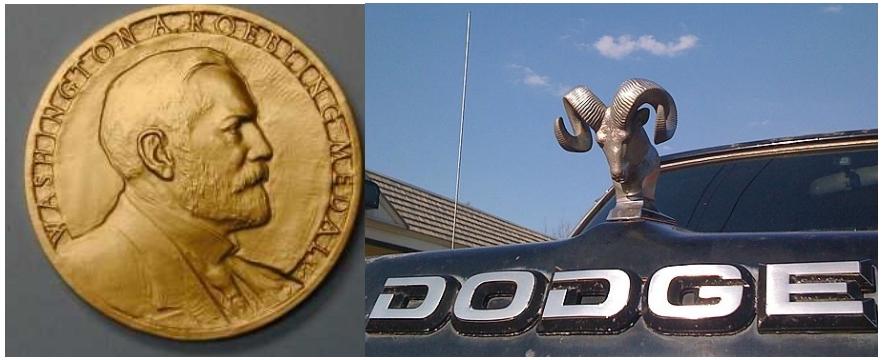
Microanalysis of Oxygen Isotope Ratios I: My Favorite Minerals

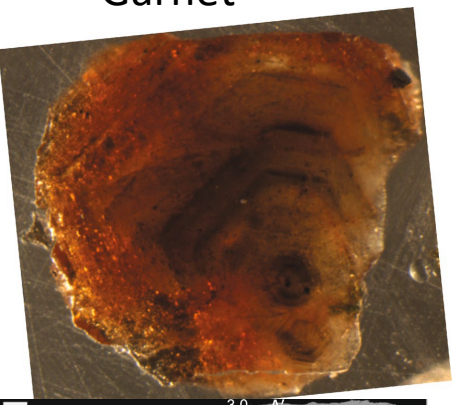
John Valley

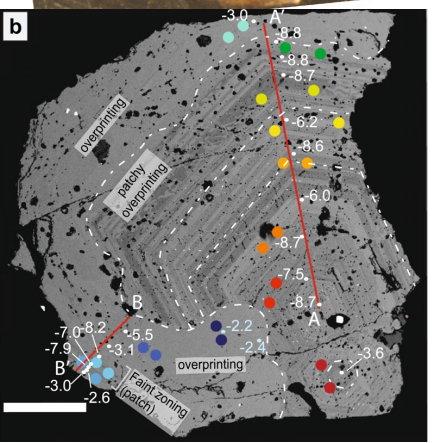
and *MANY* others

University of Wisconsin- Madison

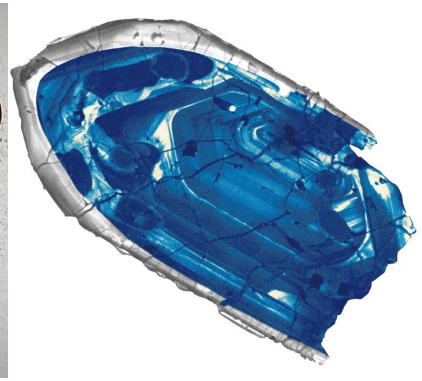


Garnet



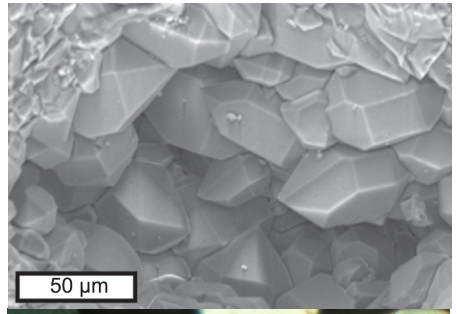


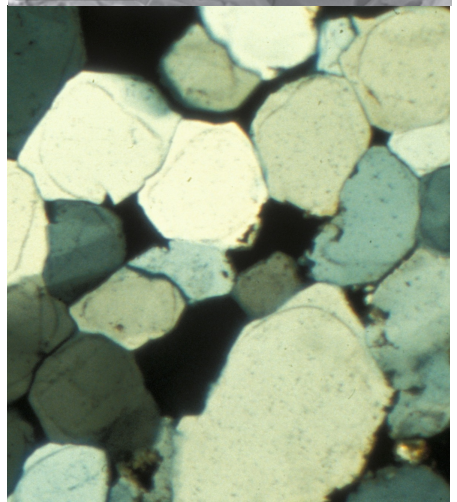
Zircon



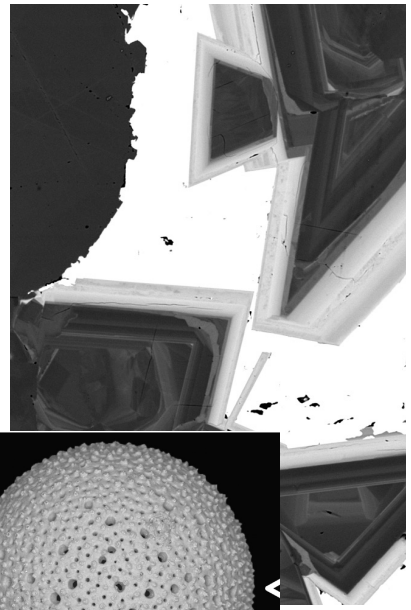
WiscSIMS is funded by
NSF-EAR as a National Facility

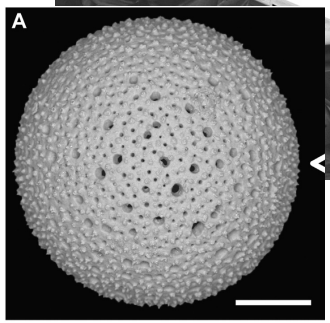
Quartz





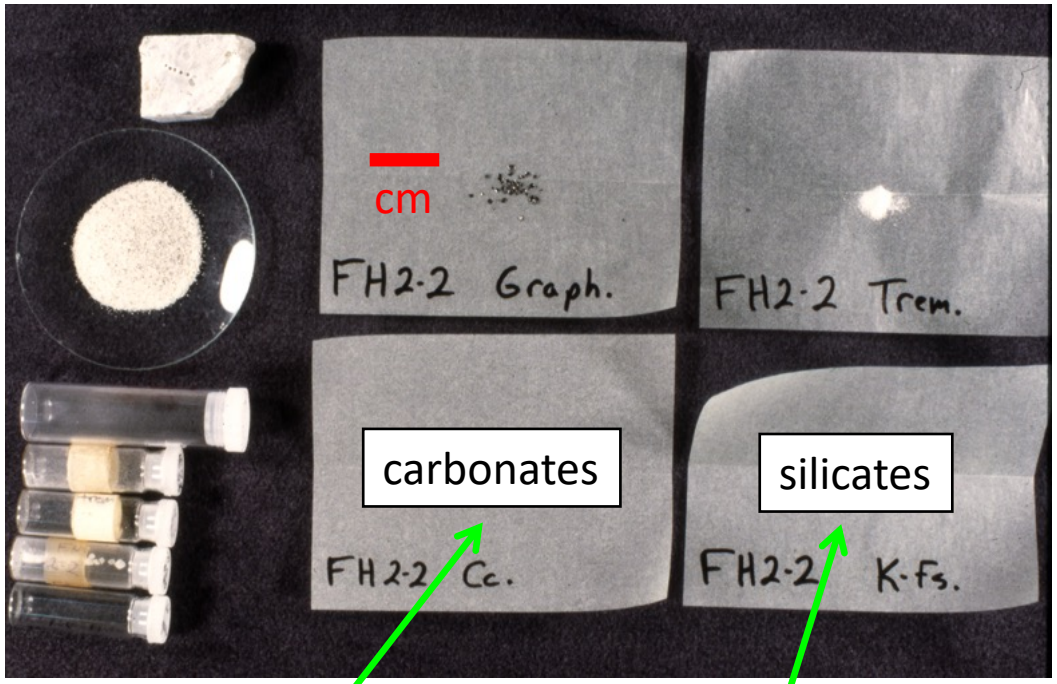
II: Carbonates (Yesterday)





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

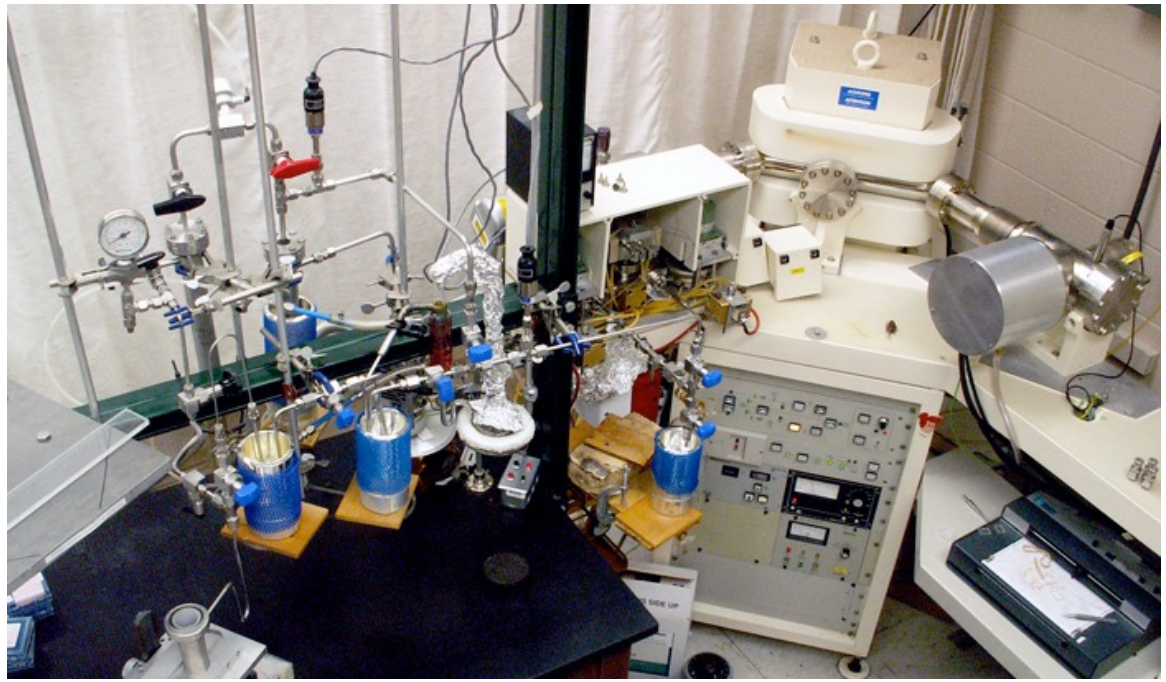
Powders & chips
mm- to cm-scale



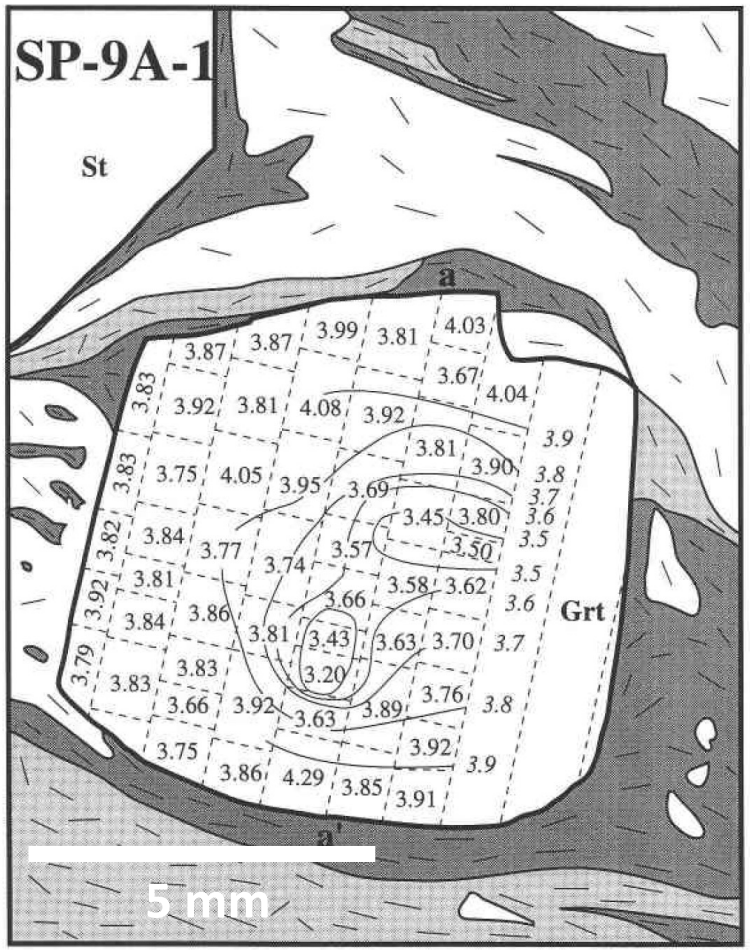
Acid extraction
10^{-2} - 10^{-5} g

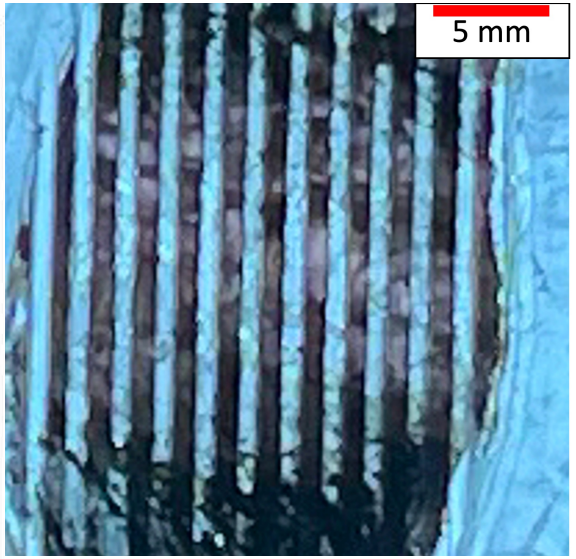
Fluorination
10^{-2} - 10^{-3} g

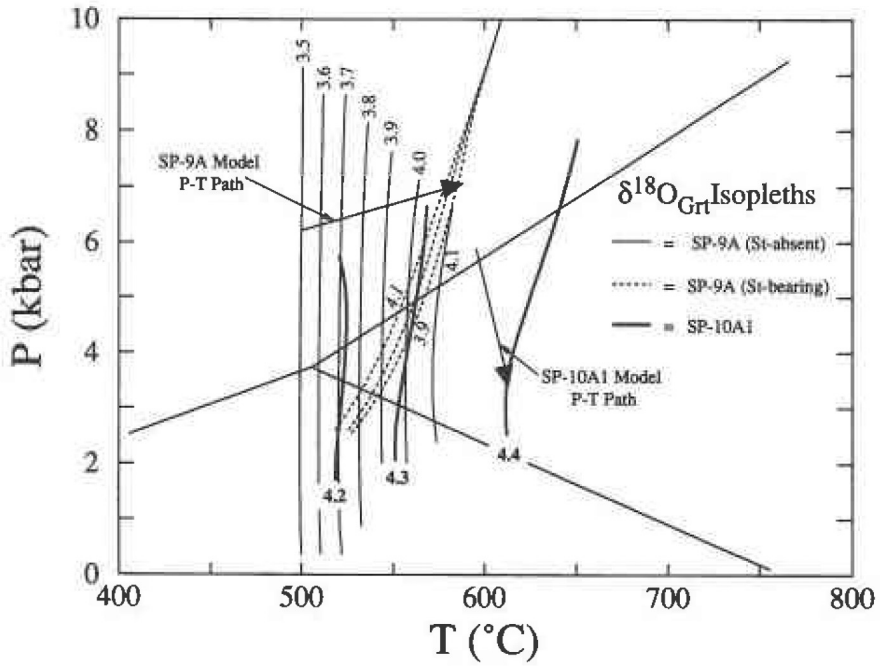
Gas-source mass spectrometer (GSMS)



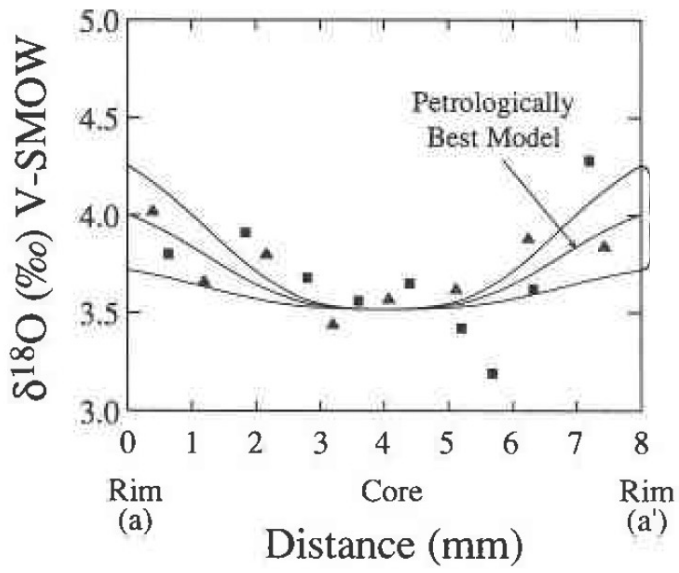
Zoned Garnets pre-SIMS





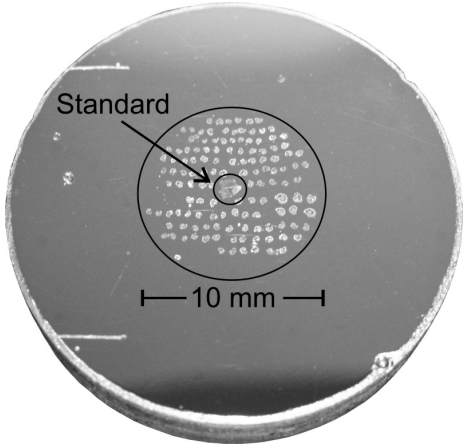


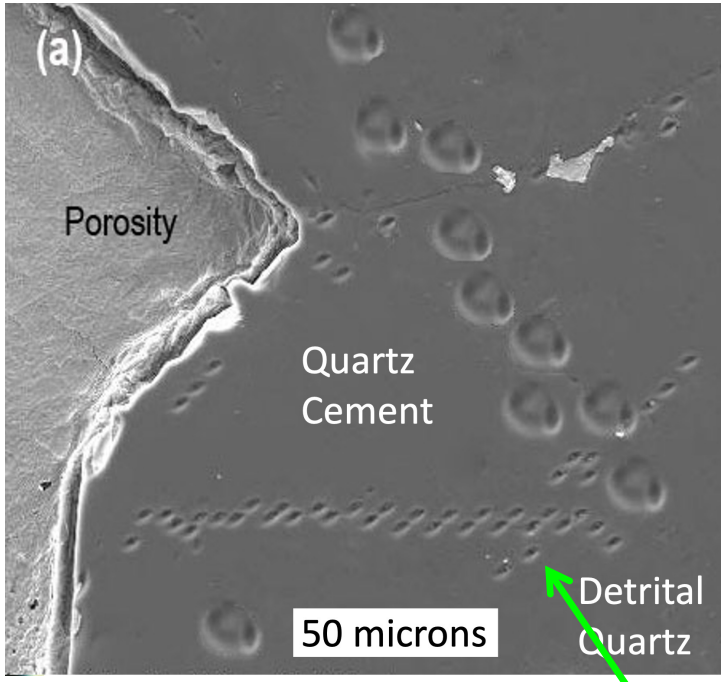
(B)



Kohn et al. 1993

SIMS





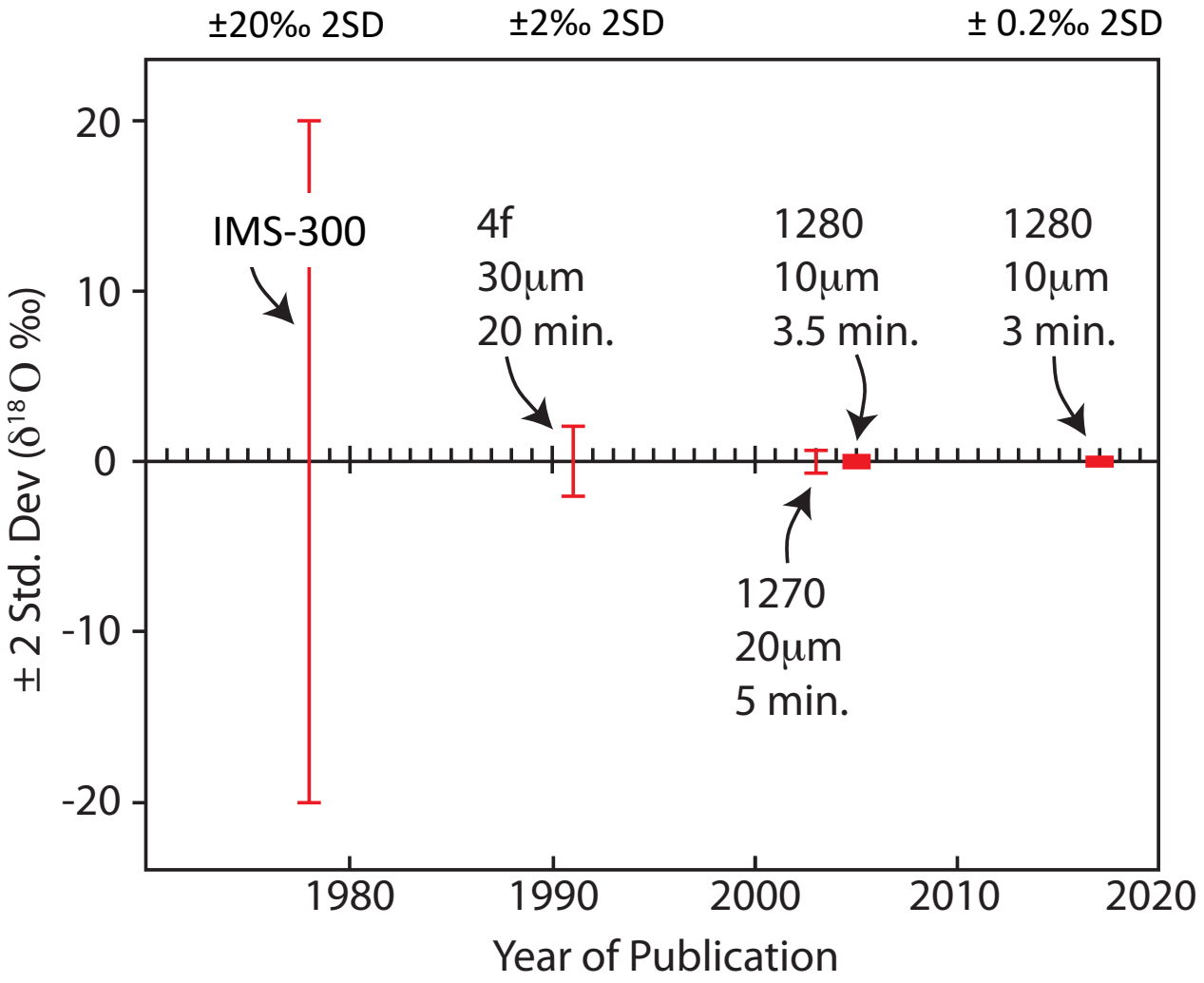
In situ analysis
1-10 micrometer spot
10^{-9} - 10^{-12} g

Million to billion times smaller
Spatially resolved

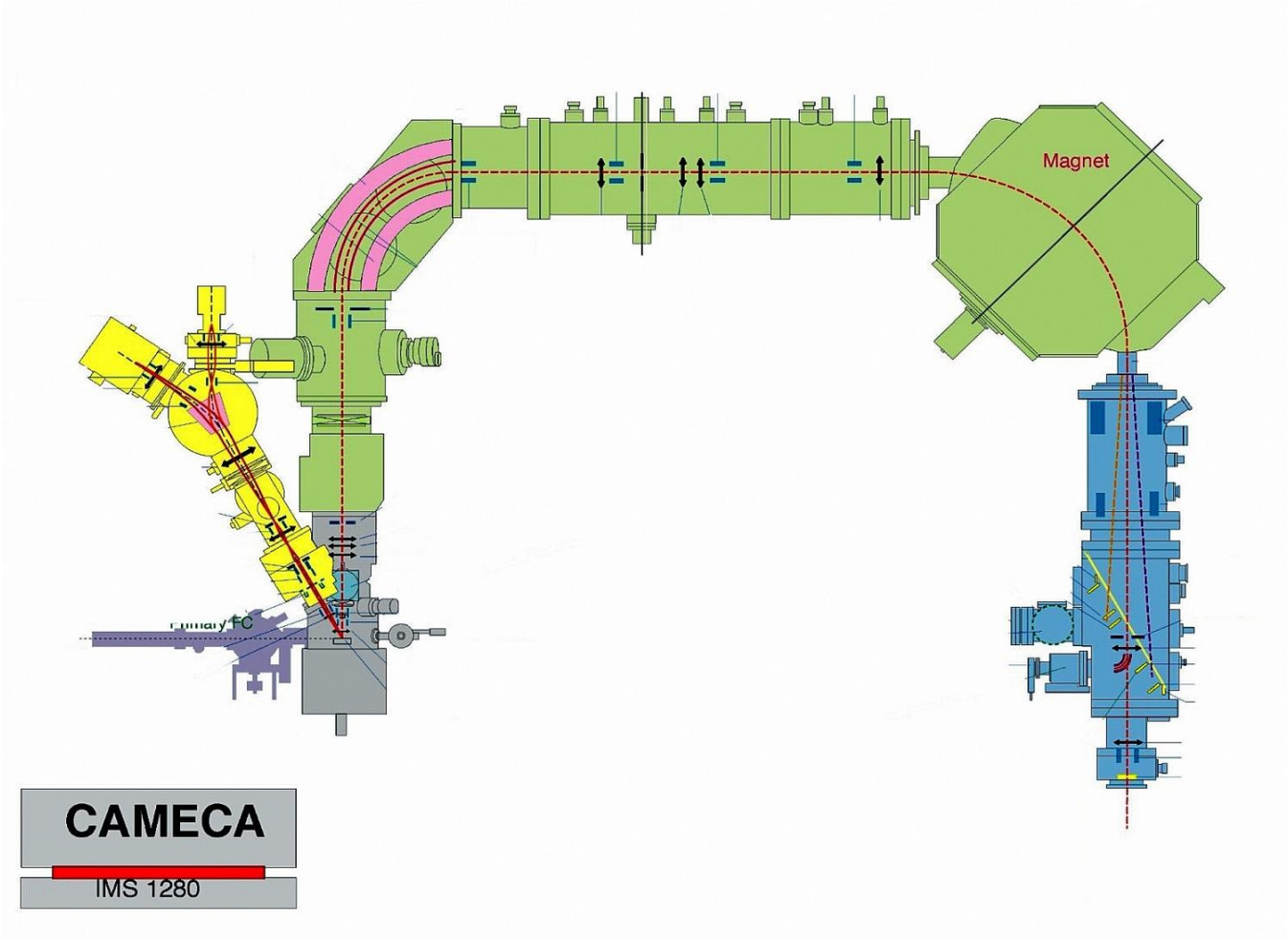
Oxygen Isotope Analysis by SIMS

40 years of Improvement

Analytical Precision
Spot size
Speed
Reliability
Accuracy



Giletti et al. 1978
Valley & Graham 1991
Cavosie et al. 2003, 2005
Tenner, Kita et al. 2017



Quality of Data

Instrument: analysis protocol & tuning

Trade-off: spot size vs. precision

Sample Preparation:

Polishing relief; Flat surface; Voids; X-Y effects

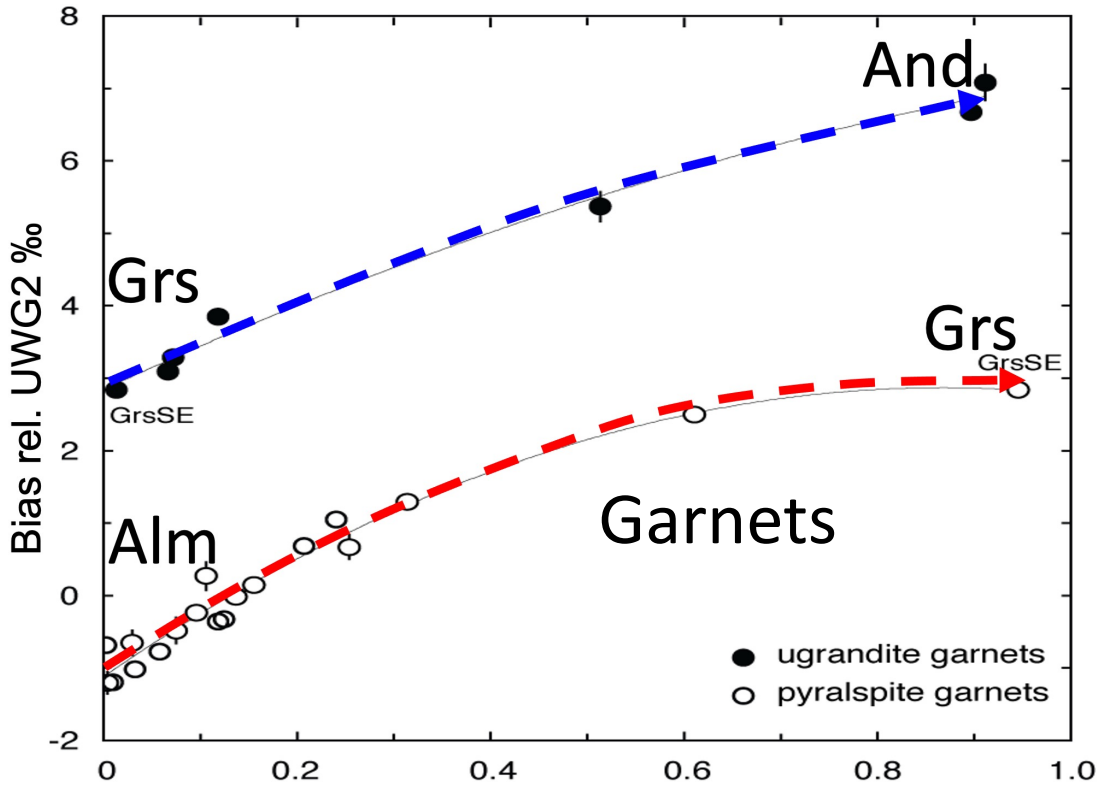
Correlate data and images, QGIS

Standards:

chemical and crystallographic match; solid solution

WiscSIMS has more than 100 standard SIMS mounts that are used in analysis

Garnets: Matrix effects of a mineral with solid solution

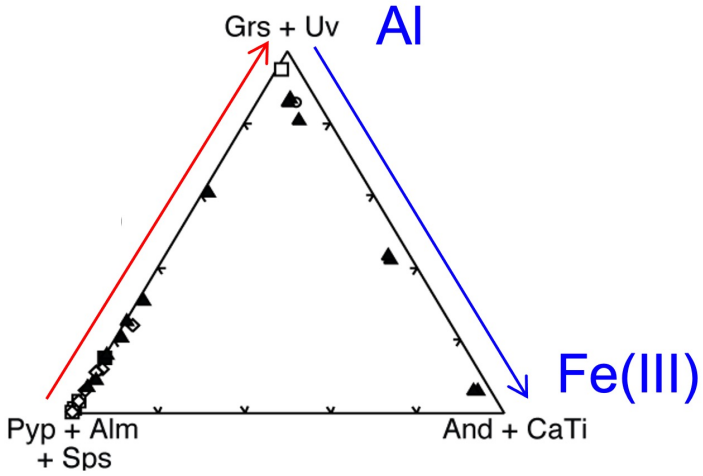


25 garnet standards

Page et al. 2010

49 garnet standards Fe^{2+}, Mg, Mn, Cr

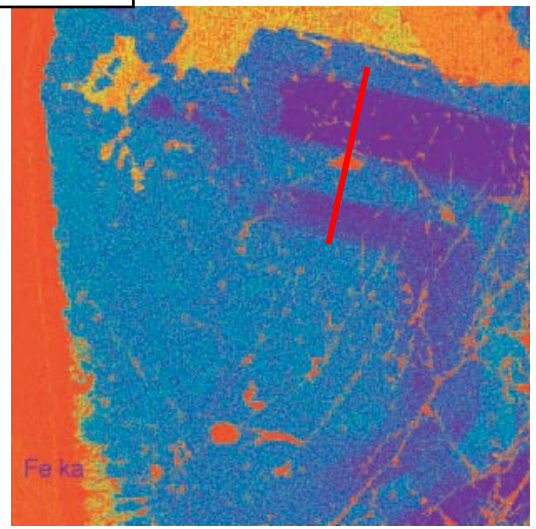
Kitajima et al. 2016



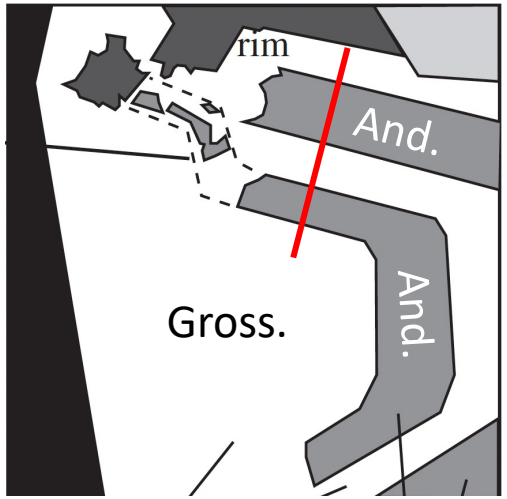
Garnets

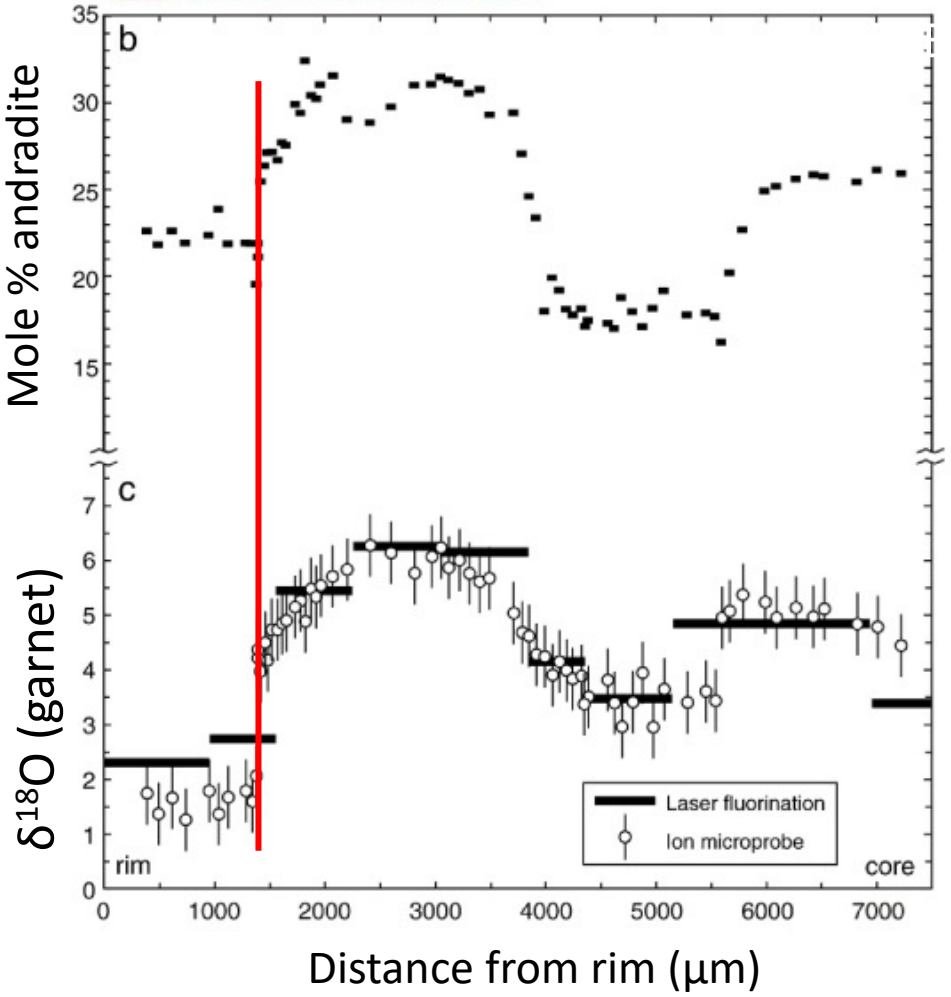
Poly-metamorphic Garnet, Willsboro, NY

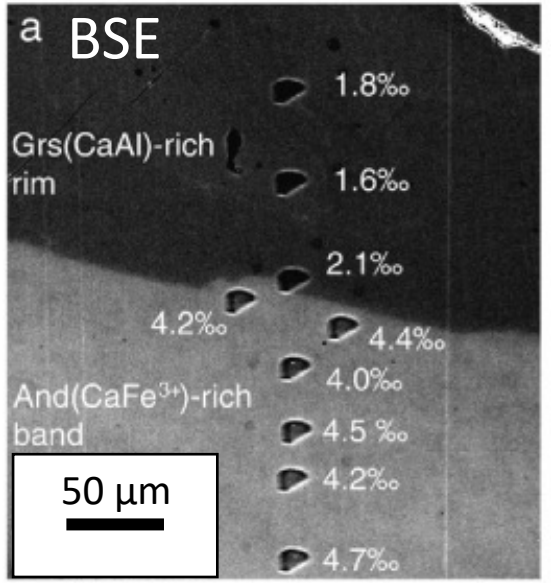
Fe Kα

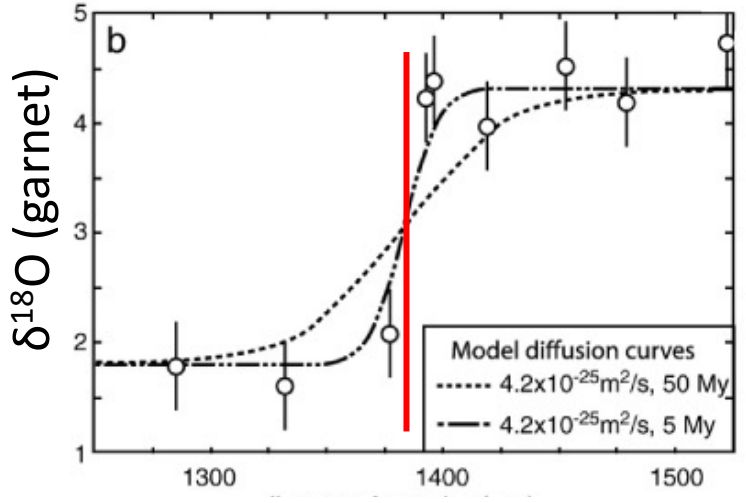


3 mm





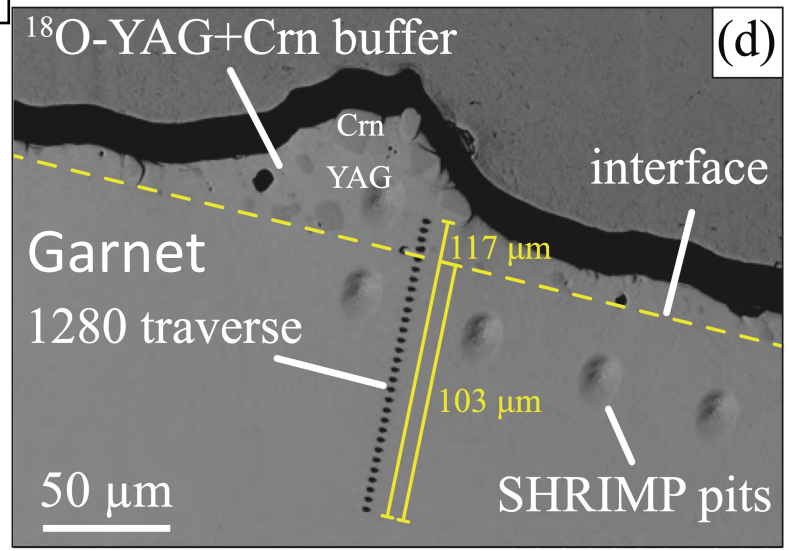


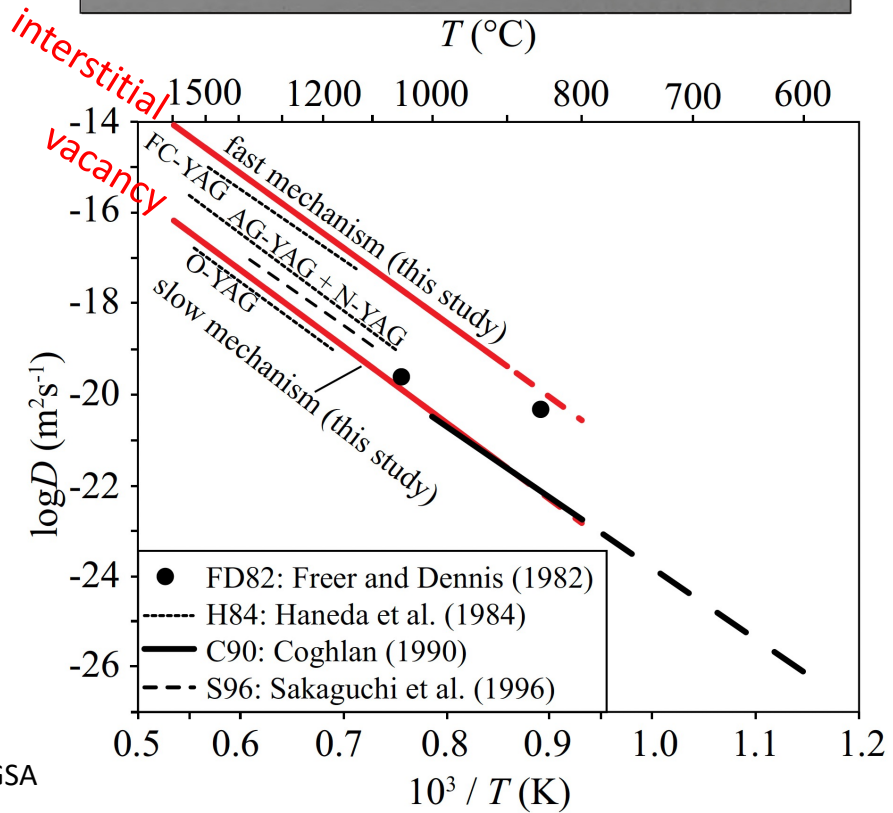


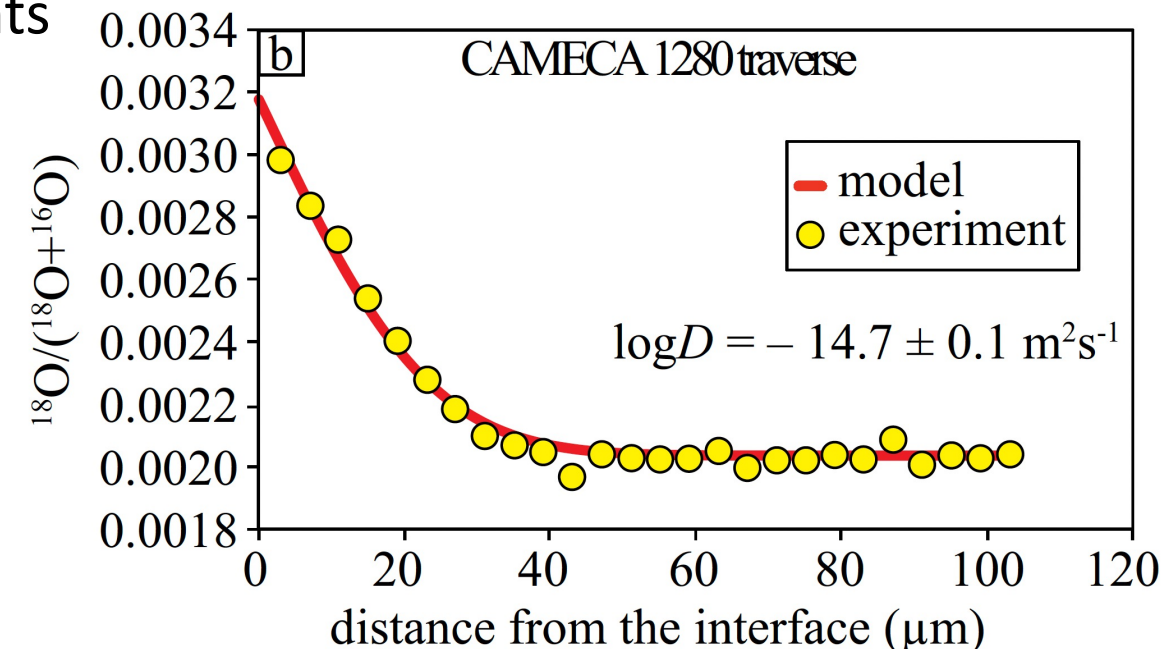
Page et al. 2010
Clechenko & Valley 2003

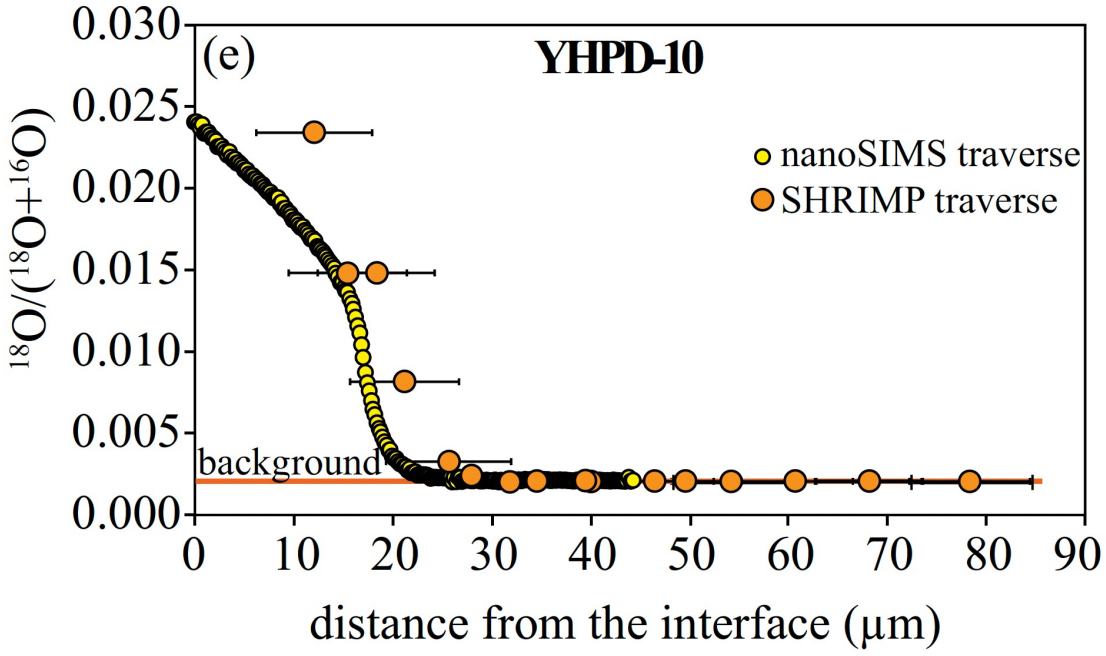
Garnets

Oxygen Diffusion in Garnets, Experiments







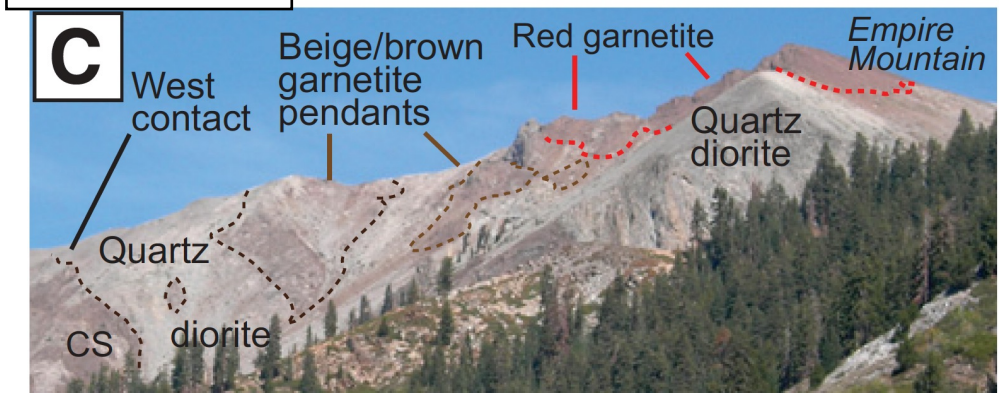


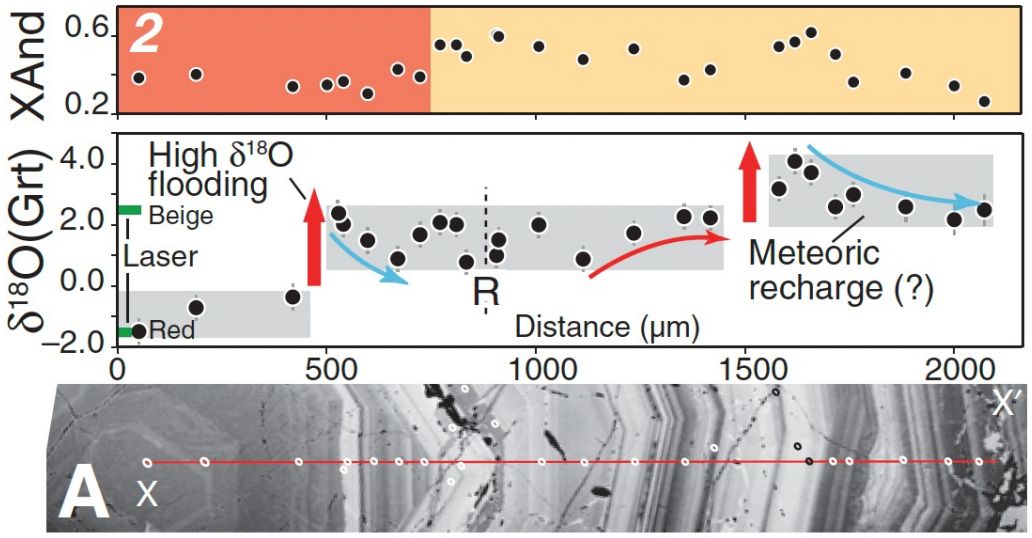
Valley 2022 GSA

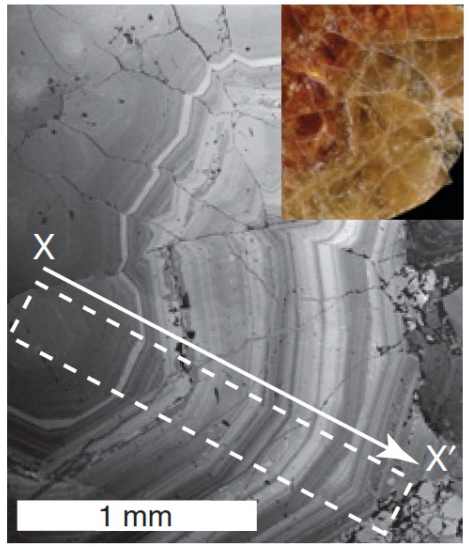
Scicchitano et al. 2022, Am. Min.

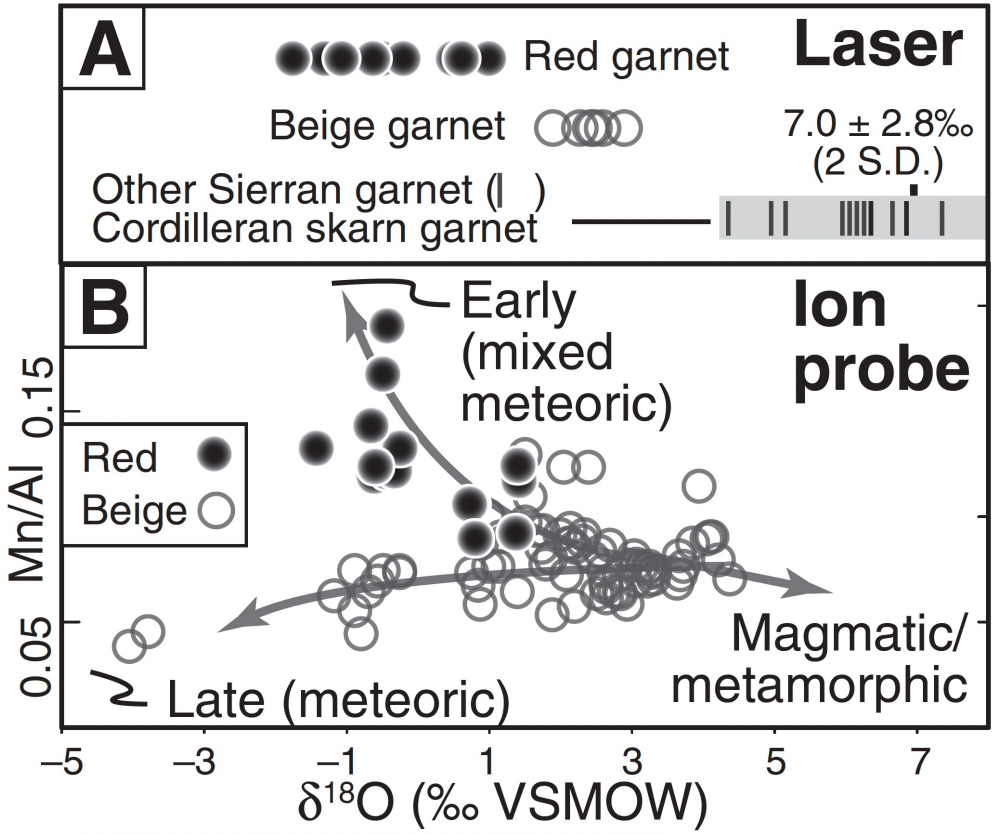
Garnets

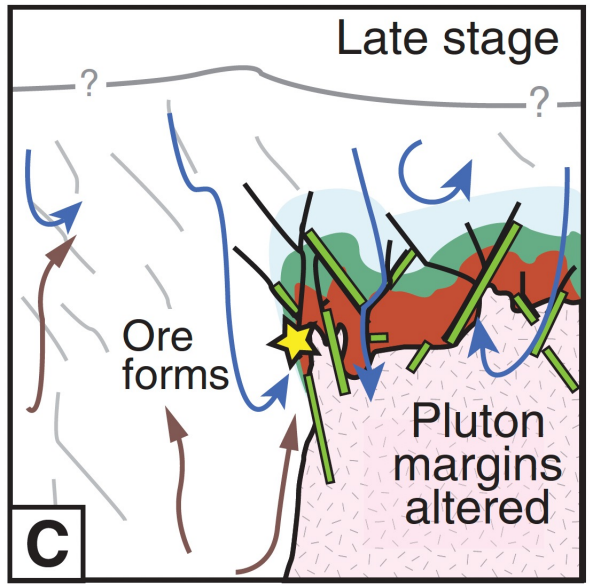
Garnet Skarn, Empire Mtn, Sierra Nevada









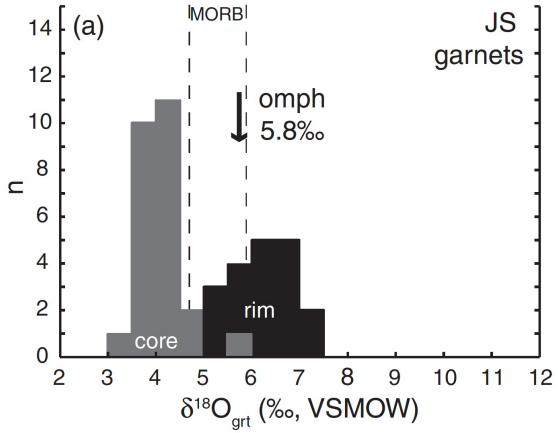


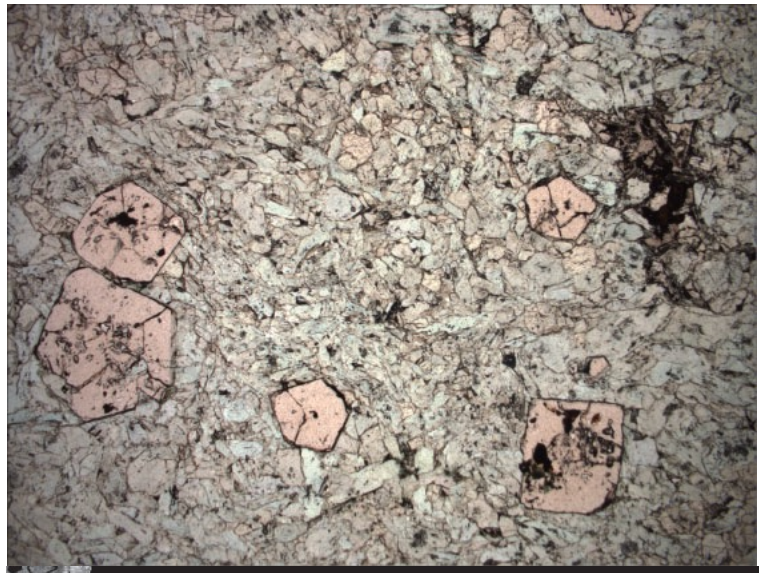
D'Errico et al. 2012

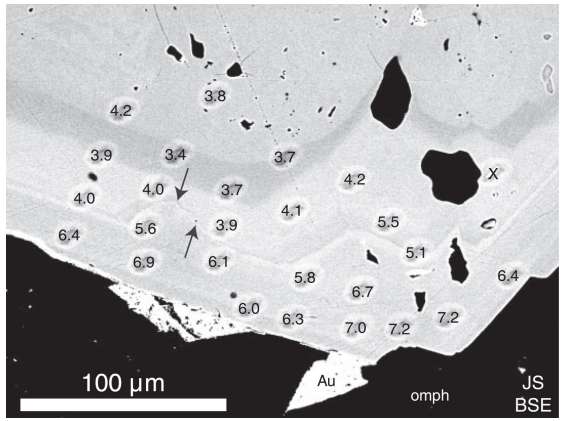
Valley 2022 GSA

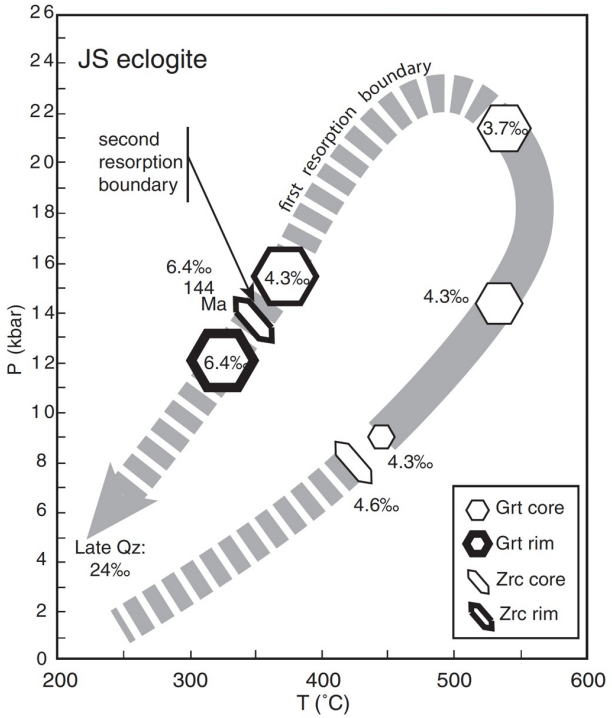
Garnets

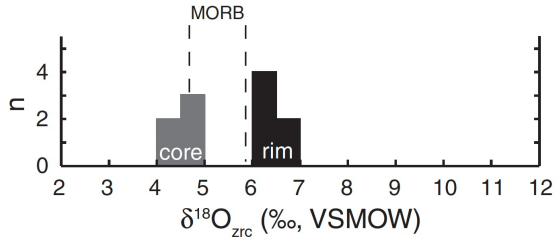
Junction School eclogite, Franciscan Complex

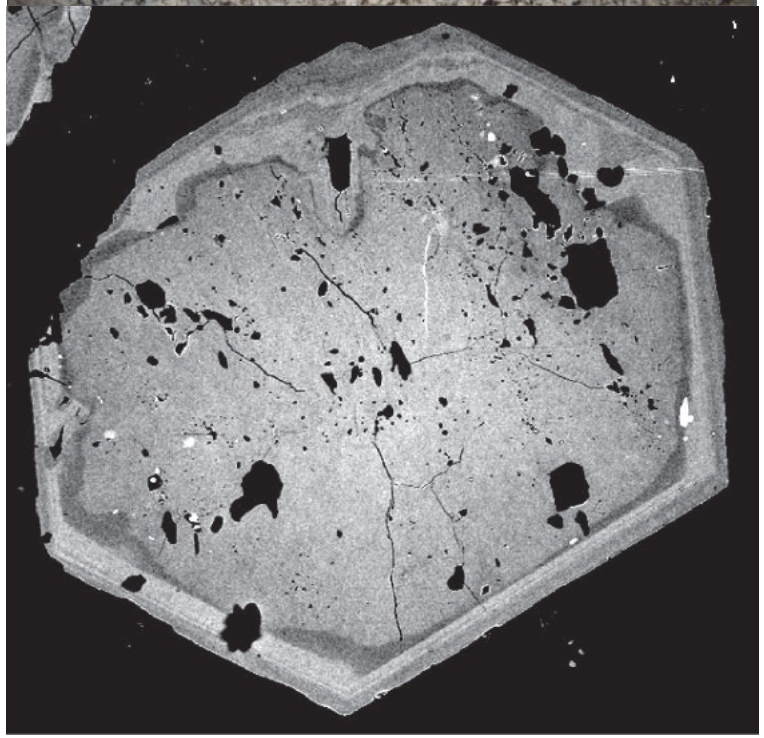


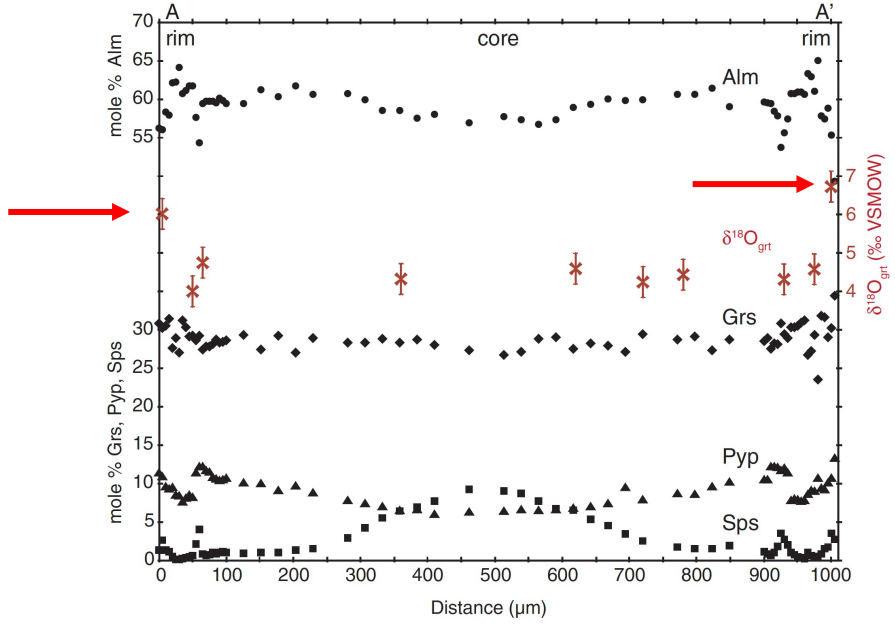








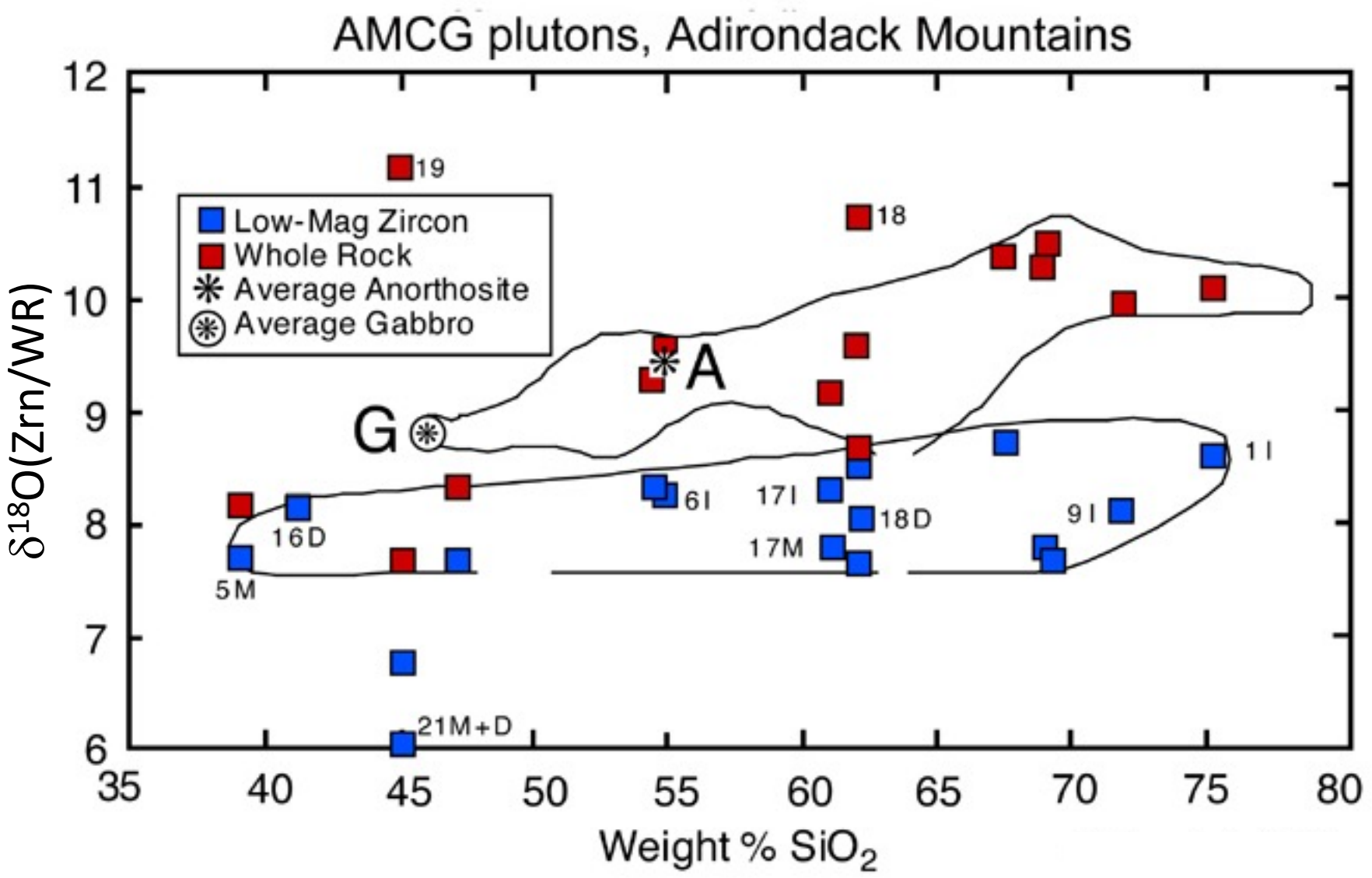




Page et al. 2014

Valley 2022 GSA

Zircons



AMCG
Anorthosite
Mangerite
Charnockite
Granite
~1155 Ma

U-Pb concordant zircons yield consistent $\delta^{18}O$ values

Radiation damaged, magnetic zircons have altered $\delta^{18}O$

Unaltered zircon has slow O diffusion, <=Pb

$\Delta^{18}O$(Zrn-Gt) ~ 0‰

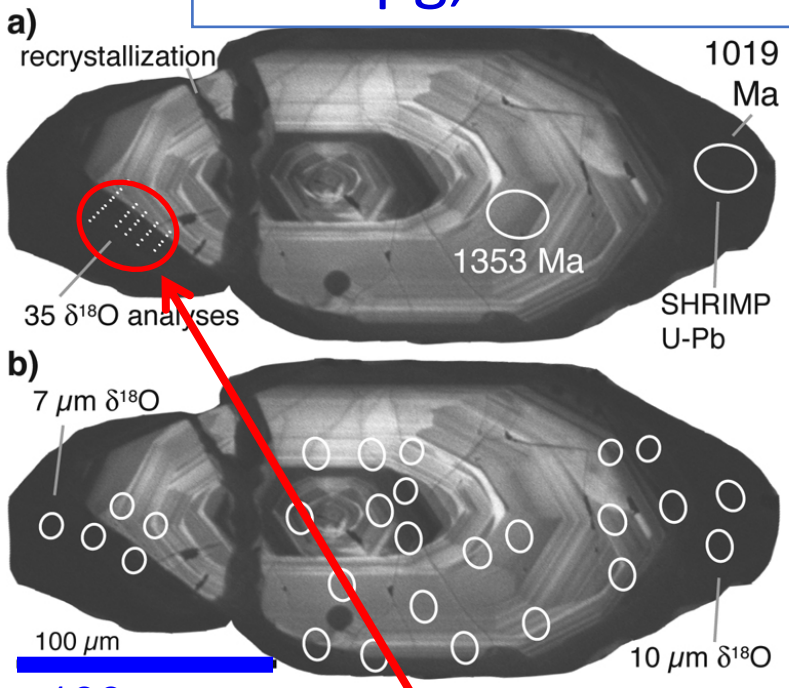
High $\delta^{18}O$ anorthosites in Adirondacks are magmatic

Valley et al. 1994

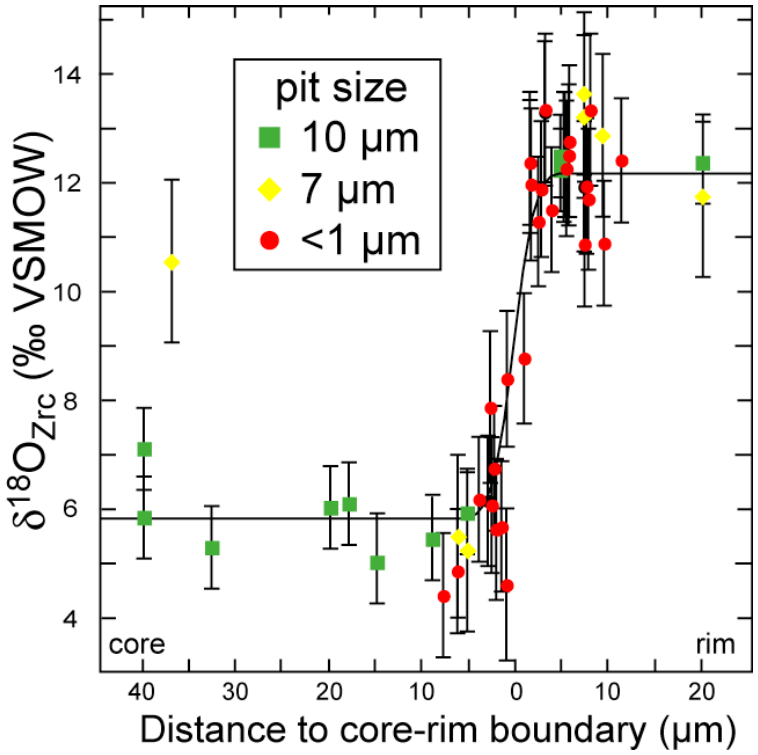
Zircons

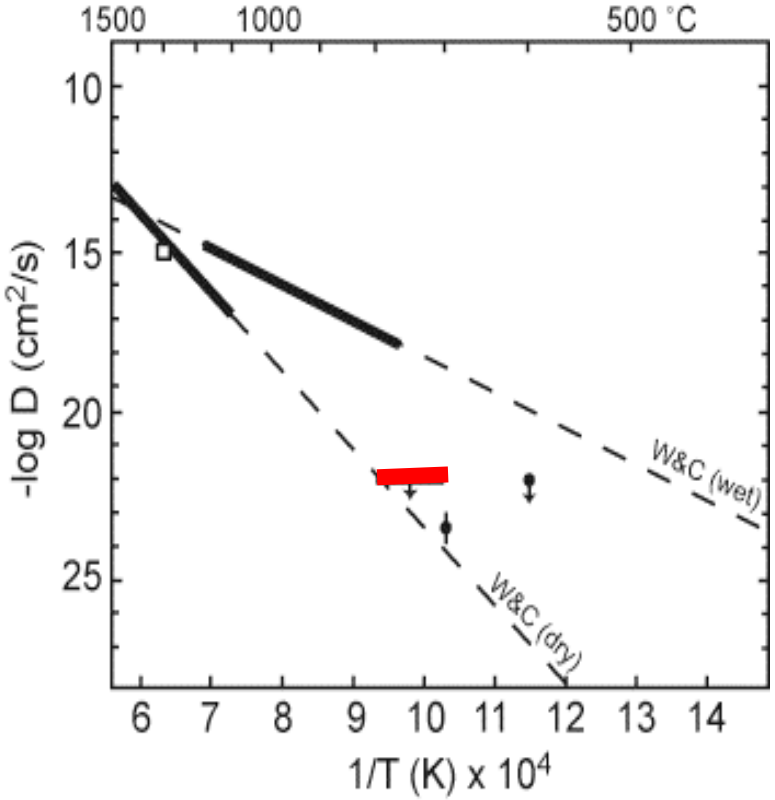
$\delta^{18}O$ sub 1-µm spot

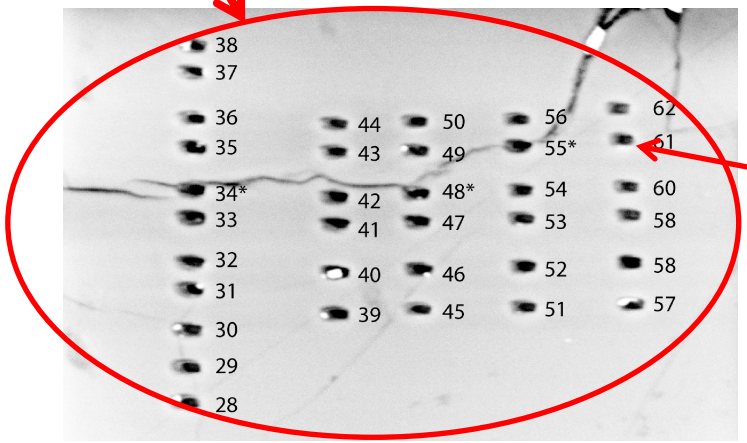
~ 1 pg, 2 SD = 2 ‰

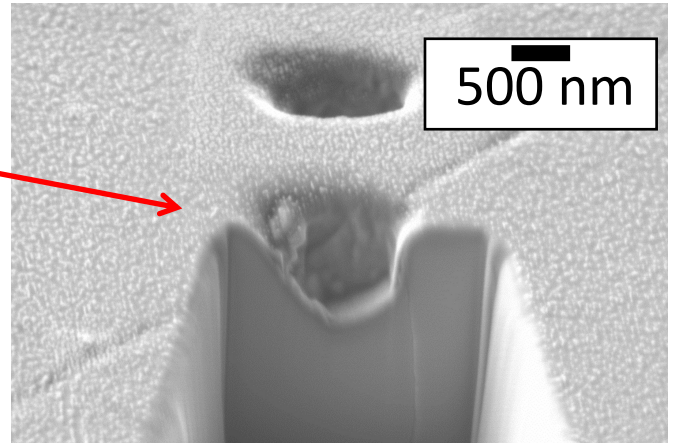


100 µm





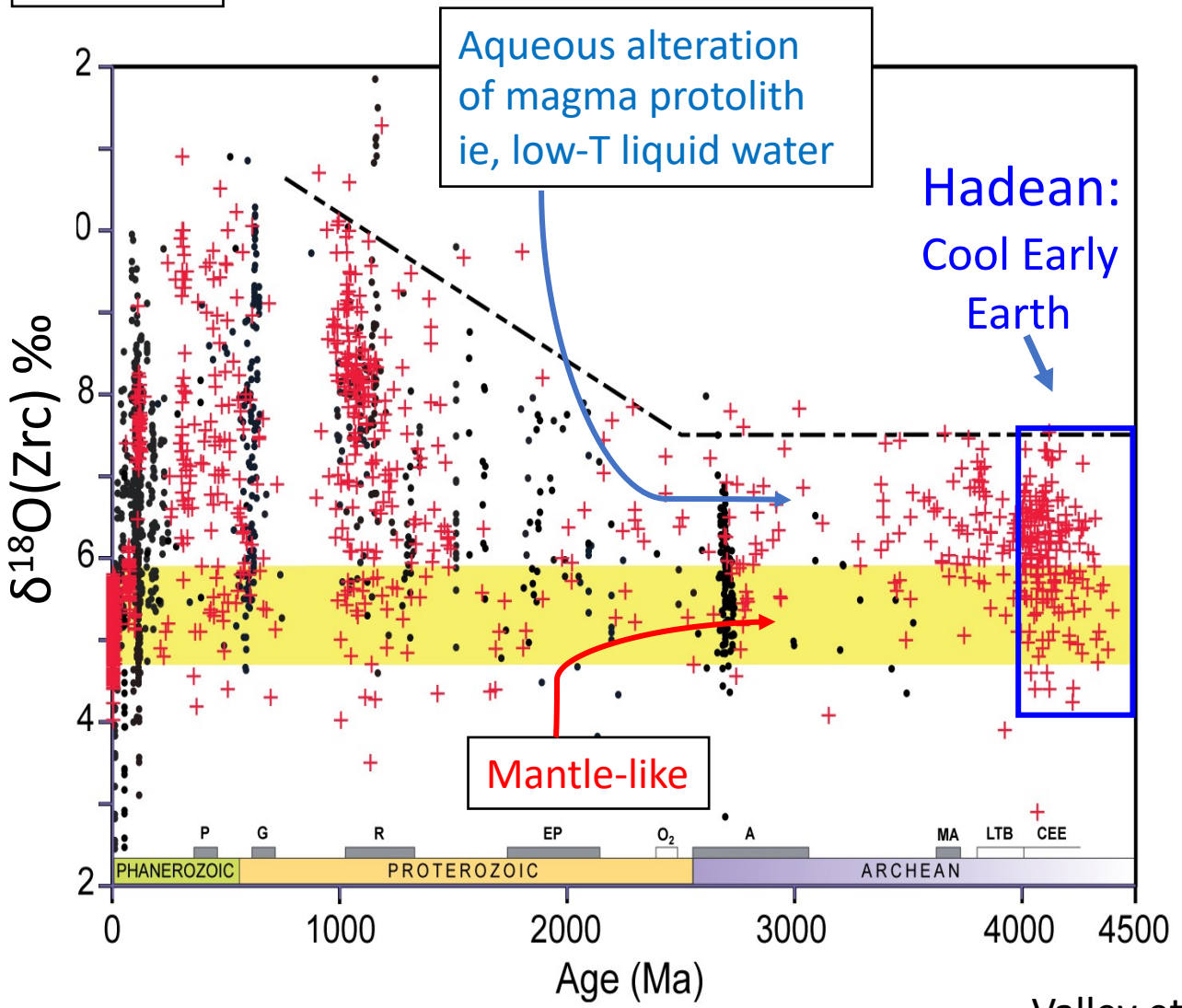




Page et al. 2007
Bowman et al. 2011

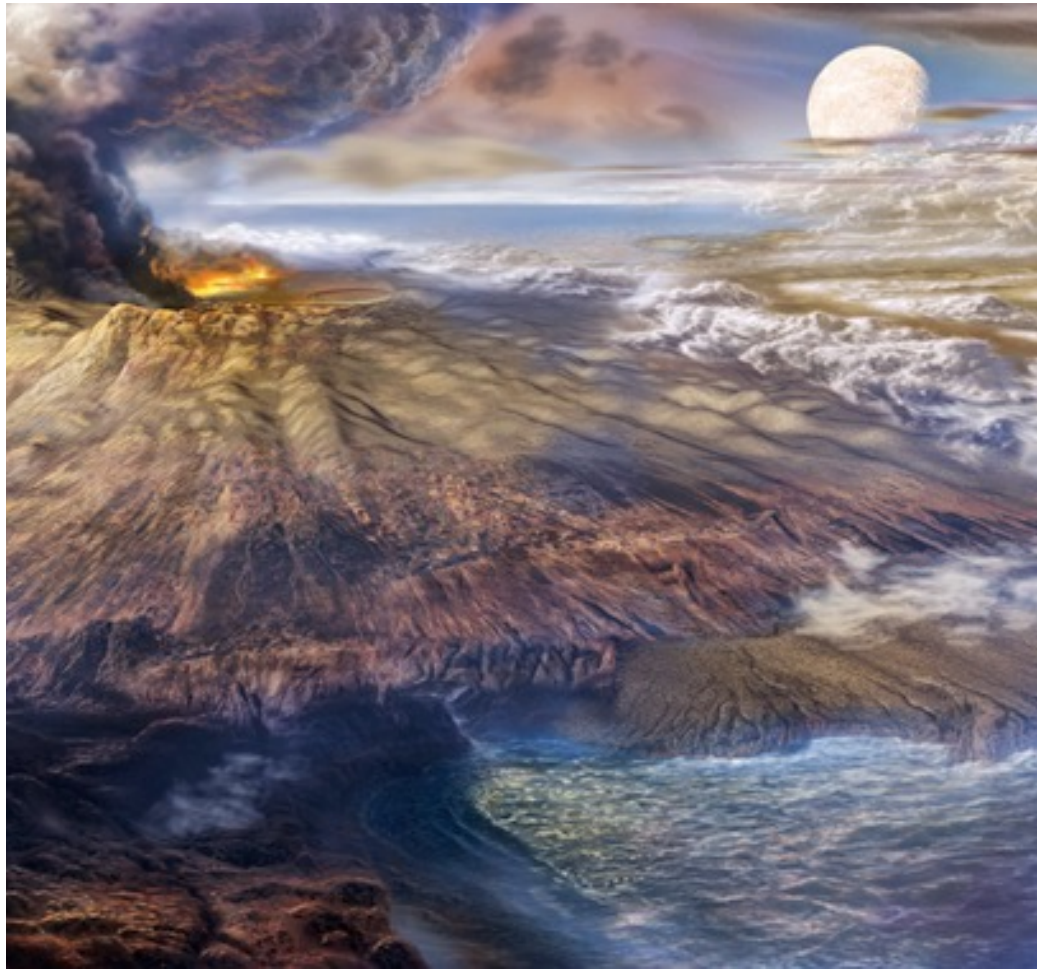
Zircons

Unaltered Igneous Zircon



Valley et al.
2005, 2015

Cool Early Earth, Oceans at 4.3 Ga.



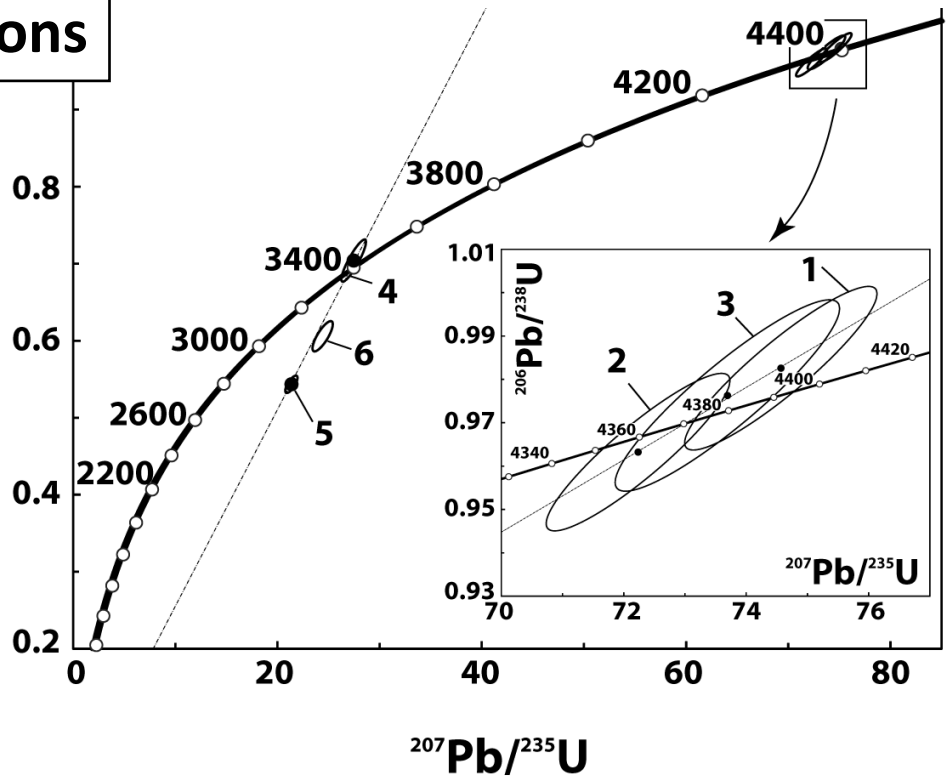
Valley 2005

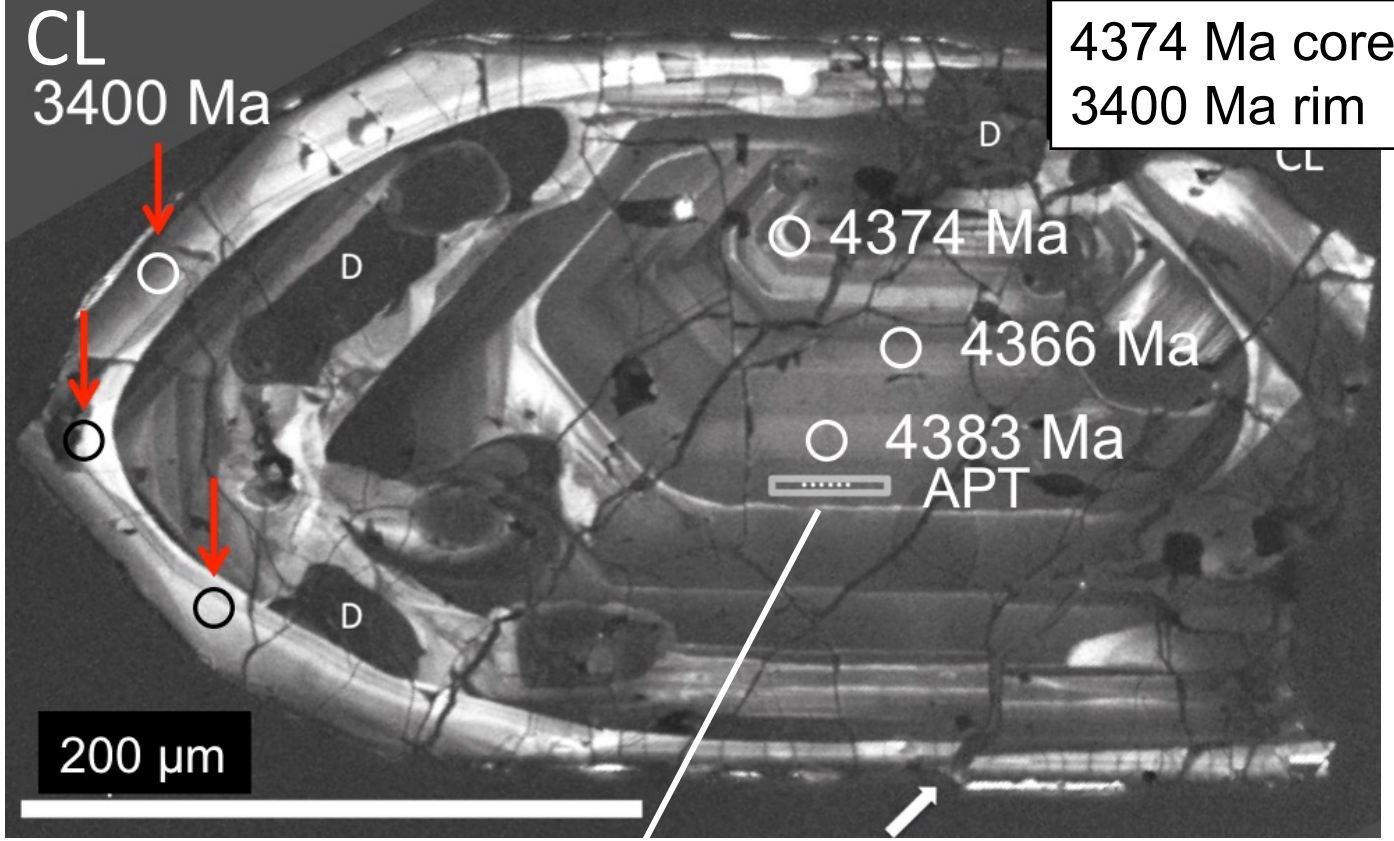
Laser $\delta^{18}O$ Data, 1 data point/rock
~2mg, low-Mag, HF

\+ SIMS $\delta^{18}O$ Data, 1 data point/zircon
~2ng, CL, OH/O, Age-concordant

Wisc SIMS

Zircons





APT: Archean/Hadean zircons

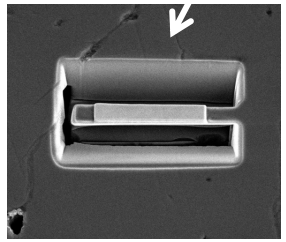
Pb mobility < 50 nm
- Linked to radiation damage

Compositions reintegrated by SIMS
- SIMS ages are accurate

Clusters date reheating events

Confirms 4.4 Ga zircon from Jack Hills

FIB-APT

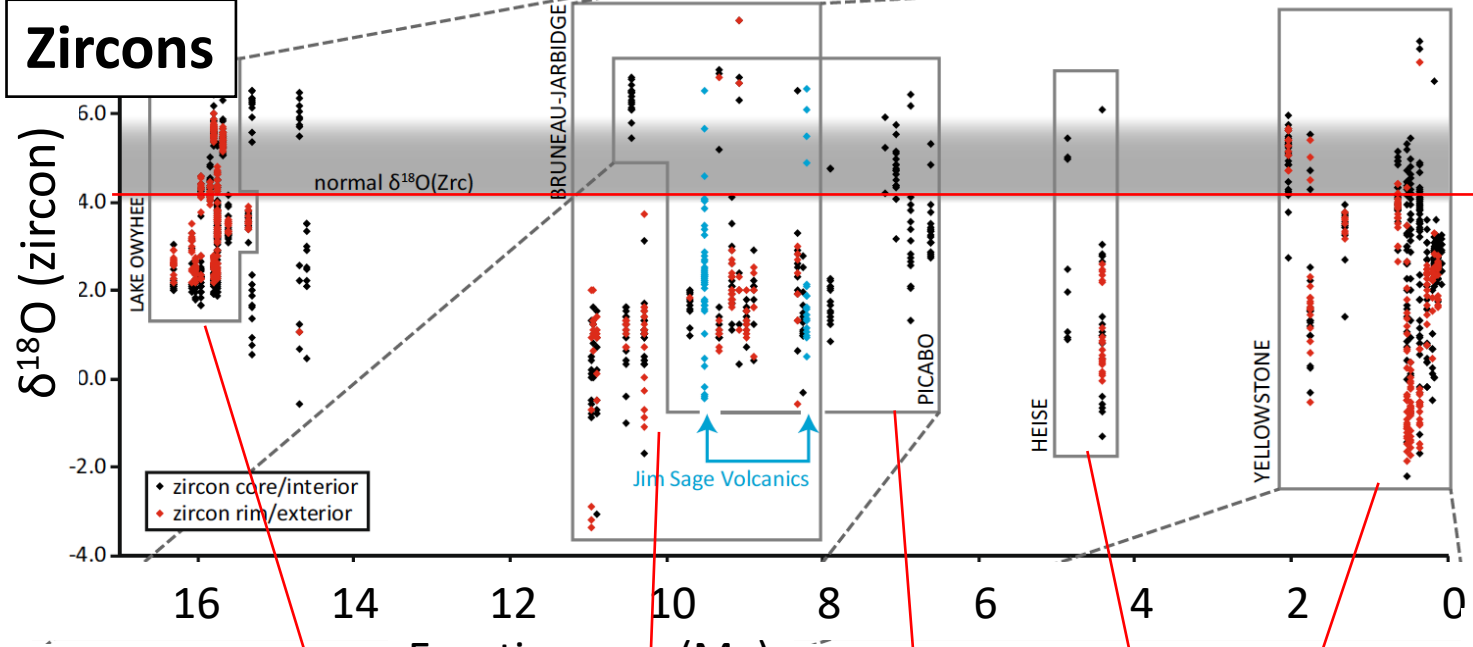


- ✓ Imaged by SEM-CL, -BSE, -SE
- ✓ Magnetism, Raman, OH/O

Valley et al. 2014, 2015

- ✓ U-Pb geochronology
- ✓ Oxygen 2 & 3-isotopes
  Hf isotopes
- ✓ APT
- ✓ Ti-in-zircon thermometry
- ✓ Ce & Eu anomalies
- ✓ REEs
  [Li] & Li isotopes
- ✓ Mineral inclusions
- ✓ Devitrified melt inclusions

Zircons



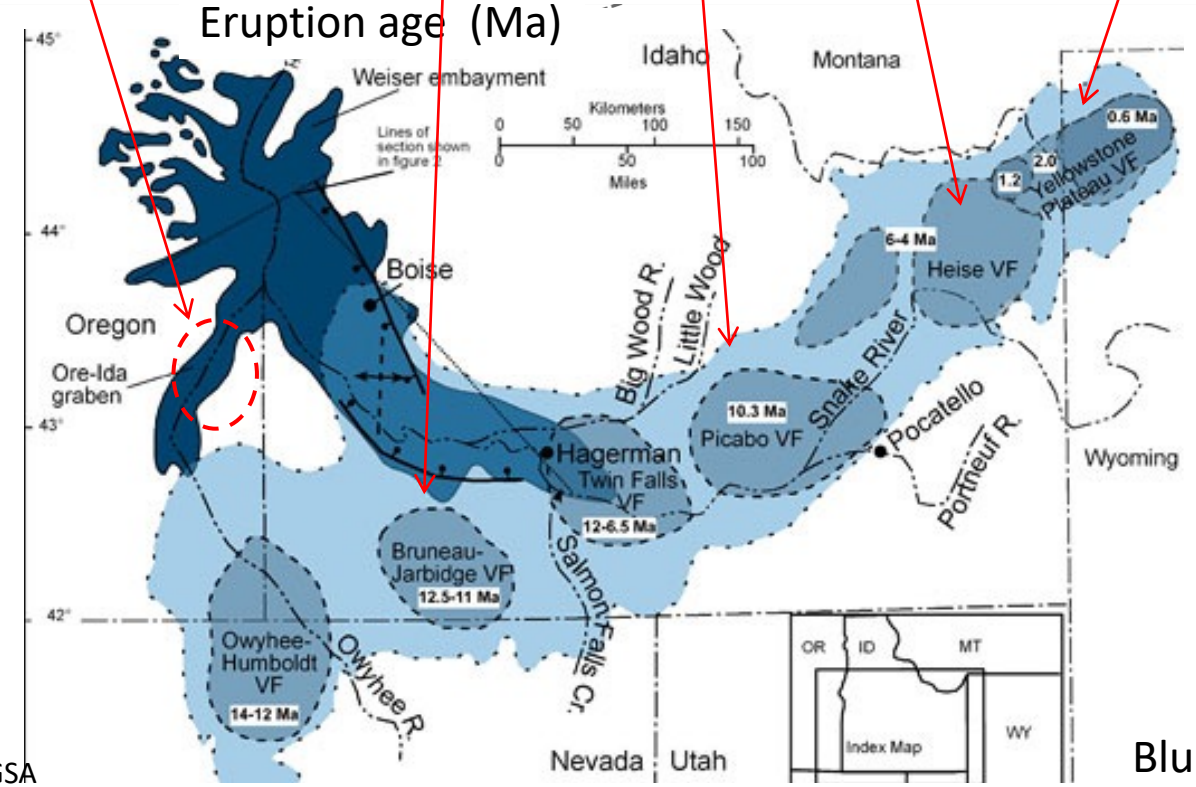
Normal $\delta^{18}O$

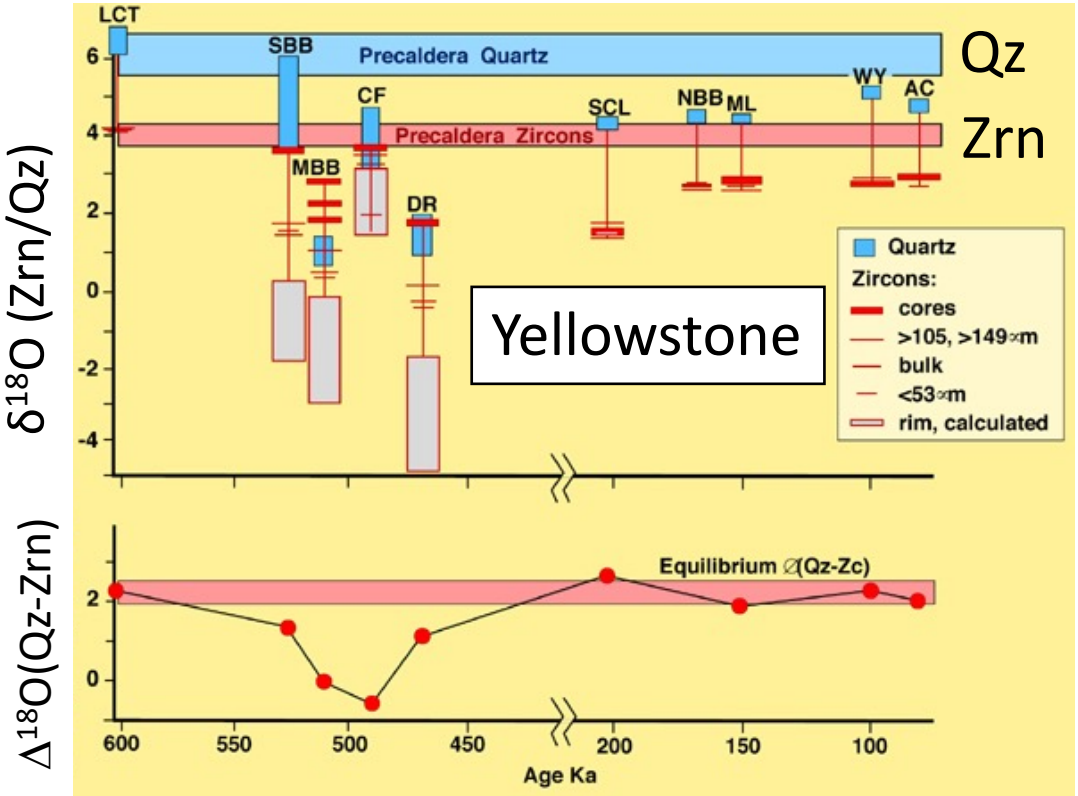
Low $\delta^{18}O$ Rhyolites

$\delta^{18}O$(WR) <6

Low $\delta^{18}O$ Rhyolite

Snake River Plain





Qz

Zrn

Bindeman & Valley 2000

Bindeman et al. 2001, 2008

Blum et al. 2016

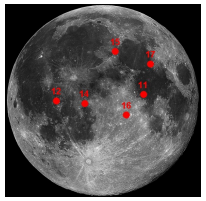
Valley 2022 GSA

Zircons

Lunar Zircons vs. Earth

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

0.1 ‰
on Moon

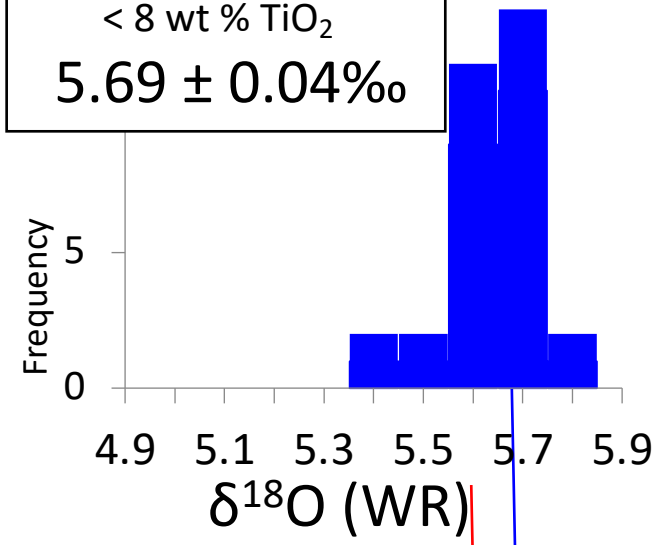


vs.
0.4 ‰
on Earth

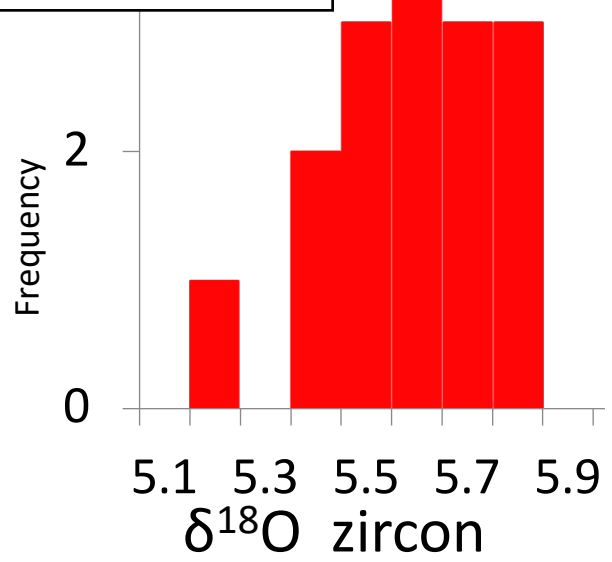
Valley et al. 2014

Valley 2022 GSA

Mare Basalt WR
< 8 wt % TiO_2
5.69 ± 0.04‰



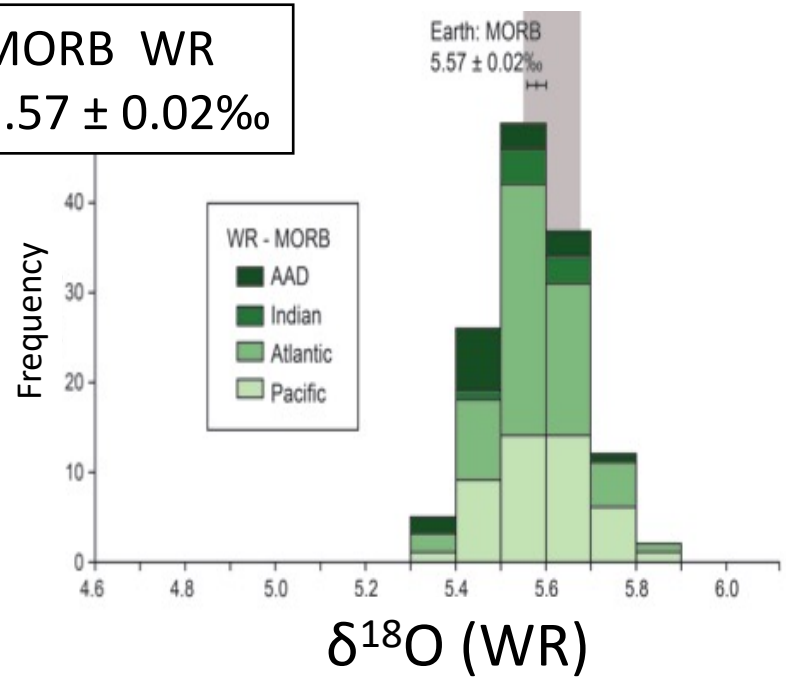
Lunar Zircons
5.59 ± 0.08‰



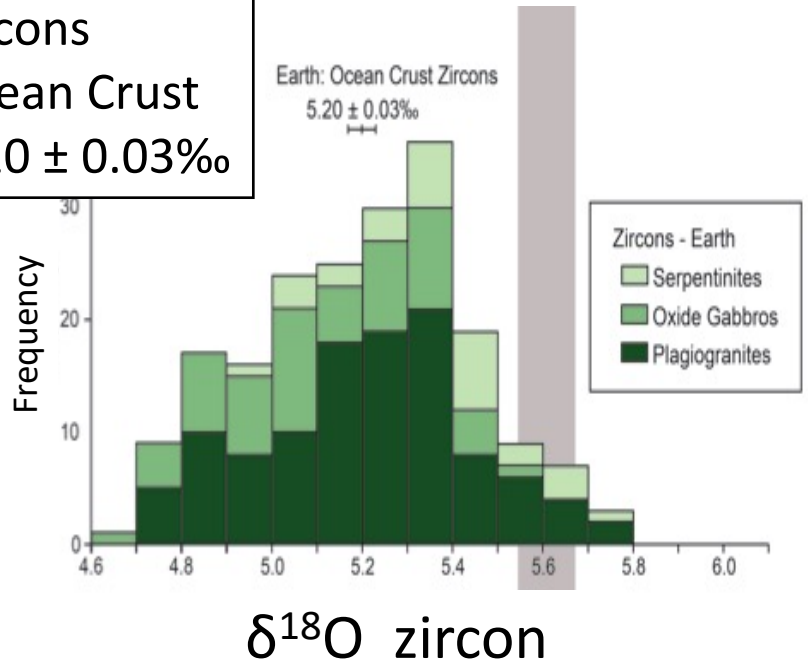
Moon

Earth

MORB WR
5.57 ± 0.02‰

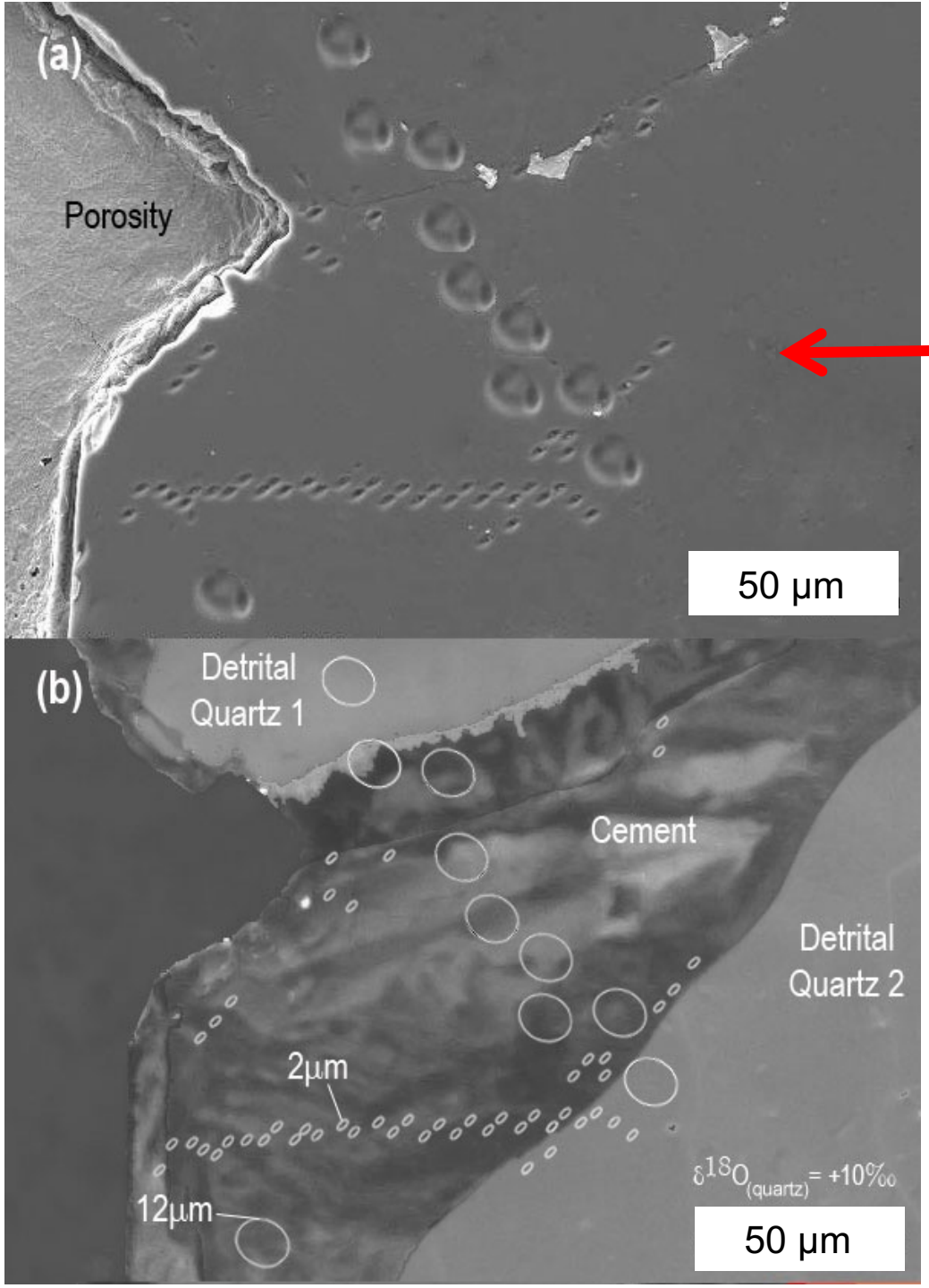


Zircons
Ocean Crust
5.20 ± 0.03‰

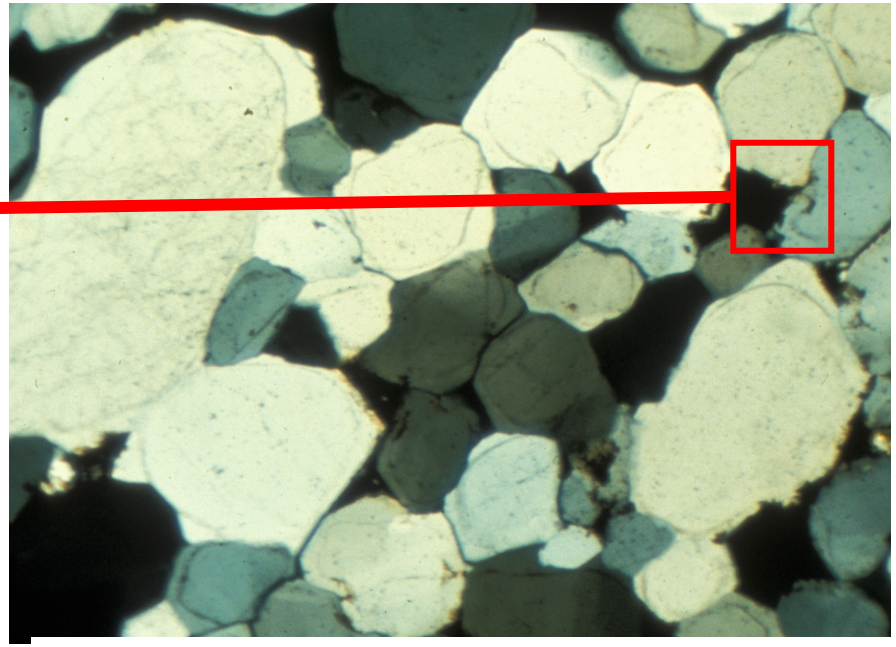


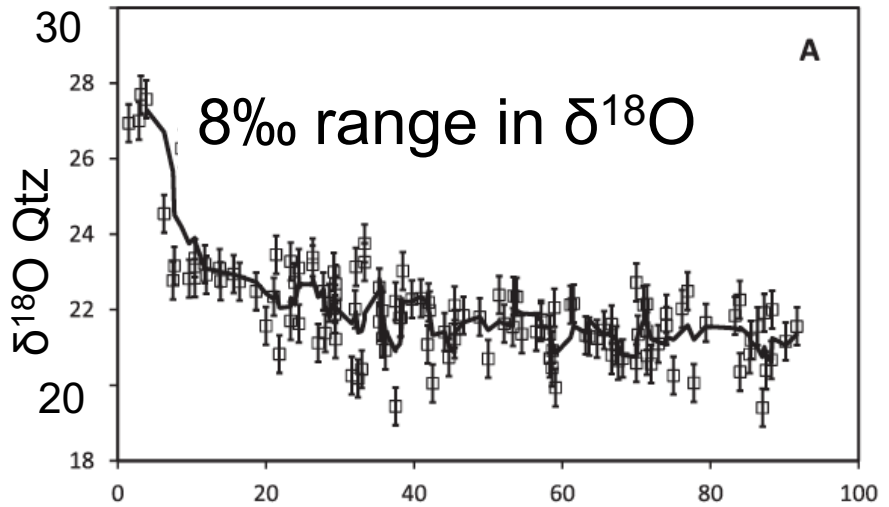
Quartz

Ness Fm.
North Sea



Quartz Overgrowths





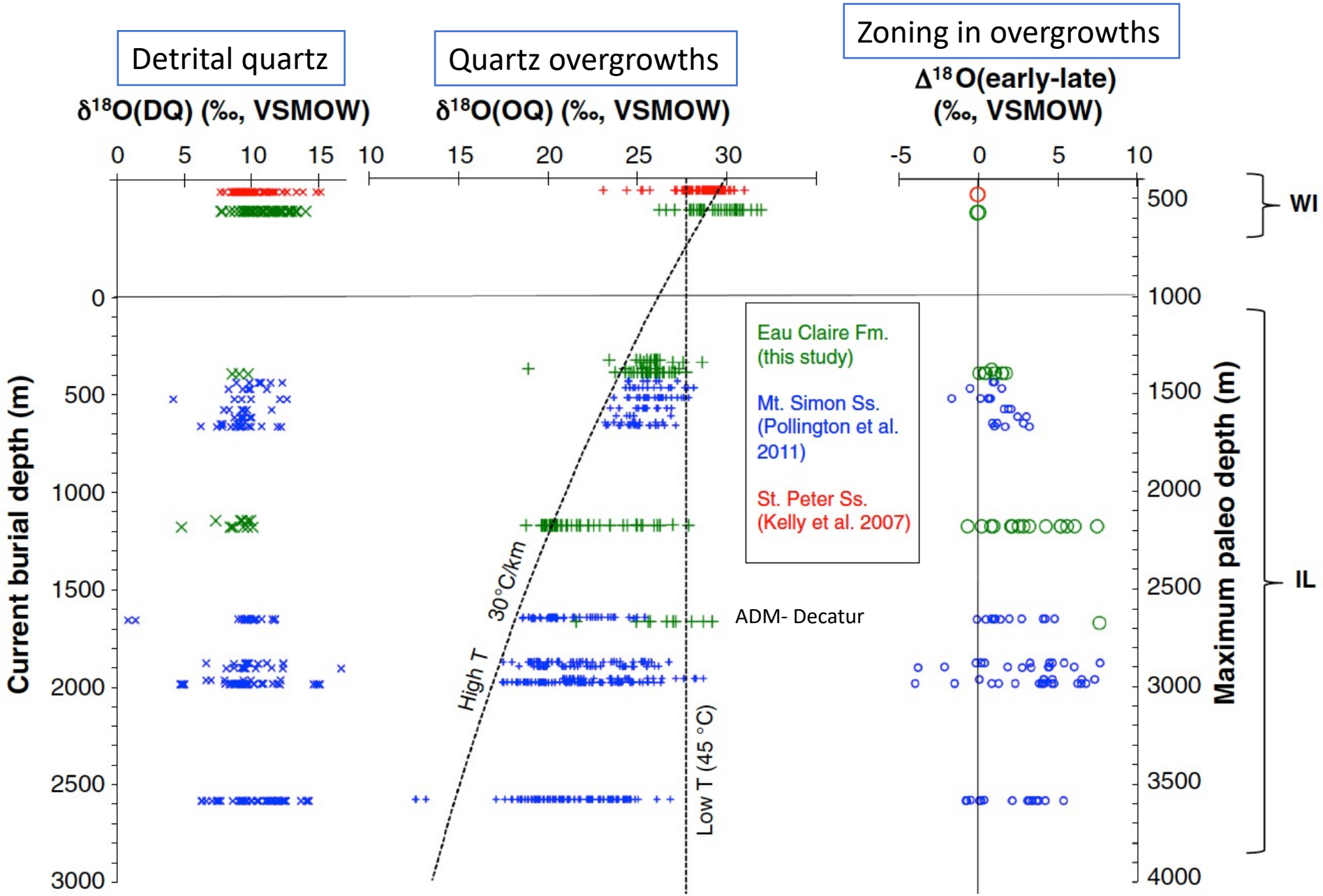
Harwood et al. 2013

Durham University

Wisc SIMS

Quartz

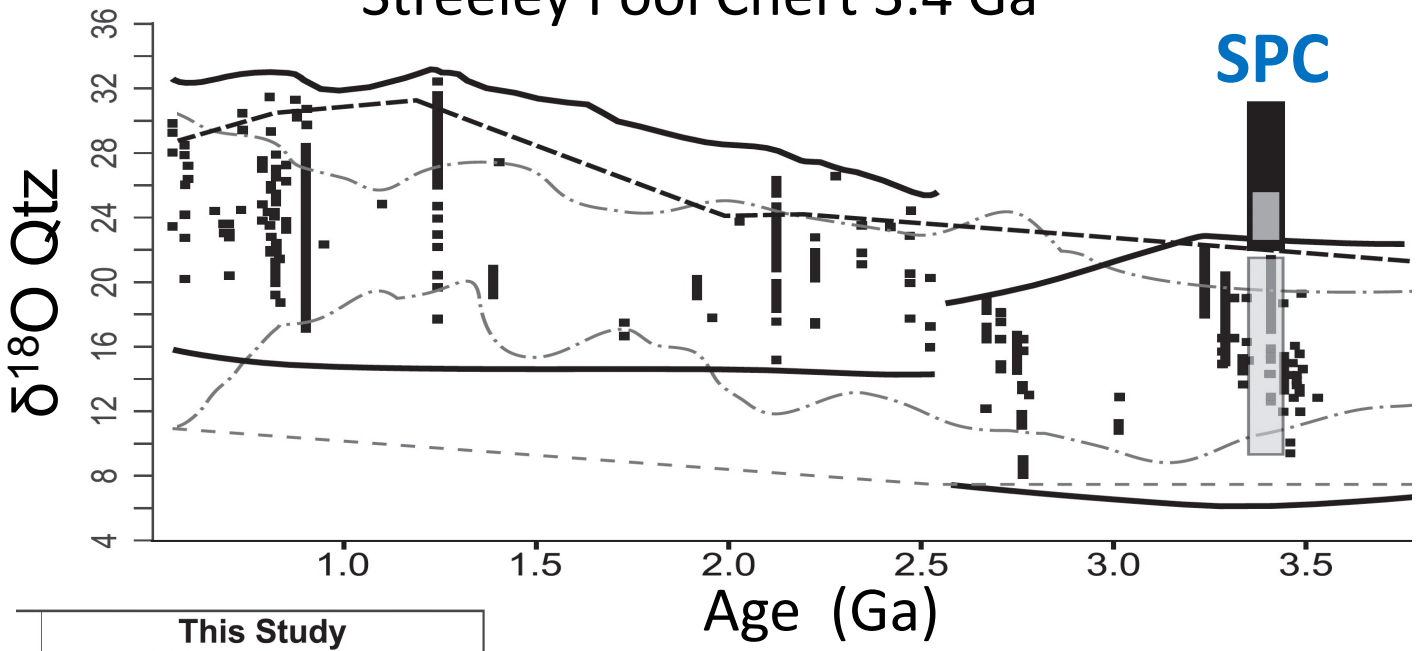
Illinois & Wisconsin- Sandstones



Pollington et al. 2011, 2016; Hyodo et al. 2014

Quartz

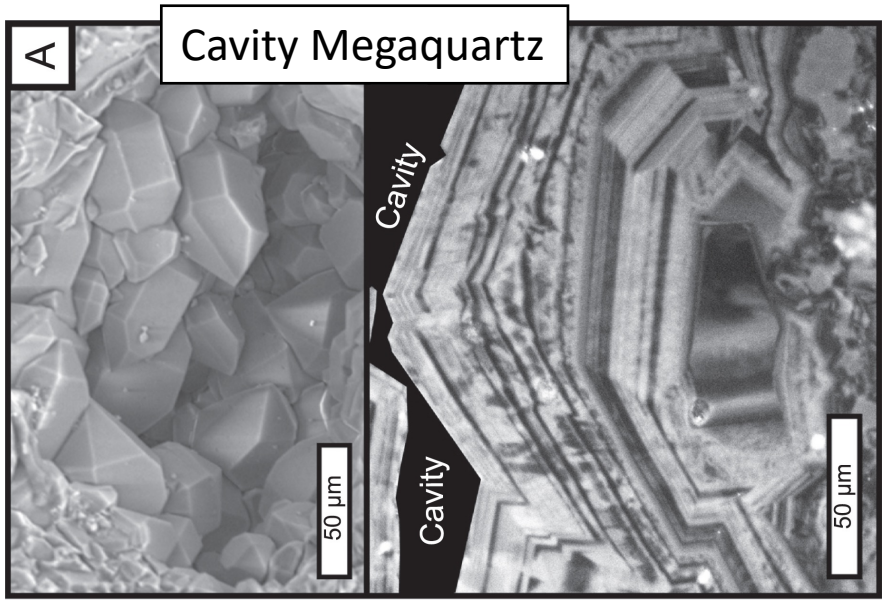
Streeley Pool Chert 3.4 Ga

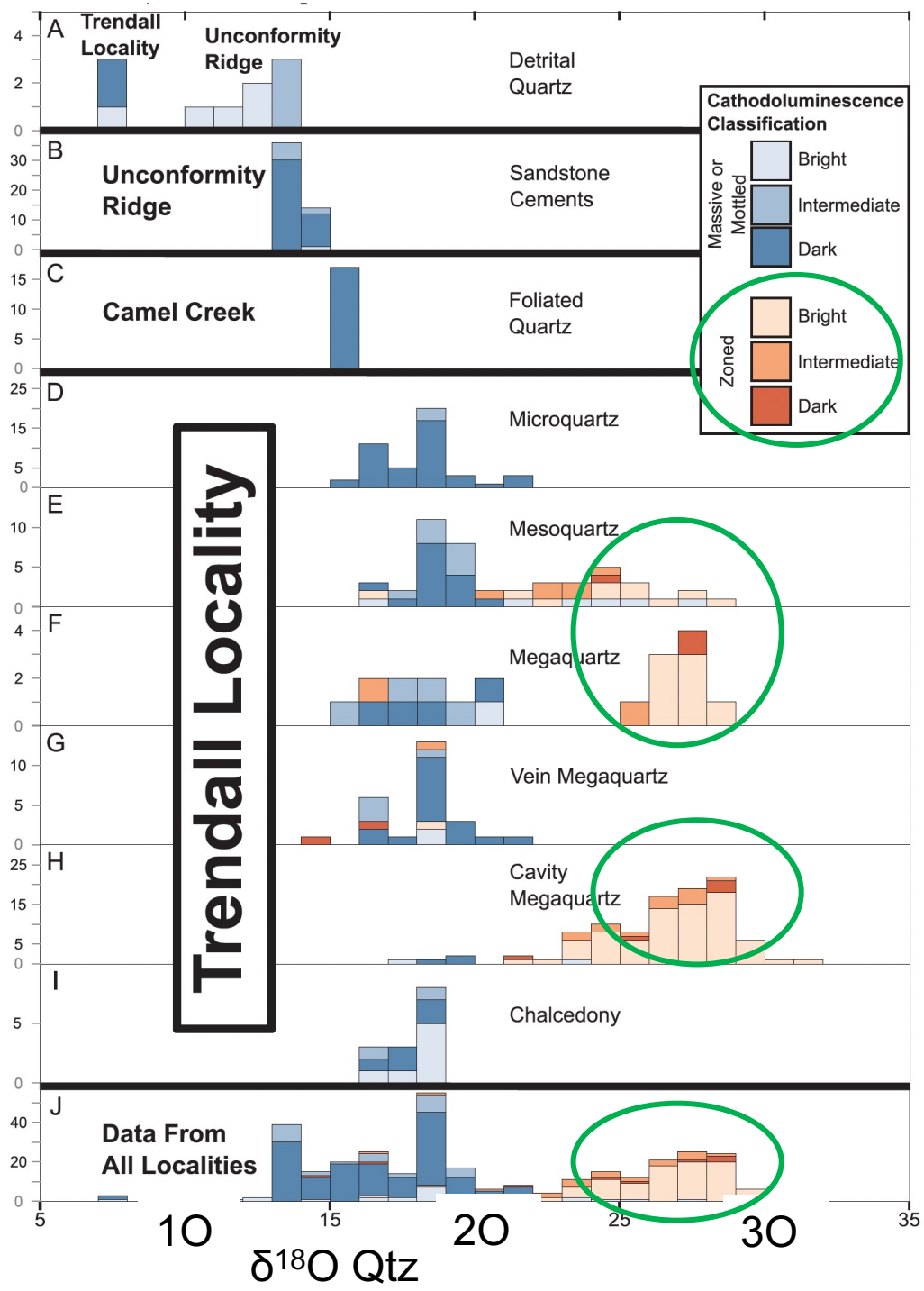


This Study
- SIMS Trendall (n = 123)
- LF Trendall (n = 11)
- LF SPF (n = 176)

LF = Laser Fluorination Data

- Chert $\delta^{18}O$
- Chert $\delta^{18}O$ range
- Chert $\delta^{18}O$ maximum
- Carbonate $\delta^{18}O$ range
- Zircon $\delta^{18}O$, upper limit



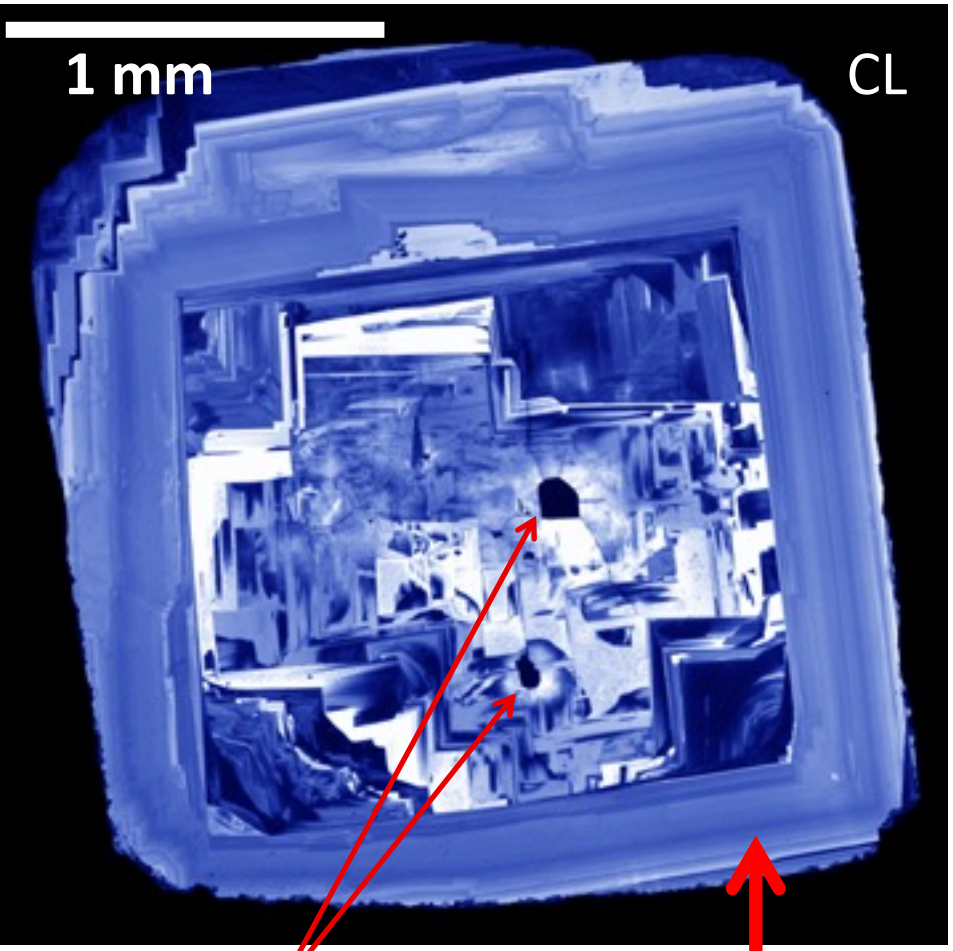


Cammack et al. 2018

Valley 2022 GSA

Inclusions

Silicate inclusions in diamonds



Coesite

$\delta^{18}O$= +10 to +16‰

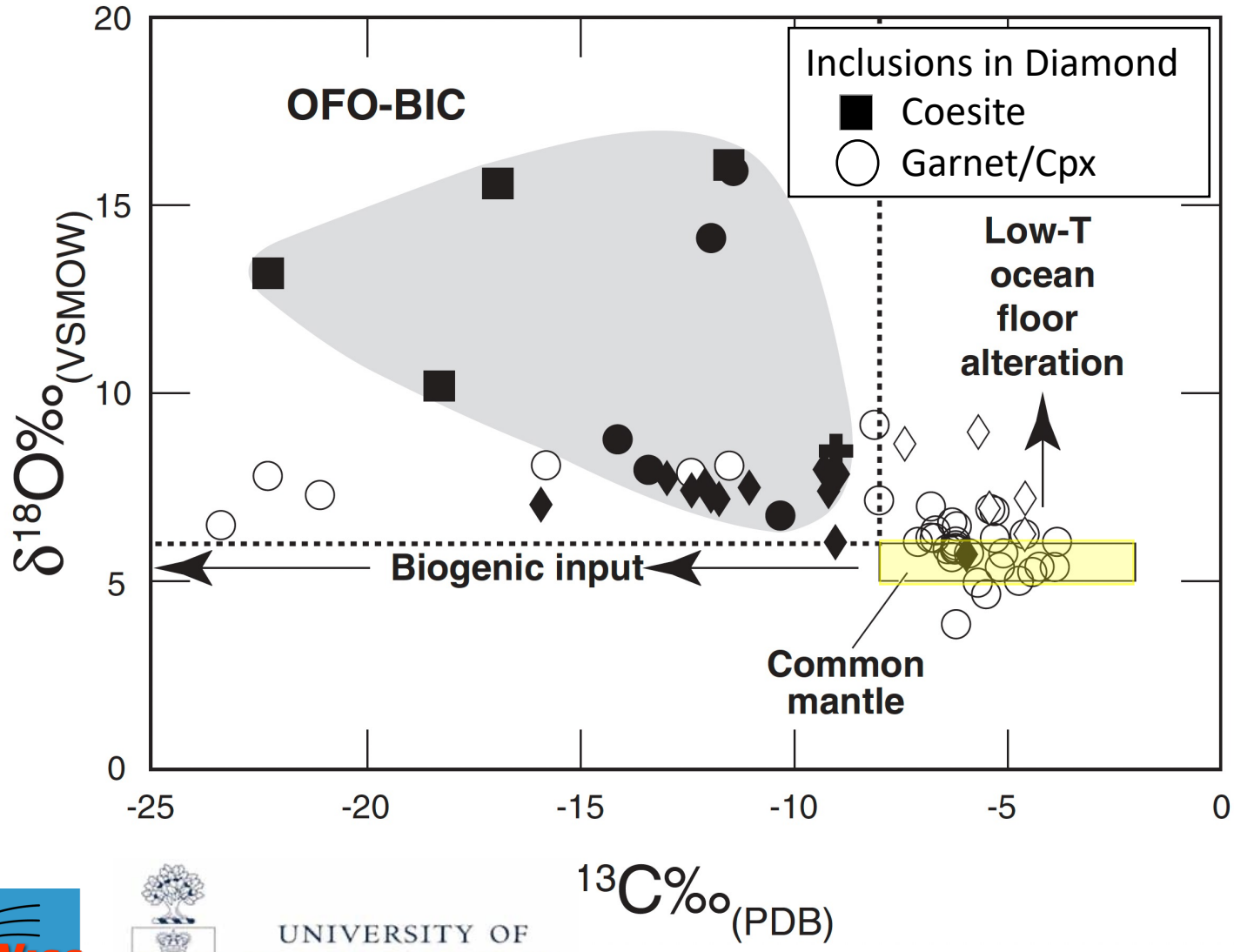
Diamond

$\delta^{13}C$= -22 to -11‰

Schulze et al. 2003

OFO-BIC

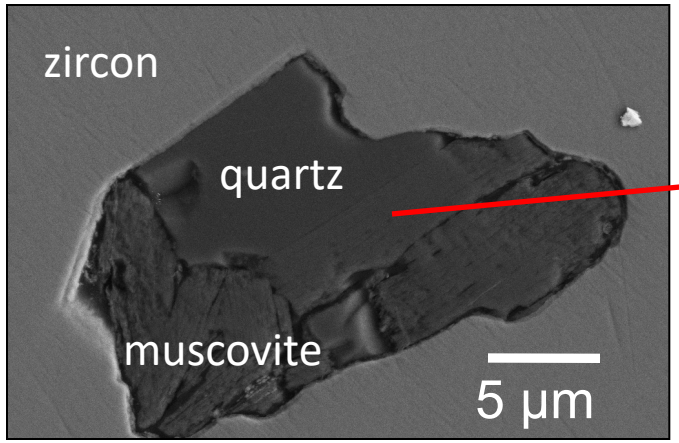
ocean floor oxygen–biogenic carbon

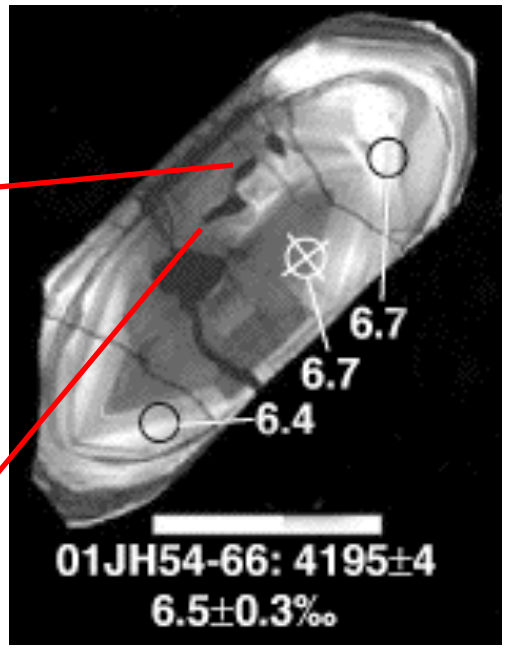


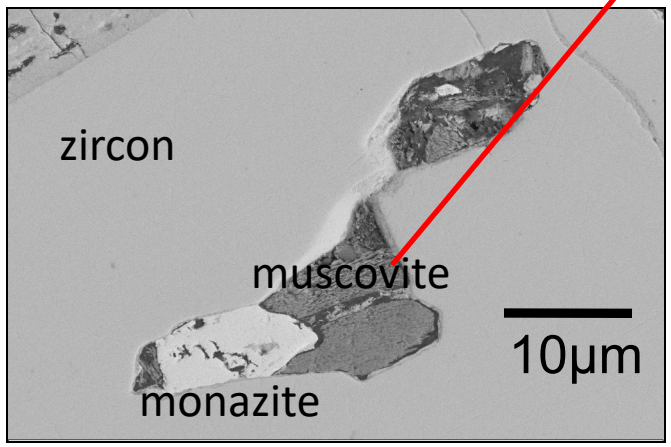
Schulze et al. 2013

Jack Hills: inclusions in >4 Ga detrital zircons

"very small rocks"







4195 Ma

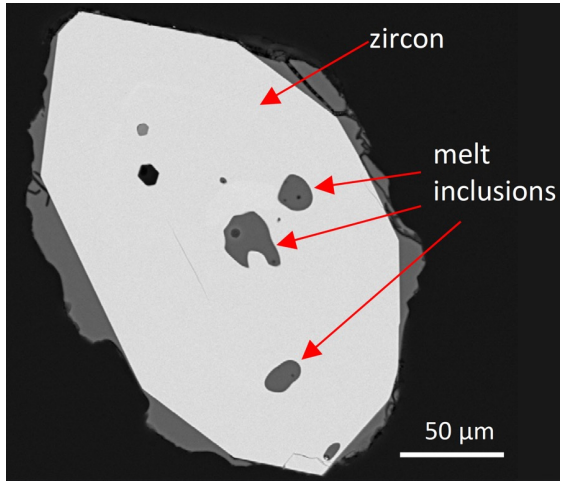
$\delta^{18}O(Zrc)$ = 6.5 ‰

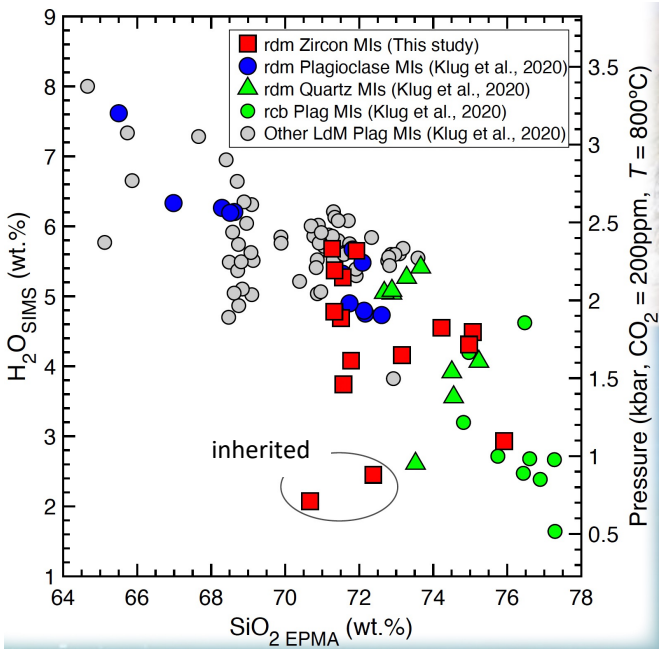
Quartz
K-feldspar
Plagioclase
Muscovite
Biotite
Hornblende
Apatite
Xenotime
Monazite
Fe-Ti-oxide
Rutile
Pyrite
~~Diamond~~
Graphite
Devitrified granitic melt?

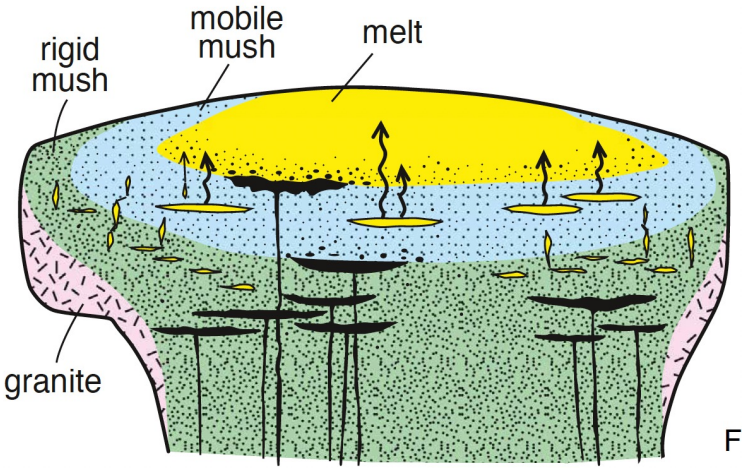
Cavosie et al. 2005
Valley et al. 2006 AGU
Ortiz 2010
Bell et al. 2015

What's Next? Melt Inclusions in Zircon

Volcanic zircons
Laguna del Maule, Chile, <100 ka

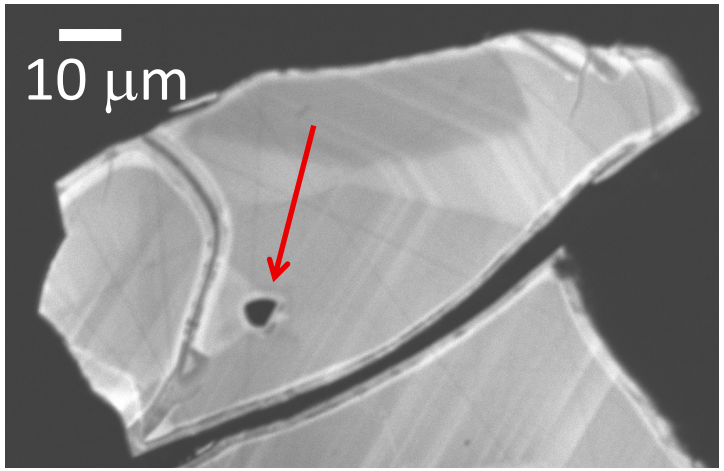






Shimizu et al. 2022
Klug et al. 2020

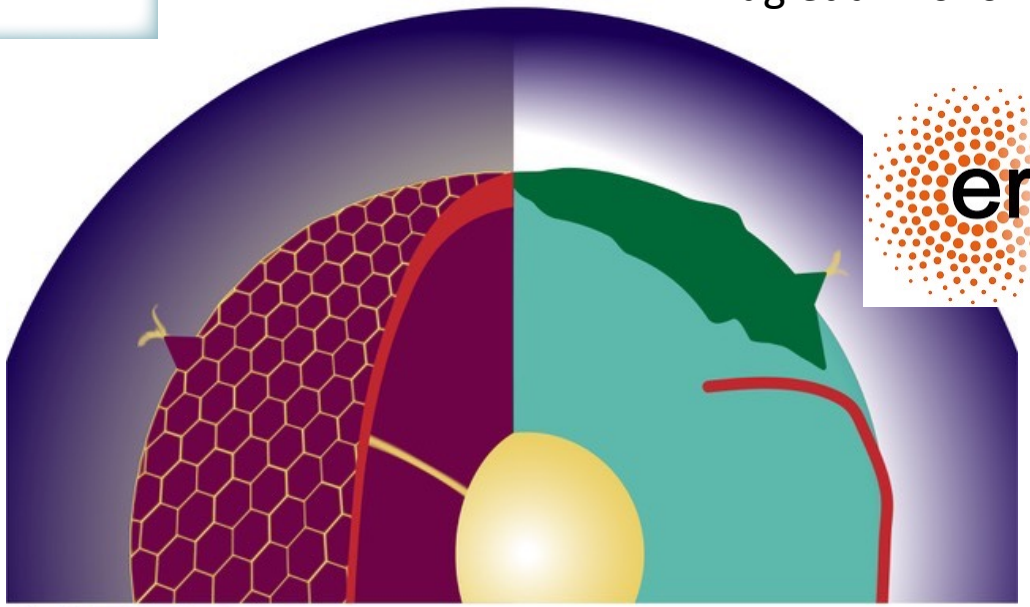
Jack Hills detrital zircons, Archean & Hadean (annealed, 4Kb)



Zircon
3.4 Ga
Glass
70% SiO_2
$\Delta^{18}O$(glass-Zrn) = 2.5‰

Valley et al., unpd

Valley 2022 GSA



MEET Monitoring Earth Evolution Through Time