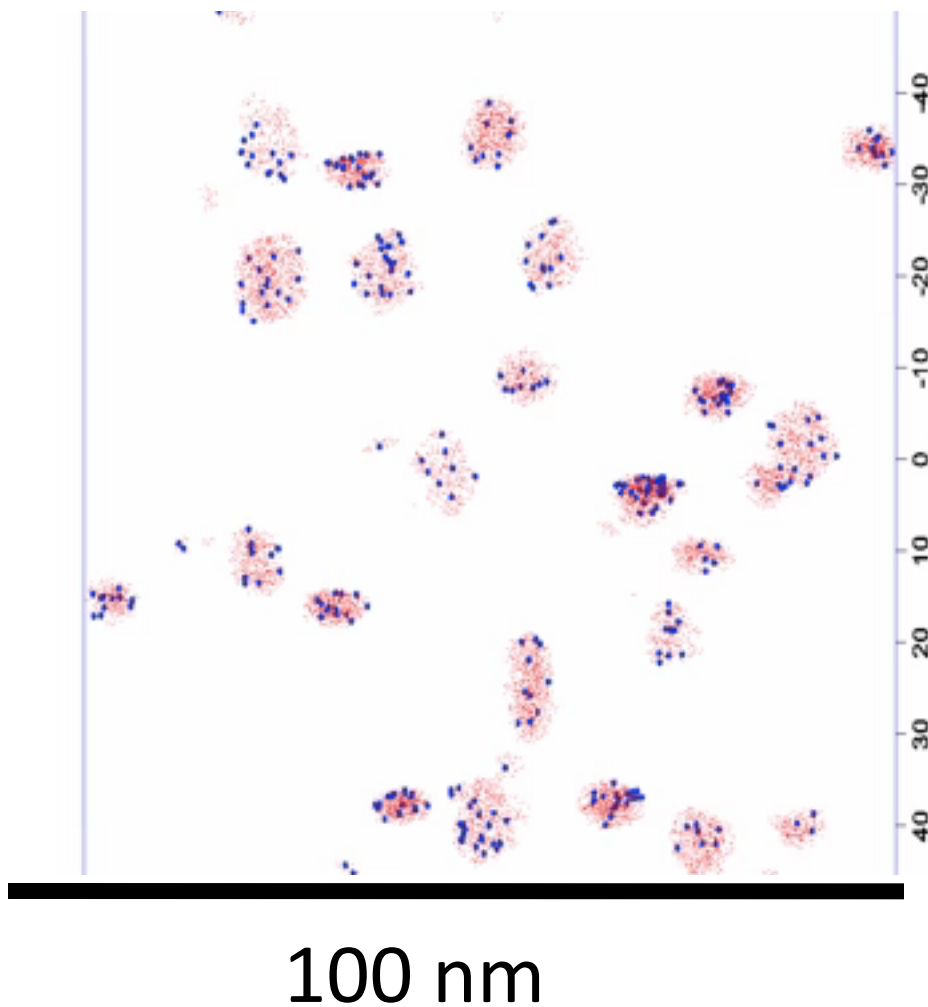
APT spectra on zircon AMU

Valley et al. 2015 Am Min



Clusters, 4.4 Ga

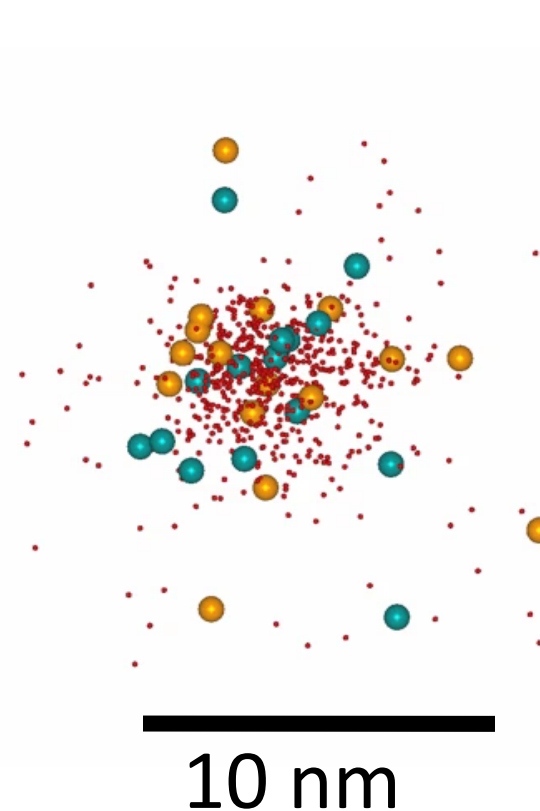
Y & Pb



^{206}Pb

^{207}Pb

Y



Valley et al. 2014 Nat. Geosci.

Valley et al. 2015 Am. Min.

Valley et al. 2016, GSA, Denver

Y

Clusters, 4.4 Ga

391 clusters, 5,287 Pb atoms
 $^{207}\text{Pb}/^{206}\text{Pb} = 1.2 \pm 0.05$

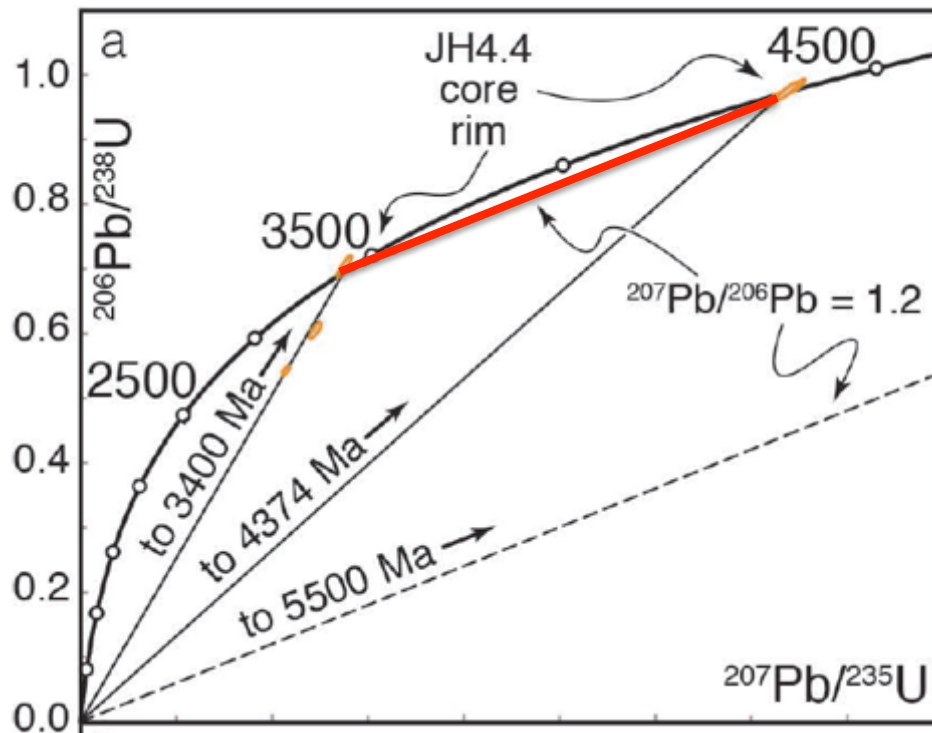
1000 nm

^{206}Pb

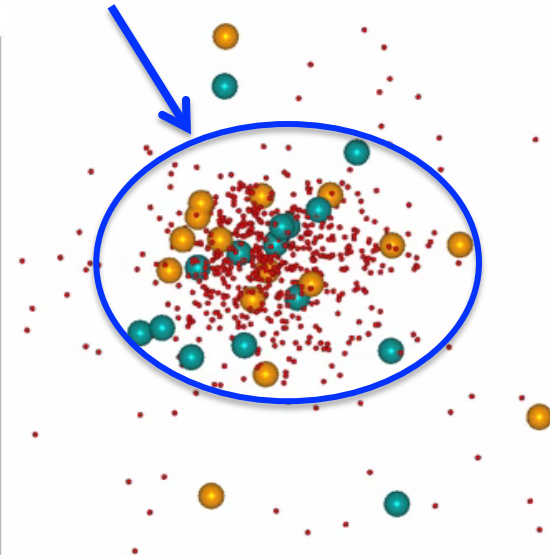
^{207}Pb

Y

1 cluster, 25 Pb atoms
 $^{207}\text{Pb}/^{206}\text{Pb} = 1.1$ (13/12)



Valley et al. 2014 Nat. Geosci.
 Valley et al. 2015 Am. Min.



10 nm

Valley et al. 2016, GSA, Denver

Small is always better..... until it isn't.





How Small is Too Small for Isotope Ratio Analysis?

Depends on the application:

$< \approx 0.5 \mu\text{m}$ for $\delta^{18}\text{O}$ at
natural abundance

$< \approx 10 \text{ nm}$ for $^{207}\text{Pb}/^{206}\text{Pb}$
in Archean clusters

	SIMS	APT
Zircons		
$^{207}\text{Pb}/^{206}\text{Pb}$		
^{208}Pb , O & Li isotopes	