Correcting for common Pb in standards

- A brief summary of VizualAge_UcomPbine (Chew, Petrus & Kamber, Chemical Geology 2014)

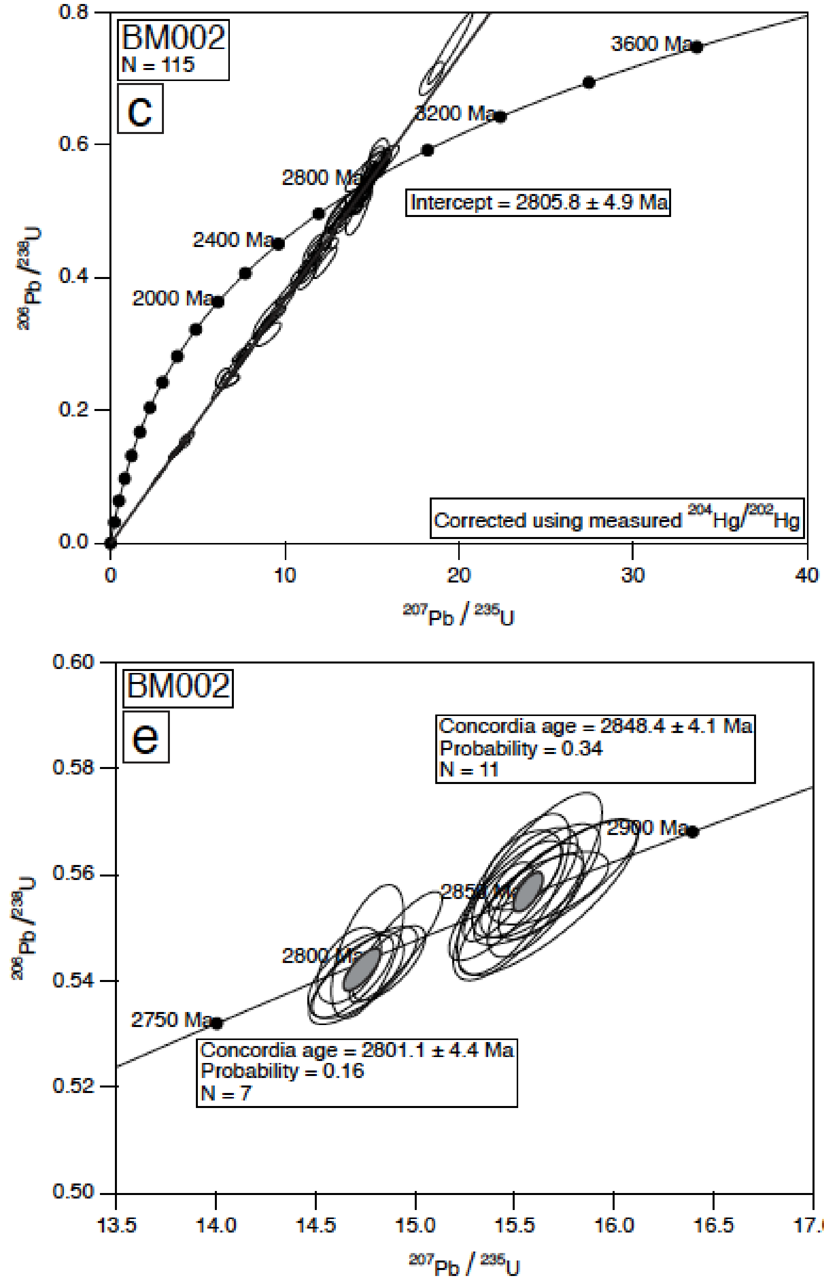
- Corrects for variable common Pb in standards (using either a ^{204}Pb-, ^{207}Pb- or ^{208}Pb correction) prior to correcting for LIEF and session drift

- It assumes:
- 1) standards are age homgenous if they didn't contain common Pb;
- 2) the "**end member**" common Pb is isotopically homogenous
- 3) However there can **be variable incorporation of the amount of common Pb** – either from standard grain to grain, or even variable amounts of common Pb during an individual TRA standard grain analysis

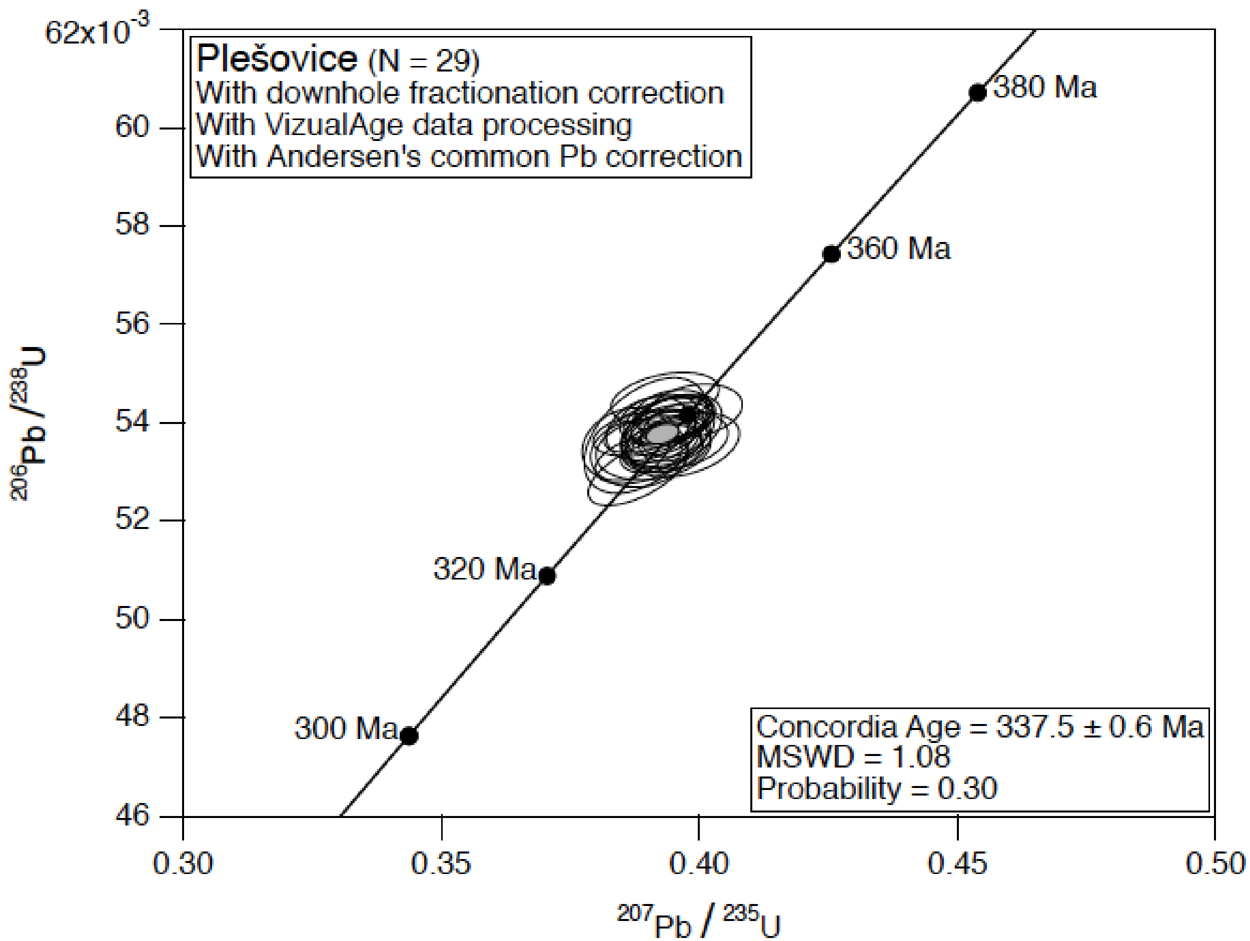
VizualAge (Petrus & Kamber, 2012)

- Data reduction scheme for Iolite

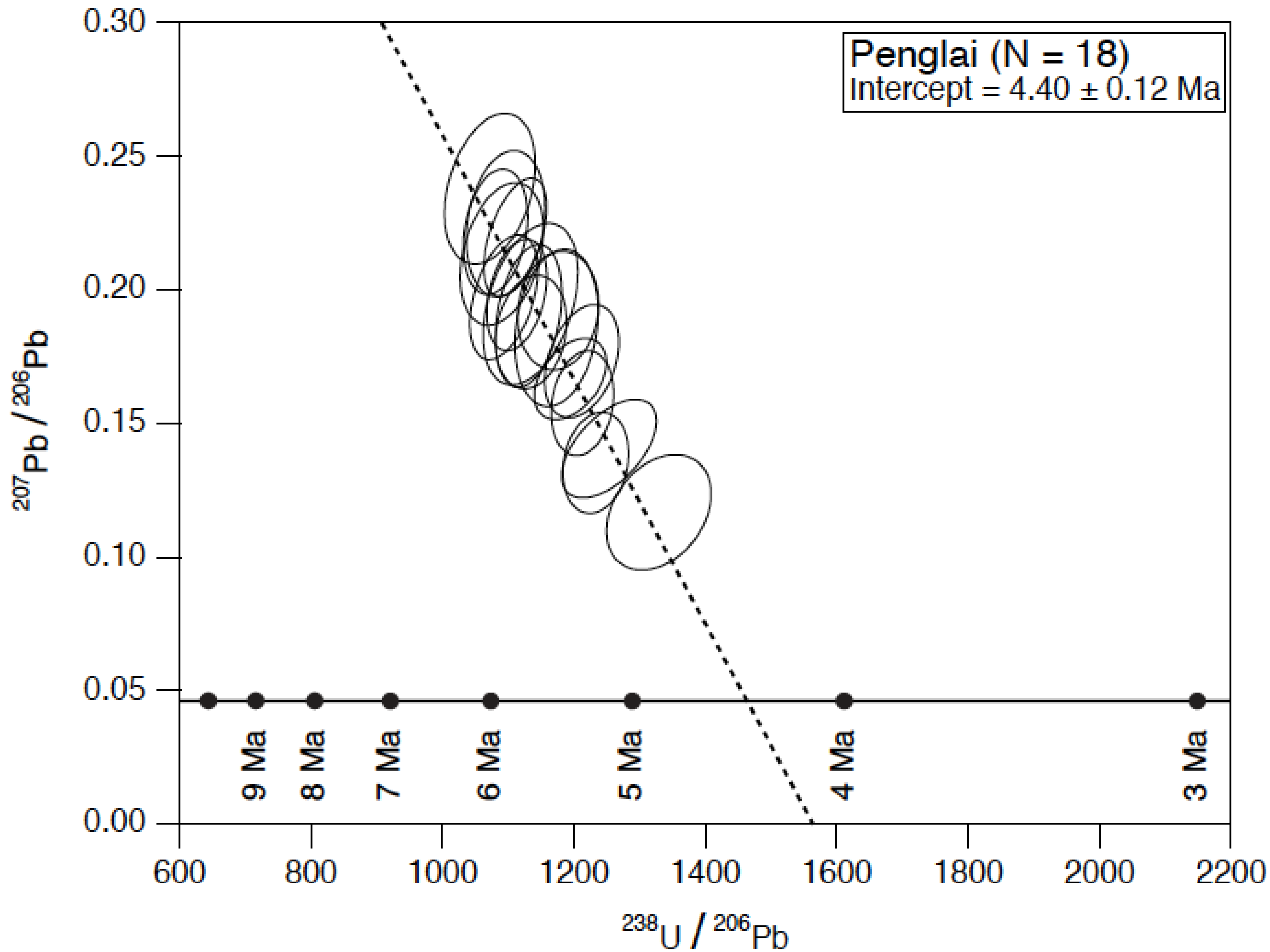
- 207*Pb/206*Pb dates;
- 'live' concordia;
- 'live' error ellipses;
- ^{204}Pb common Pb to unknowns



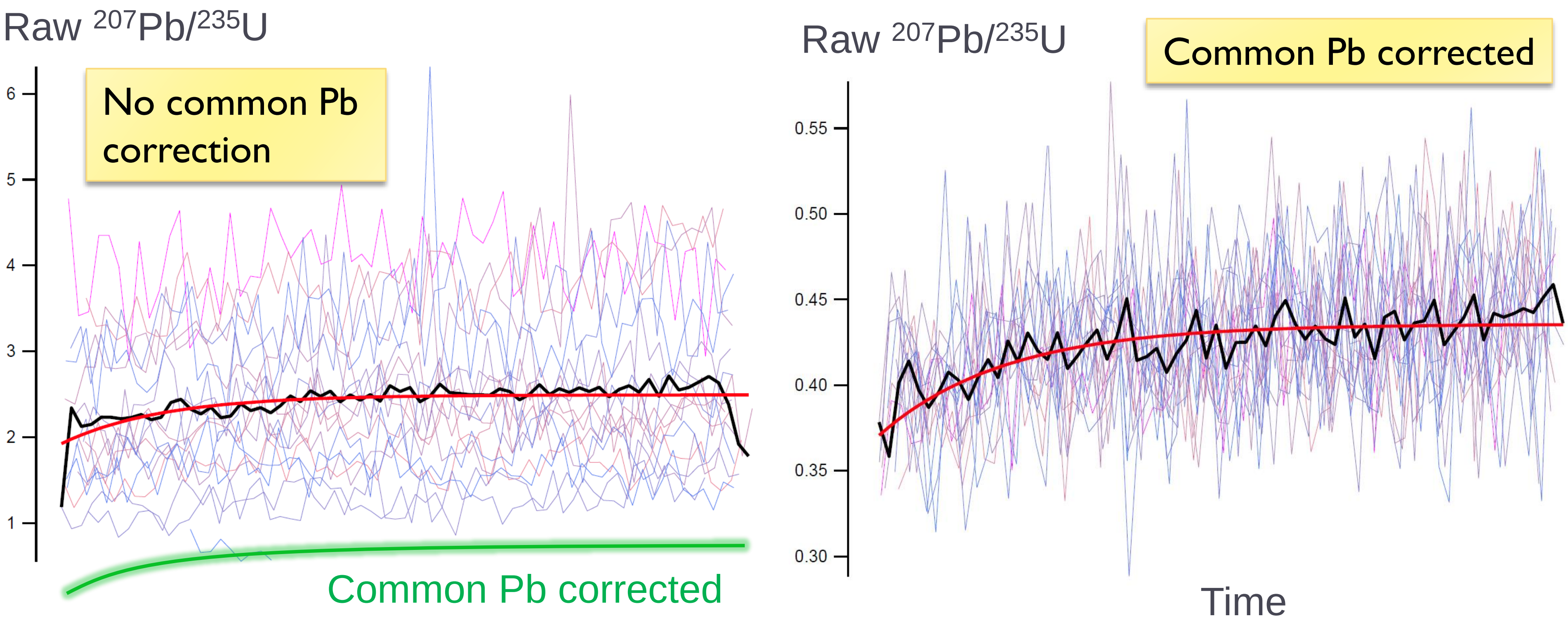
VizualAge example 1



VizualAge example 2



The problem of common Pb in standards

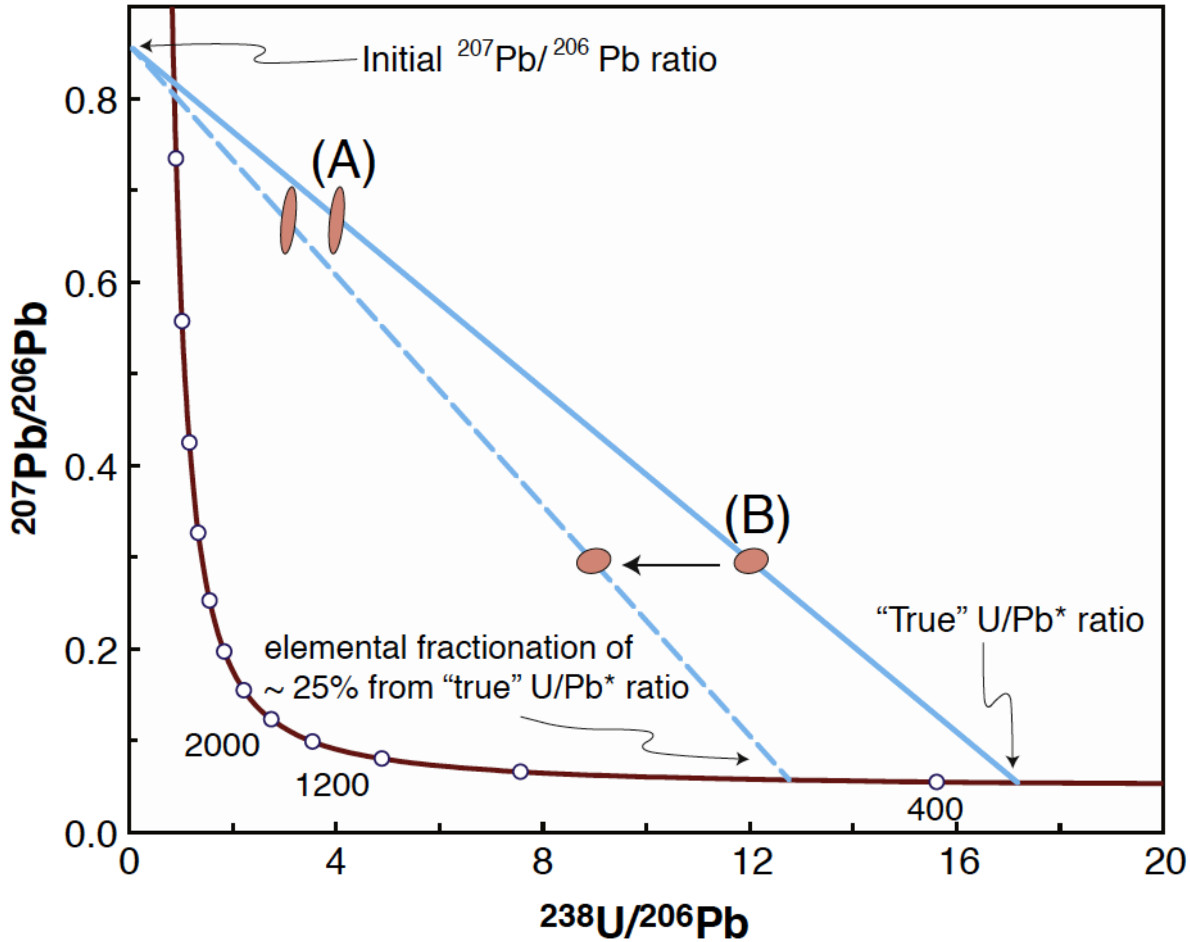


Standard: *c.* 523.5 Ma McClure Mountain apatite

Chew et al. (2014), Chemical Geology

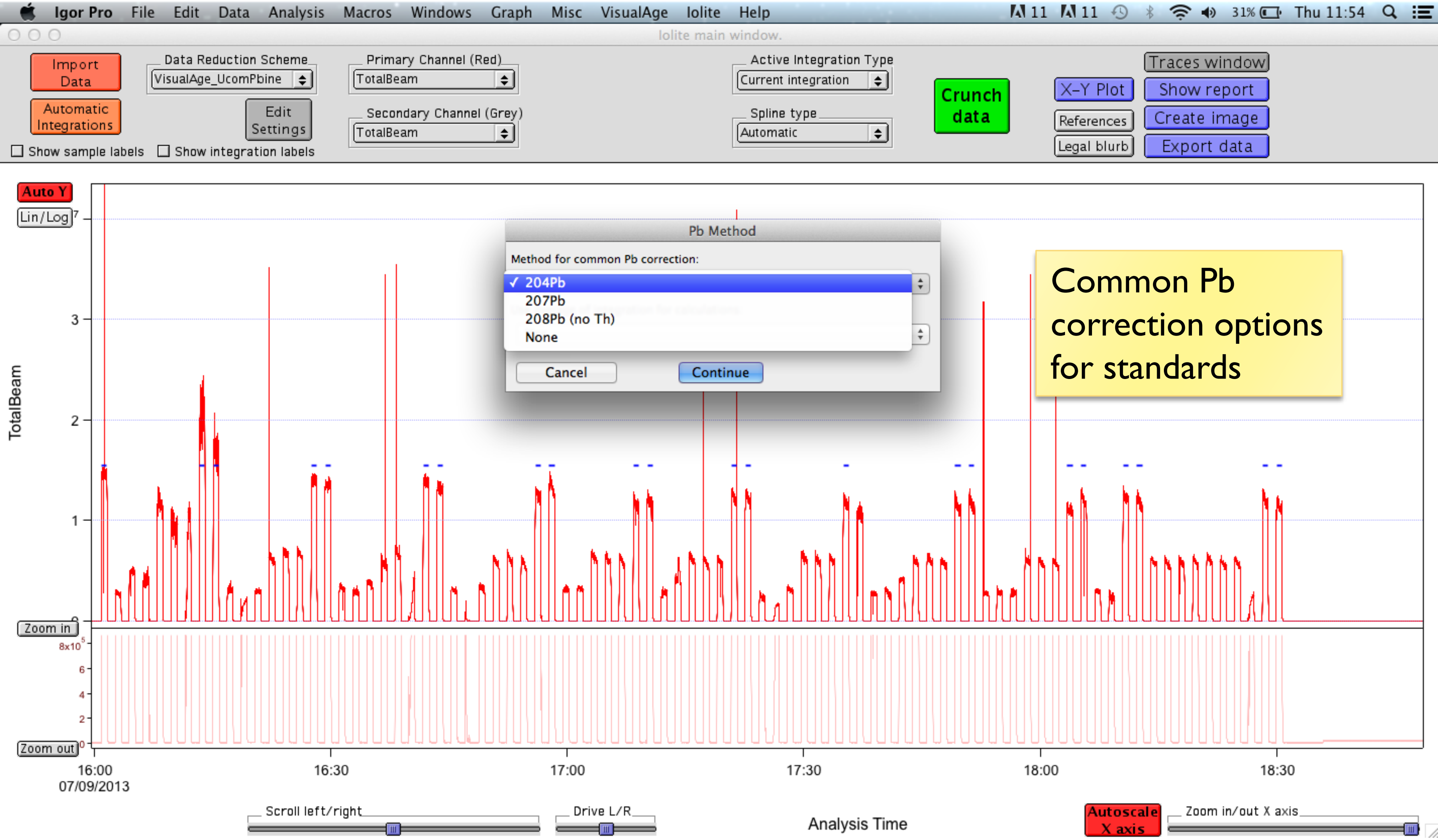
VizualAge_UcomPbine

- Assume Pb isotopic ratios are essentially unaffected by LIEF
- Correct standards for common Pb prior to downhole fractionation correction
- Deviation from "true" U/Pb ratio is due to elemental fractionation
- Correct for this by sample-standard bracketing



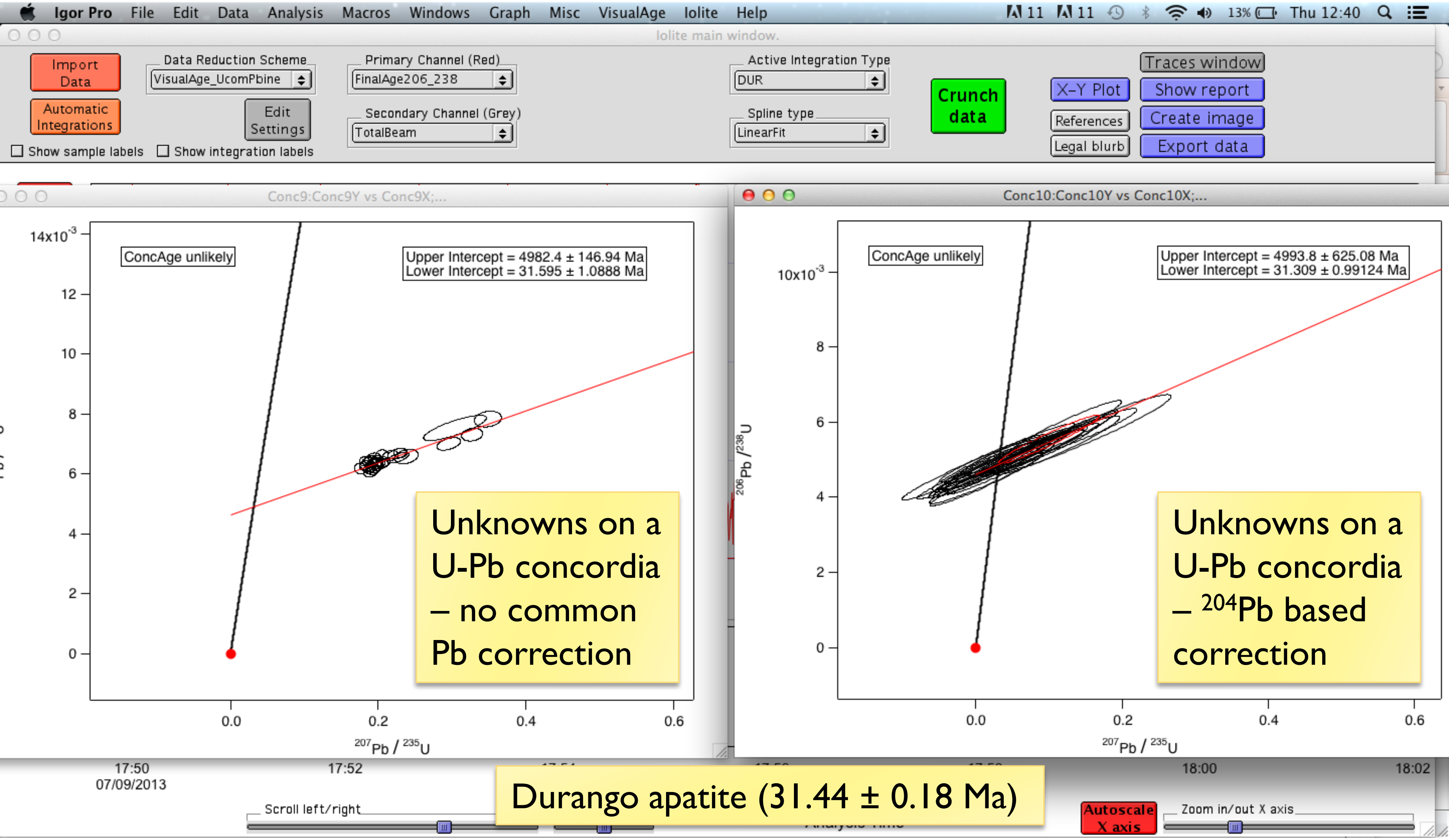
Chew et al. (2014), Chemical Geology

VizualAge_UcomPbine



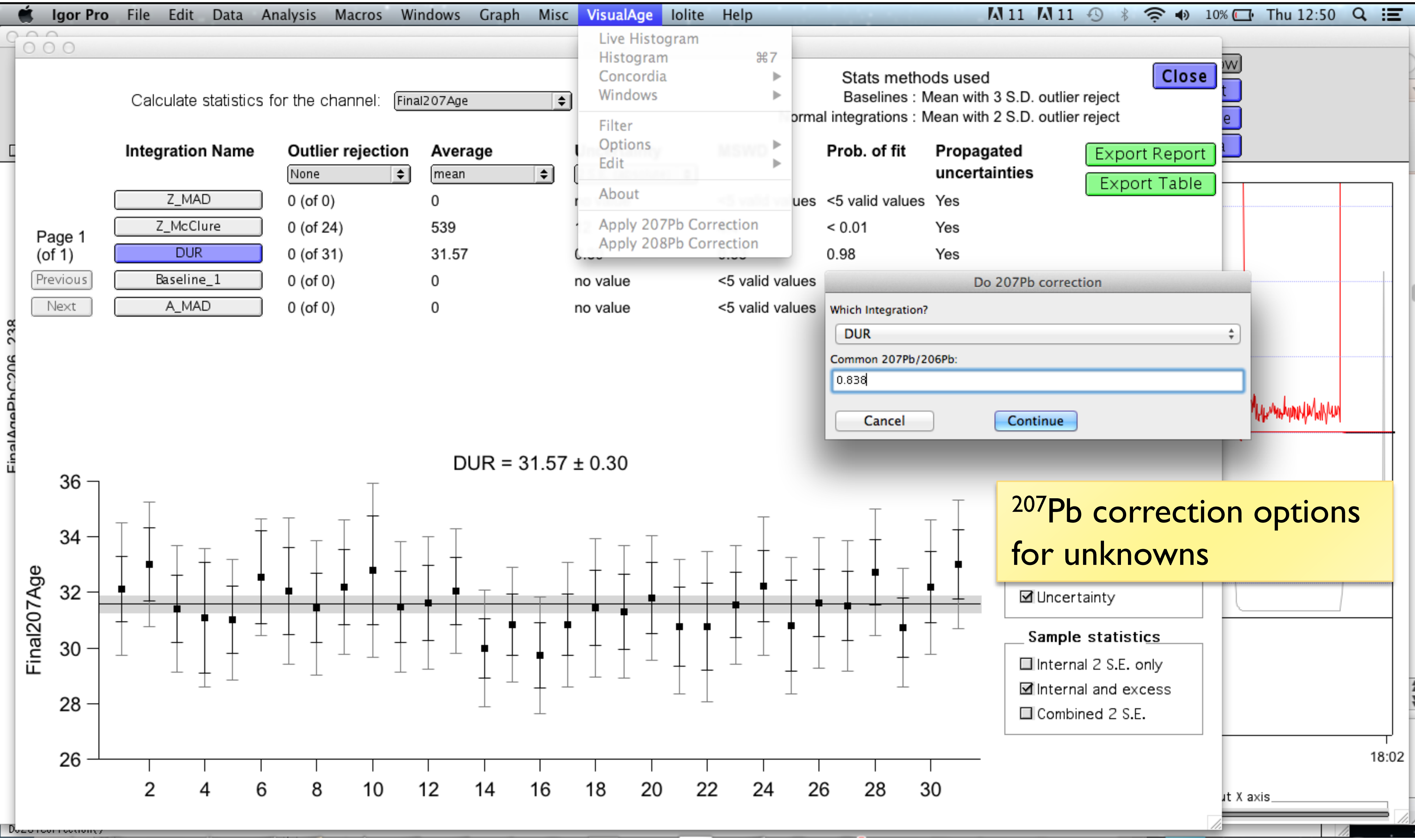
Chew et al. (2014), Chemical Geology

VizualAge_UcomPbine



Chew et al. (2014), Chemical Geology

VizualAge_UcomPbine



Chew et al. (2014), Chemical Geology

VizualAge_UcomPbine: summary

COMMON Pb CORRECTION TO STANDARDS:

- 3 methods: ^{204}Pb-, ^{207}Pb- and ^{208}Pb-correction

COMMON Pb CORRECTION TO UNKNOWNS:

- ^{204}Pb-, ^{207}Pb- and ^{208}Pb-correction. ^{204}Pb method uses conventional VizualAge correction; ^{207}Pb- and ^{208}Pb-correction user inputs initial Pb ratio

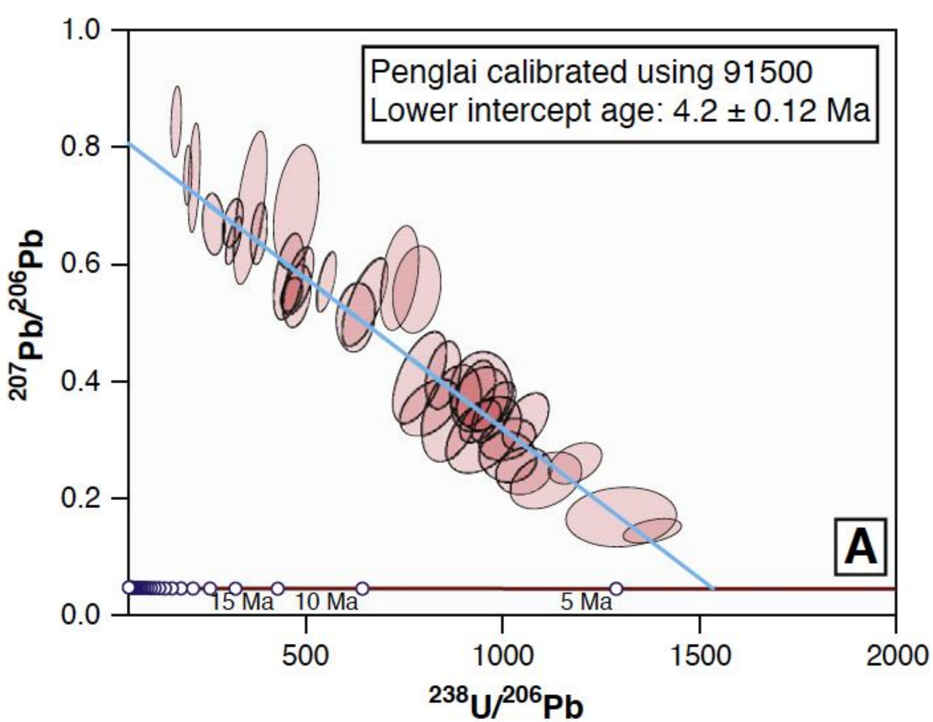
CONCORDIA OPTIONS:

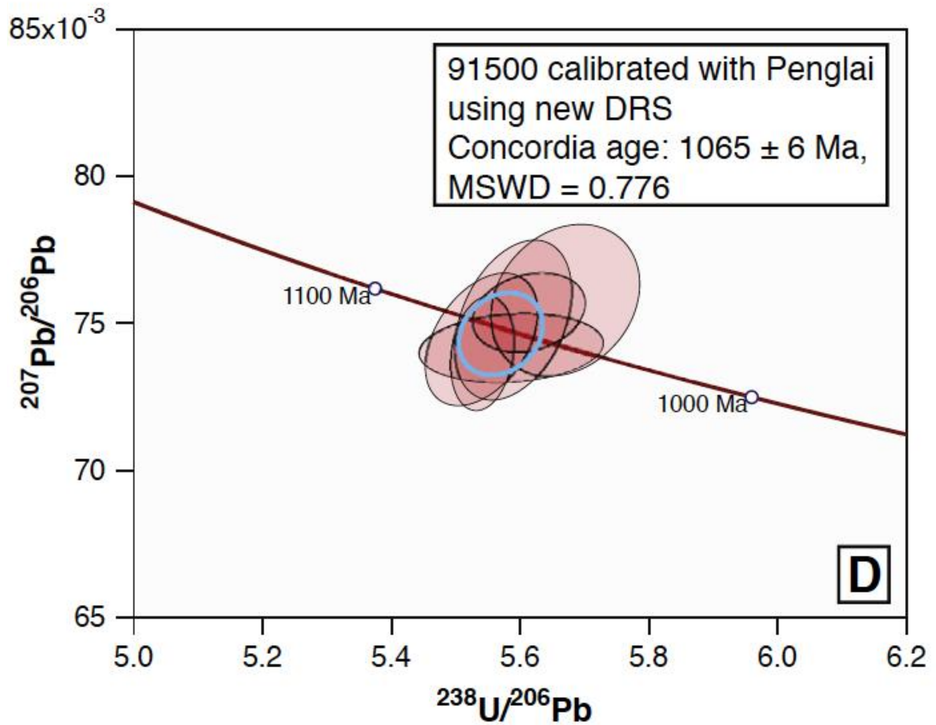
- Live Concordias; Wetherill and Tera-Wasserburg: non-corrected or ^{204}Pb and ^{208}Pb-correction

Chew et al. (2014), Chemical Geology

VizualAge_UcomPbine: nice example!

30 micron zircon spot analyses





This is a common Pb-infested Penglai zircon (4.1 Ma), with some analyses plotting close to modern day common Pb. 91500 used as the primary.

Same session – but we used the common Pb infested Penglai as the primary and treated 91500 as the unknown – comes out at 1065 Ma.

1. Application-specific strategies

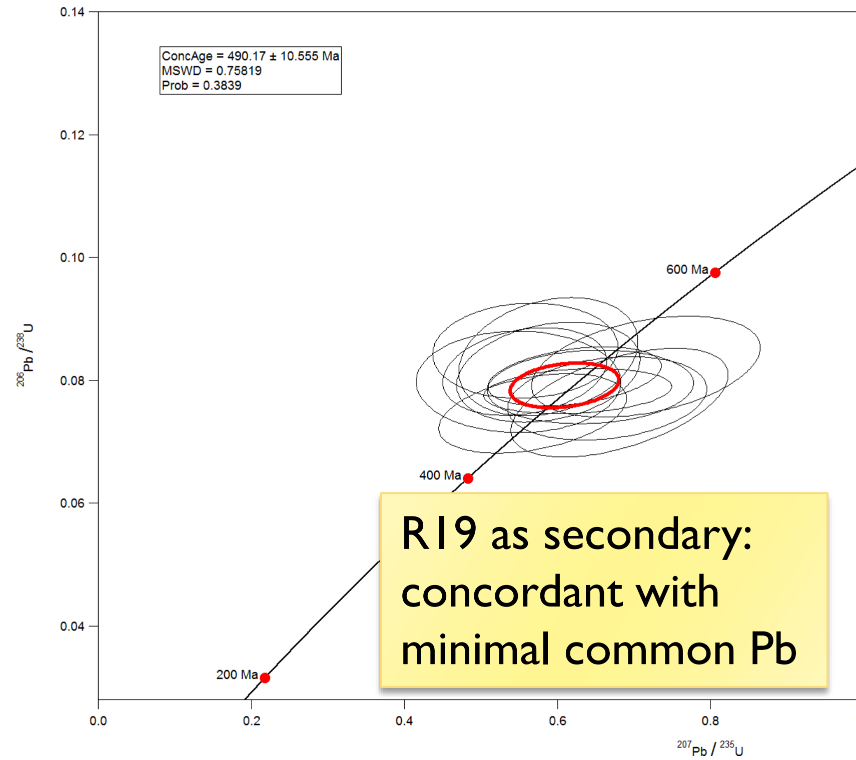
Listed in (a crude) order of increasing common Pb

- 1. Rutile
- 2. Titanite
- 3. Apatite
- 4. Calcite

- In Trinity College Dublin, we use a Photon Machines Analyte Exite ArF Excimer laser coupled to a Thermo Scientific iCAP Qc
- For rutile, apatite and titanite, a spot size of 30 to 60 microns (depending on the U and Pb contents in the session), 5Hz rep rate, 45 sec ablation, 25 sec background, 1 primary and 2 secondaries (blocks of 6 standards then 20 unknowns)
- All standards corrected for common Pb prior to LIEF and sample-standard bracketing using a modified version of Vizual Age (VizualAge_UcomPbine)

Rutile

- Main standards:
  - R10/R10b (Luvizotto et al. 2009) ← Primary
  - R19 (Zack et al., 2011)
  - Both standards contain minimal common Pb and are typically concordant



- Rutile ideally suited to a ^{208}Pb correction due to low Th
- If no Th present, all ^{208}Pb assumed common
- Some Th can be present in unknowns. As standards contain no Th how do we determine $^{232}Th/^{208}Pb$ fractionation? Tune on NIST with Th/U~1 and measure $^{232}Th/^{238}U$ of NIST during the session?
- So can do ^{204}Pb, ^{207}Pb and ^{208}Pb corrections and compare

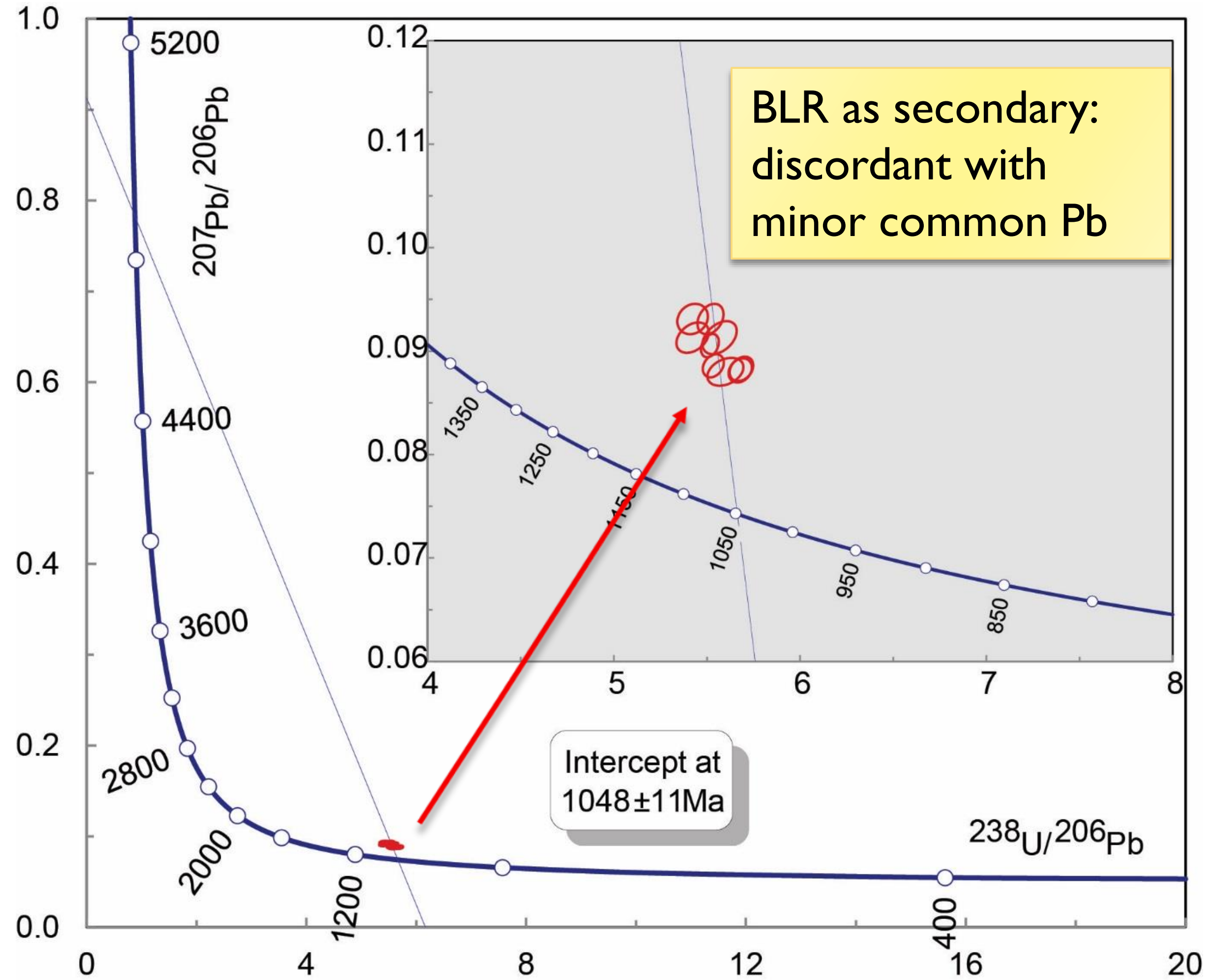
Titanite

Primary

- Some crystal standards:
  - OLT1 (Kennedy et al., 2010)
  - BLR (Aleinikoff et al., 2007; UCSB group)
  - Khan (Heaman et al., 2009)
  - These are large crystal standards that contain minor common Pb- typically minor discordance but analyses overlap

- Mineral separates
  - Fish Canyon tuff
  - McClure Mountain syenite (Schone and Bowring, 2006)
  - Variable common Pb from grain to grain

Titanite



- We do correct standards for common Pb (can get variations of 1 to 2% in U/Pb ratio due to variable common Pb). Our chips of Khan seem to suffer from minor Pb loss.

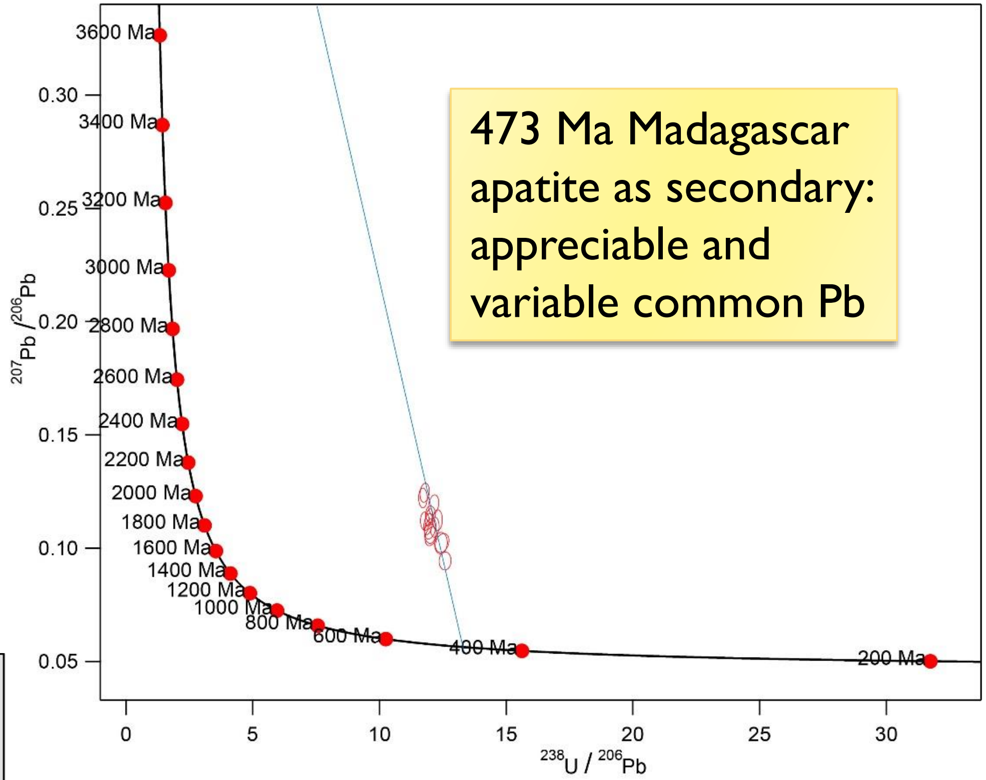
Apatite

Primary

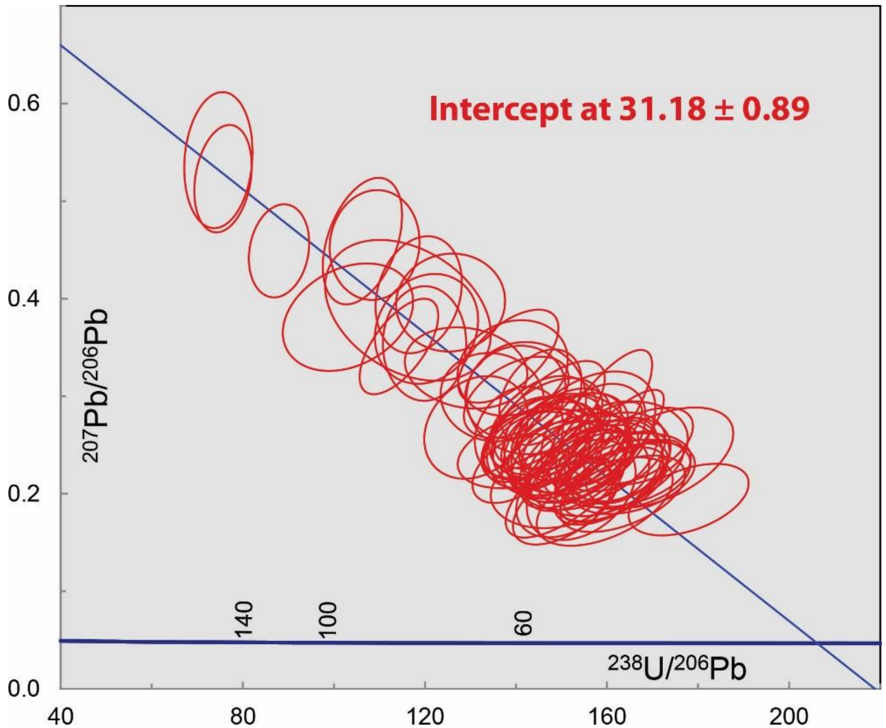
- Crystal standards:
  - Madagascar (Thomson et al., 2012)
  - Durango (McDowell et al., 2005)
  - These are large crystal standards that contain minor to appreciable common Pb
  - Standard analyses require common Pb correction

- Mineral separates
  - McClure Mountain syenite (Schoene and Bowring, 2006)
  - Variable common Pb from grain to grain

Apatite



473 Ma Madagascar apatite as secondary: appreciable and variable common Pb



31.44 Ma Durango apatite as secondary: appreciable and variable common Pb

Calcite

- Age standards:
  - "Troy" speleothem calcite (Li et al., 2014 Chemical Geology)

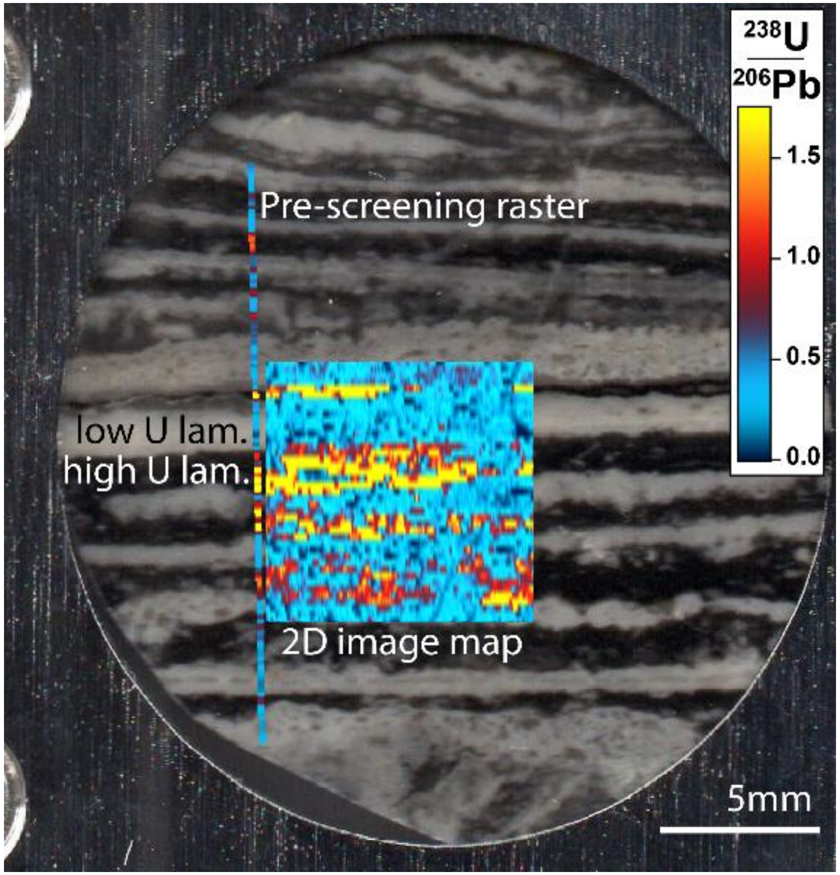
    and that is it….

- Very tricky – often very low U (100 ppb – 1ppm), lots of common Pb.

- Li et al. (2014) used LA-MC-ICPMS spot analyses with NIST 614 glass and Troy Calcite (TIMS age of 251±2Ma) as SRMs

- Alternative approach described here is image age mapping ("rastering") by LA-Q-IPCMS.
- It can often circumvent the problems of low U contents and/or high initial Pb by identifying zones of high U high U/Pb ratio on LA-ICPMS image maps. U-Pb ages are generated from these same image maps. Same standards used as Li et al. (2014)

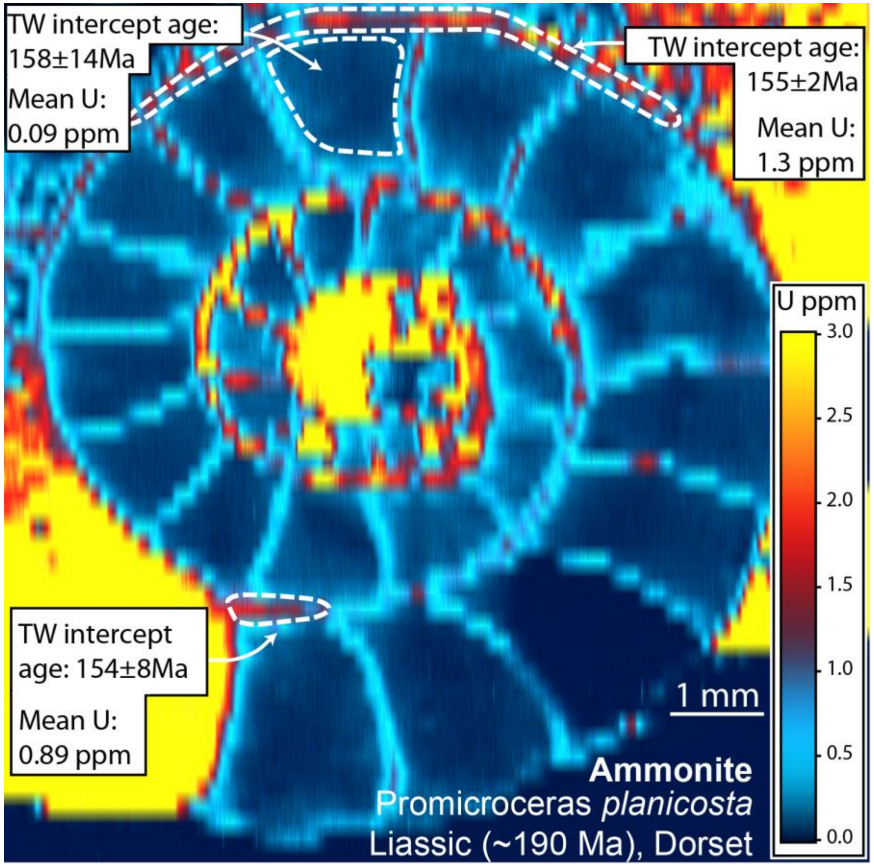
Calcite



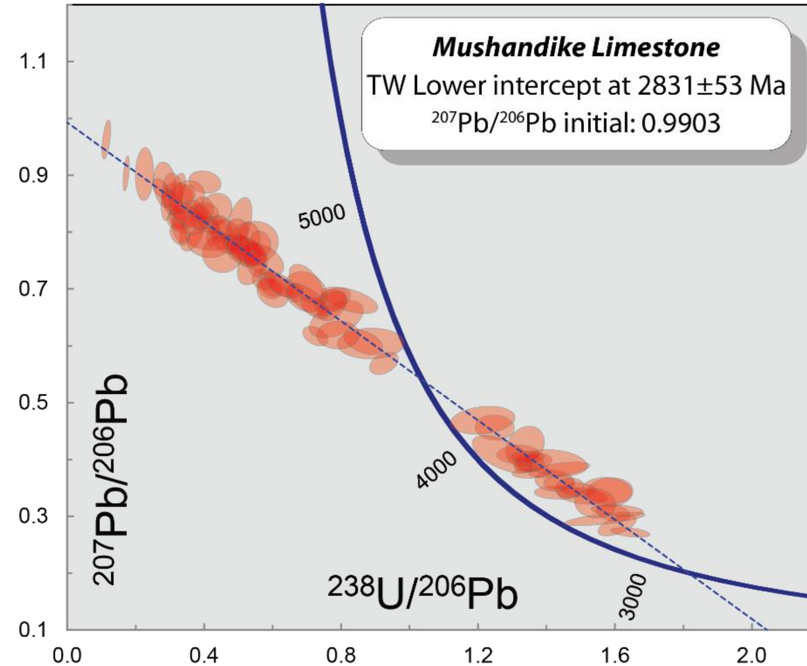
LA-ICPMS $^{238}U/^{206}Pb$ map of a laminated Neoproterozoic microbial dolomite illustrating dark laminae with high $^{238}U/^{206}Pb$ ratios. The image map is overlain on a scanned sample image using IOLITE

- Rationale - no way to know in advance of analysis if a sample has a viable U/Pb ratio, so many carbonates are not datable.
- Do a pre-screening raster to identify highly radiogenic subzones (low common Pb and/or high U) that are the key to precise ages.
- Then map highly radiogenic subzones and generate U-Pb ages from these maps

Calcite – example data



LA-ICPMS U concentration map of a diagenetic calcite cement in a Liassic ammonite with U-Pb calcite ages marked

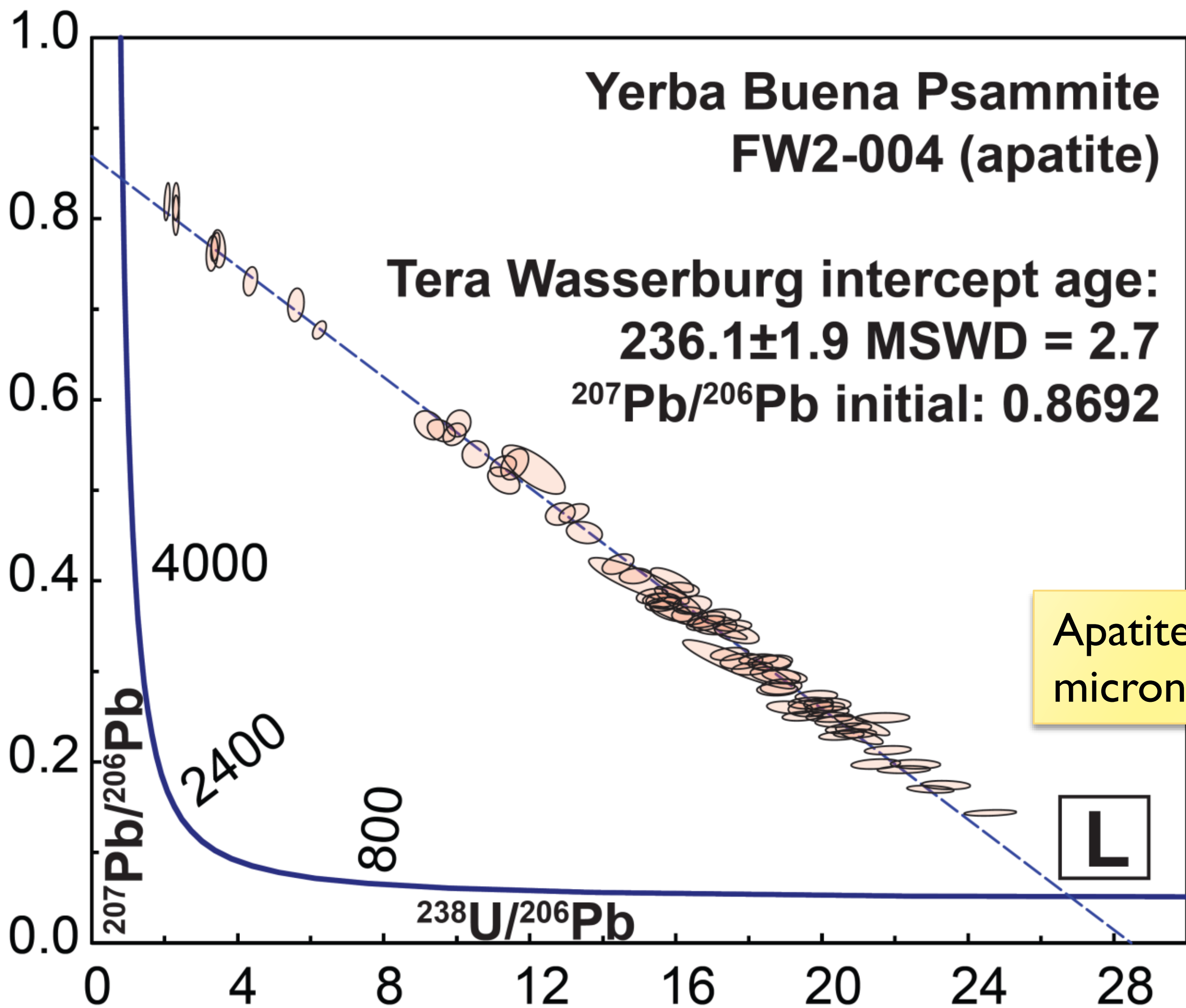


LA-ICPMS U-Pb calcite dating of the Mushandike limestone (2839±33 Ma TIMS age; Moorbath et al., 1987).

2. Tera-Wasserburg discordia examples

- CASE A. Well constrained – no anchor required. Data alone define intercept age.
- CASE B. Moderately constrained, close to Concordia. Data alone define intercept age but a very conservative choice of common Pb anchor improves precision
- CASE C. Poorly constrained and plot close to common Pb intercept. Data alone should define intercept age and anchoring with initial Pb should not be employed.
- CASE D. Poorly constrained intercept (analyses cluster with no spread) but close to Concordia. A very conservative choice of common Pb anchor should be used.

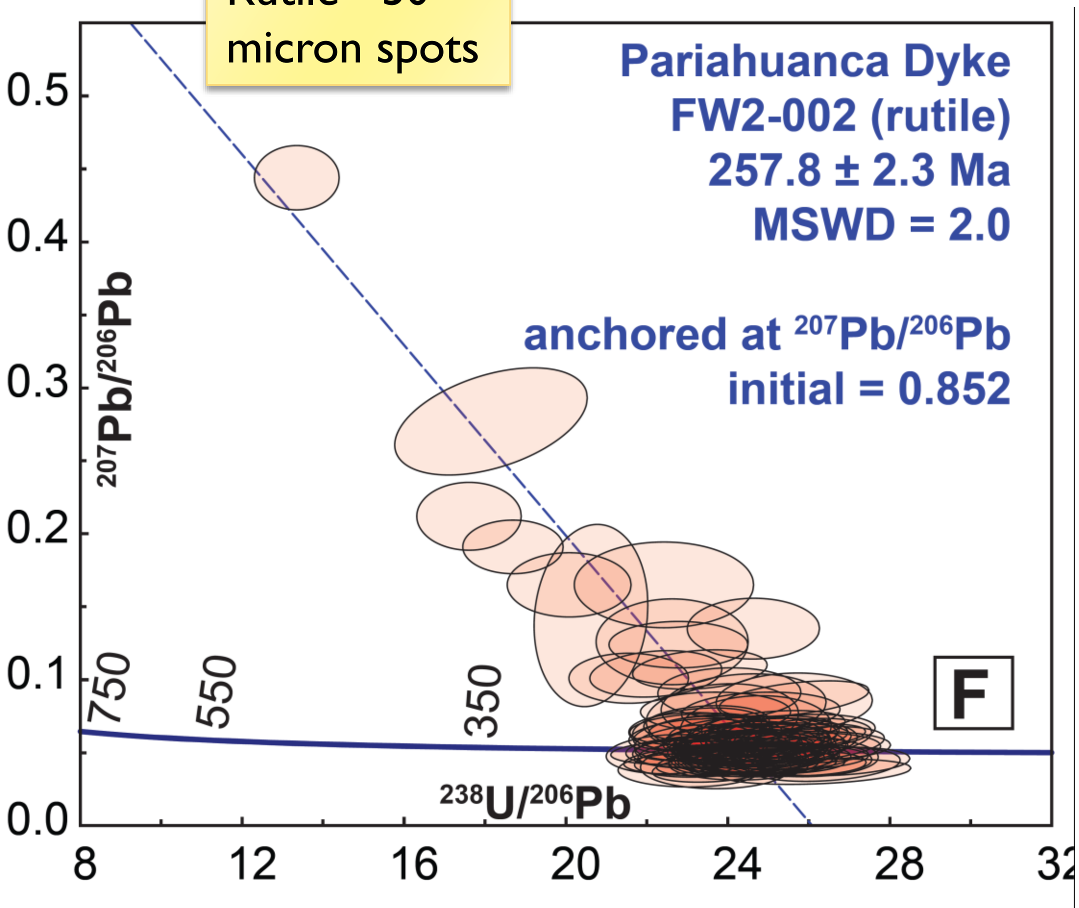
CASE A: Data alone define intercept



Apatite - 50 micron spots

CASE A: Data alone define intercept

Rutile - 50 micron spots



TW Intercept age anchored at $^{207}Pb/^{206}Pbc = 0.83 \pm 0.02$
257.3 ± 2.3 Ma, MSWD = 2

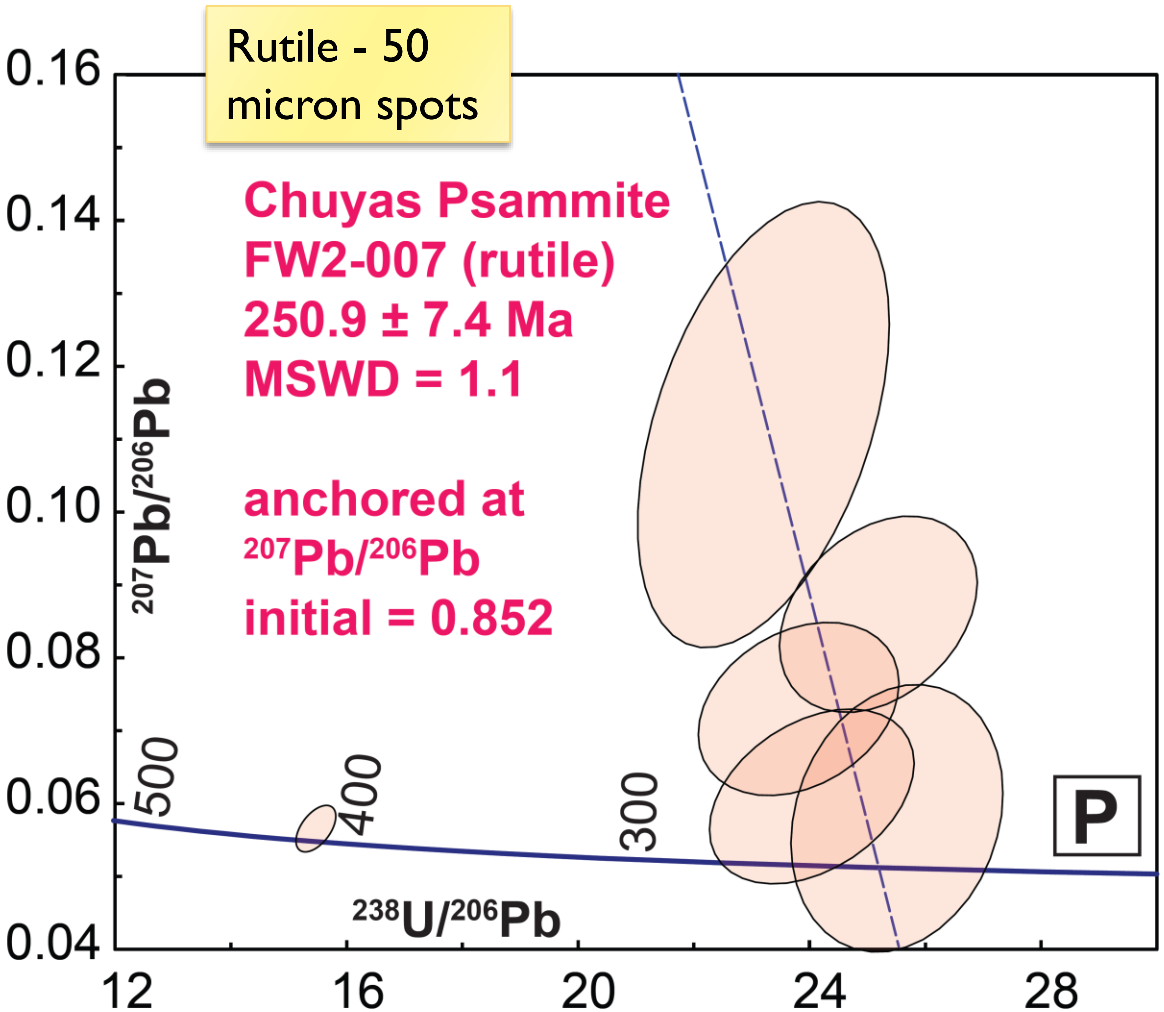
TW Intercept age anchored at $^{207}Pb/^{206}Pbc = 0.874 \pm 0.02$
257.9 ± 2.3 Ma, MSWD = 2

Unanchored TW Intercept age
257.8 ± 2.4 Ma, MSWD = 2

⇒ Large enough spread in data to give a well constrained unanchored intercept

⇒ Unanchored and anchored ages virtually identical

CASE B: Moderately constrained isochron



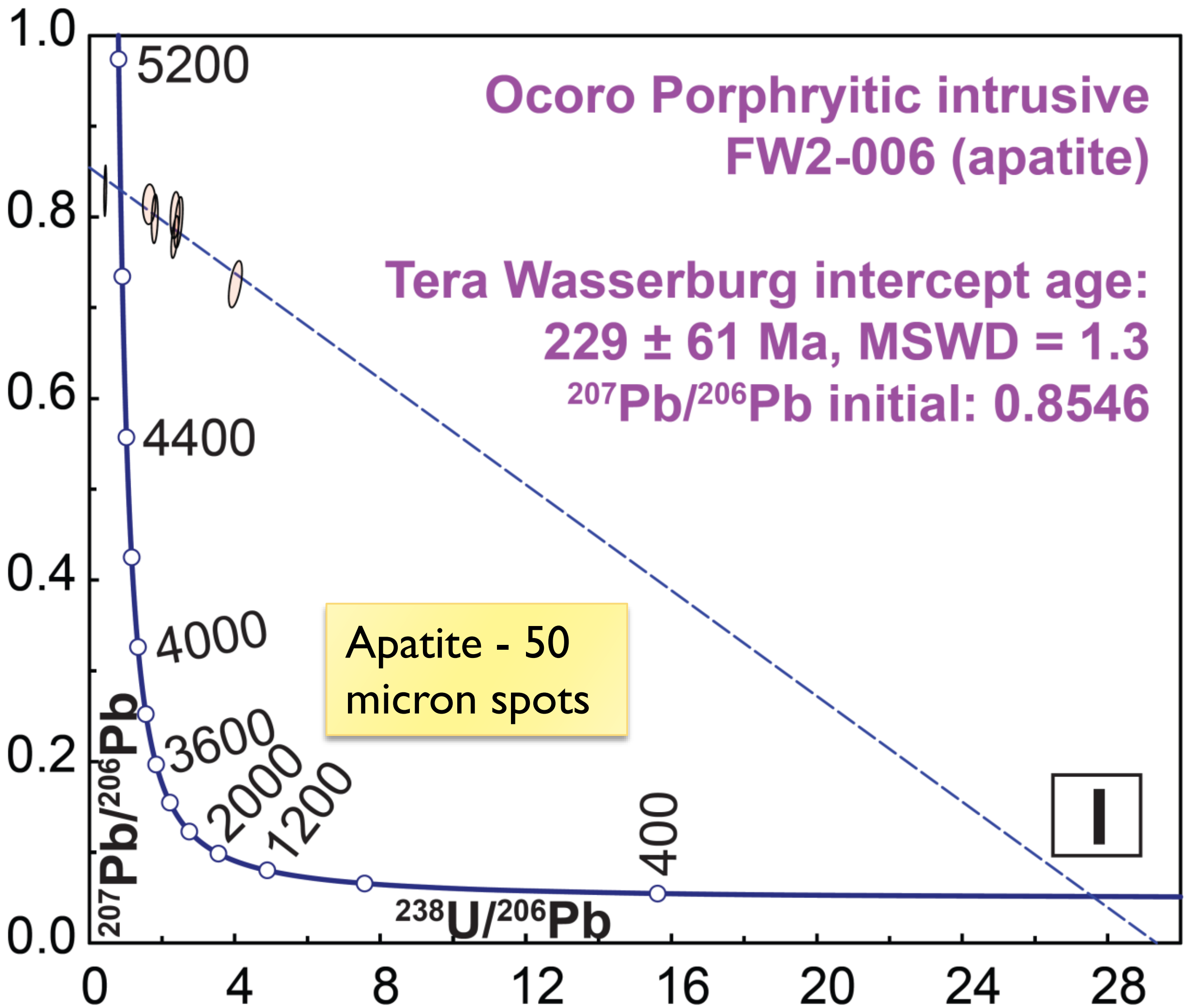
TW Intercept age anchored at $^{207}Pb/^{206}Pbc$ =0.83±0.02
250.7 ± 7.4 Ma, MSWD = 1.1

TW Intercept age anchored at $^{207}Pb/^{206}Pbc$ =0.874±0.02
251.1 ± 7.4 Ma, MSWD = 1.1

Unanchored TW Intercept age
252.0 ± 12 Ma, MSWD = 1.4

⇒ Would seem reasonable to anchor isochron at Stacey & Kramers with large uncertainty – not enough spread in data to give a well constrained unanchored intercept

CASE C: Poorly defined intercept; data plot close to common Pb



TW Intercept age using $^{207}Pb/^{206}Pbc = 0.85 \pm 0.02$
227 ± 57 Ma, MSWD = 1.1

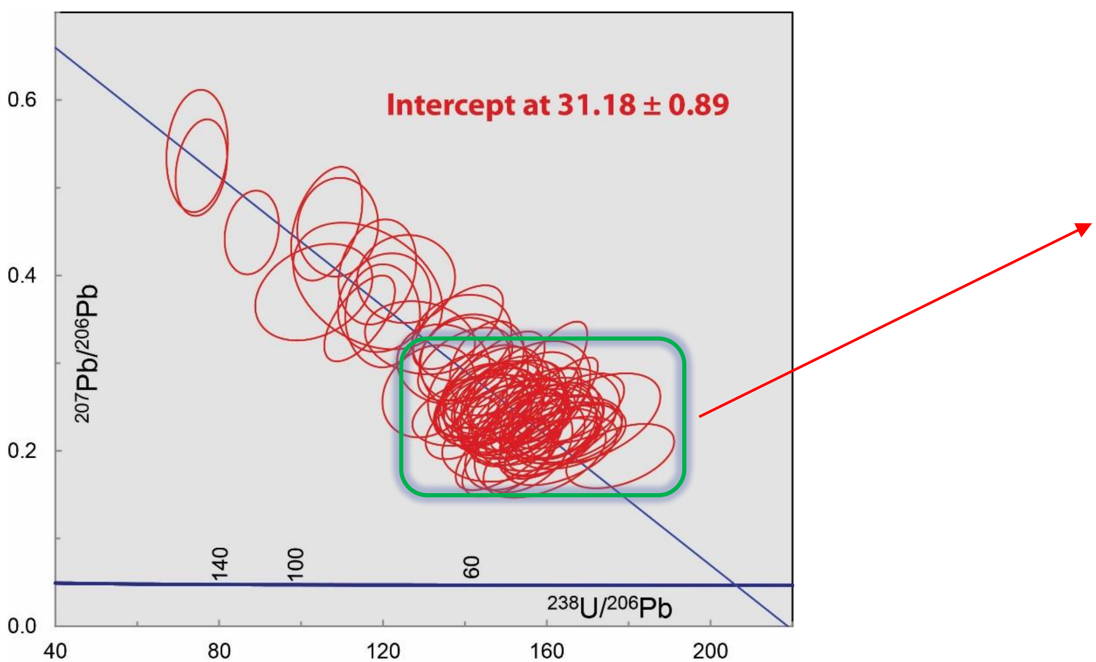
Unanchored Intercept age
229 ± 61 Ma, MSWD = 1.3

⇒ No spread in data to give a well constrained unanchored intercept

⇒ Need to employ conservative uncertainty in initial composition of Pb; does not help precision

CASE D: Poorly defined intercept; data plot close to concordia

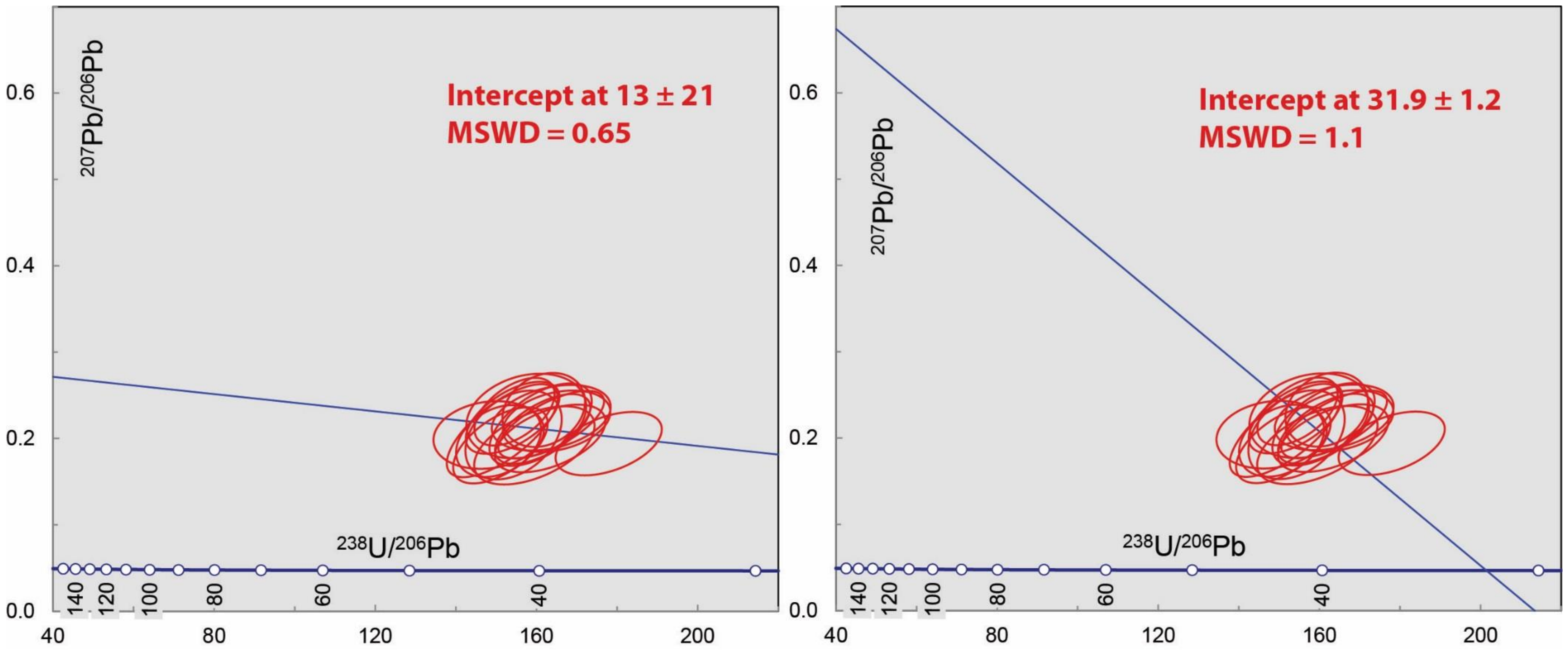
Durango apatite - 50 micron spots
=CASE A (well constrained)



Will take a subset of the data to make an overlapping cluster of points close to concordia

CASE D: Poorly defined intercept; data plot close to concordia

31.44 Ma Durango apatite - 50 micron spots



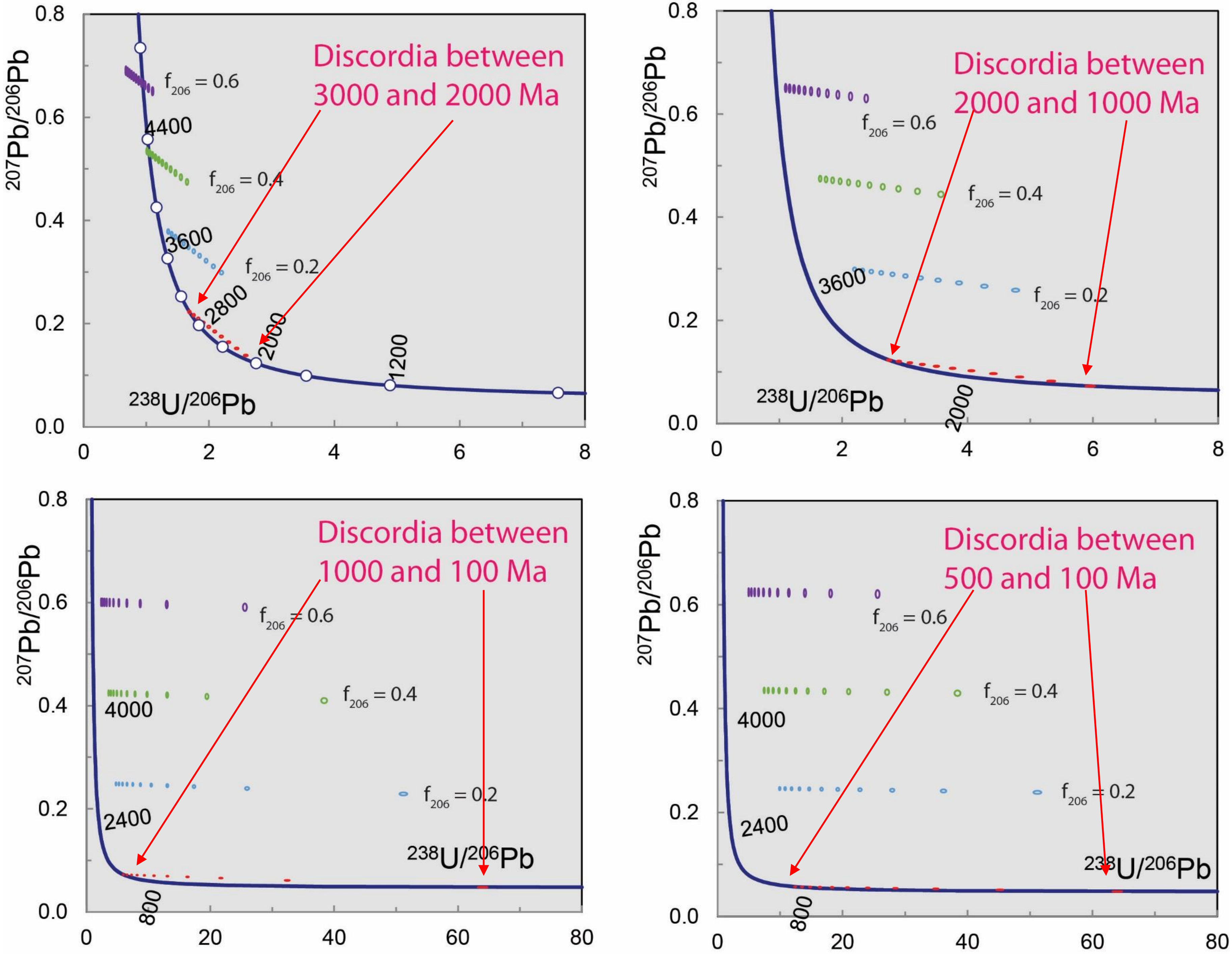
Data alone define intercept

Data anchored at $^{207}Pb/^{206}Pb_c$ = 0.84±0.03

3. When to use ^{204}Pb correction vs ^{207}Pb correction?

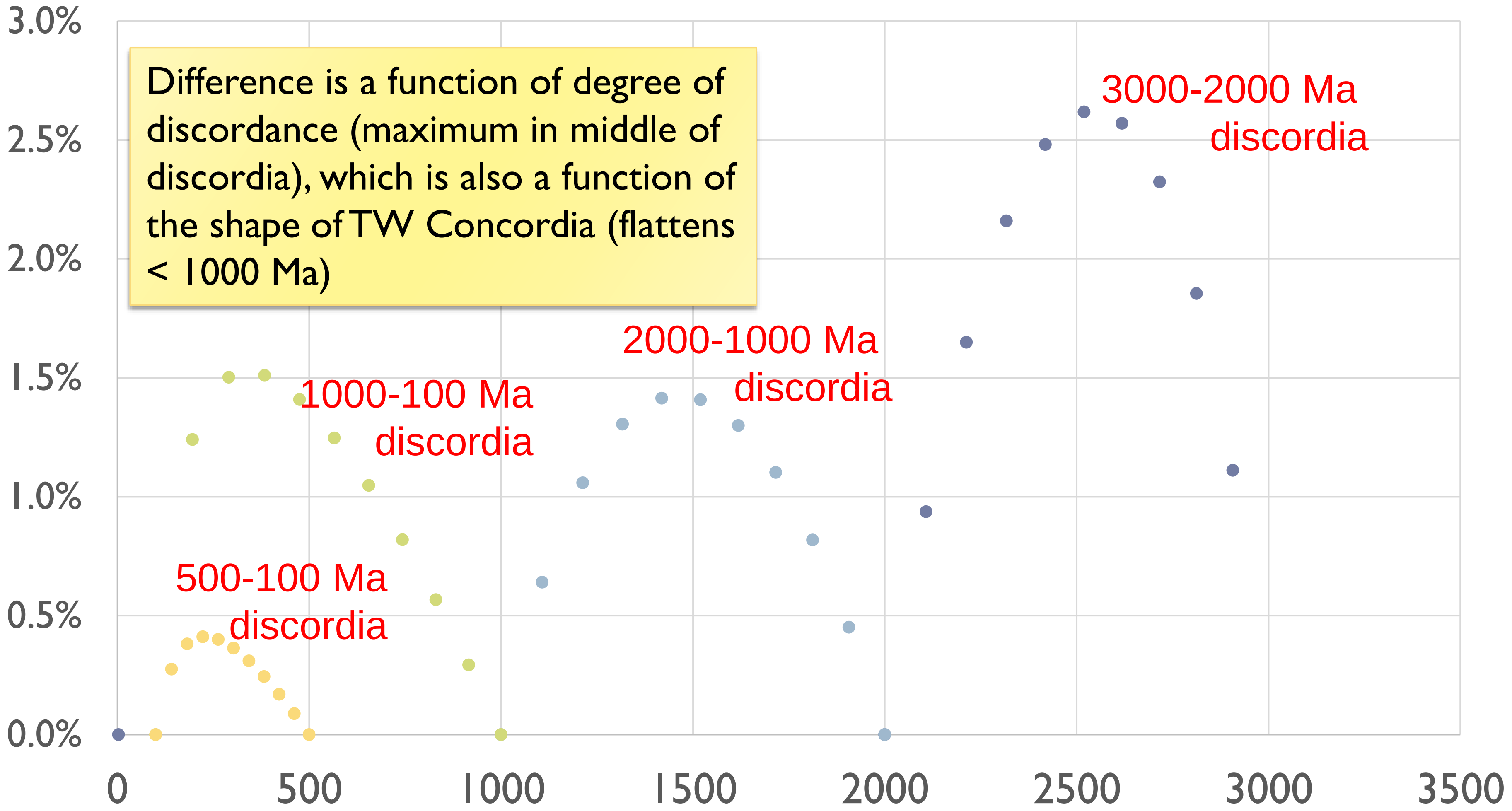
[A theoretical discussion independent of analytical setup]

- A ^{207}Pb correction assumes concordance so should never be used for strongly discordant data (e.g. zircon with significant Pb loss)
- Rutile, titanite and apatite generally are happier incorporating Pb in their structure (they accept common Pb) and so Pb loss is often less significant
- But apatite in particular can lose Pb due to slow cooling through the closure temperature window (Tc = 550 – 375°C depending on grain size and cooling rate)
- Following diagrams illustrate 4 discordias on TW Concordia (with incorporation of common Pb at f_{206} = 0.2, 0.4 and 0.6)
- Difference in the ^{207}Pb- vs ^{204}Pb-corrected age is then calculated



Discordia between 3000 and 2000 Ma
Discordia between 2000 and 1000 Ma
Discordia between 1000 and 100 Ma
Discordia between 500 and 100 Ma
$f_{206} = 0.6$
$f_{206} = 0.4$
$f_{206} = 0.2$
$^{207}Pb/^{206}Pb$
$^{238}U/^{206}Pb$
4400
3600
2800
2000
1200
4000
2400
800

^{207}Pb corrected vs ^{204}Pb corrected ages (difference %)



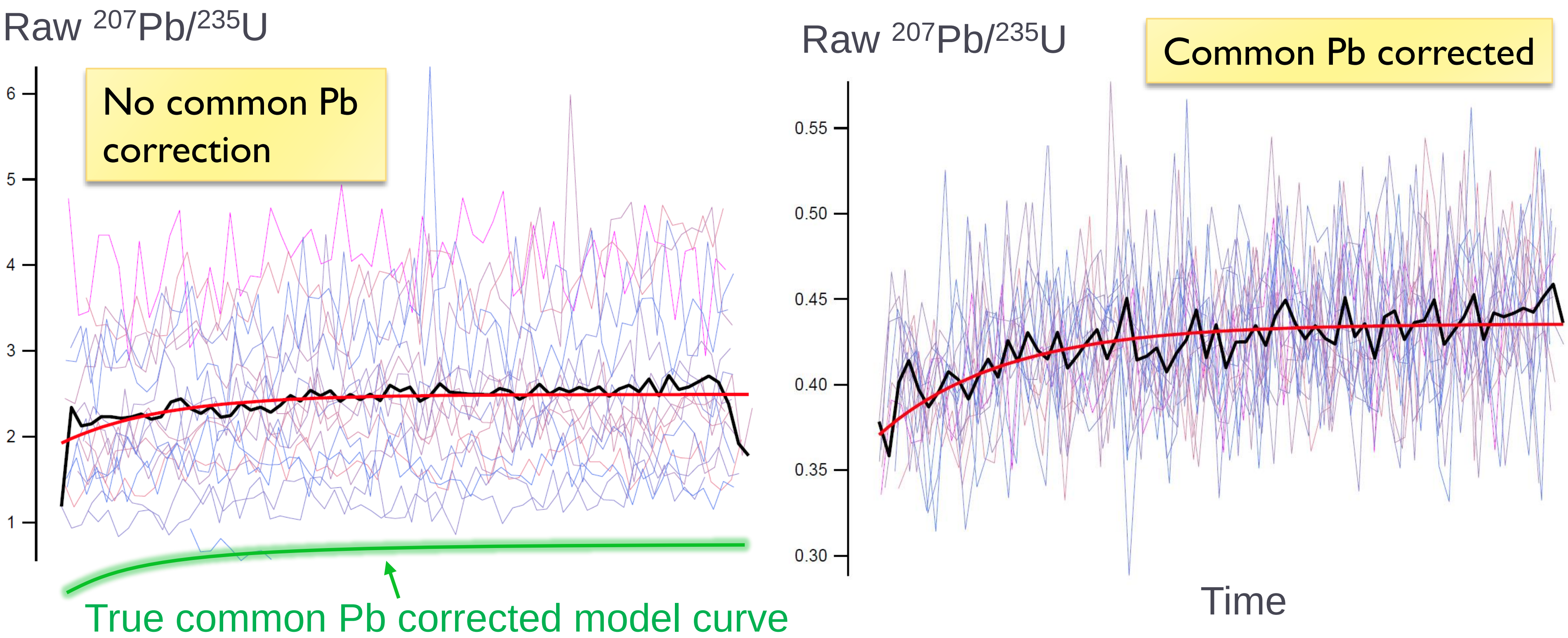
4. Correcting for common Pb in standards

- A brief summary of VizualAge_UcomPbine (Chew et al. Chemicla Geology 2014)

- Corrects for variable common Pb in standards (using either a ^{204}Pb-, ^{207}Pb- or ^{208}Pb correction) prior to correcting for LIEF and session drift

- It assumes:
- 1) standards are concordant if they didn't contain common Pb;
- 2) the "**end member**" common Pb is isotopically homogenous
- 3) However there can **be variable incorporation of the amount of common Pb** – either from standard grain to grain, or even variable amounts of common Pb during an individual TRA standard grain analysis

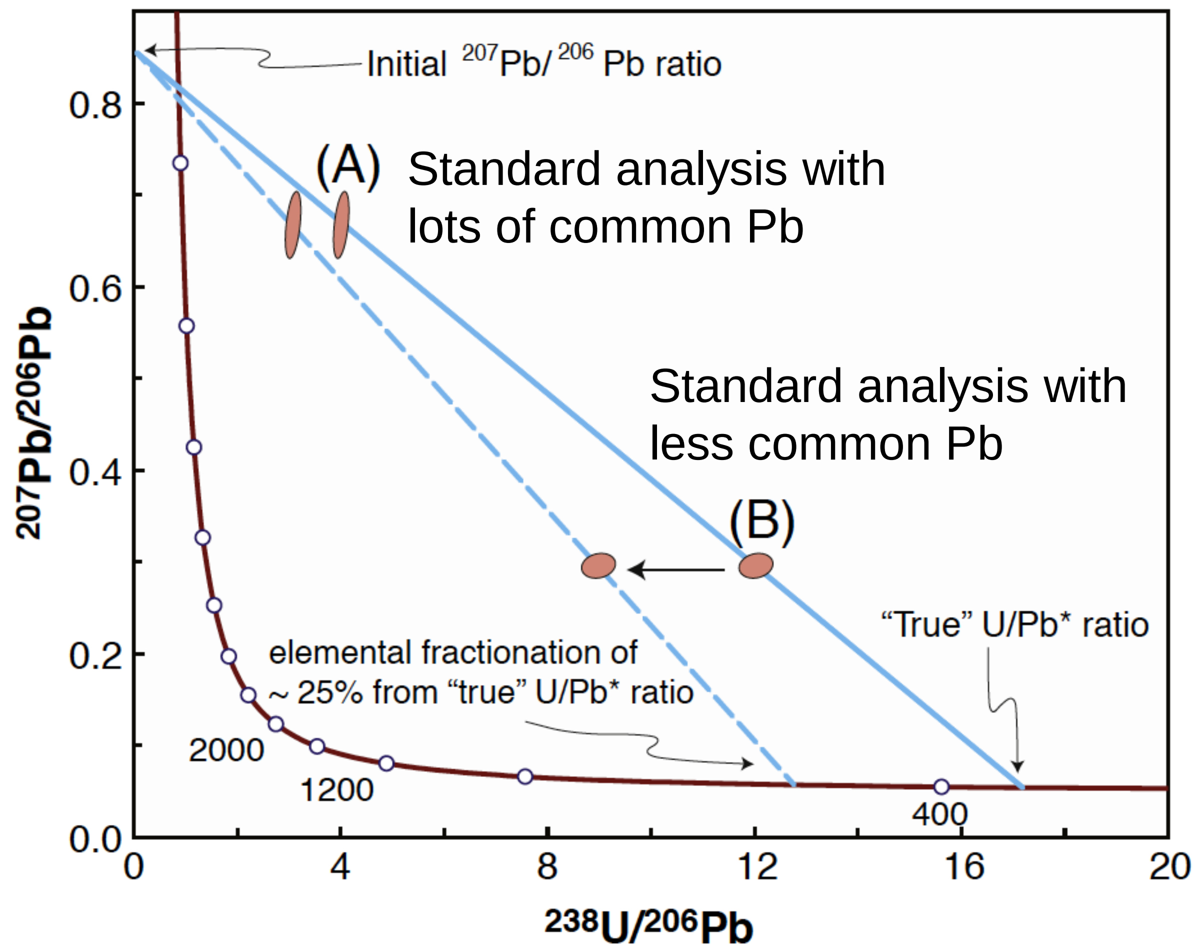
VizualAge_UcomPbine – correct for common Pb prior to downhole fractionation correction



Standard: *c.* 523.5 Ma McClure Mountain apatite

Correct for session drift by sample-standard brackting

- Assume Pb isotopic ratios are unaffected by elemental fractionation
- Correct standards for common Pb
- Deviation from "true" U/Pb ratio is due to elemental fractionation
- Correct for this by sample-standard bracketing



VizualAge_UcomPbine: summary

Common Pb correction to standards :

- 3 methods: ^{204}Pb-, ^{207}Pb- and ^{208}Pb-correction

Common Pb correction to unknowns:

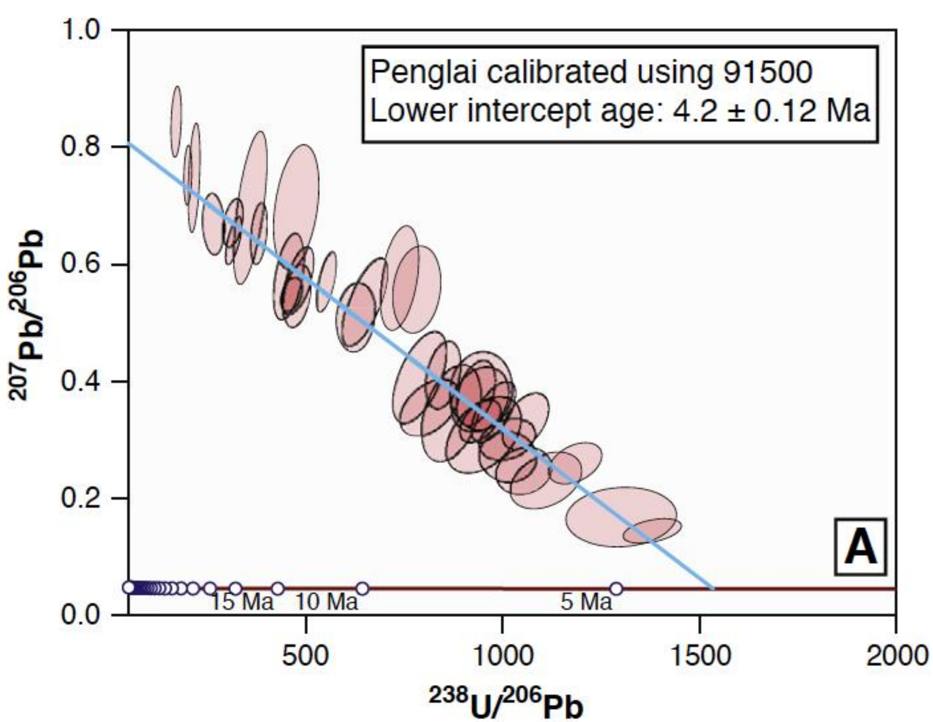
- ^{204}Pb-, ^{207}Pb- and ^{208}Pb-correction. ^{204}Pb method uses conventional VizualAge correction; ^{207}Pb- and ^{208}Pb-correction user inputs initial Pb ratio

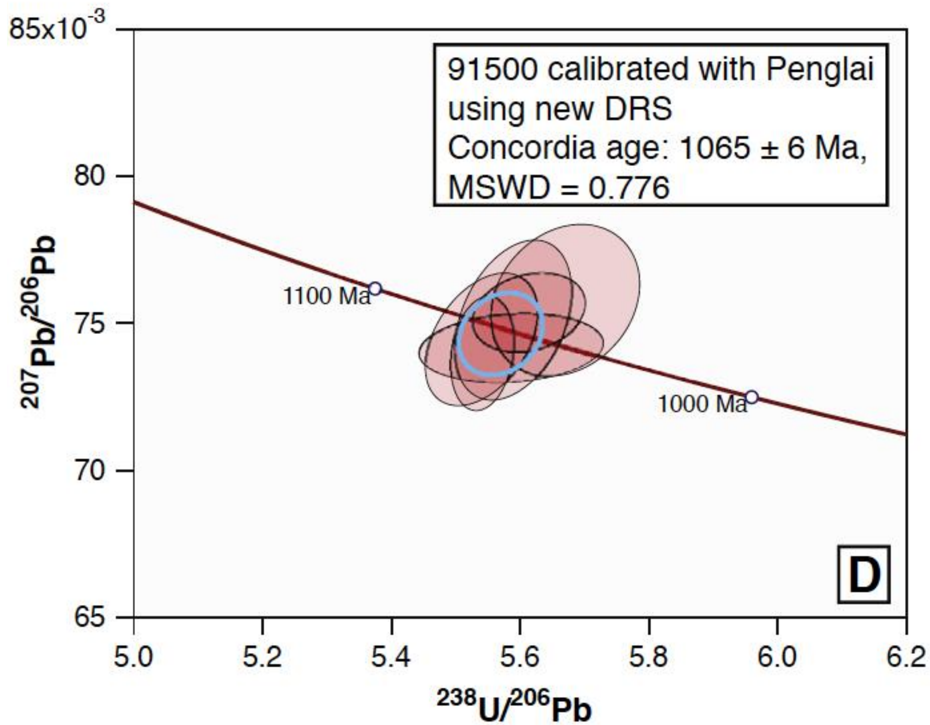
Concordia Options:

- Wetherill and Tera-Wasserburg: non-corrected or ^{204}Pb and ^{208}Pb-correction

VizualAge_UcomPbine: nice example!

30 micron zircon spot analyses





This is a common Pb-infested Penglai zircon (4.1 Ma), with some analyses plotting close to modern day common Pb. 91500 used as the primary.

Same session – but we used the common Pb infested Penglai as the primary and treated 91500 as the unknown – comes out at 1065 Ma.