# When good zircons go bad

## ›› Redistribution of Radiogenic Pb in Granulite Grade Zircon, Snowbird Tectonic Zone, Canada

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# J.C. Roddick Ion Microprobe Laboratory, Geological Survey of Canada

- **Lab dominantly involved in geochronological applications, closely integrated with TIMS facility.**

- **Projects defined by GSC program activities, with component of work from external sources (universities, provincial geological surveys, industry).**

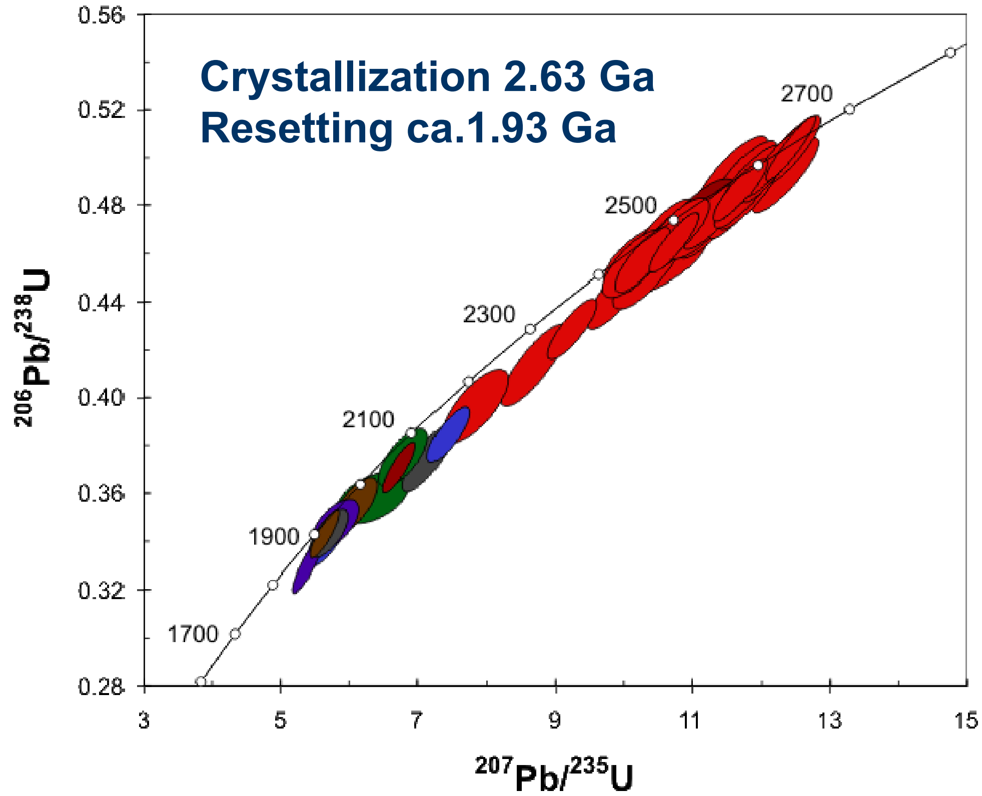
- **Currently three dedicated operational staff: Nicole Rayner (project scientist), Tom Pestaj (technologist), Bill Davis (research scientist).**

- **WHEN GOOD ZIRCONS GO BAD:**
    - ***the patient***
    - ***the symptoms***
    - ***the treatment***
    - ***the diagnosis***
    - ***a possible cure?***

# Redistribution of Pb in zircon

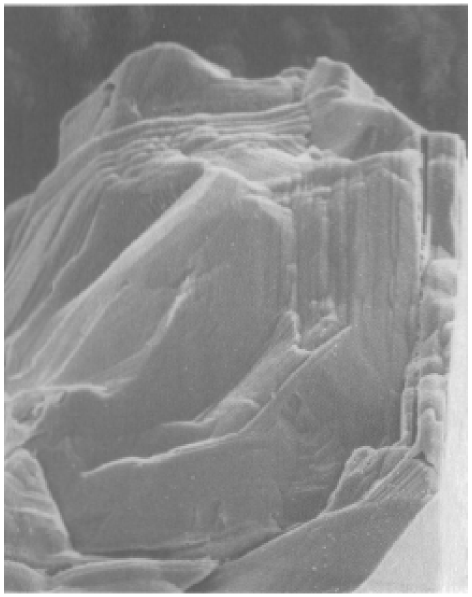
- **Typically seen as Pb-loss with respect to U**
- **Recognized by discordance of U-Pb system**
  - Recrystallization/growth
  - Leaching
  - Alteration
  - Deformation
  - Diffusive loss
- **Pb redistribution can be a good thing**
  - can be used to calibrate secondary processes affecting a rock

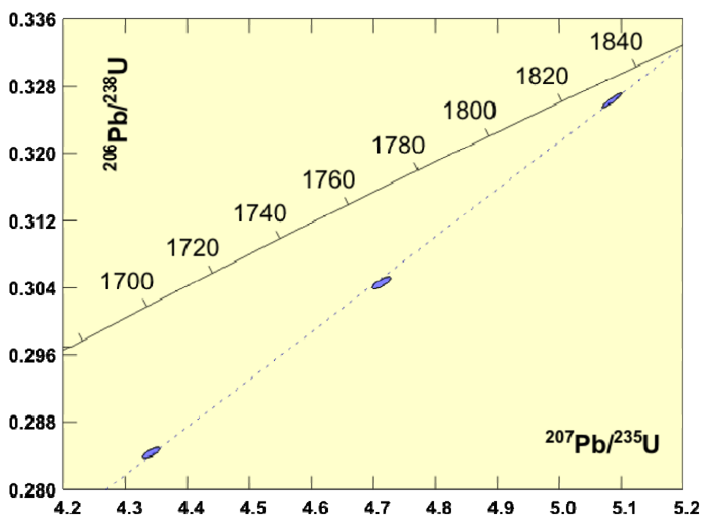
## Sample 8811, pegmatitic norite



# Scale of redistribution

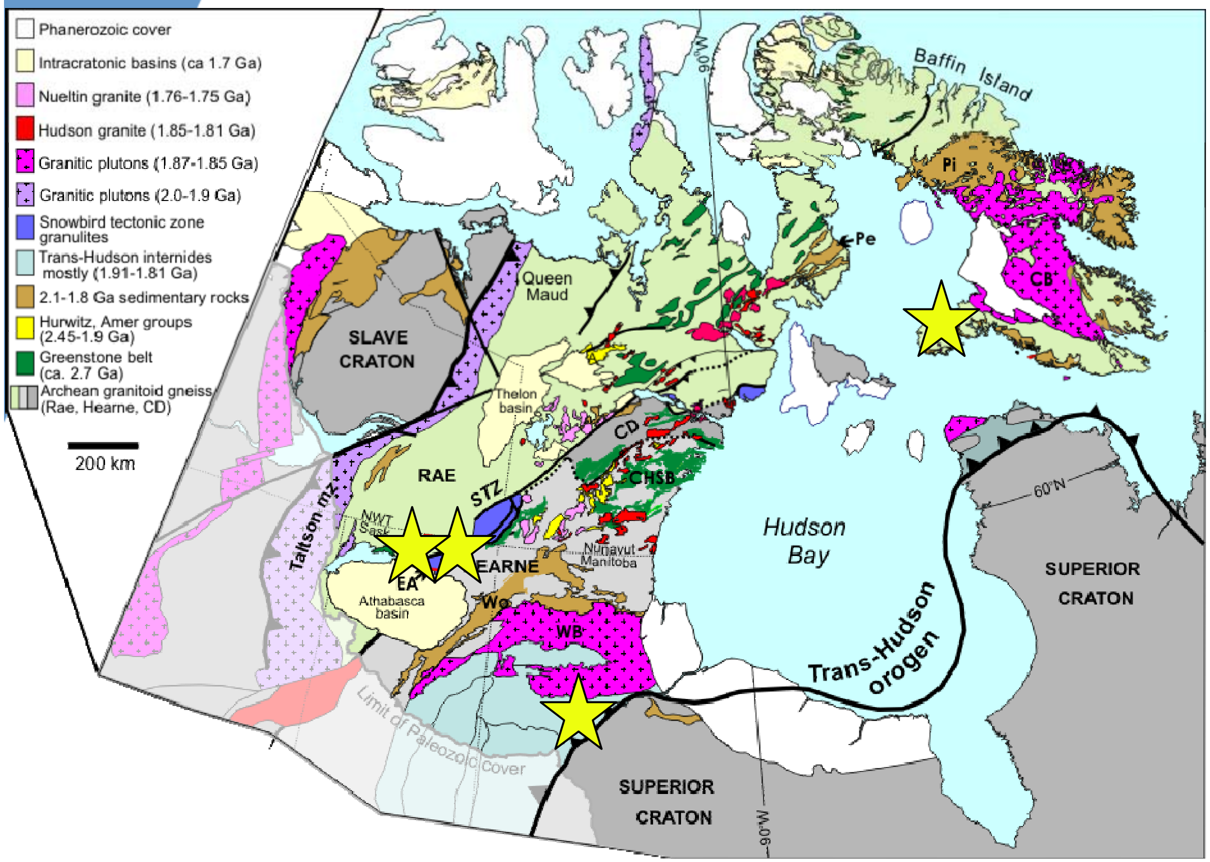
- **Local redistribution via recoil processes (nm or less)**
  - High U zone adjacent to low U zone (Mattinson et al. 1996)






- **Unmixing at a given scale (um or less, domains of Pb-loss vs no loss)**
  - expelled from the zircon

# The patient:
# Mafic granulites from Snowbird Zone

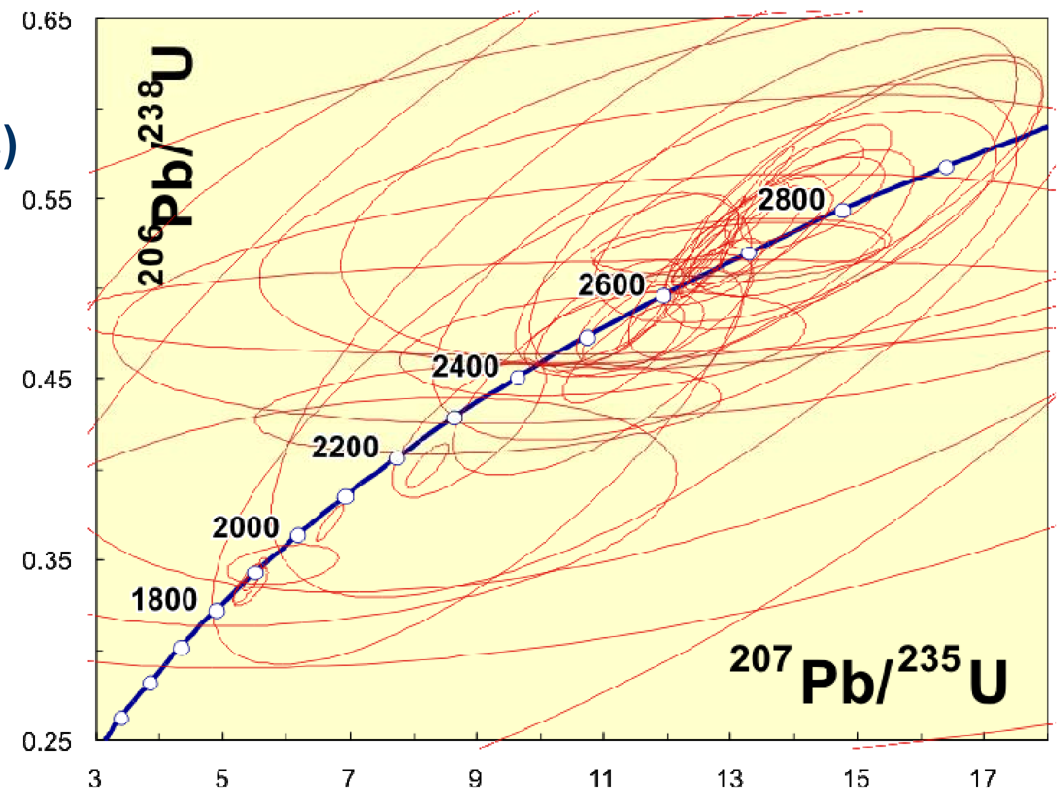



- Unusual Pb ionization behaviour that doesn't correlate with "classical" Pb-loss
- Always seen in granulite grade rocks (but not in all granulite grade rocks)
- Approximately 10 documented cases, all within the Trans-Hudson Orogen or reworked margins

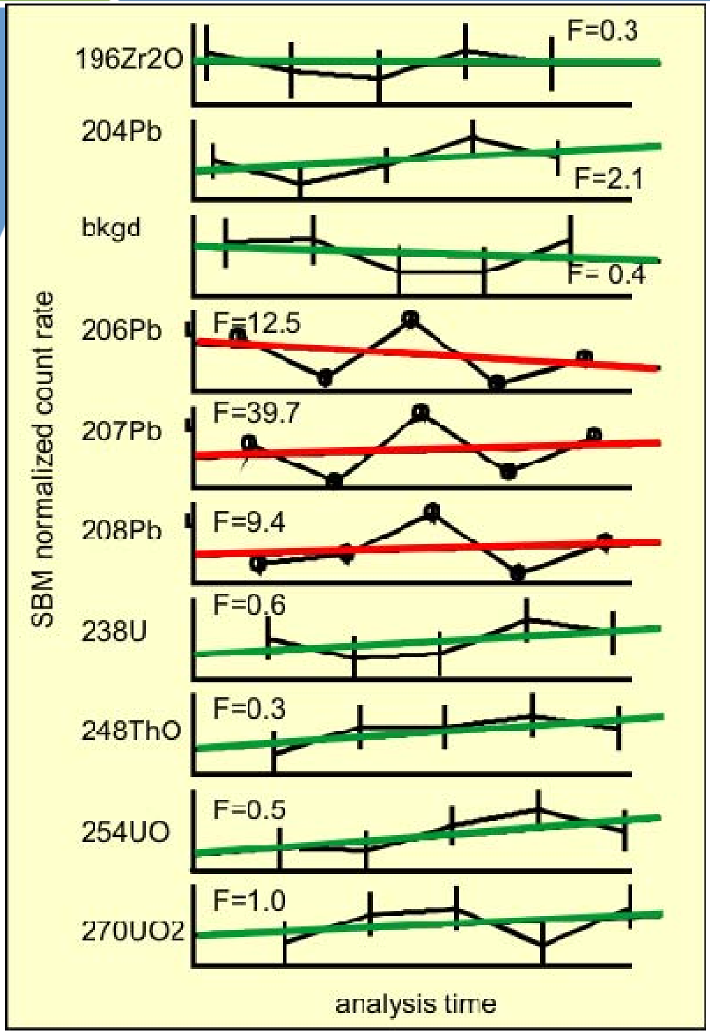
# The patient: Mafic granulites from Snowbird Zone

## Sample 8617

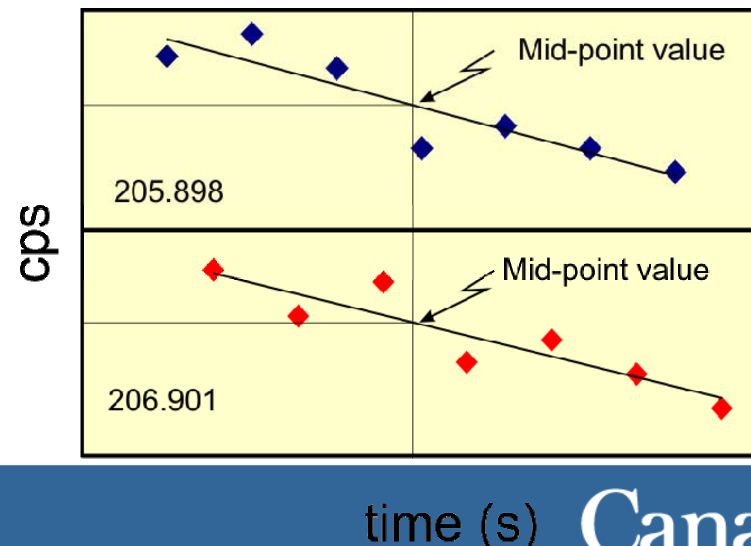
- Extremely large errors on some analyses (2σ ellipses)
- Domainal within individual zircon grains
- Excess scatter does not correlate with age (i.e. degree of Pb-loss)
- Excess scatter does not correlate with composition (i.e. U ppm)



# The symptom:
# Unusual Pb secondary ion yields

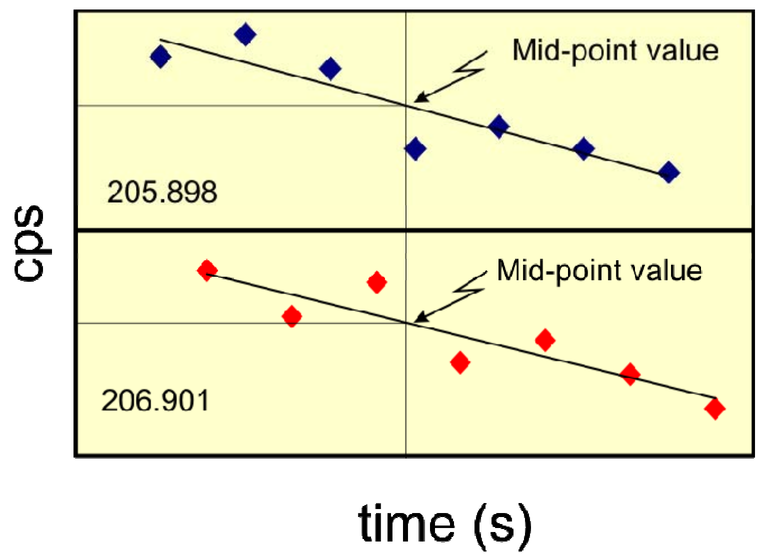



- **Non-linear ionization of Pb isotopes**
- **Normal ionization of Zr, Th, U**
- **Not seen in other samples during same analytical session**
- **"Snapshot" method of calculating a single count rate/isotope**
- **Ratios calculated from individual cps "snapshots"**
- **Strongly affected by outliers**

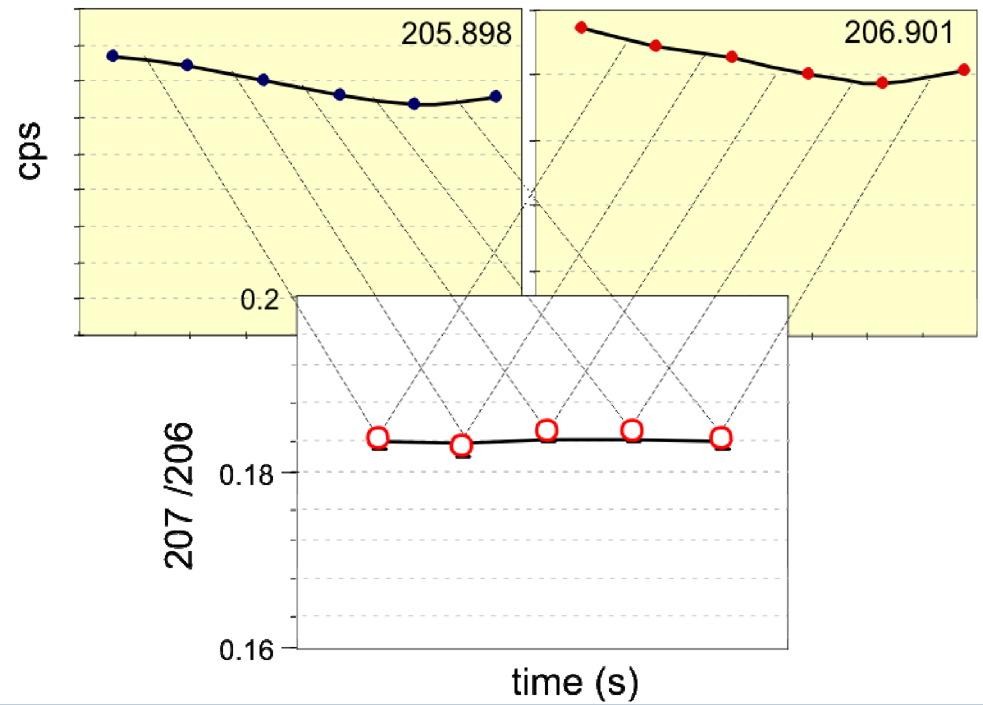


# PRAWN vs SQUID

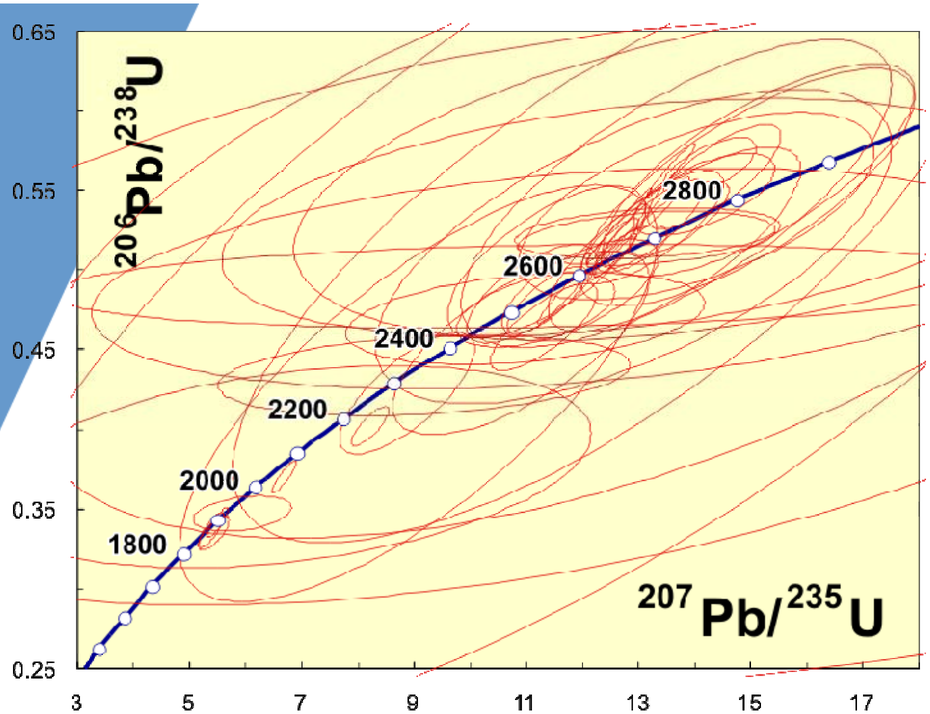
- "Snapshot" method of calculating a single count rate/isotope
- Ratios calculated from individual cps "snapshots"
- Strongly affected by outliers



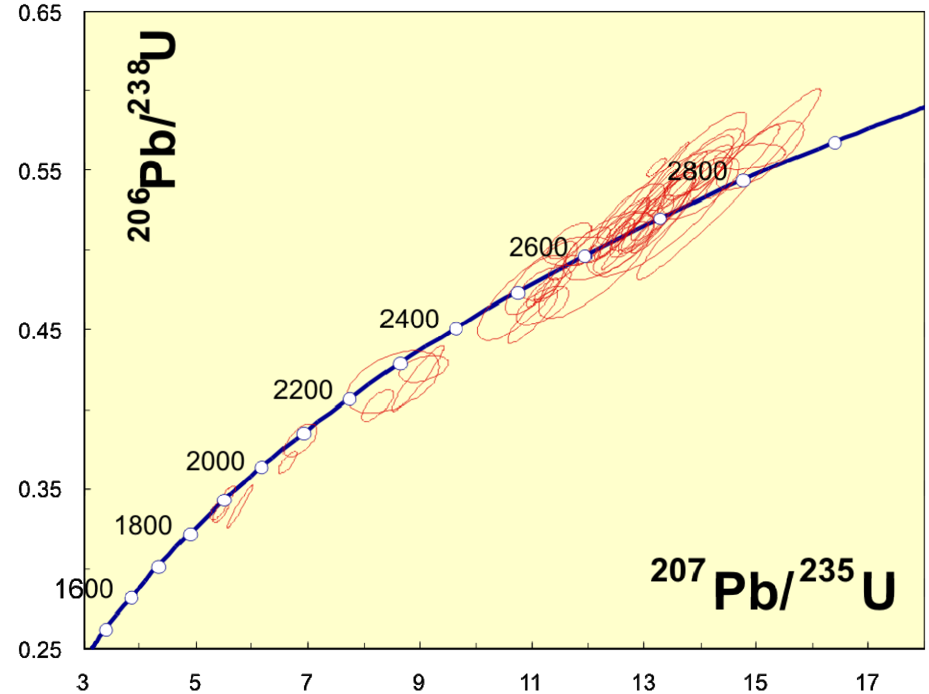

- Dodson double-interpolation to calculate N-1 ratios at mean time between each double pair of peaks
- Takes robust mean of N-1 ratios
- Resistant to outliers



# The treatment: SQUID



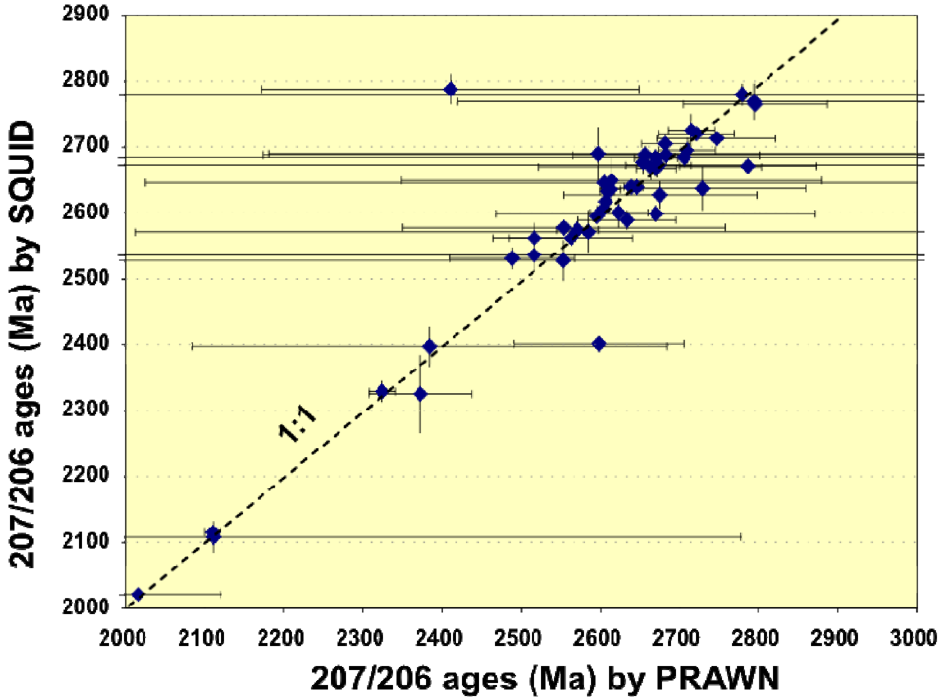

**PRAWN**




**SQUID**

- Much improved but excess scatter remains even after SQUID – still something unusual with these zircon

# The treatment: SQUID




- Excellent reproducibility of results regardless of data reduction scheme
- Note that there is no correlation between age and excess scatter; this isn't related to loss of Pb from the zircon

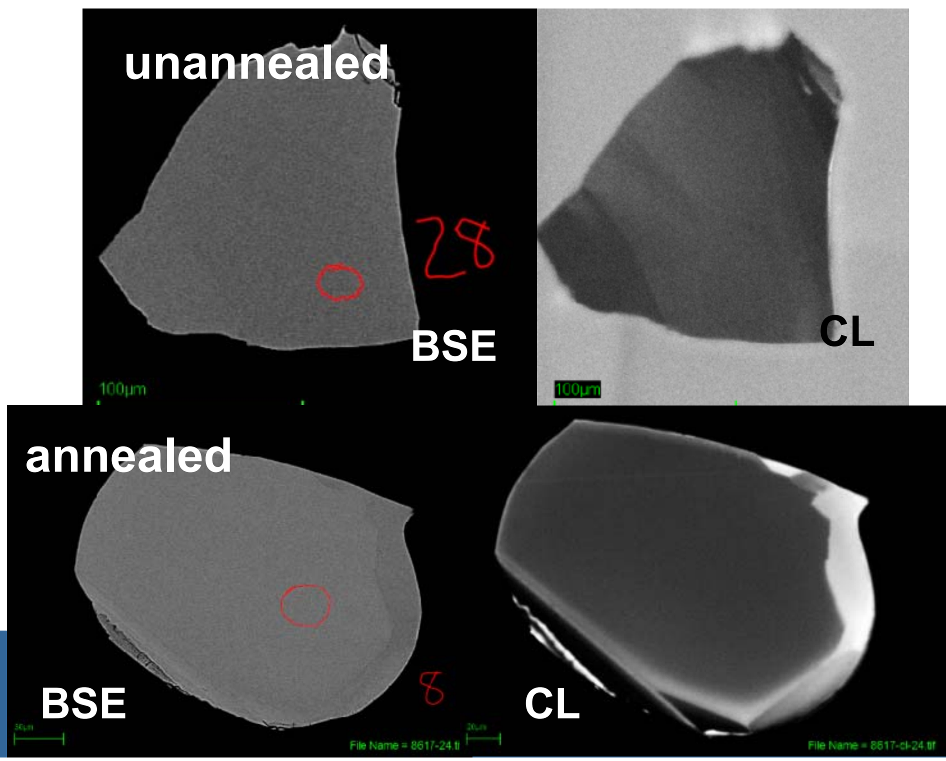
# Secondary Ionization of Pb in zircon

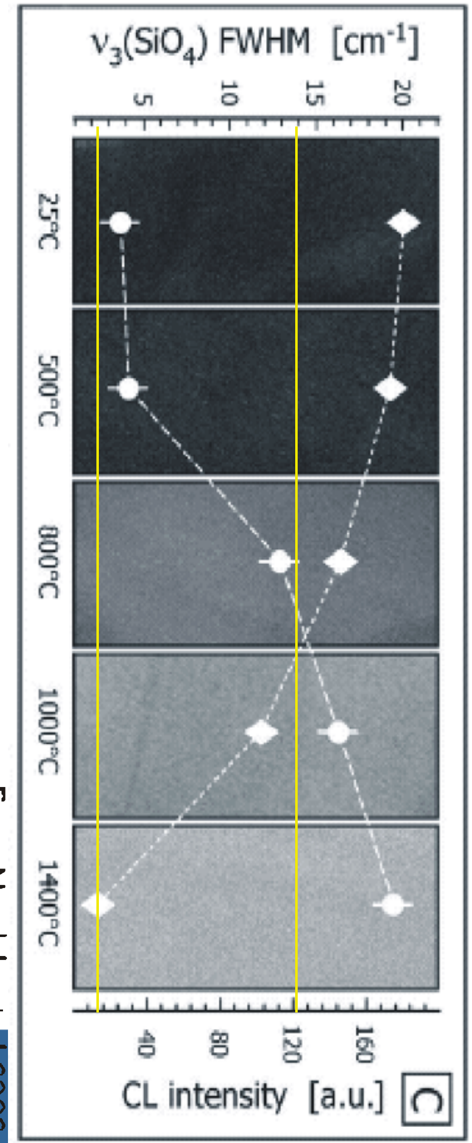
## Matrix effects

- **Microstructural state**
  - annealing experiments
- **Severely metamict/altered**
  - Wiedenbeck, 1995; MacLaren et al, 1994
  - ionization behaviour correlates with chemical composition e.g. elevated 204Pb, high LREE
- **Compositional controls (U, REE content)**
  - Williams and Hergt, 2000; Black et al 1991; Black et al 2004
  - affects Pb/U ratios but not Pb/Pb ratios

# The diagnosis: Microstructural state?

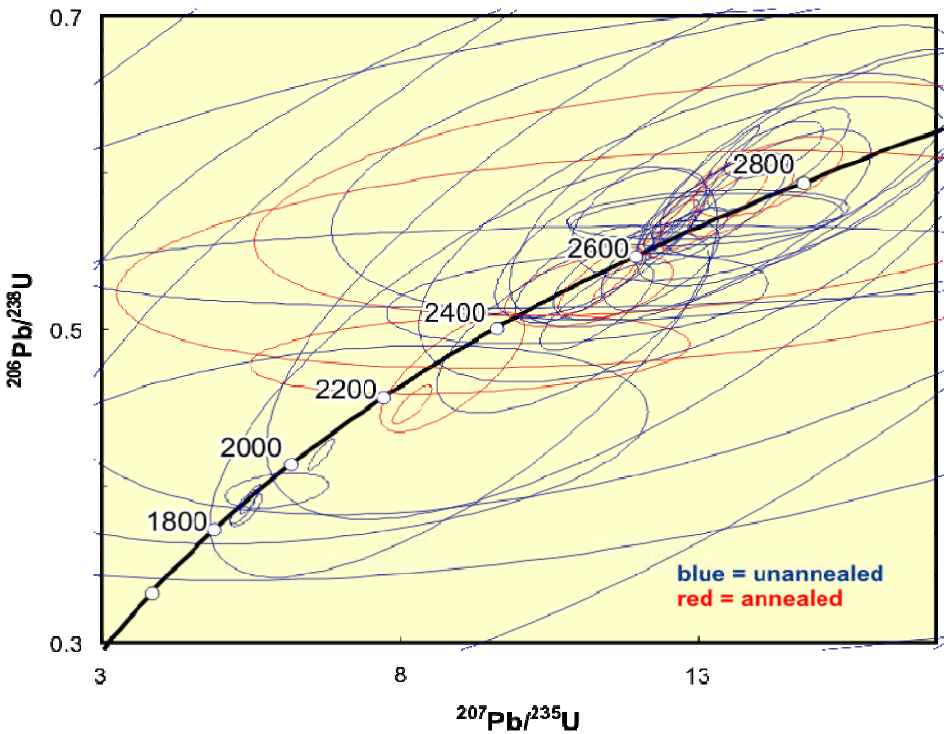
- Annealing experiment
- Dramatic recovery of CL response in annealed zircon
- Expected recovery of crystal lattice (Nasdala et al. 2002)
- Annealing does not reduce excess scatter




From Nasdala et al 2002

# The diagnosis: Microstructural state?




- Annealing experiment
- Dramatic recovery of CL response in annealed zircon
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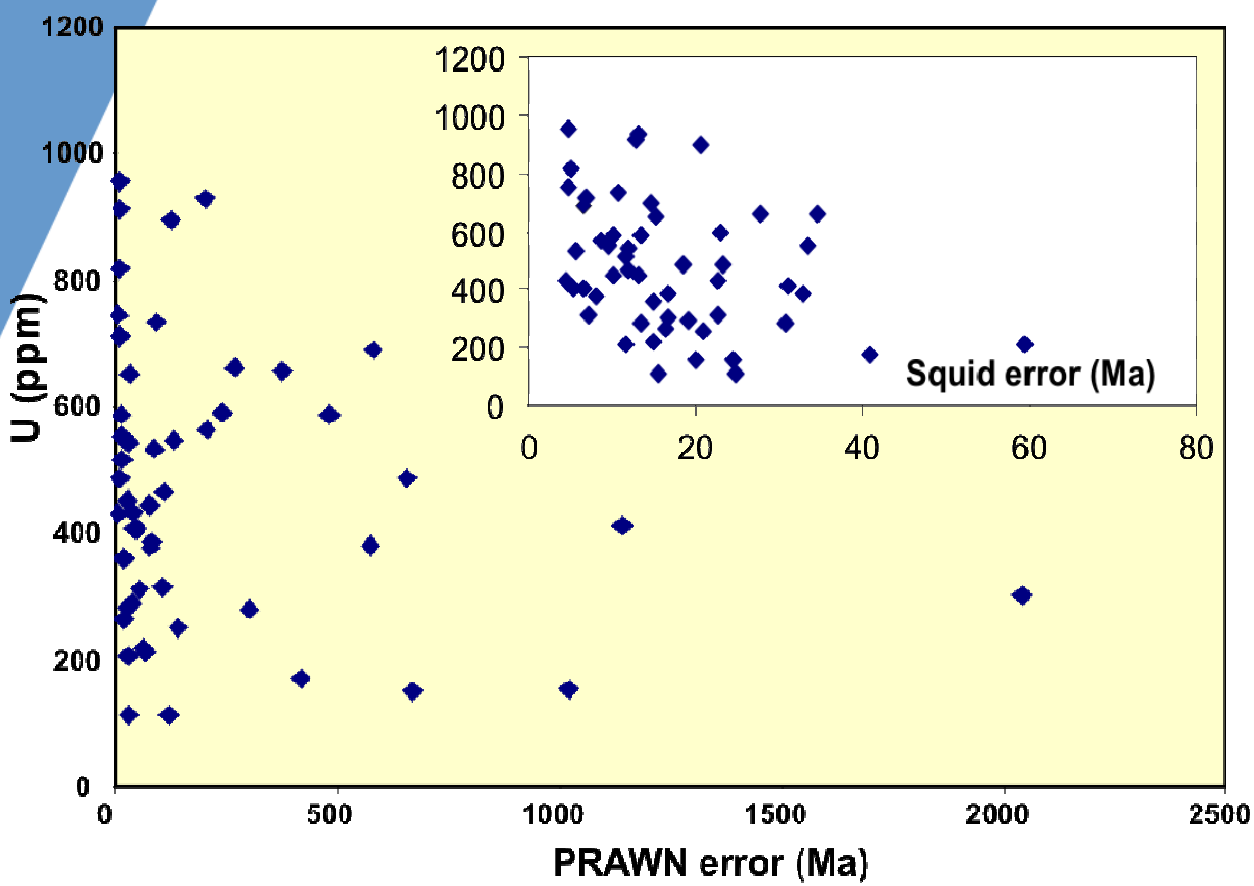
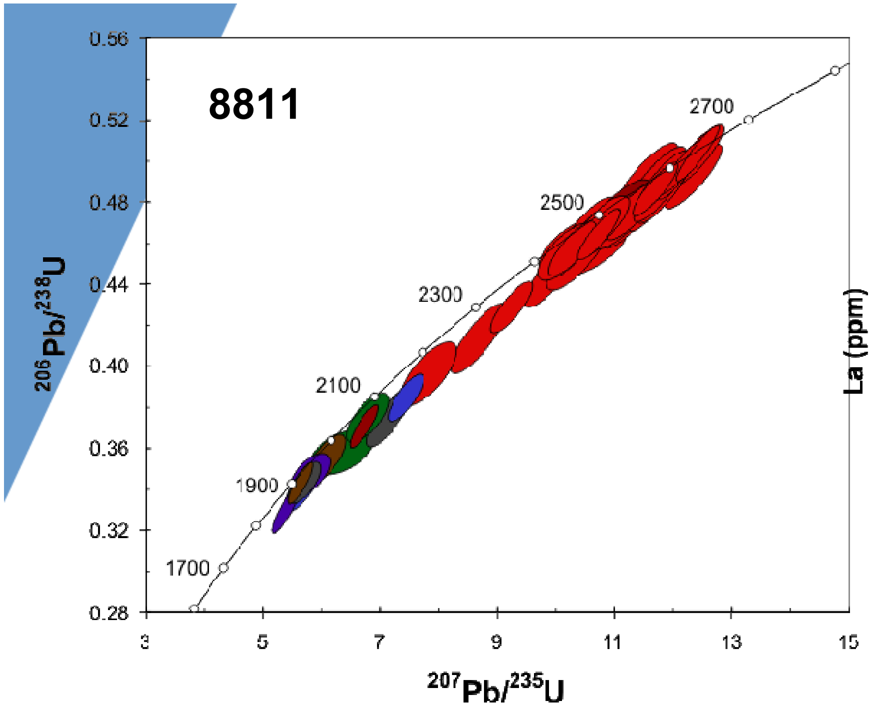
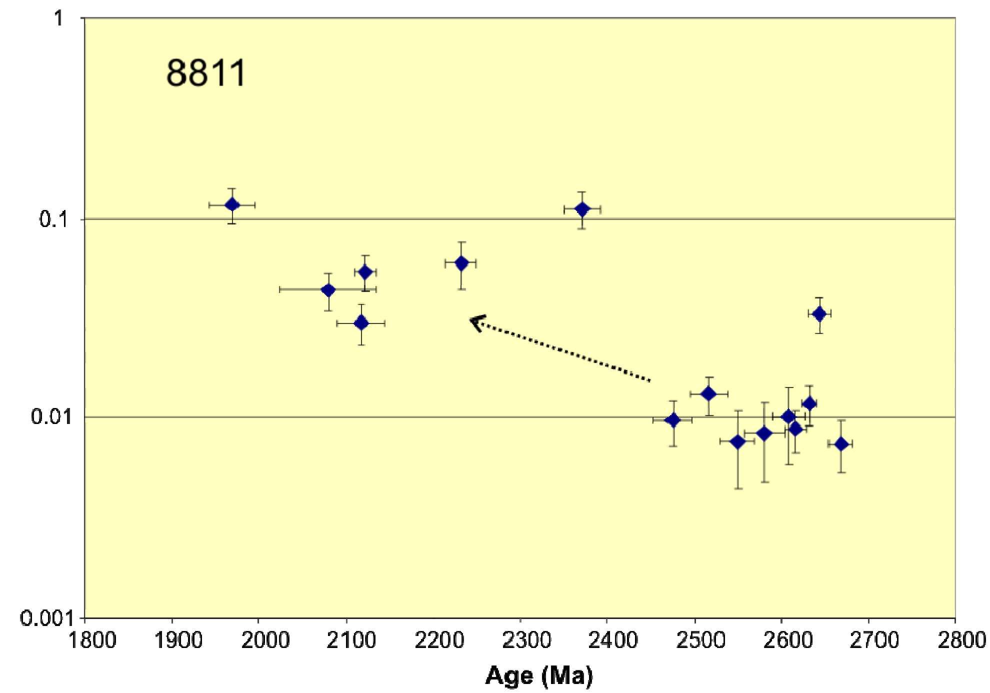
# The diagnosis: Trace elements?




- No correlation between excess scatter and U content
- Scatter in excess of counting statistics remains after SQUID

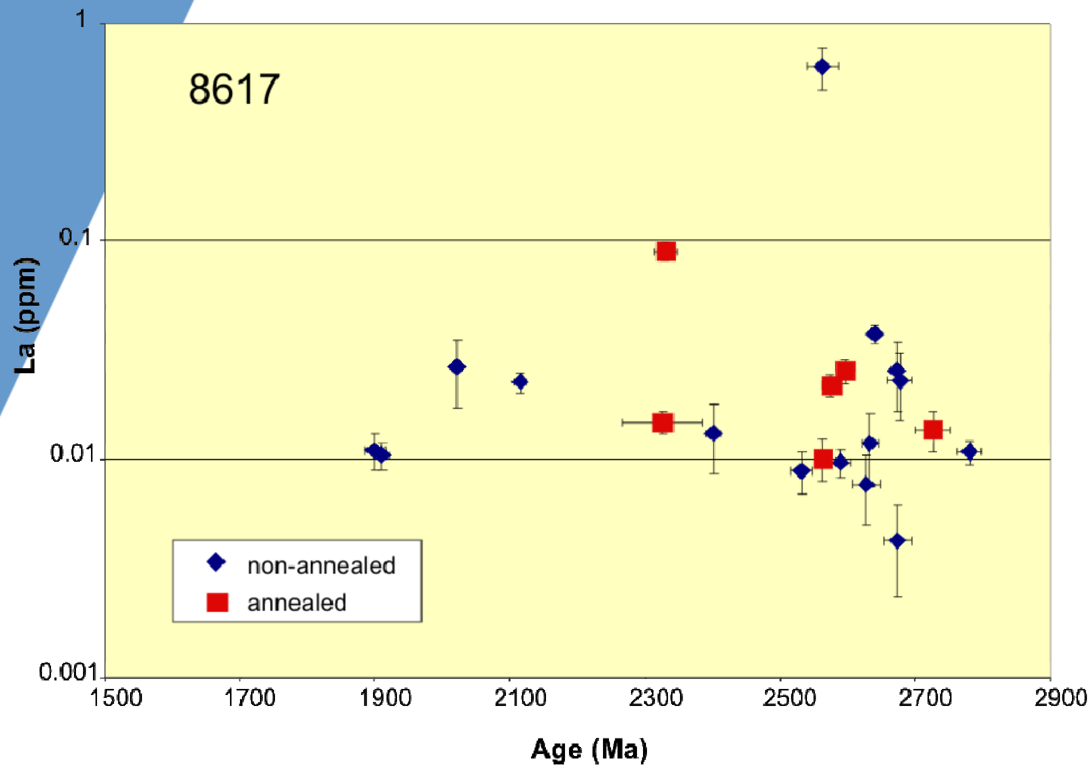
# The diagnosis: Trace elements?



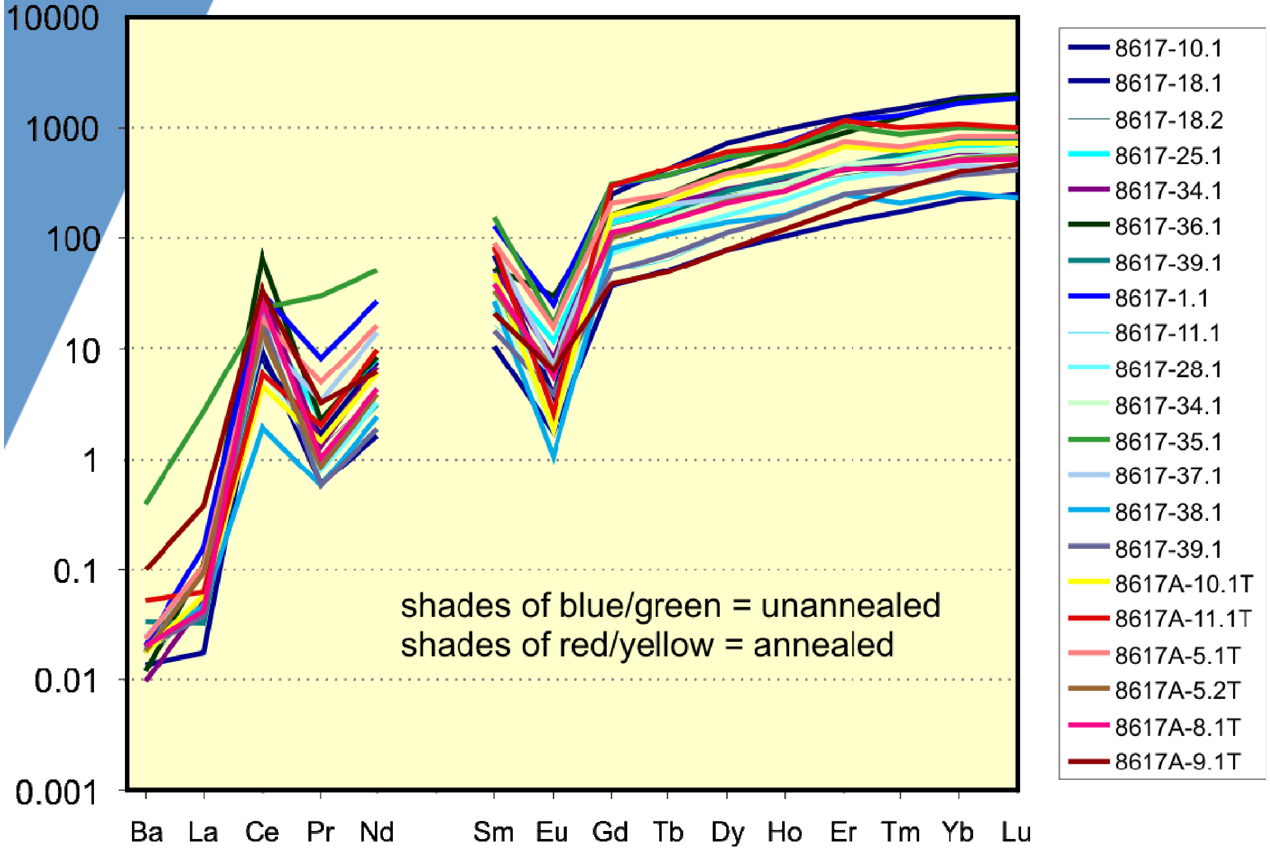

- Some instances of Pb redistribution (Pb-loss) can be accompanied by changes in the trace element composition
- Indication of recrystallization/new growth (fluid-mediated?) as operating process

# The diagnosis: Trace elements?



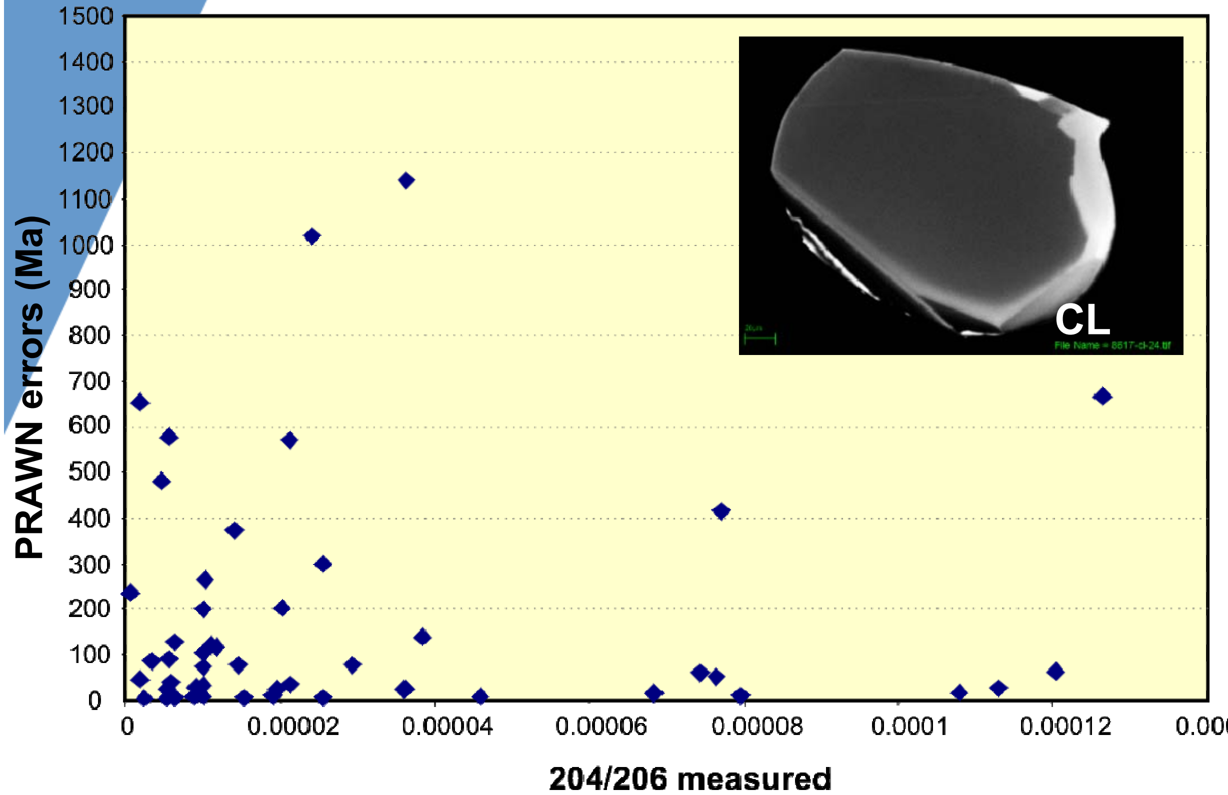

- No correlation between age and La content (unlike 8811)
- No effect of annealing on age
- Same recrystallization/new growth process not occuring
- Alteration (increase in 204 and LREE) not responsible

# The diagnosis: Trace elements?

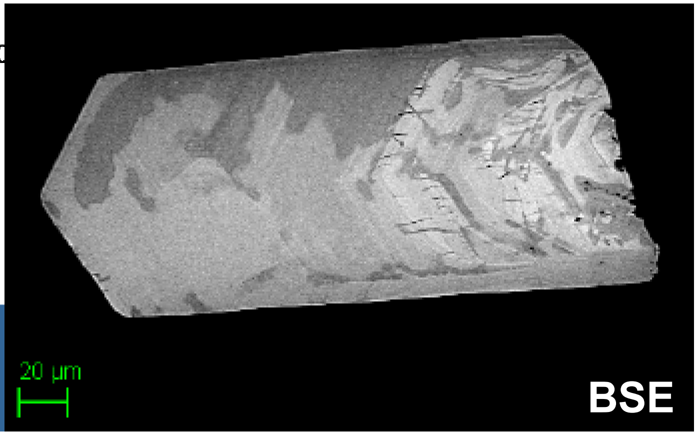



- **No difference in REE patterns between annealed/ unannealed zircon**
- **No difference in REE between zircon with excess scatter or without**

# The diagnosis: Alteration?

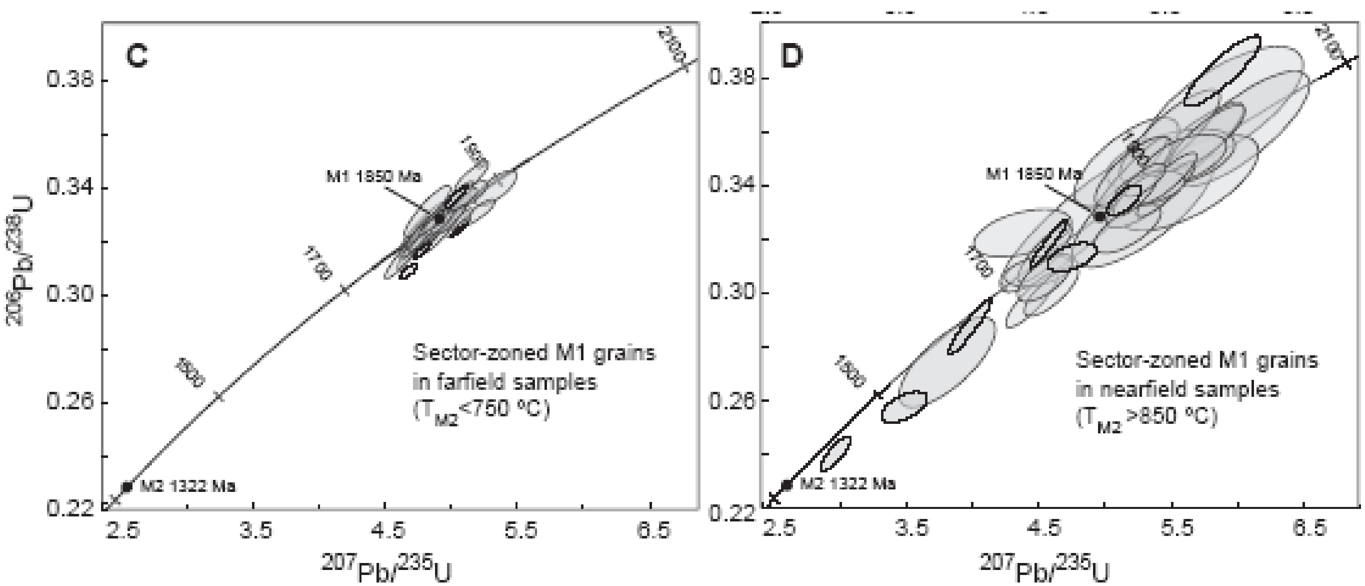


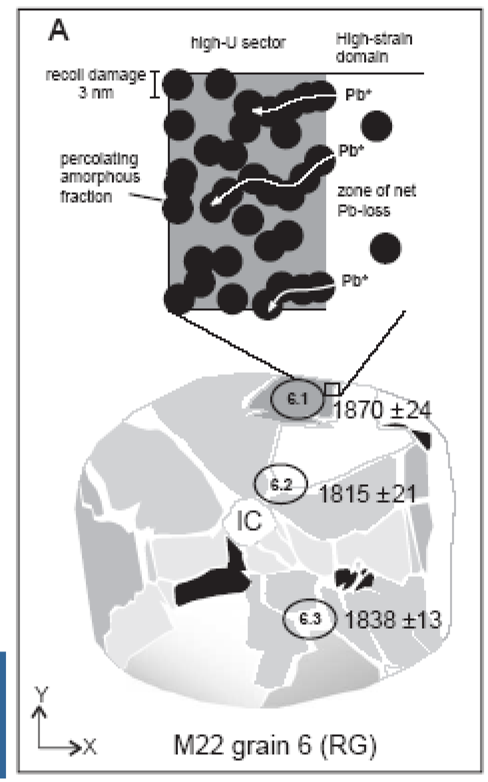

- No evidence from images of alteration
- No correlation with 204Pb (or LREE) content
- Detailed post-SHRIMP imaging of problem grains did not show mineral intergrowths or inclusions at the µm scale



# The diagnosis: Redistribution of Pb during metamorphism

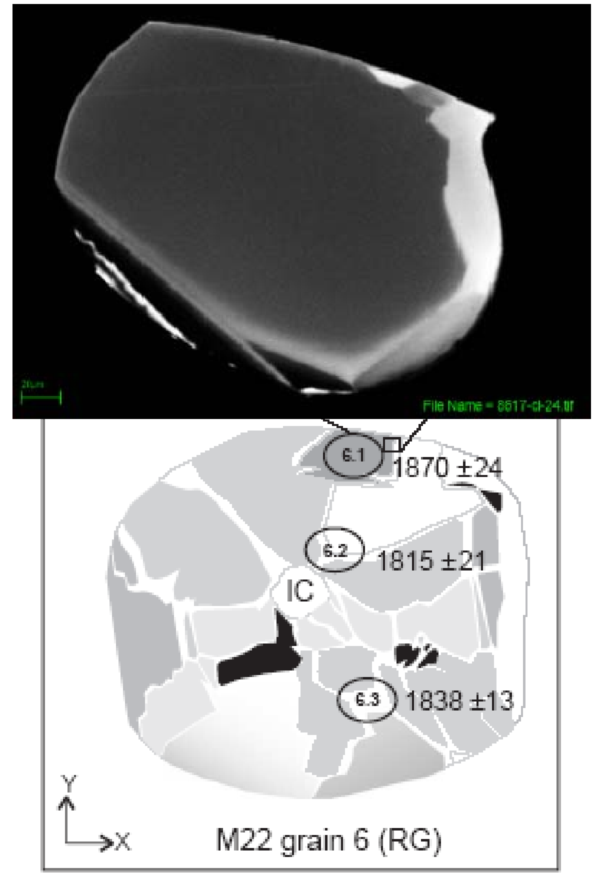
- **Lack of correlation of excess scatter with age (not related to extent of Pb loss)**
- **Similar effect documented by Macfarlane et al. 2005**
  - **contact metamorphism setting (nearfield vs farfield)**
  - **extent of redistribution ascribed to lattice structure (defect density, U concentration) and consequently ion probe pit location relative to zoning**

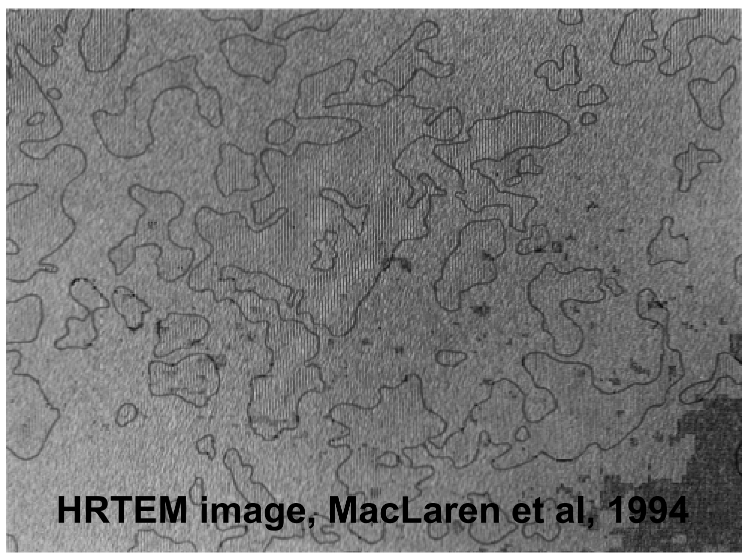


# The diagnosis: Redistribution of Pb during metamorphism

- We do not consistently observe a relationship with U, REE, microstructure, zoning
- Possibly a smaller scale process exploiting the crystalline to metamict transition (MacLaren et al. 1994 and others)



HRTEM image, MacLaren et al, 1994

# The diagnosis:
# Redistribution of Pb during metamorphism

## How do we tell if the same process is at work with different expression, or a different process altogether?

- Microstructure (EBSD, Raman, microXRD)

- Geological control (why Pb-redistribution instead of Pb-loss)
  - multiple granulite grade events?
  - effects of fluids

- Utility of time-series data reduction