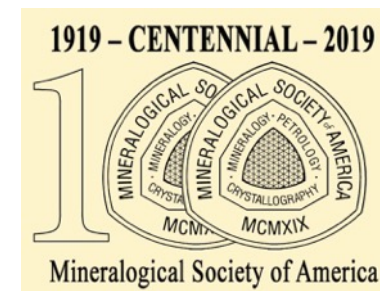


The Microanalysis Revolution in Isotope Geochemistry

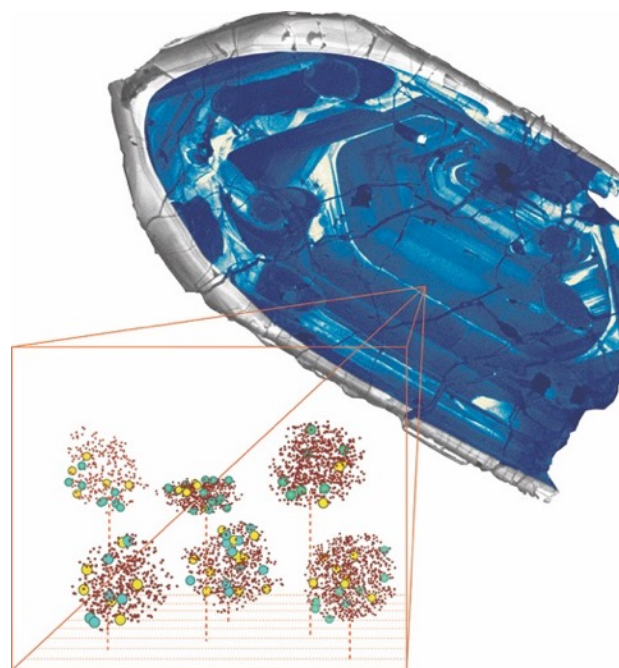


John Valley

TB Blum, EM Cameron
UW- Madison

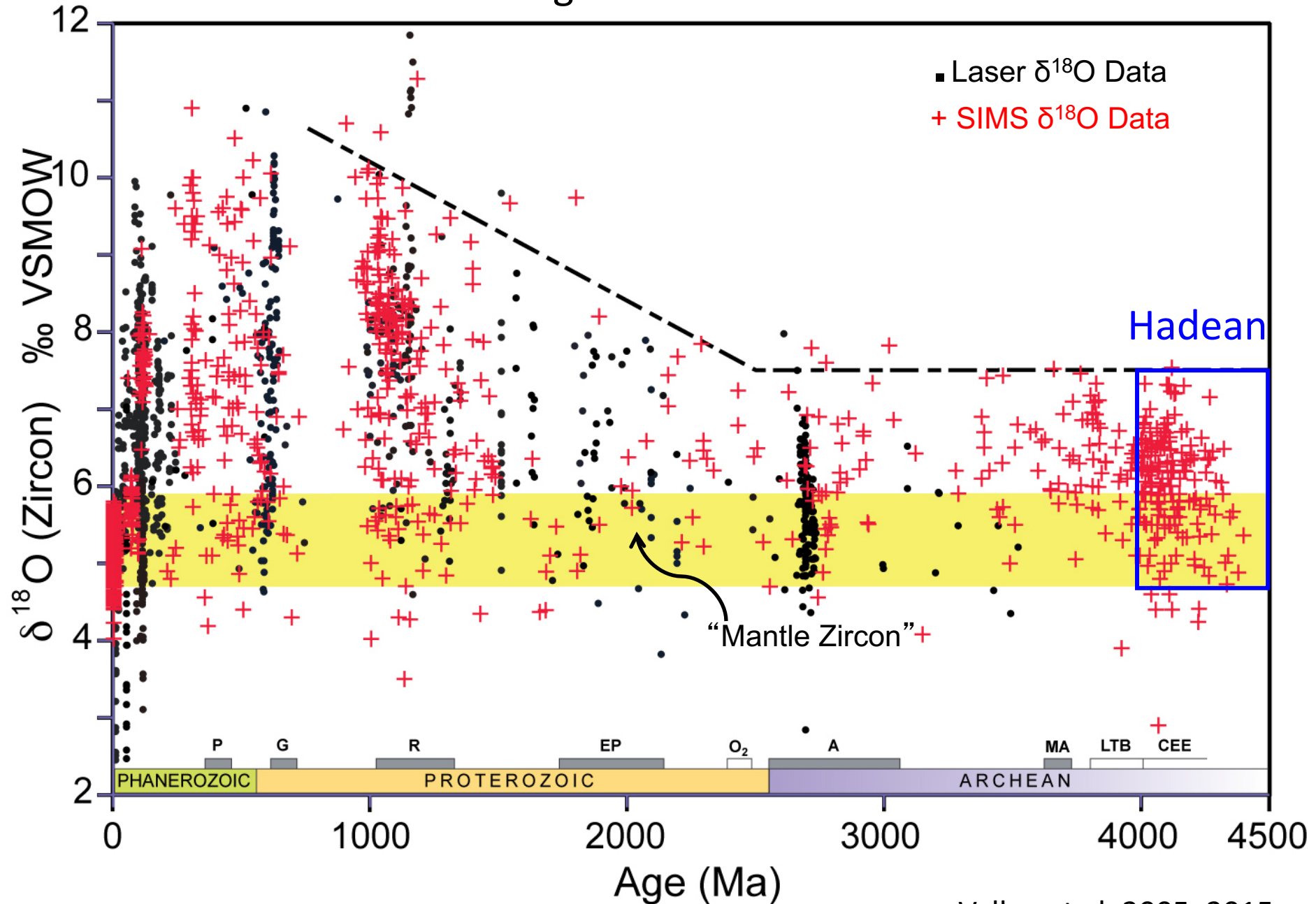


Hadean Earth



Unaltered Igneous Zircon

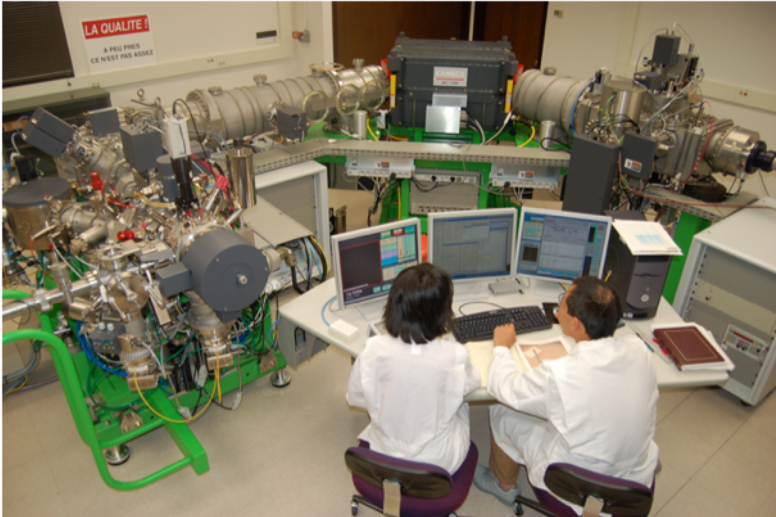
$\delta^{18}\text{O}$
vs.
Age



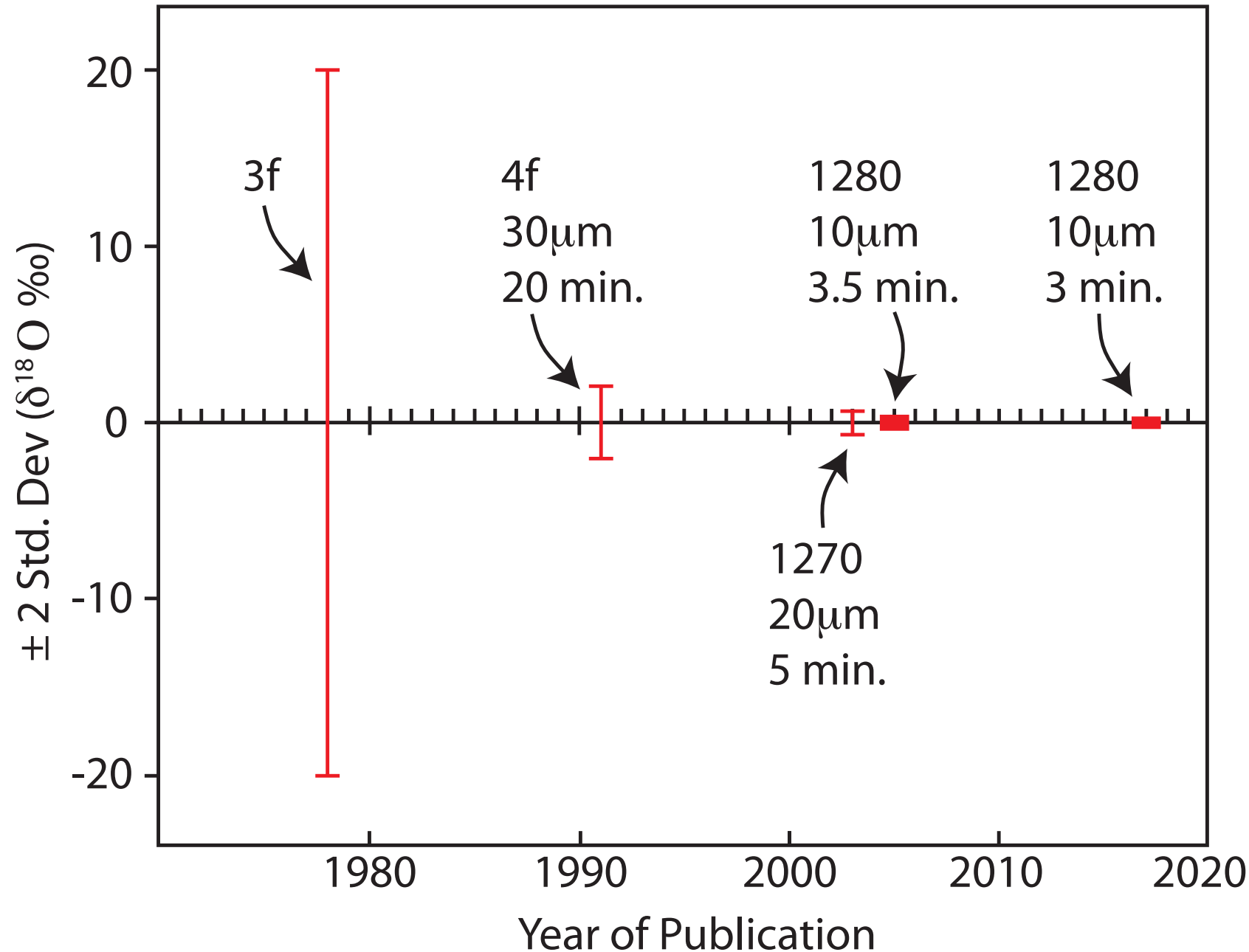
Valley et al. 2005, 2015

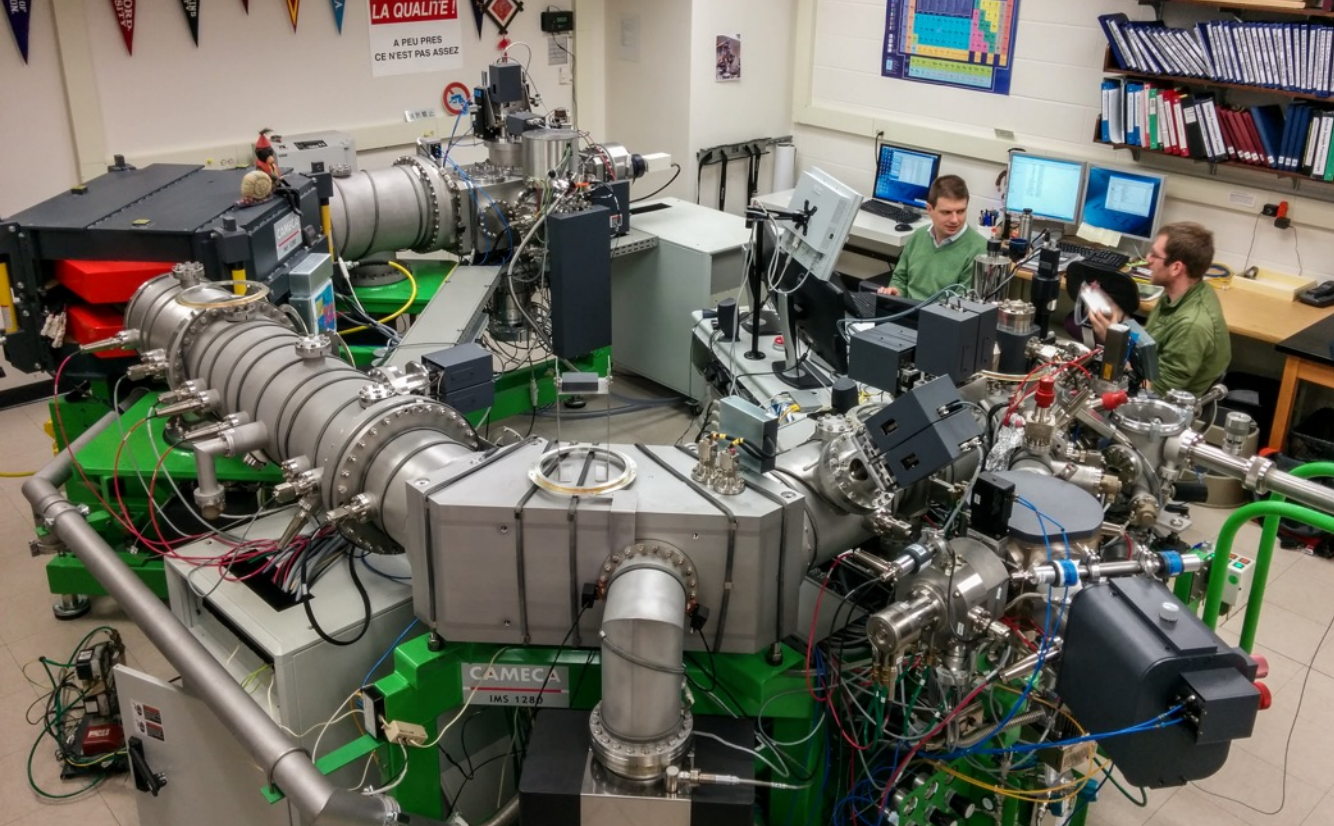
Oxygen Isotopes

SIMS Analytical Precision
40 years of Improvement



Valley et al. 2019 GSA

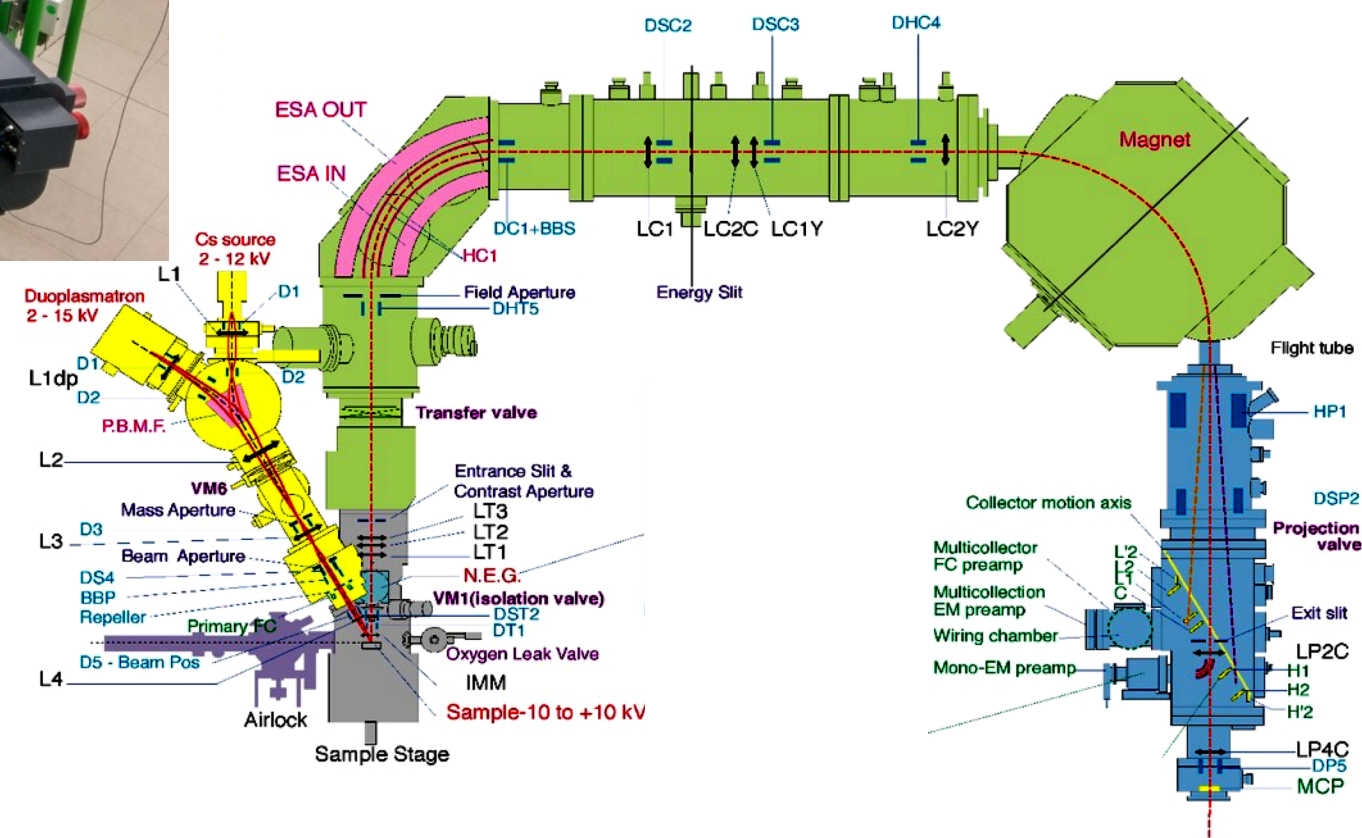




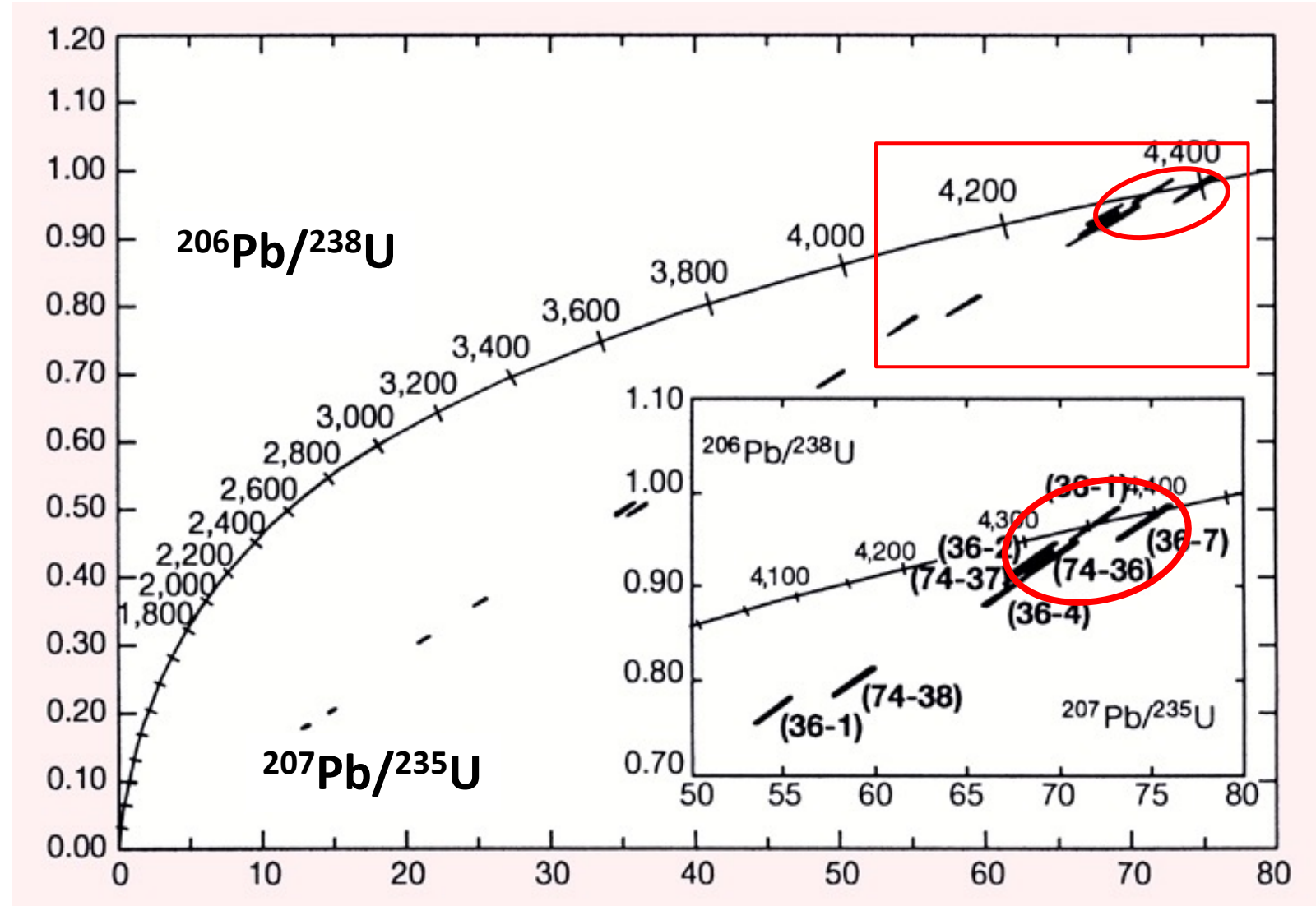
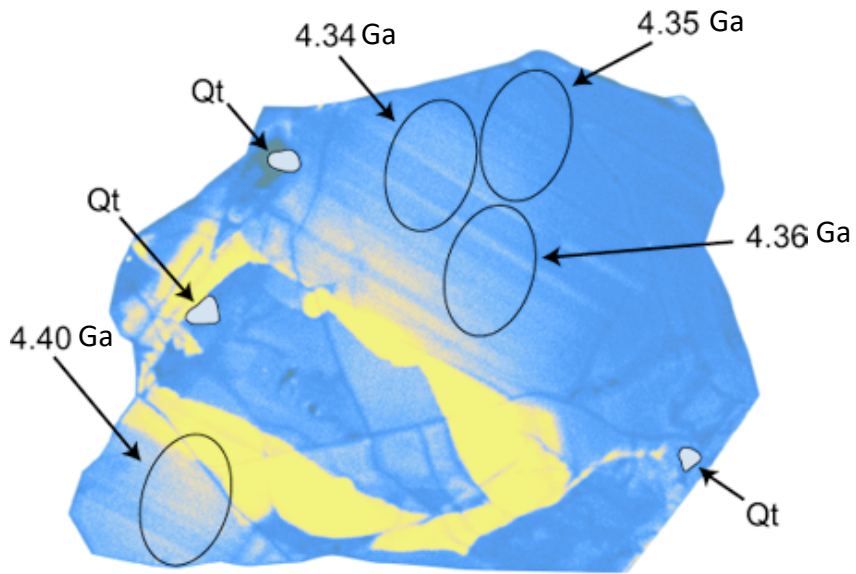
Secondary Ion Mass Spectrometer SIMS Ion Microprobe



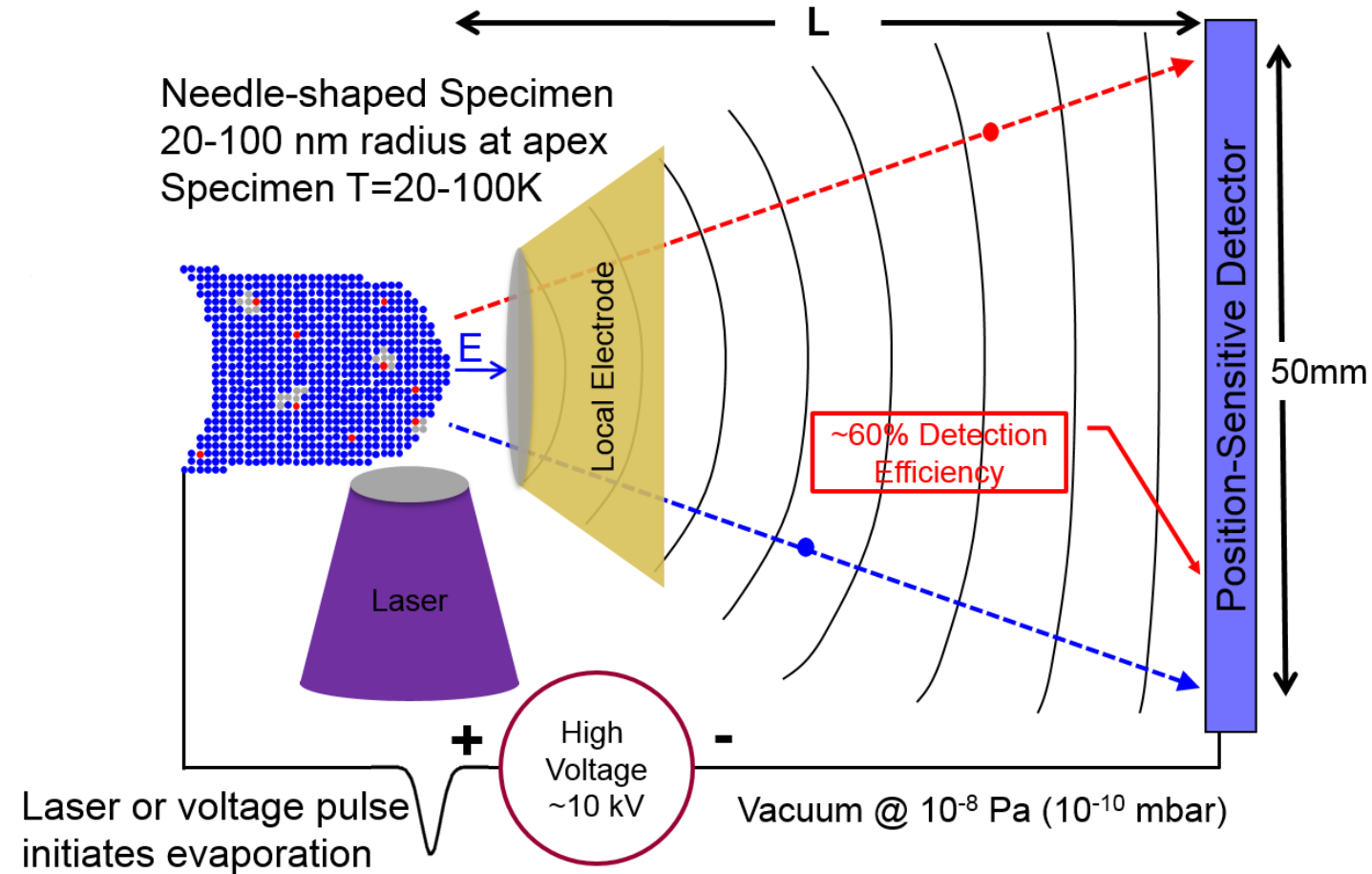
CAMECA IMS-1280
UW-Madison



Hadean detrital zircon

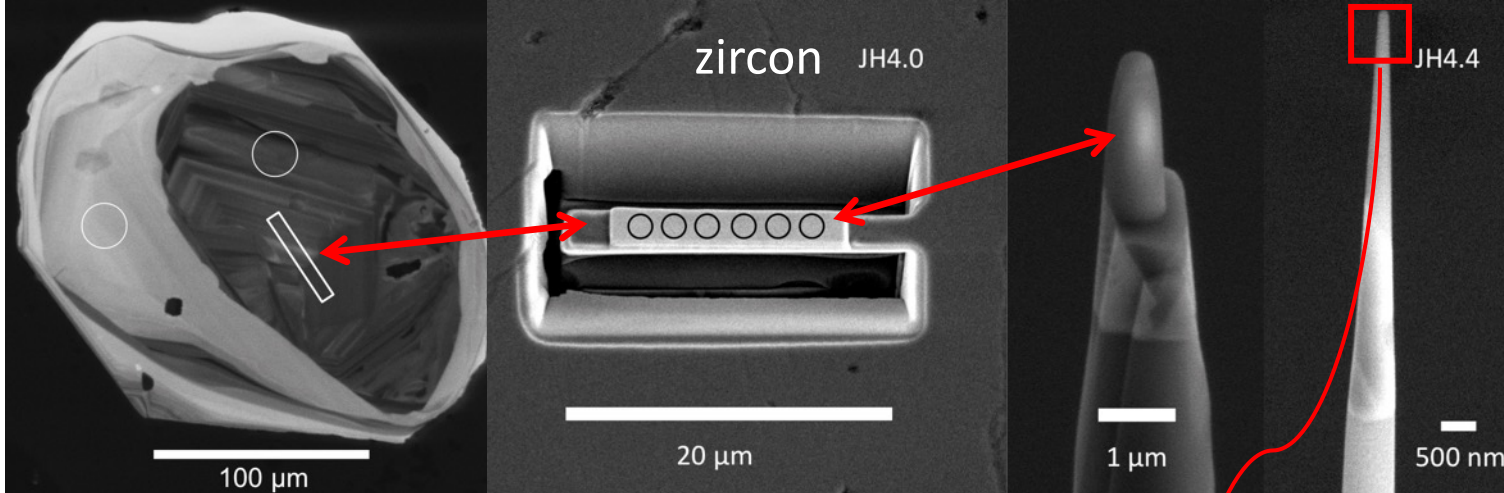


Atom Probe Tomography APT



Valley et al. 2015 Am Min

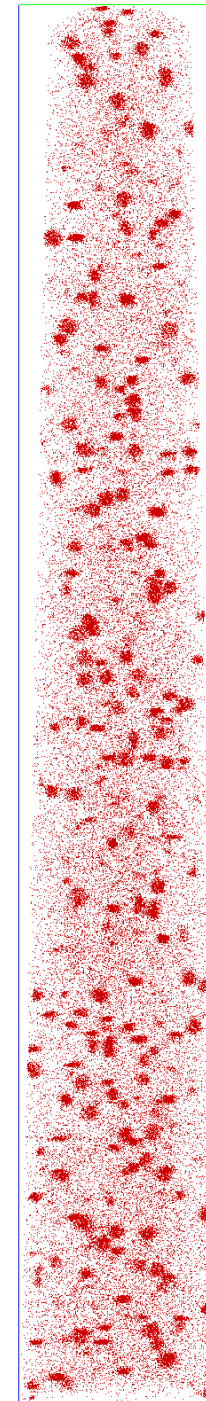
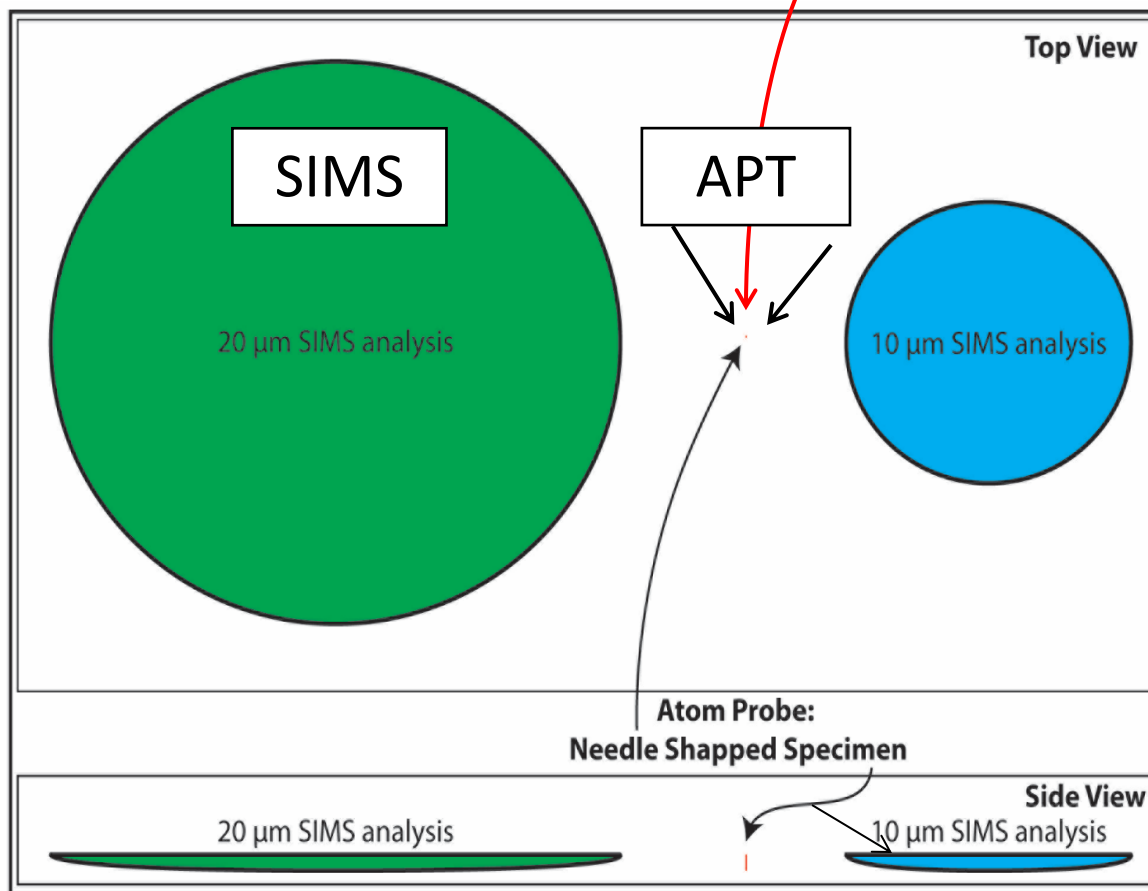
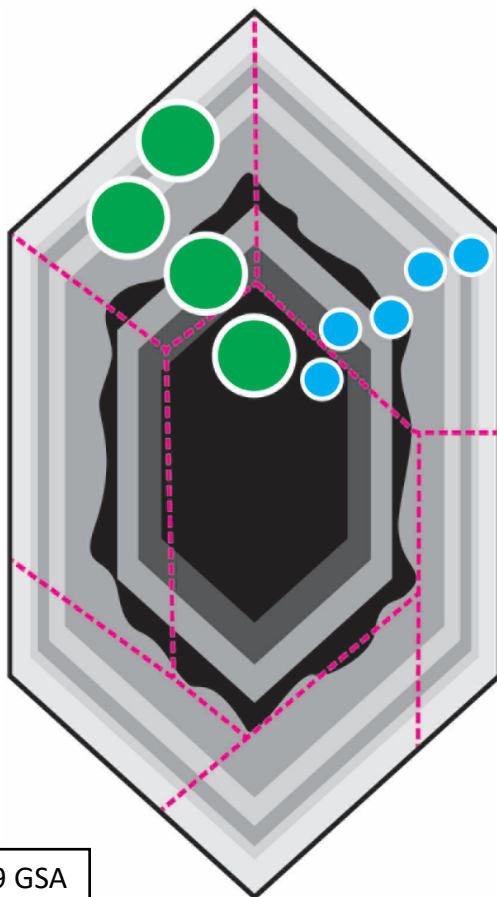
FIB
lift-out



APT
Y & Pb clusters
in zircon

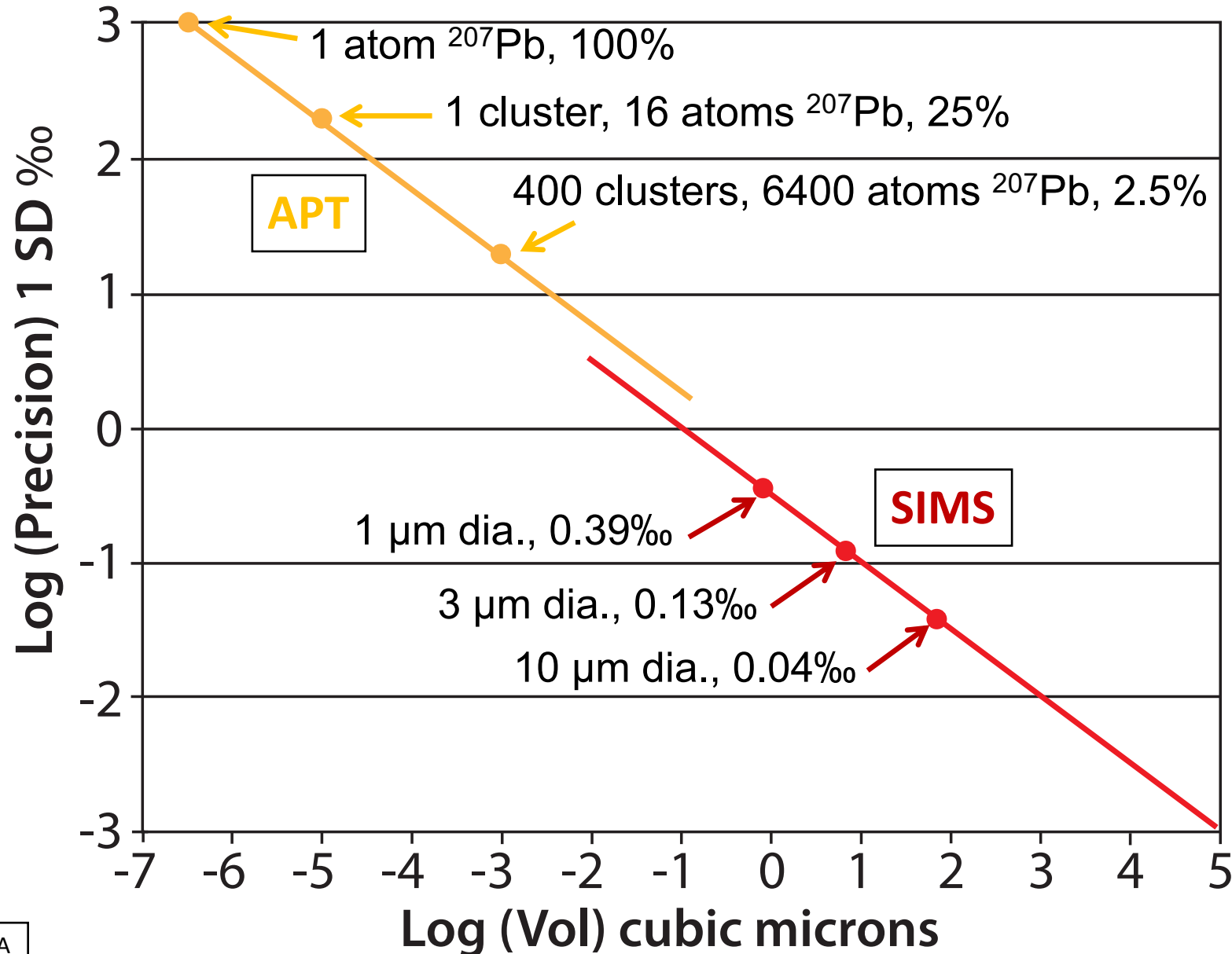
100 nm

SIMS
vs.
APT



Valley et al. 2014

Precision vs. Analysis Volume: Theoretical Limit ($1\sigma = \sqrt{N}$)



SIMS

$^{18}\text{O}/^{16}\text{O} \sim 0.002$

Zircon

670,000 ppma

7% yield

APT (sample specific)

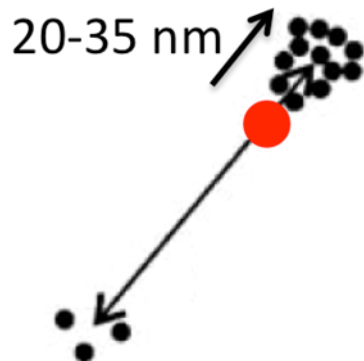
$^{207}\text{Pb}/^{206}\text{Pb} \sim 1$

Pb clusters

800 ppma

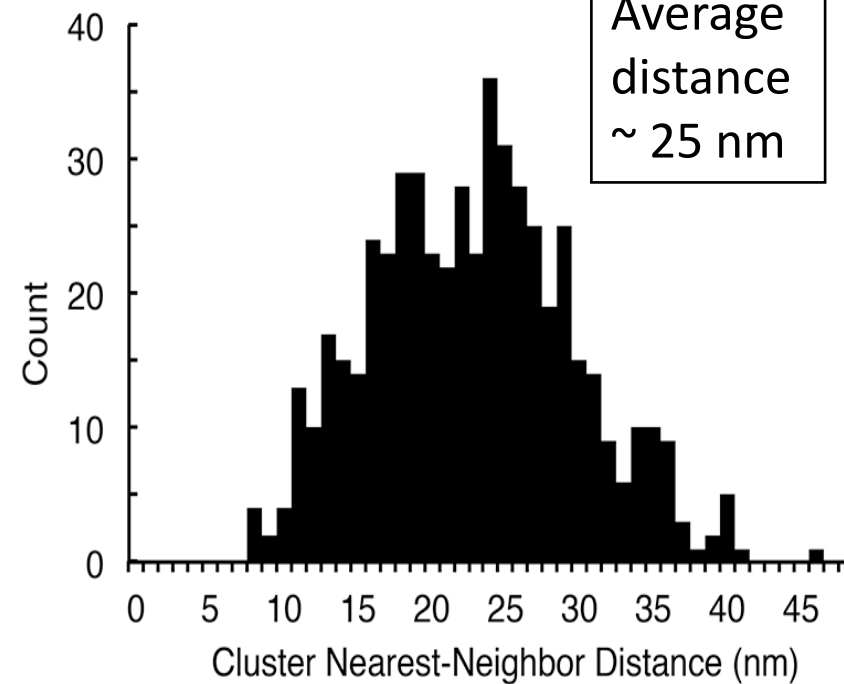
80% yield

Radiation damage: α -recoil



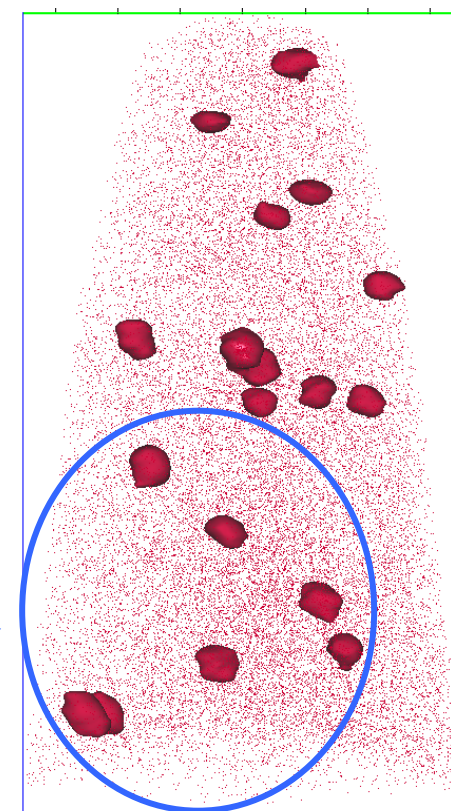
Clusters in 4.4 Ga Zircon

Average distance
~ 25 nm



Y & Pb clusters 2.5 Ga Zircon

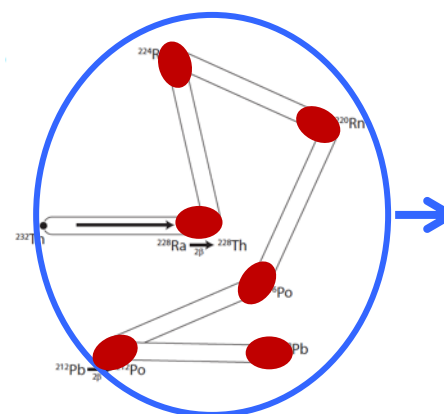
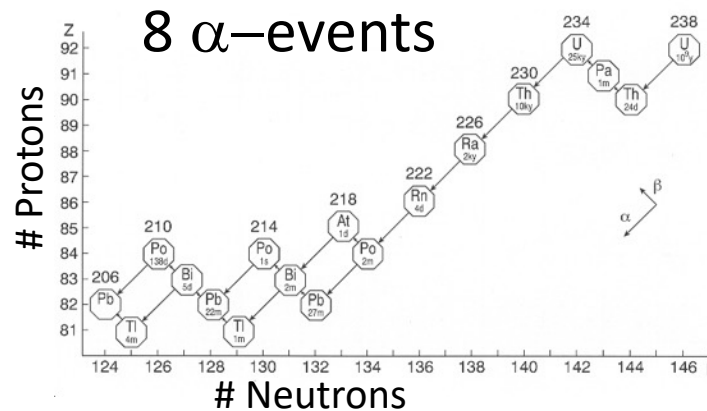
100 nm



250 nm

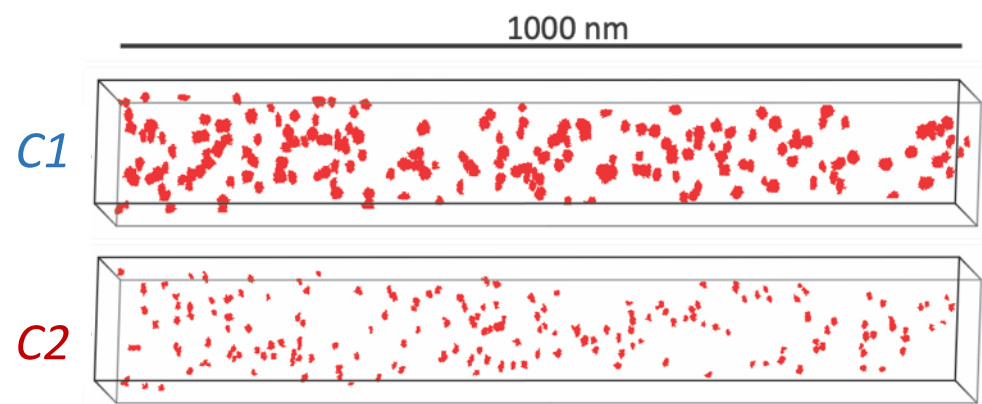


8 α -events



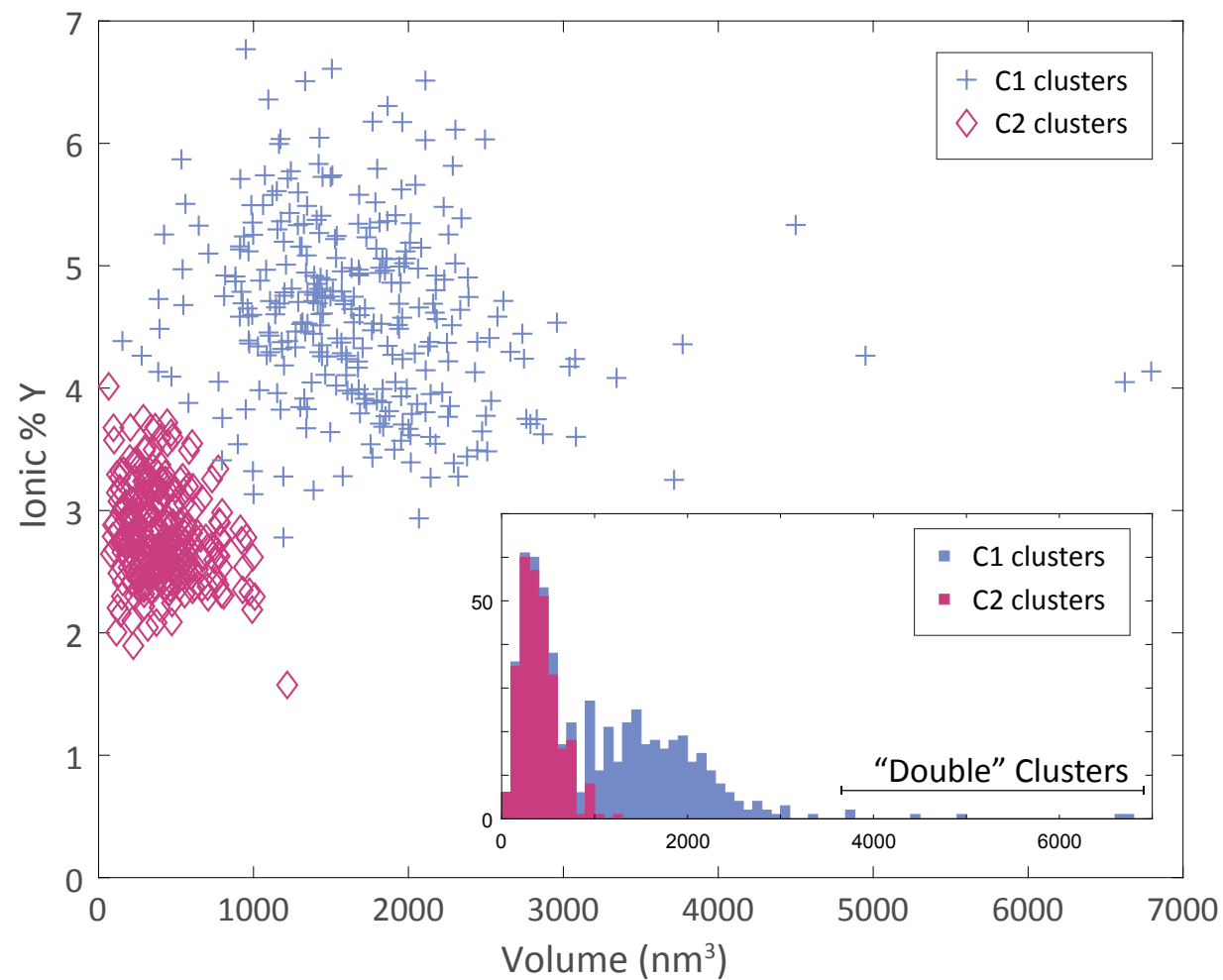
2 Generations of clusters

4.4 Ga zircon



Y in clusters

C1 $^{207}\text{Pb}/^{206}\text{Pb} \sim 1.4$
C2 $^{207}\text{Pb}/^{206}\text{Pb} \sim 0.9$



SIMS

$^{207}\text{Pb}/^{206}\text{Pb}$

JH 4.4

4374 Ma core
inside clusters

0.548

outside clusters
3400 Ma rim

0.291

APT

$^{207}\text{Pb}/^{206}\text{Pb}$

10,255 Pb atoms

0.52

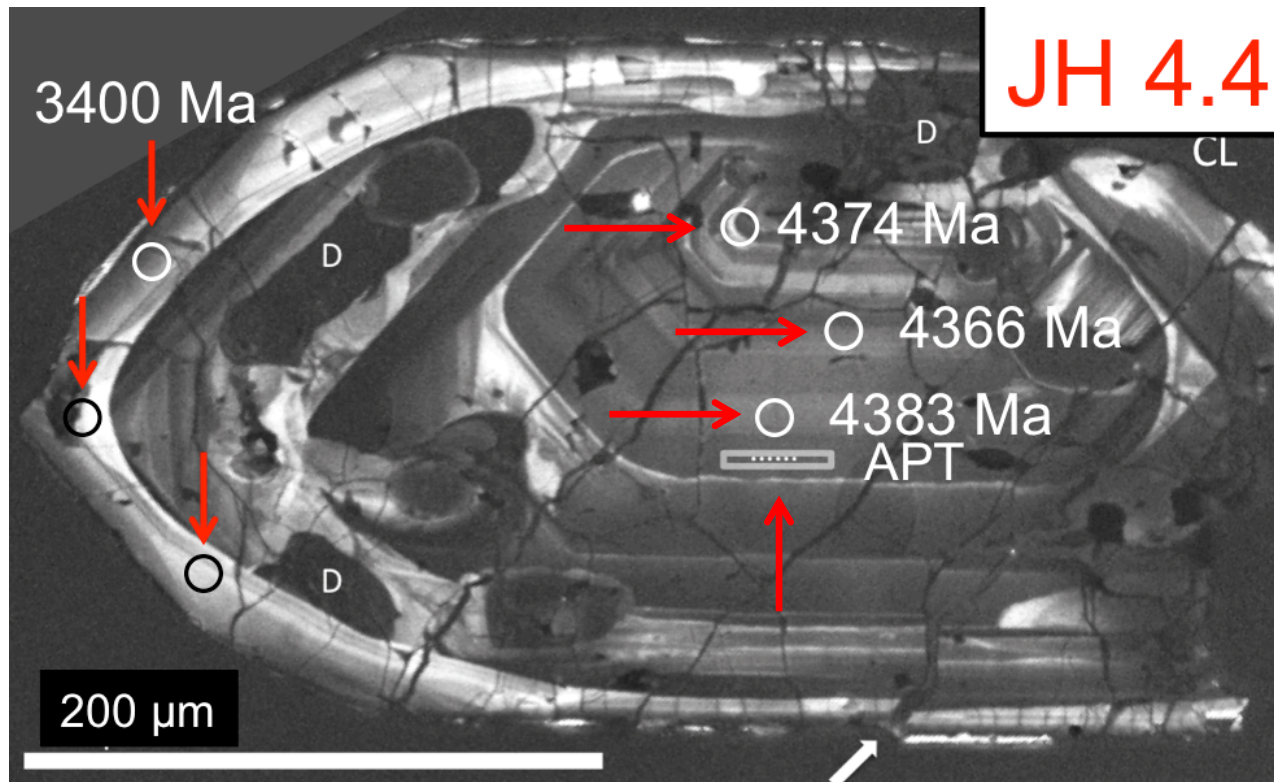
1.2 C1 1.4

C2 0.9

0.30

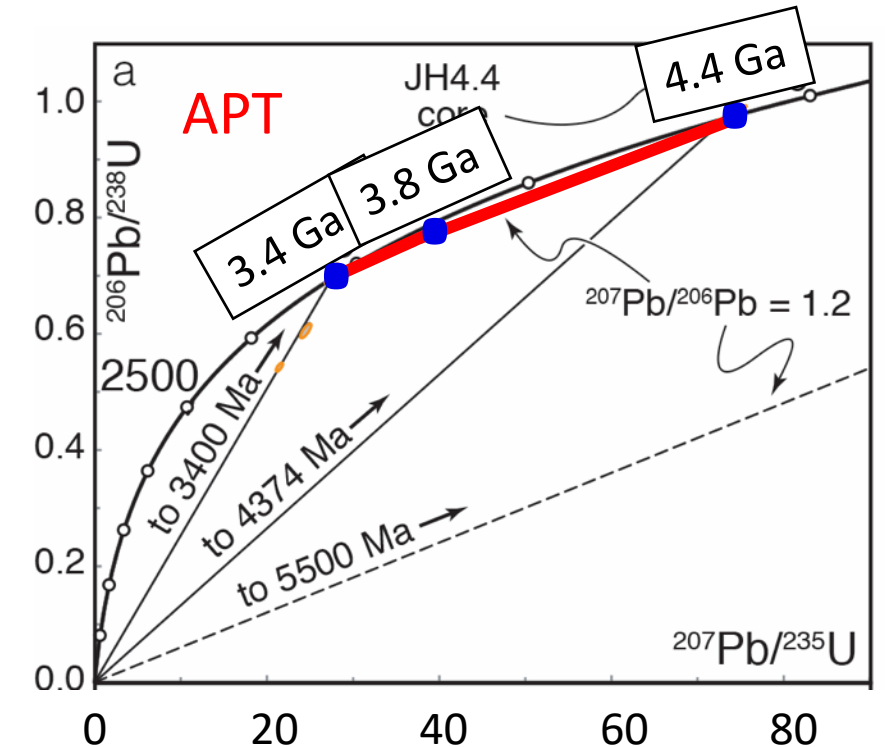
Jack Hills

4.374 Ga



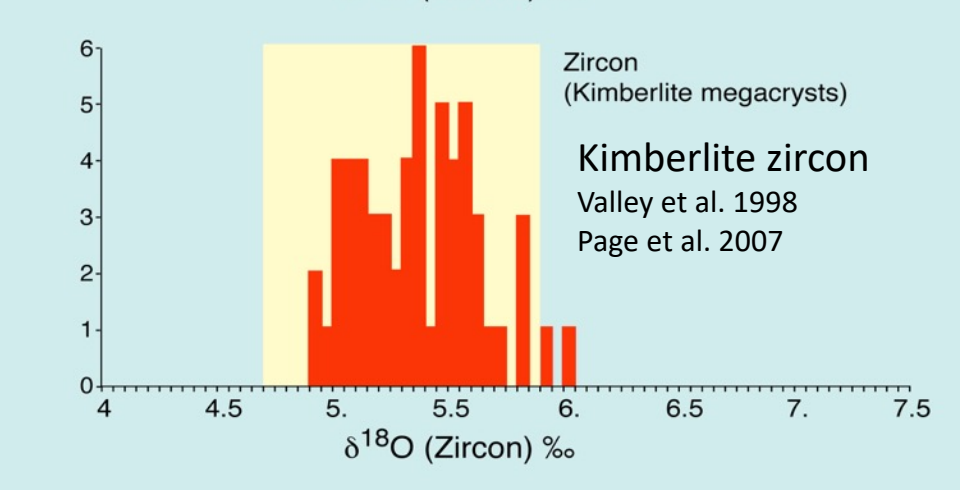
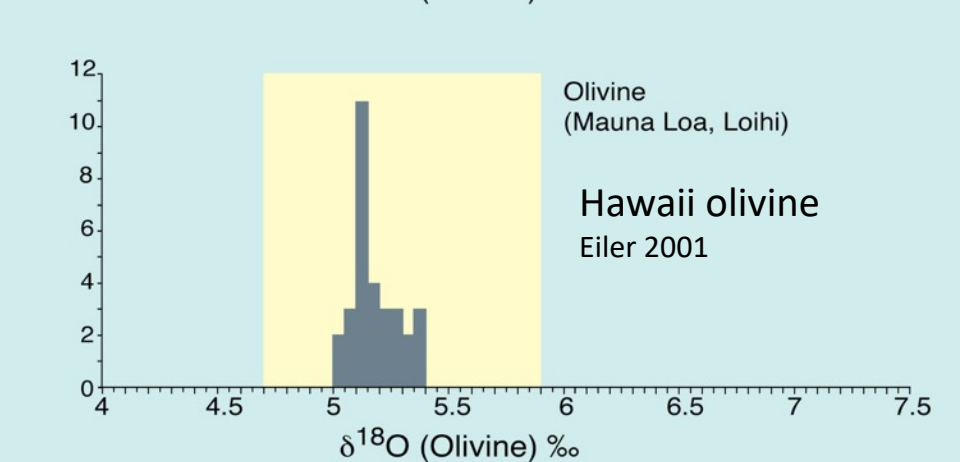
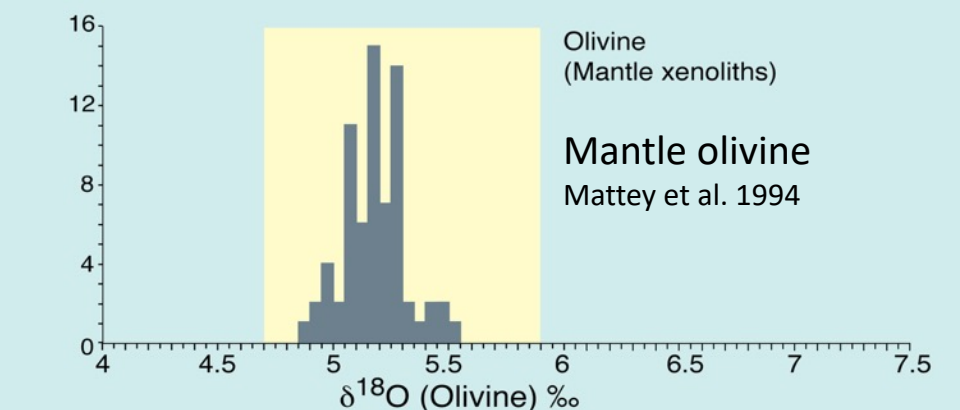
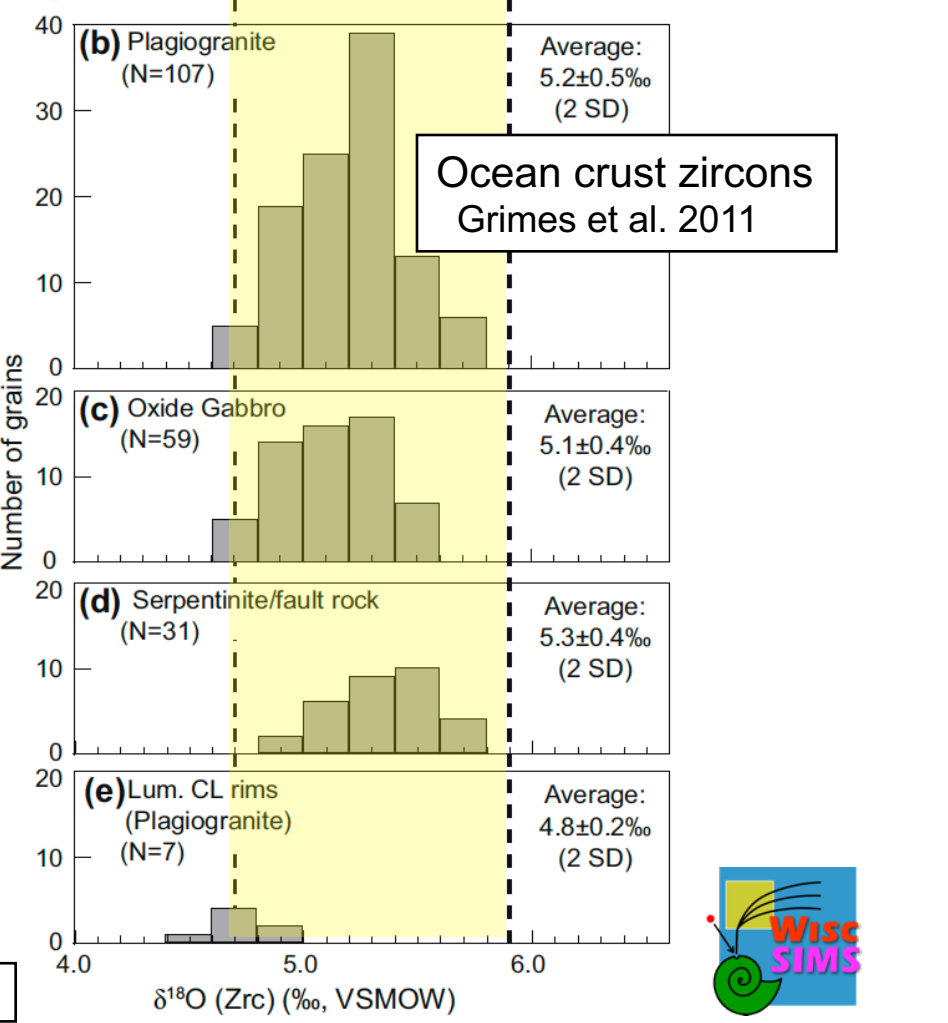
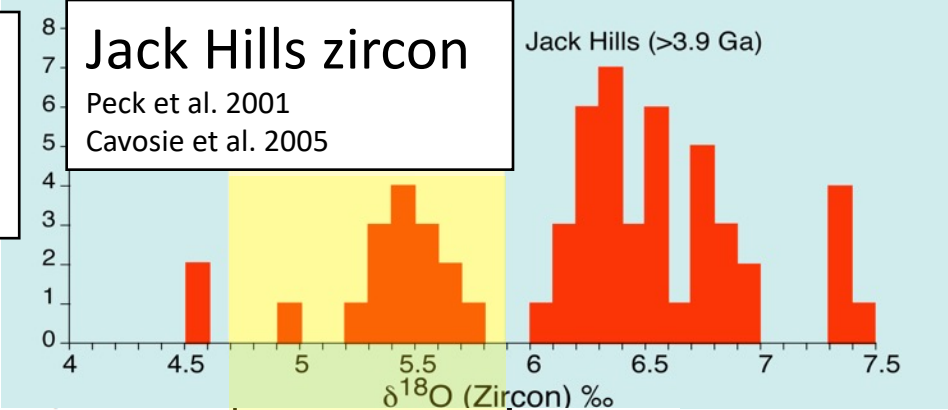
Valley et al. 2019 GSA

Valley et al. 2014



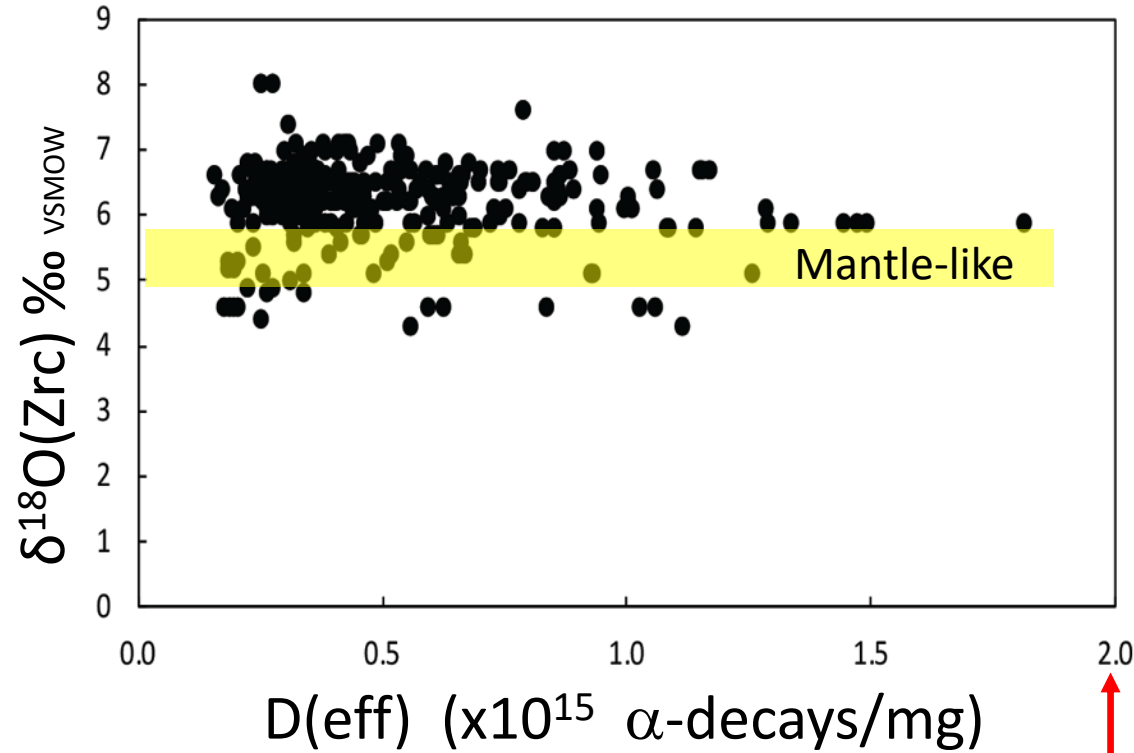
Blum et al. 2020

Oxygen Isotopes

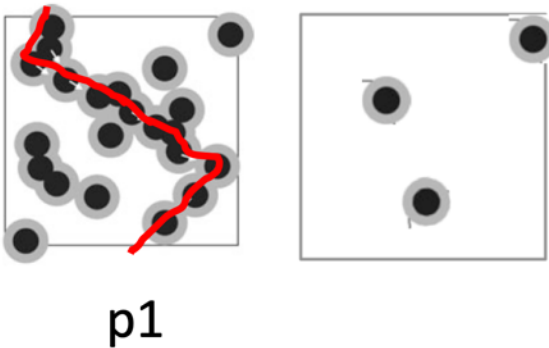


These Hadean zircons are pristine (CL, concordant ages, low-magnetism, Raman, low-[OH])

Below p1, the first percolation point.

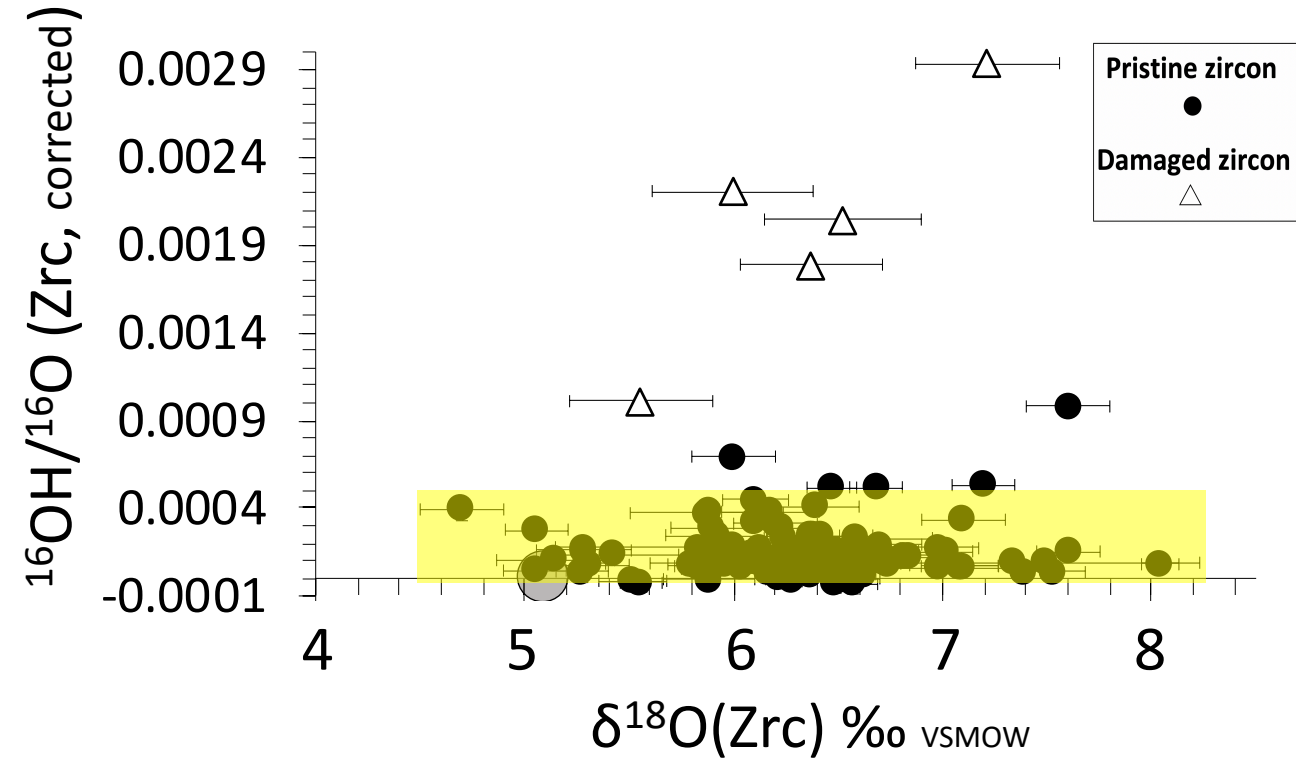


Trachenko et al. 2004



1st Percolation Point
(2x10¹⁵ α-decays/mg)

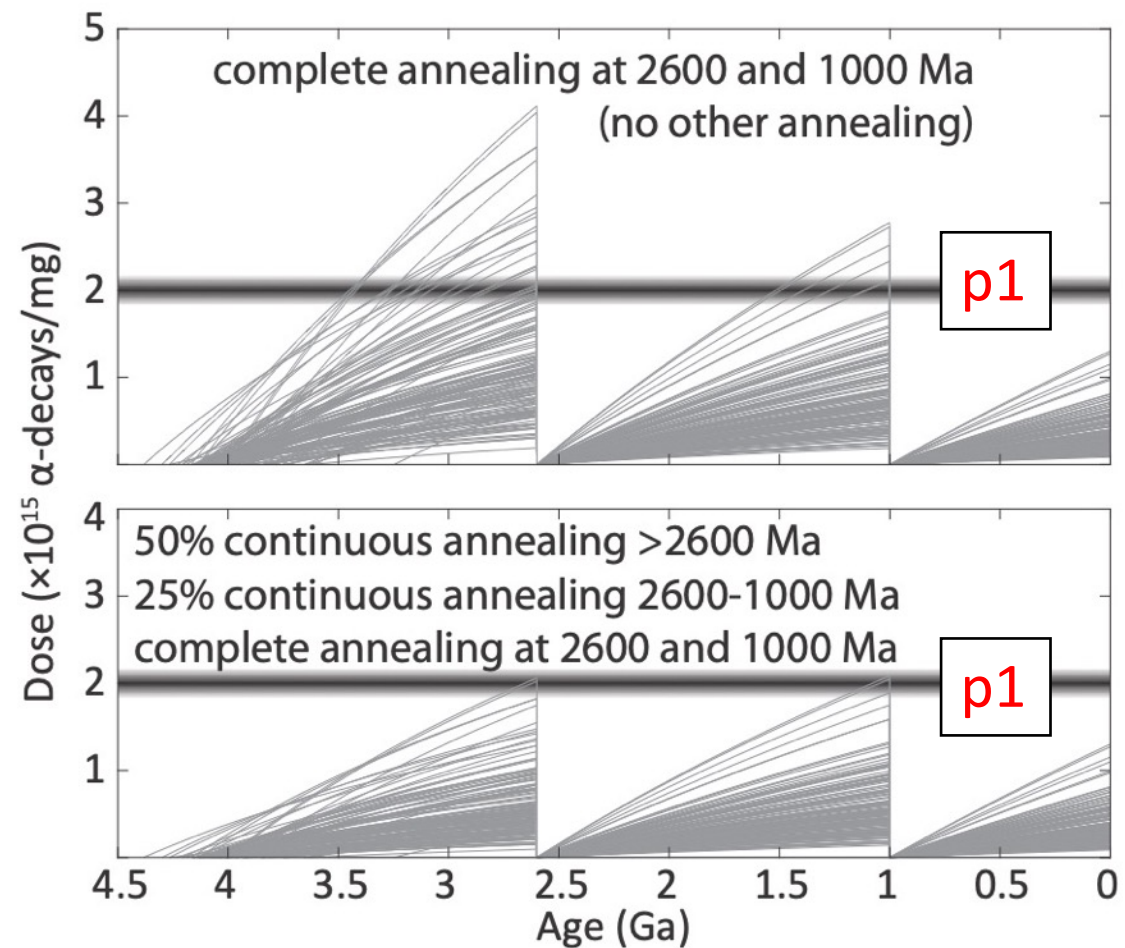
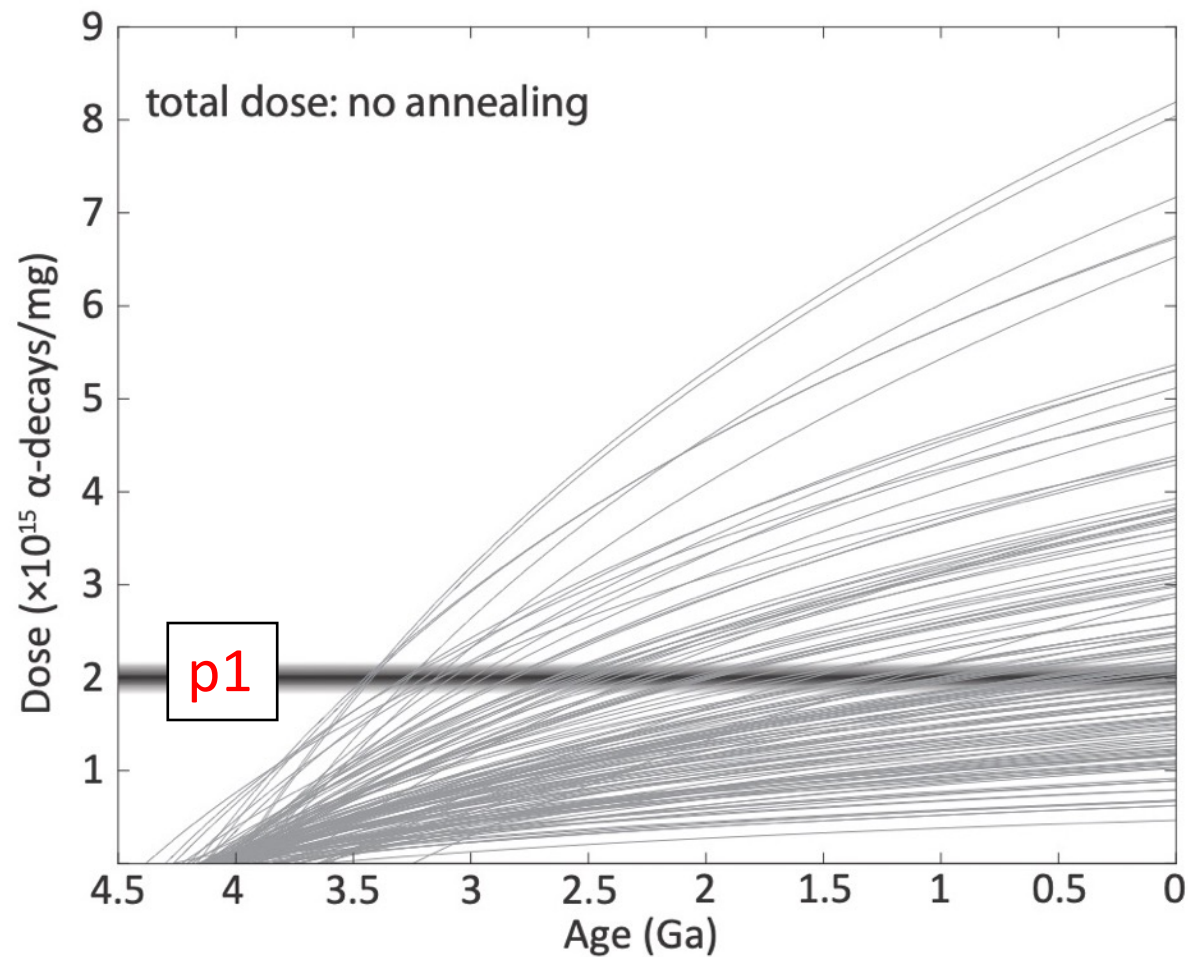
Not hydrous.



Cameron et al., 2020

Valley et al. 2019 GSA

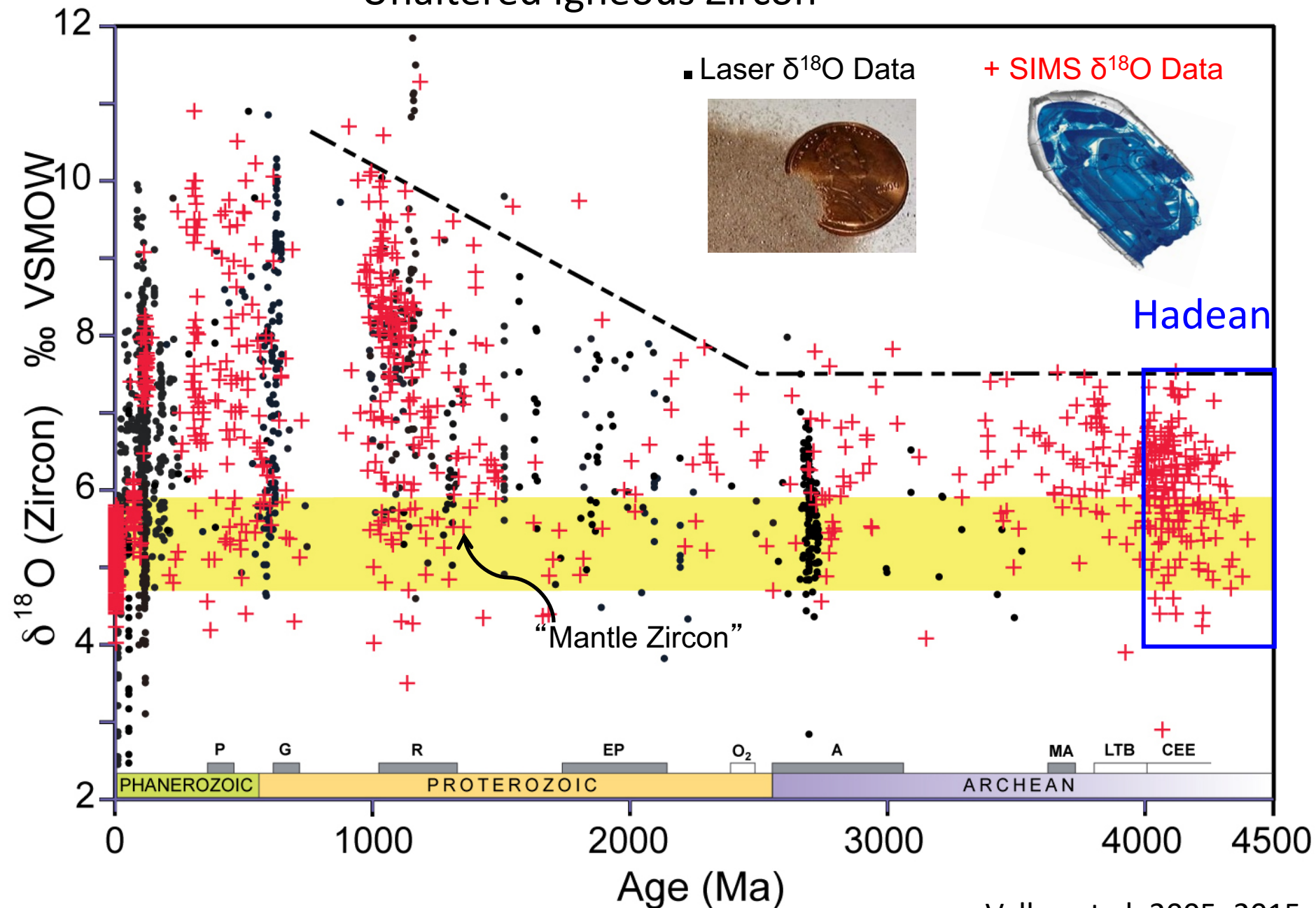
Did these Hadean zircons ever exceed the first percolation point?





Cavosie et al. 2004, 2005, 2006

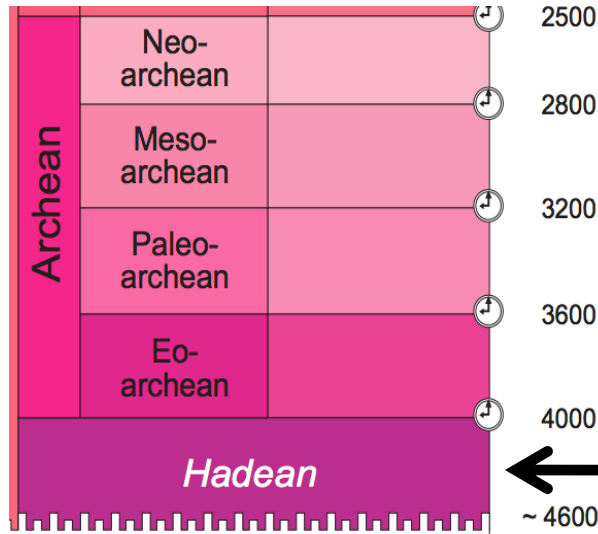
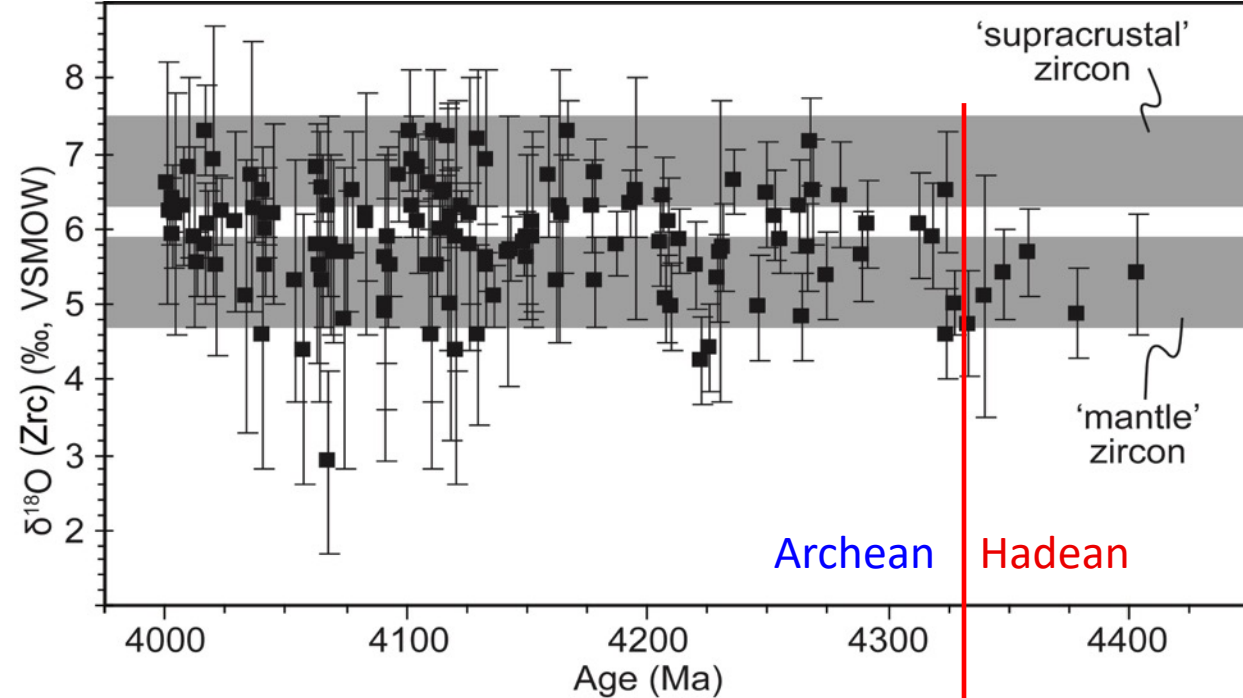
Unaltered Igneous Zircon



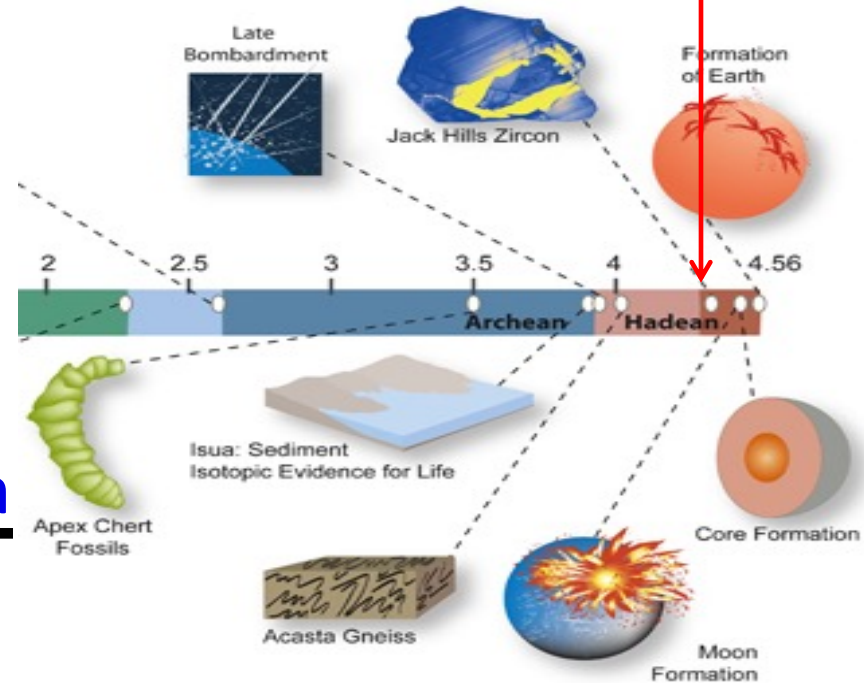
Valley et al. 2019 GSA

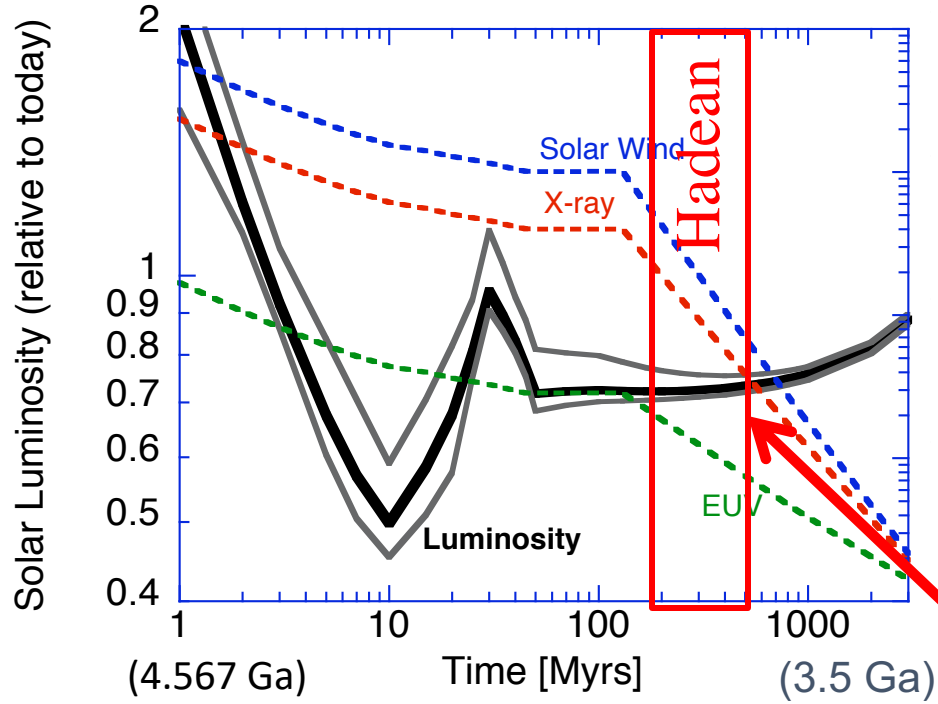
Valley et al. 2005, 2015

When was the end of the Hadean Eon?



↓
Archean
← Hadean



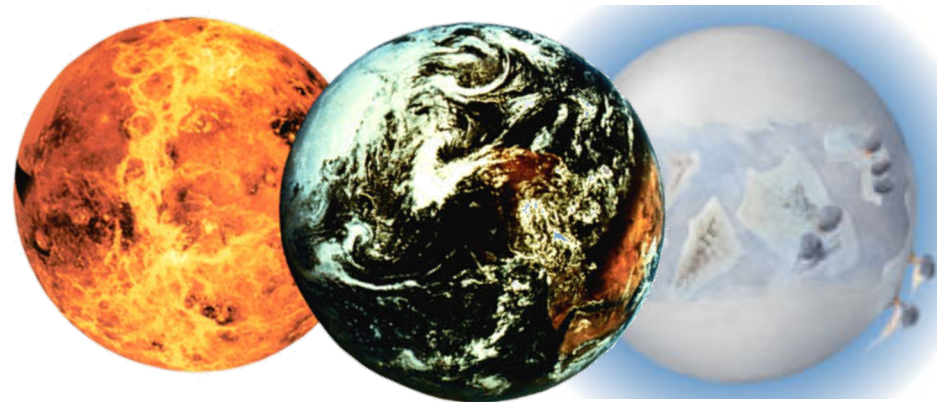


Zahnle 2006



Faint Young Sun
~70% luminosity @ 4.4-4.0 Ga

Hadean vs. Snowball Earth?

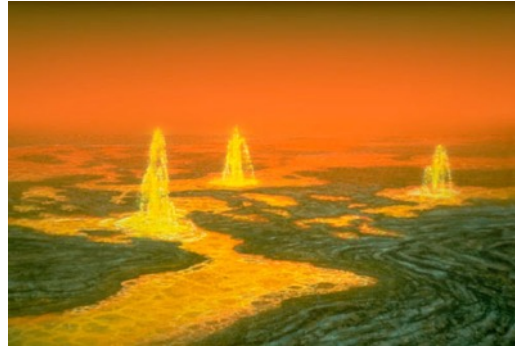


What Destroyed Pre-4 Ga Rocks?

Melting ?

Meteorite Impact ?

Subduction/ Mantle Overturn ?



Don Dixon

But,
the zircons survived.

Weathering ?

~50°C +

CO₂-rich atmosphere

= Acid Sauna

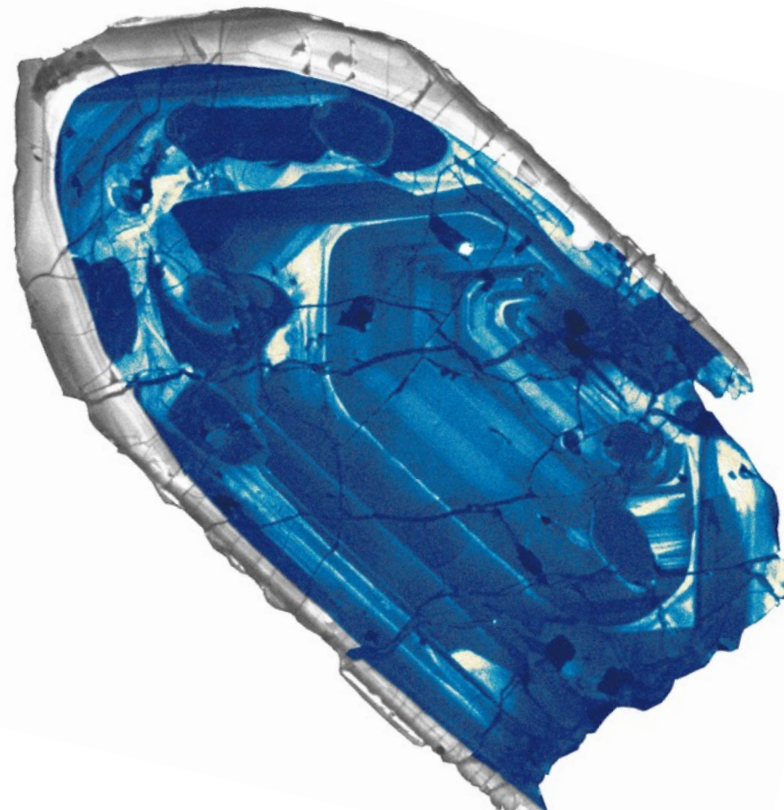




Feb. 19, 2014

IAN GAVAN/GETTY IMAGES

Beyoncé wore a glittering blue Vrettos Vrettakos gown that featured 400,000 blue zircon crystals.



nature
geoscience

LETTERS

PUBLISHED ONLINE: 23 FEBRUARY 2014 | DOI: 10.1038/NGEO2075

Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography

John W. Valley^{1*}, Aaron J. Cavosie^{1,2}, Takayuki Ushikubo¹, David A. Reinhard³, Daniel F. Lawrence³, David J. Larson³, Peter H. Clifton³, Thomas F. Kelly³, Simon A. Wilde⁴, Desmond E. Moser⁵ and Michael J. Spicuzza¹

Feb. 23, 2014

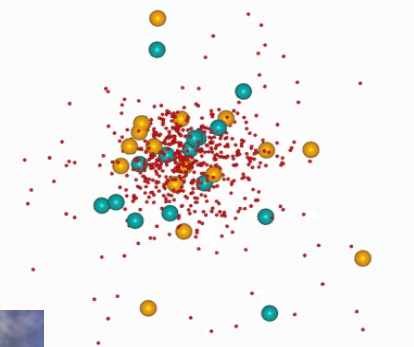
Valley et al. 2019 GSA



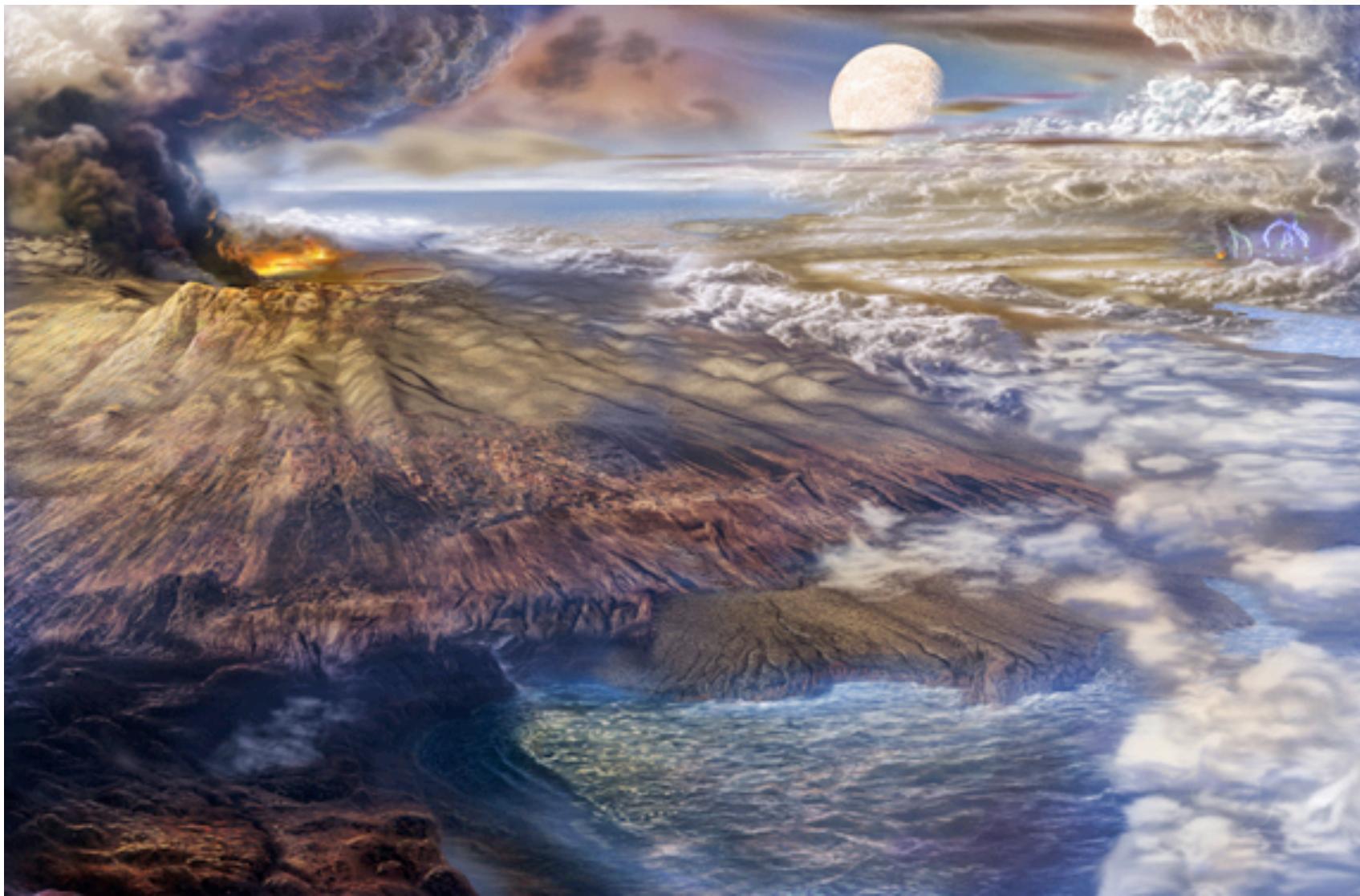


Cool Early Earth

4.4 Ga Protocontinental Crust
>4.3 Ga End of Hadean, Oceans, Life?



^{206}Pb ●
 ^{207}Pb ●



Earth
4.3 Ga

Valley et al. 2019 GSA

Don Dixon

