Instytut Geofizyki
Polskiej Akademii Nauk

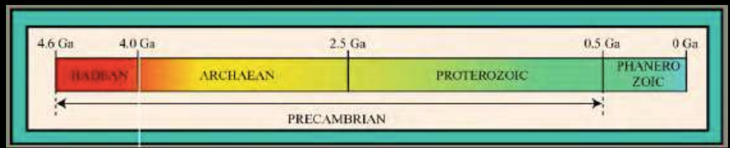
Frozen in Time
-Pb nanospheres in zircon

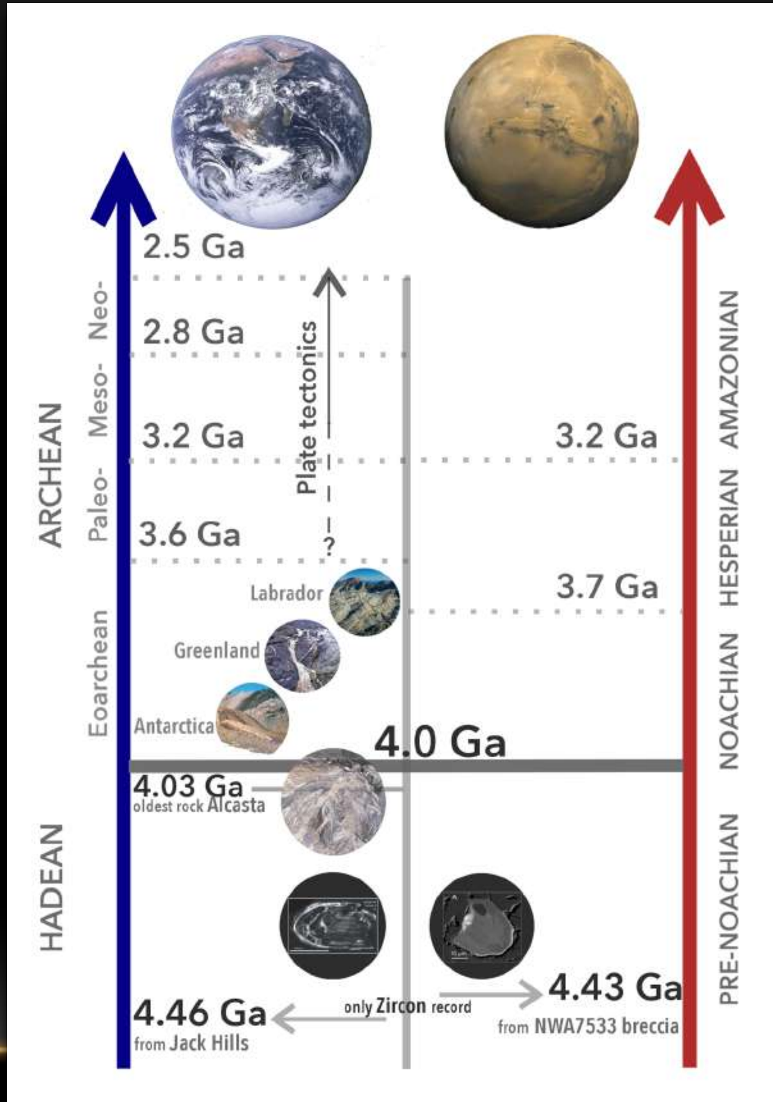
Monika A. Kusiak
IGF PAN
monika.kusiak@igf.edu.pl

Alexander von Humboldt Stiftung/Foundation

MARIE CURIE ACTIONS

OLDEST ROCKS ON EARTH





ZIRCONS ARE FOREVER

$ZrSiO_4$

Common mineral in igneous, metamorphic and sedimentary rocks

Trace amount of: U, Th, Y, Hf and REE

Most commonly used U-Pb geochronometer

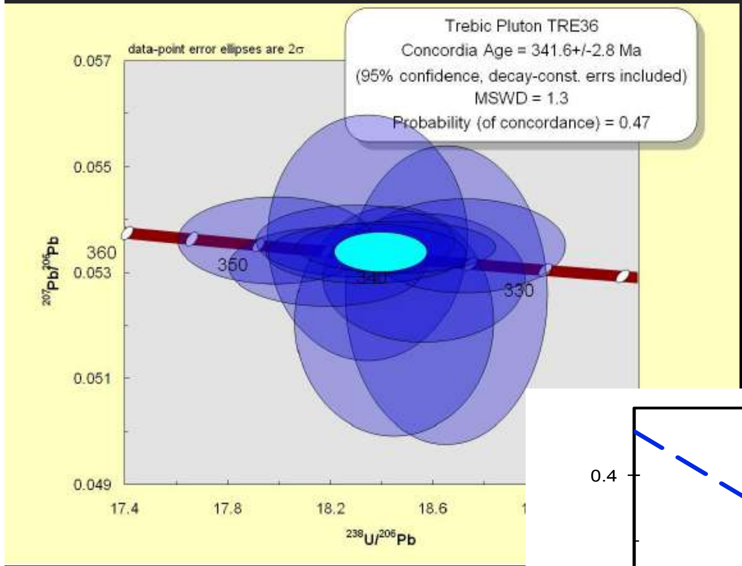
UNIQUE SITUATION OF U-PB

- Decay of two U-isotopes allows the determination of three ages ($^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$, $^{207}Pb/^{206}Pb$) by analysing the concentrations as well as the Pb-isotopes from any zircon

But

These three ages have a tendency to disagree for most zircon analyses!

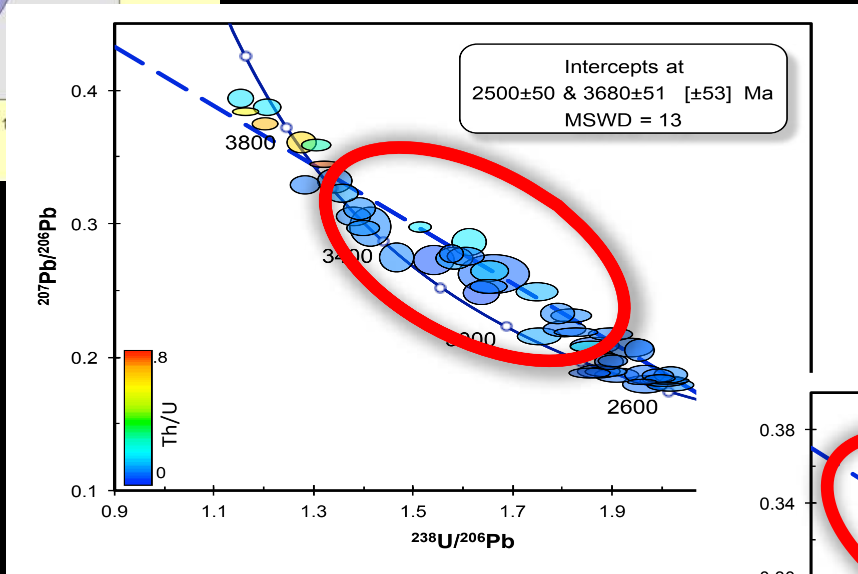
Concordant



Kusiak et al. 2010; GR

Discordant

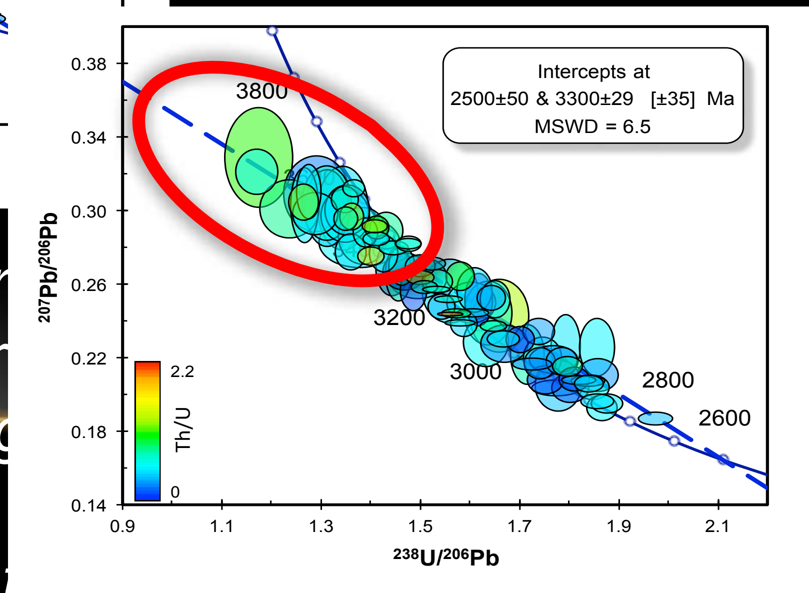
Pb/Pb > U/Pb



Kusiak et al. 2013; Geology

Reverse discordant

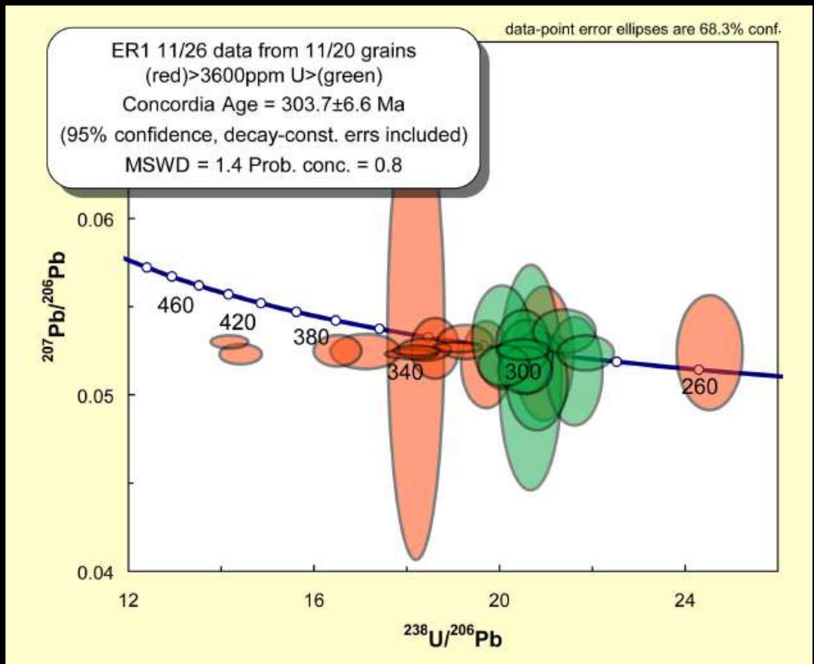
Pb/Pb < U/Pb



- *Open system behaviour*
- *Physical mixing of older component with a young overgrowth*
- *Common Pb contamination*

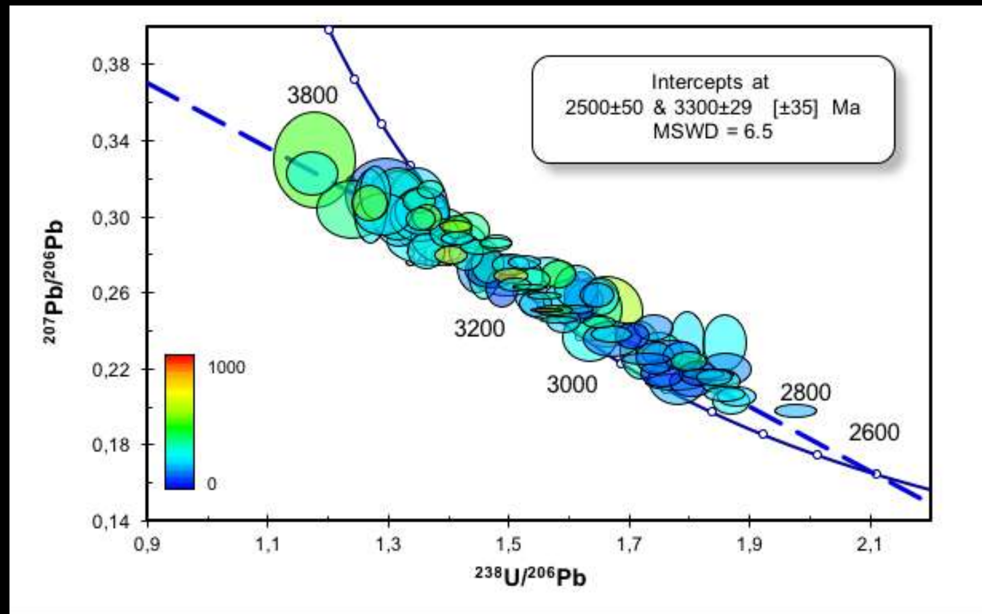
REVERSE DISCORDANCE

Analytical artefact



Kusiak et al. 2009; Geology

Real physical phenomenon



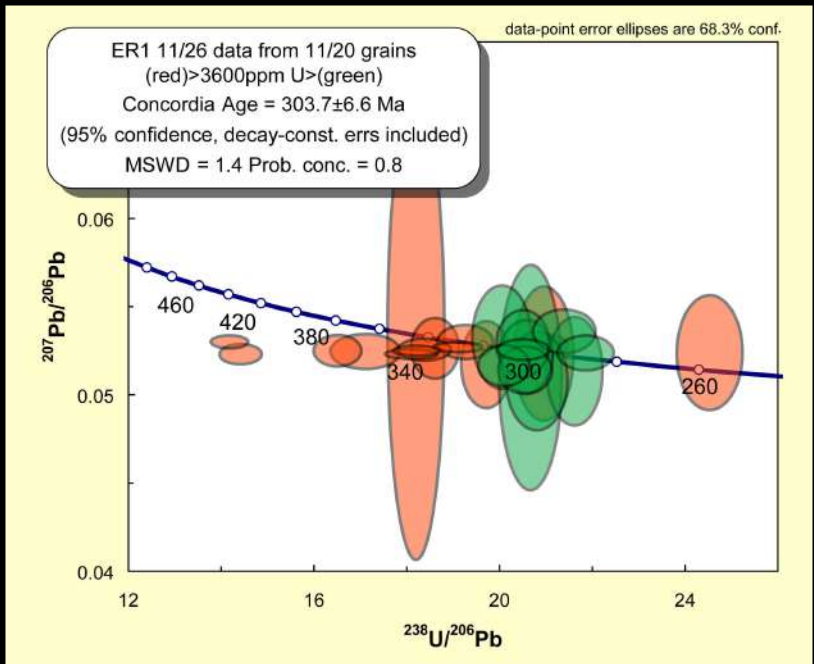
Kusiak et al. 2013; Geology

Uranium content

- > 3600 ppm
- <3600 ppm

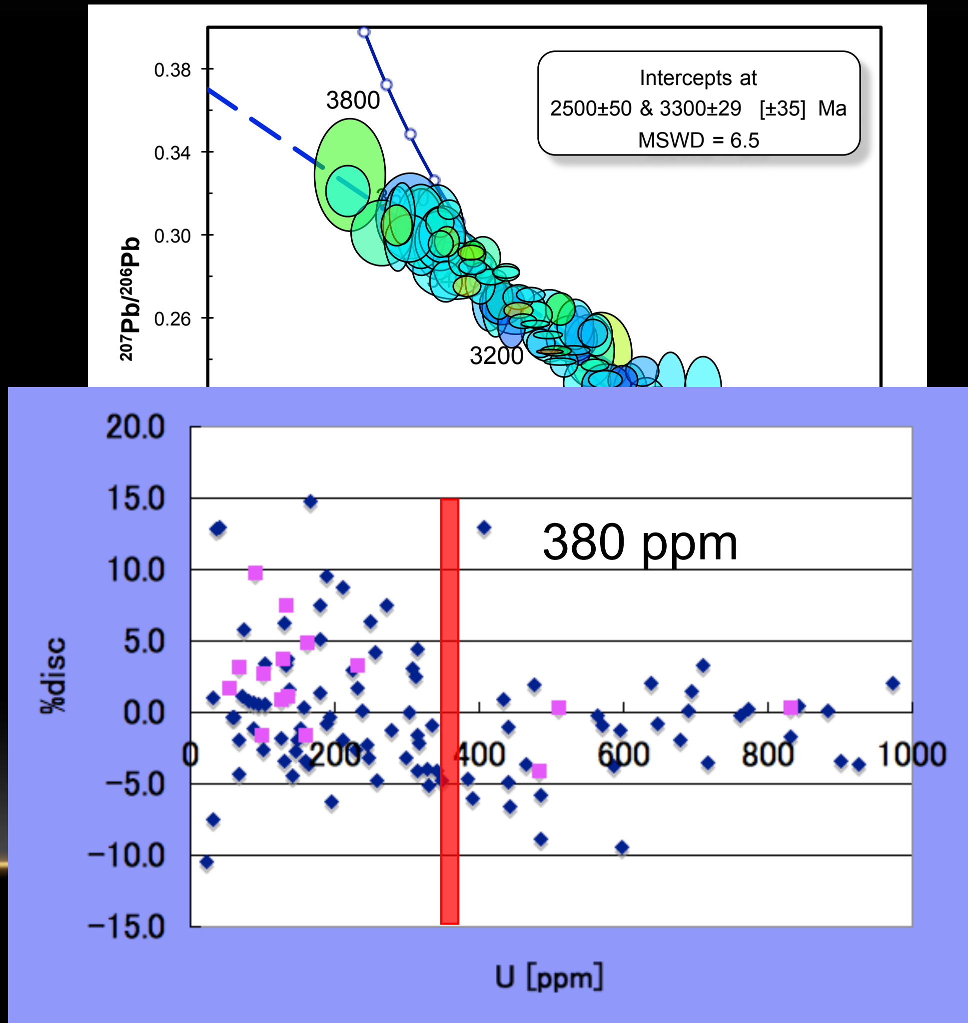
REVERSE DISCORDANCE

Analytical artefact



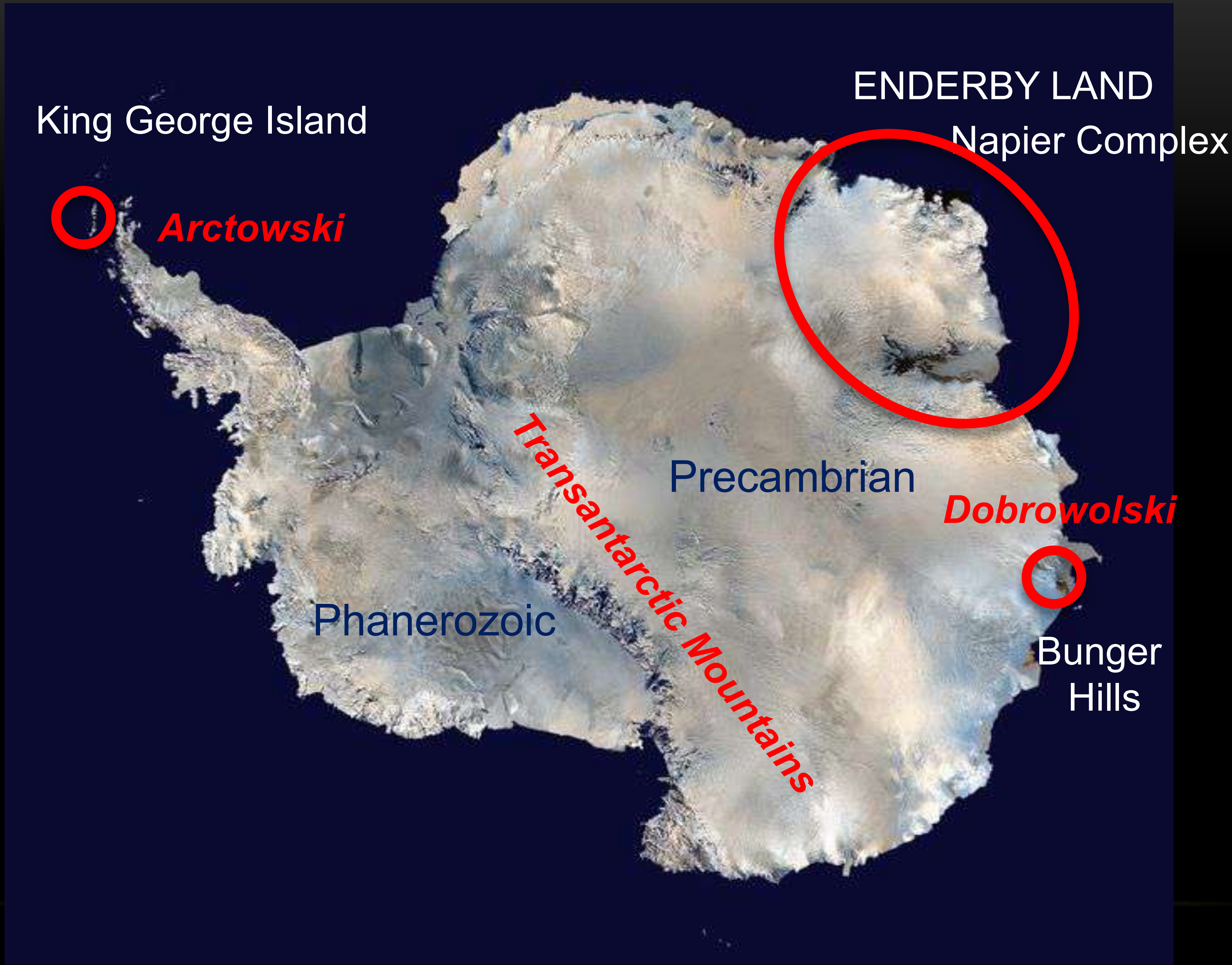
Kusiak et al. 2009; Geology

Real physical phenomenon

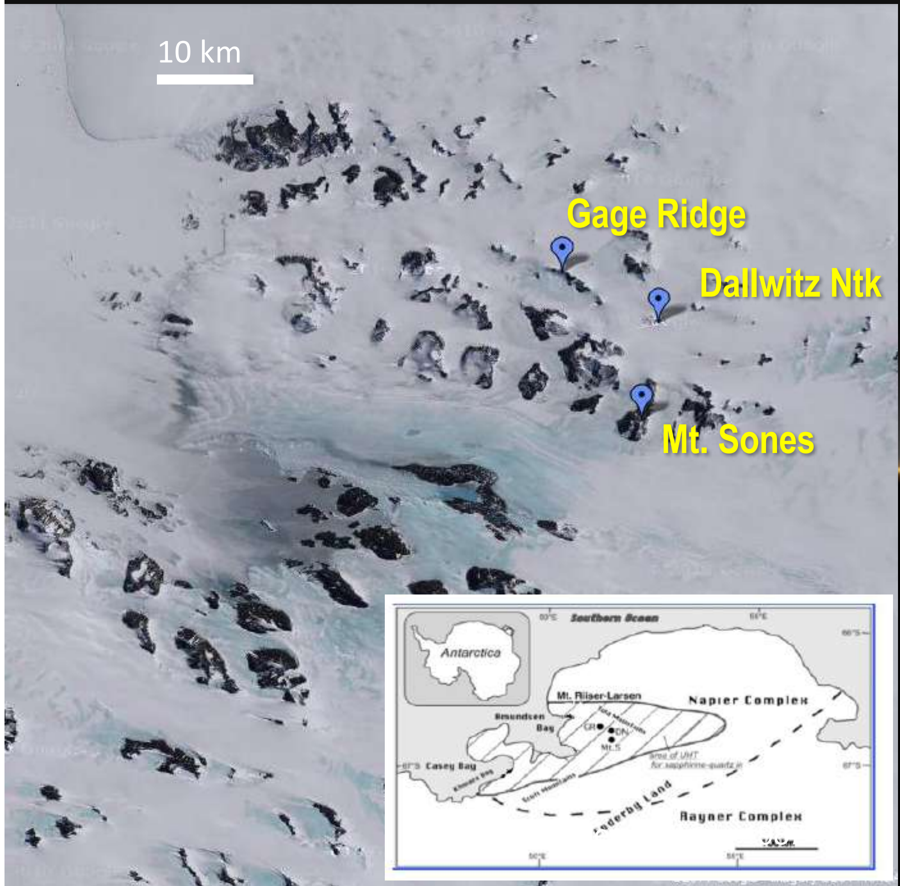


Uranium content

- > 3600 ppm
- <3600 ppm


King George Island
Arctowski
ENDERBY LAND
Napier Complex
Precambrian
Transantarctic Mountains
Dobrowolski
Phanerozoic
Bunger
Hills

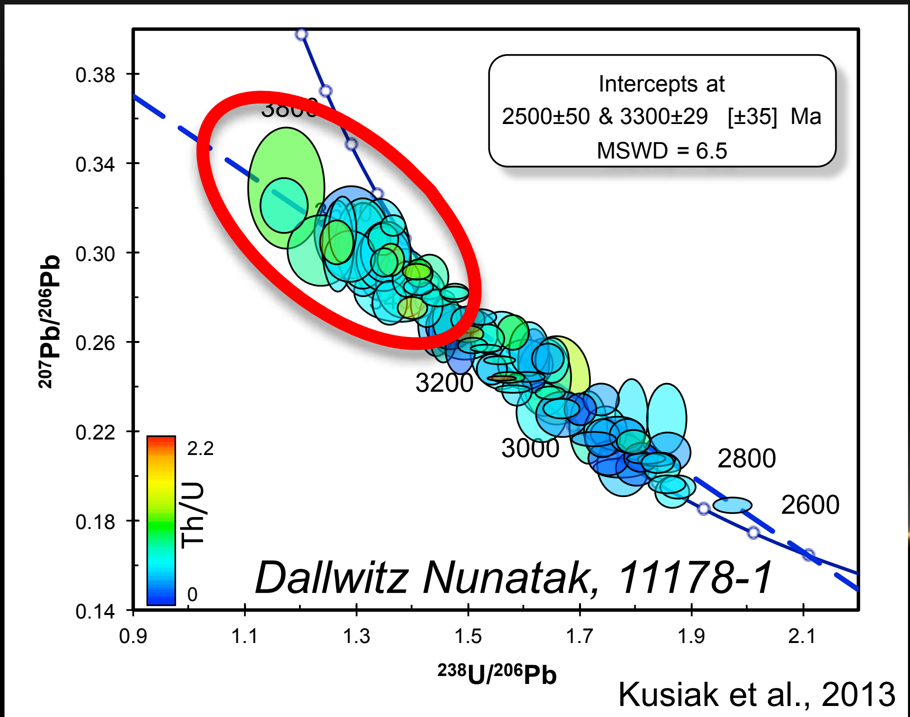
Napier Complex, Antarctica

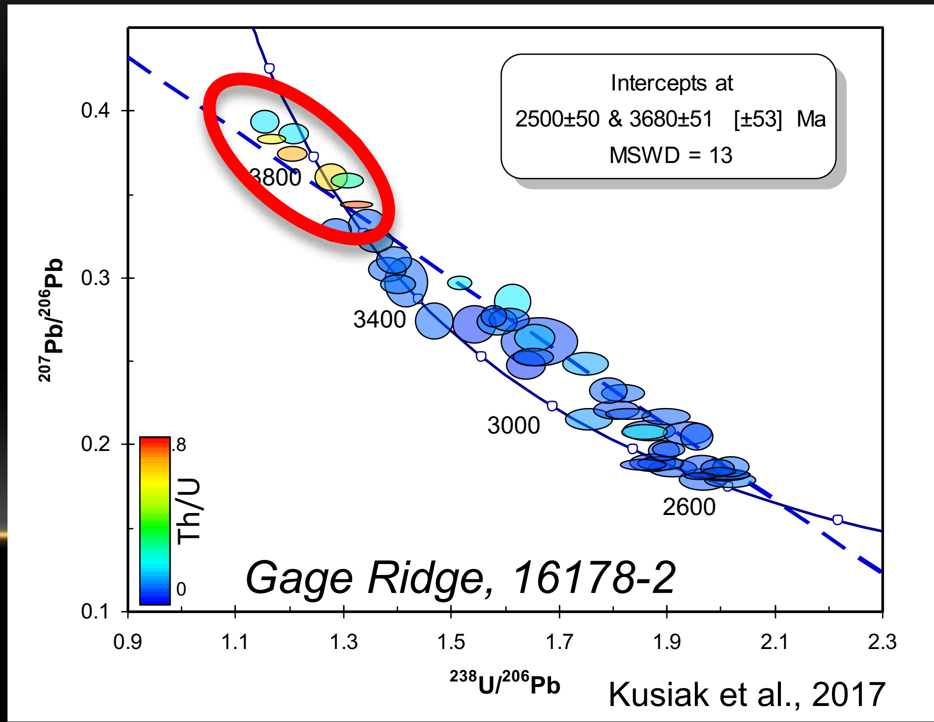


- One of several known Archaean blocks within the East Antarctic Precambrian Shield
- Parts of Napier Complex >3.8 Ga

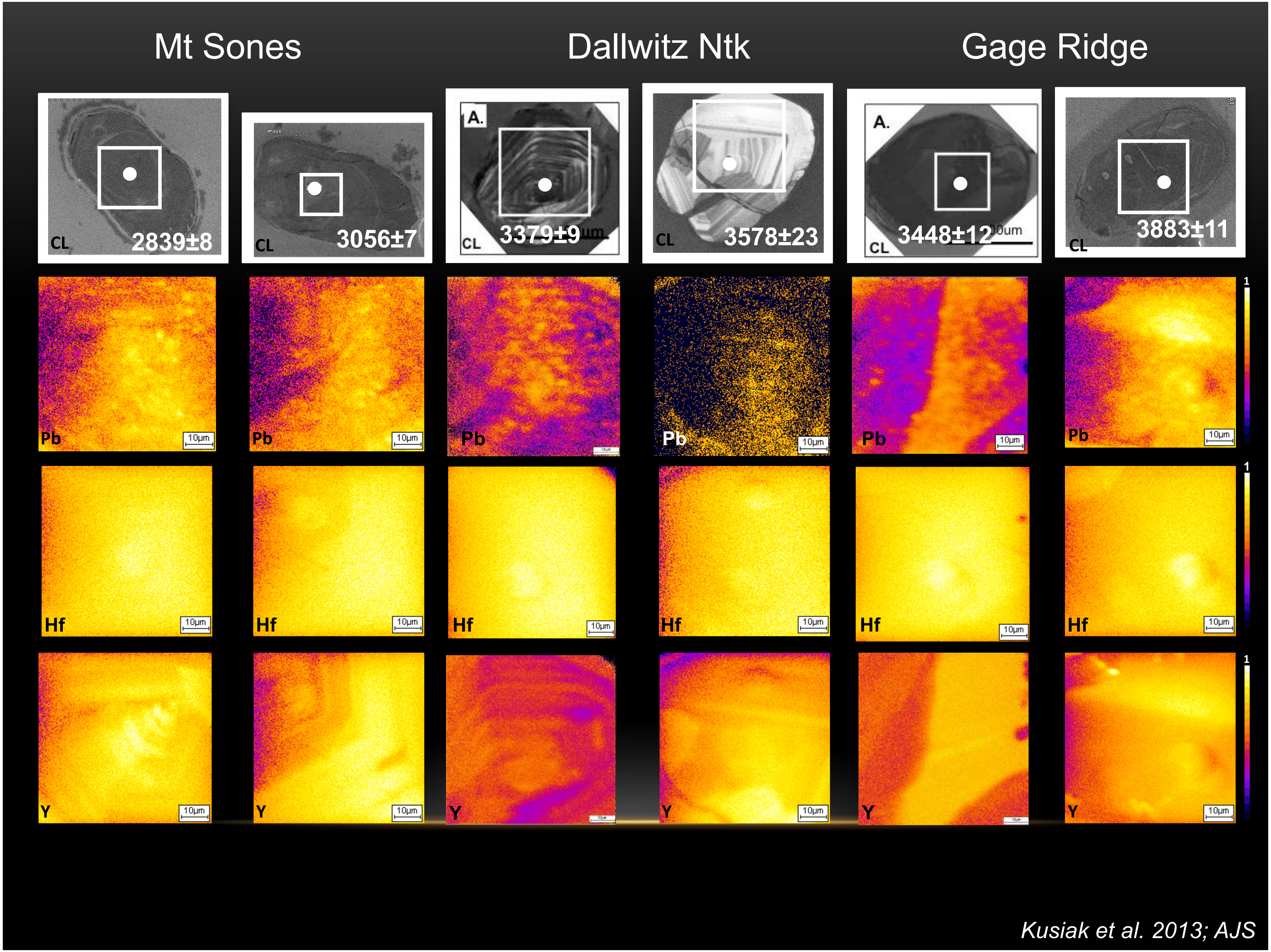
- Highly deformed at 2.8 Ga & 2.5 Ga
- UHT metamorphism (>1000ºC)
- Complexity of zircon reported by early SIMS U-Pb studies (Williams et al., 1984; Black et al., 1986; Harley et al., 2019)

Napier Complex, Antarctica

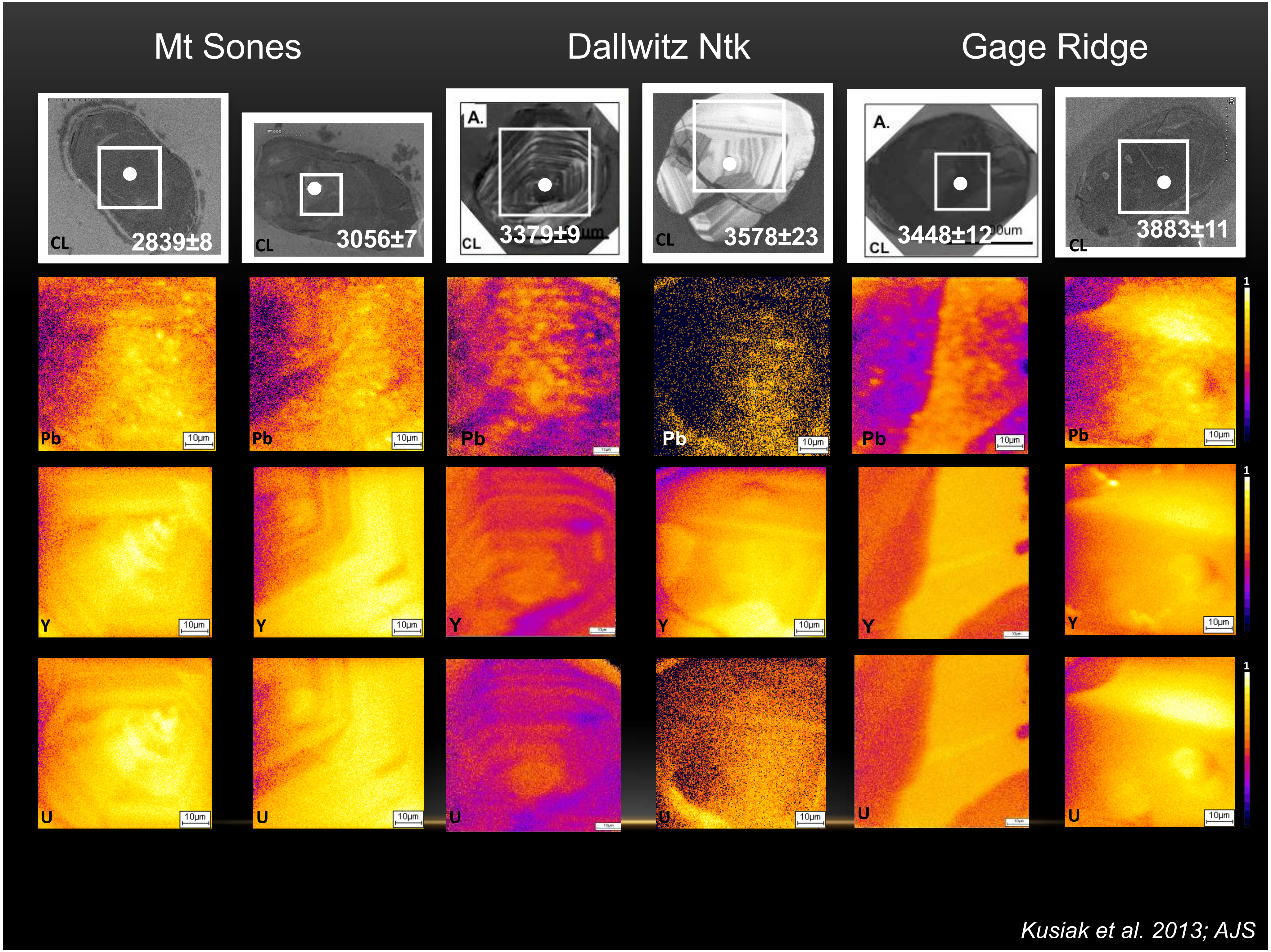




- Reverse discordance pattern in some zircon populations despite low U concentration
- Individual $^{207}Pb/^{206}Pb$ ages appear too old
- Unusually large errors on some analyses
- True age hard to define

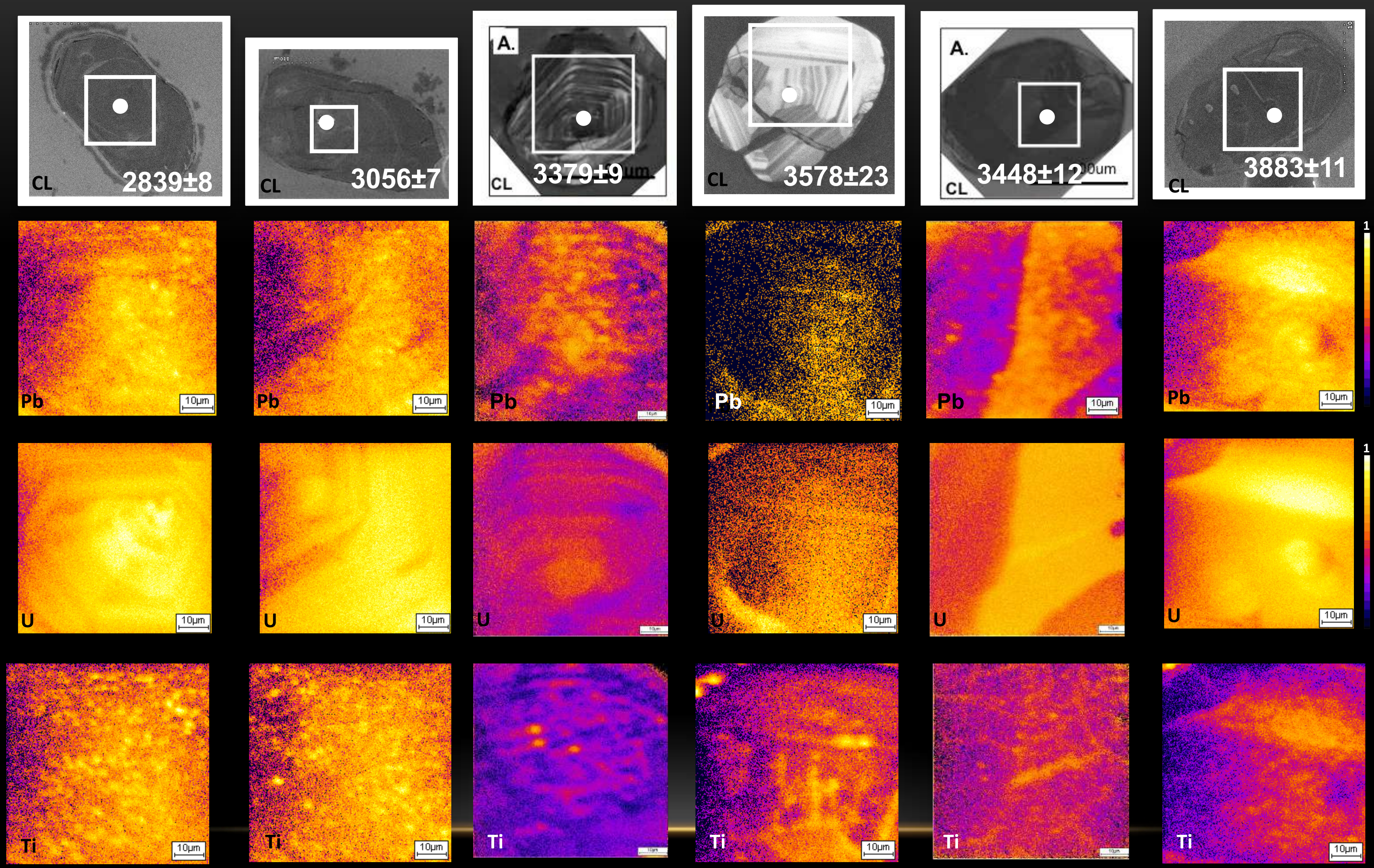


Mt Sones
Dallwitz Ntk
Gage Ridge
CL
2839±8
3056±7
3379±9
3578±23
3448±12
3883±11
A.
Pb
Hf
Y
10μm
Kusiak et al. 2013; AJS



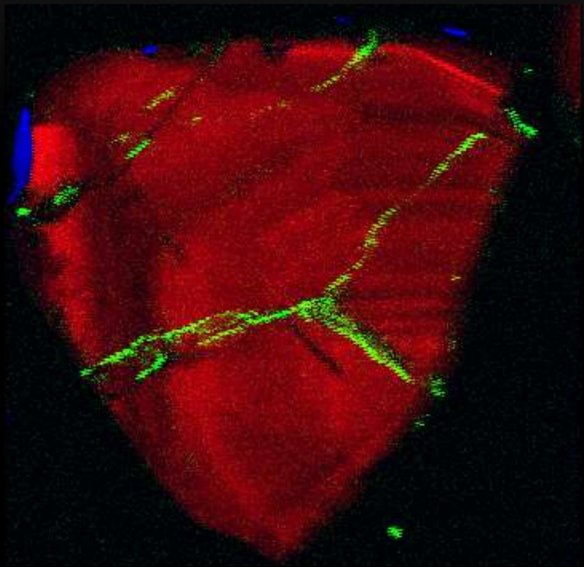
Mt Sones
Dallwitz Ntk
Gage Ridge
CL
2839±8
CL
3056±7
A.
CL
3379±9
CL
3578±23
A.
CL
3448±12
CL
3883±11
Pb
Y
U
10µm
1
Kusiak et al. 2013; AJS

Mt Sones Dallwitz Ntk Gage Ridge

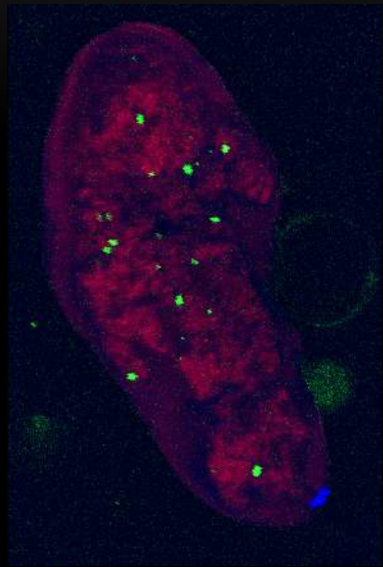


Kusiak et al. 2013; AJS

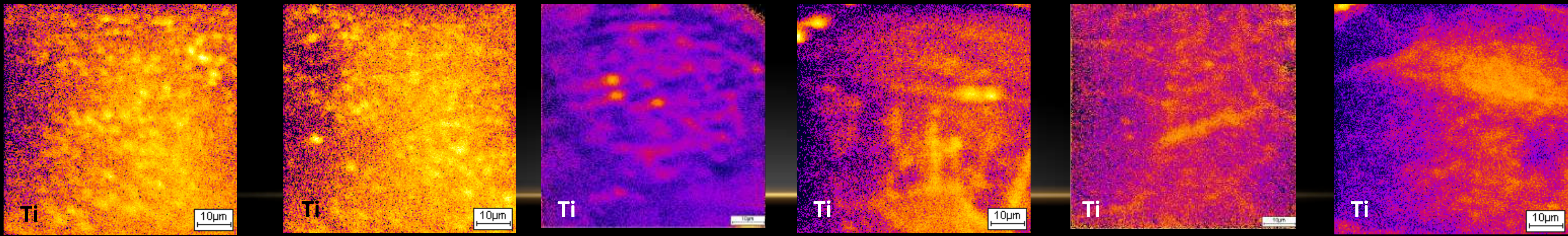
TI MAPPING



Ti in cracks

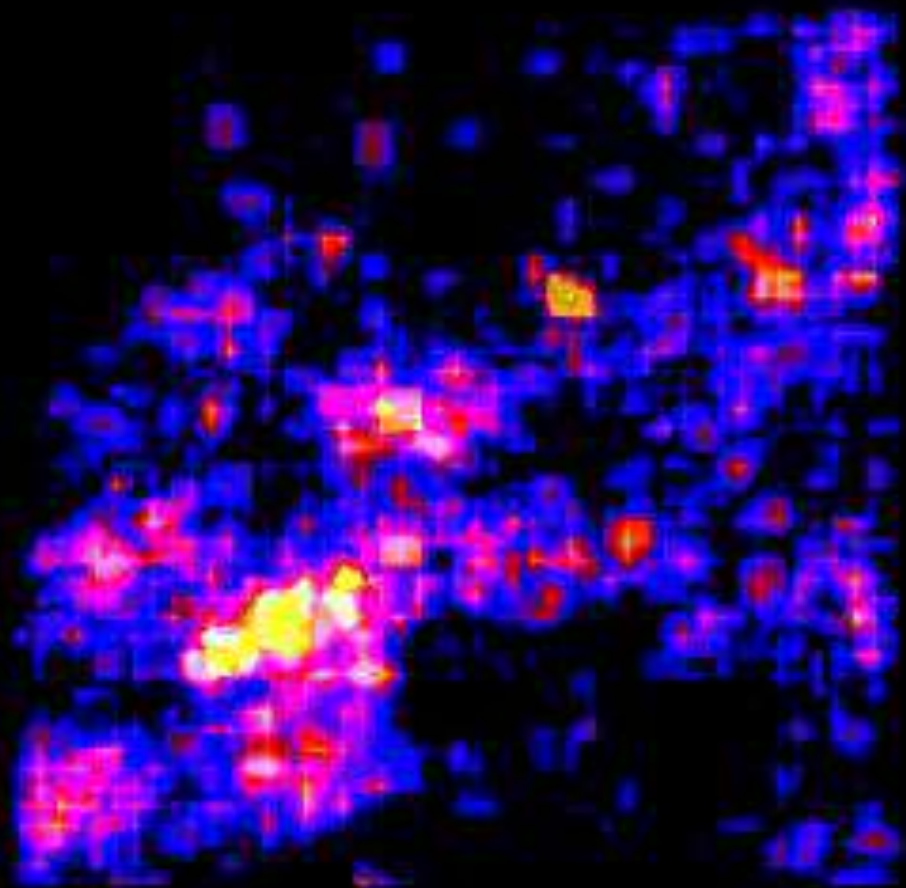


Rutile inclusions

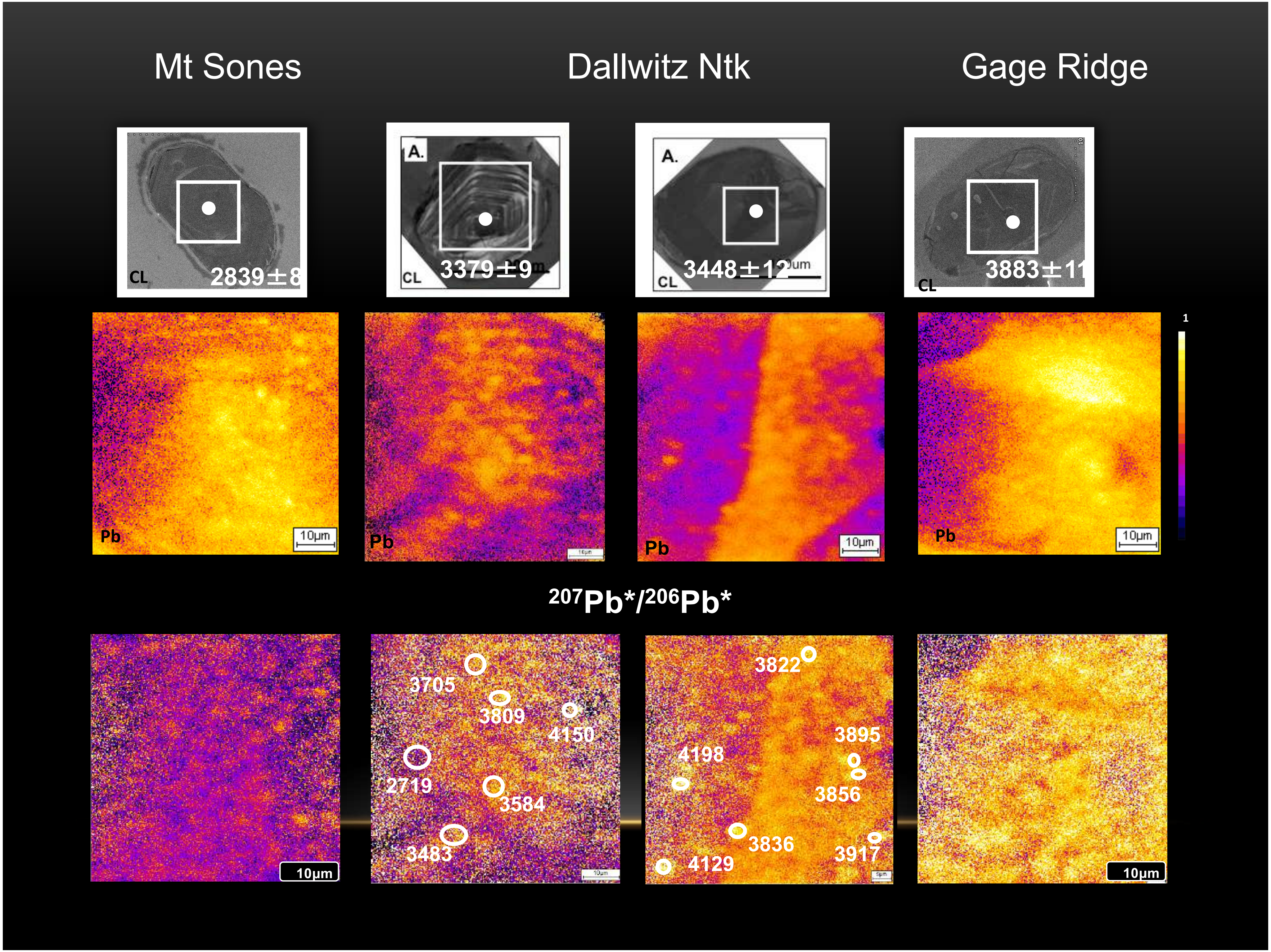


RECONSTRUCTION OF 3D VOLUME ~1MM X 0.7MM X 0.3 MM

Red ^{27}Al
Yellow ^{48}Ti
Blue ^{206}Pb

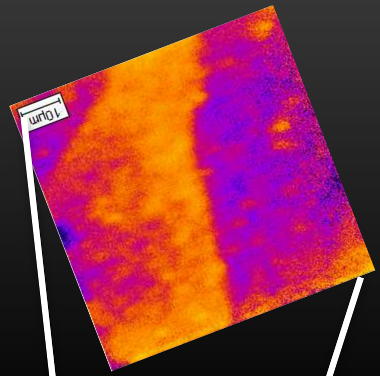


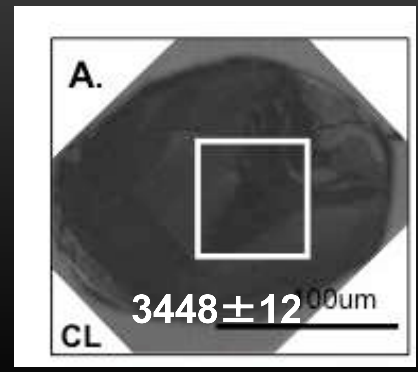
Lyon et al. 2019; Sci Rep

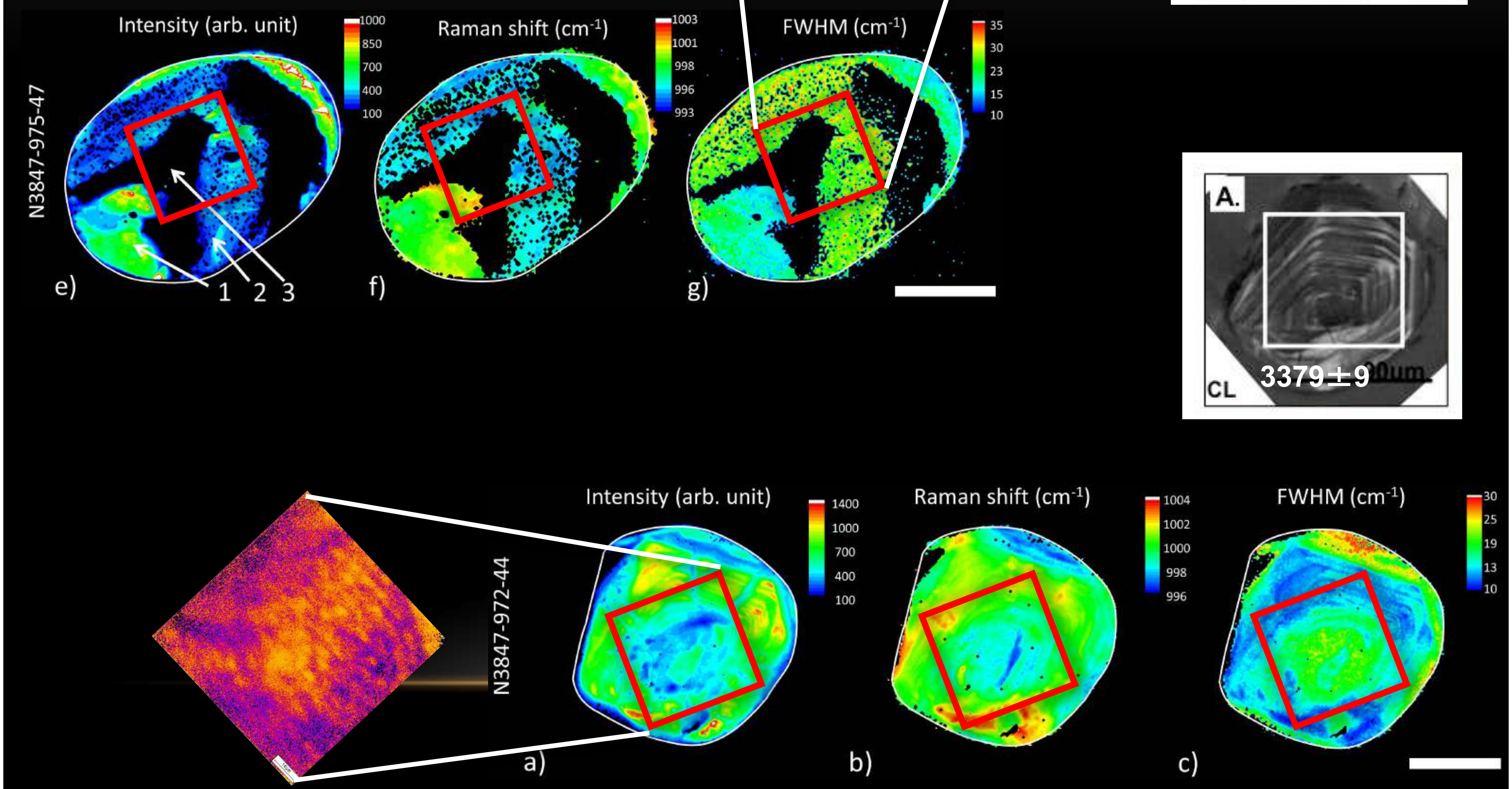


Mt Sones
Dallwitz Ntk
Gage Ridge
CL
2839±8
A.
CL
3379±9
A.
CL
3448±12
CL
3883±11
Pb
10μm
Pb
Pb
10μm
Pb
10μm
1
$^{207}Pb^*/^{206}Pb^*$
10μm
3705
3809
4150
2719
3584
3483
3822
3895
4198
3856
3836
3917
4129
10μm

1. A medium radiation damaged zone;
2. Amorphous area;
3. Glassy area



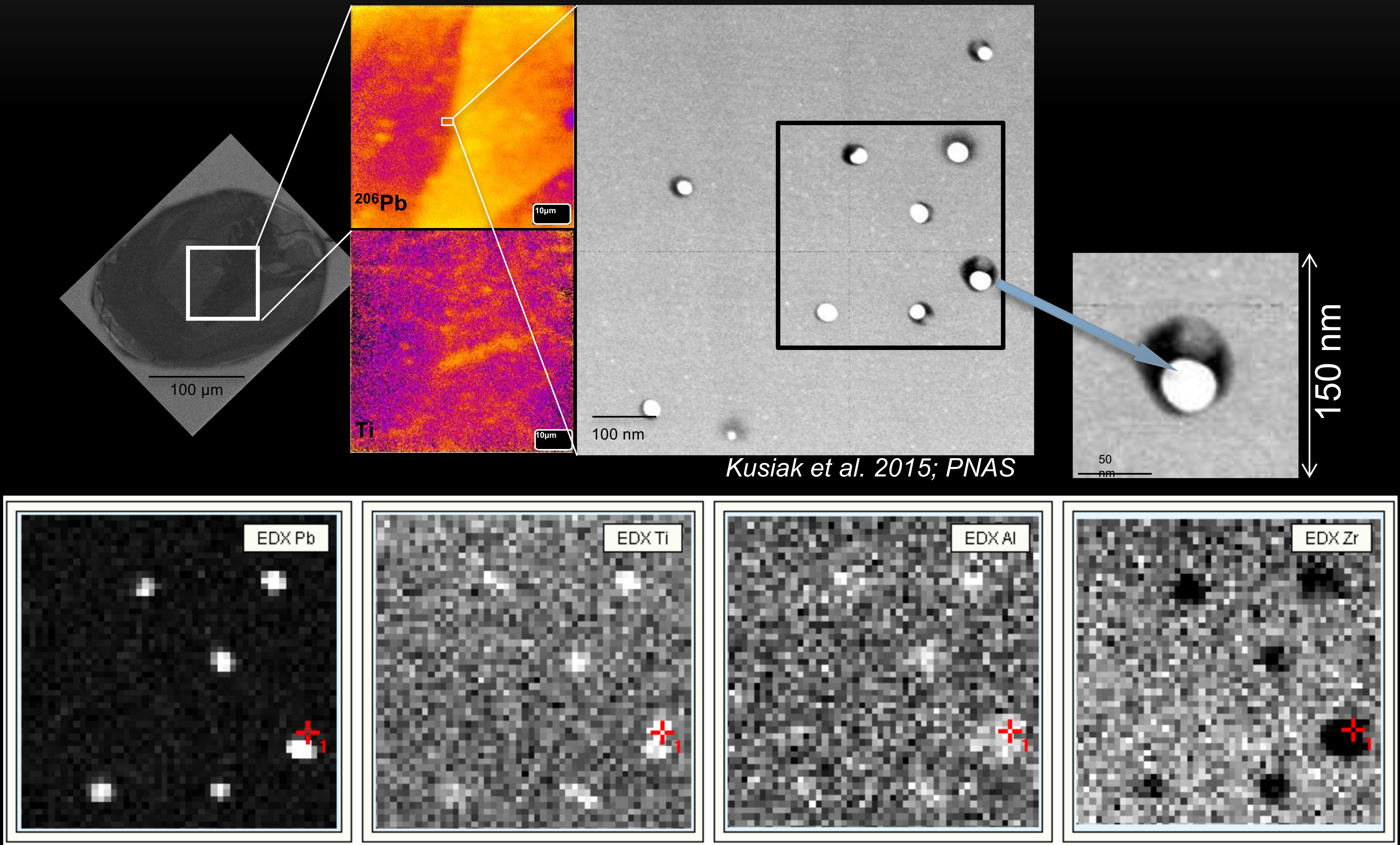




Kusiak et al. 2013; AJS

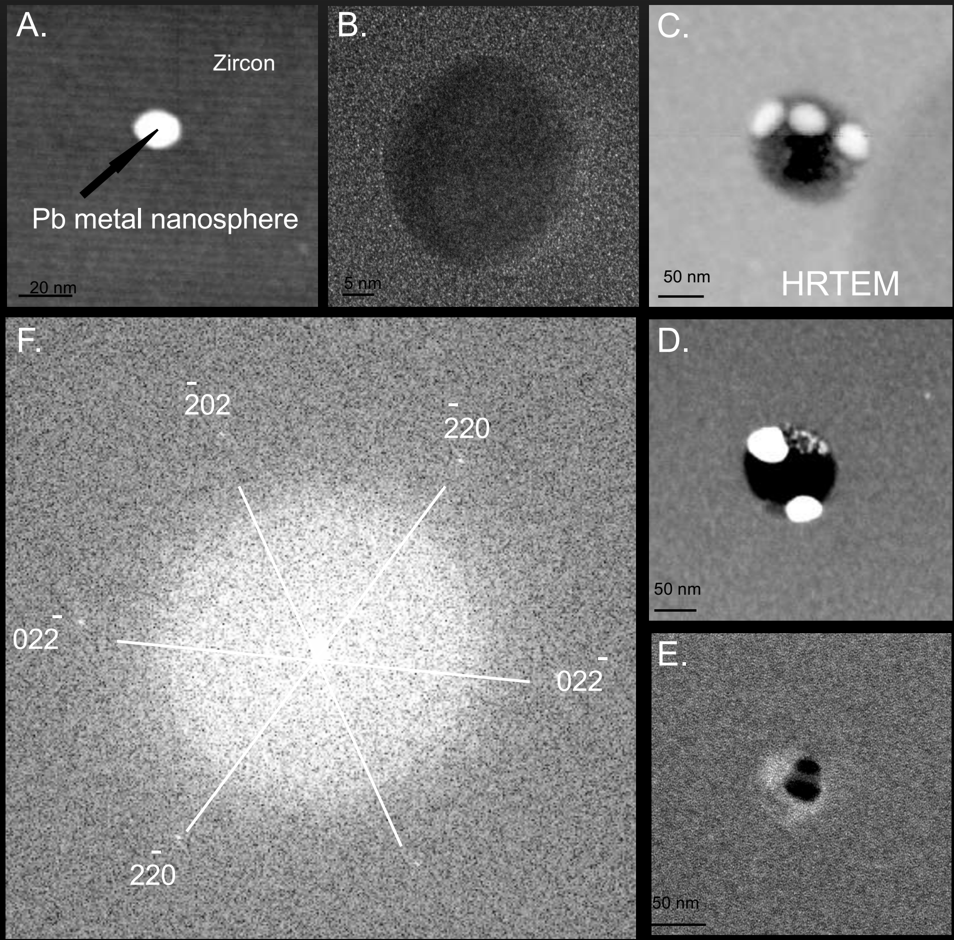
Not Pb in zircon but Pb nanoinclusions!

Some inclusions contain multiple phases



Kusiak et al. 2015; PNAS

HAADF TEM images of the Pb nanospheres in zircon

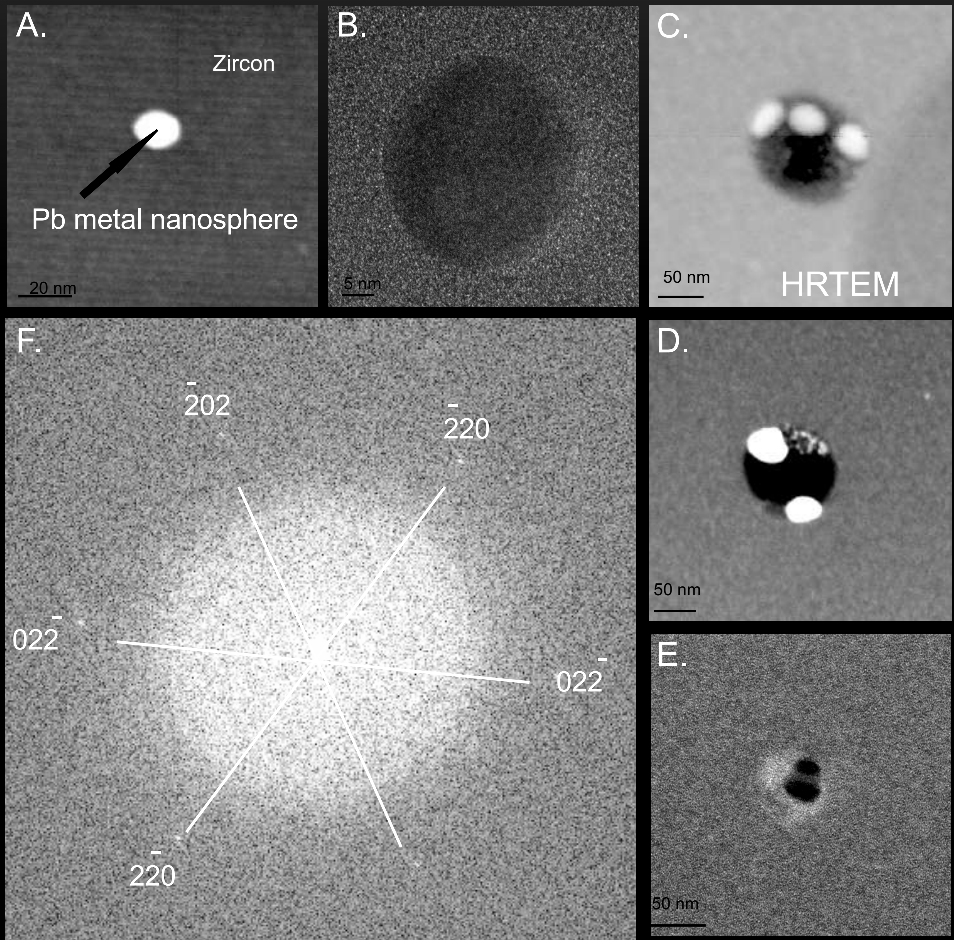


Pb nanospheres are randomly oriented with respect to crystallographic axes demonstrating that they are individual crystals, not atoms concentrated in the crystal lattice of host zircon.

HAADF – High-angle annular dark-field

Kusiak et al. 2015; PNAS

HAADF TEM images of the Pb nanospheres in zircon



- All vectors have lengths of 1.78 Å (*in agreement with Pb*)
- the angles between planes are 60°

Diffraction pattern indexed as cubic Pb

HAADF – High-angle annular dark-field

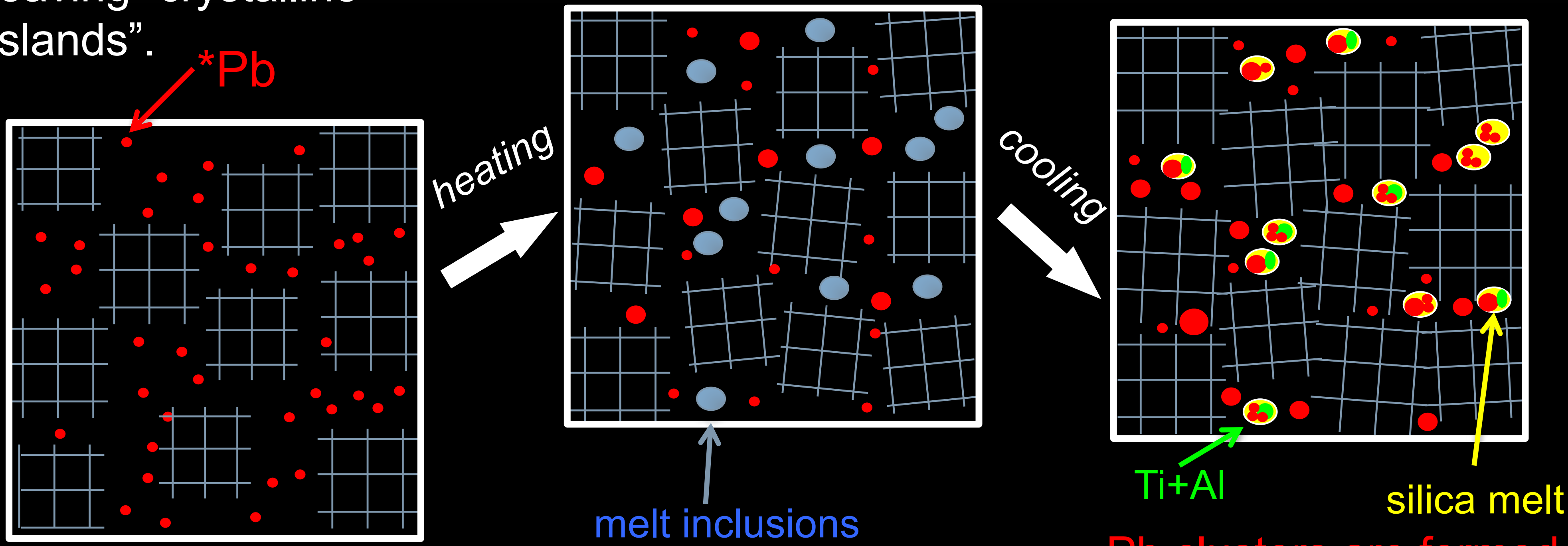
Kusiak et al. 2015; PNAS

Model of Pb-nanosphere formation

Zircon structure damaged during the radioactive decay leaving “crystalline islands”.

Individual incompatible elements are concentrated in the non-crystalline areas forming melt inclusions.

Metal melt (Pb) separates from the Si-rich phase forming nanospheres.



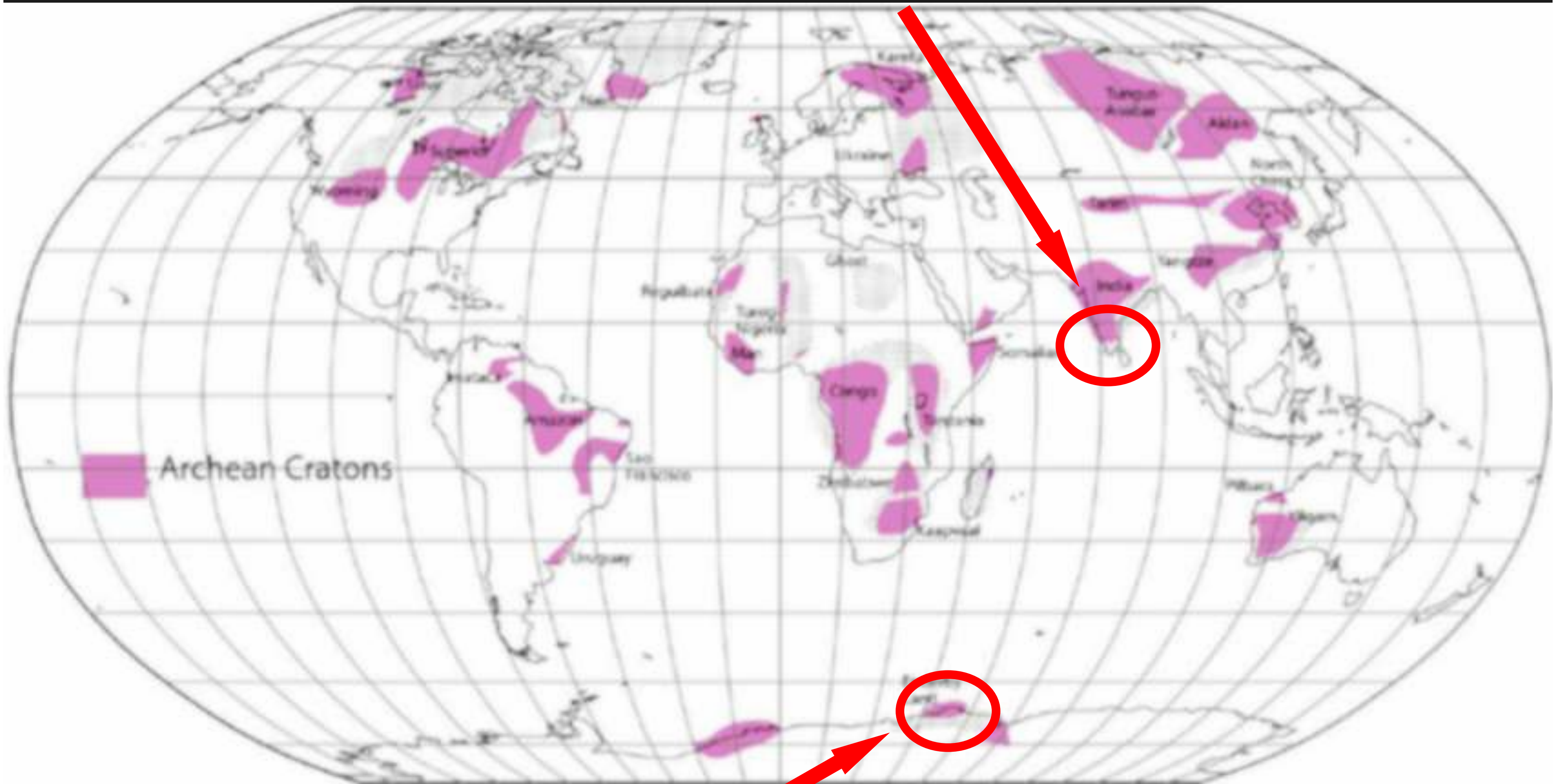
*Pb is distributed in the non-crystalline areas.

Larger *Pb spheres form at the expense of smaller ones thus minimizing surface energy (Ostwald ripening).

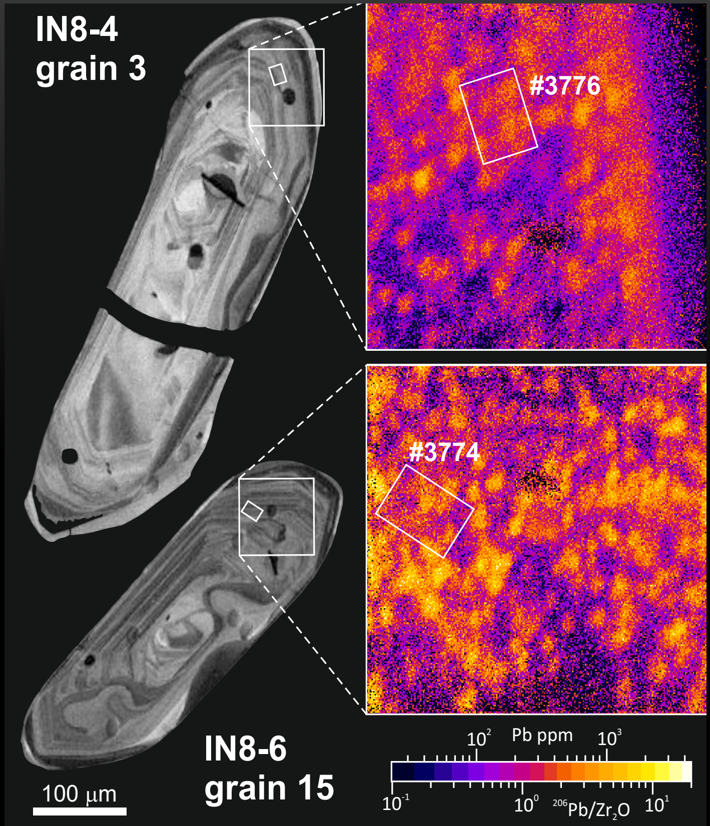
Pb clusters are formed and are commonly associated with silica melt locally enriched in Al and Ti.

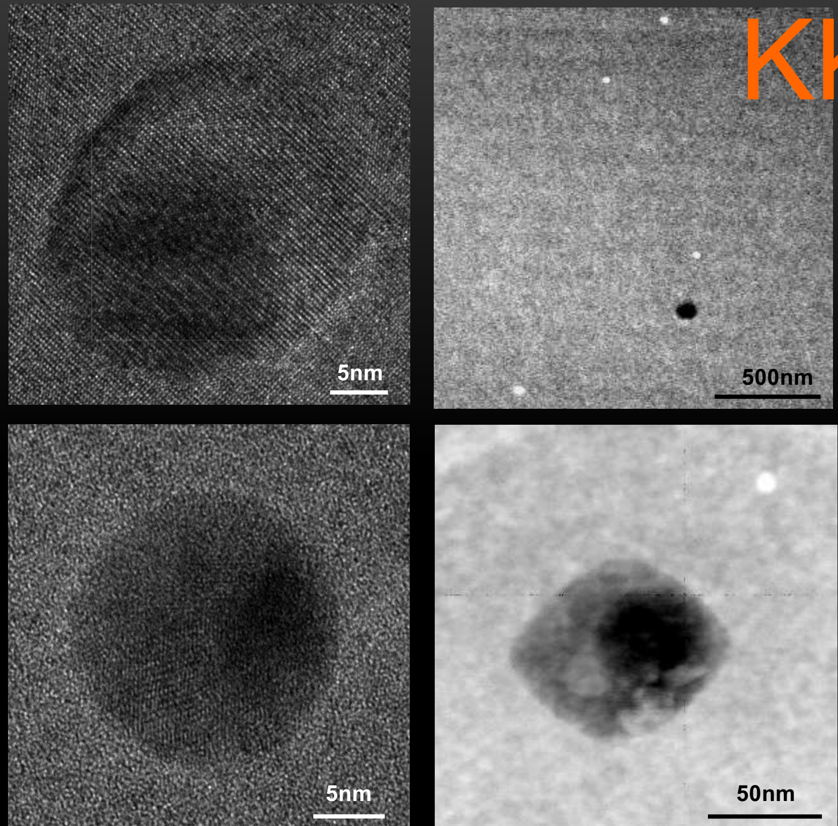
Kusiak et al. 2015; PNAS

Kerala Khondalite Belt, S India; 1.85 Ga, T 900 ºC



Napier Complex, Antarctica; up to 4.0 Ga, T 1100 ºC



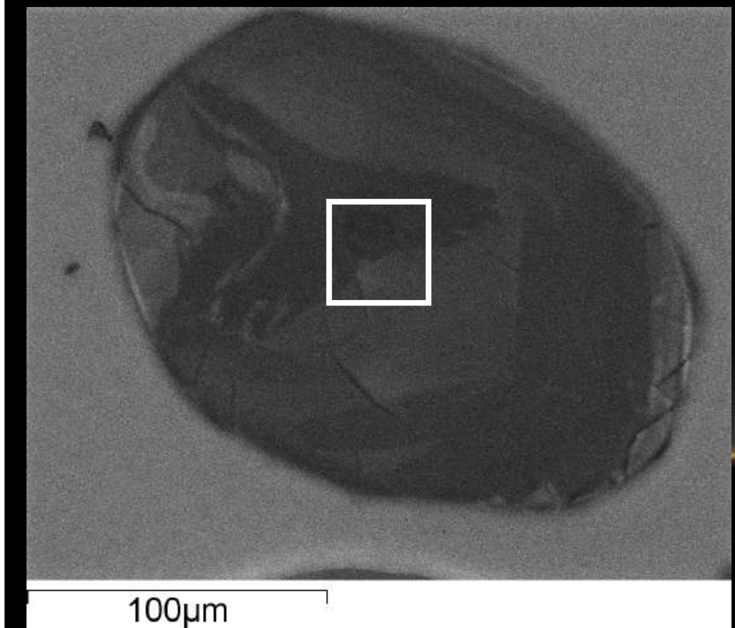


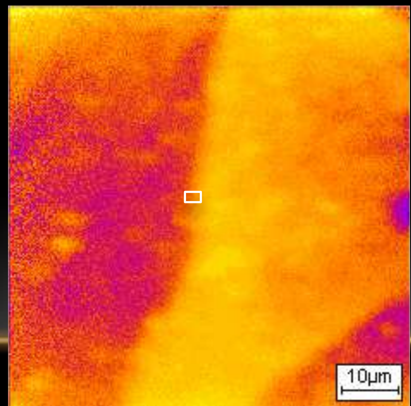
KKB, India

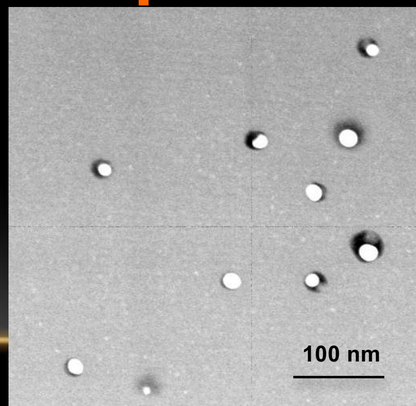
Protolith
1850 Ma
Metamorphism
560 Ma-T 900 ºC
510 Ma - ?

Whitehouse et al. 2017; Min & Pet

Napier Antarctica



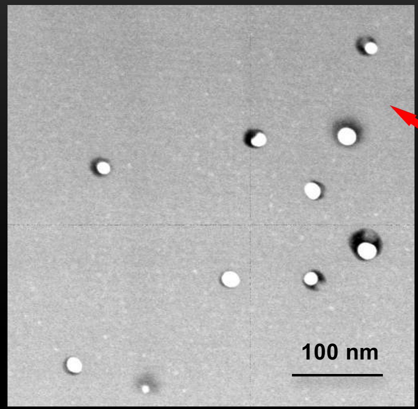




Protolith
up to 4.0 Ga
Metamorphism
2800 Ma
2500 Ma-T1100ºC

Kusiak et al. 2015; PNAS
Kusiak et al., 2017; AGU monograph

Napier, Antarctica



Pb spheres

up to 35 nm

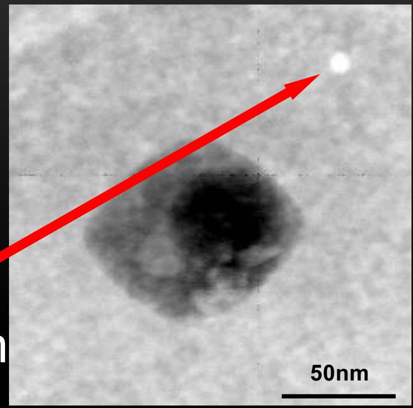
up to 20 nm

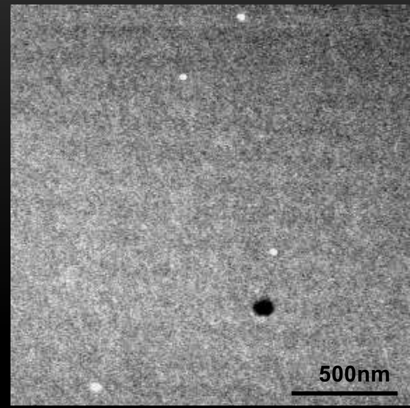
Protolith up to 4.0 Ga

Metamorphism 2800 Ma - ?

2500 Ma-T1100ºC

KKB, India





Protolith 1850 Ma

Metamorphism 560 Ma-T 900 ºC

510 Ma - ?

Similarities

- Pb spheres are heterogeneously distributed
- They represent metal Pb
- Metamictization is not a prerequisite for Pb nanosphere formation

Differences

- Pb spheres either single, or with Si, Ti-Al
- Si-rich phase never observed without a Pb
- Clusters of spheres

- Pb spheres never observed with Si
- Si-rich phases larger than Pb spheres
- Si-rich phases less common
- Zircon crystal highly crystalline
- Traces of Fe

Conclusions from Antarctic zircons

- The occurrence of metallic Pb nanospheres in UHT zircon can explain the unusual U-Pb behaviour of such grains during SIMS U-Pb analysis.
- Inhomogeneity in the distribution of radiogenic lead, and possible matrix effects, may result in inaccurate age estimates of such zircon when analysed by microbeam techniques.

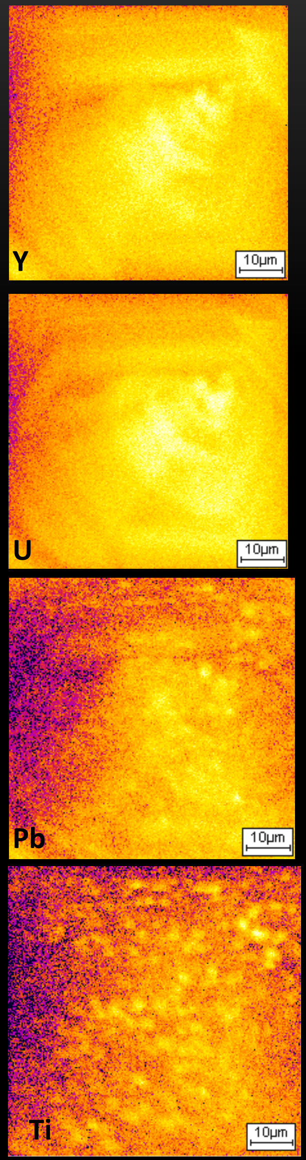
Conclusions from Indian zircons

- Since UHT metamorphism is common to both regions, the mechanism to generate Pb nanospheres appears to be related to these extreme metamorphic conditions.

- Separate occurrence of metallic Pb nanospheres and Si-rich phase rules out operation of a liquid immiscibility mechanism that has been proposed for Enderby Land.

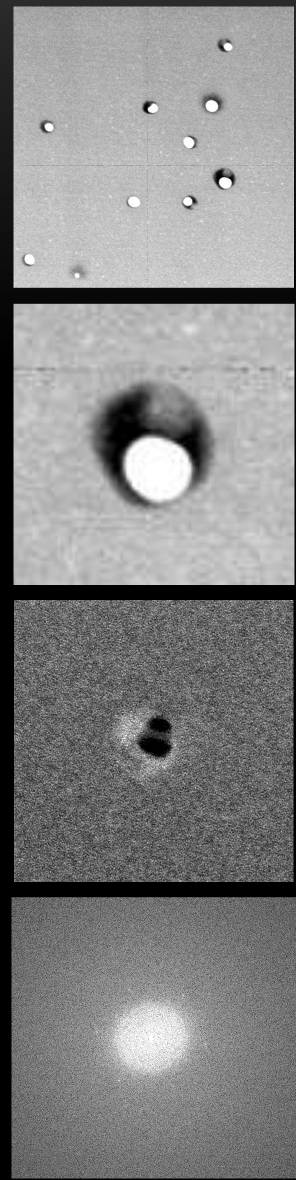
Micro Observations:

- Zr, Hf, Y, U and Th: distributions reflect growth zoning in original (protolith) zircon
- Pb and Ti: distributions reflect growth zoning, but also concentrated into sub-micron domains
- Pb is radiogenic, and not compatible in crystalline zircon, but Ti was originally in solid solution in protolith zircon
- If Ti behaves in a similar way as Pb, then it's compatibility in zircon has been reduced (e.g. lower temperature?)



Nano Observations:

- Pb is present as a metal spheres of 10-30 nm in size, randomly distributed in zircon
- The spheres might be associated with a quench phase, rich of Ti-Al;
- Y or Fe cloths might be present
- Pb and/or Ti-Al sometimes present in as inclusions with silica glass (only Antarctica)



Nanospheres represent melt inclusions

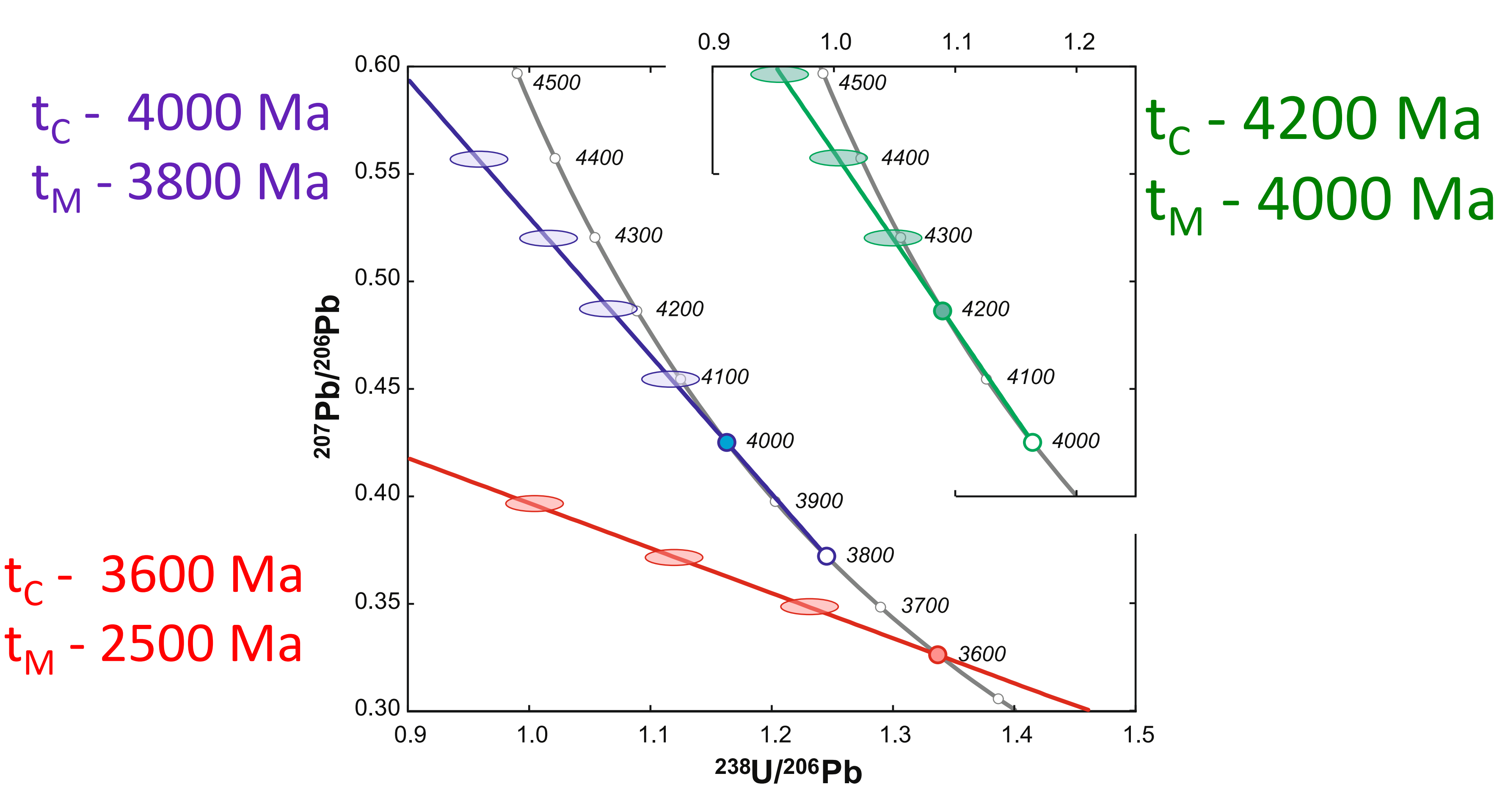
(must be above 327°C).

Conclusions 1:

- Pb and other elements are present as nanoinclusions in annealed zircon after (U)HT
- Multi-phase nanoinclusions are melt inclusions
- All APT work documented clustering of Pb atoms in zircon, but no formation of Pb spheres similar to those observed zircon by TEM
- Pb clusters can be interpreted as precursor of the formation of Pb nanospheres.

Conclusions 2:

- Pb nanospheres can result in spuriously old or young ages by SIMS analysis.
- Nanospheres <10 nm are too small to affect Pb count rates on SIMS.
- Regardless of the mechanism of Pb nanosphere formation, their presence can prevent the loss of radiogenic Pb from a zircon and, hence complete resetting to the (U)HT metamorphic age.



- readily recognized as such at apparent $^{207}Pb/^{206}Pb$ ages that are only slightly in excess of t_C
- resolvable as discordant only at apparent $^{207}Pb/^{206}Pb$ ages > 4200 Ma
- only resolved as discordant when the apparent $^{207}Pb/^{206}Pb$ age exceeds 4400 Ma

Rhodope Metamorphic Complex, Greece; 2.1 Ga, T 800 ºC

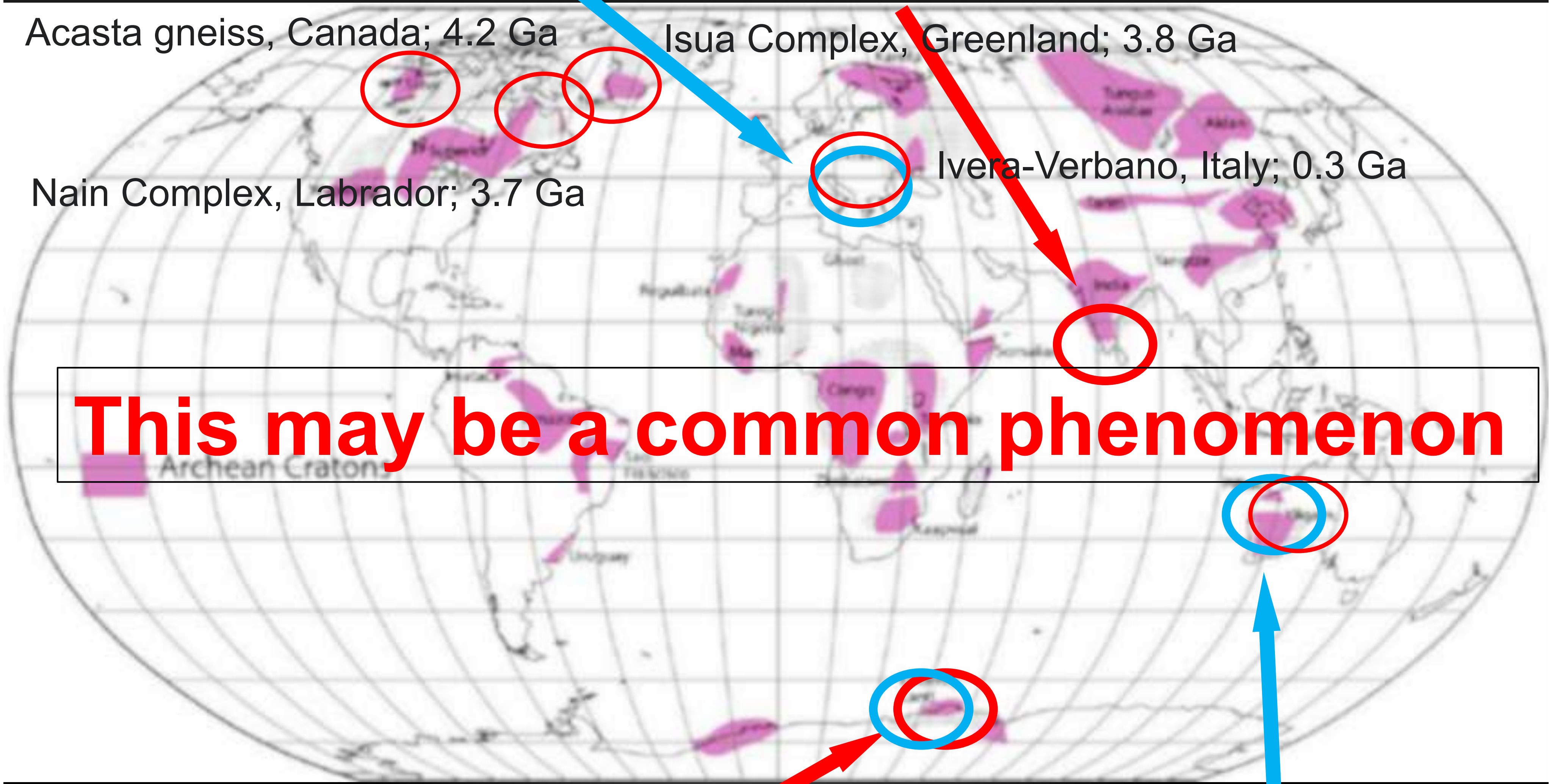
Kerala Khondalite Belt, S India; 1.85 Ga, T 900 ºC

Acasta gneiss, Canada; 4.2 Ga

Isua Complex, Greenland; 3.8 Ga

Nain Complex, Labrador; 3.7 Ga

Ivera-Verbano, Italy; 0.3 Ga



This may be a common phenomenon

Napier Complex, Antarctica; up to 4.0 Ga, T 1100 ºC

Jack Hills, W Australia; 4.4 Ga, T ˜450 ºC

Instytut Geofizyki
Polskiej Akademii Nauk

Thank you!

Richard Wirth
Daniel J. Dunkley
Martin J. Whitehouse
Simon A. Wilde
Ian Lyon
Martina Menneken
Chutimun N. Chanmuang
Katarina Marquadt
Christian Schmidt
Lutz Nasdala
Tsuyoshi Iizuka

A. B. DOBROWOLSKI POLISH ANTARCTIC STATION

Alexander von Humboldt
Stiftung/Foundation

MARIE CURIE ACTIONS

What was done?

1. Williams et al. 1984, CMP; SHRIMP; Napier
2. Kusiak et al., 2013, Geology; 1280; Napier
3. Kusiak et al., 2013, AJS; 1280, Raman; Napier
4. Valley et al, 2014, NatGe; APT; JH
5. Whitehouse et al., 2014, CMP; 1280; KKB
6. Valley et al., 2015, AM, APT; JH
7. Kusiak et al., 2015, PNAS; TEM, Napier
8. Peterman et al., 2016, ScieAdv; APT, Rhodope
9. Piazolo et al., 2016, NatCom; APT, Napier
10. Whitehouse et al., 2017, MinPet; 1280,TEM; KKB
11. Kusiak et al., 2017, AGU; 1280,TEM,Synch; Napier
12. Ge et al., 2018, Geology; 1280; JH
13. Kusiak et al., 2019, GCA; TEM
14. Lyon et al. 2019, Sci Rep.; NanoSIMS, Napier