# LA-ICP-MS U-Th-Pb Network shortcourse Boston Goldschmidt 2018

# Welcome & Logistics

- Fire exits, Toilets, Coffee & lunch times
- Ask Q's!

# Programme

- <u>**Operating variables impacting U-Pb reproducibility**</u> – *how do issues such as pulse energy, focus, water vapour in the cell and resin mount degassing impact U-Pb data? Testing cells for U-Pb reproducibility.*
- **Coffee (11:00-11:30)**
- <u>**Data handling Principles**</u>
- **Definitions** - Error vs uncertainty, s vs sigma, random vs systematic errors/uncertainty
- **Reference values** – Using ratios not geological ages. Which are the right ones? With CA, without? Excess Th corrected?
- **Data reporting.** Importance of data reporting standards. Description of content of data tables. Reporting of validation data, metadata and x/y/z uncertainties.
- **Lunch (1:00-2:00)**

# Programme (cont.)

- **Implementing uncertainty propagation in LA-ICP-MS U-Th-Pb data**
- Coffee (3:30-4:00)
- Data Interpretation
- **Resolution of scatter with low precision data points.** - fundamental assumption of MSWD calculation.
- **Ability to interpret data in a relative sense** without full uncertainty propagation. Understanding resolution, precision/accuracy and MSWD.
- Clinic/Q&A?

# Over to Simon

# Data Handling Principles - Intro

- Mostly recommendations from Community paper
- None of this is cast in stone – a new (improved) line in the sand from which we can progress and are evolving with better understanding.
- Some of the viewpoints herein represent this evolution (i.e. not necessarily all derived from community discussions)
- More complicated now, that’s progress!
- Therefore requires more consideration, understanding and time. Arguably more subjective assessment required but within better defined constraints
- Requires ‘ethical geochronology’ on your part!
- Not rocket science, common sense applied to analysis.

Terminology & Fundamentals review

# Repeatability vs reproducibility

- Repeatability - the variation in measurements taken by a single person or instrument on the same item, under the same conditions, and in a short period of time.
- Reproducibility - the ability of an entire experiment or study to be duplicated, either by the same researcher or by someone else working independently.

# Accuracy vs precision

**Accuracy**

How do I know the result is correct?

A measurement of the difference between an experimental result and the truth (*'you can't handle the truth'* - you can never know the true value because any assigned value always has an uncertainty associated with it)

**Precision**

How well do I know the value?

A measurement of the repeatibility of an experimental result, without regard to the truth

# Error vs bias vs uncertainty

Error - a single value (e.g., 0.1), deviation from the expected
- not known unless a reference value exists to compare against.

Measurement error can be

1) random (unpredictably offset from the measurand value), or
2) systematic (consistently or predictably offset from a reference value).

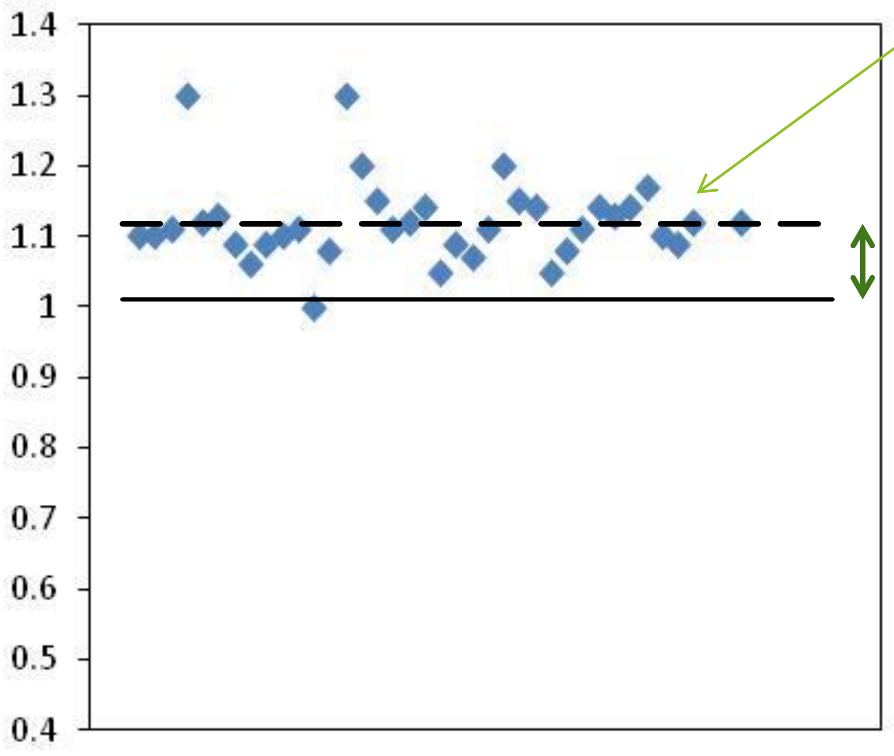
Bias - once quantified, a systematic error is referred to as a bias.

The impact of measurement error is to make the result uncertain. This uncertainty can be quantified and is commonly referred to as systematic or random in reference to the error to which it relates.

Uncertainty - a range (e.g., ± 0.1, 2*s*) within which the measurand is expected to lie with a given probability.

# Error vs bias vs uncertainty

*Components of error*

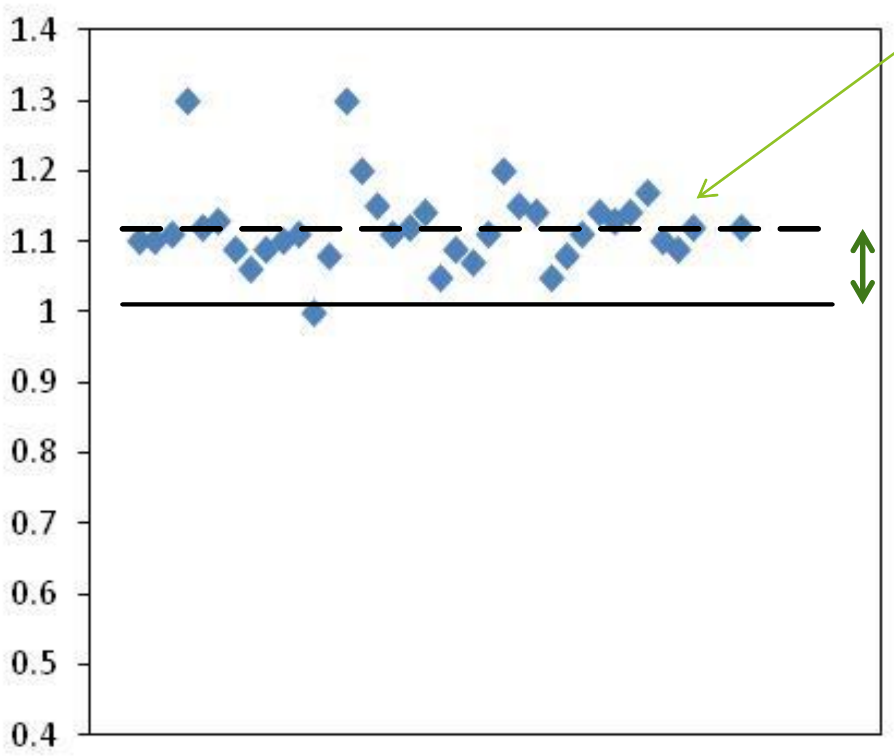



**Random component** – from random fluctuations in the signal you're measuring. The uncertainty resulting from this can be reduced by increasing the number of observations.

**Systematic component** – remains constant or varies predictably, no matter how many measurements you make. The uncertainty resulting from this cannot therefore be reduced further. To reduce the uncertainty this contributes, the bias must be reduced or the error eliminated.

# Error vs bias vs uncertainty

*Components of error*




**Random component** – from random fluctuations in the signal you're measuring. The uncertainty resulting from this can be reduced by increasing the number of observations.

**Systematic component** – remains constant
or varies predictably, no matter how many
measurements you make. The uncertainty resulting from this cannot therefore be reduced further. To reduce the uncertainty this contributes, the bias must be reduced or the error eliminated.

# Classifying Uncertainties

- Uncertainties related to random error:
  - Measurement processes (ion beam size, baseline/background variation, etc)
  - Repeatibility, short term over-dispersion (excess variance)

**Fundamentally limiting!**
**You cannot do better than this!**

- Uncertainties related to systematic error:
  - Decay constants
  - Long-term over-dispersion (excess variance) of the analytical method
  - (Composition of common lead used for correction)
  - Reference material ratios

# Propagating Uncertainty

General rule of thumb:

Use $\sqrt{a^2 + b^2}$

Uncertainties for random errors always need to be propagated to represent a measurement value.

Uncertainties for systematic errors need to be propagated when a total uncertainty is required e.g. when comparing values determined under different conditions (i,e they have experienced different systematic errors…)

e.g. decay constant uncertainties: they are systematic - they apply to everything dated by that technique.
A mineral dated by U-Pb can be compared to another mineral dated by U-Pb without incorporating the uncertainty in the U decay constants.

BUT, if you're comparing K-Ar dates to U-Pb dates, the uncertainty in decay constants is important and requires inclusion in the final age uncertainty!

Sometimes it is not so clear...

# Tools for quantifying uncertainty: MSWD/reduced Chi-squared statistic

- MSWD - Mean Square Weighted Deviation

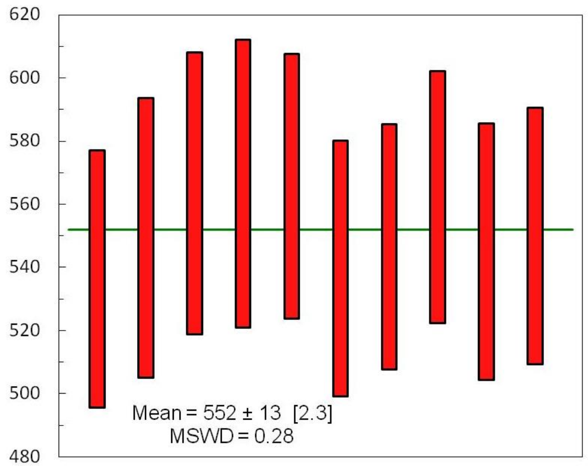
  (same as reduced chi-squared test)

  - a measure of the goodness of fit of a series of datapoints around the defined mean taking into account the datapoint uncertainty

"…it should average about 1 when the observed deviations from the regression line or plane are within analytical error and there is no additional scatter (geological error)"
Wendt & Carl, 1991

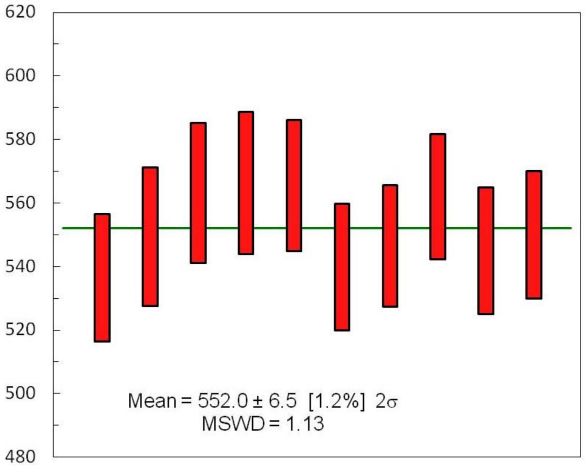
# MSWD

underdispersed



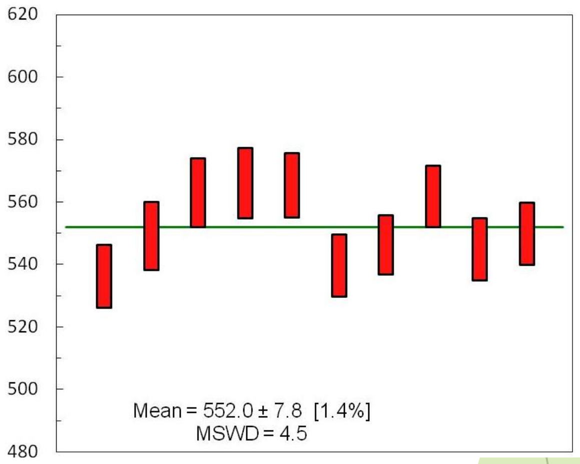

Analytical uncertainties
overestimated?

ideal




Analytical uncertainties
estimated correctly,
single population of data.

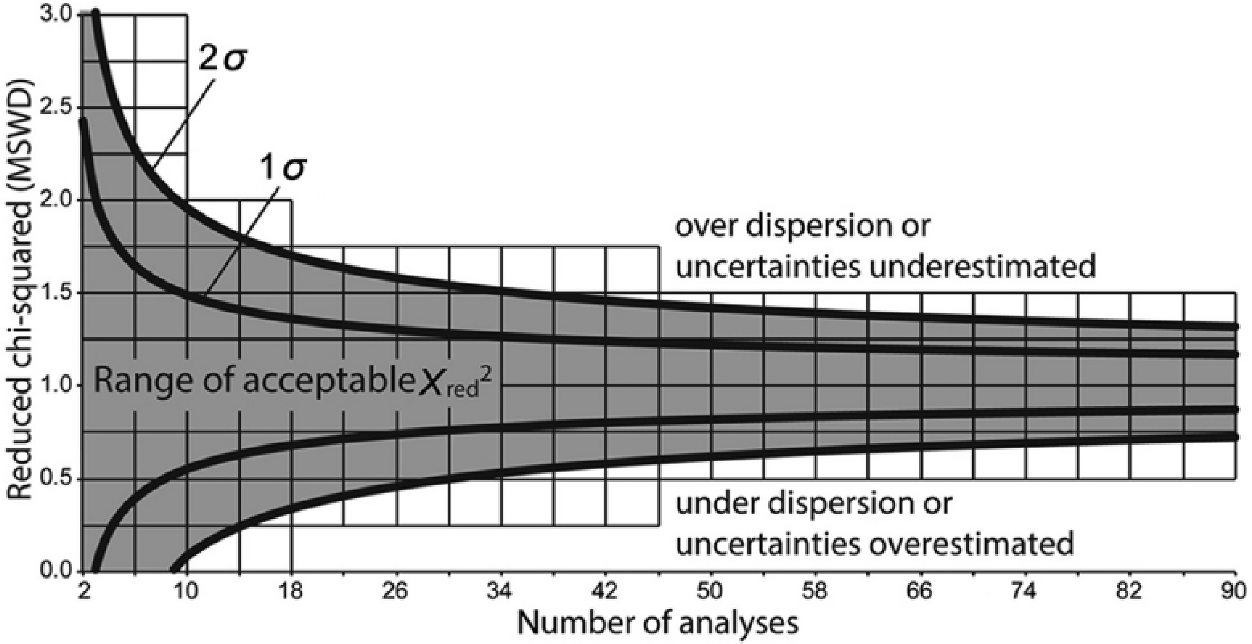
overdispersed




Analytical uncertainties
underestimated?
OR real geological scatter
(i.e. not a single population of data)

# Range of acceptable MSWD values scales with n

- MSWD

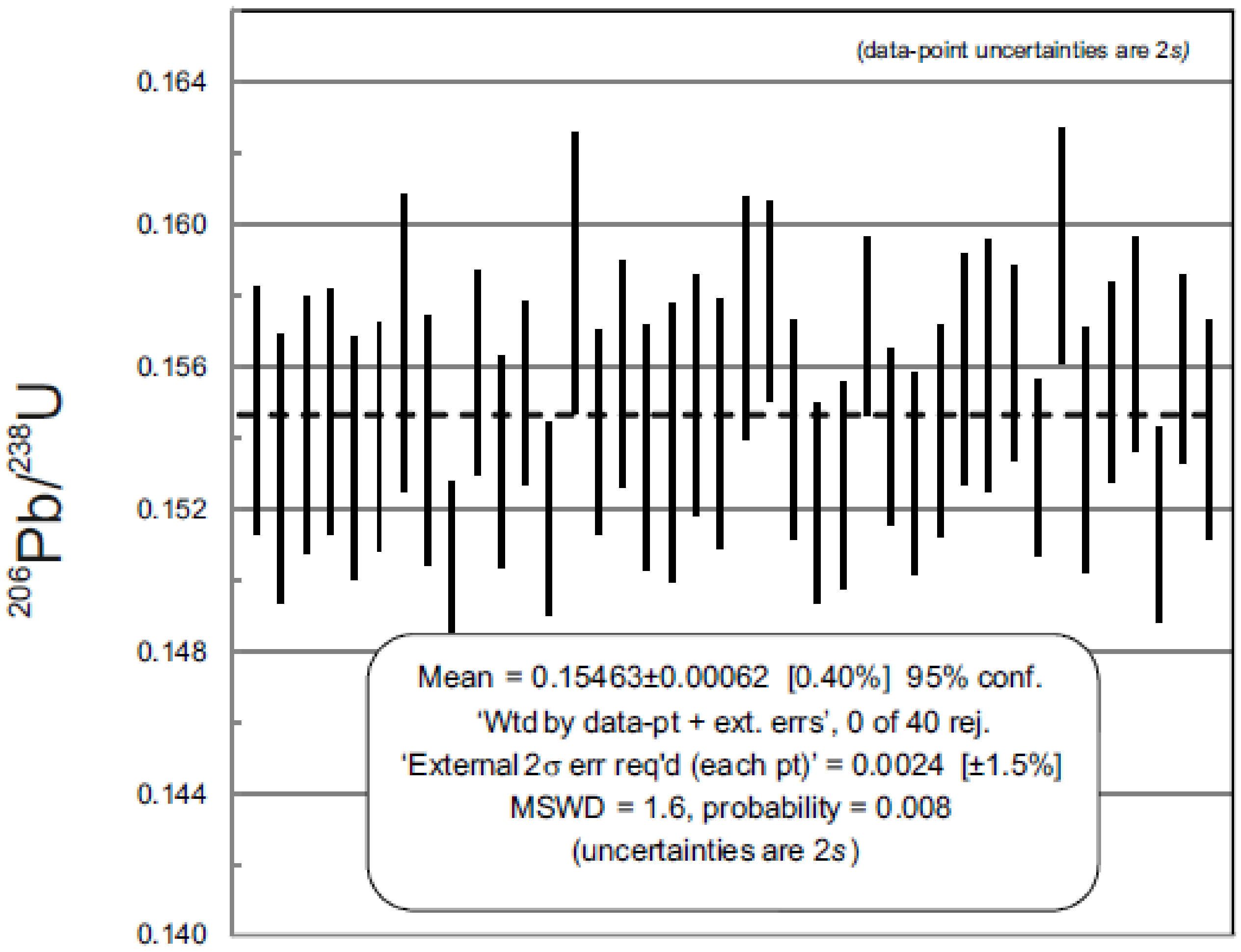


# Tools for quantifying uncertainty: Excess variance/overdispersion

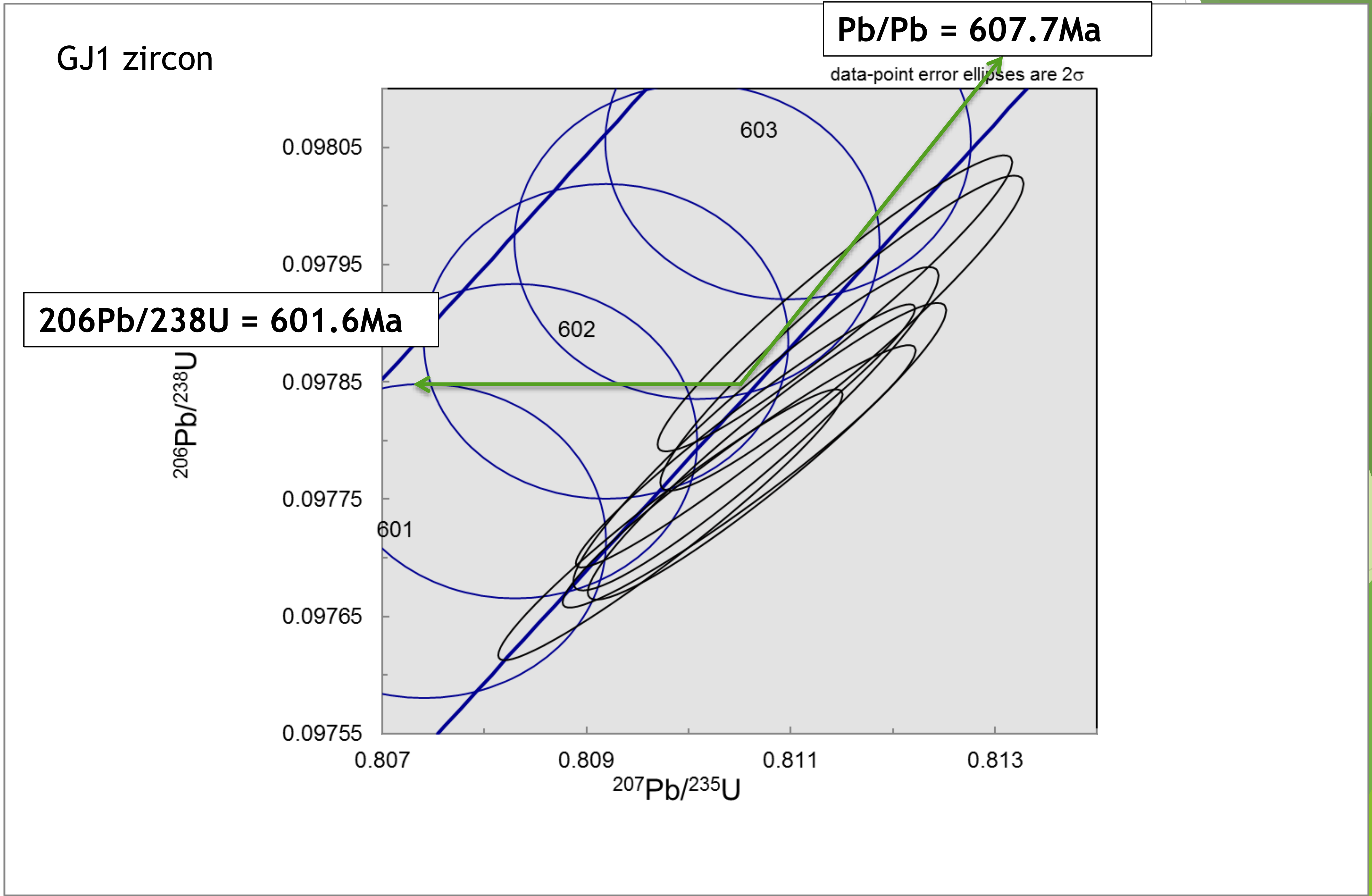
- **overdispersion** is the presence of greater variability in a data set than would be expected based on a given statistical model.
- Overdispersion is a very common feature in applied data analysis because in practice, populations are frequently heterogeneous (non-uniform) contrary to the assumptions implicit within widely used simple parametric models.

*(wikipedia May 2016)*

# Quantifying overdispersion



# Reference values – use ratios not ages



‘Stern’ or Moacyr monazite

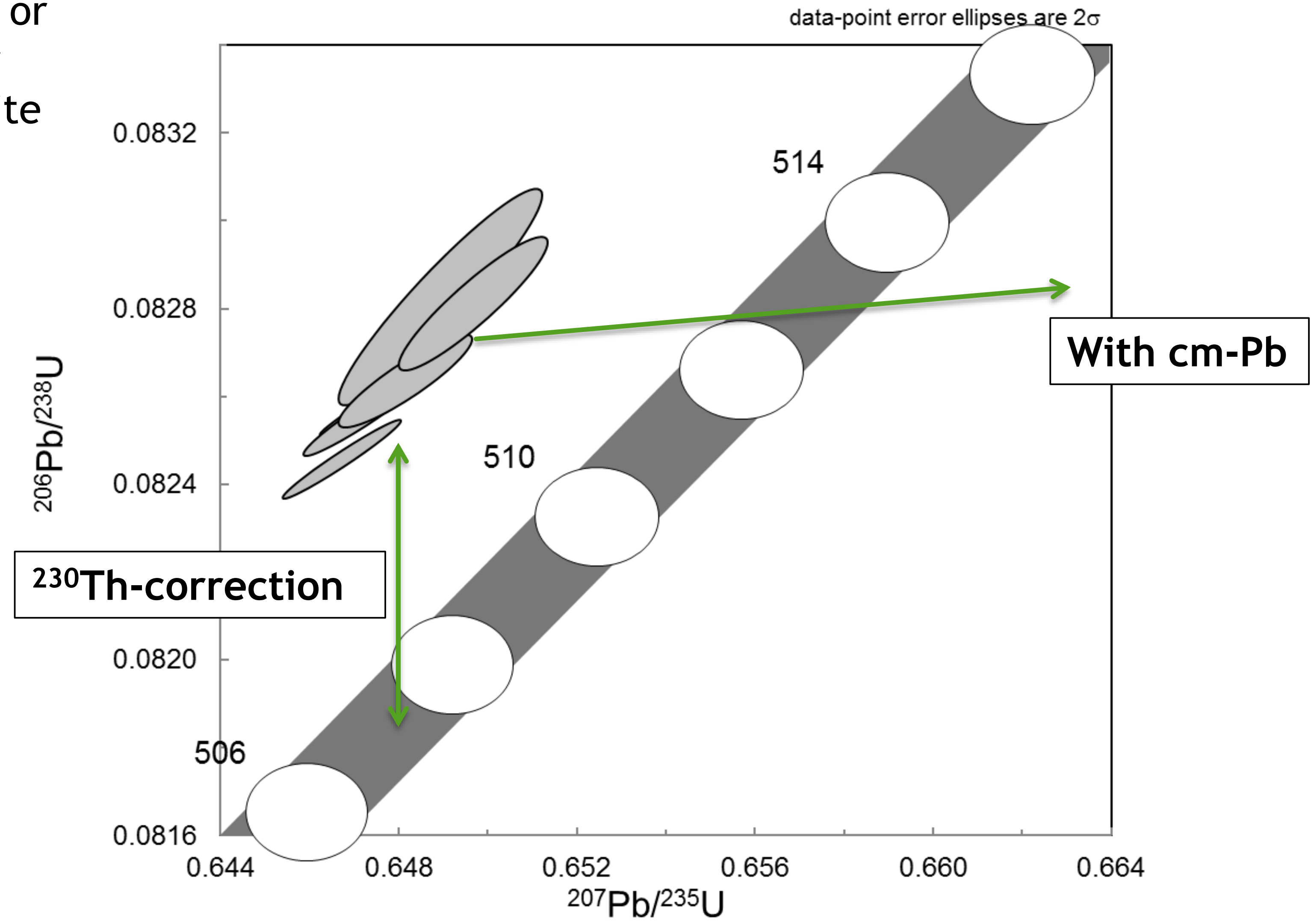
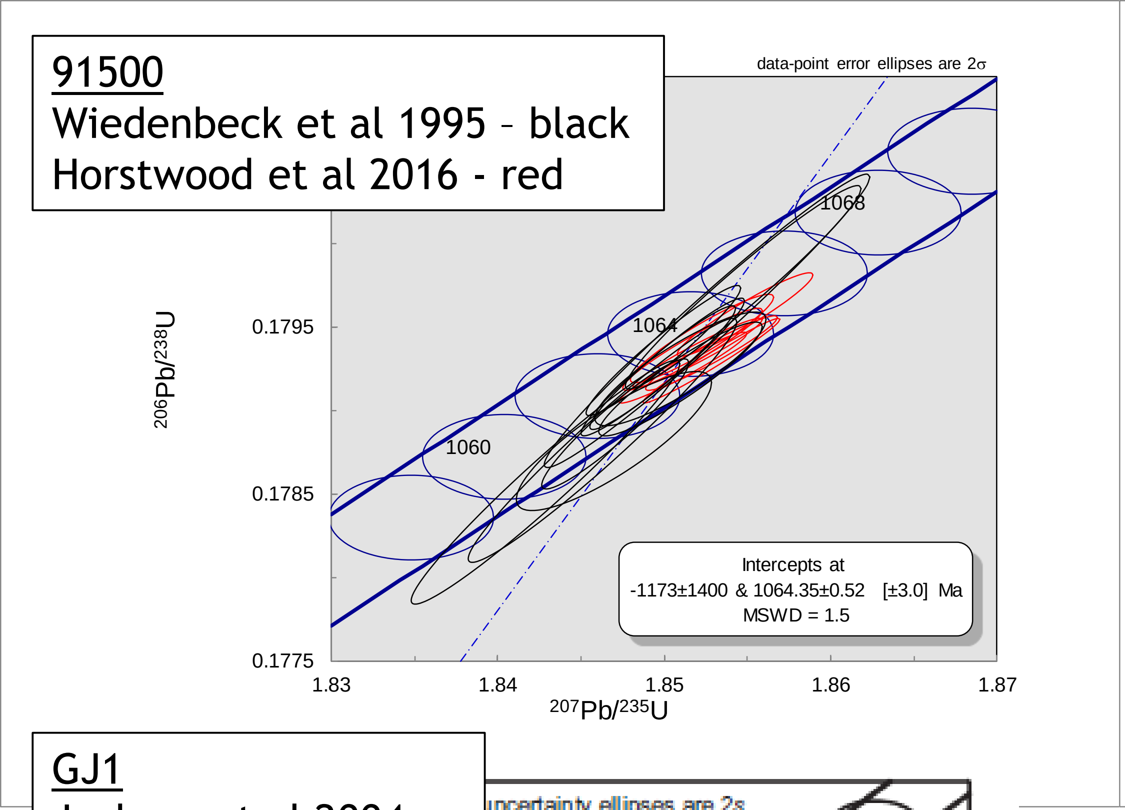
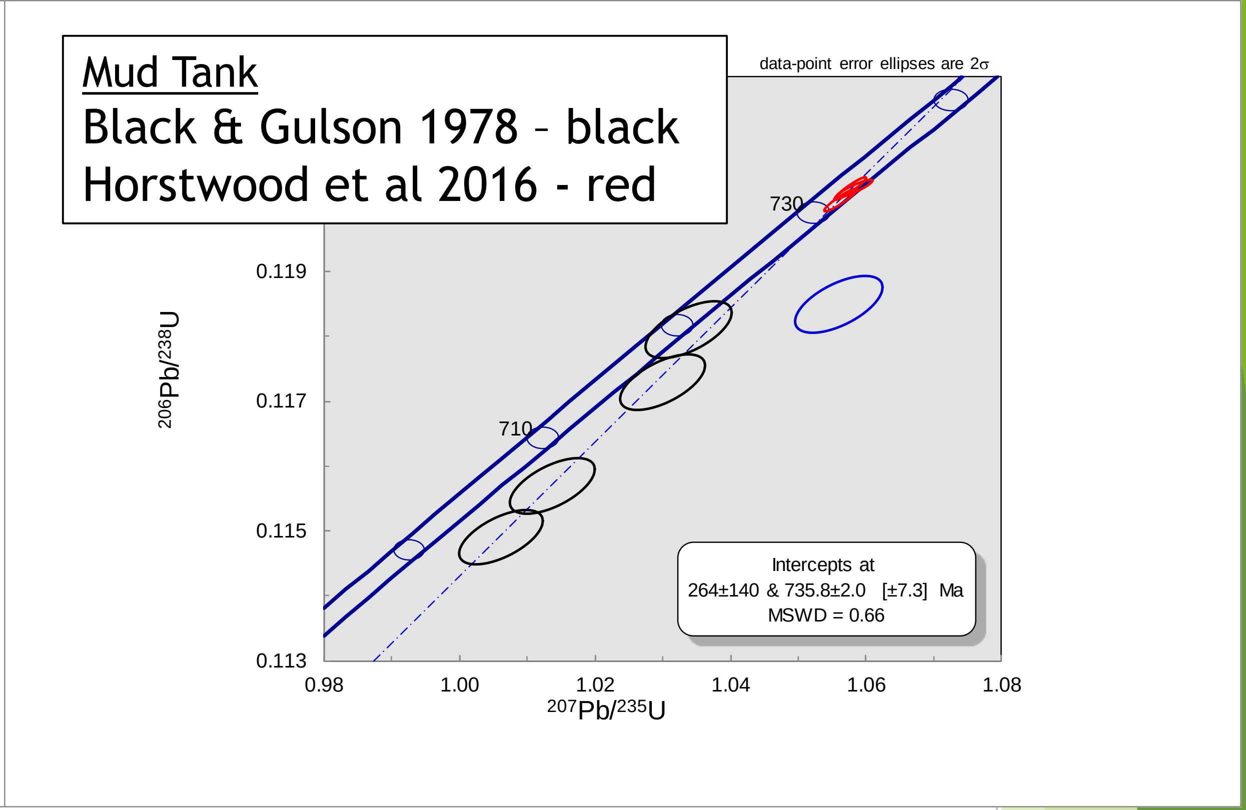


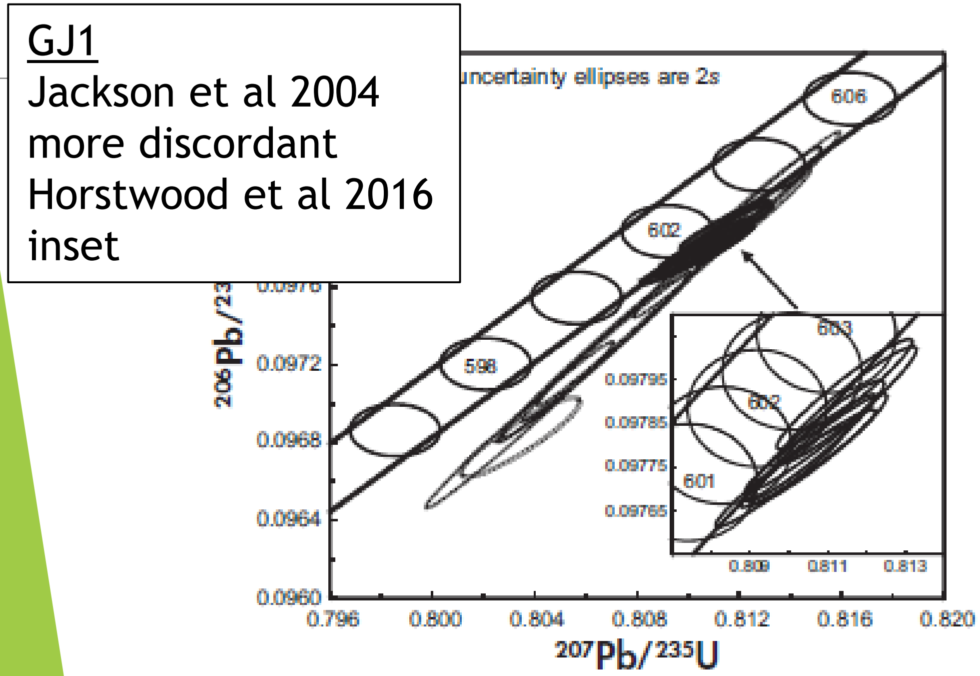
Table 2.
Reference values for some reference materials commonly used in LA-ICP-MS U-Pb dating

| Reference material | *n* | Radiogenic ratios[a] | | | | | | Ages | | | | | | Hiess *et al.* (2012) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^{207}Pb/^{206}Pb$ | ± % | $^{207}Pb/^{235}U$ | ± % | $^{206}Pb/^{238}U$ | ± % | $^{207}Pb/^{206}Pb$ | ± | $^{207}Pb/^{235}U$ | ± | $^{206}Pb/^{238}U$ | ± | $^{238}U/^{235}U$ |
| GJ1 | 7 | 0.060139 | 0.031 | 0.81117 | 0.065 | 0.097860 | 0.065 | 607.70 | 0.67 | 603.11 | 0.30 | 601.86 | 0.37 | 137.824 |
| Mud Tank | 6 | 0.063802 | 0.048 | 1.0569 | 0.11 | 0.120188 | 0.071 | 734.4 | 1.0 | 732.29 | 0.55 | 731.65 | 0.49 | 137.836 |
| Plešovice | 10 | 0.053244 | 0.027 | 0.39396 | 0.057 | 0.053694 | 0.034 | 337.96 | 0.61 | 337.26 | 0.16 | 337.16 | 0.11 | 137.803 |
| 91500 xl | 7 | 0.074941 | 0.030 | 1.8525 | 0.066 | 0.179365 | 0.040 | 1066.01 | 0.61 | 1064.32 | 0.44 | 1063.51 | 0.39 | (137.818) |
| Stem | 6 | 0.056872 | 0.037 | 0.64715 | 0.14 | 0.08261 | 0.25 | 484.68 | 0.81 | 506.73 | 0.57 | 511.7 | 1.2 | 137.763 |
| Moacyr | 2 | 0.056824 | 0.072 | 0.64831 | 0.13 | 0.082830 | 0.064 | 482.5 | 1.6 | 507.44 | 0.52 | 512.99 | 0.31 | 137.743 |
| Ontario 2 | 6 | 0.074373 | 0.11 | 1.820 | 0.60 | 0.17753 | 0.61 | 1050.7 | 2.2 | 1052.6 | 3.9 | 1053.5 | 5.9 | (137.818) |
| **Reference material** | ***n*** | **Ratios with initial Pb[b]** | | | | | | **Ages** | | | | | | **Hiess *et al.* (2012)** |
| | | $^{207}Pb/^{206}Pb$ | ± % | | | $^{206}Pb/^{238}U$ | ± % | $^{207}Pb/^{206}Pb$ | ± | | | $^{206}Pb/^{238}U$ | ± | $^{238}U/^{235}U$ |
| GJ1 | 7 | 0.060171 | 0.08 | | | 0.097877 | 0.07 | 608.8 | 1.8 | | | 601.95 | 0.40 | 137.824 |
| Mud Tank | 6 | 0.06402 | 1.0 | | | 0.12021 | 0.14 | 741 | 21.4 | | | 731.8 | 1.0 | 137.836 |
| Plešovice | 9 | 0.05332 | 0.19 | | | 0.053707 | 0.04 | 341.6 | 4.4 | | | 337.24 | 0.13 | 137.803 |
| 91500 xl | 7 | 0.074989 | 0.075 | | | 0.17942 | 0.07 | 1067.3 | 1.5 | | | 1063.78 | 0.65 | (137.818) |
| Stem | 6 | 0.05735 | 0.26 | | | 0.08265 | 0.29 | 504.1 | 5.7 | | | 511.9 | 1.5 | 137.763 |
| Moacyr | 2 | 0.0613 | 3.8 | | | 0.08327 | 0.36 | 648[$] | 32 | | | 515.6[$] | 1.0 | 137.743 |
| Ontario 2 | 6 | 0.1187 | 1.9 | | | 0.1874 | 0.66 | 1935 | 33 | | | 1107.4 | 6.7 | (137.818) |

- You must decide which are appropriate – unresolved common-Pb in there or common-Pb free?




# To CA or not CA?

# Prague 2015 workshop – Network recommendations

- Annealing improves accuracy of results (on the whole)
- CA even better where appropriate
- Use reference material appropriate to sample – if sample is CA'd, use CA'd reference materials
- Note that for thin section work CA is not an option so non-CA'd reference values will still be needed

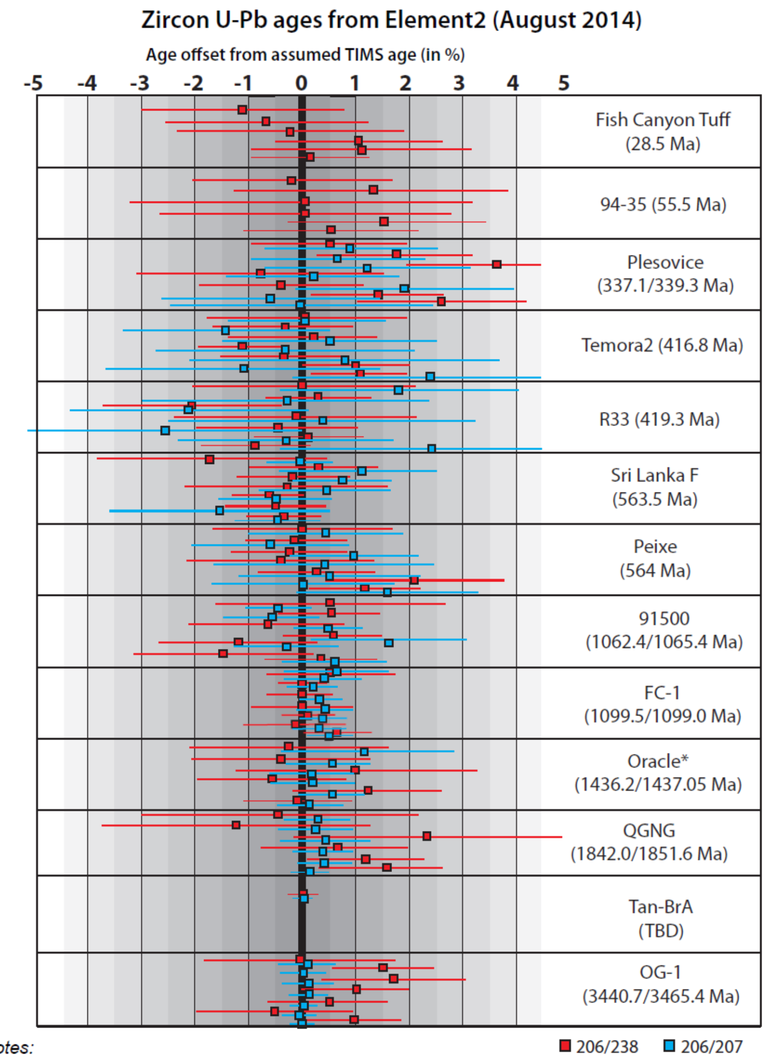
# Data reporting

- Importance of data reporting standards
- Excel data reporting table
- Word metadata reporting table

# Validation

- **Method validation** is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use. Results from **method validation** can be used to judge the quality, reliability and consistency of analytical results; it is an integral part of any good analytical practice.

| **Reference Material** | **wtd mean, 95% conf** | **MSWD, n** | **Bias** | **Long term excess variance, 2s** | **Comment** |
|---|---|---|---|---|---|
| Mud Tank 207-206 | 0.06370 +/- 0.35% | 2.3, n= 26 | -0.5% | 1.2% | Validation accurate within excess variance (bias < variance) |
| Mud Tank 206-238 | 0.11996 +/- 0.48% | 4.3, n= 27 | -0.21% | 2.1% | Validation accurate within excess variance (bias < variance) |
| GJ1 207-206 | 0.060238 +/- 0.12% | 0.56, n= 27 | +0.11% | - | Validation accurate within uncertainty |
| GJ1 206-238 | 0.09775 +/- 0.30% | 1.5, n= 27 | -0.13% | - | Validation accurate within uncertainty |




*Notes:*
*-- FC-1 used as the primary standard*
*-- ages corrected for common Pb based on measured $^{204}$Pb*
*-- composition of common Pb from Stacey and Kramers (1975)*
*-- each symbol represents the weighted mean of 15-30 analyses (outliers rejected by Isoplot)*
*-- horizontal bar represents the weighted mean uncertainty, shown at 2-sigma*
*-- Reference ages are from ID-TIMS unless indicated with * (for CA-TIMS ages)*
*-- Data from Element2 single collector ICPMS and Photon Machines Analyte G2 laser (with HeLex cell).*

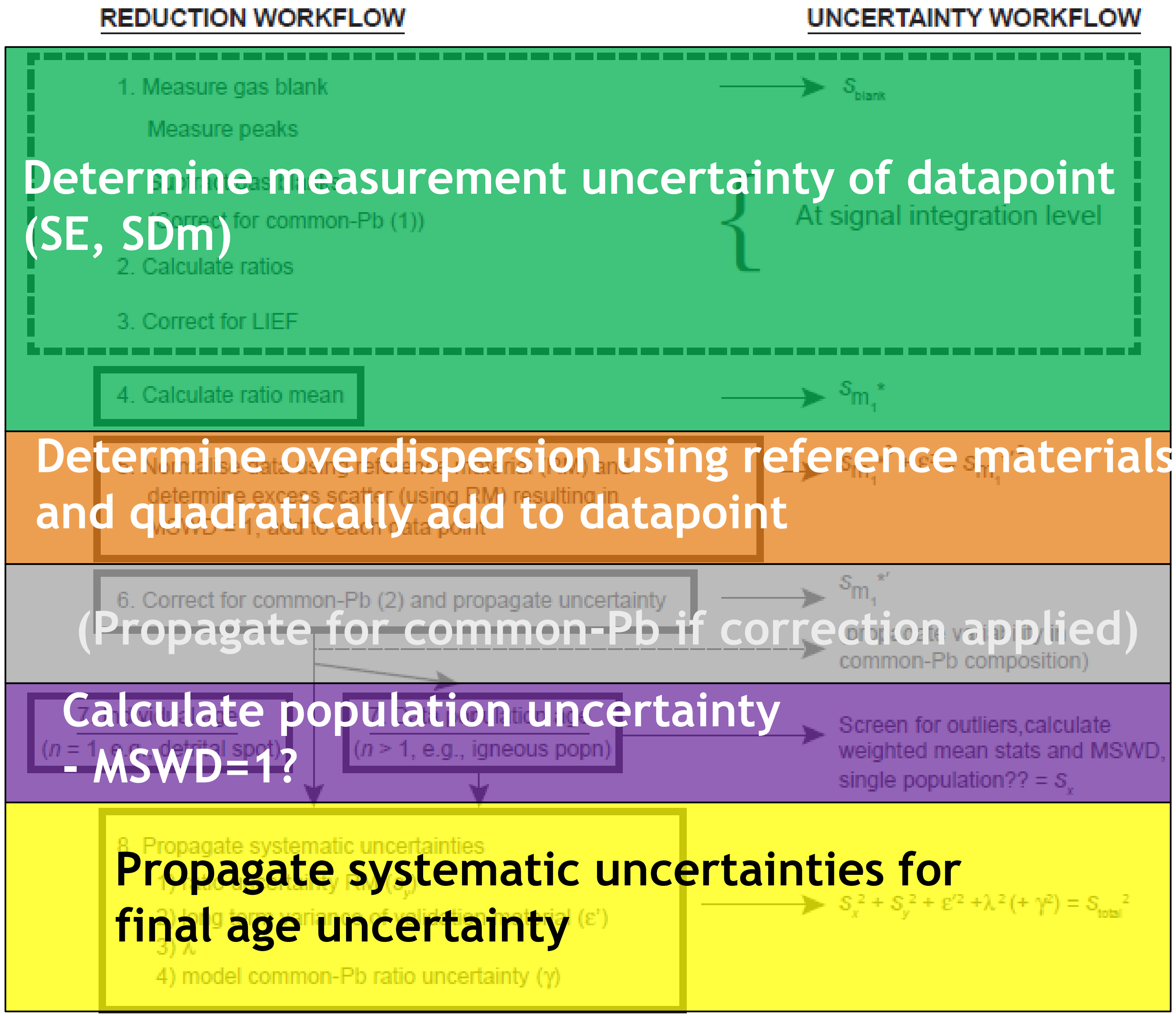
# Reporting α/β & ref mat heterogeneity

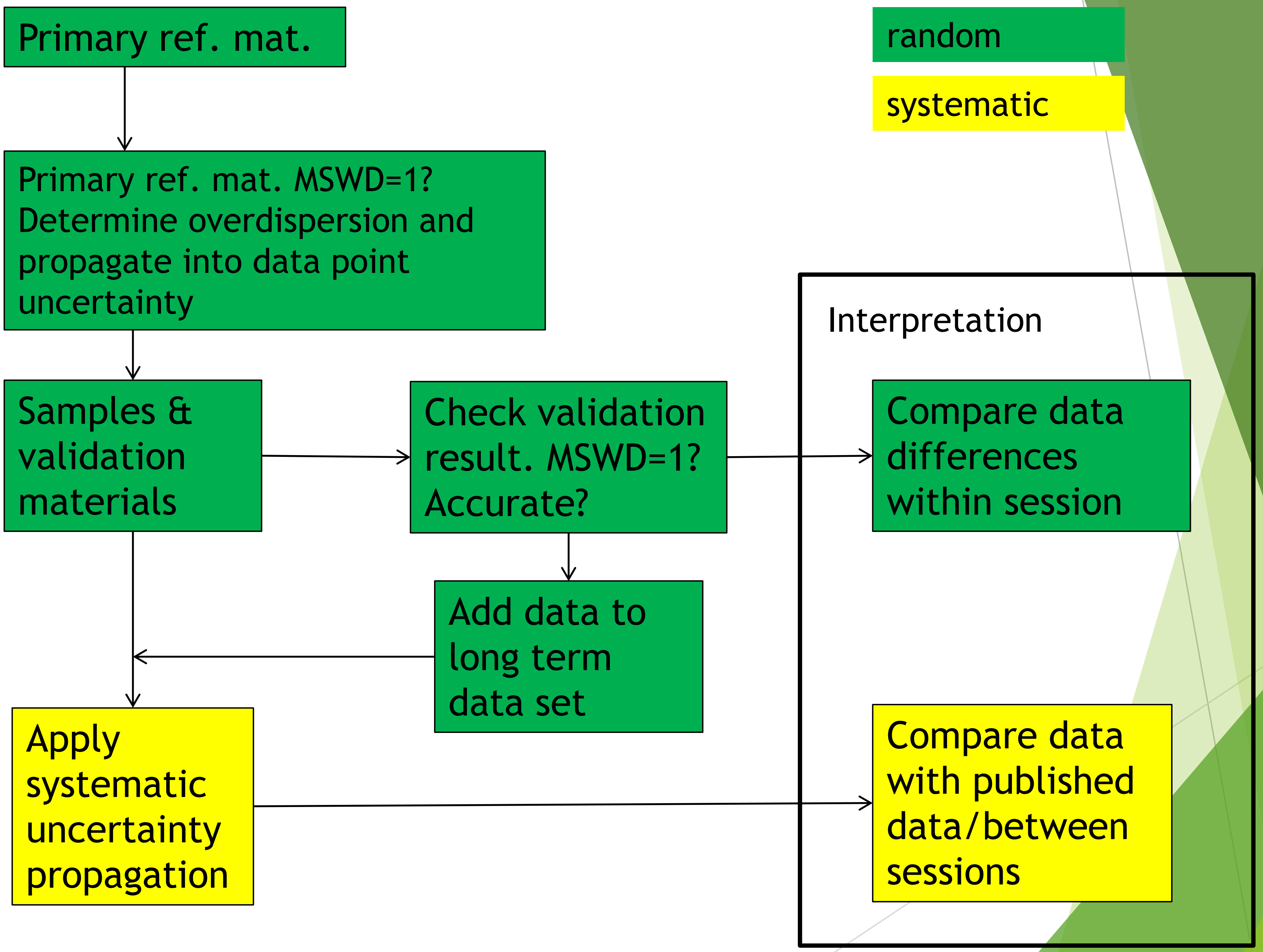
| Systematic uncertainties (1s %) | 206/238 | 207/235 | 207/206 |
|---|---|---|---|
| age uncertainty primary ref. Mat. | 0.062 | 0.065 | 0.030 |
| long term scatter/variance | 1.35 | 1.55 | 0.30 |
| decay constant uncertainties | 0.05 | 0.10 | 0.11 |
| common-Pb compositional variation | 1 | 1 | 1 |
| **Total** | **1.35** | **1.55** | **0.32** |

| Systematic uncertainties (1s %) | 206/238 | 207/235 | 207/206 |
|---|---|---|---|
| age uncertainty primary ref. Mat. | 1 | 1.4 | 1 |
| long term scatter/variance | 1.35 | 1.55 | 0.30 |
| decay constant uncertainties | 0.05 | 0.10 | 0.11 |
| common-Pb compositional variation | 1 | 1 | 1 |
| **Total** | **1.68** | **2.10** | **1.05** |

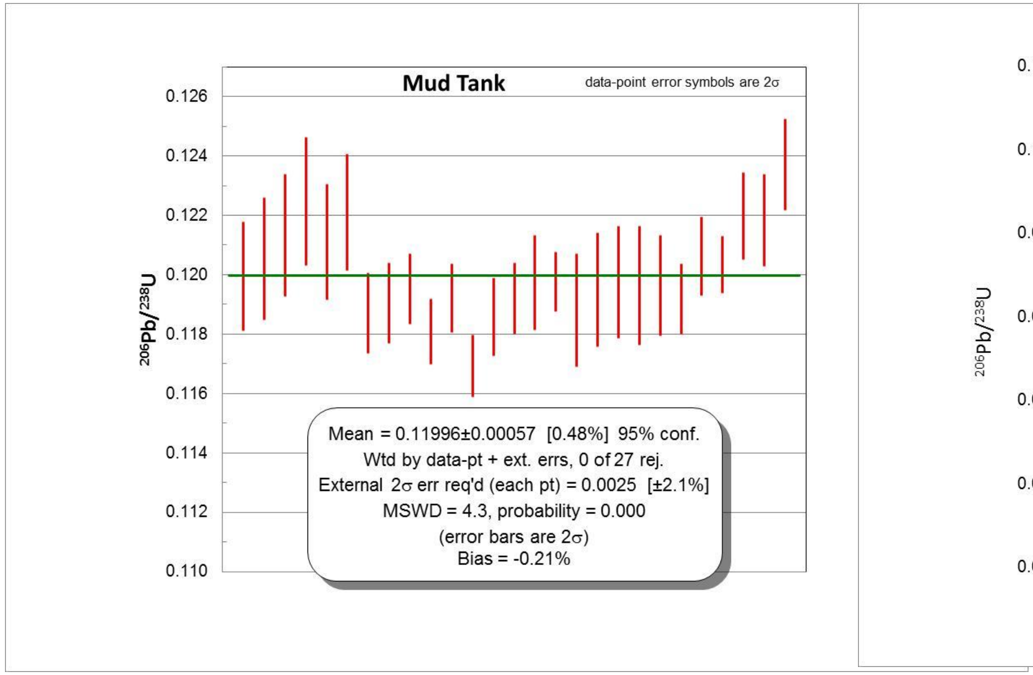
# Implementing uncertainty propagation

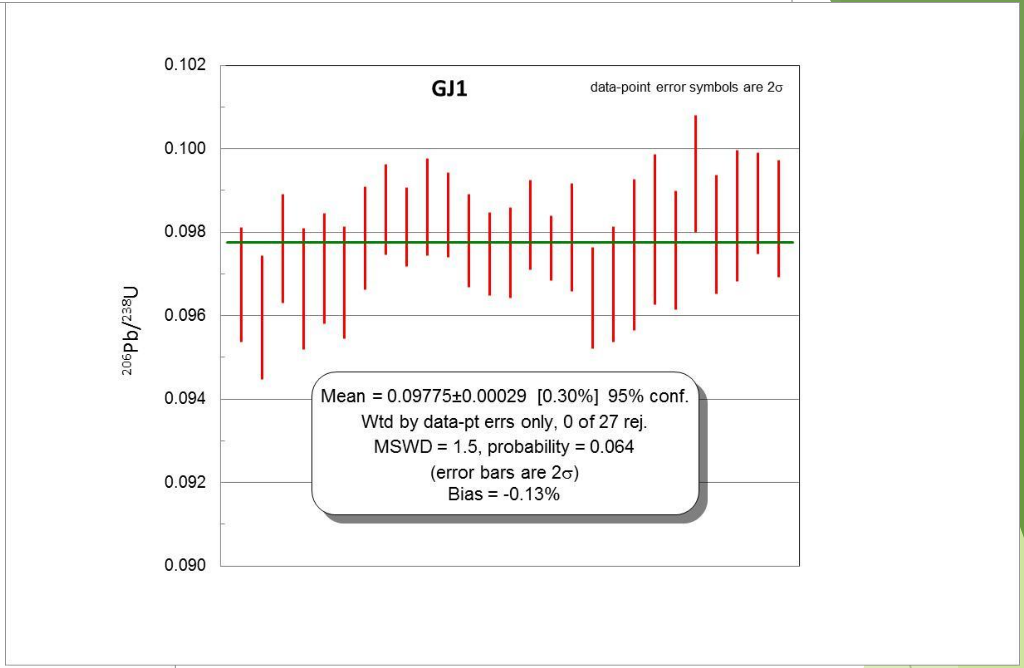
# Data reduction workflow and uncertainty propagation in LA-ICP-MS U-Pb geochronology




Primary ref. mat.
Primary ref. mat. MSWD=1? Determine overdispersion and propagate into data point uncertainty
Samples & validation materials
Check validation result. MSWD=1? Accurate?
Add data to long term data set
Apply systematic uncertainty propagation
random
systematic
Interpretation
Compare data differences within session
Compare data with published data/between sessions

# Long term validation $^{206}Pb/^{238}U$



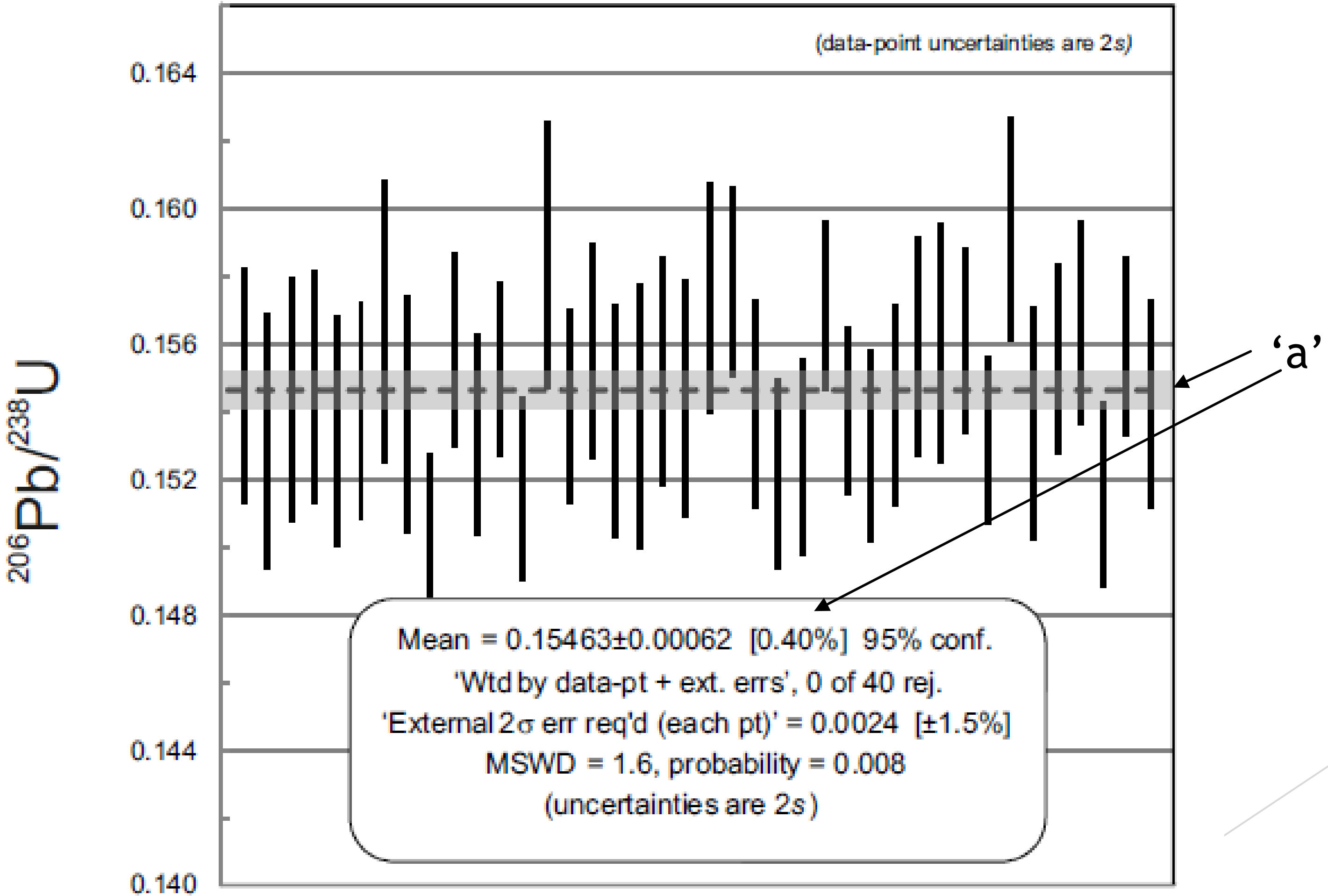
# Igneous vs detrital long-term excess variance assessment – data population vs stand-alone quantification

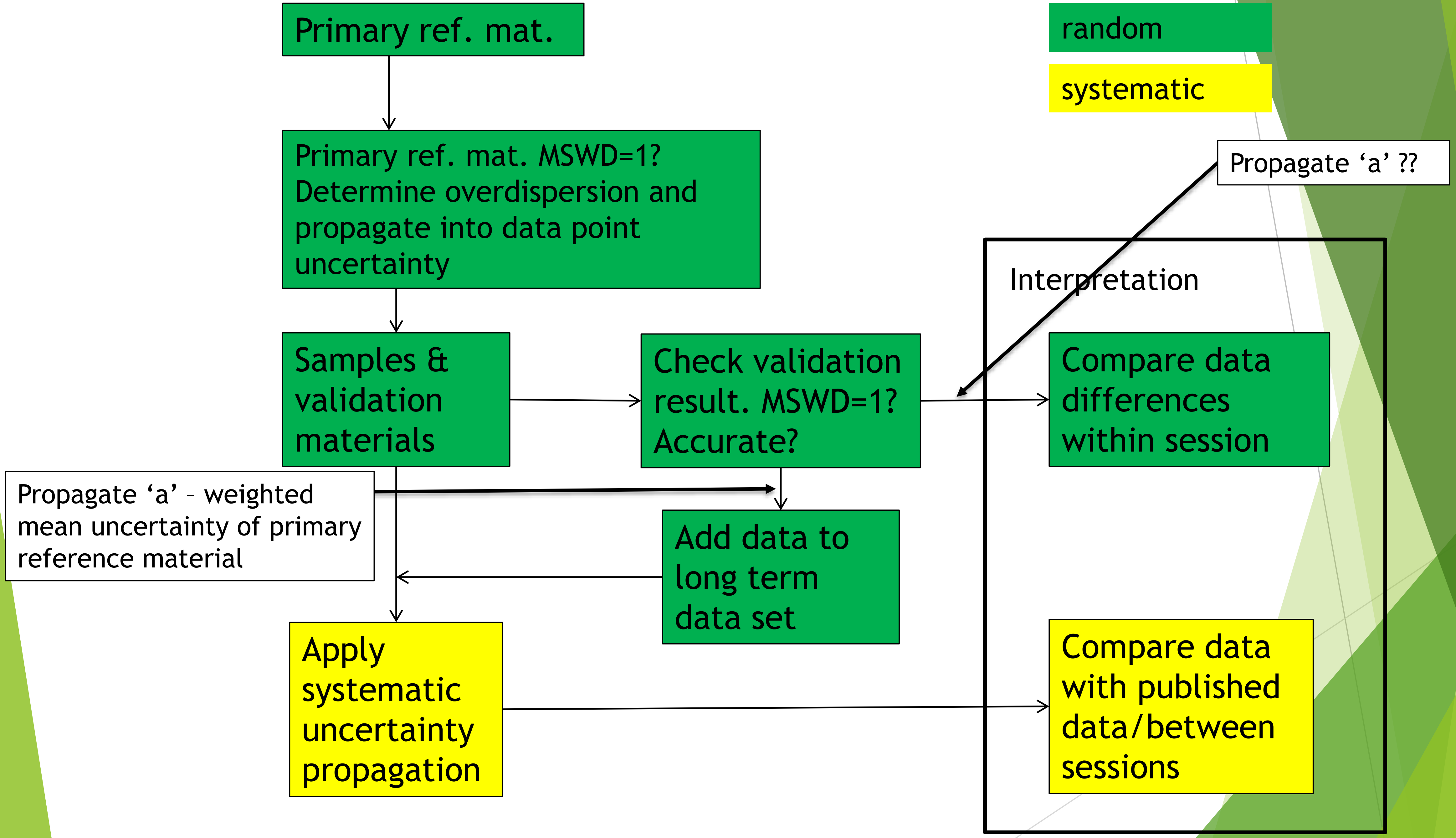
- Don’t exclude any for detrital assessment – this could be one of your grains?
- Wtd ave of 10 compilation – allows rejection as in igneous population. Excess variance therefore lower?

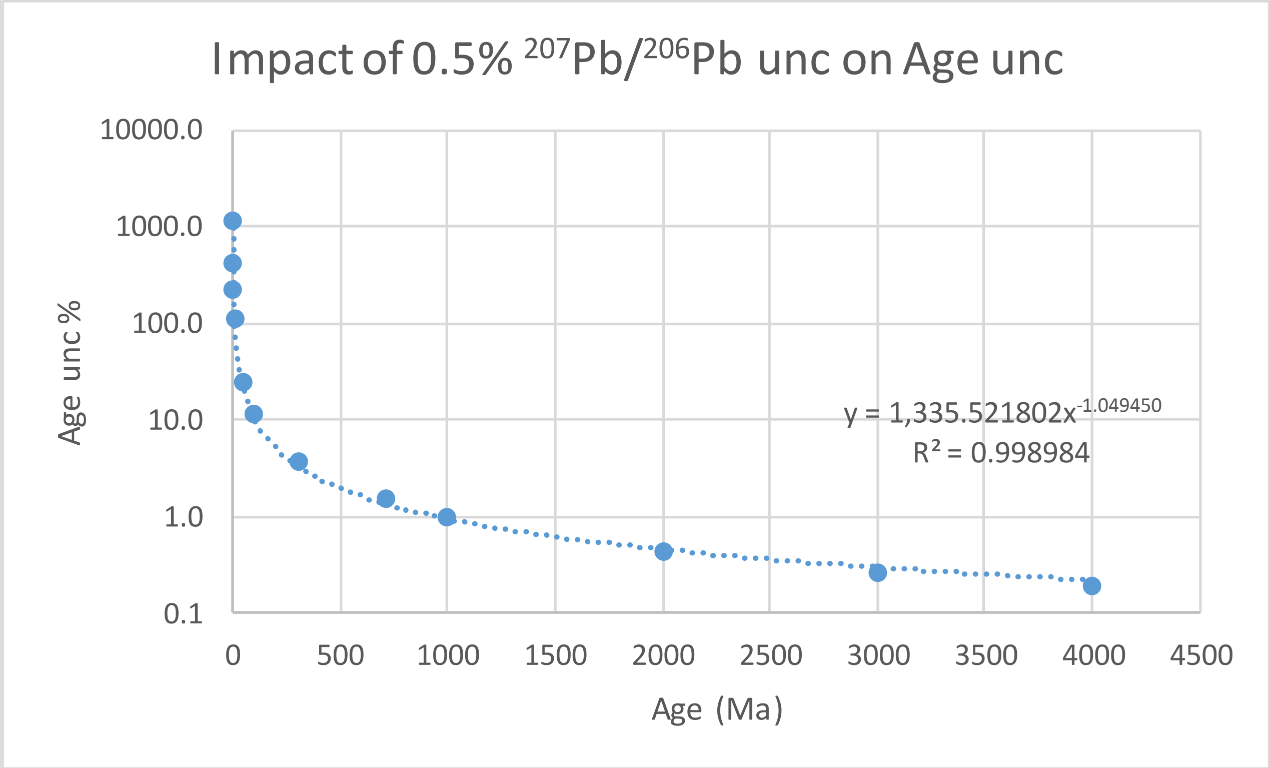
# Propagation of ‘a’

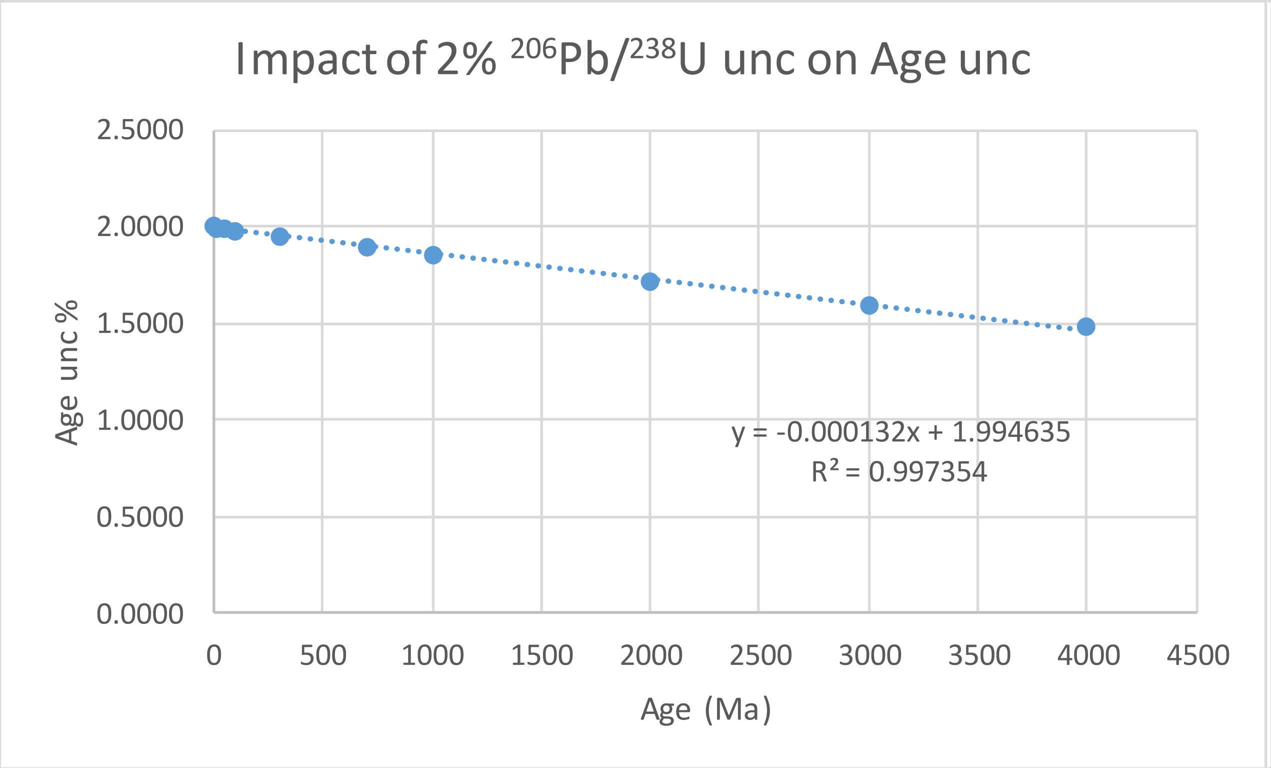
- Propagation of wtd mean uncertainty of primary reference material
  - performed by SQUID
  - part of workflow in McLean et al 2016 – ET_Redux
  - performed by Iolite?
- Limiting uncertainty on session accuracy
- An obvious omission from recommended LA workflow.
- This will reduce long term excess variance component so will not add to the total overall uncertainty
- Important when considering comparison of data

# Quantifying overdispersion




Primary ref. mat.
random
systematic
Primary ref. mat. MSWD=1? Determine overdispersion and propagate into data point uncertainty
Propagate 'a' ??
Interpretation
Samples & validation materials
Check validation result. MSWD=1? Accurate?
Compare data differences within session
Propagate 'a' – weighted mean uncertainty of primary reference material
Add data to long term data set
Apply systematic uncertainty propagation
Compare data with published data/between sessions




- 337Ma – 0.5% ratio unc = 3% Age unc
- 1065Ma – 0.5% ratio unc = 0.9% Age unc
- 3450Ma – 0.5% ratio unc = 0.26% Age unc

- 337Ma – 2% ratio unc = 1.95% Age unc
- 1065Ma – 2% ratio unc = 1.85% Age unc
- 3450Ma – 2% ratio unc = 1.54% Age unc

## Propagate uncertainties by ratio NOT by age

# Combining multiple results which include systematic uncertainty

- "How do we do this Noah?"
- "With a block diagonal matrix"

$$
\mathbf{V} = \begin{pmatrix}
\sigma_c^2+\sigma^2 & \sigma_c^2 & \sigma_c^2 & \sigma_c^2 & 0 & 0 & 0 & 0 & 0 \\
\sigma_c^2 & \sigma_c^2+\sigma^2 & \sigma_c^2 & \sigma_c^2 & 0 & 0 & 0 & 0 & 0 \\
\sigma_c^2 & \sigma_c^2 & \sigma_c^2+\sigma^2 & \sigma_c^2 & 0 & 0 & 0 & 0 & 0 \\
\sigma_c^2 & \sigma_c^2 & \sigma_c^2 & \sigma_c^2+\sigma^2 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \sigma_c^2+\sigma^2 & \sigma_c^2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \sigma_c^2 & \sigma_c^2+\sigma^2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \sigma_c^2+\sigma^2 & \sigma_c^2 & \sigma_c^2 \\
0 & 0 & 0 & 0 & 0 & 0 & \sigma_c^2 & \sigma_c^2+\sigma^2 & \sigma_c^2 \\
0 & 0 & 0 & 0 & 0 & 0 & \sigma_c^2 & \sigma_c^2 & \sigma_c^2+\sigma^2
\end{pmatrix}
$$

- "Something a little simpler perhaps?!"

# Combining multiple results which include systematic uncertainty

- Check for single population status – MSWD =1?
- Remove systematic uncertainty component but leave ‘a’ – limiting session uncertainty
- Take weighted mean
- Propagate systematic uncertainty back on top

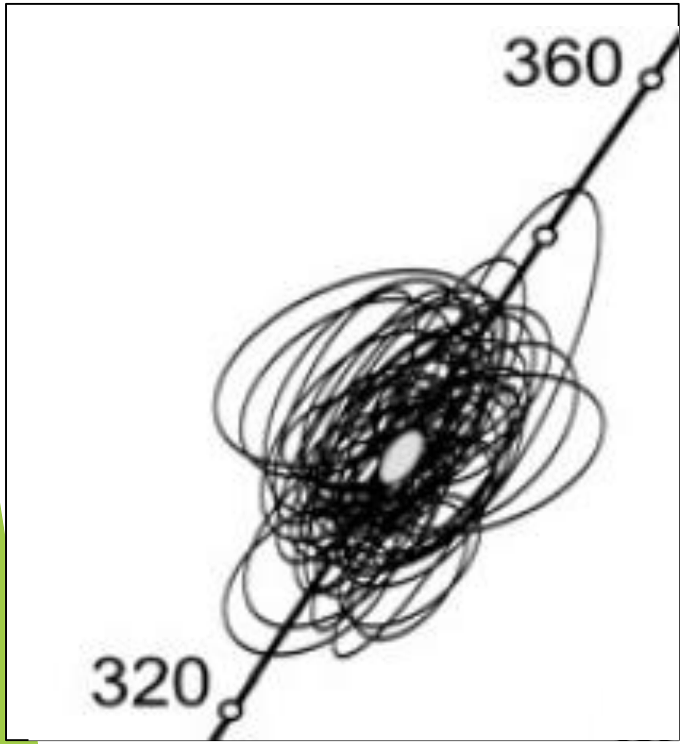
# Walk-through excel exercise

- Uncertainty propagation in excel

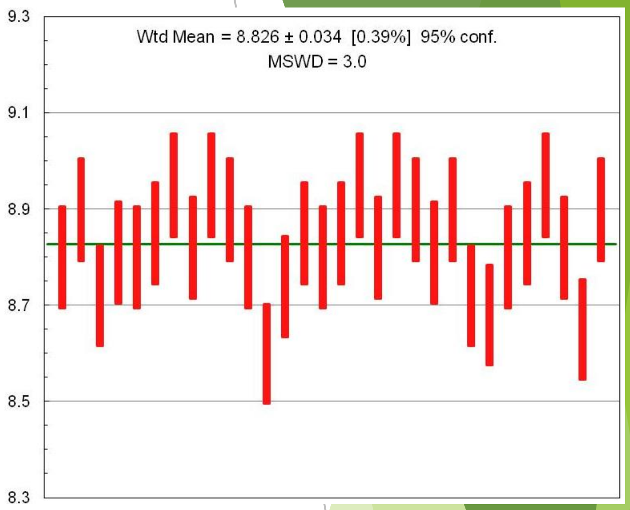
# Data Interpretation

- **Resolution of scatter with low precision data points.** - fundamental assumption of MSWD calculation.
- **Ability to interpret data in a relative sense** without full uncertainty propagation. Understanding resolution, precision/accuracy and MSWD.

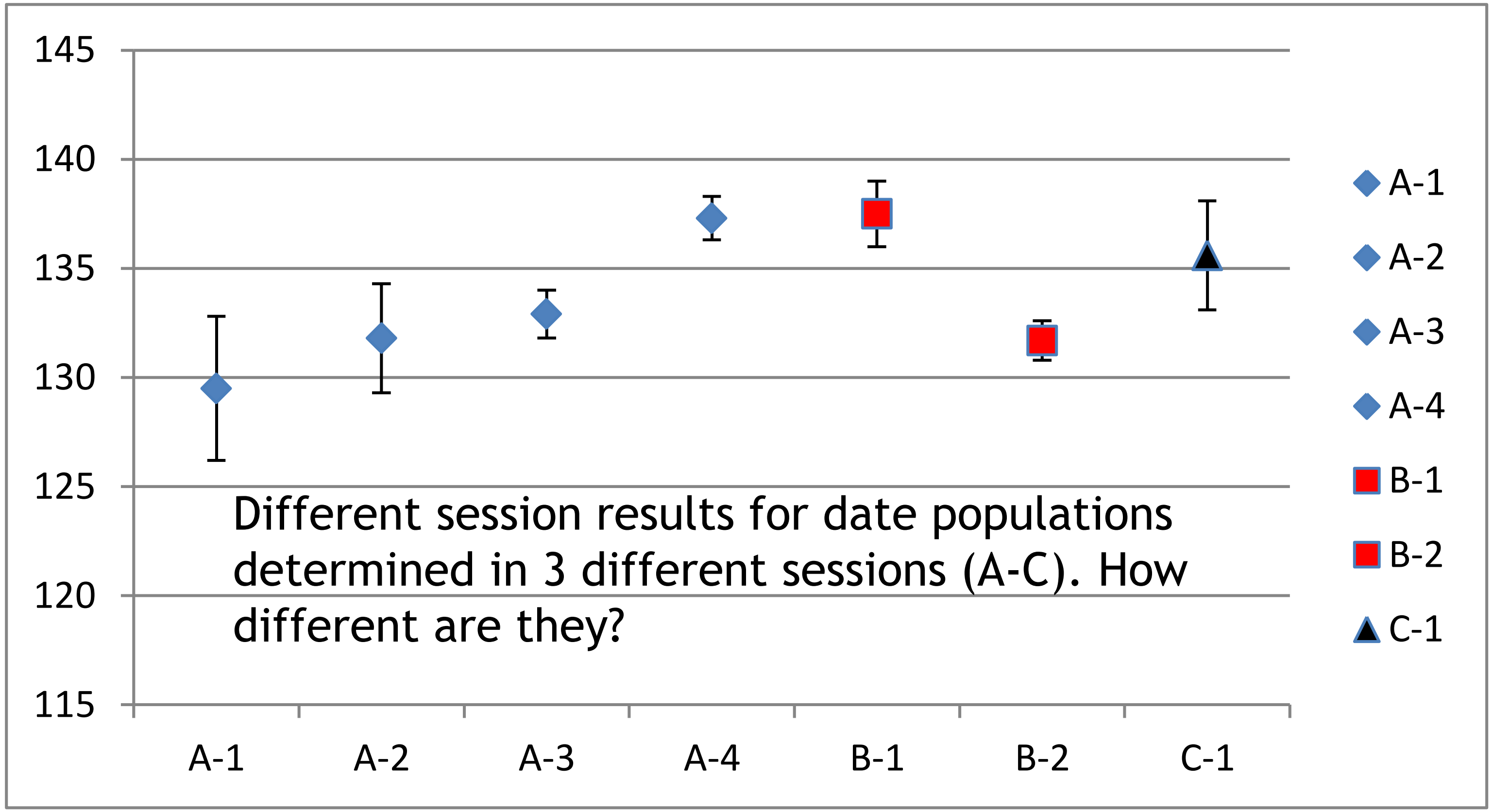
# Resolution of scatter with low precision data points




"Even in the best cases, the reported age uncertainty will not be much better than the analytical error [sic] of the most precise analyses. [This] accords with the concept that the real limit on accuracy for U/Pb dates is only a factor of two or so better than the analytical error [sic] of the individual analyses, rather than amenable to arbitrary improvement by increasing the number of analyses alone. This concept follows statistical limitations on the ability to resolve complexity in the true age structure of a suite of analyses arising from open system behaviour, presence of xenocrysts, or a variable and non-zero magma-residence-time." Ludwig (2012)



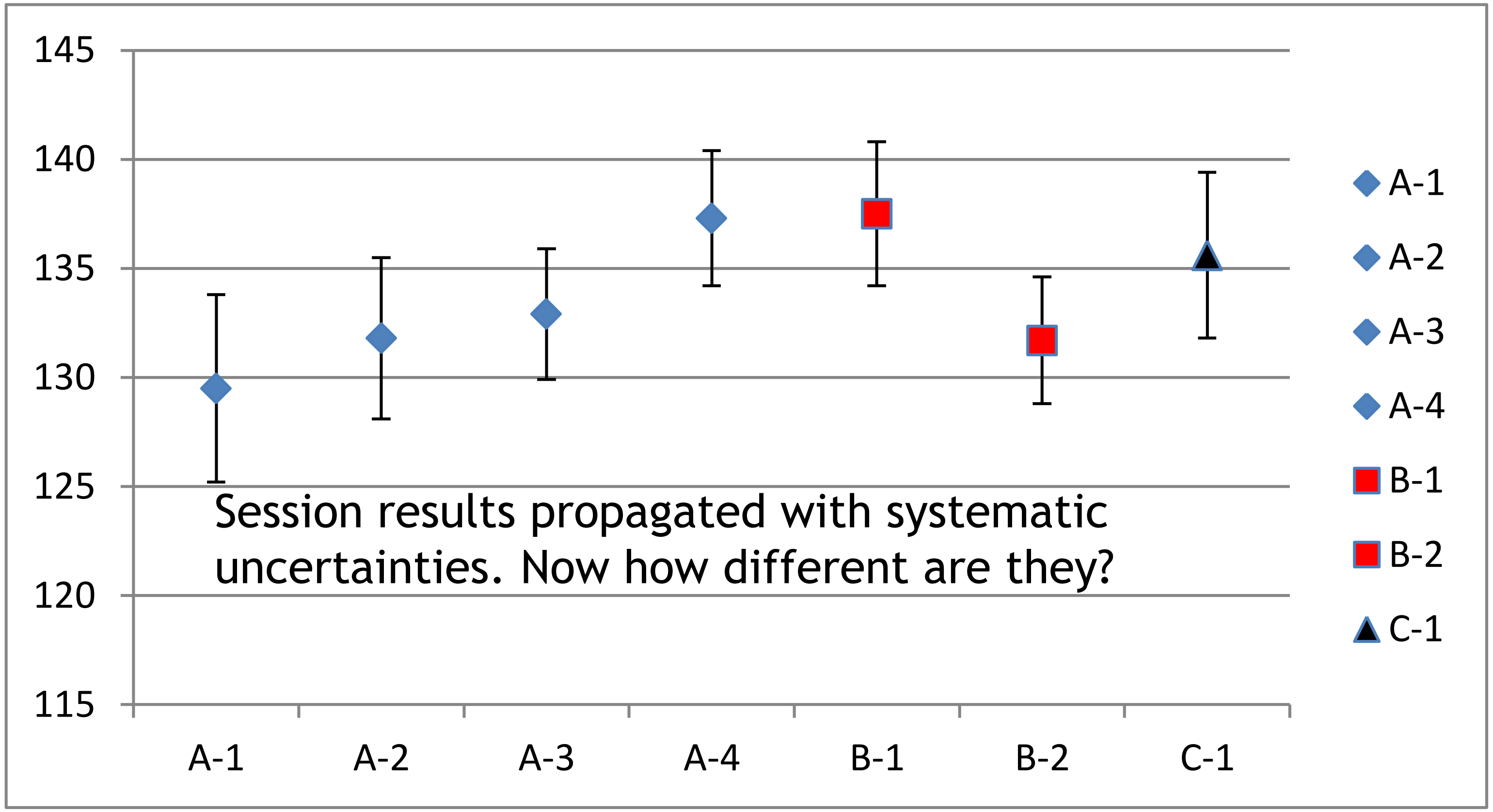

# Interpreting data at different levels of uncertainty propagation




Is A4 different to A3 and the same as B1?
What age is A4?
Is C1 more similar to B1 or B2?
What is the age difference between B2 and A4?

A4 and A3 are clearly different, by 2-6Ma.
A4 looks the same as B1. A4 is 137+/-1Ma
C1 looks like it might be more similar to B1.
B2 and A4 look about 5Ma different.

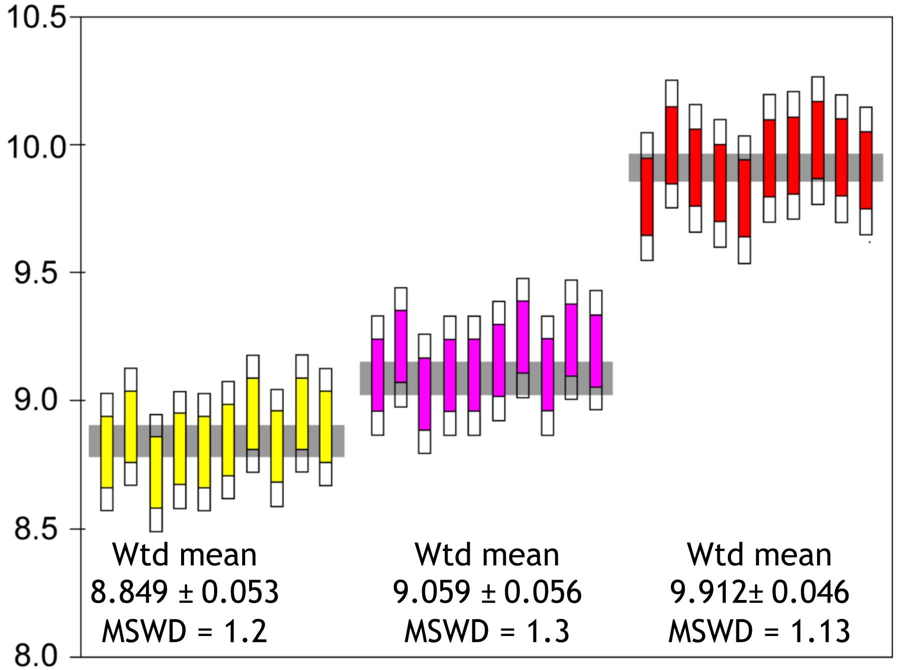
# Interpreting data at different levels of uncertainty propagation




A4 and A3 were analysed in the same session so the relative difference of 2-6Ma stands.
At the level of measurement precision achievable, A4 could be different to B1. They would need analysing together in the same session to discriminate this.
A4 is 137+/-3Ma. A3 is 133 +/- 3Ma (note A3 & A4 ages overlap) but definitely 2-6Ma younger than A4.

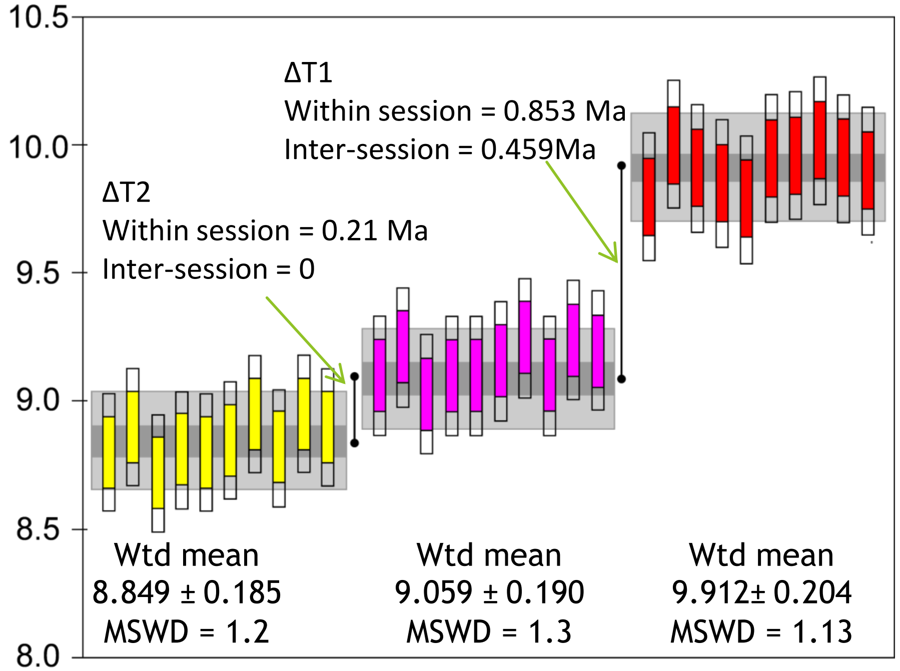
C1 could be the same as either B1 or B2.
B2 and A4 could be the same age.
Analyse together A4, B2 & C1 (+/-B1) to discriminate.

# Interpreting data at different uncertainty levels




Weighted means with no systematic uncertainties propagated

# Interpreting data at different uncertainty levels




Weighted means with systematic uncertainties propagated

# Interpreting detrital data

- PDP's etc – use session uncertainties
- But comparison between sessions is more difficult – see discussion in Anderson et al 2018 (sampling error likely more significant)
- Use dt when discussing differences between dates within session
- Use systematic uncertainties when discussing grain ages
- Interpreting detrital grain age = X +/- $\alpha/\beta$; but grain D is XMa younger than grain Z (in the same data set) using uncertainty $\alpha$.

# Summary

- So you see its got more complex, nuanced, subtle, but we've got better understanding and guidelines to work by
- Starting on new ground now.
- Be clear about what you have and haven't done and report that. Then valid consideration/review of your work can be made and commentary provided.
- Without reporting what you've done, questionable results/conclusions are more likely to be dismissed. Doesn't make for good science and informed debate.

# Clinic/Q&A

- Discussion of issues & problem data sets