Monazite U–Th–Pb age mapping: A tool to understand complex metamorphism

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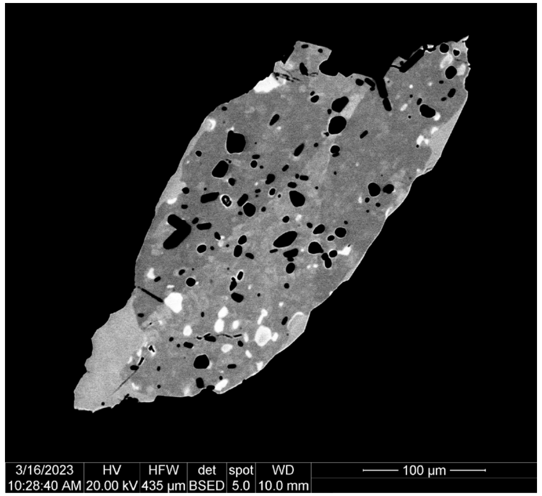
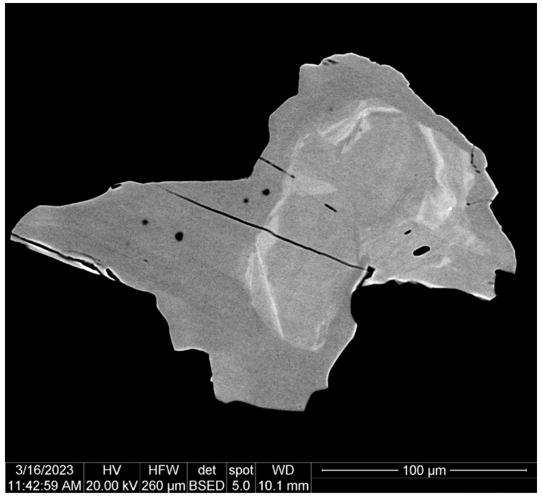
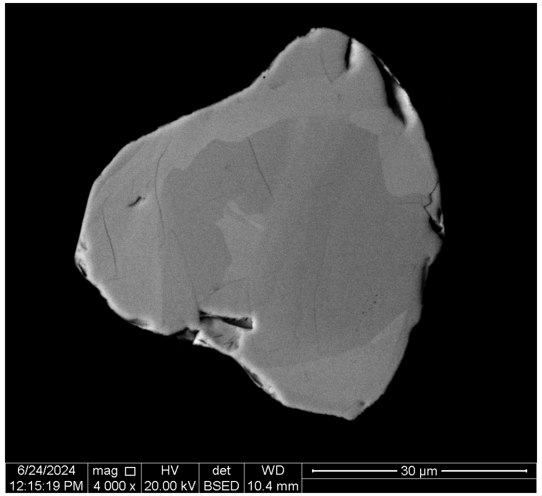
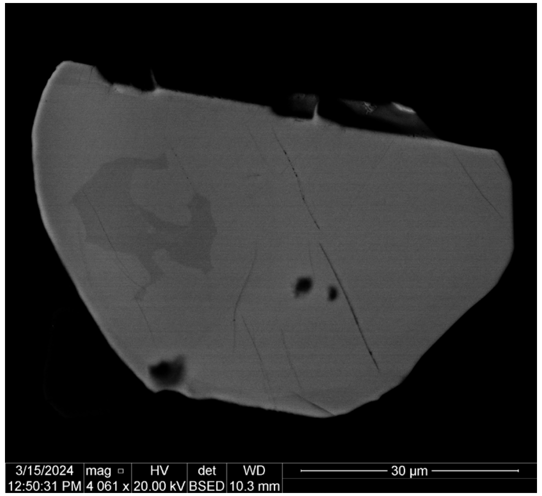
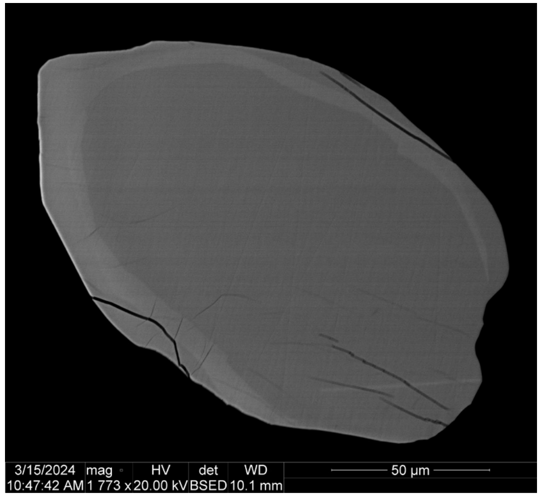
Why age mapping?

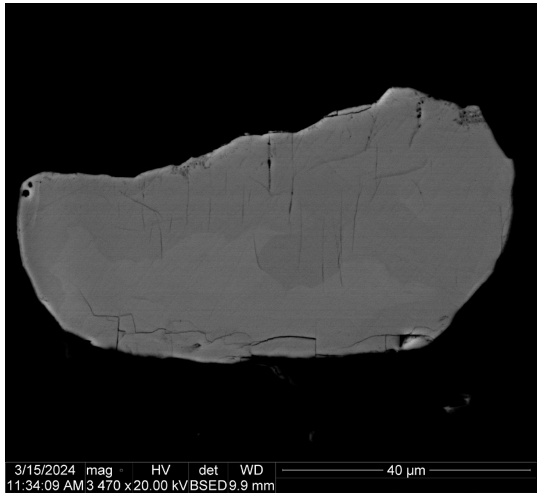


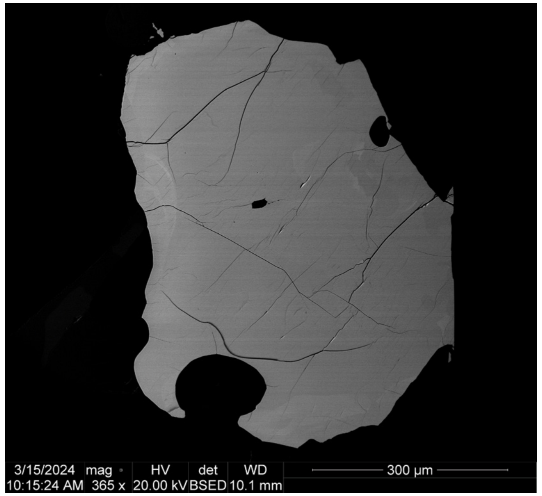


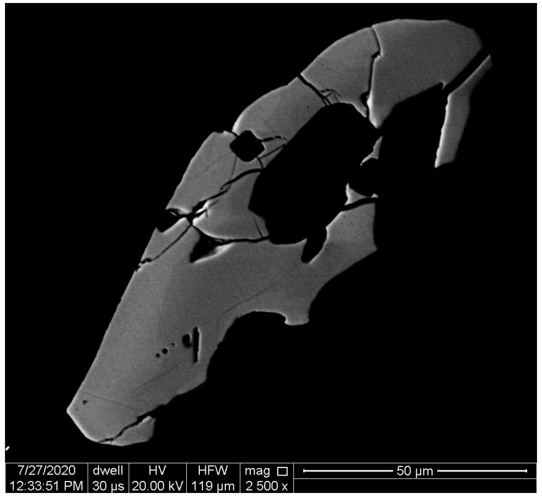










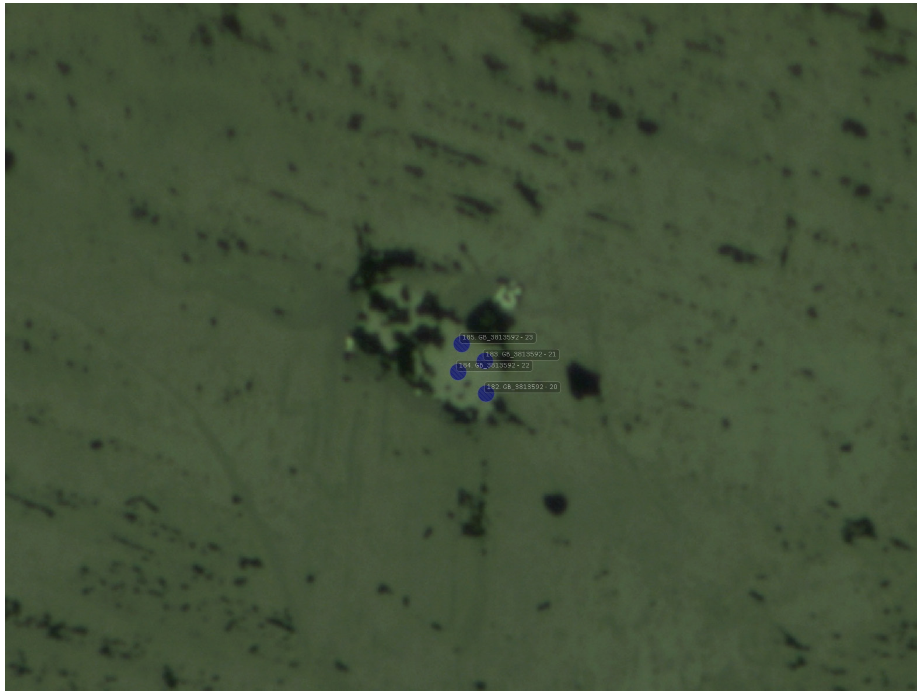


Why not stick to spot data?

Compared to mapping, collecting spot data is **slow** and **labour intensive**

Spot targeting can be cumbersome due to poor image quality and small target domains (+ cracks and inclusions to avoid)

Spot analyses are subject to downhole uncertainty – **we can't see in 3D** (yet…)

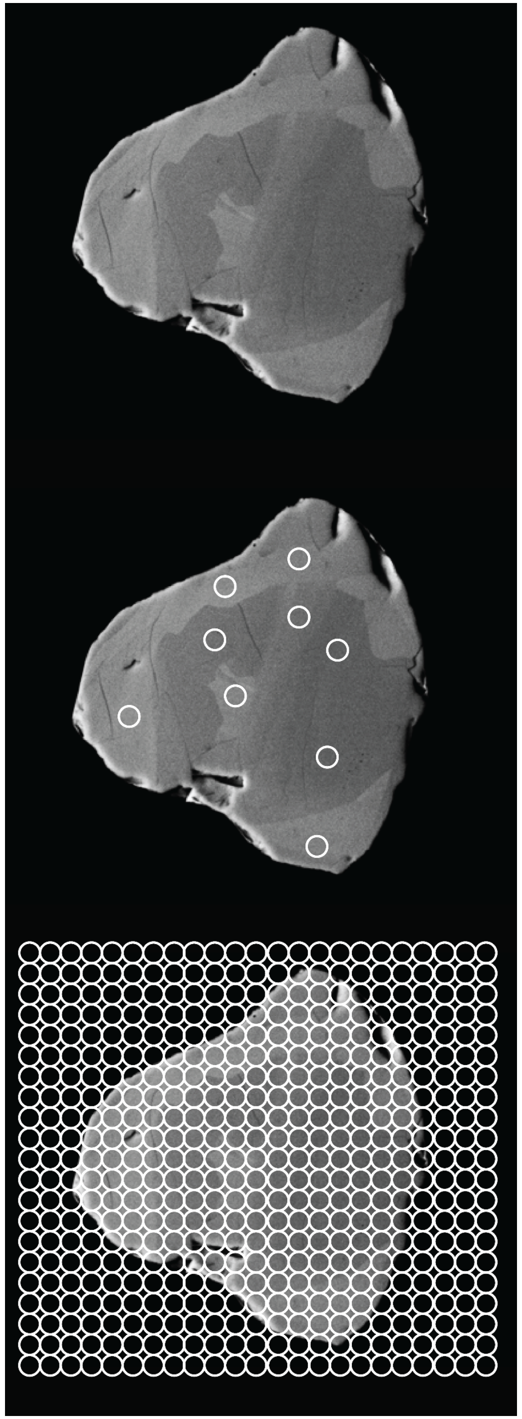


A conventional 'grid of spots' on a single grain takes a long time on conventional LA-ICP-MS (typically, ~1.5 mins/spot)

With our mapping setup 1 spot ≈ 0.02 s

We achieve this with two advanced pieces of kit:

1. Time-of-Flight mass (ToF) spectrometry
2. Fast-washout laser ablation cell



Time-of-Flight mass spectrometry (ToF-MS)

icpTOF R manufactured by tofwerk, Switzerland – housed at UniSA

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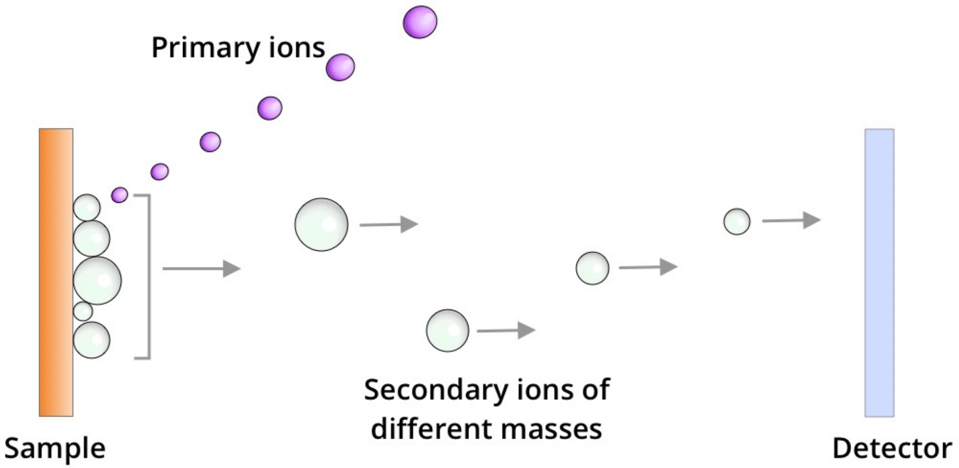
Mass-to-charge ratio (m/z) is determined by measuring an ions ‘time of flight’

Ions are accelerated by an electric field, all receiving the same kinetic energy

Lighter ions (**or ions with higher charge**) travel faster and **reach the detector sooner**

Heavier ions (**or ions with lower charge**) travel slower and **arrive later**

Because velocity depends on an ion’s mass-to-charge ratio (m/z), **the time it takes to reach the detector uniquely identifies the ion**



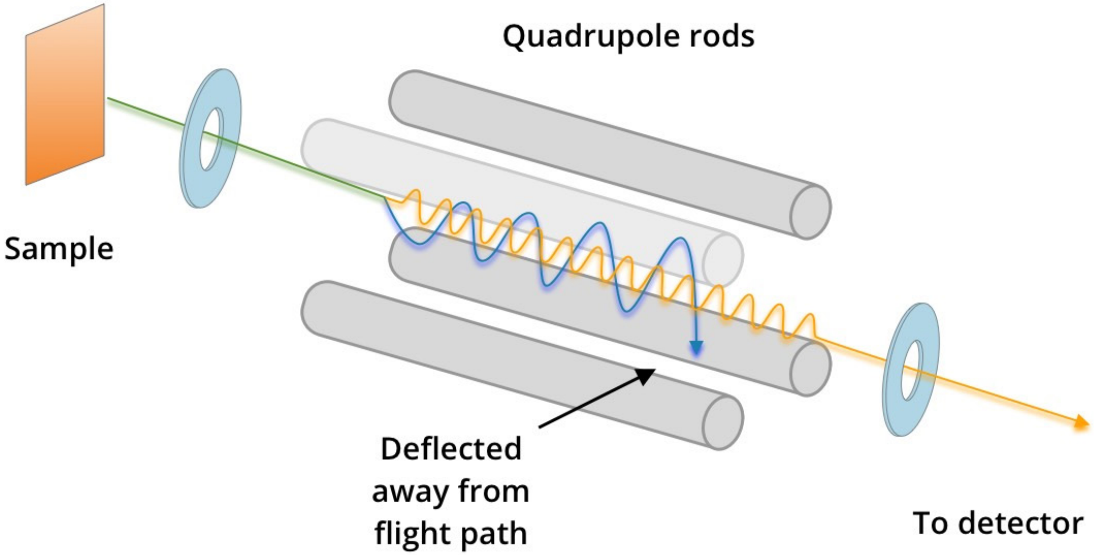
ToF vs Quadrupole mass analysers

Quadrupole:
Sweep time (20–30 isotopes) ≈ **200–300 ms**

Rate limited by sequential isotope measurement

ToF:
Full mass spectrum ≈ **0.03 ms (33 kHz)**

Rate limited by LA washout time



myscope.training

ToF offers slightly worse sensitivity, but much faster data acquisition and every mass…

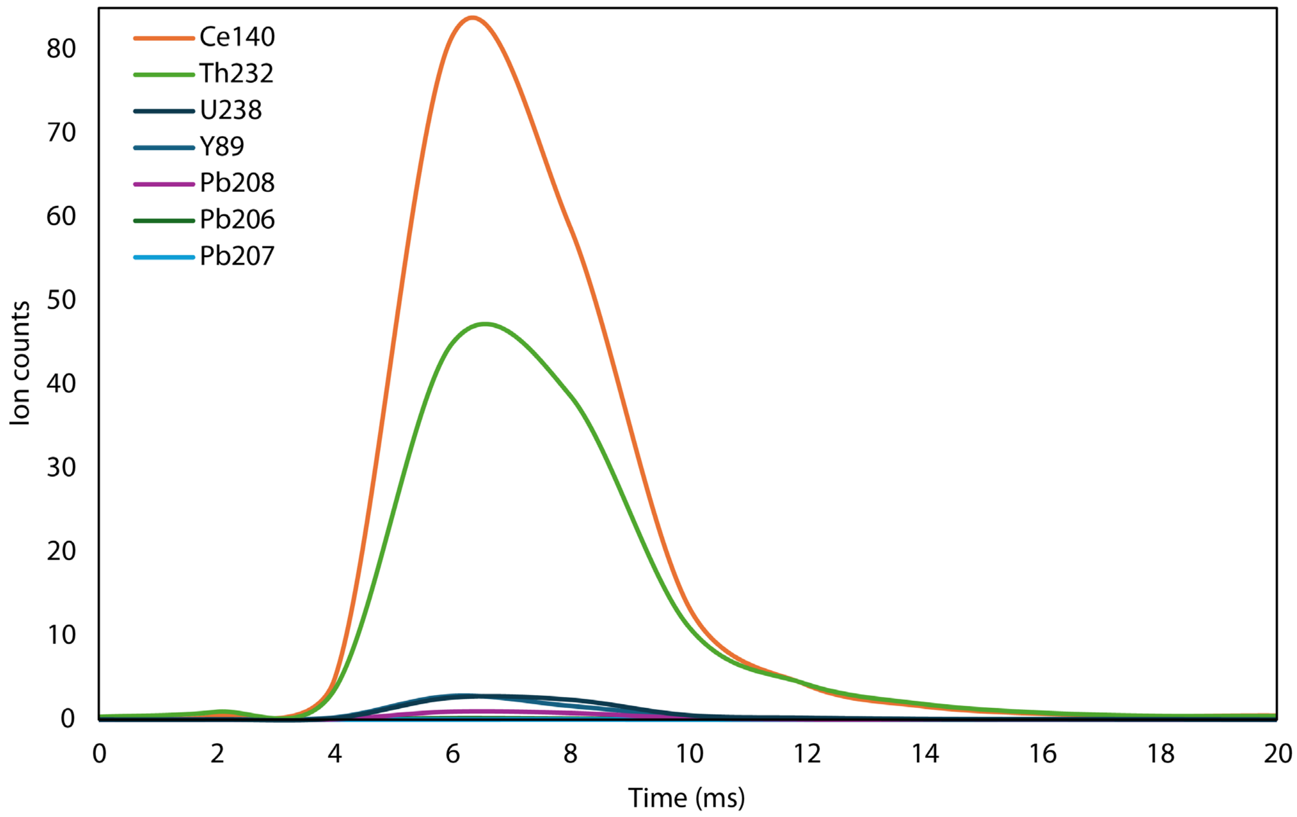
Fast washout laser ablation cell

Washout is the time it takes for the ablated material to clear out of the sample cell and tubing before the signal returns to baseline

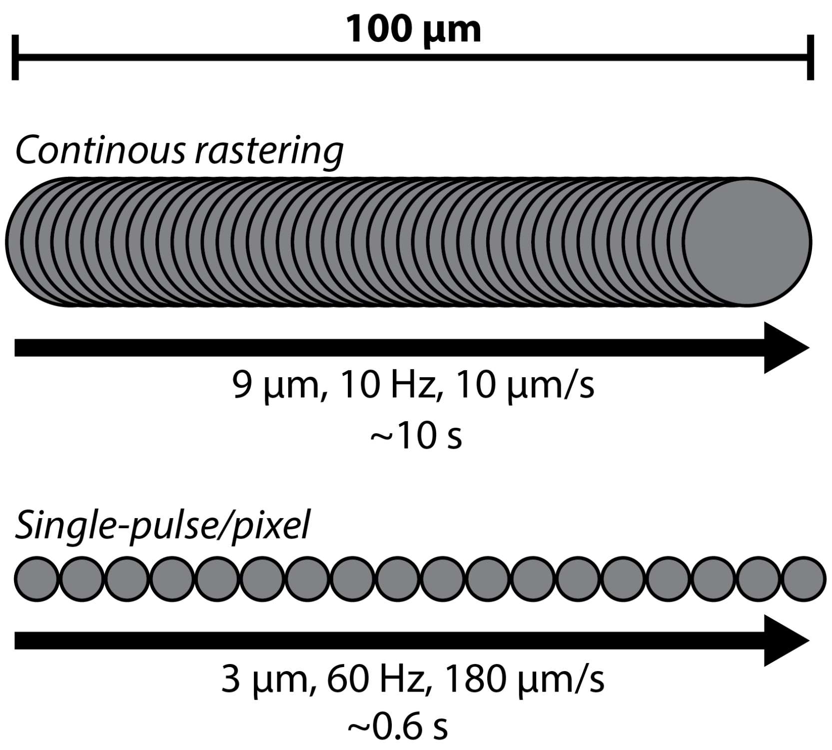
Quadrupoles have long sweep times (~300 ms) and need multiple sweeps for good statistics – no benefit in having fast washout

ToF can generate mass spectra every 0.03 ms – **allowing data to be collected from single laser pulses**

This requires a fast washout cell



Single pulse mapping



100 µm

Continous rastering

9 µm, 10 Hz, 10 µm/s
~10 s

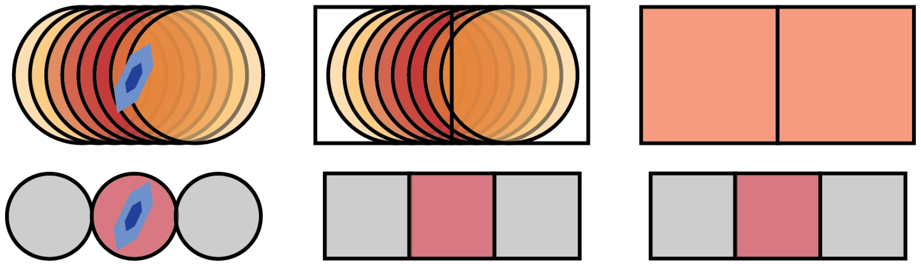
Single-pulse/pixel

3 µm, 60 Hz, 180 µm/s
~0.6 s

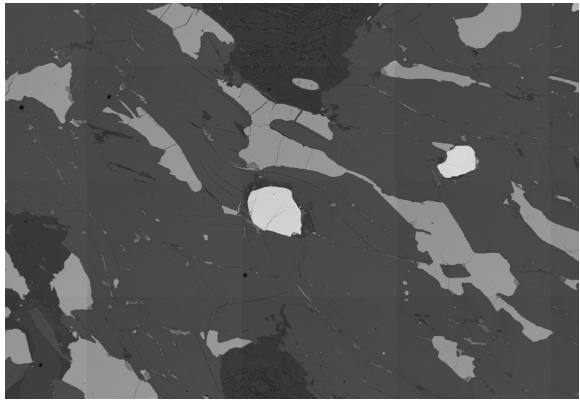
Continuous rastering homogenises signal over multiple pixels

This can result in issues when there are orders of magnitude concentration changes over small spatial resolutions

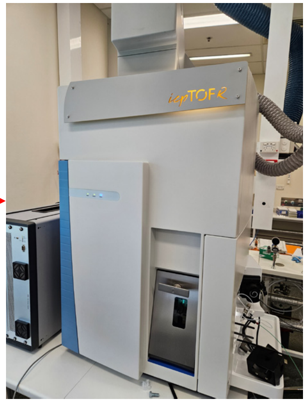
When converted into a pixel map, inclusions, or other spurious data are more discrete



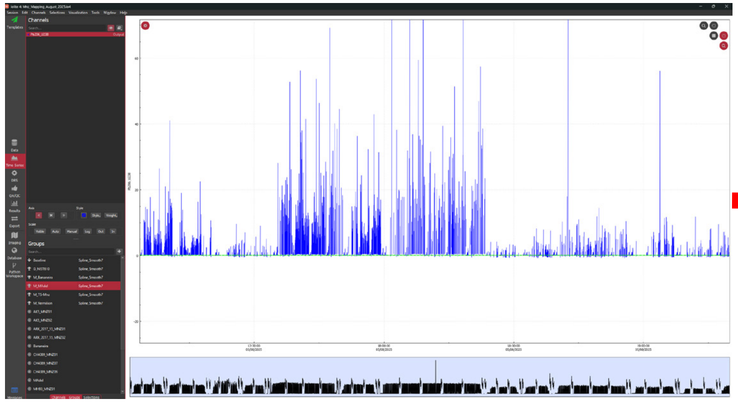
U–Th–Pb age mapping workflow



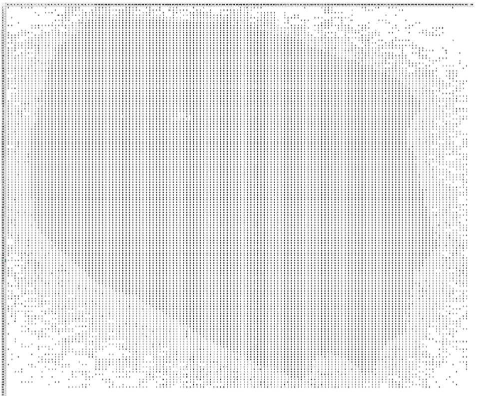
Identify monazite in situ
(>50 µm, the bigger the better)



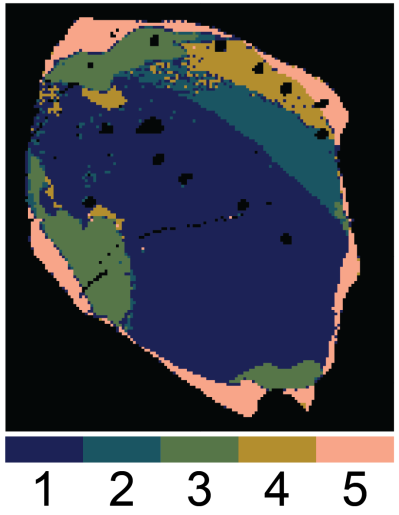
Collect isotopic data
LA-ICP-ToF-MS



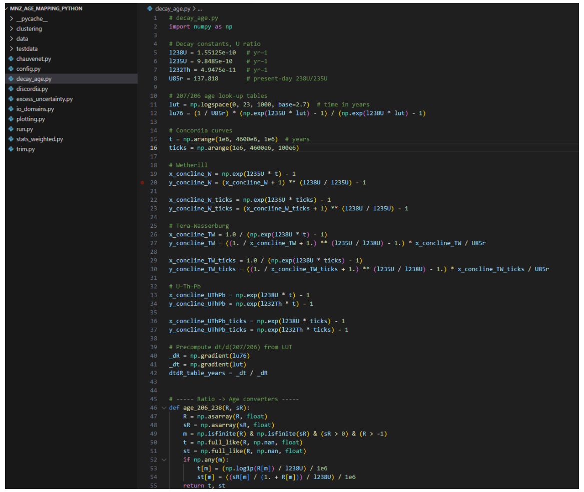
Calibrate data in iolite4
(background subtraction, drift correction)



Export each map as a 2D matrix

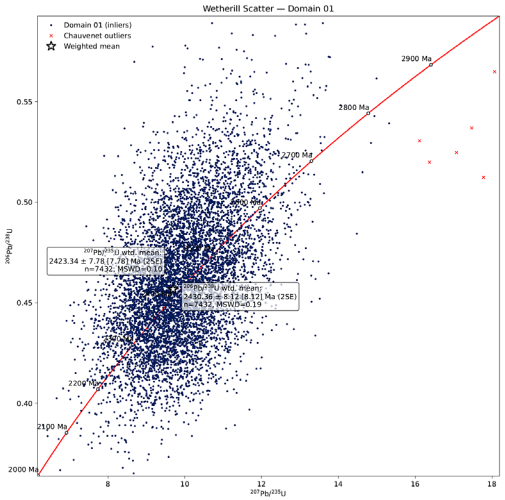


Identify monazite domains



```python
# decay_age.py
import numpy as np

# Decay constants, U ratio
l238U = 1.55125e-10   # yr-1
l235U = 9.8485e-10    # yr-1
l232Th = 4.9475e-11   # yr-1
U85r = 137.818        # present-day 238U/235U

# 207/206 age look-up tables
lut = np.logspace(0, 23, 1000, base=2.7)  # time in years
lu76 = (1 / U85r) * (np.exp(l235U * lut) - 1) / (np.exp(l238U * lut) - 1)

# Concordia curves
t = np.arange(1e6, 4600e6, 1e6)  # years
ticks = np.arange(1e6, 4600e6, 100e6)

# Wetherill
x_concline_W = np.exp(l235U * t) - 1
y_concline_W = (x_concline_W + 1) ** (l238U / l235U) - 1

x_concline_W_ticks = np.exp(l235U * ticks) - 1
y_concline_W_ticks = (x_concline_W_ticks + 1) ** (l238U / l235U) - 1

# Tera-Wasserburg
x_concline_TW = 1.0 / (np.exp(l238U * t) - 1)
y_concline_TW = ((1. / x_concline_TW + 1.) ** (l235U / l238U) - 1.) * x_concline_TW / U85r

x_concline_TW_ticks = 1.0 / (np.exp(l238U * ticks) - 1)
y_concline_TW_ticks = ((1. / x_concline_TW_ticks + 1.) ** (l235U / l238U) - 1.) * x_concline_TW_ticks / U85r

# U-Th-Pb
x_concline_UThPb = np.exp(l238U * t) - 1
y_concline_UThPb = np.exp(l232Th * t) - 1

x_concline_UThPb_ticks = np.exp(l238U * ticks) - 1
y_concline_UThPb_ticks = np.exp(l232Th * ticks) - 1

# Precompute dt/d(207/206) from LUT
_dR = np.gradient(lu76)
_dt = np.gradient(lut)
dtdR_table_years = _dt / _dR


# ----- Ratio -> Age converters -----
def age_206_238(R, sR):
    R = np.asarray(R, float)
    sR = np.asarray(sR, float)
    m = np.isfinite(R) & np.isfinite(sR) & (sR > 0) & (R > -1)
    t = np.full_like(R, np.nan, float)
    st = np.full_like(R, np.nan, float)
    if np.any(m):
        t[m] = (np.log1p(R[m]) / l238U) / 1e6
        st[m] = ((sR[m] / (1. + R[m])) / l238U) / 1e6
    return t, st
```

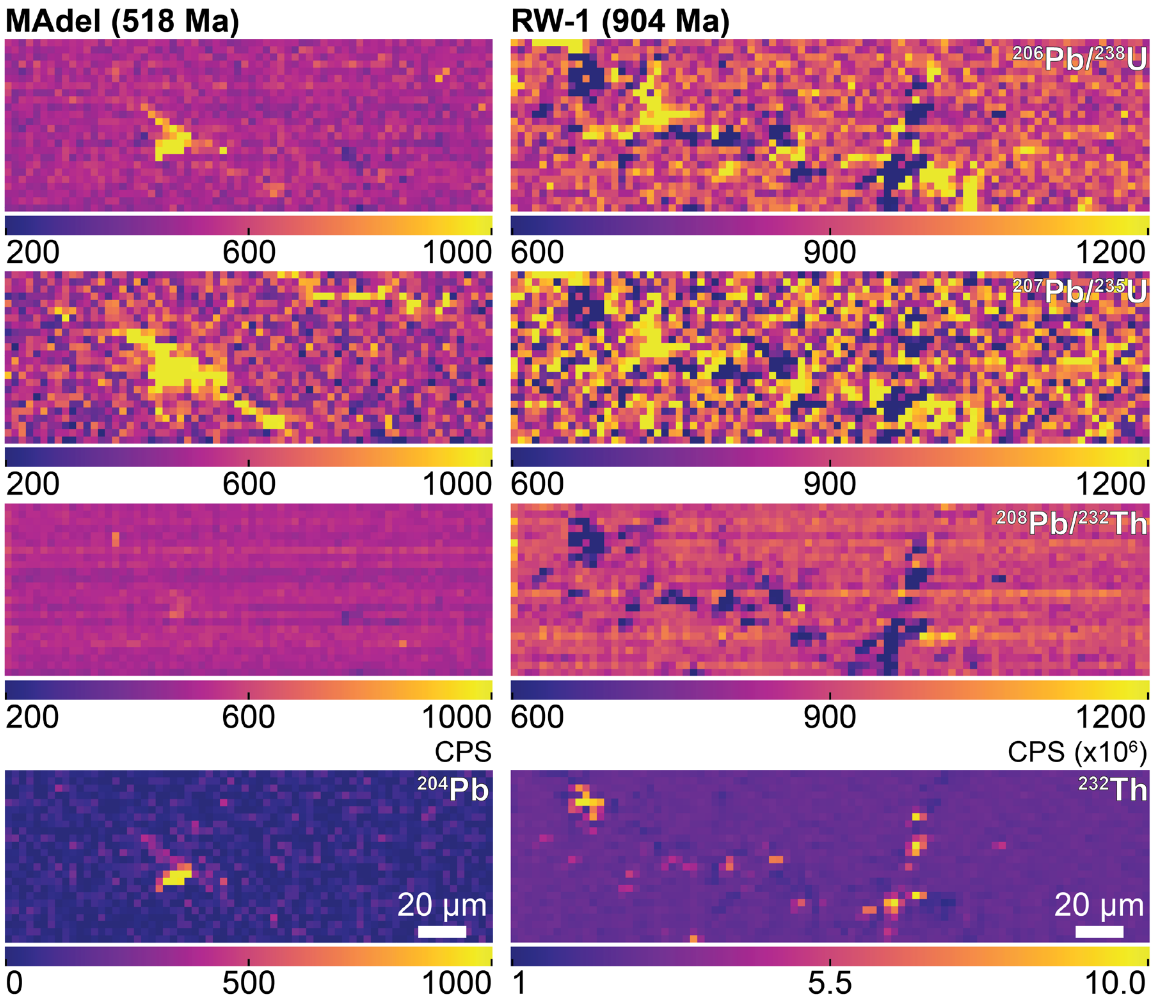
Extract isotope ratios for each domain

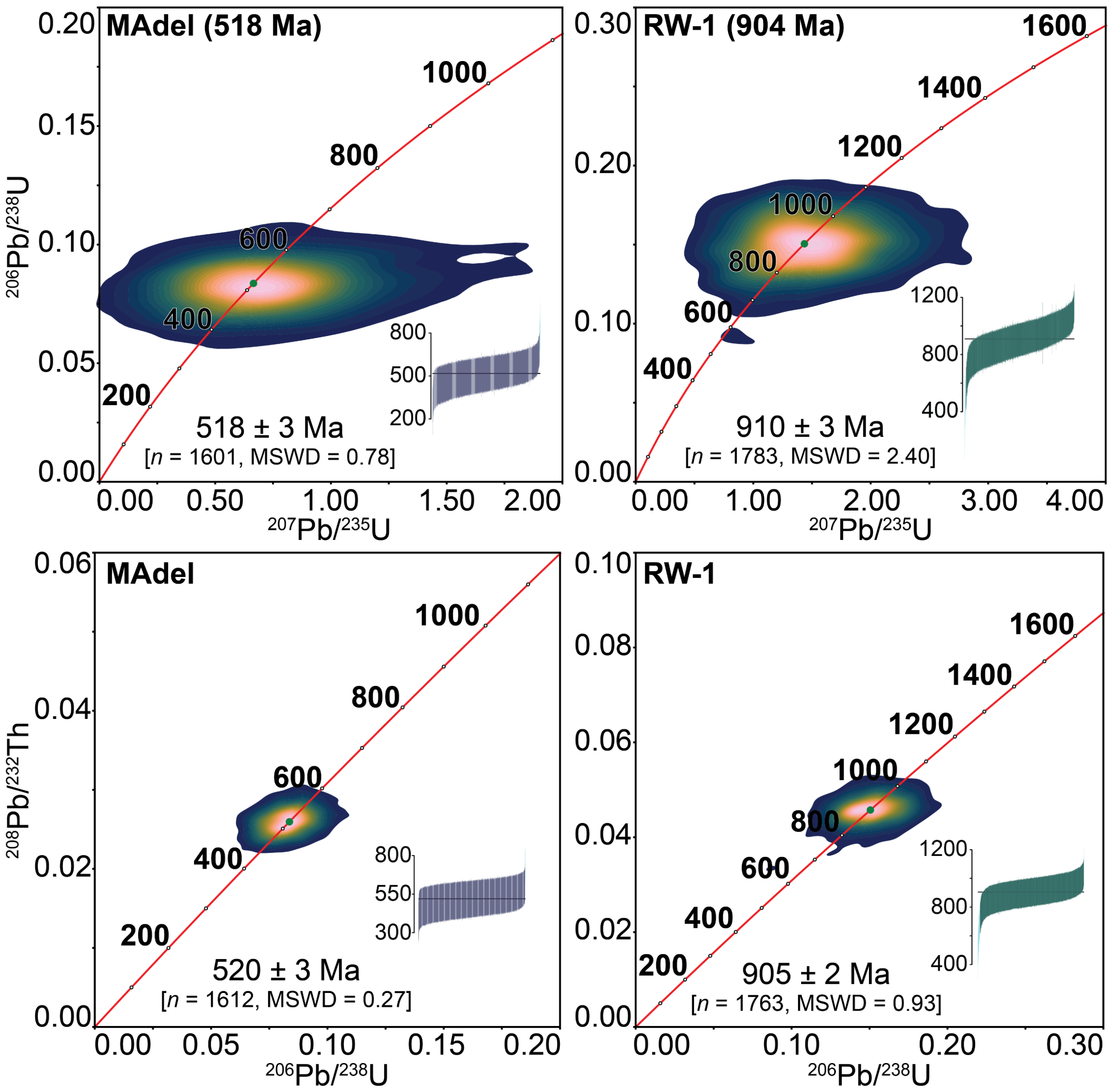


Compute concordia plots and
weighted mean ages for each domain

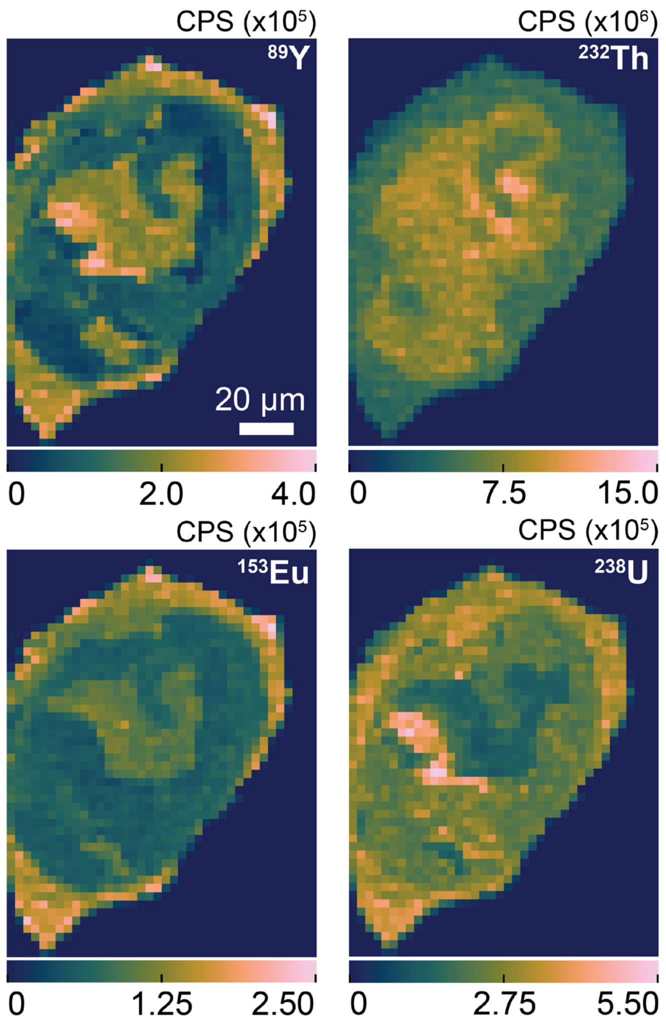
Reference material validation

Reference materials yield their expected ages ✓





94-222 – Harts Range, central Australia

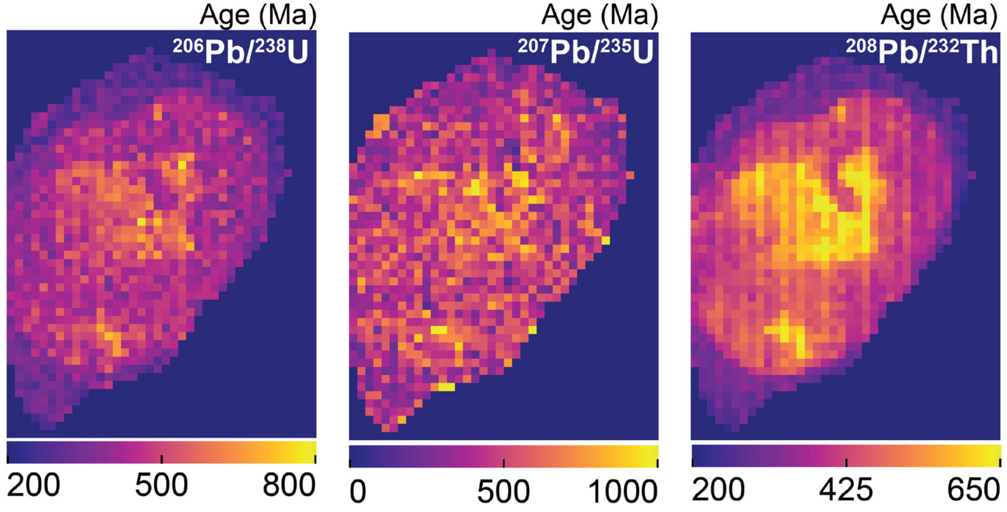


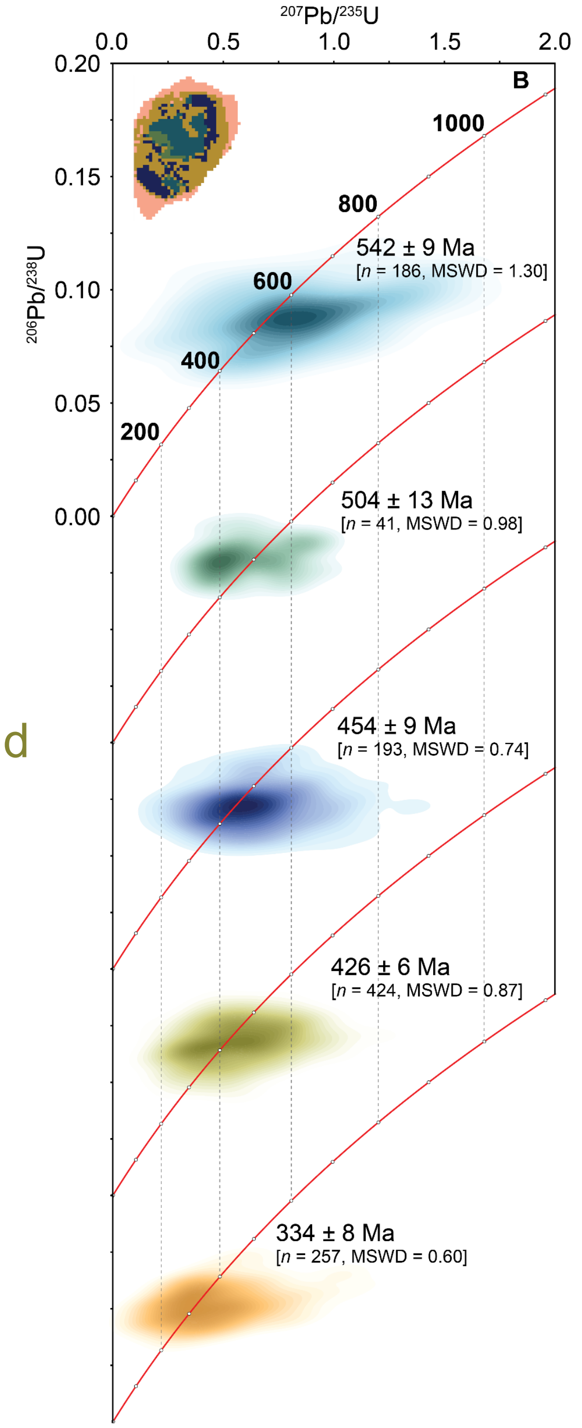
Inner Core: Detrital cores yield ages of **c. 542 & 504 Ma**

Outer Core: Metamorphic overgrowth dating the onset of the Alice Springs Orogeny (ASO) at **c. 454 Ma**

Rim: Later metamorphic overgrowth corresponding to the final stage of the ASO (peak *P*–*T*) – **c. 334 Ma**

Outer Core: Displays isotopic mixing between early and late ASO domains (likely driven by dissolution-precipitation) – **c. 426 Ma**





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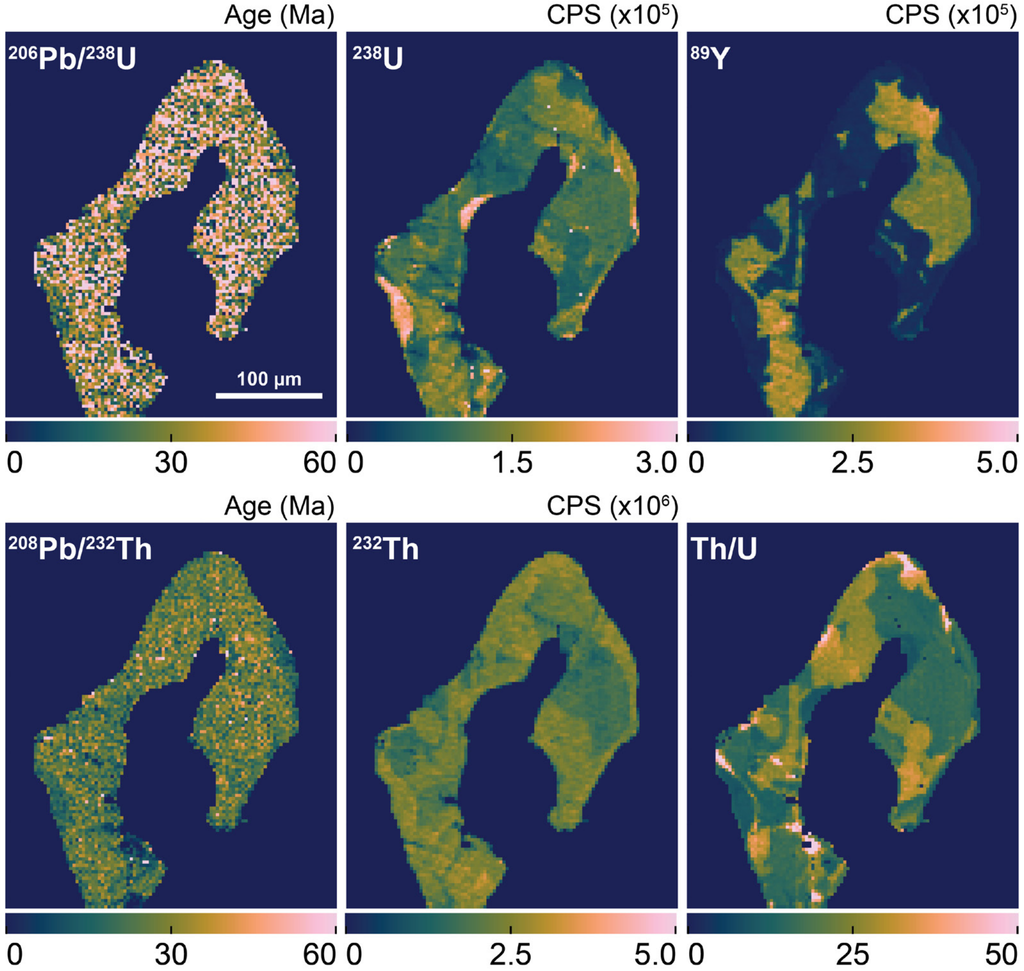
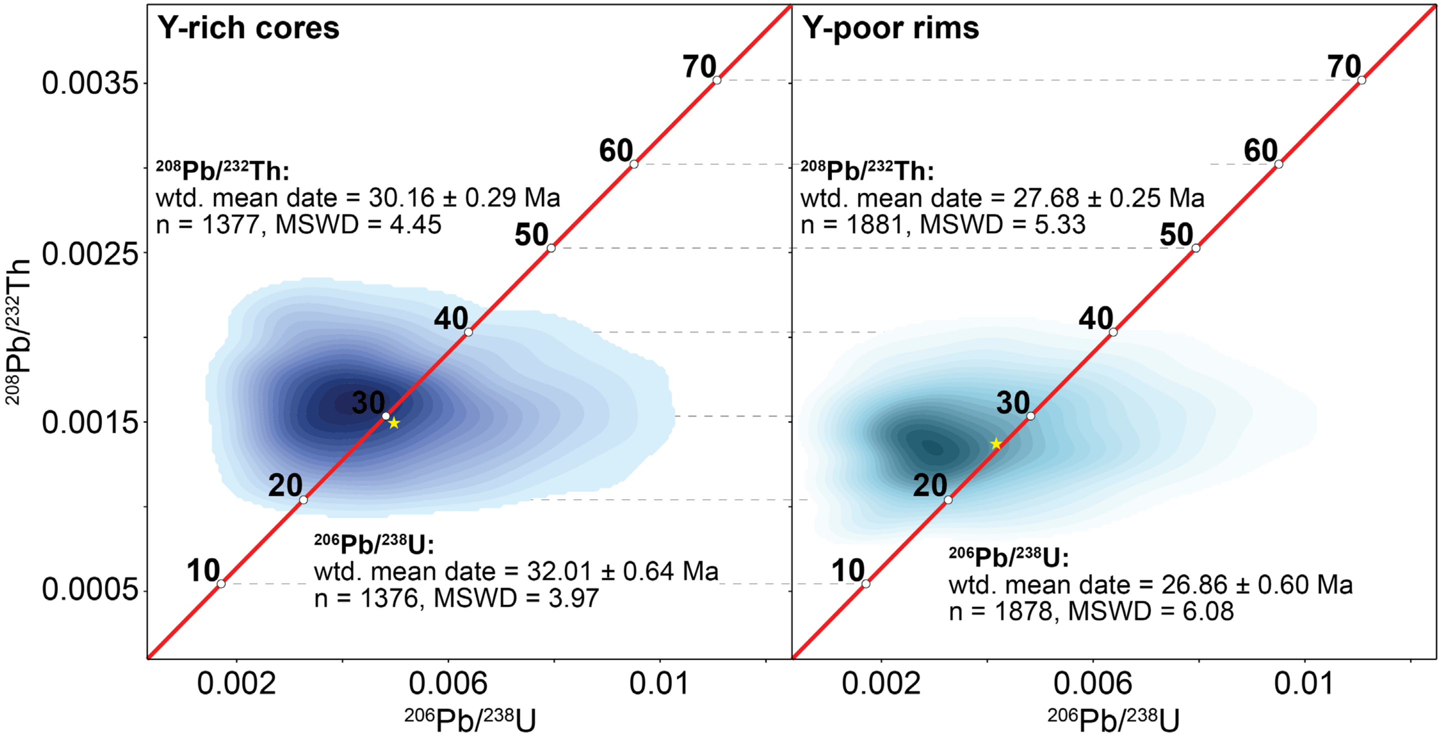
MH93 – Nanga Parbat, western Himalaya

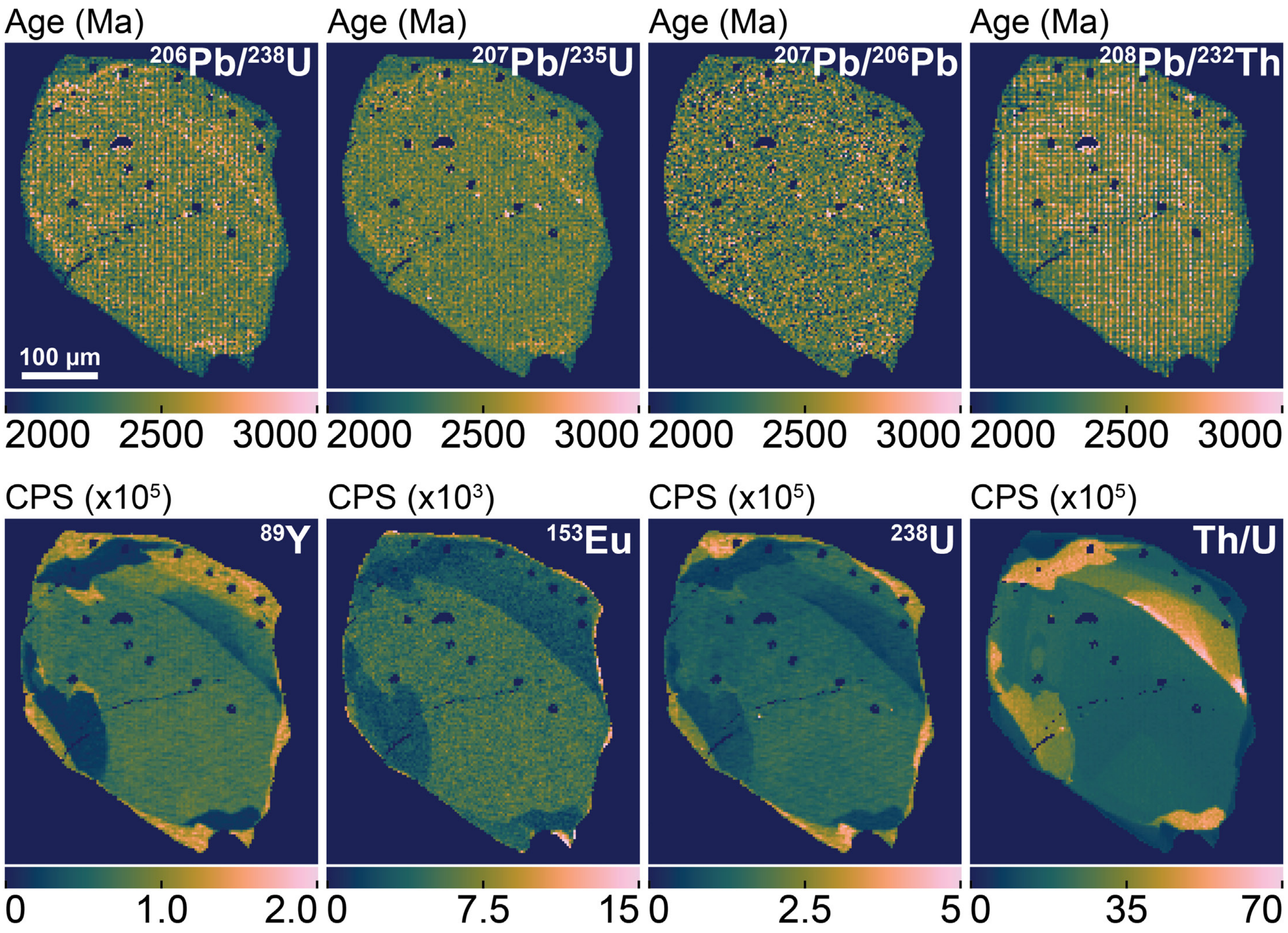


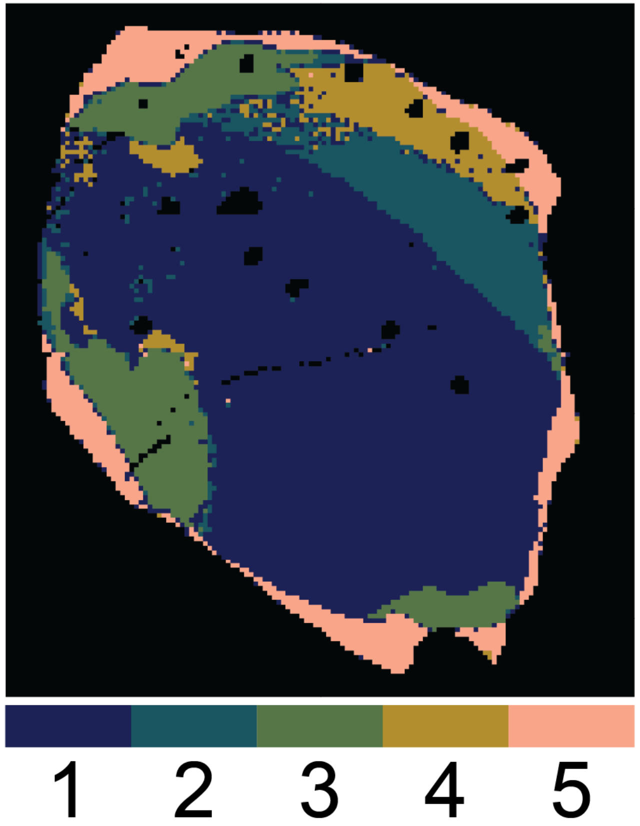
Testing lower limits of age resolution

^{208}Pb/^{232}Th are very useful at such young ages

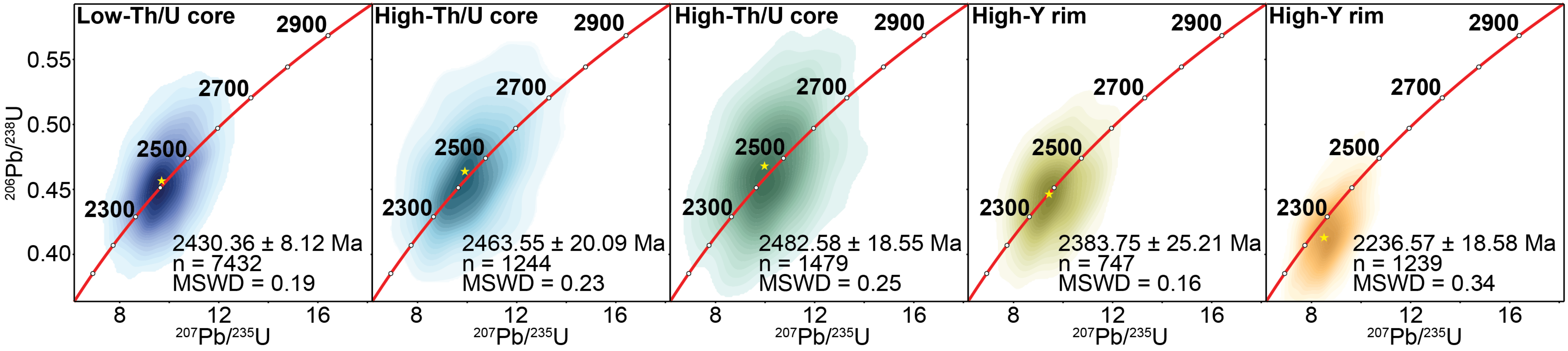


CH4389 – Challenger, western Gawler Craton





CH4389 – Challenger, western Gawler Craton

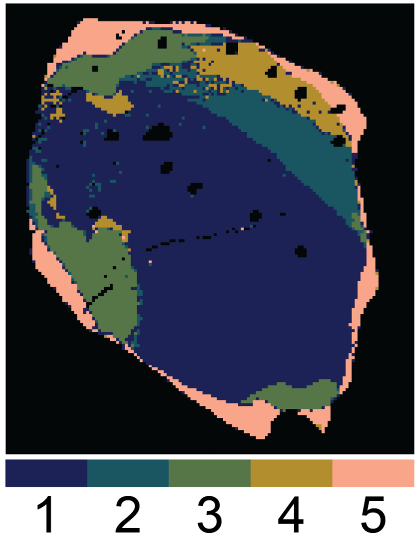


Inner core domain likely records **peak metamorphism and anatexis at c. 2430 Ma** – aligns with other data from the Mulgathing Complex

U-poor (high Th/U) domains exhibit anomalously old, reversely discordant ages – excess 206Pb?

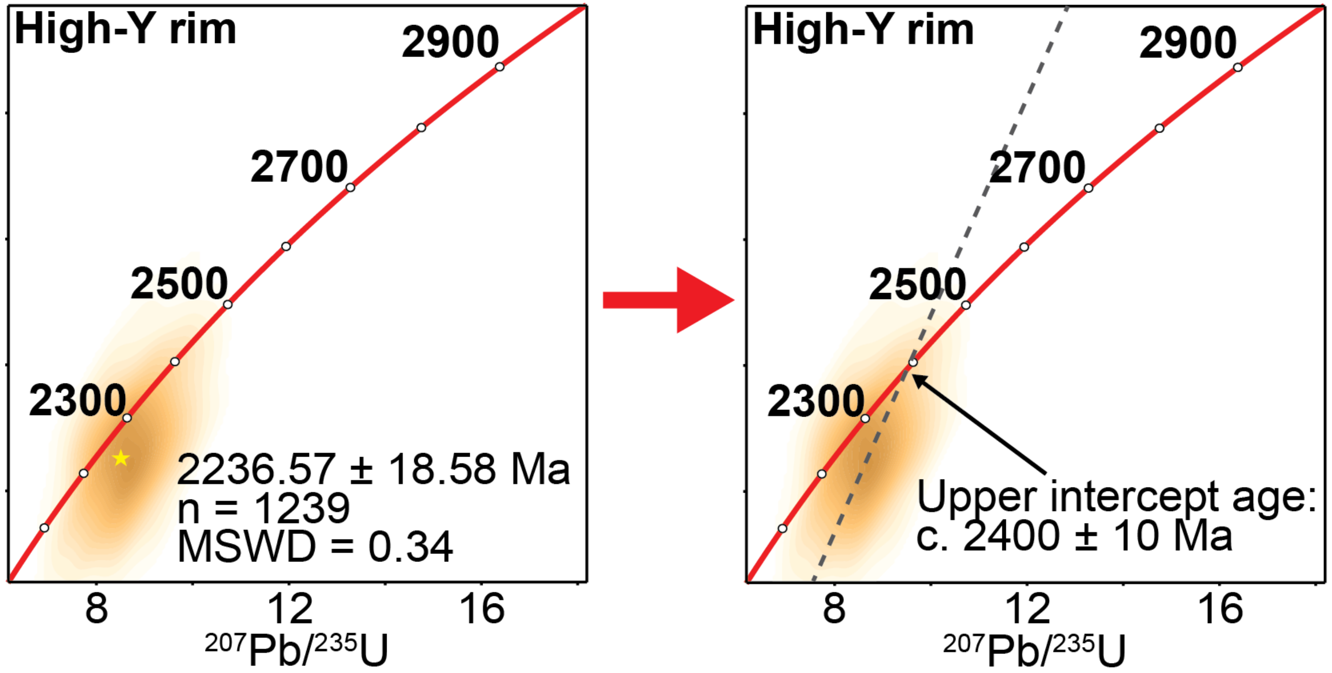
Inner Y-rich rim isn't as affected by Pb-loss and **likely records late melt crystallisation at c. 2380 Ma**

Outermost Y-rich rim exhibits significant Pb-loss (corresponds to Eu enrichment)



Where to from here?

1. Implement discordia fitting to calculate upper and lower intercept ages



2236.57 ± 18.58 Ma
n = 1239
MSWD = 0.34

Upper intercept age:
c. 2400 ± 10 Ma

2. Expand to other minerals (zircon, apatite)

3. Begin applying to geological problems across South Australia

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