# Ancient Zircons, APT and SIMS:
## Hadean Zircons are not from Hell

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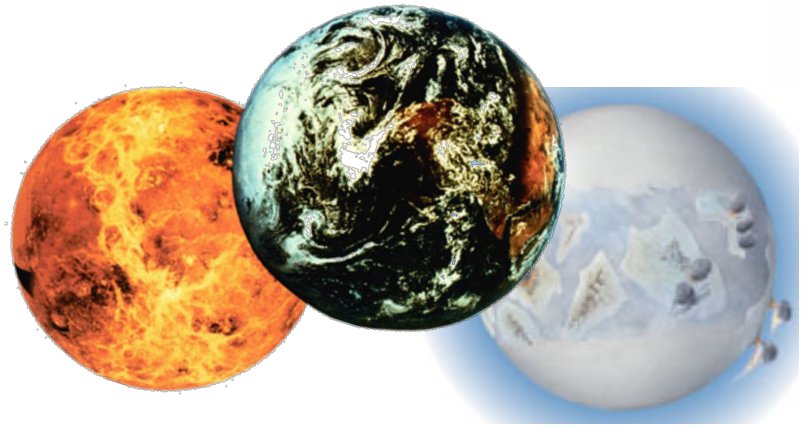
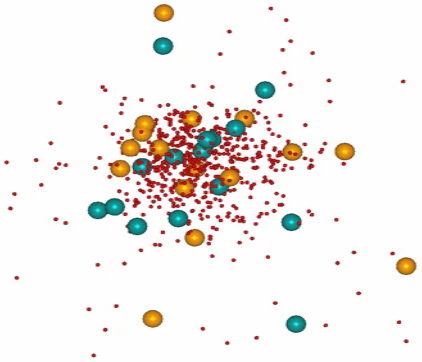
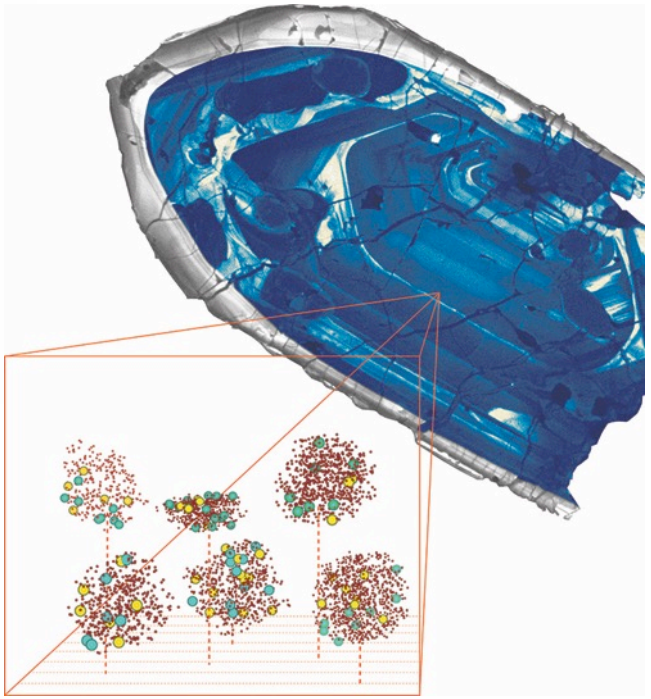
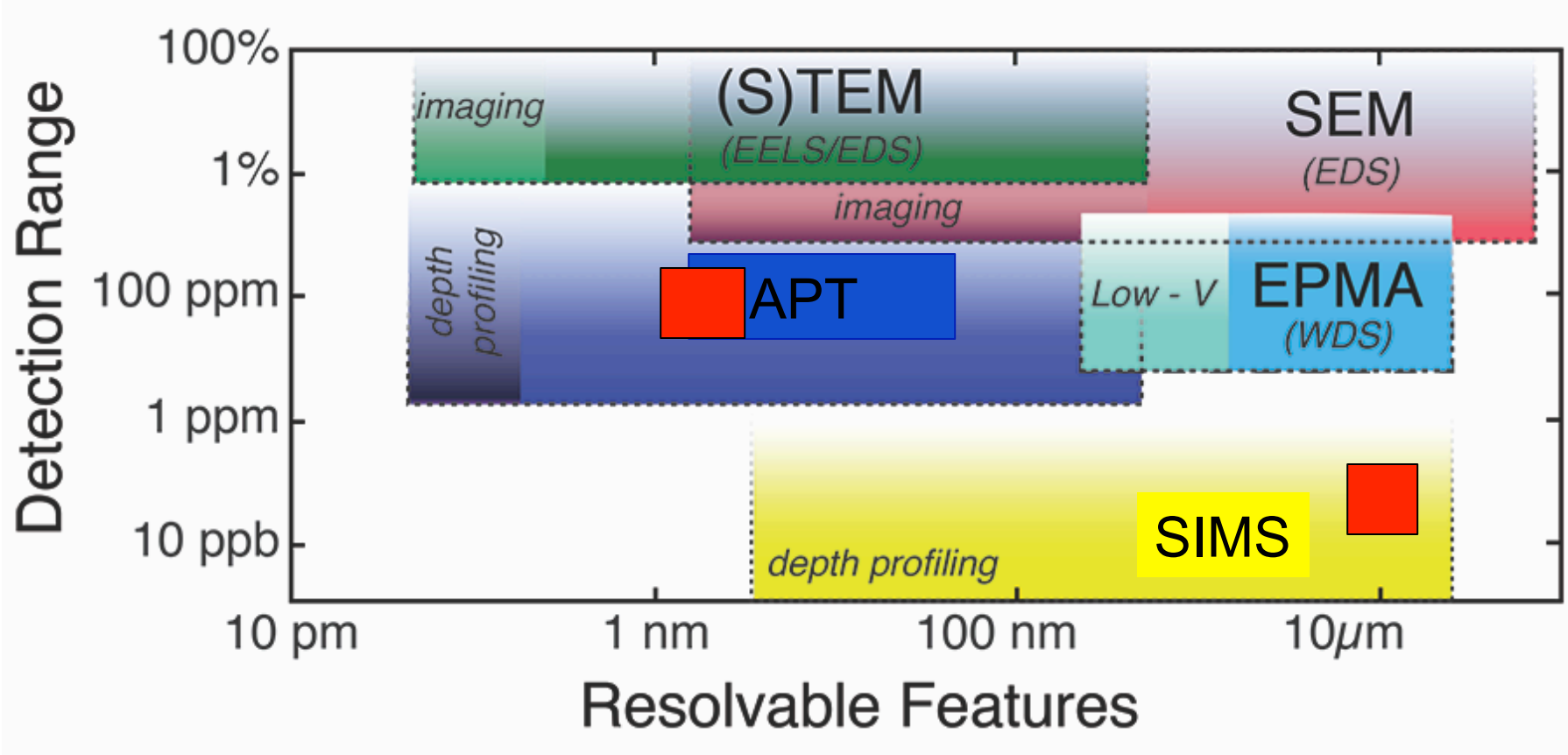
P Clifton, TF Kelly, DJ Larson, DF Lawrence, David Reinhard
D Moser, D Snoeyenbos, SA Wilde







NASA Astrobiology Institute

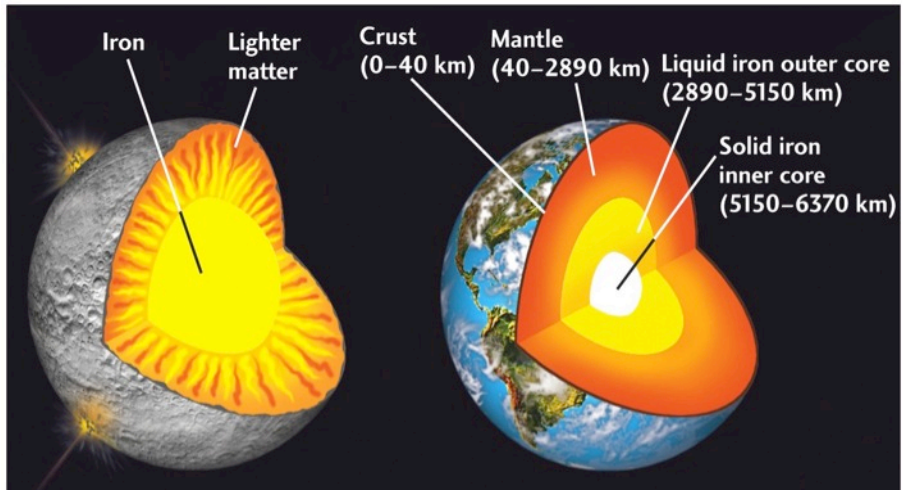


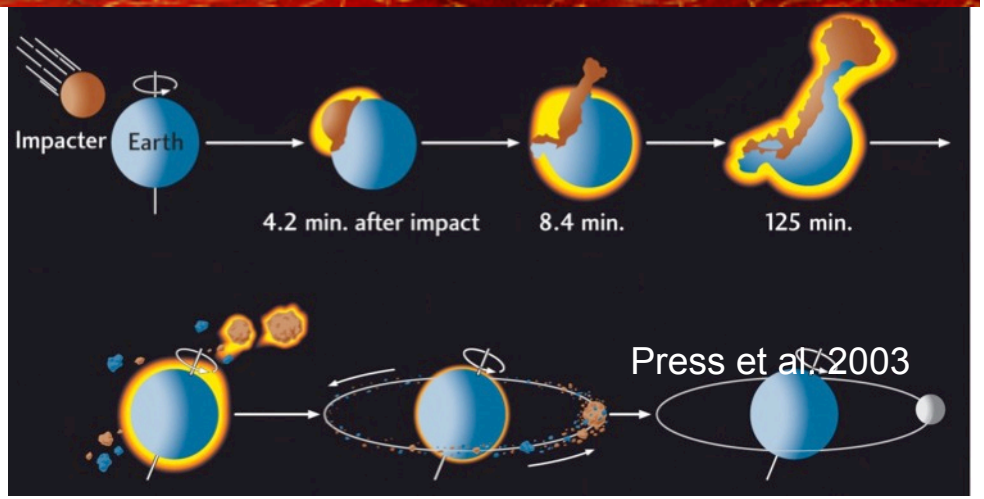

zircons

Valley et al. 2015
Modified from Gault et al. 2012

# Hot Hadean Earth

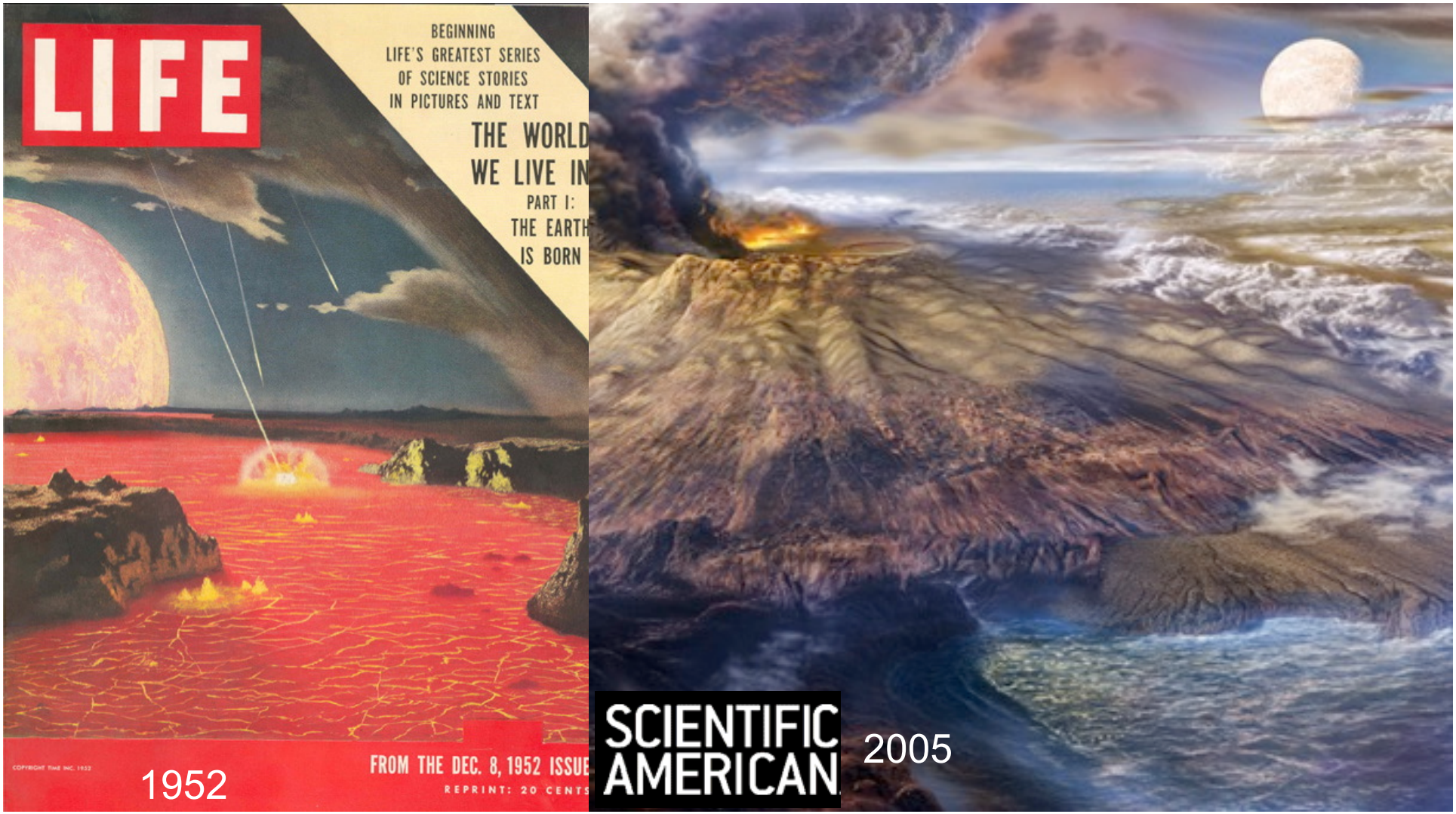
Chesley Bonestell 1952

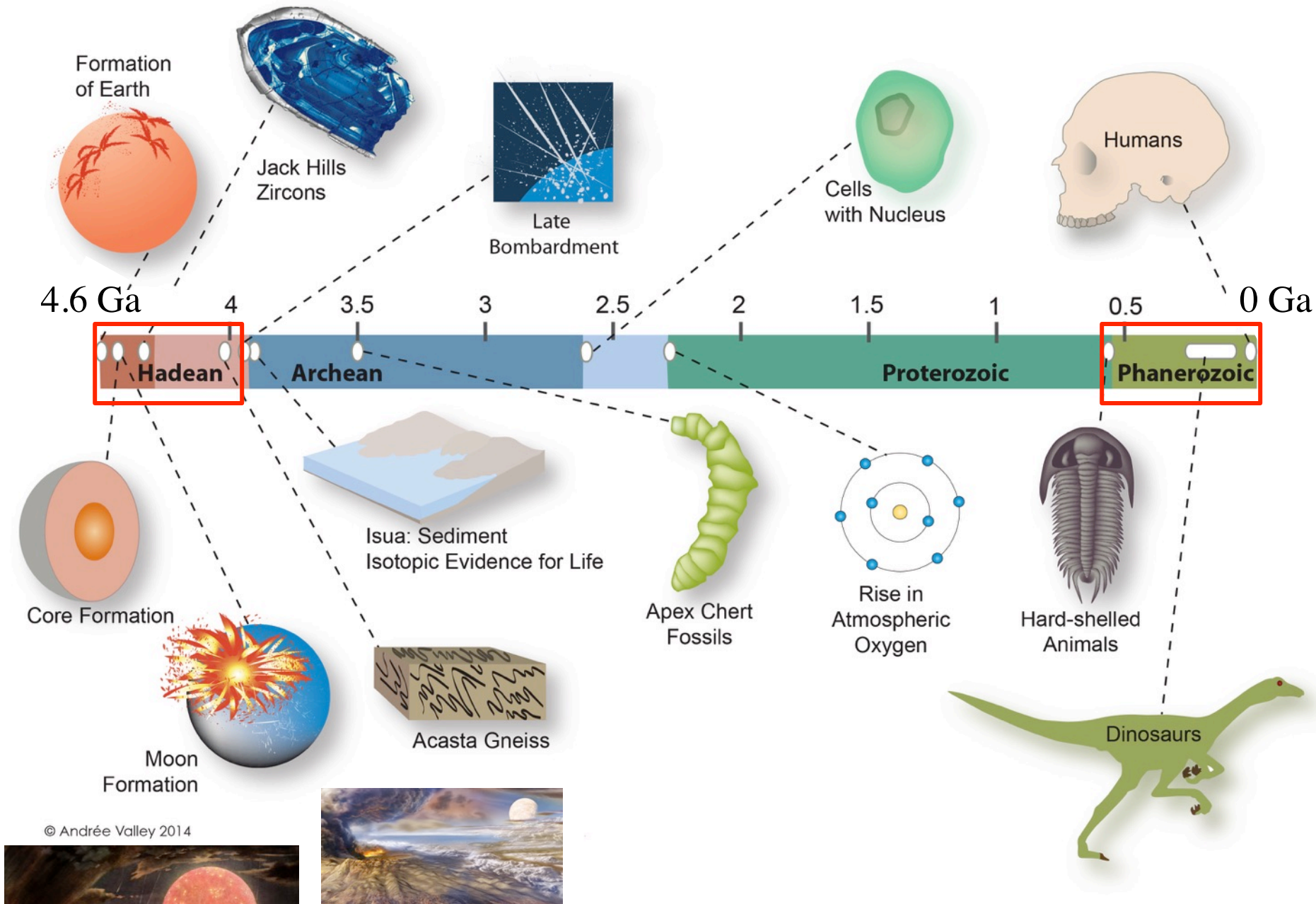


# Hot Earth - Cool Earth

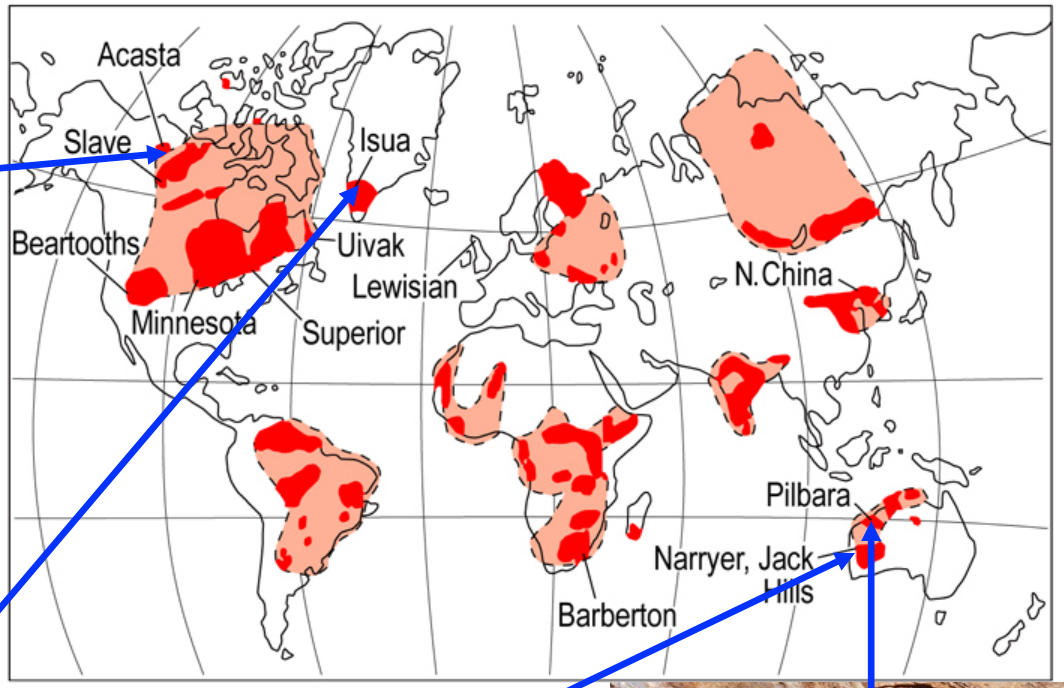
When were the first Oceans, Continents, Life?




Formation of Earth
Jack Hills Zircons
Late Bombardment
Cells with Nucleus
Humans
4.6 Ga
4
3.5
3
2.5
2
1.5
1
0.5
0 Ga
Hadean
Archean
Proterozoic
Phanerozoic
Core Formation
Isua: Sediment Isotopic Evidence for Life
Apex Chert Fossils
Rise in Atmospheric Oxygen
Hard-shelled Animals
Moon Formation
Acasta Gneiss
Dinosaurs
© Andrée Valley 2014

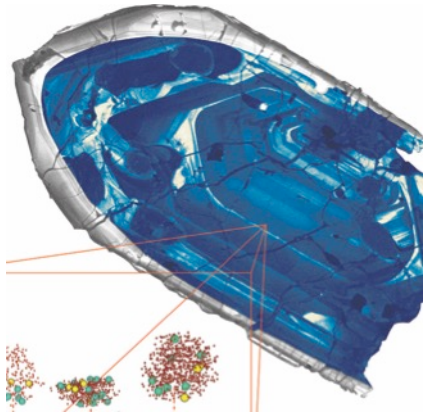
# Archean- Rocks older than 2.5 Ga

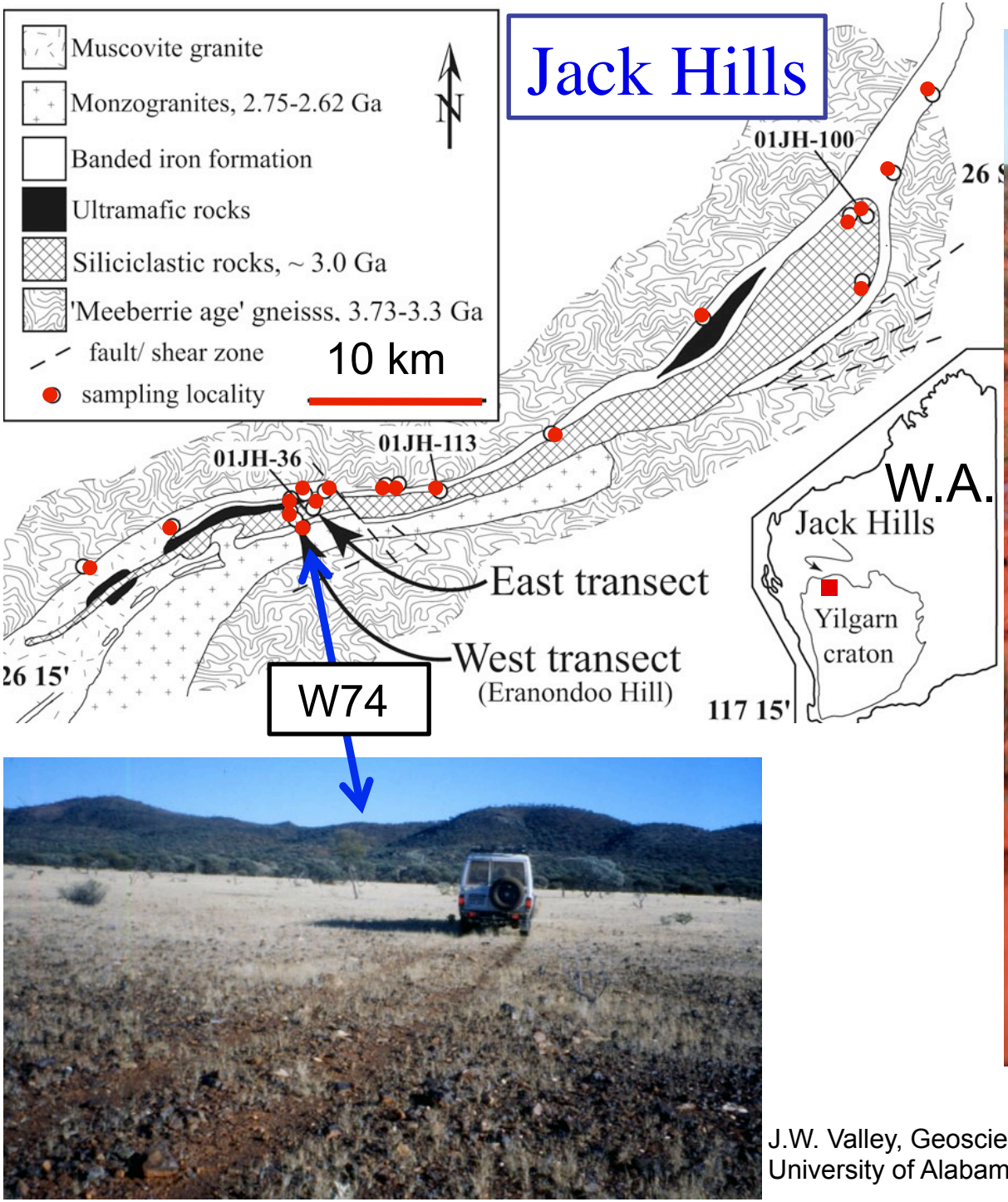
Acasta 4 Ga



Isua 3.8 Ga

Jack Hills 4.4 Ga



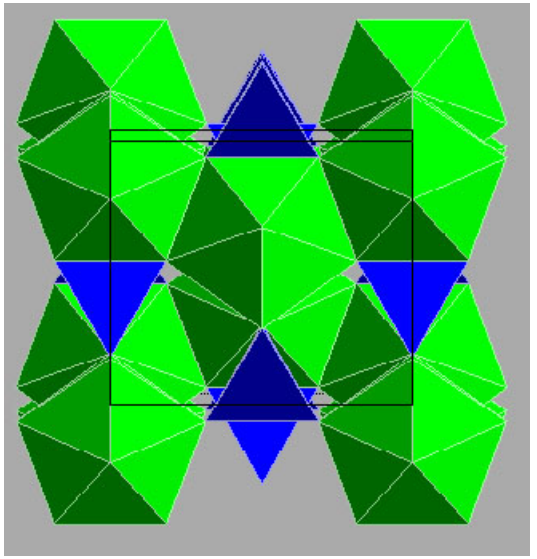

Jack Hills
Muscovite granite
Monzogranites, 2.75-2.62 Ga
Banded iron formation
Ultramafic rocks
Siliciclastic rocks, ~ 3.0 Ga
'Meeberrie age' gneisss, 3.73-3.3 Ga
fault/ shear zone
sampling locality
10 km
N
01JH-100
01JH-36
01JH-113
East transect
West transect
(Eranondoo Hill)
W74
W.A.
Jack Hills
Yilgarn
craton
26 15'
117 15'

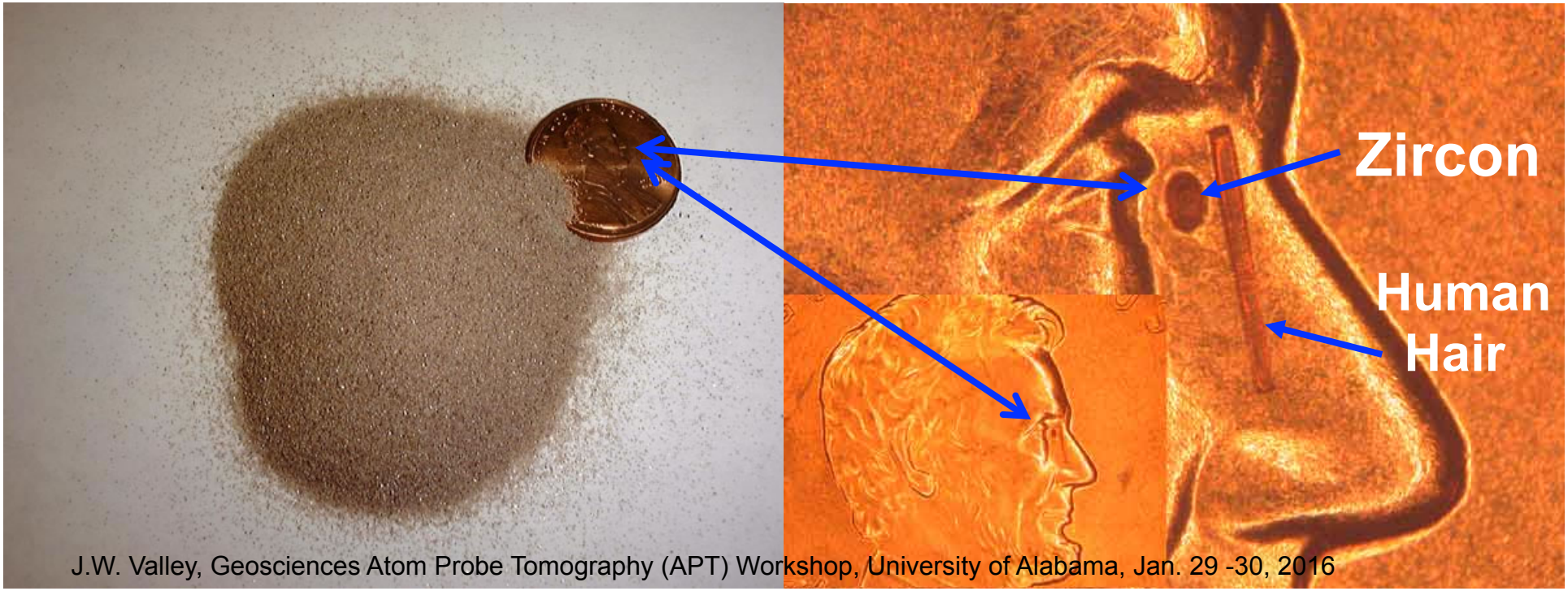
# Jack Hills Metaconglomerate

$SiO_2$ > 95%
Zr: 40-500 ppm
Cr: up to 5300 ppm

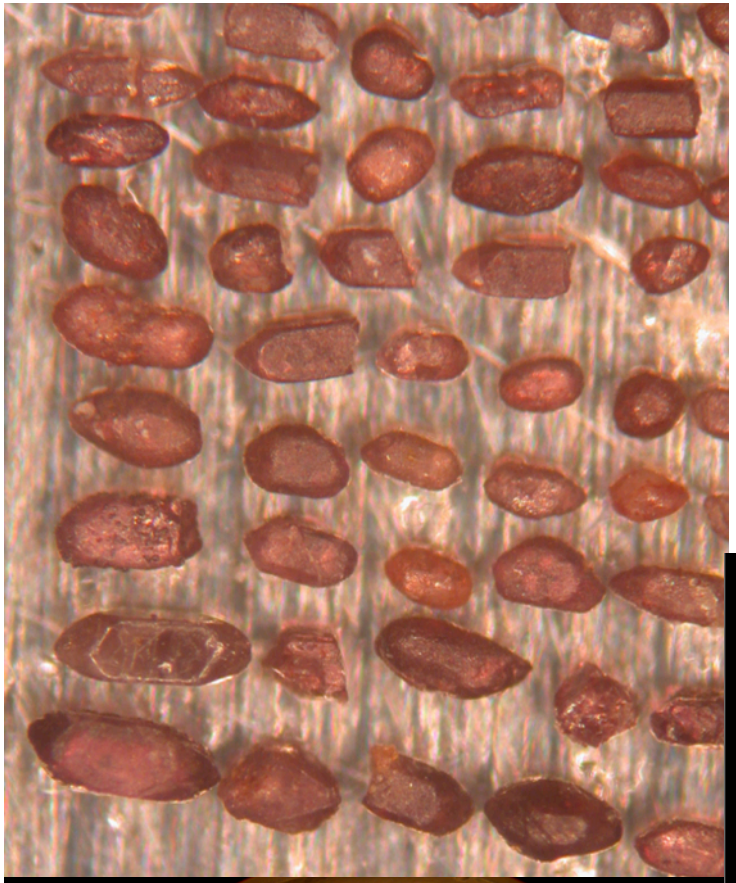
# Zircon $ZrSiO_4$

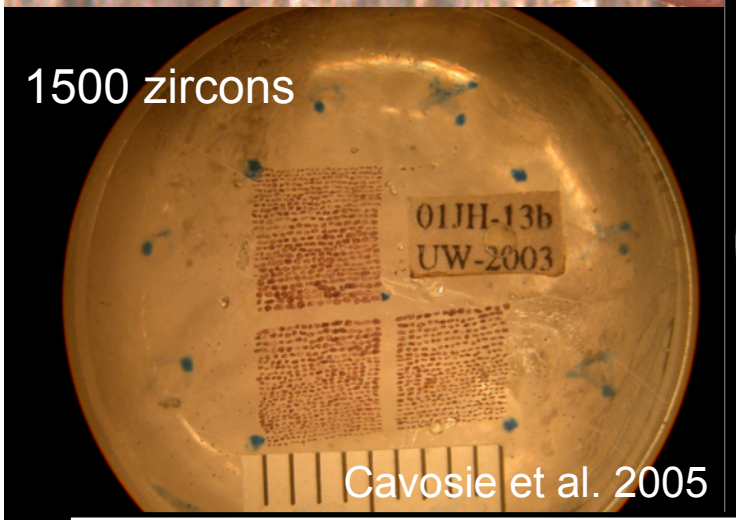
| | Ionic Radius |
|---|---|
| $^{VIII}Zr^{+4}$ | 0.84 Å |
| $^{VIII}U^{+4}$ | 0.95 Å |
| $^{VIII}Pb^{+2}$ | 1.29 Å |





# EVIDENCE from >4 Ga ZIRCONS






Imaging
U-Pb age
Oxygen isotopes
[Li] & Li isotopes
REEs, Ti
Mineral inclusions

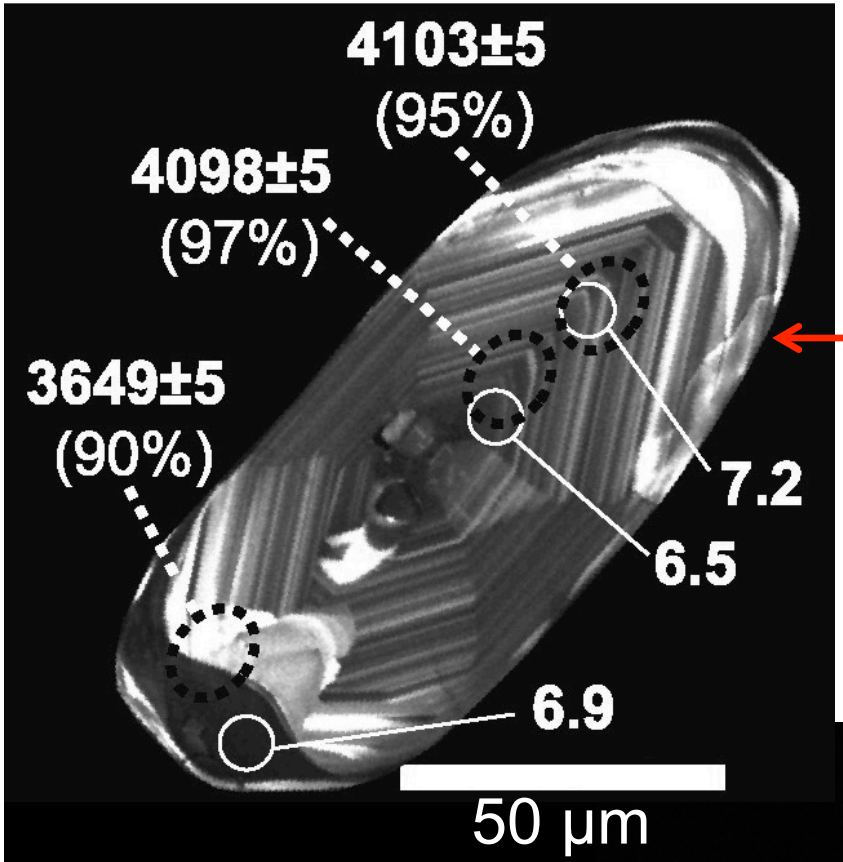
Ti-in-zircon thermometry
Phengite barometry
Hf isotopes
~~Diamond inclusions~~

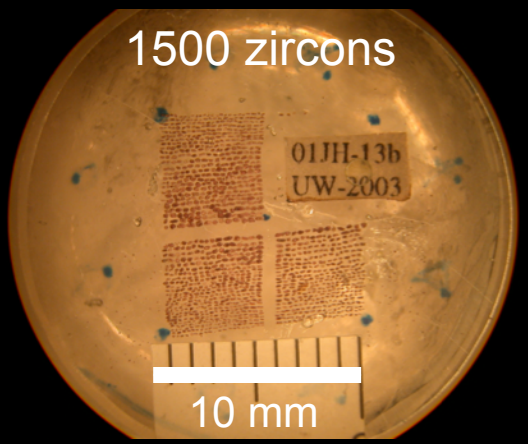
# Correlated analyses

(U-Pb, O, Li isotopes, TE's)

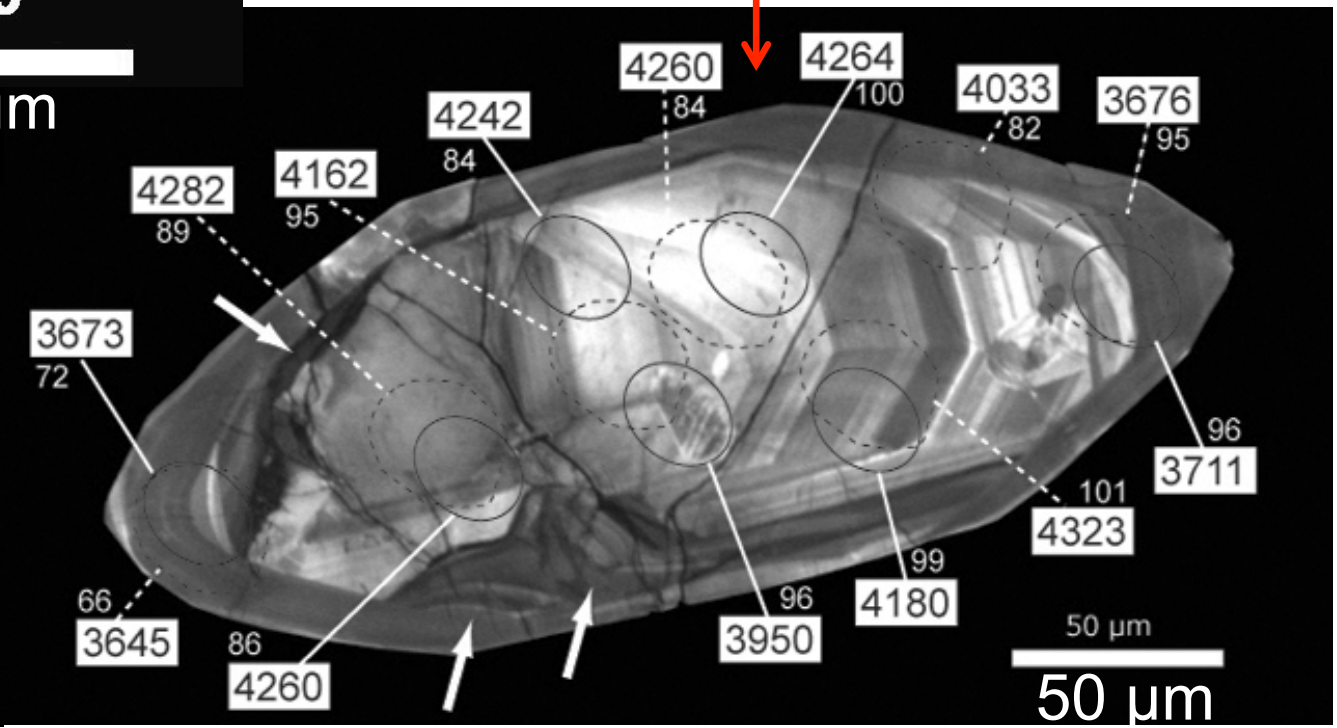
Core: 4.1 Ga igneous
Rim: 3.7 Ga metamorphic

Core: 3.9 - 4.3 Ga disturbed igneous
Rim: 3.7 Ga metamorphic

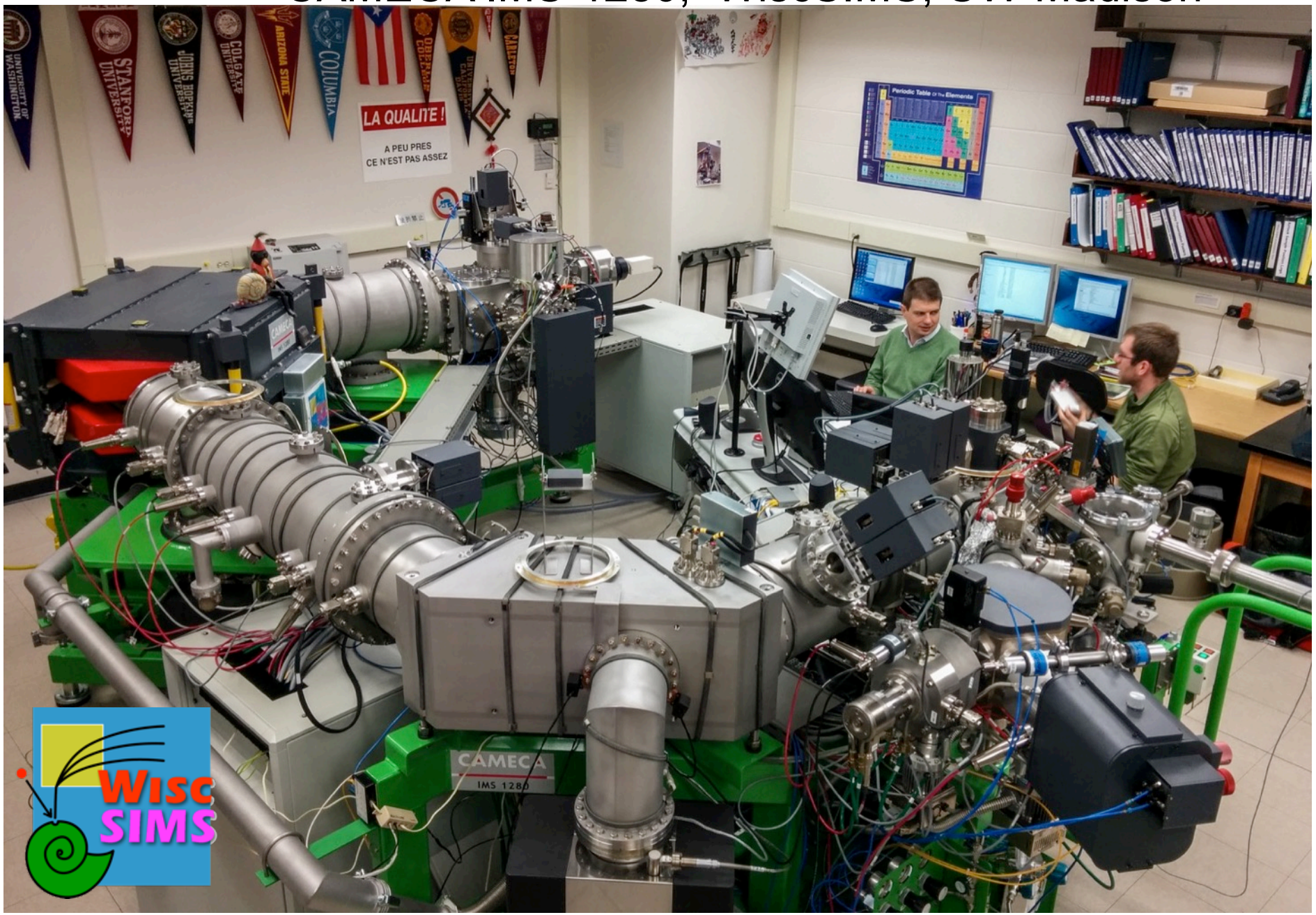


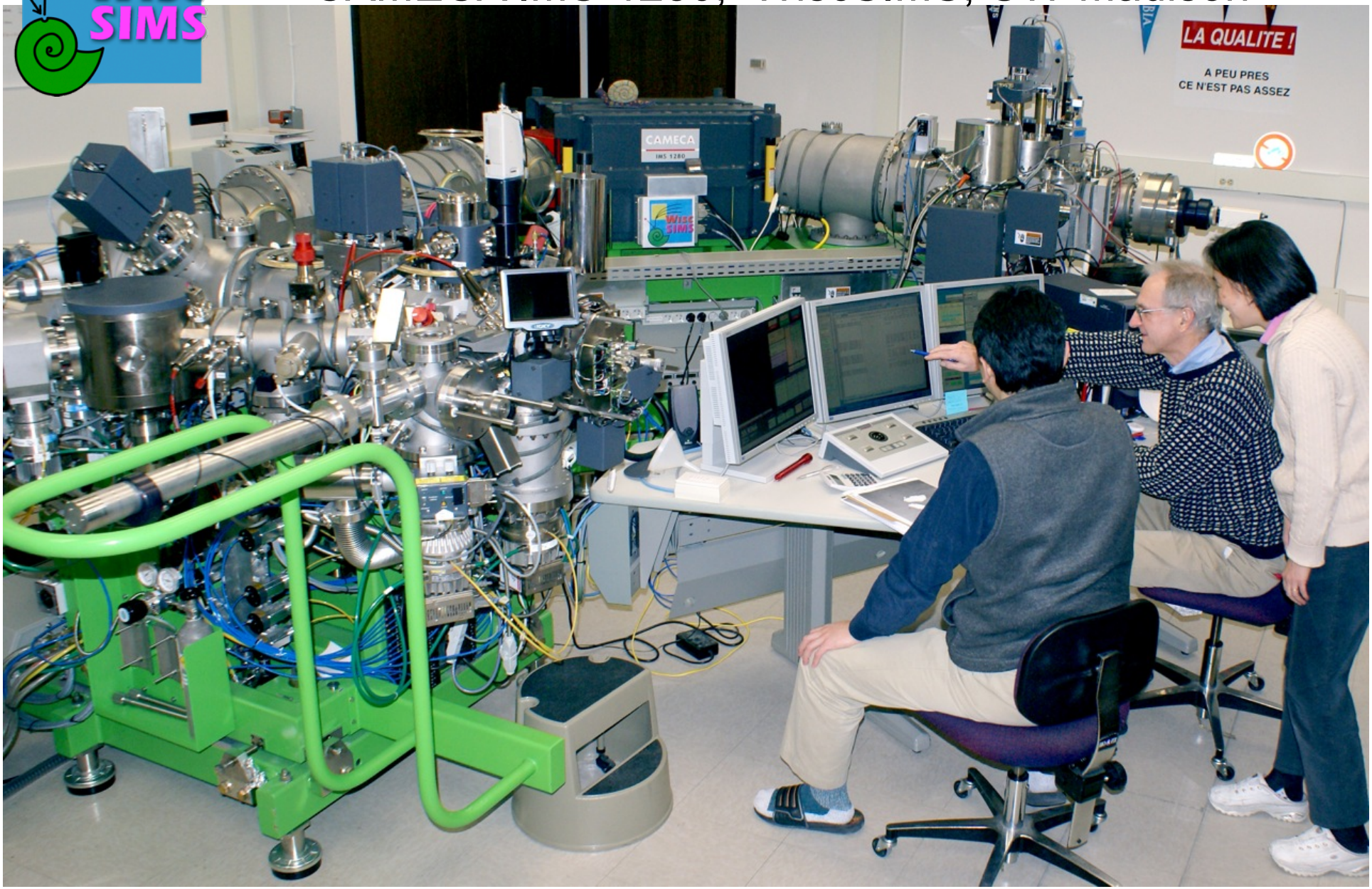

Cavosie et al. 2006



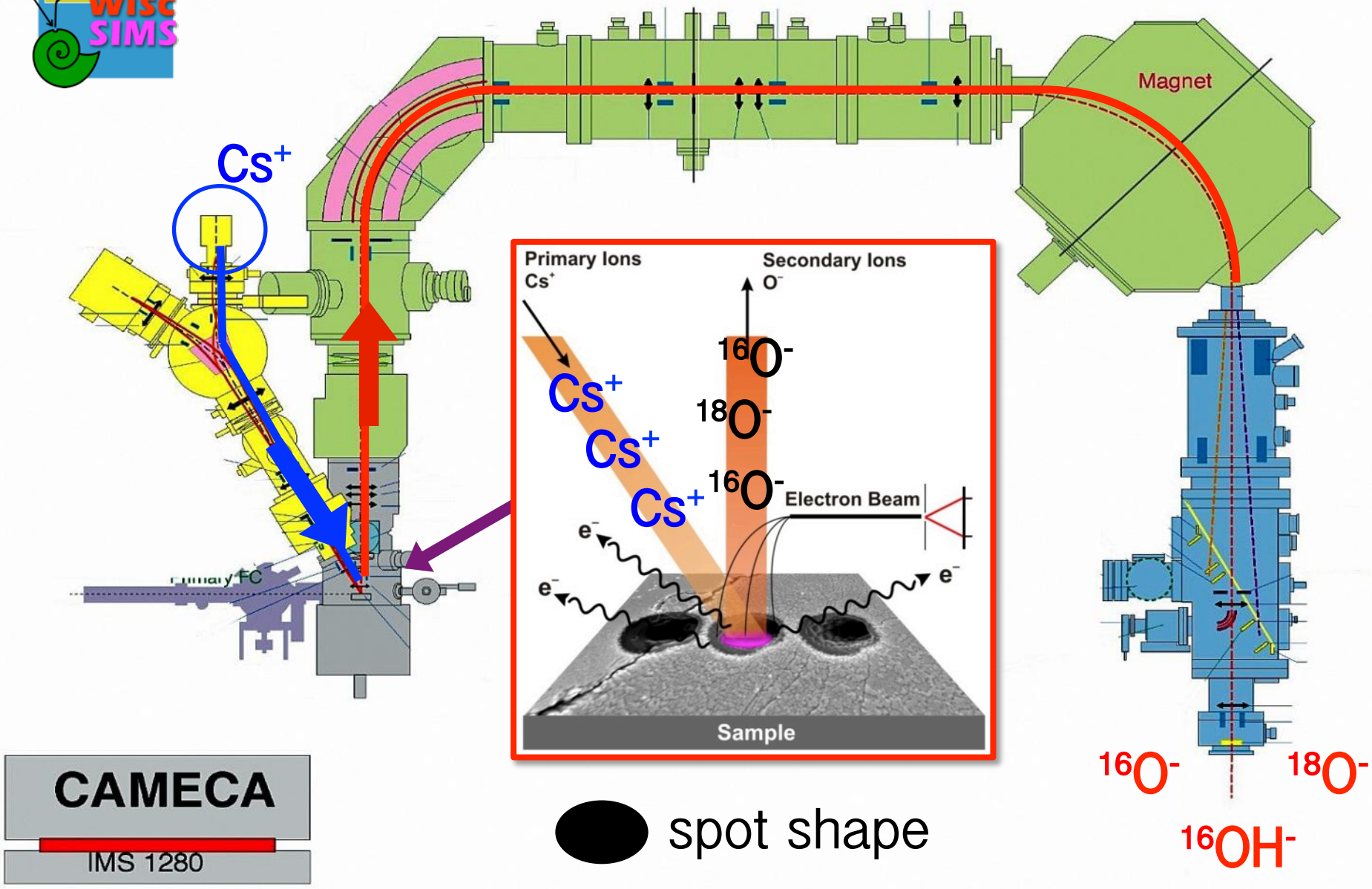
# CAMECA IMS-1280, WiscSIMS, UW-Madison

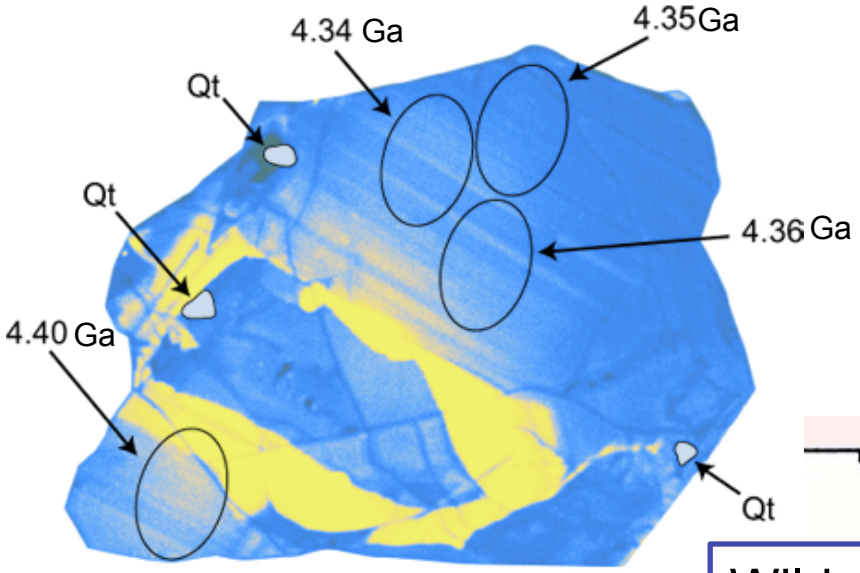


# CAMECA IMS-1280, WiscSIMS, UW-Madison



# SIMS - Secondary Ion Mass Spectrometer





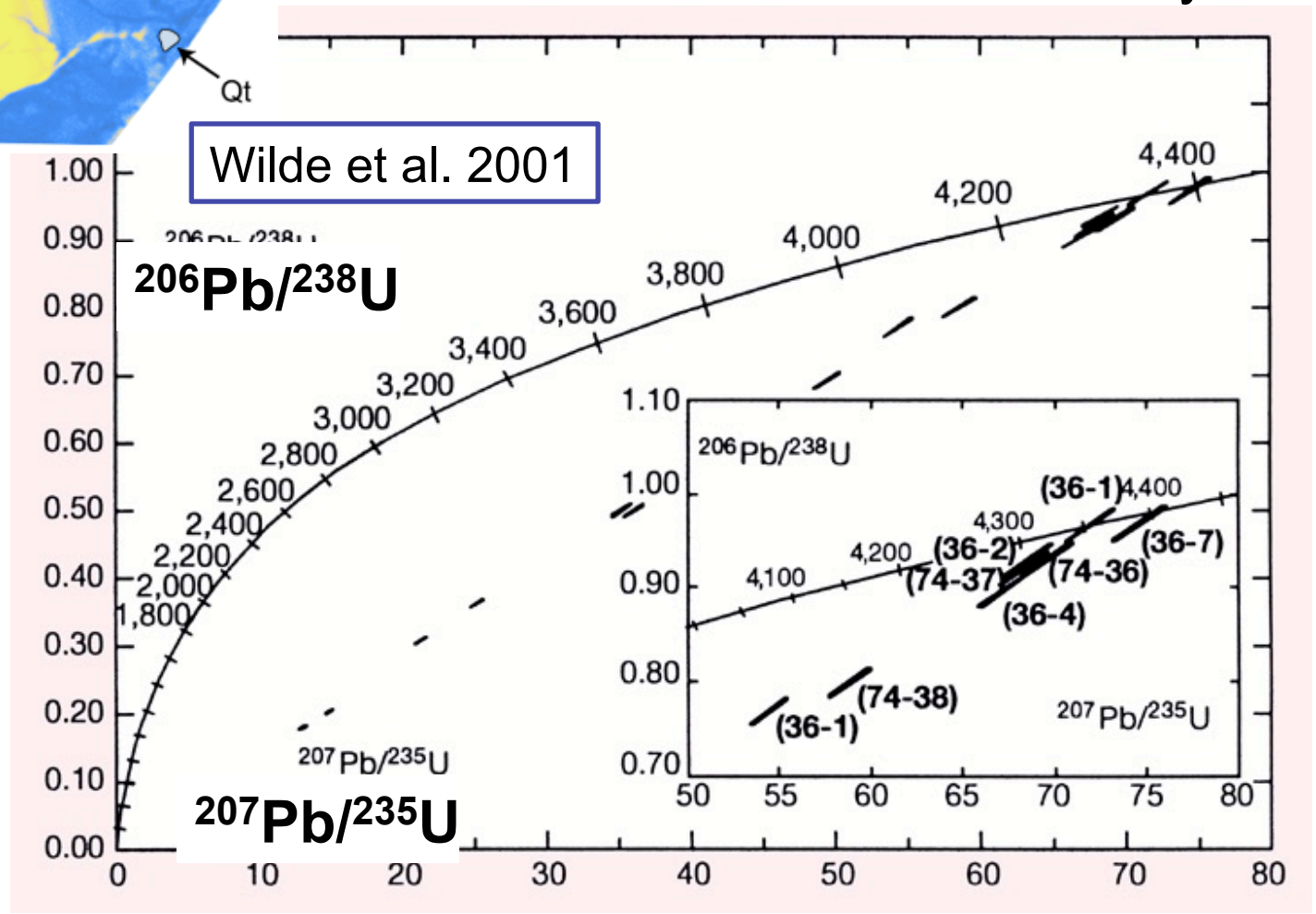

# Zircon

## Uranium- Lead Geochronology

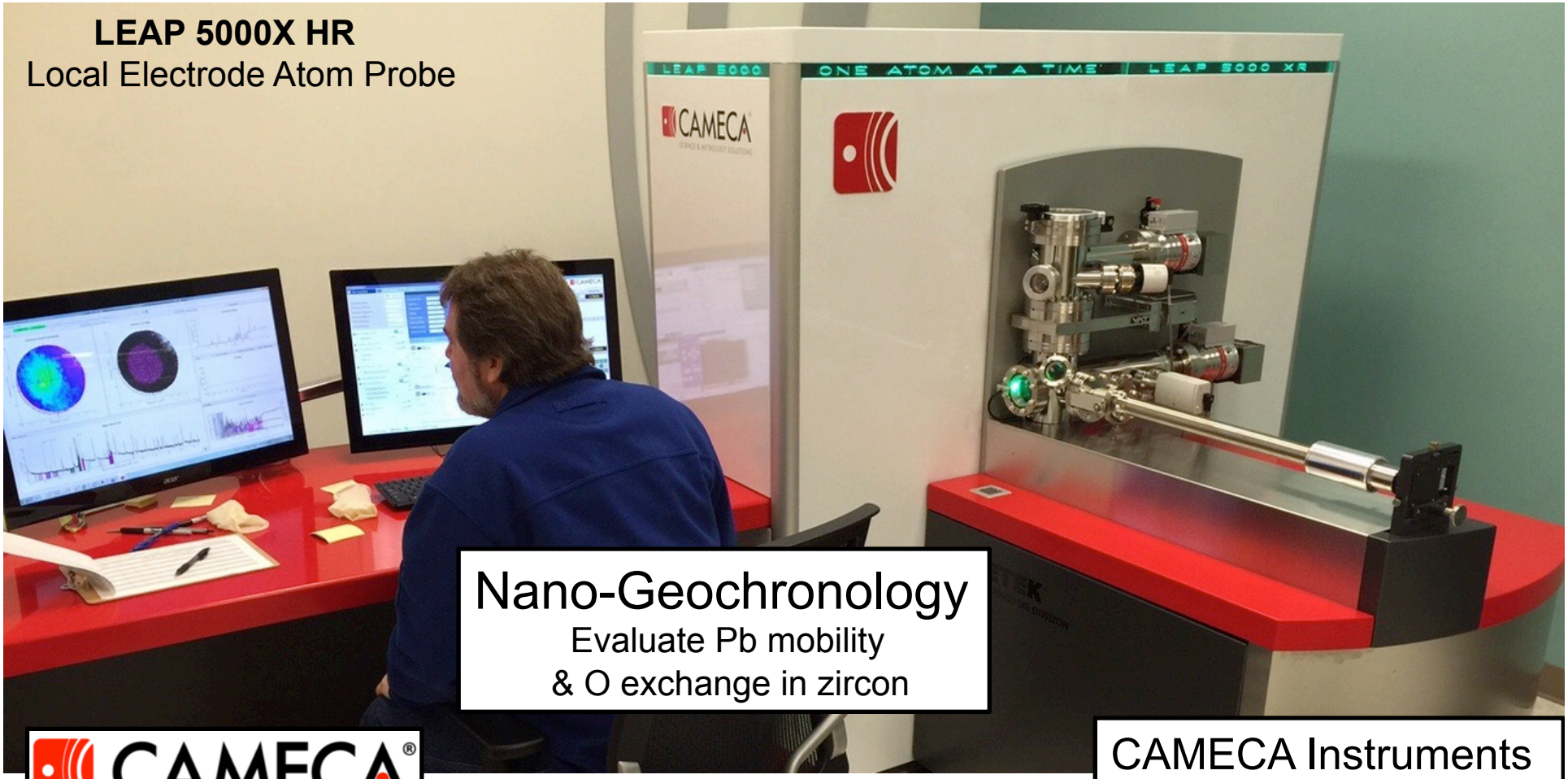
$^{238}U \rightarrow {}^{206}Pb$ Half-life = 4470 myr.

$^{235}U \rightarrow {}^{207}Pb$ Half-life = 700 myr.

Froude et al. 1983
Compston & Pidgeon 1986
Cavosie et al. 2004, 2007
Harrison et al. 2009
Holden et al. 2009
Valley et al. 2014, 2015



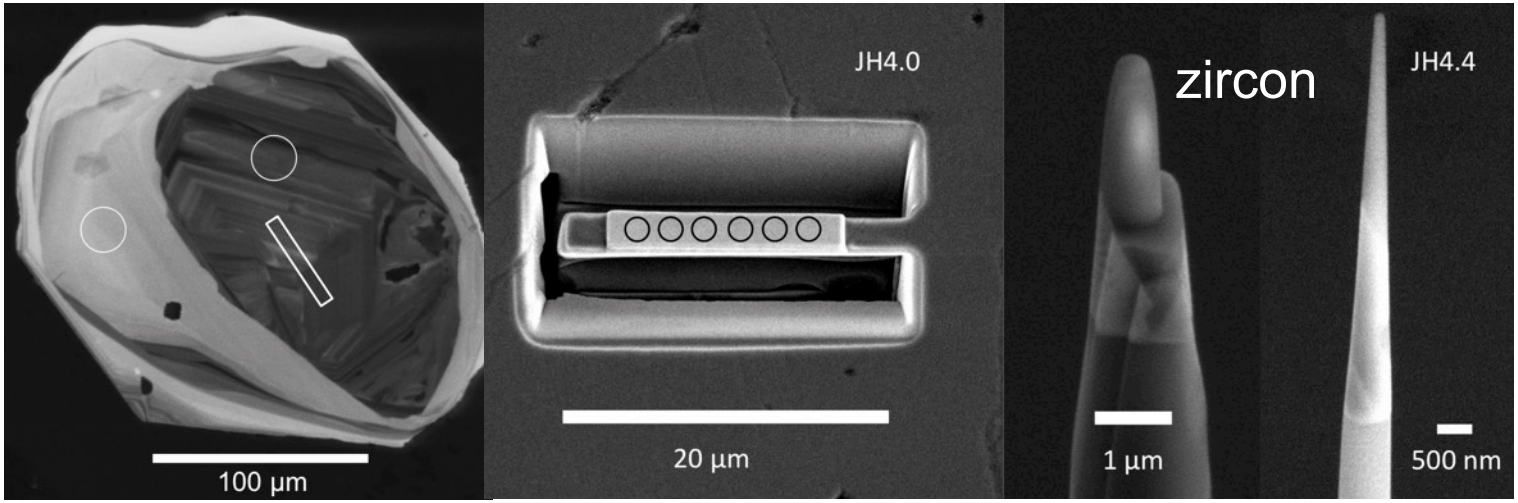
**LEAP 5000X HR**
Local Electrode Atom Probe

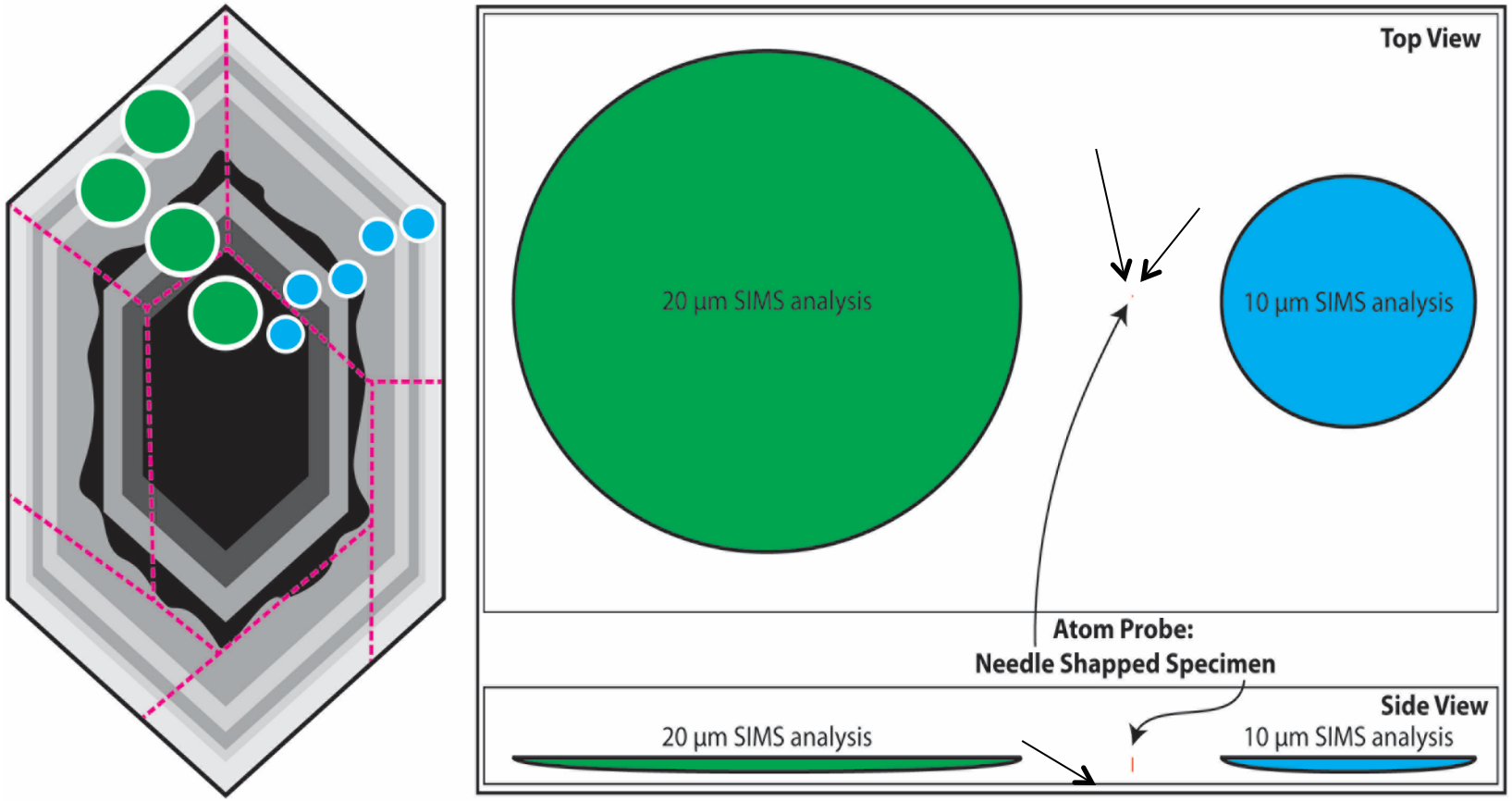



Nano-Geochronology
Evaluate Pb mobility
& O exchange in zircon

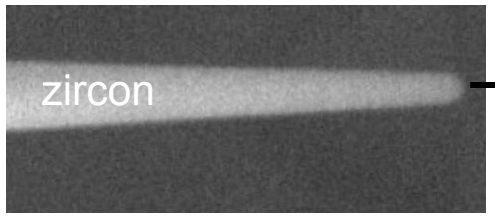
CAMECA®

CAMECA Instruments
Factory, Madison, WI


100 µm
JH4.0
20 µm
zircon
JH4.4
1 µm
500 nm


Top View
20 µm SIMS analysis
10 µm SIMS analysis
Atom Probe:
Needle Shapped Specimen
Side View
20 µm SIMS analysis
10 µm SIMS analysis

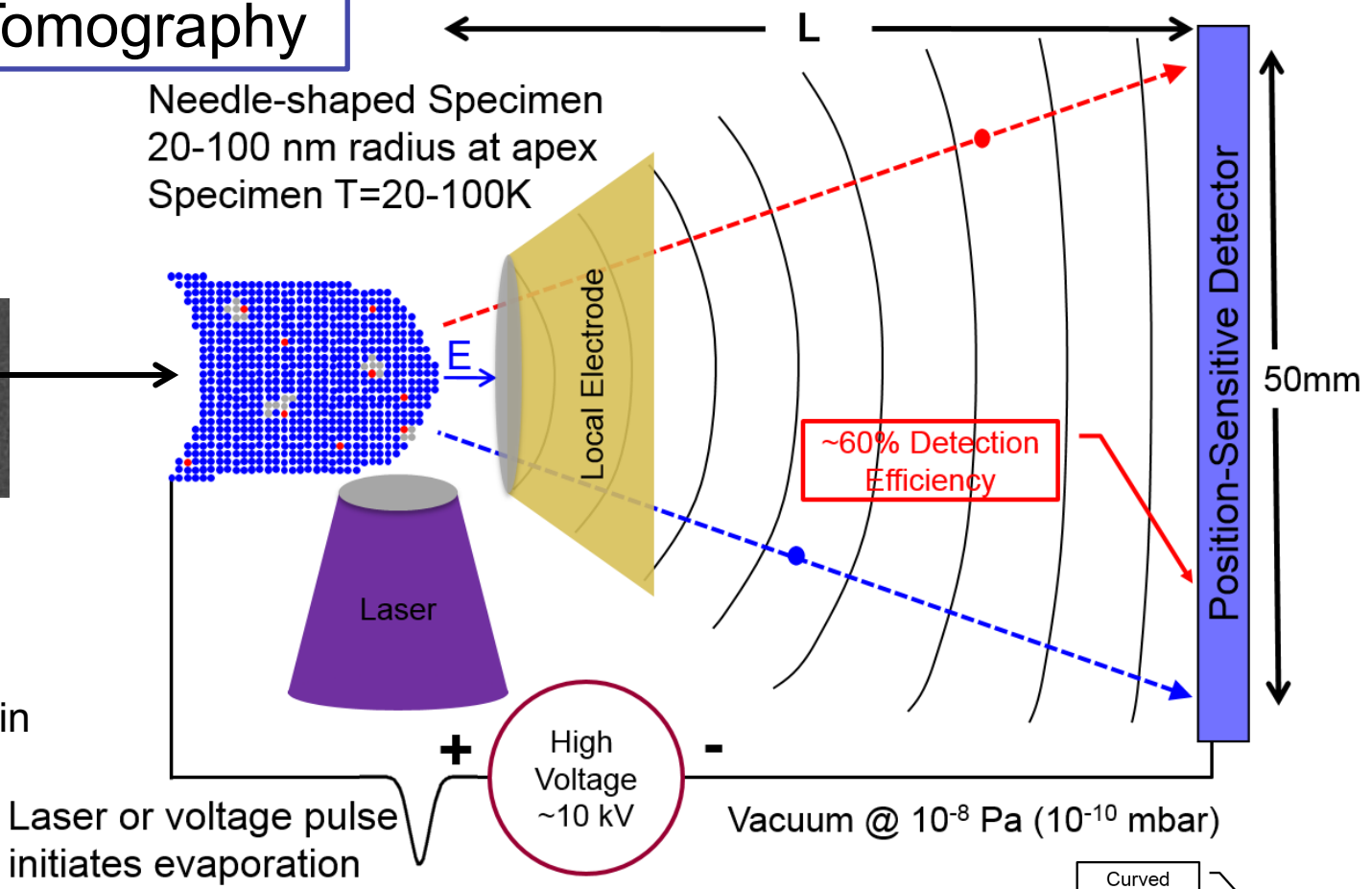
# Atom Probe Tomography

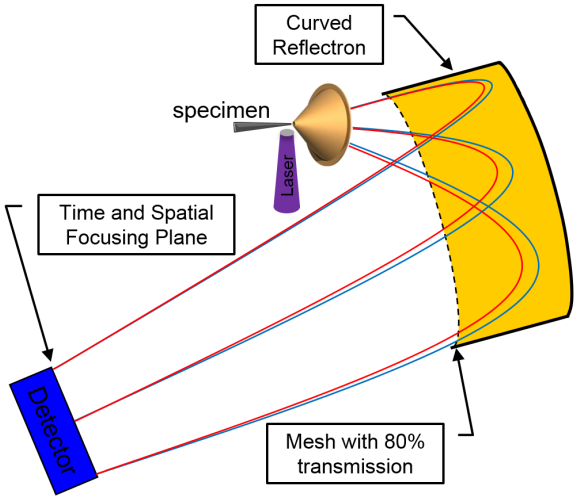



Sample zircon

100 nm

Valley et al. 2015 Am Min



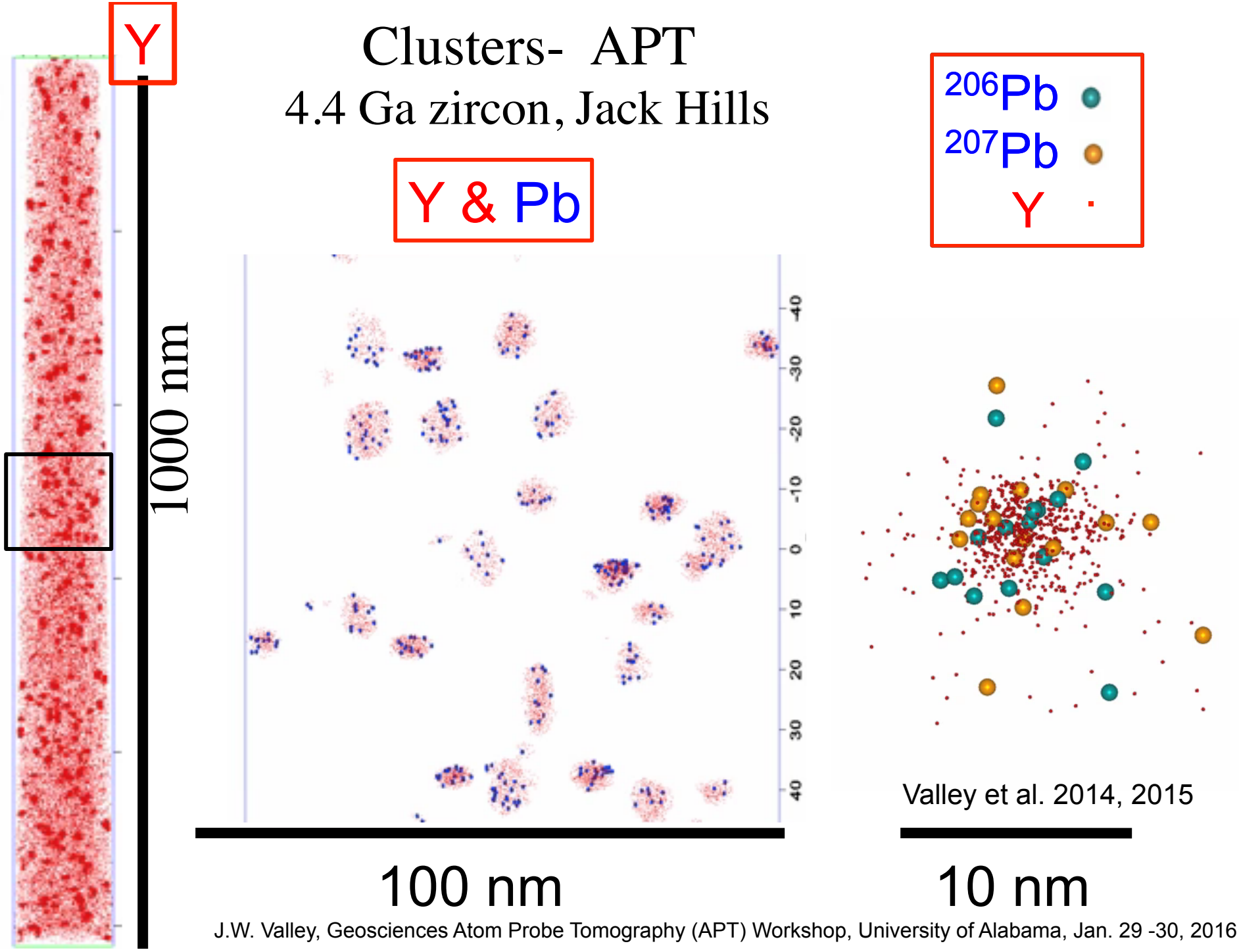



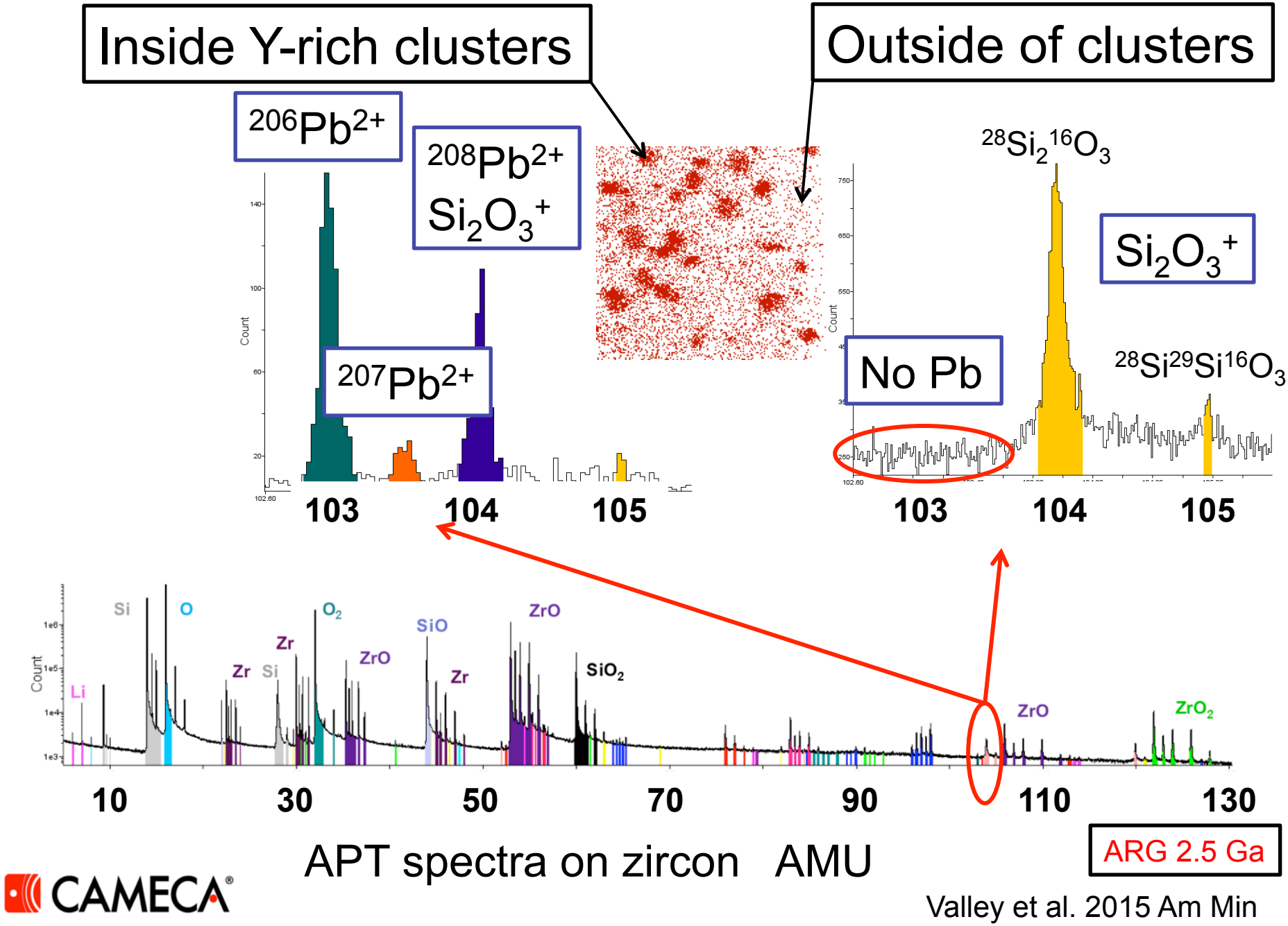

CAMECA

J.W. Valley, Geosciences Atom Probe Tomography (APT) Workshop, University of Alabama, Jan. 29 -30, 2016

# Clusters- APT

## 4.4 Ga zircon, Jack Hills



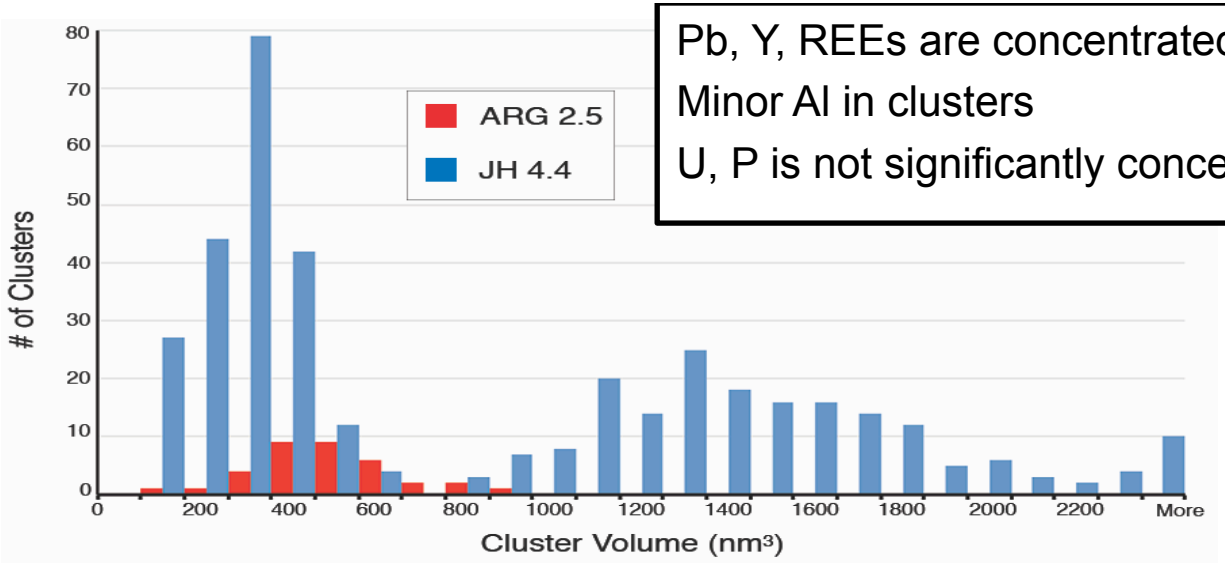


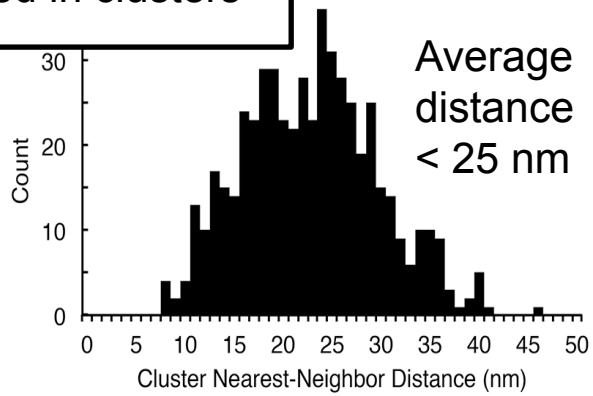

Valley et al. 2015 Am Min

Pb, Y, REEs are concentrated in clusters

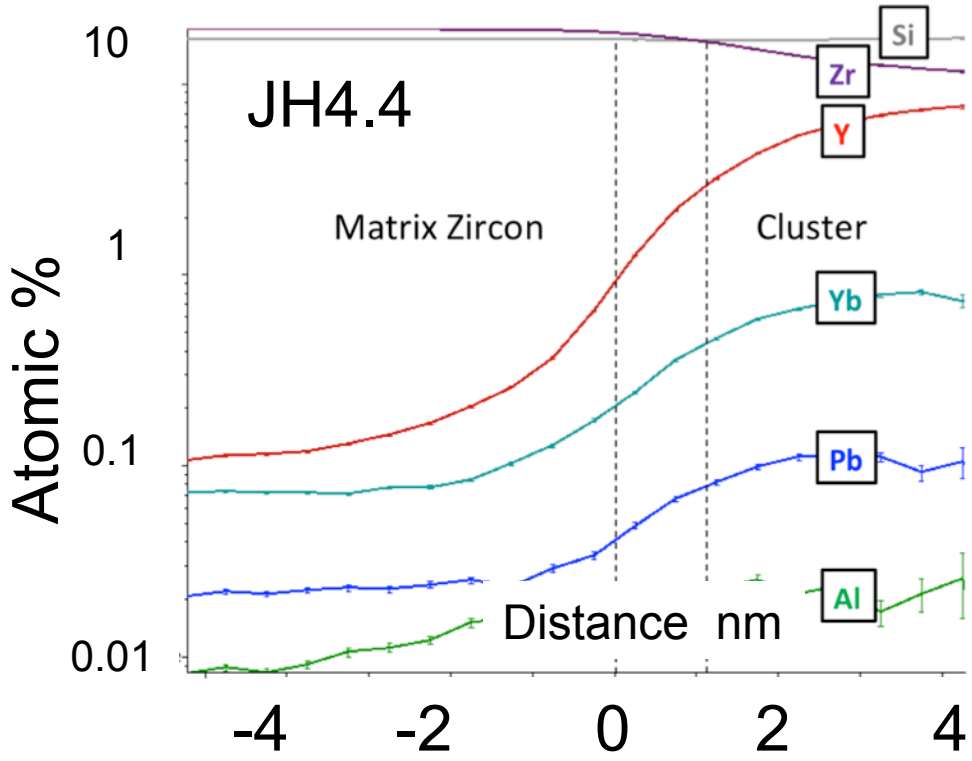
Minor Al in clusters

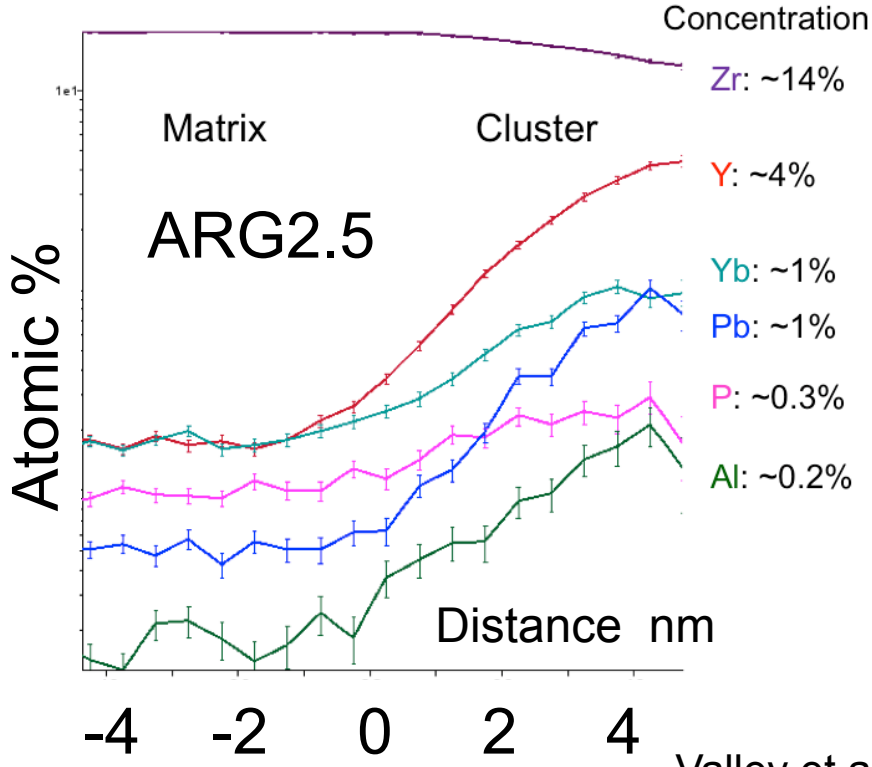
U, P is not significantly concentrated in clusters




Average distance < 25 nm




Concentration

Zr: ~14%

Y: ~4%

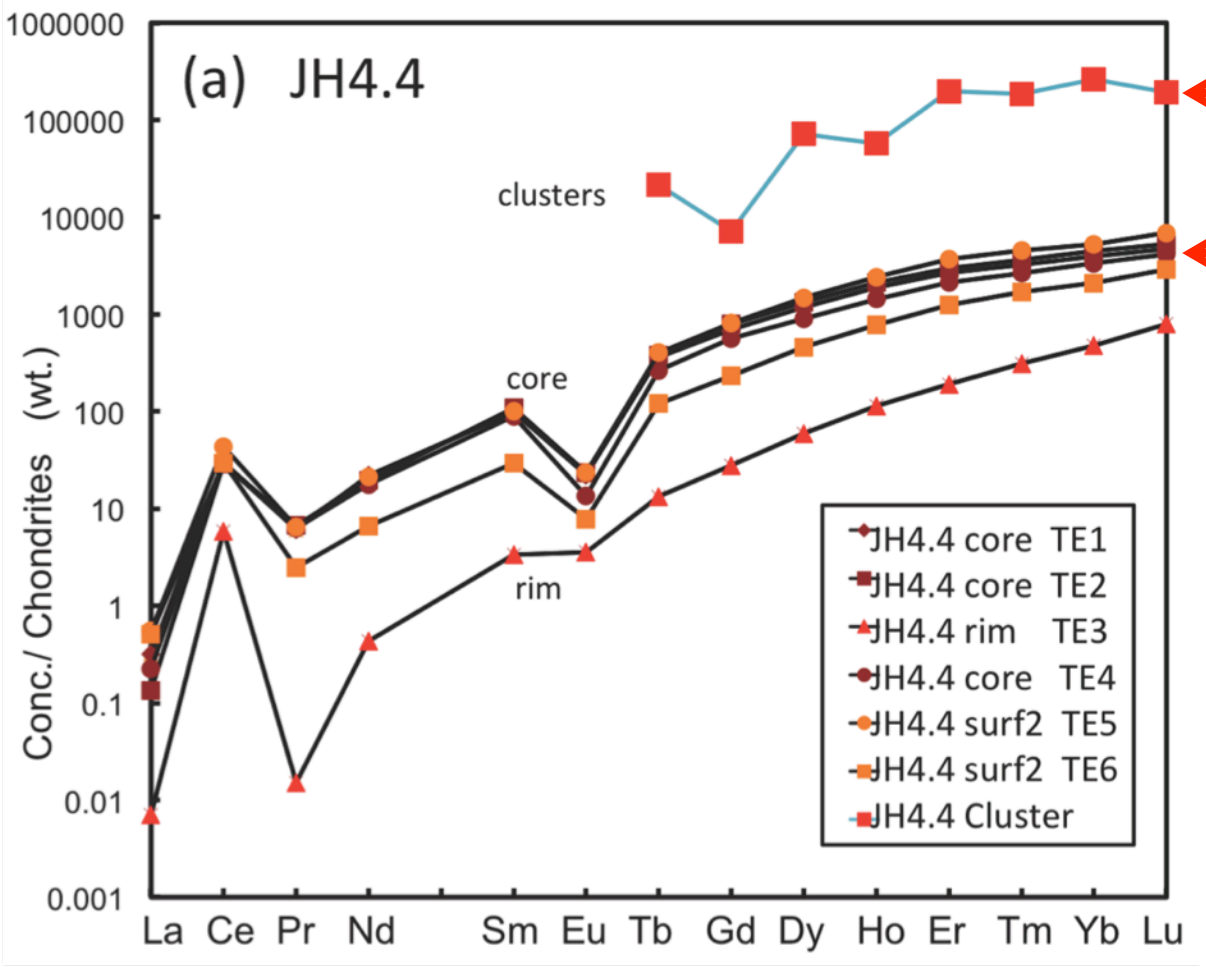
Yb: ~1%

Pb: ~1%

P: ~0.3%

Al: ~0.2%

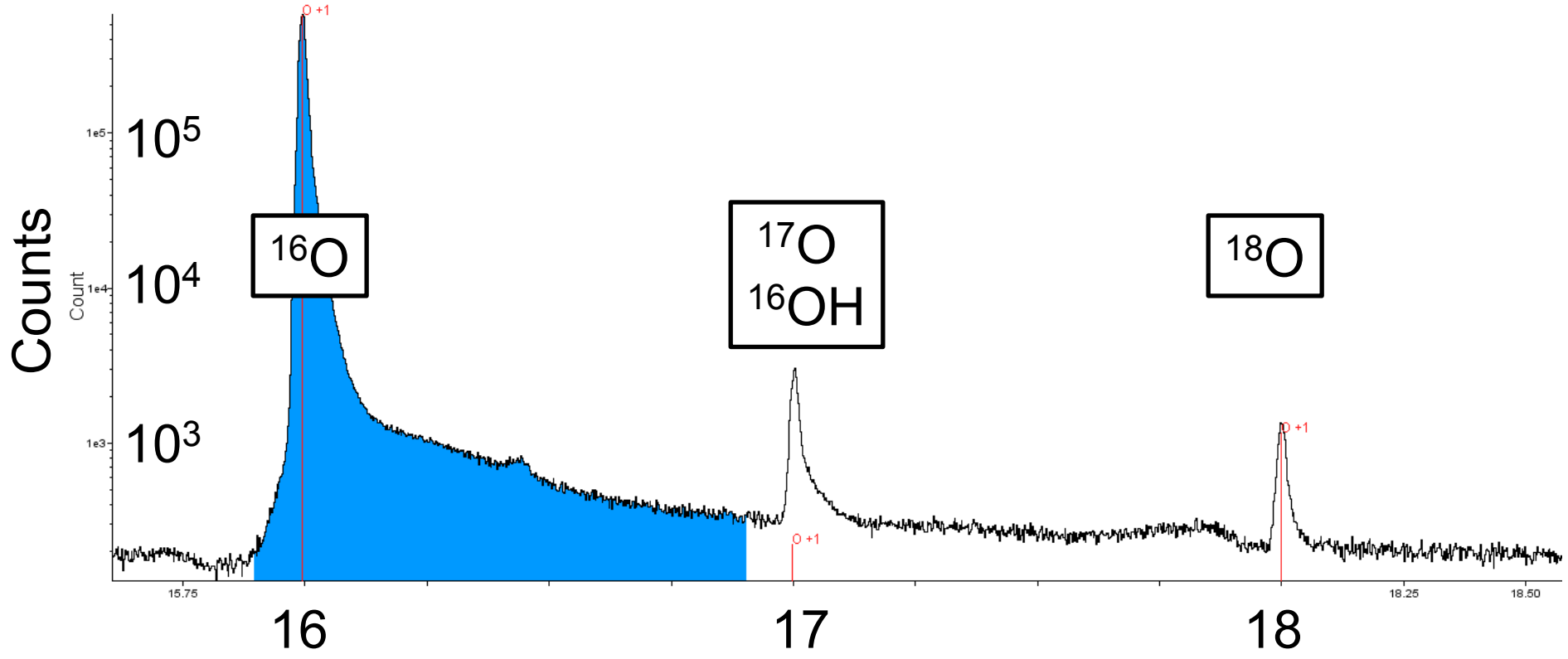
Valley et al. 2015

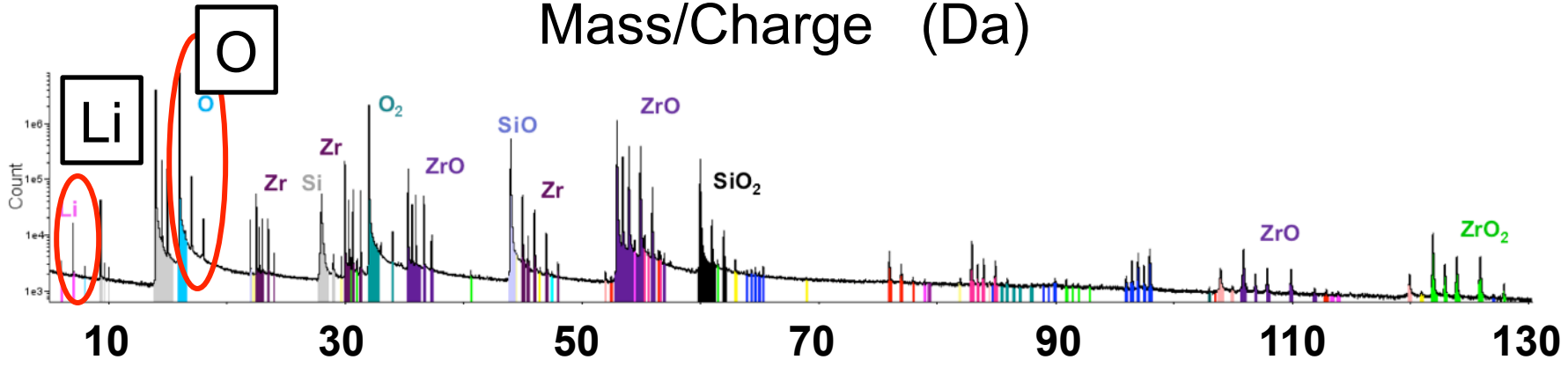



Within Clusters- APT

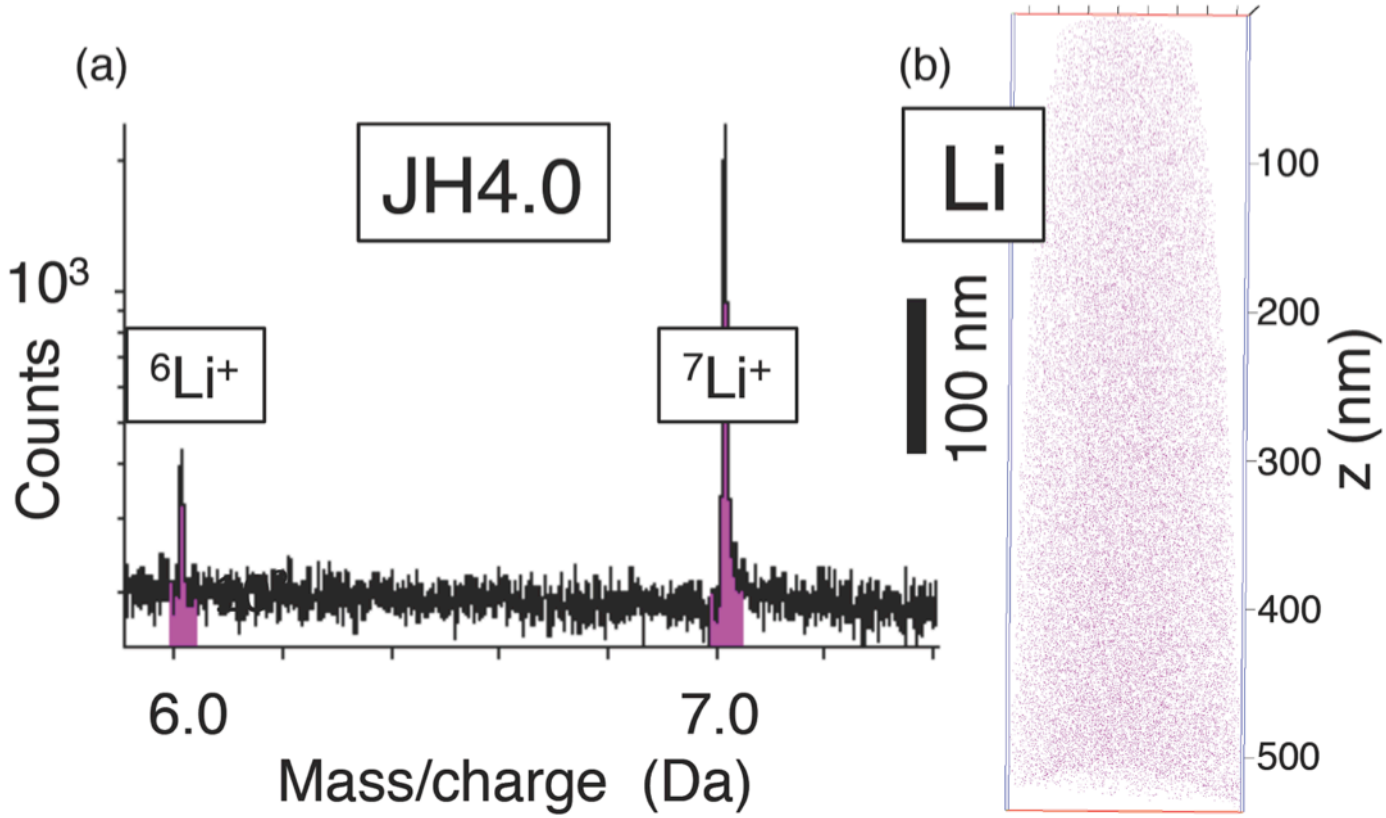
Outside Clusters- SIMS

Valley et al. 2015 Am Min


Counts
$10^5$
$10^4$
$10^3$
Count
$^{16}O$
$^{17}O$
$^{16}OH$
$^{18}O$
O +1
15.75
18.25
18.50
16
17
18
Mass/Charge (Da)


Li
O
Count
Li
O
Zr
Si
Zr
$O_2$
ZrO
SiO
Zr
ZrO
$SiO_2$
ZrO
$ZrO_2$
10
30
50
70
90
110
130
APT spectra on zircon (Da)

CAMECA

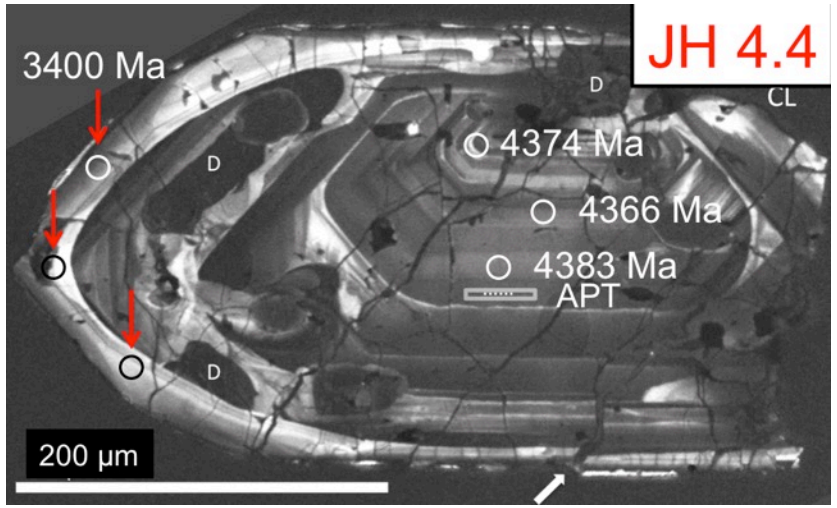



~237ppm (atomic)

Li distribution uniform

CAMECA

| Jack Hills | SIMS $^{207}Pb/^{206}Pb$ | APT $^{207}Pb/^{206}Pb$ |
|---|---|---|
| JH 4.4 Ga | | |
| (10,255 Pb atoms) | | |
| 4374 Ma core | 0.548 | 0.52 |
| inside clusters | | 1.2 |
| outside clusters | | 0.30 |
| 3400 Ma rim | 0.291 | |




## APT: Archean/Hadean zircons

Pb mobility < 50 nm

Linked to radiation damage

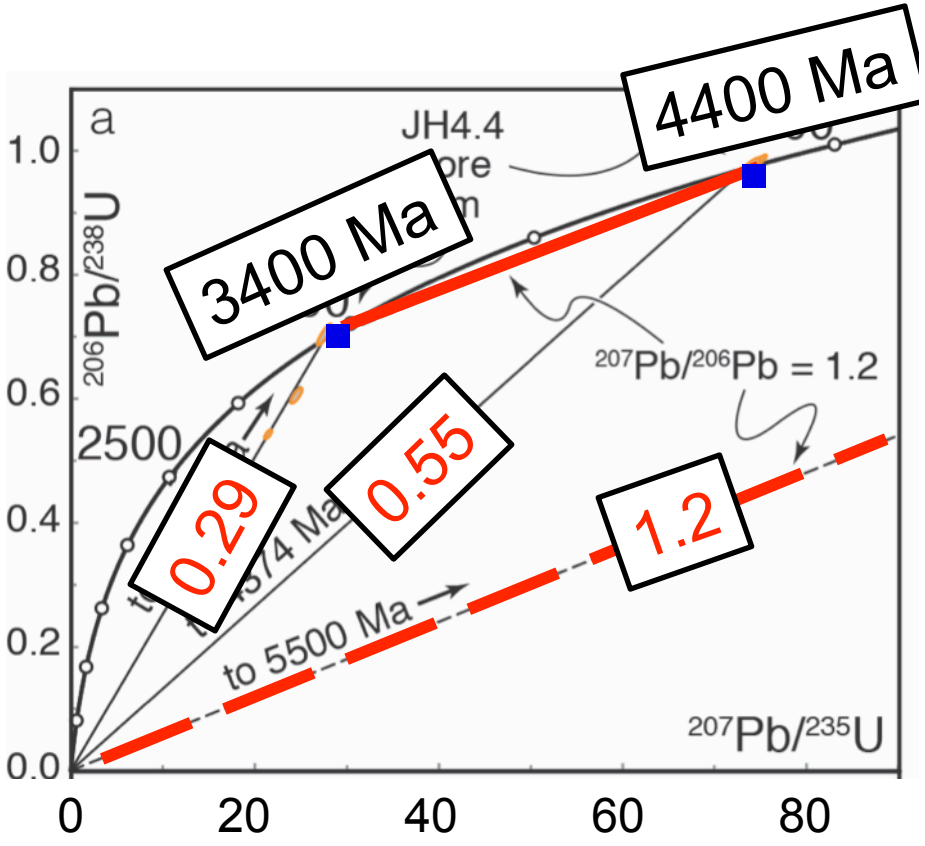
Compositions reintegrated by SIMS

SIMS ages are accurate

Clusters date reheating events

Confirms 4.4 Ga zircon from Jack Hills

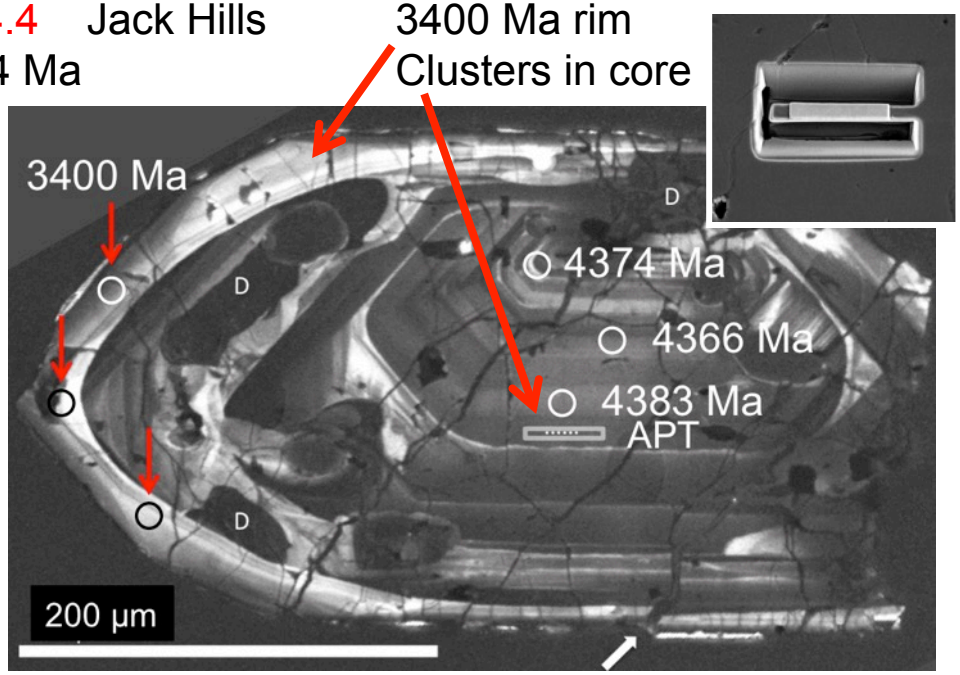
Valley et al. 2014, 2015



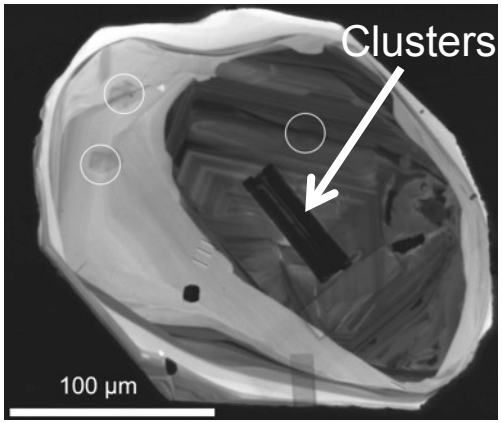
## 3 with Clusters

JH 4.4 Jack Hills
4374 Ma

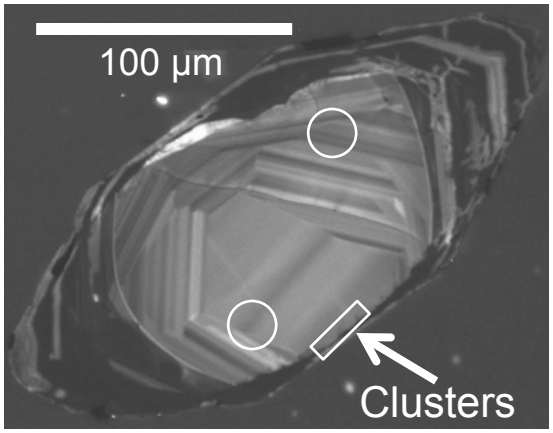
3400 Ma rim
Clusters in core




ARG 2.5 Grouse Ck Mts
2542 Ma Core, 29 Ma rim

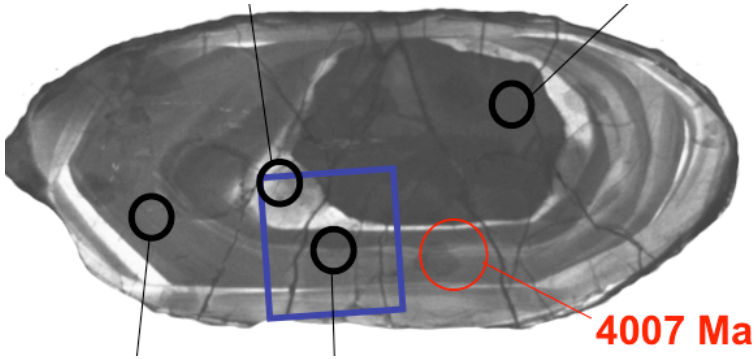



BT5-13 Beartooth Mts
3775 Ma Core, ~2700 Ma meta.

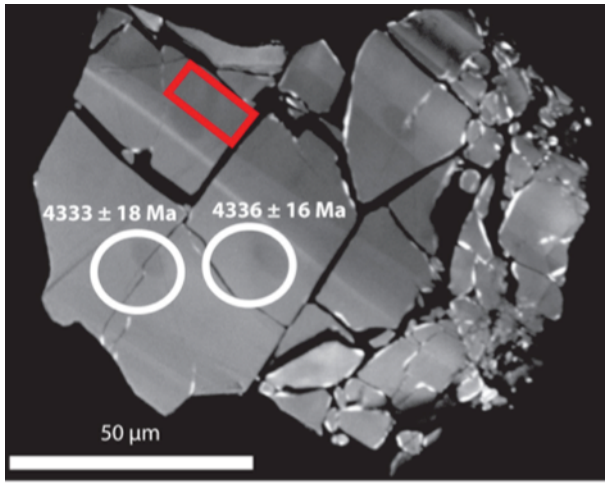



## 2 with No Clusters

JH 4.0 Jack Hills 4007 Ma
No rim, No clusters



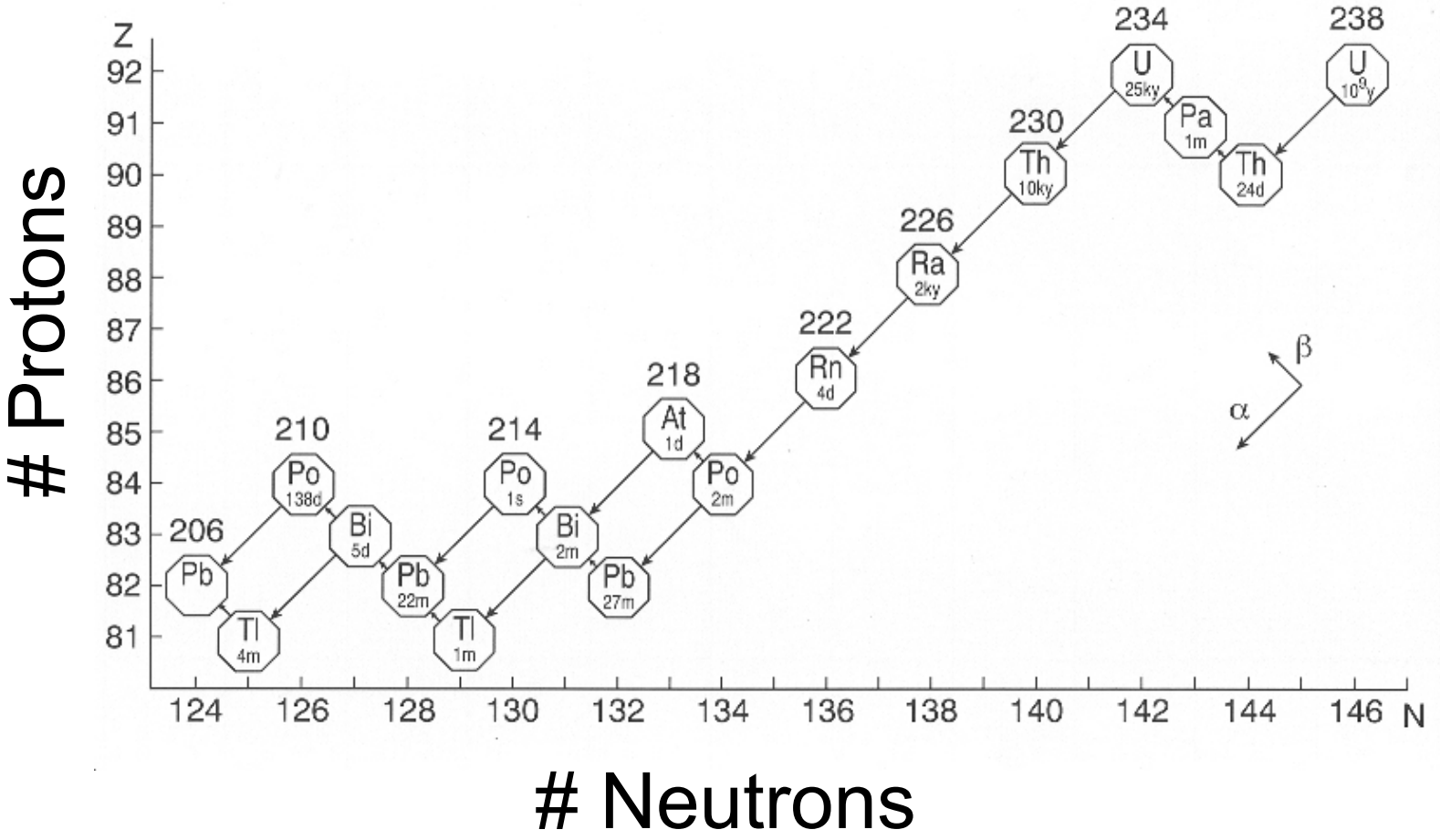

14Q4 Apollo 14, Moon, QMD 4335 Ma
No rim, No clusters




Valley et al. 2014, 2015
Blum et al. 2014, unpd.

# What causes clusters in zircon ?

$^{238}U \rightarrow {}^{206}Pb$ Half-life = 4470 myr.

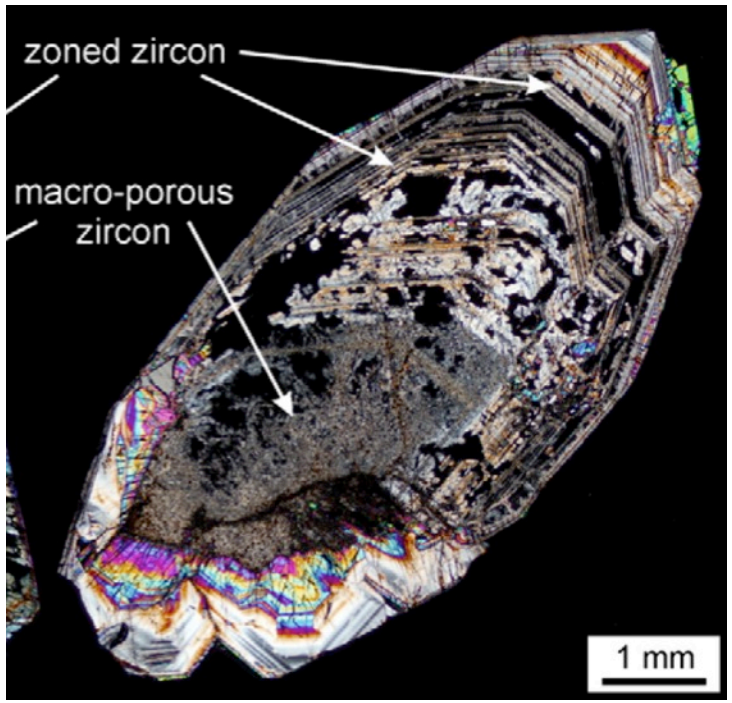



# Protons

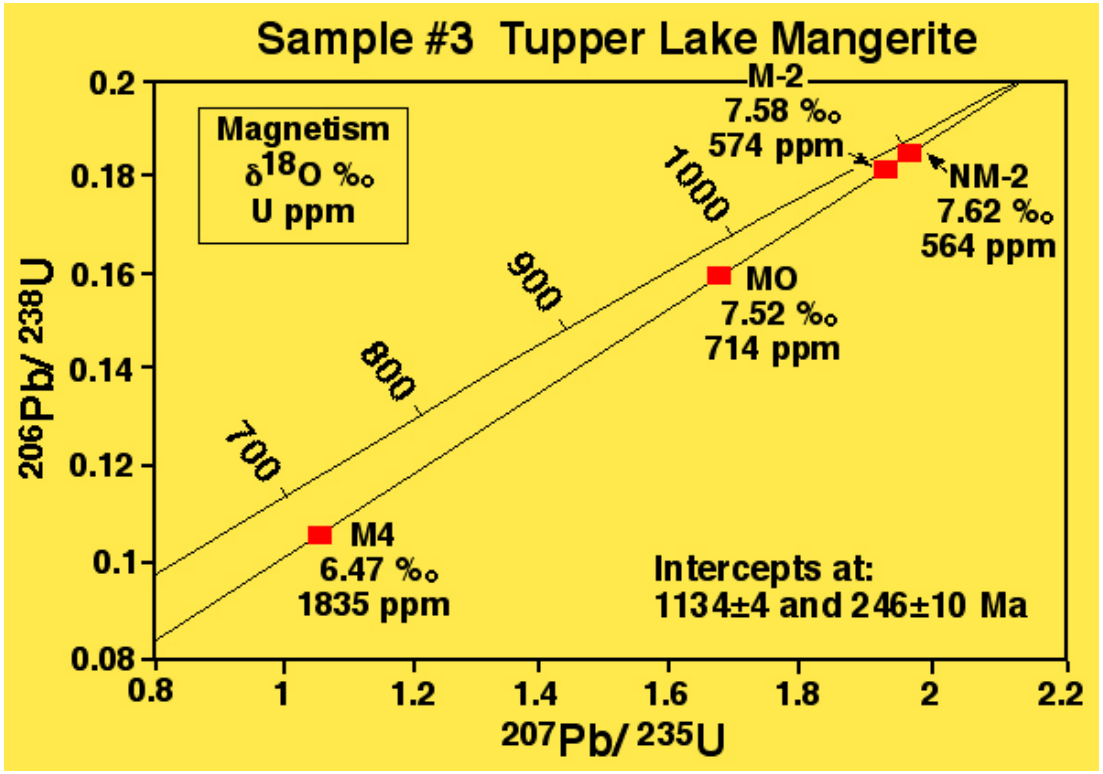
# Neutrons

## Radiation damage affects:

- Density
- Birefringence
- $H_2O$ content
- Microcracks
- HF solubility
- U-Pb discordance
- $\delta^{18}O$, & trace elements




Nasdala et al. 2010




Valley et al. 1994
Valley 2003

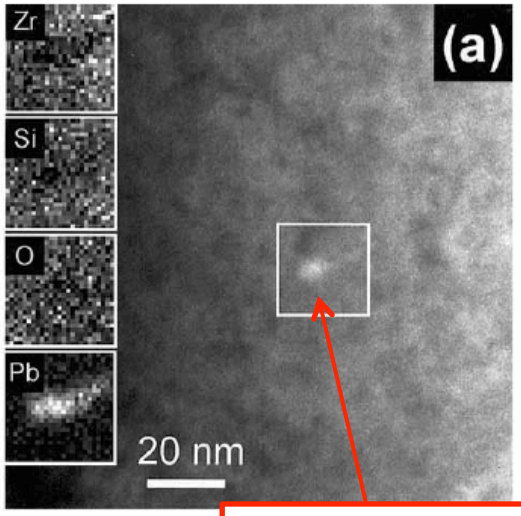
## Avoid damage by:

- Imaging
- Magnetic separation
- HF leach
- Laser Raman
- U-Pb
- Trace elements

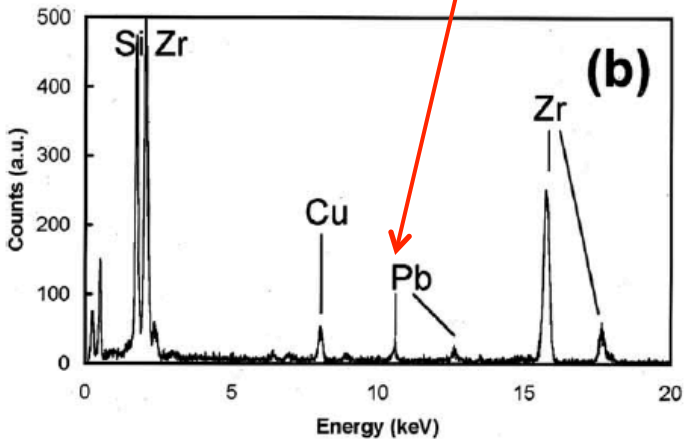
**Examine Your Zircons**

# Radiation damage in zircon- *a*-recoil

Pb in zircon

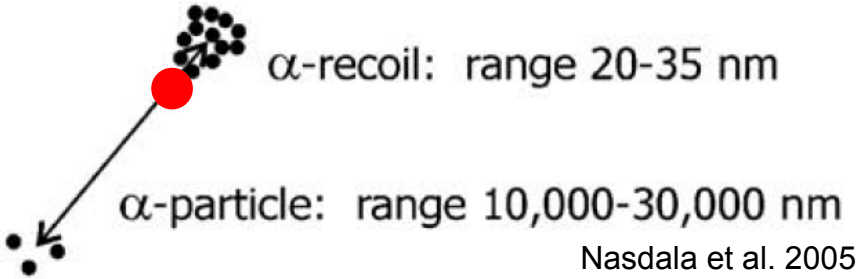



5.6 wt.% Pb

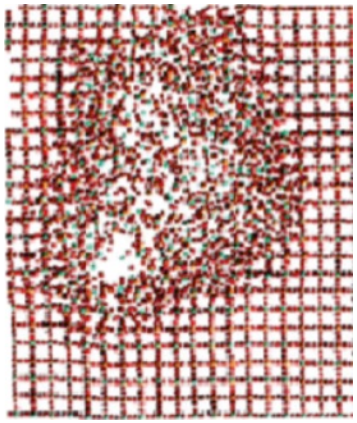



HAAD-STEM
High-Angle Annular Dark Field
Utsunomiya et al. 2004

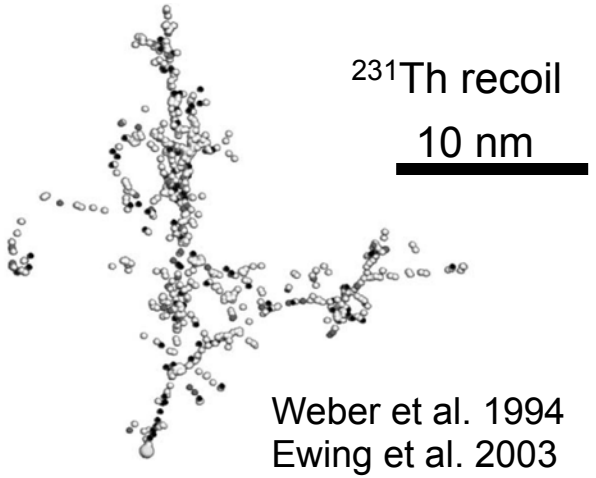
EDX




Nasdala et al. 2005

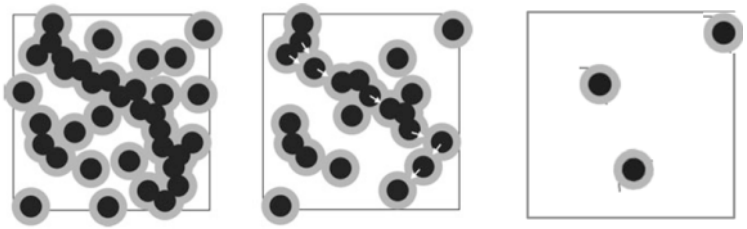


Geisler et al. 2007




Weber et al. 1994
Ewing et al. 2003

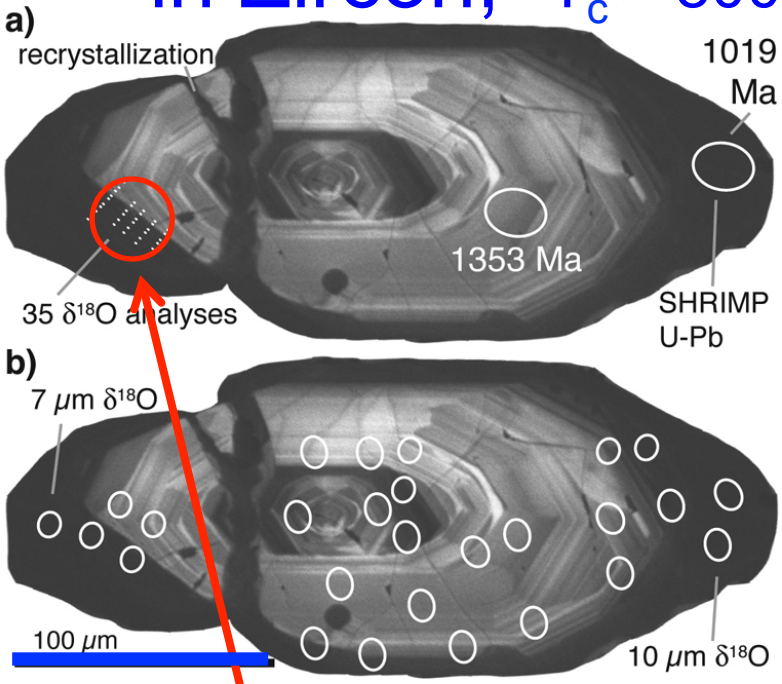
Percolation Theory

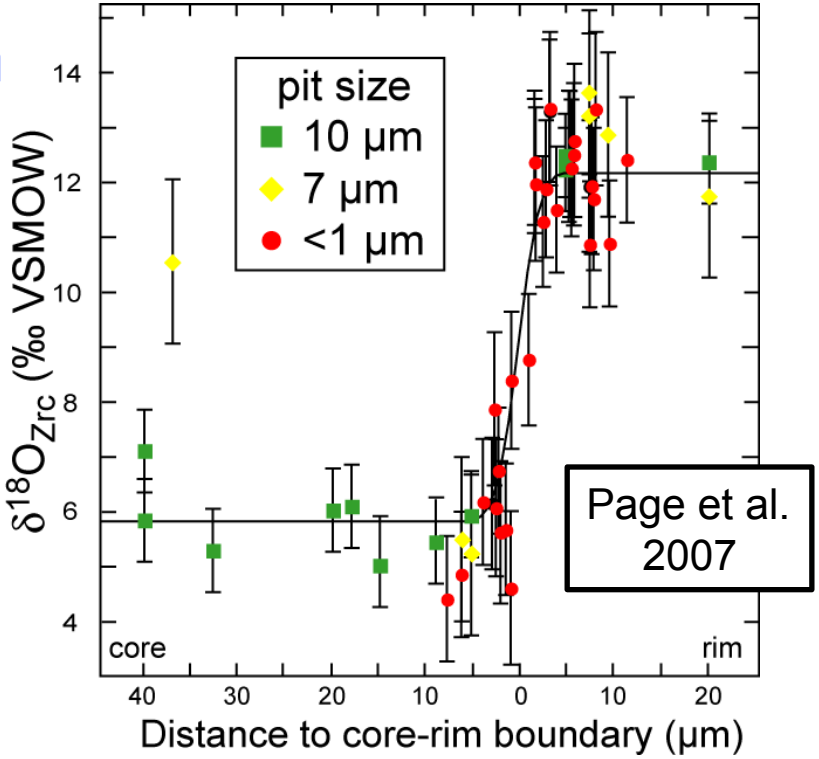


p2 p1

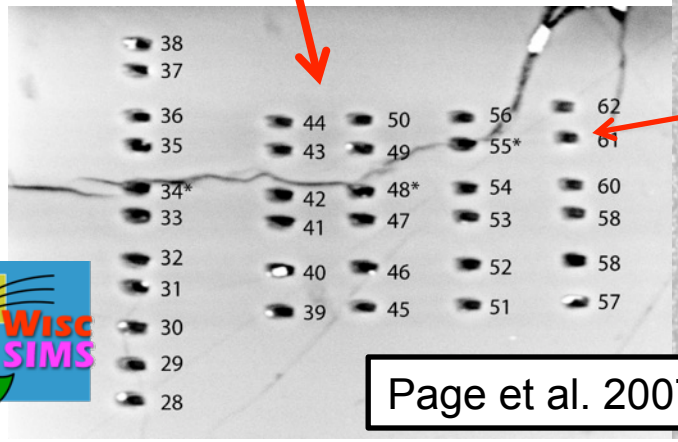
Trachenko et al. 2004

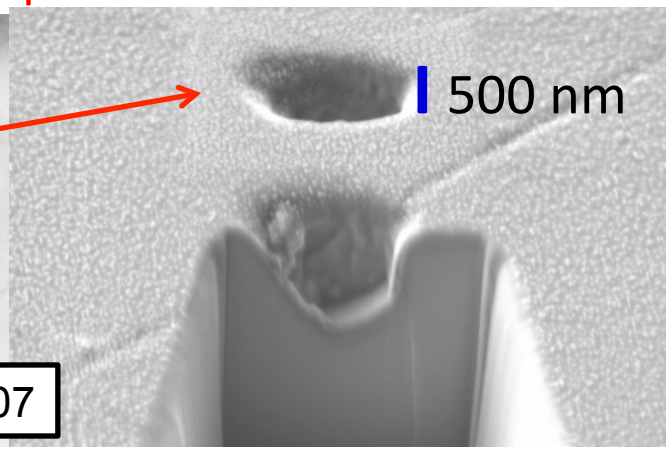
# $\delta^{18}O$ is not reset by Diffusion in Zircon, $T_c > 800^oC$



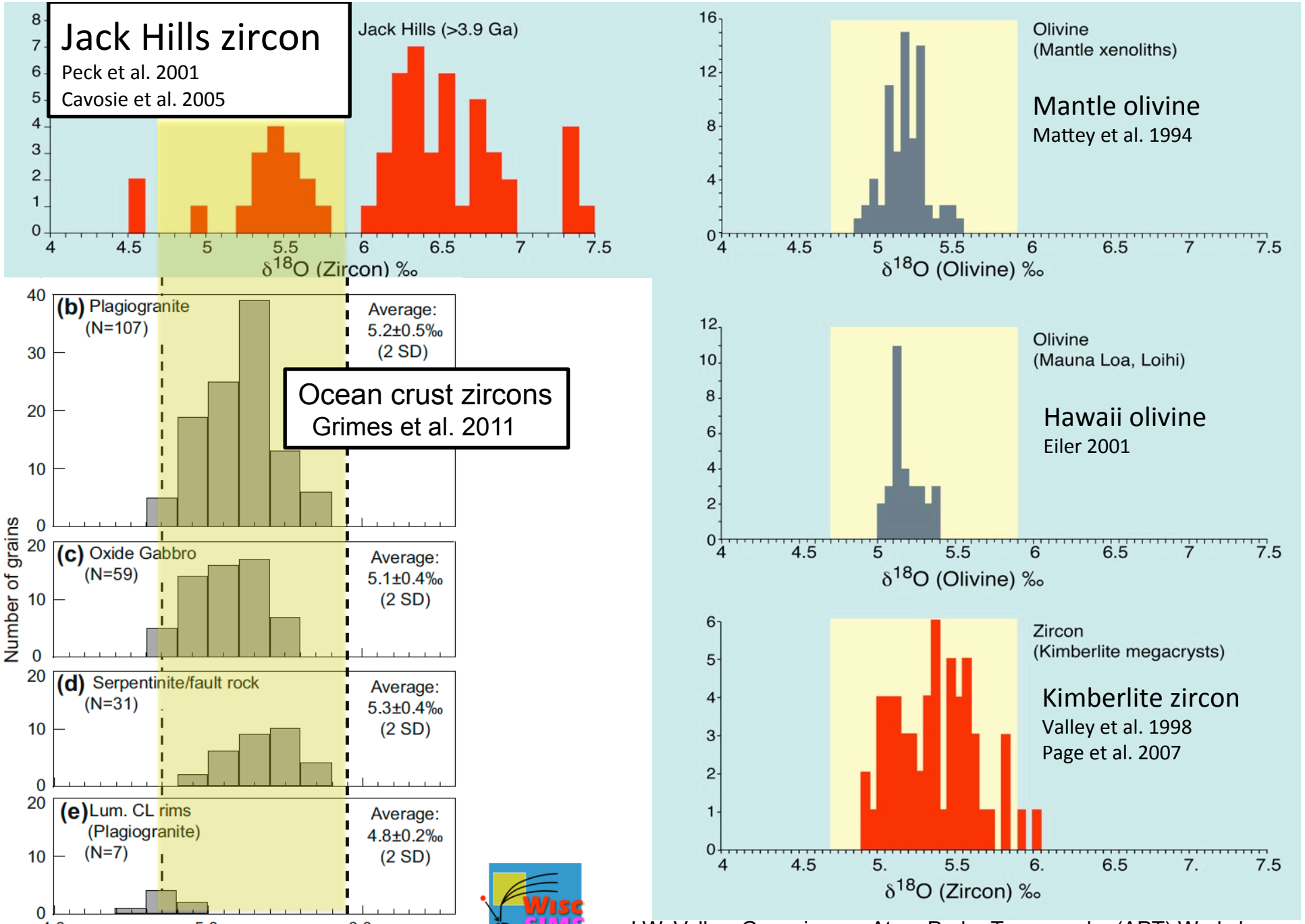



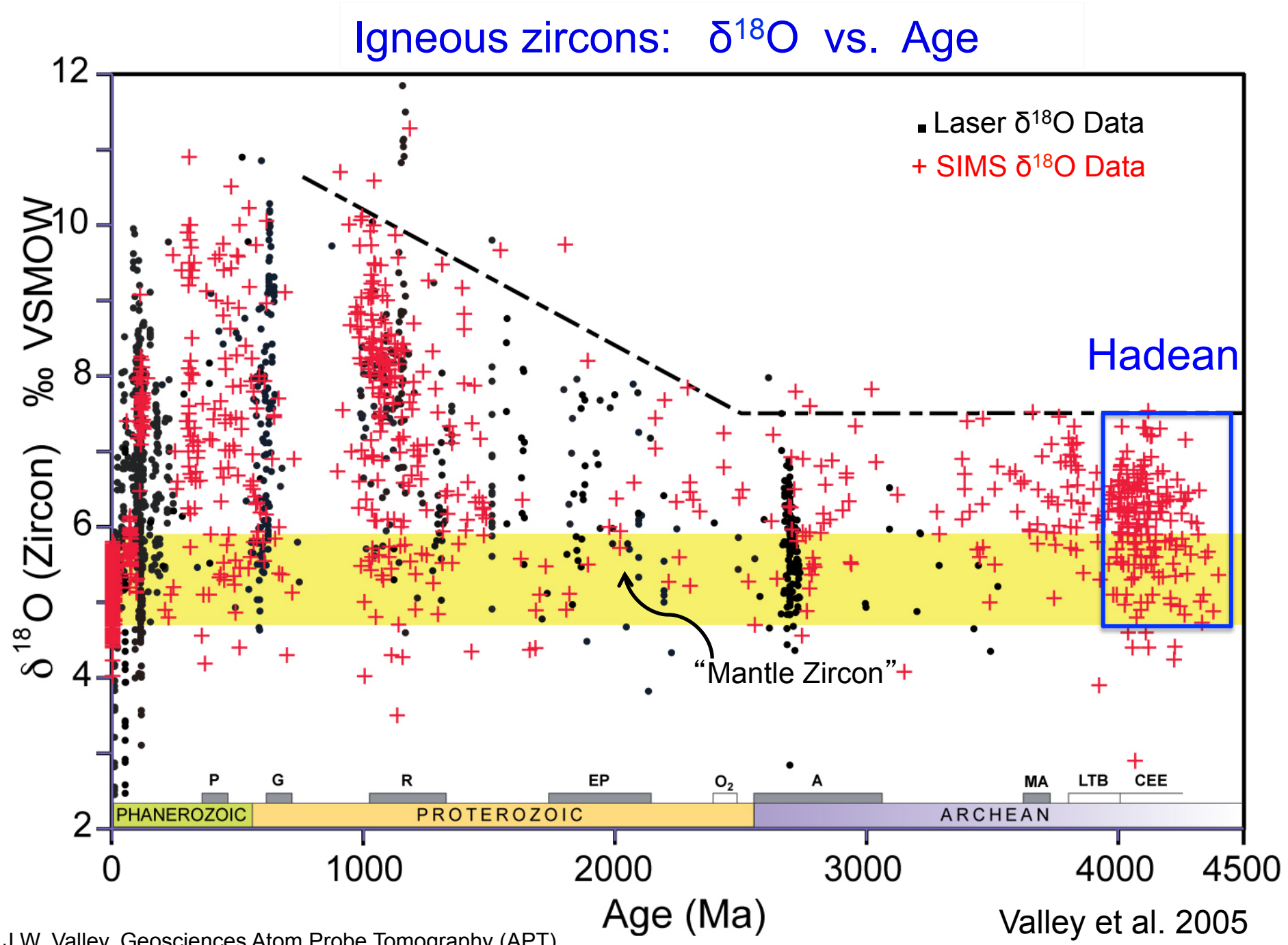

Sub-micron spot - $\delta^{18}O$



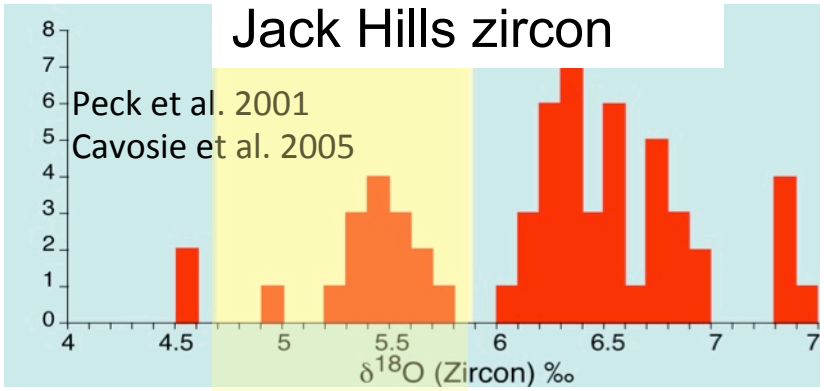

Granulite & amphibolite facies migmatites
UHP eclogites
Bowman et al. 2011

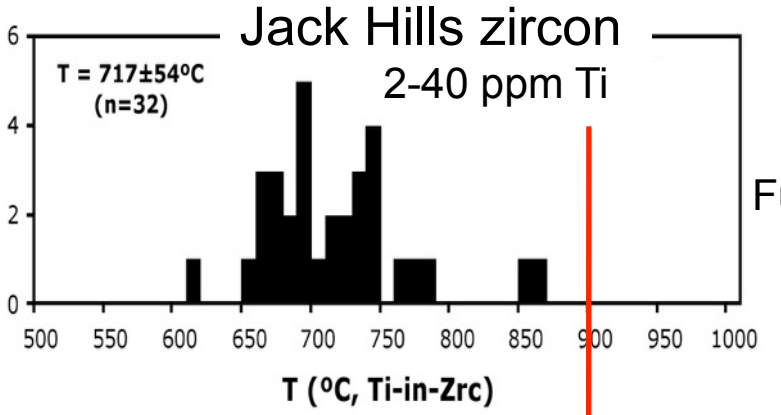

Jack Hills zircon
Peck et al. 2001
Cavosie et al. 2005
Jack Hills (>3.9 Ga)
δ18O (Zircon) ‰
Olivine
(Mantle xenoliths)
Mantle olivine
Mattey et al. 1994
δ18O (Olivine) ‰
Olivine
(Mauna Loa, Loihi)
Hawaii olivine
Eiler 2001
δ18O (Olivine) ‰
Zircon
(Kimberlite megacrysts)
Kimberlite zircon
Valley et al. 1998
Page et al. 2007
δ18O (Zircon) ‰
Ocean crust zircons
Grimes et al. 2011
(b) Plagiogranite
(N=107)
Average:
5.2±0.5‰
(2 SD)
(c) Oxide Gabbro
(N=59)
Average:
5.1±0.4‰
(2 SD)
(d) Serpentinite/fault rock
(N=31)
Average:
5.3±0.4‰
(2 SD)
(e) Lum. CL rims
(Plagiogranite)
(N=7)
Average:
4.8±0.2‰
(2 SD)
Number of grains
δ18O (Zrc) (‰, VSMOW)
Wisc SIMS




Valley et al. 2005
Valley et al. 2015

# Are pre-4 Ga zircons like the Moon? No: $\delta^{18}O$, Ti

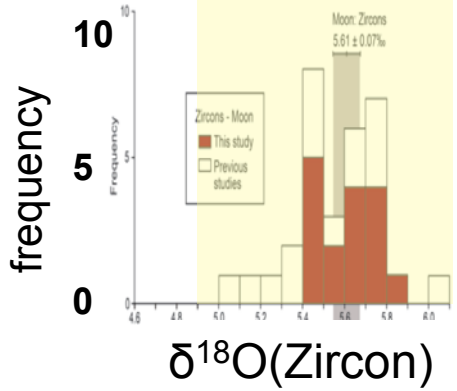



Fu et al. 2008

$\delta^{18}O$(Zircon)

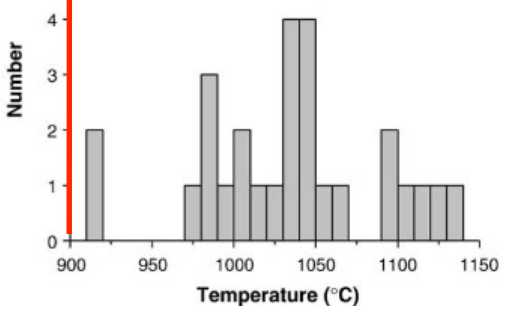
Ti-in-Zircon, uncorrected T's




Lunar zircon
5.61 ±0.07

Valley et al. 2014
Whitehouse & Nemchin 2010

Lunar zircon
50-250 ppm Ti

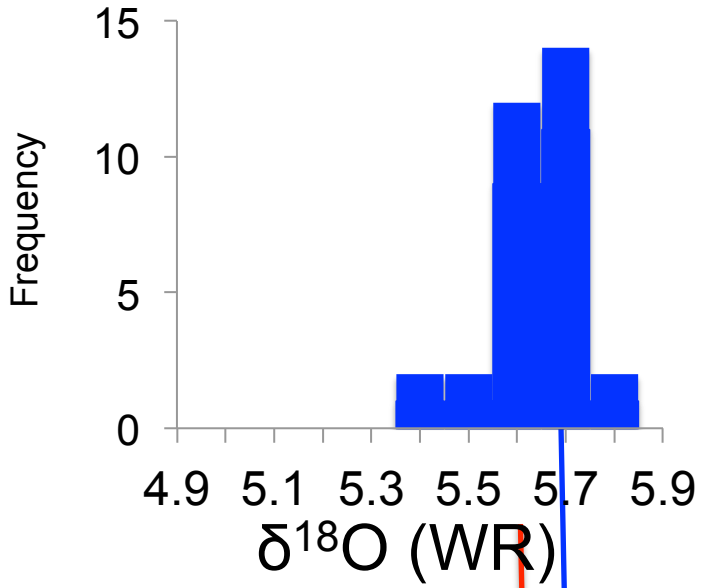



Taylor et al. 2009
Spicuzza et al. 2011

Mare Basalt WR

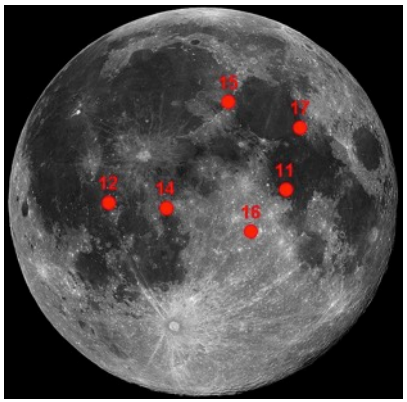
< 8 wt % $TiO_2$

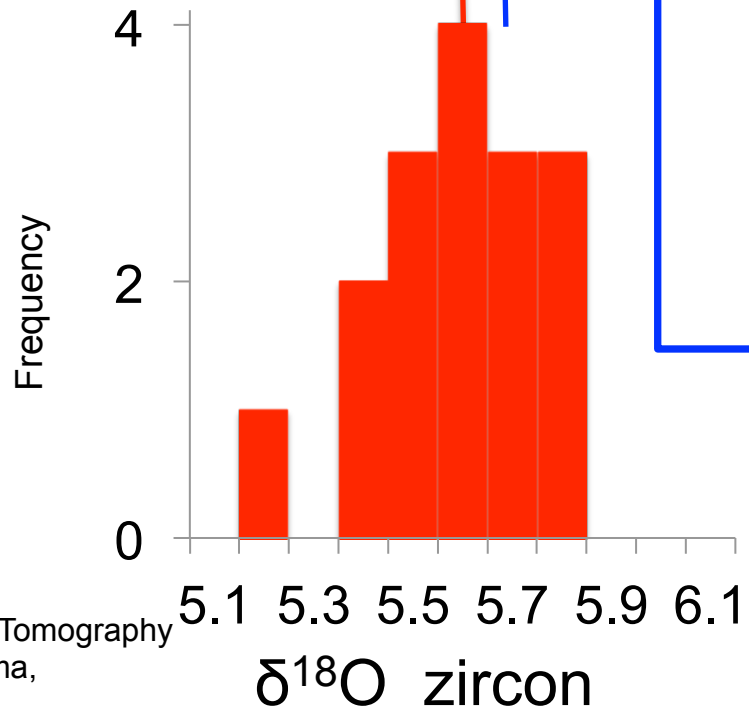
5.69 ± 0.04‰




Lunar Zircons

5.59 ± 0.08‰




$\Delta^{18}O(WR\text{-}Zrc)$ =

0.1 ‰ on Moon

vs.

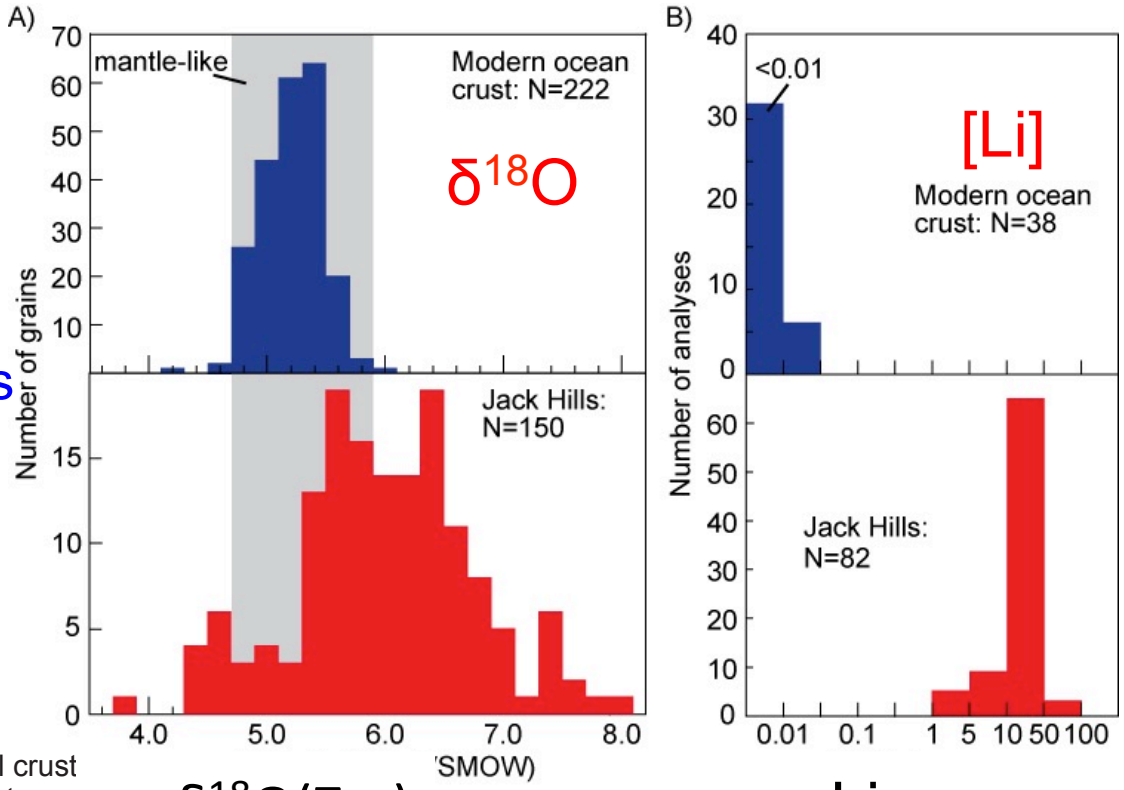
0.4 ‰ on Earth

J.W. Valley, Geosciences Atom Probe Tomography (APT) Workshop, University of Alabama, Jan. 29 -30, 2016

Valley et al. 2014 CMP

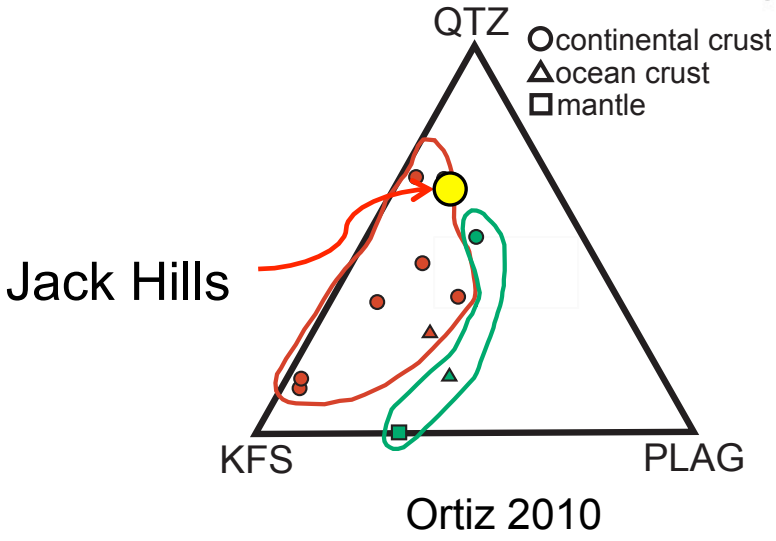
# Are Pre-4 Ga Zircons from Ocean-crust?

No: $\delta^{18}O$, Li, TE's, Inclusions

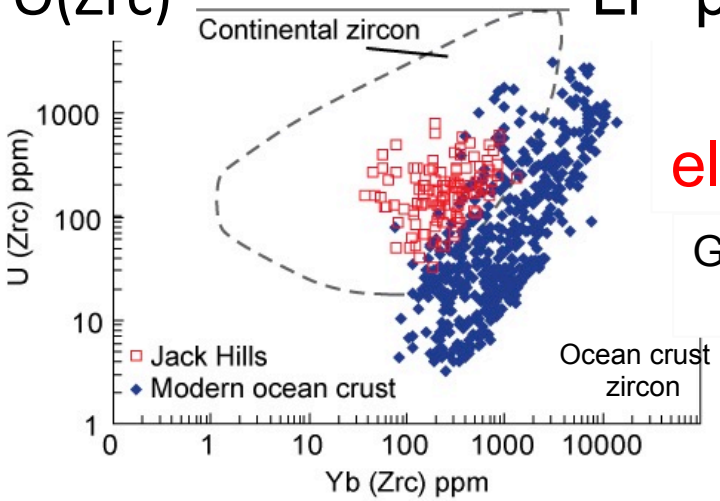



$\delta^{18}O$(Zrc)

Li ppm




Ortiz 2010



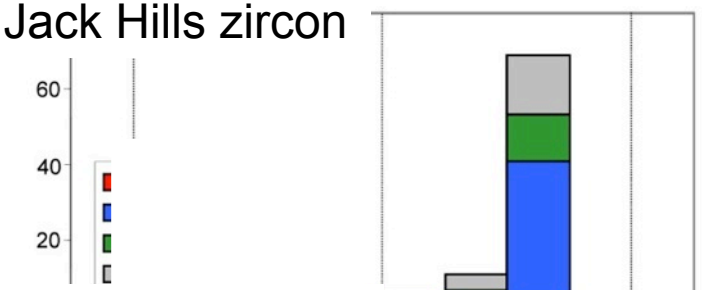

trace elements

Grimes et al. 2011

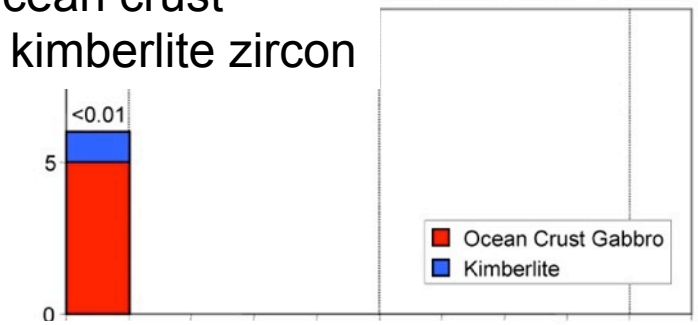
# Are > 4 Ga Zircons from Granitic Rocks?

## Mostly Yes.

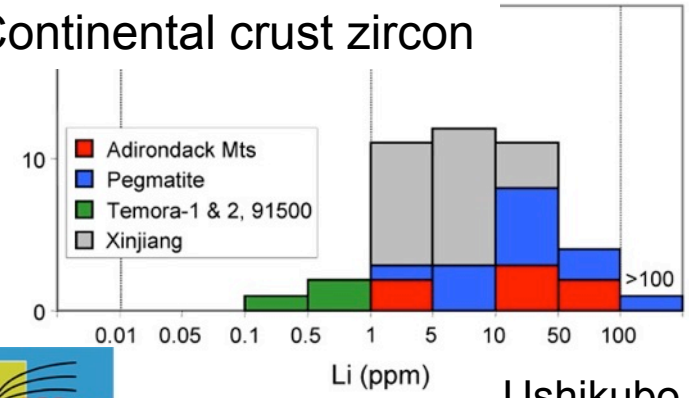
Jack Hills zircon




Ocean crust
& kimberlite zircon




Continental crust zircon

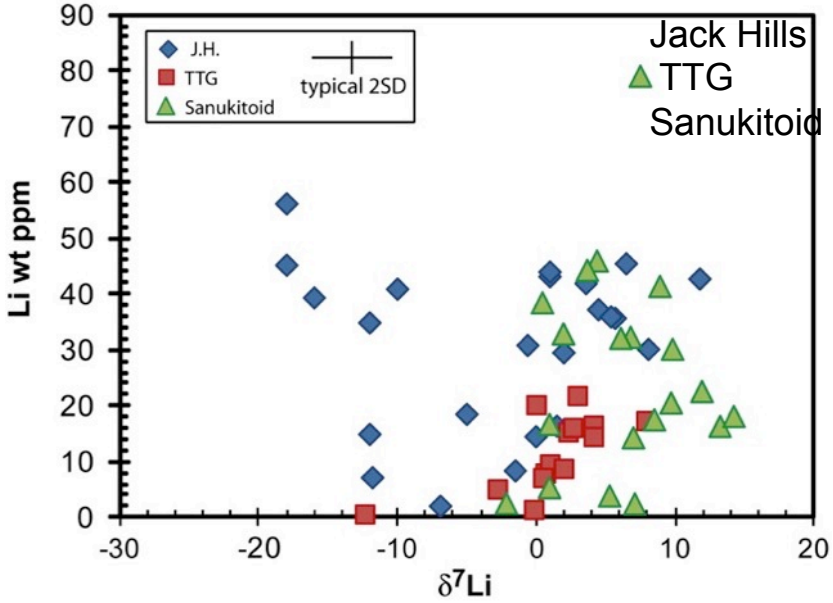



Ushikubo et al. 2008

Inclusions in >4 Ga zircon

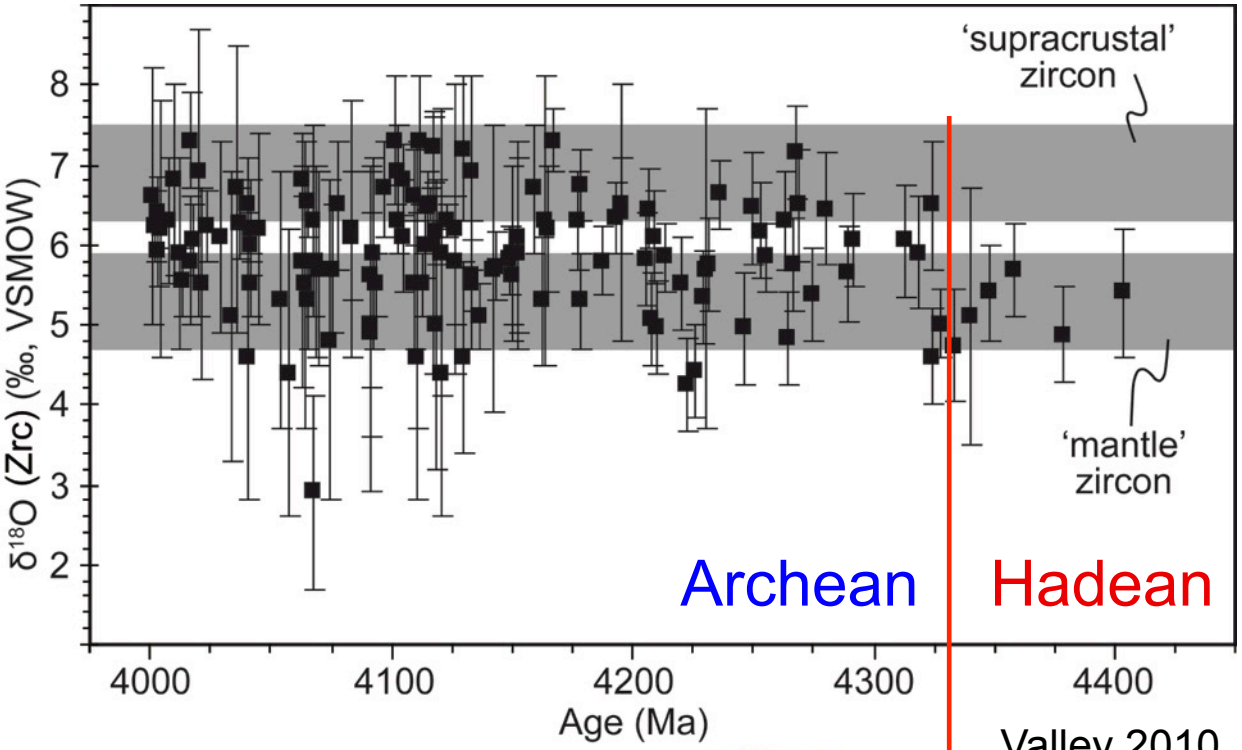
Quartz
K-feldspar
Plagioclase
Muscovite
(Devitrified granitic melt?)

Biotite
Hornblende
Apatite
Xenotime
Monazite
Fe-Ti-oxide
Rutile
Pyrite

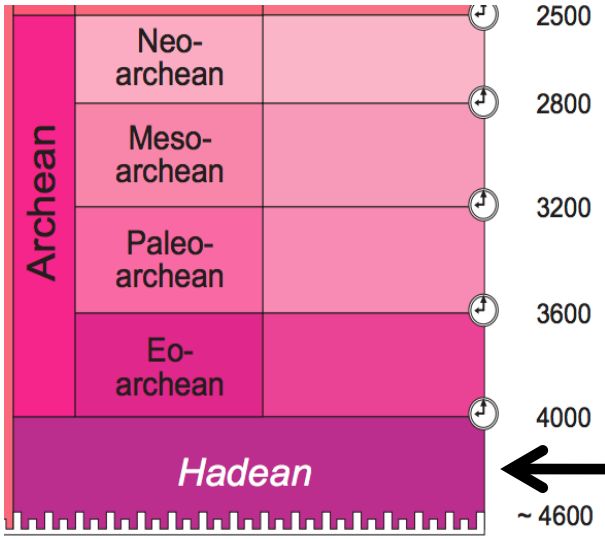



Bouvier et al. 2011

When was the end of the Hadean Eon?



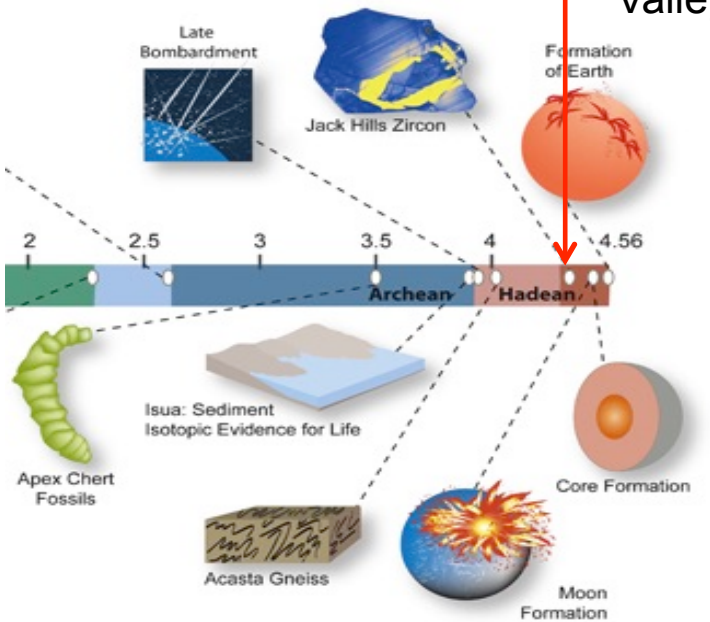

Valley 2010

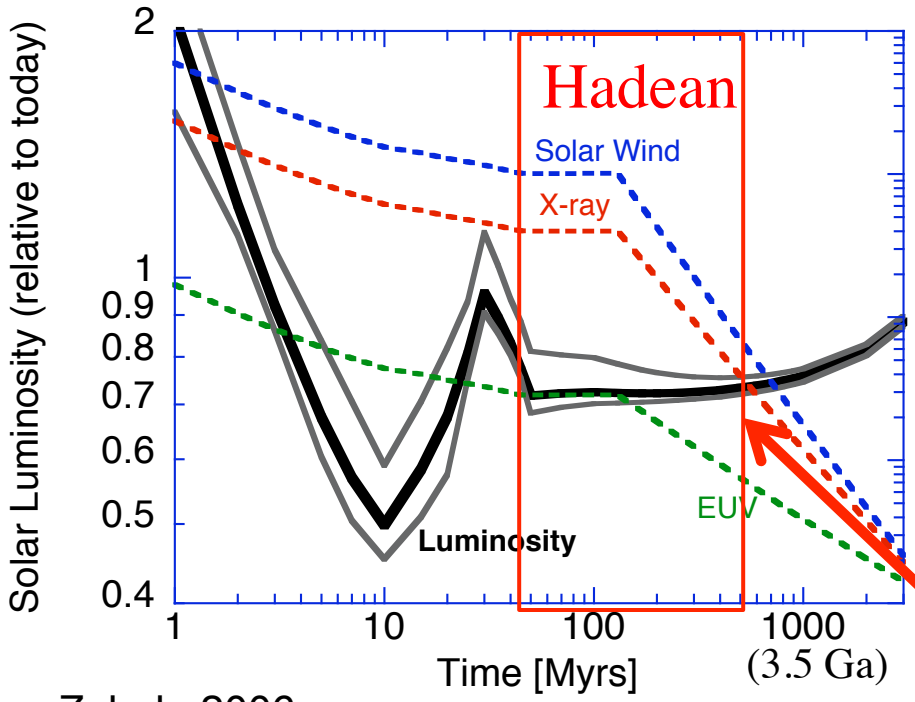



ICS 2013

Archean

Hadean



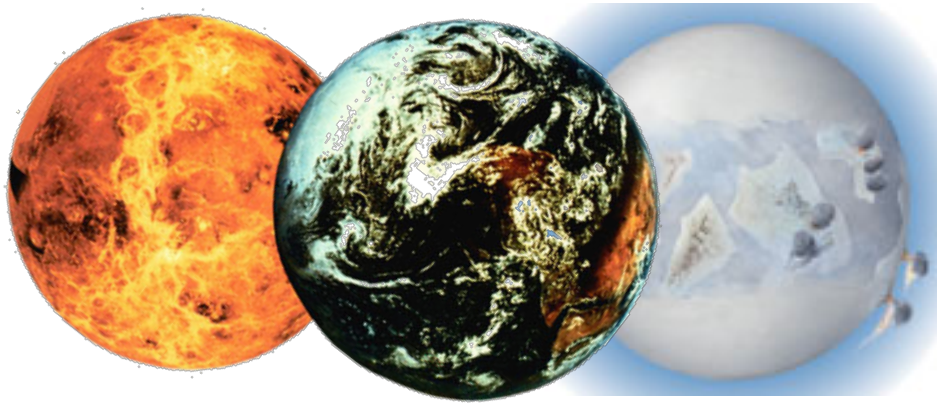



Zahnle 2006

Faint Young Sun

~70% luminosity @ 4.4-4.0 Ga

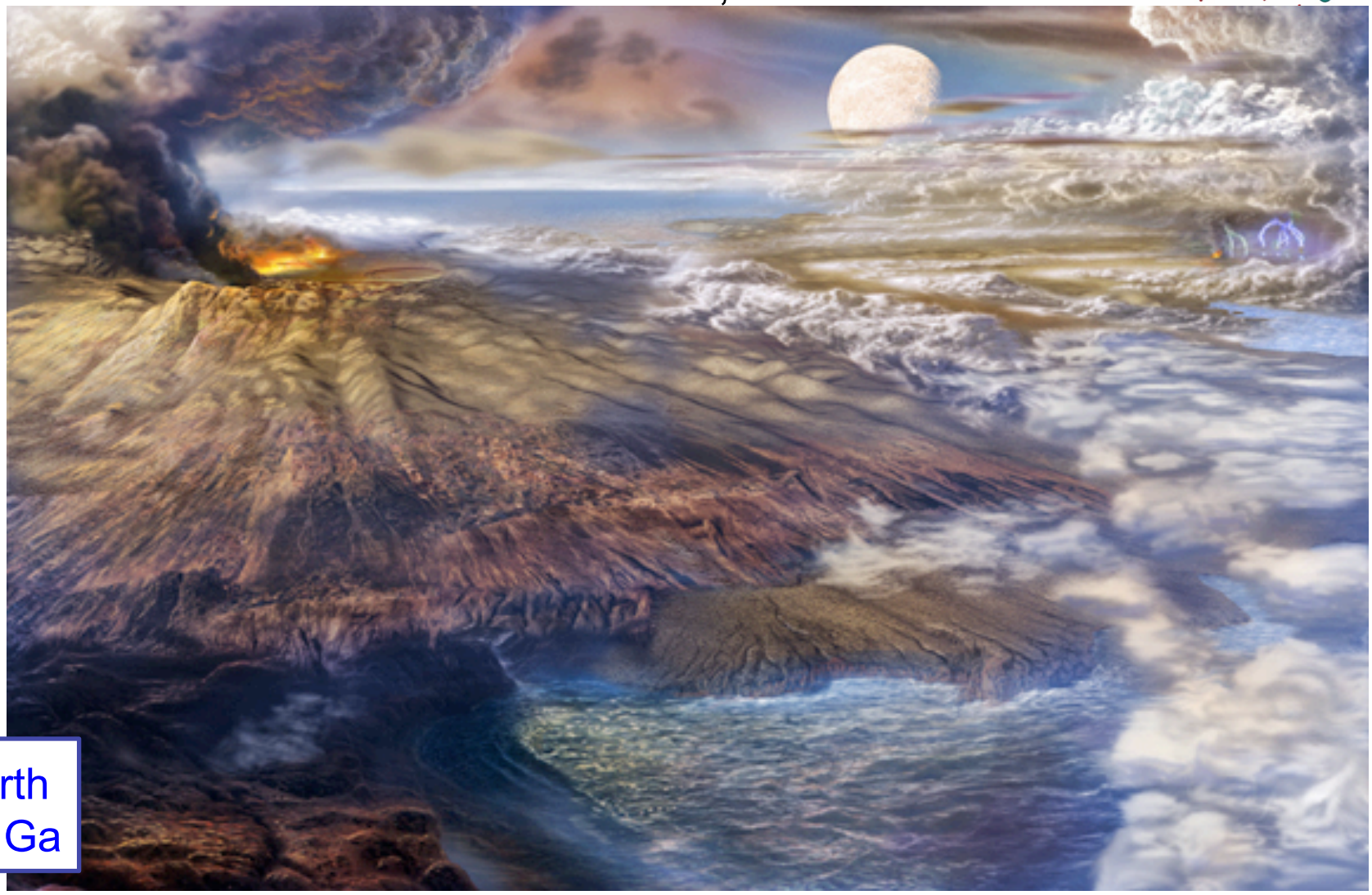
# Hadean vs. Snowball Earth?



# Cool Early Earth

4.4 Ga  Protocontinental Crust

>4.3 Ga  End of Hadean,
Oceans, Life?



Earth
4.3 Ga

Don Dixon