

U-Pb_Redux




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Outline:

1. Uncertainty propagation protocol/workflow
2. Common Pb correction methods, if applicable
3. Method of inter-element and inter-isotope fractionation correction
4. Weighted Mean/Linear regression support, if applicable
5. Rejection criteria
6. Handling/storage of reference values for normalization
7. Key differences from other available packages

Workflow: Sample Setup



EARTHTIME PROJECT MANAGER

Project Name: Green River Basin Session 3**Project Type:** U-Pb LA-ICP MS Data acquisition and reduction

Choose file handling protocol: NU Plasma MC Faraday File

Choose raw data template: Arizona NUPlasma

Choose analysis purpose:

Load Raw Data using chosen File Handling Protocol and Raw Data Template

Details: This is the default protocol for handling file faraday analysis on the NU-Plasma. This handler v runs.

Organize Samples:

Name: Sri Lanka Zircon Std

EARTHTIME SriLanka Standard v... View

AQUIPE01-SL [21:47:44 23.Jun]
AQUIPE01-SL.1 [21:48:39 23.Jun]
AQUIPE01-SL.2 [21:49:28 23.Jun]
AQUIPE01-SL.3 [21:50:20 23.Jun]
AQUIPE01-SL.4 [21:51:26 23.Jun]
AQUIPE01-SL.5 [21:52:13 23.Jun]
AQUIPE01-SL.6 [21:53:06 23.Jun]
AQUIPE01-5SL [21:59:47 23.Jun]
AQUIPE01-10SL [22:04:54 23.Jun]
AQUIPE01-15SL [22:10:17 23.Jun]
AQUIPE01-20SL [22:16:42 23.Jun]
AQUIPE01-25SL [22:22:21 23.Jun]
AQUIPE01-30SL [22:27:22 23.Jun]

Name: Ent-09-123

Role: Unknown

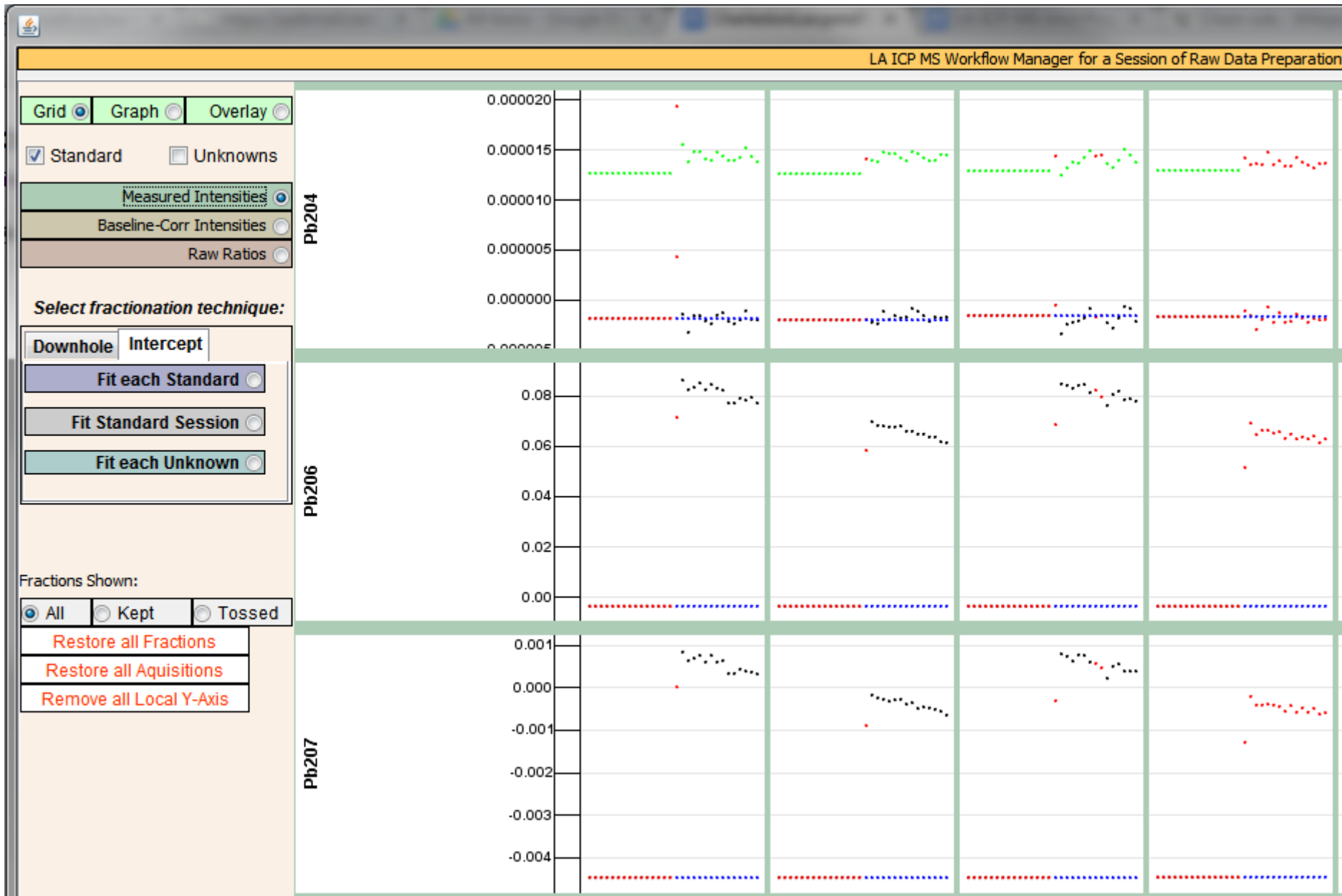
AQUIPE01-1 [21:55:22 23.Jun]
AQUIPE01-2 [21:56:14 23.Jun]
AQUIPE01-3 [21:57:10 23.Jun]
AQUIPE01-4 [21:58:04 23.Jun]
AQUIPE01-5 [21:58:54 23.Jun]
AQUIPE01-6 [22:00:40 23.Jun]
AQUIPE01-7 [22:01:34 23.Jun]
AQUIPE01-8 [22:02:23 23.Jun]
AQUIPE01-9 [22:03:13 23.Jun]
AQUIPE01-10 [22:04:05 23.Jun]
AQUIPE01-11 [22:05:50 23.Jun]
AQUIPE01-12 [22:06:45 23.Jun]
AQUIPE01-13 [22:07:34 23.Jun]

Name: R33 Zircon Std

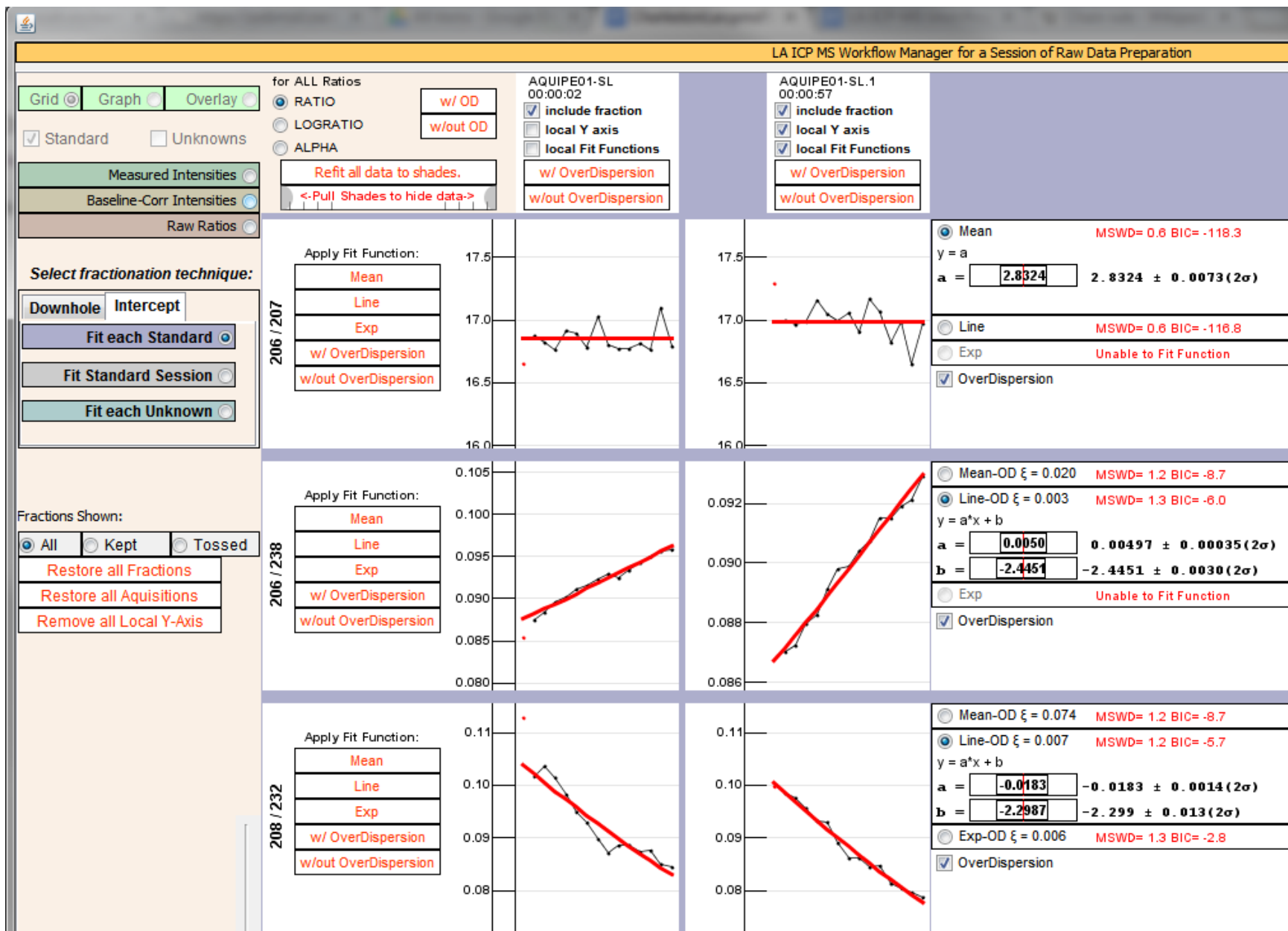
Role: Secondary STD

AQUIPE01-R33 [21:54:10 23.Jun]
AQUIPE01-110R33 [00:03:25 24.Jun]
AQUIPE01-110R33.1 [00:04:11 24.Jun]

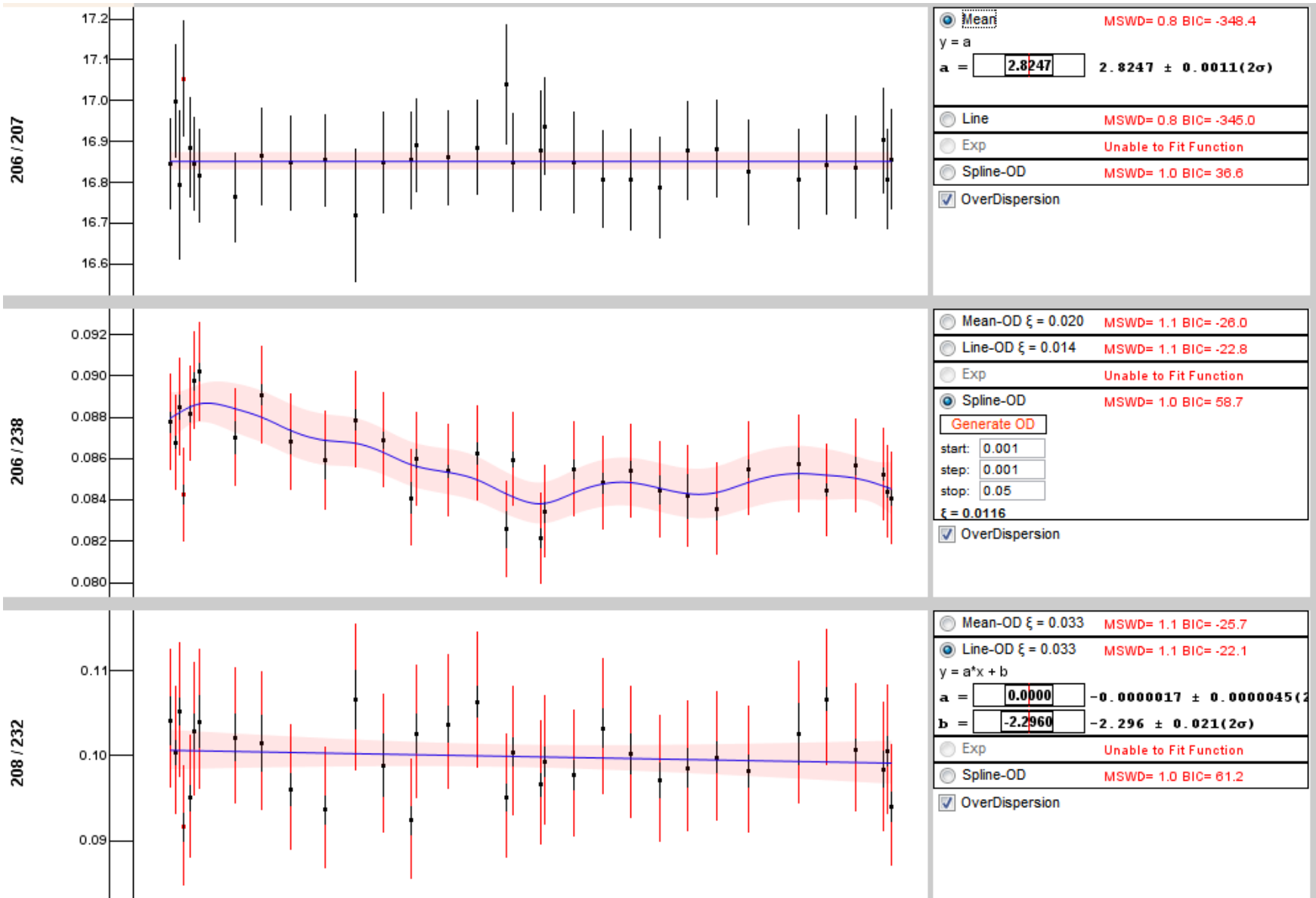
Workflow: Raw Ratios



Workflow: Fit Standards



Workflow: Fit Session



Workflow: Fit Unknowns

LA ICP MS Workflow Manager for a Session of Raw Data Preparation

Grid ☒ Graph ☐ Overlay ☐

☐ Standard ☒ Unknowns

for ALL Ratios
☒ RATIO ☐ LOGRATIO ☐ ALPHA
☐ w/ OD ☐ w/out OD
☐ Refit all data to shades.
☐ <-Pull Shades to hide data->

AQUIPE01-R33
00:06:28
☒ include fraction
☐ local Y axis
☐ local Fit Functions
☐ w/ OverDispersion ☐ w/out OverDispersion

AQUIPE01-1
00:07:40
☒ include fraction
☐ local Y axis
☐ local Fit Functions
☐ w/ OverDispersion ☐ w/out OverDispersion

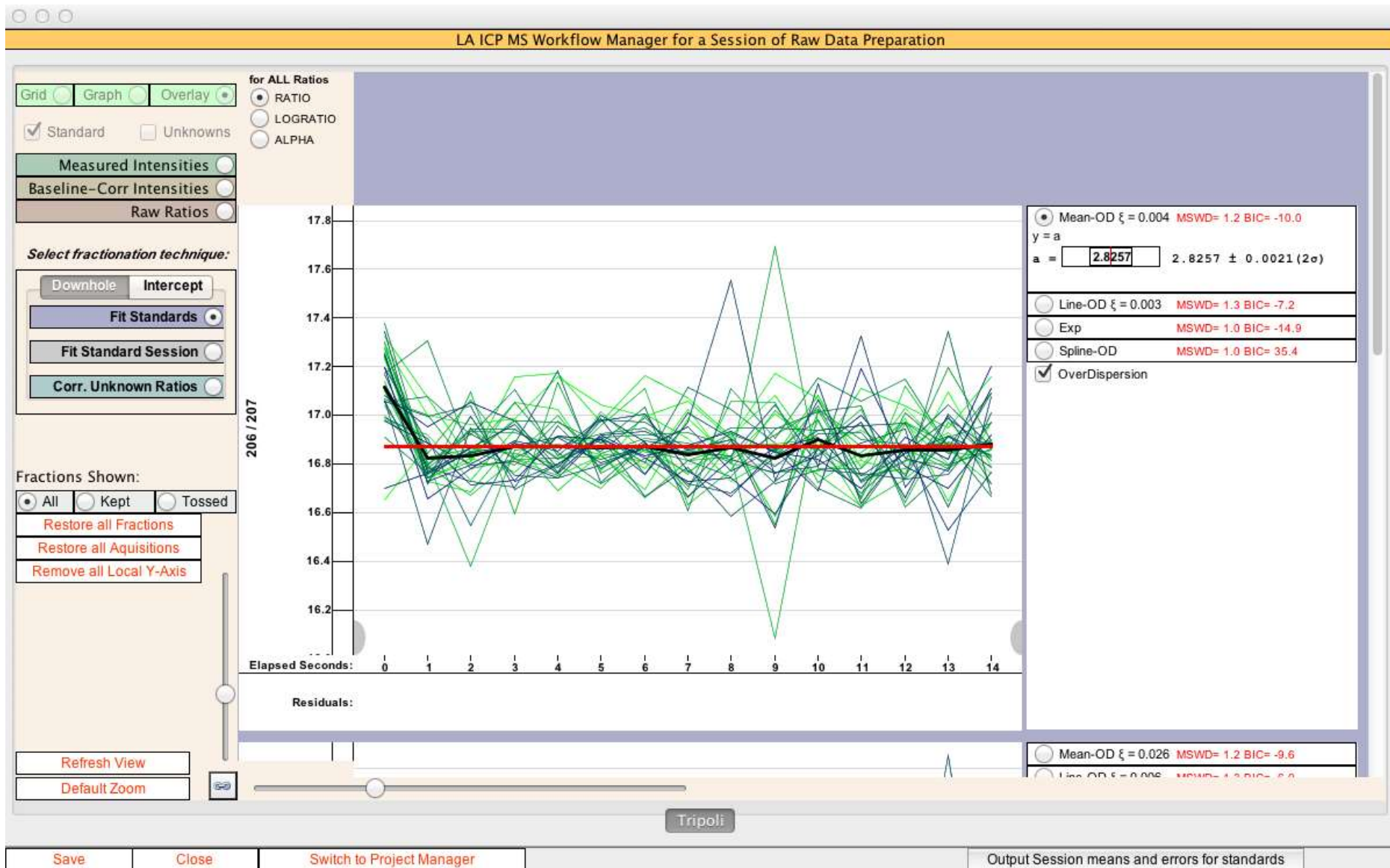
Measured Intensities ☒
Baseline-Corr Intensities ☐
Raw Ratios ☐

Select fractionation technique:
Downhole ☐ Intercept ☐
Fit each Standard ☐
Fit Standard Session ☐
Fit each Unknown ☒

Fractions Shown:
☒ All ☐ Kept ☐ Tossed
Restore all Fractions
Restore all Aquisitions
Remove all Local Y-Axis

Sample	Apply Fit Function:	Graph	Fit Parameters
206 / 207	<input checked="" type="radio"/> Mean <input type="radio"/> Line <input type="radio"/> Exp <input type="checkbox"/> w/ OverDispersion <input type="checkbox"/> w/out OverDispersion		<input type="radio"/> Mean MSWD= 0.7 BIC= -114.7 <input checked="" type="radio"/> Line MSWD= 0.8 BIC= -112.0 $y = a \cdot x + b$ $a = 0.0001 \pm 0.0014 (2\sigma)$ $b = 2.5304 \pm 0.012 (2\sigma)$ <input type="radio"/> Exp Unable to Fit Function <input checked="" type="checkbox"/> OverDispersion
206 / 238	<input type="radio"/> Mean <input checked="" type="radio"/> Line <input type="radio"/> Exp <input type="checkbox"/> w/ OverDispersion <input type="checkbox"/> w/out OverDispersion		<input type="radio"/> Mean-OD $\xi = 0.021$ MSWD= 1.2 BIC= -8.7 <input checked="" type="radio"/> Line-OD $\xi = 0.006$ MSWD= 1.3 BIC= -6.1 $y = a \cdot x + b$ $a = 0.0050 \pm 0.00076 (2\sigma)$ $b = -1.6189 \pm 0.0065 (2\sigma)$ <input type="radio"/> Exp Unable to Fit Function <input checked="" type="checkbox"/> OverDispersion
208 / 232	<input type="radio"/> Mean <input type="radio"/> Line <input checked="" type="radio"/> Exp <input type="checkbox"/> w/ OverDispersion <input type="checkbox"/> w/out OverDispersion		<input type="radio"/> Mean-OD $\xi = 0.082$ MSWD= 1.2 BIC= -8.7 <input type="radio"/> Line-OD $\xi = 0.026$ MSWD= 1.3 BIC= -6.0 <input checked="" type="radio"/> Exp-OD $\xi = 0.009$ MSWD= 1.4 BIC= -3.3 $y = a \cdot e^{(b \cdot x)} + c$ $a = 0.3524 \pm 0.029 (2\sigma)$ $b = -0.1793 \pm 0.034 (2\sigma)$ $c = -1.7717 \pm 0.034 (2\sigma)$ <input checked="" type="checkbox"/> OverDispersion

Workflow: Downhole (Iolite)



Workflow: Interactive Data Table

U-Pb Redux TRIPOLIZED Project: Empty Project <C:\Users\noahm\Documents\ReduxCalcCheck\LA-ICP-MS CalcCheck 6-Jan-13\Gehrels_6149_3-04-13.redux>

Project Sample Aliquots Fractions Lab Data Reports References Web Resources Tools Help

Aliquot	Incl	Note	Fraction	206/204	206/207	206/208	206/205	207/205	208/205	202/205	238/235	233/235	233/236
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Active Fractions Rejected Fractions

Dates (Ma) Isotopic Ratios

Fraction	206Pb/ 238U ^a	±2σ abs	207Pb/ 235U ^a	±2σ abs	207Pb/ 206Pb ^a	±2σ abs	% disc ^b	206Pb/ 238U ^c	±2σ %	207Pb/ 235U ^c	±2σ %	207Pb/ 206Pb ^c
Sort	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼	▲▼
AQUIPE01::AQUIPE01												
[N] AQUIPE01-1	1212	32	1200	21	1177	16	-3.04	0.2069	2.9	2.259	3.0	0.07918
[N] AQUIPE01-2	592	16	589	14	577	19	-2.60	0.0962	2.9	0.786	3.0	0.05927
[N] AQUIPE01-3	925	27	922	32	913	88	-1.38	0.1544	3.2	1.478	5.4	0.0695
[N] AQUIPE01-4	1565	43	1561	25	1557	11	-0.54	0.2748	3.1	3.65	3.2	0.09645
[N] AQUIPE01-5	635	18	631	22	615	78	-3.24	0.1036	3.0	0.862	4.8	0.0603
[N] AQUIPE01-6	1224	32	1219	21	1211	12	-1.10	0.2091	2.9	2.322	3.0	0.08055
[N] AQUIPE01-7	590	16	592	17	601	52	1.78	0.0958	2.9	0.792	3.8	0.0599
[N] AQUIPE01-8	1066	28	1066	19	1068	11	0.22	0.1798	2.9	1.859	2.9	0.07498
[N] AQUIPE01-9	598	17	596	14	589	27	-1.50	0.0971	2.9	0.798	3.2	0.05959
[N] AQUIPE01-11	1369	39	1437	71	1540	160	11.12	0.2365	3.2	3.12	9.6	0.0956
[N] AQUIPE01-12	898	26	916	21	959	28	6.38	0.1494	3.1	1.464	3.4	0.07105
[N] AQUIPE01-13	574	16	576	16	585	46	1.86	0.0932	2.9	0.764	3.6	0.0595
[N] AQUIPE01-14	620	17	622	15	629	31	1.46	0.1009	2.8	0.845	3.2	0.06071
[N] AQUIPE01-15	10.68	0.81	95.7	8.7	9010	1300	99.88	0.00166	7.6	0.0989	9.6	0.432
[N] AQUIPE01-20	31.11	0.95	36.2	5.2	387	290	91.97	0.00484	3.0	0.0363	15	0.0544
[N] AQUIPE01-21	1502	39	1498	24	1493	14	-0.60	0.2624	2.9	3.37	3.0	0.09325
[N] AQUIPE01-22	567	15	567	13	567	19	0.00	0.0920	2.8	0.748	3.0	0.05901
[N] AQUIPE01-23	42.9	1.3	43.6	1.8	82	66	47.97	0.00667	3.0	0.0439	4.1	0.0477
[N] AQUIPE01-24	226.2	6.4	239.0	8.9	368	67	38.46	0.0357	2.9	0.265	4.2	0.0539
[N] AQUIPE01-25	25.52	0.90	46.8	8.5	1344	320	98.10	0.00397	3.5	0.0472	19	0.086
[N] AQUIPE01-26	981	26	989	30	1007	78	2.54	0.1644	2.8	1.649	4.9	0.0727
[N] AQUIPE01-27	654	18	670	47	724	180	9.61	0.1068	3.0	0.935	9.7	0.0635
[N] AQUIPE01-28	600	16	599	17	597	54	-0.51	0.0975	2.9	0.804	3.8	0.0598
[N] AQUIPE01-29	1830	45	1853	24	1879.8	8.0	2.64	0.3283	2.8	5.21	2.9	0.11499
[N] AQUIPE01-32	1365	36	1368	22	1373	14	0.62	0.2358	2.9	2.848	3.0	0.08759
[N] AQUIPE01-34	1005	27	1023	20	1061	28	5.24	0.1687	2.9	1.738	3.2	0.0747
[N] AQUIPE01-35	628	17	631	15	640	34	1.89	0.1024	2.8	0.862	3.2	0.06103
[N] AQUIPE01-37	624	17	626	17	631	48	1.10	0.1017	2.8	0.852	3.6	0.0608
[N] AQUIPE01-38	221.9	6.2	222.6	8.4	230	70	3.36	0.03503	2.8	0.245	4.2	0.0508

Report Settings Manager

Categories (double-click to hide / show)

- Fraction
- Dates (Ma)
- Composition
- Isotopic Ratios
- Correlation Coefficients
- Fraction

Columns for Selected Category (double-click to hide / show)

- 206Pb/204Pb
- 208Pb/206Pb
- 206Pb/238U
- 207Pb/235U
- 207Pb/206Pb
- 206Pb/238U (Th-corrected)
- 207Pb/235U (Pa-corrected)
- 207Pb/206Pb (Th-corrected)
- 207Pb/206Pb (Pa-corrected)
- 207Pb/206Pb (Th- and Pa-corrected)
- Correlation coefficient

Column Details

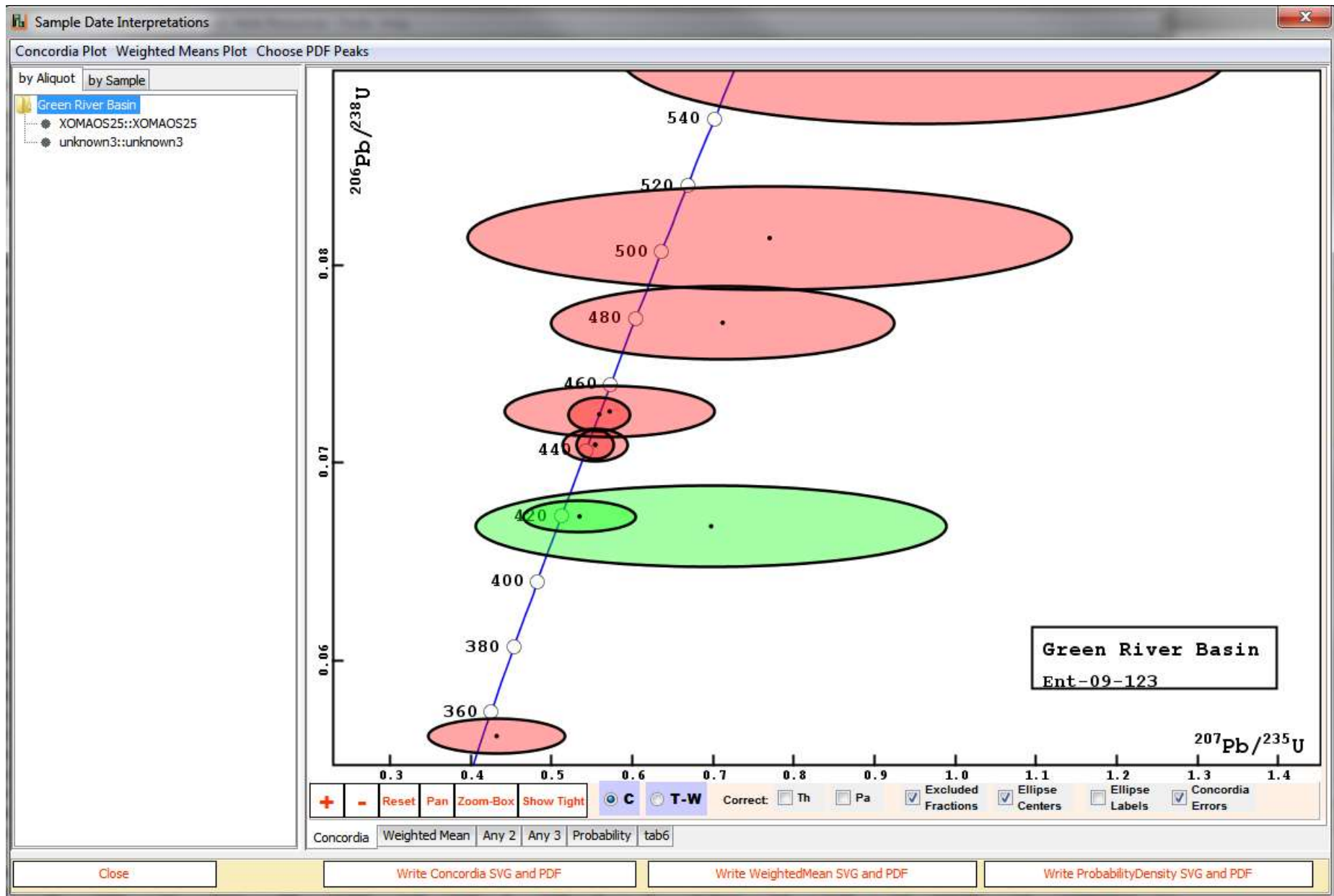
206Pb/238U

☒ sigfig ☐ arbit. digit count = n/a 2

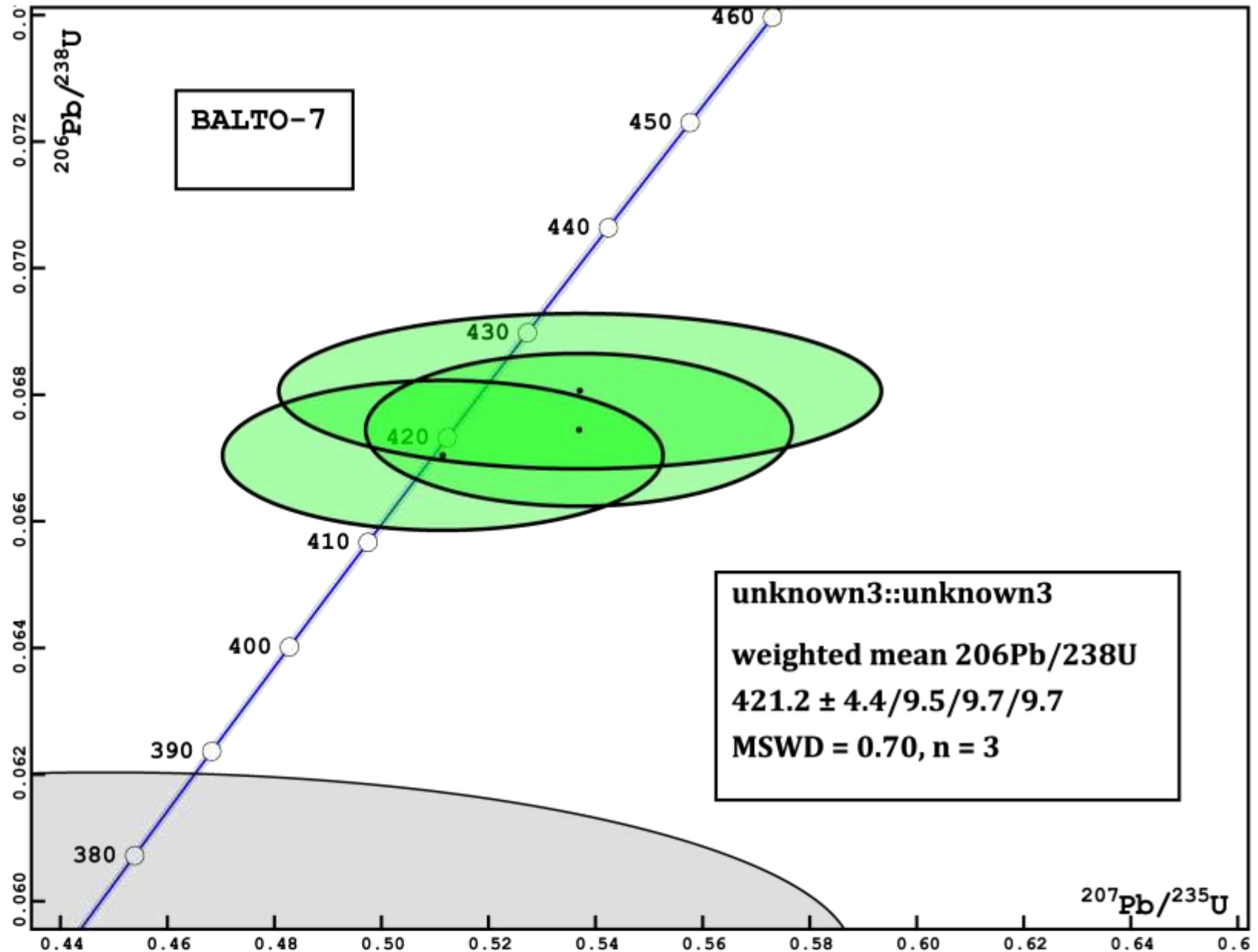
±2σ % ☒ unct col visible for this value

☒ sigfig ☐ arbit. digit count = 2

Workflow: Interactive Concordia Plots



Workflow: Interactive Concordia Plots



2. Common Pb corrections

- Isochron regression methods available (upper/lower intercept from TIMS)

3. Fractionation Correction

$$\left(\frac{x}{y}\right)_{true} = A \left(\frac{x}{y}\right)_{meas}$$

$$\log \left(\frac{x}{y}\right)_{true} = \alpha + \log \left(\frac{x}{y}\right)_{meas}$$

4. Weighted Mean/Linear Regression

- Weighted means take into account reported in the form $X/Y/Z/W$, where
 - **X** is the analytical uncertainty, and takes into account the uncertainty correlations from sample-standard bracketing
 - **Y** also includes the lab's observed variability in multiple standards of the same mineral
 - **Z** additionally includes uncertainties in the mineral standard IC
 - **W** adds in decay constant uncertainties

5. Rejection Criteria

- None: user-based rejection.
 - Open to suggestions, but 2σ ends up underestimating uncertainties

6. Handling/Storage of Reference Values

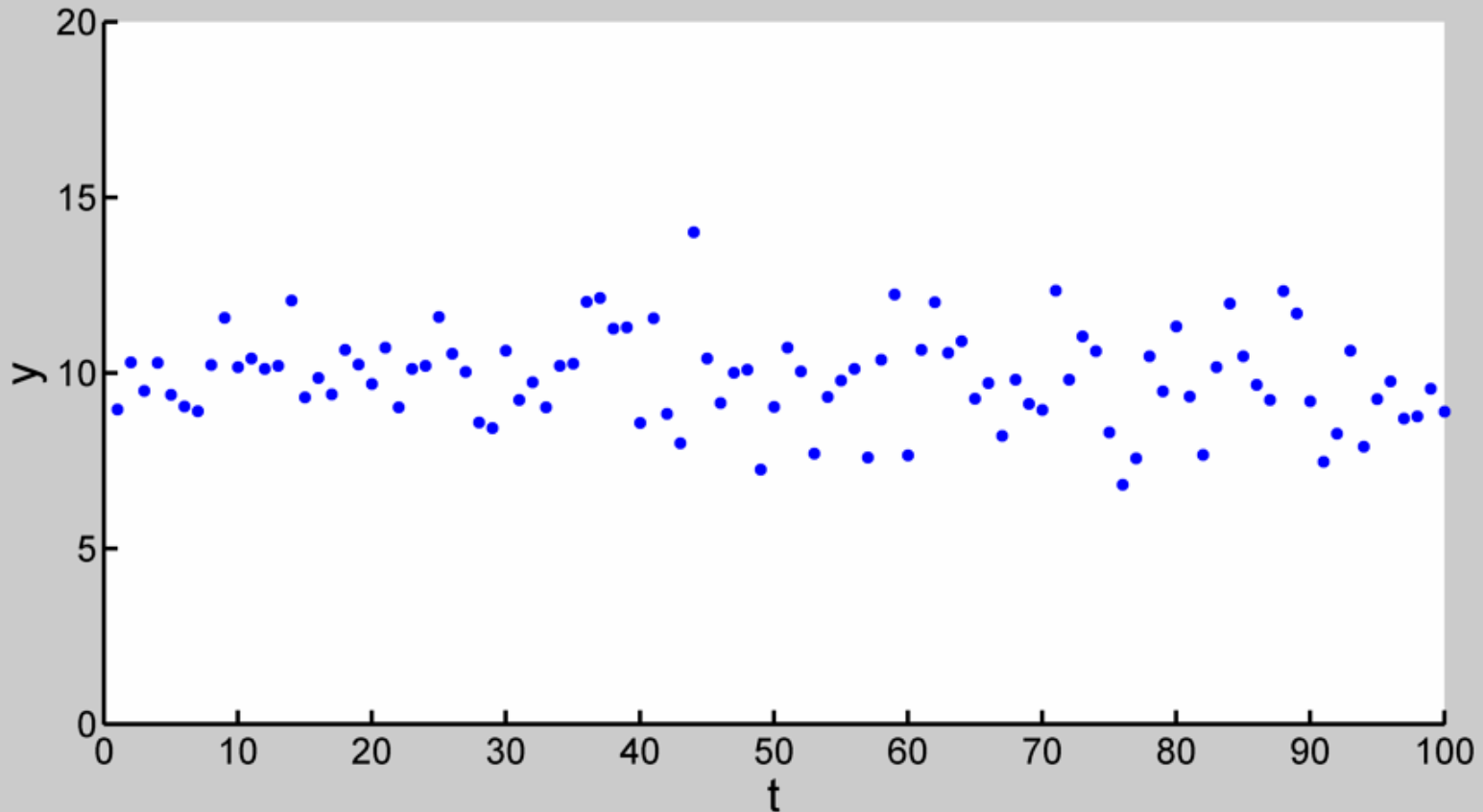
- Model stored publicly online as xml
 - Separately records radiogenic end-member and common Pb ICs, with covariance matrix to describe the uncertainties in each

7. Key Differences

- A. Treats heteroscedastic and overdispersed data
- B. Log-ratio analysis of compositional data
- C. Propagates systematic uncertainties between integrations – dead time, detector grains/non-linearity
- D. Provides model selection guidance (BIC)
- E. Treats systematic uncertainties between measurements from sample-standard bracketing
- F. Plugs into ID-TIMS Redux for plotting, weighted means, databasing capabilities

A. Heteroscedastic data

- Uncertainty in each data point is different

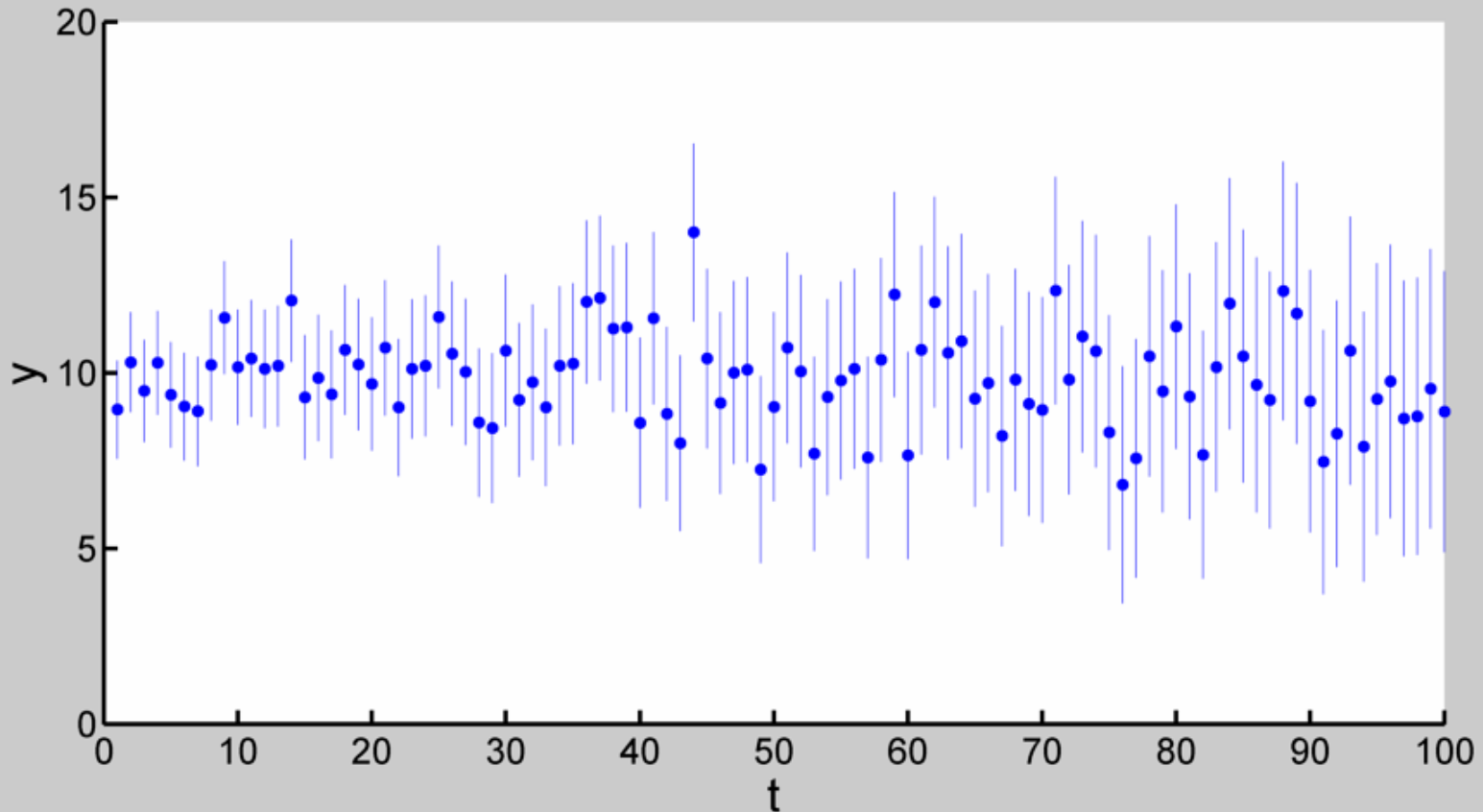


Mean: 9.86

$\pm 2\text{SE}$: 0.26

A. Heteroscedastic data

- Uncertainty in each data point is different



Mean: 9.86

$\pm 2SE$: 0.26

Wtd Mean: 9.94

$\pm 2\sigma$ 0.24

A. Heteroscedastic data

- Estimate uncertainty in each analysis
 - Total counts (shot noise)
 - Amplifier behavior (Johnson noise)
- If the measured variability in the data is larger than the estimated uncertainties, make up the difference with overdispersion (excess variance)

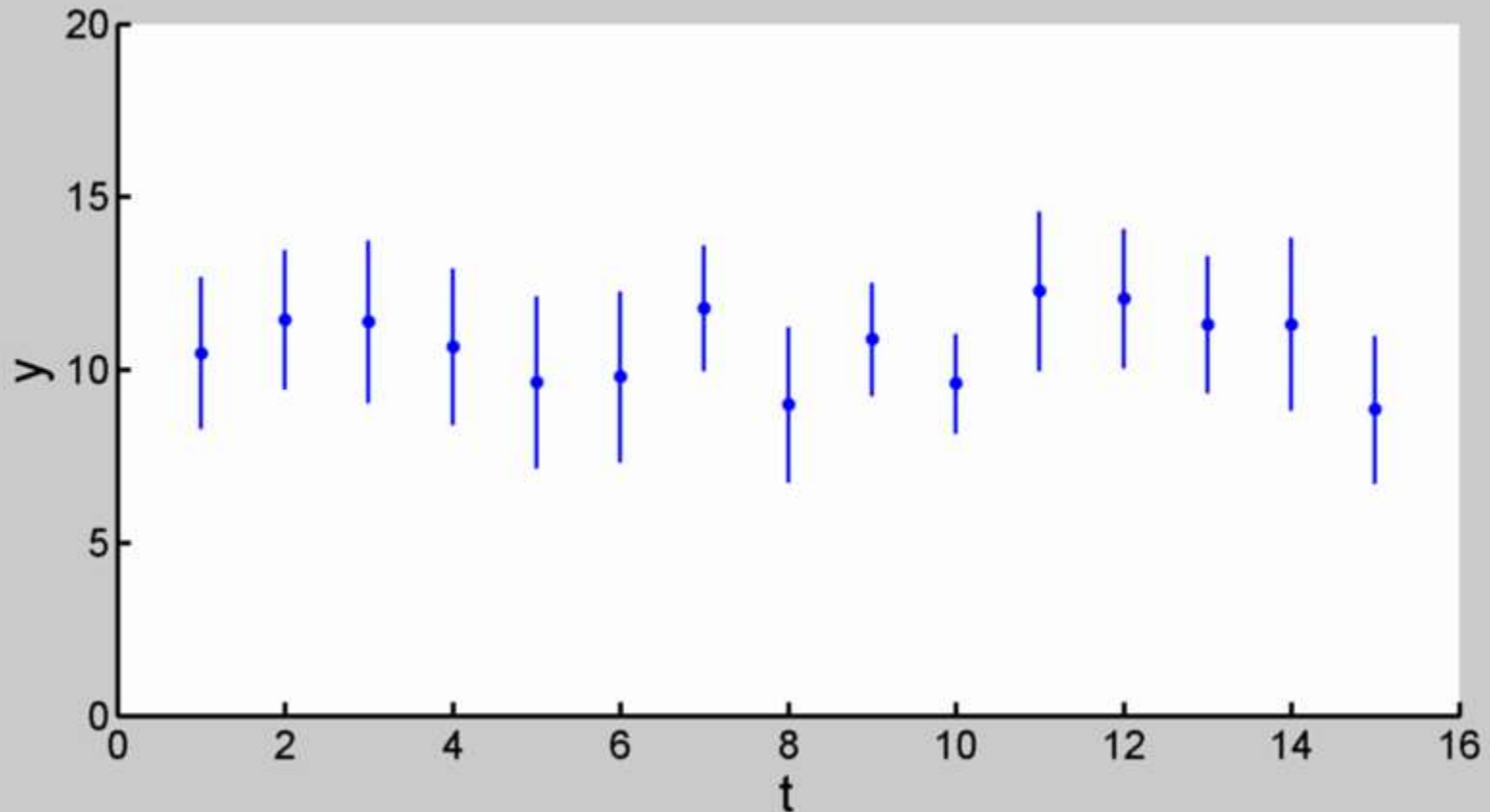
B. Log-ratios of compositional data

- Resolves the age-old problem: ratio of the mean vs. mean of the ratios?
- Differences between isotope ratios do not obey the rules of 'distances': evaluating means and standard deviations generates internally inconsistent results.
- Instead, use e.g. $\log(207/206)$, $\log(208/206)$
- Evaluate math in log-ratio space, then exponentiate. More Thursday!

C. Propagate systematic uncertainties between successive integrations

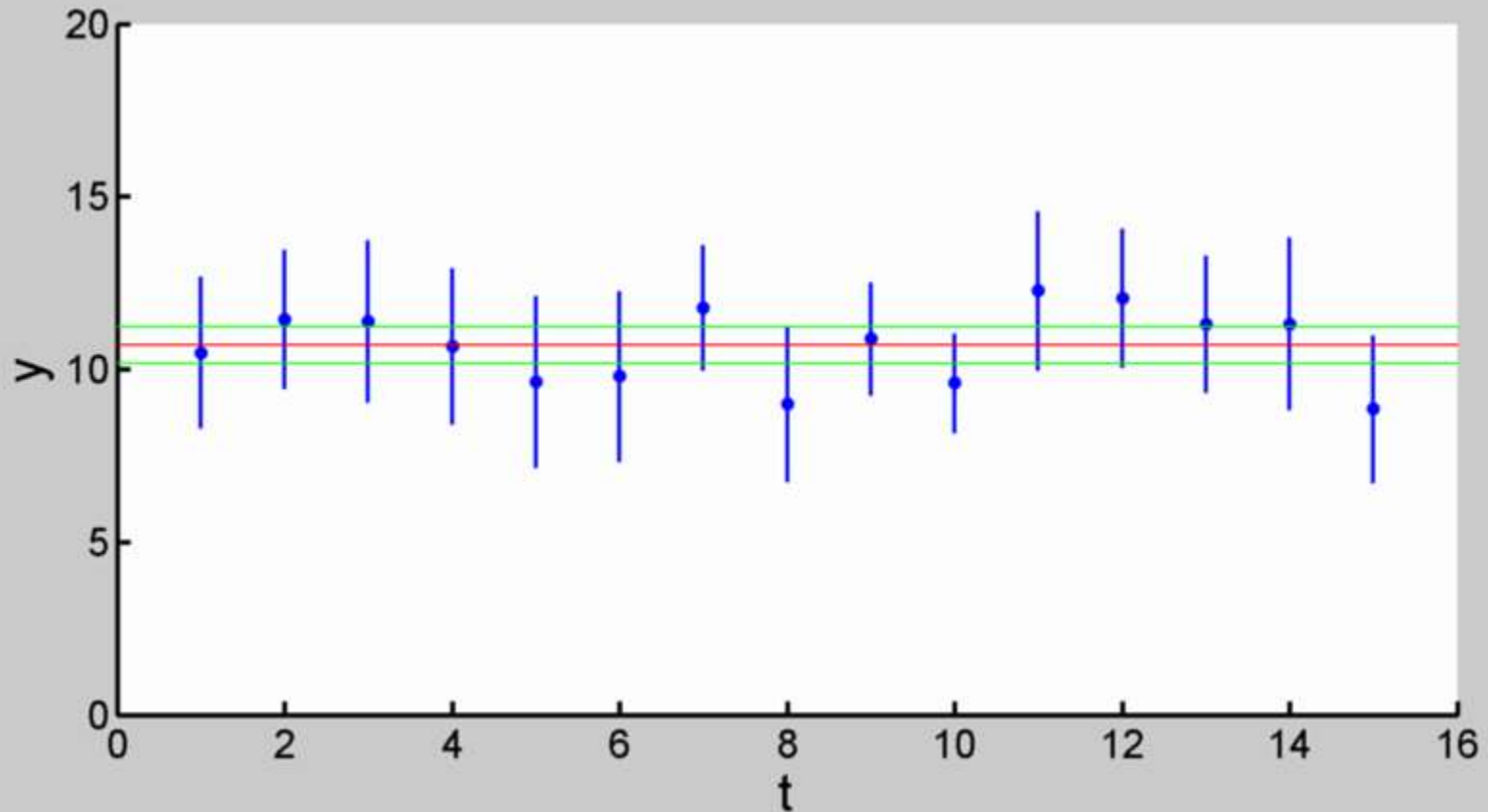
- Not as important for LA-ICP-MS at present, but will become more so as uncertainties continue to come down
- **Dead time**, ion counter non-linearity, gain inter-calibration between detectors.

D. Model Selection



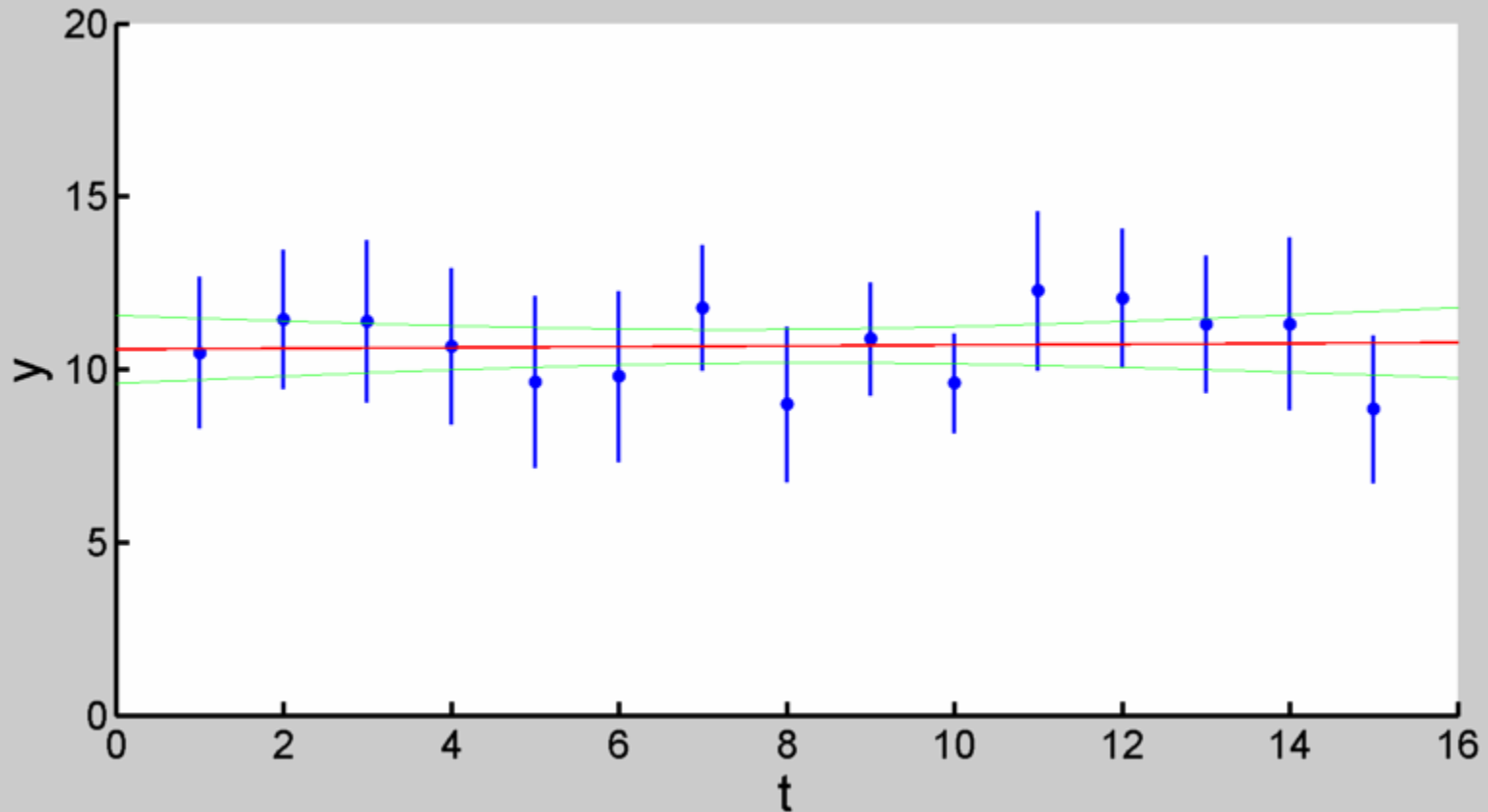
Do these measured data have a trend? Should I use a mean or a linear fit to describe the data?

D. Model Selection



Weighted mean: 10.69 ± 0.53 (2σ), MSWD = 1.38

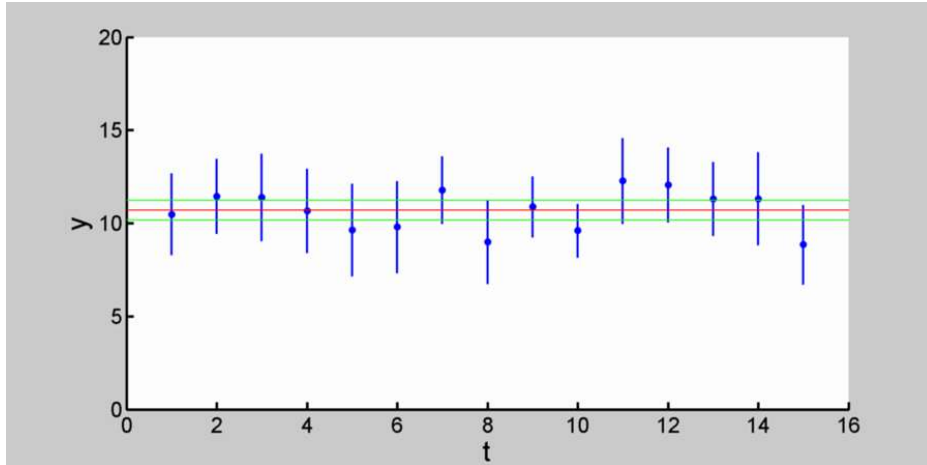
D. Model Selection



Line fit: $(0.012 \pm 0.11)t + (10.58 \pm 0.98)$, MSWD = 1.13

$$\rho_{ab} = -0.871$$

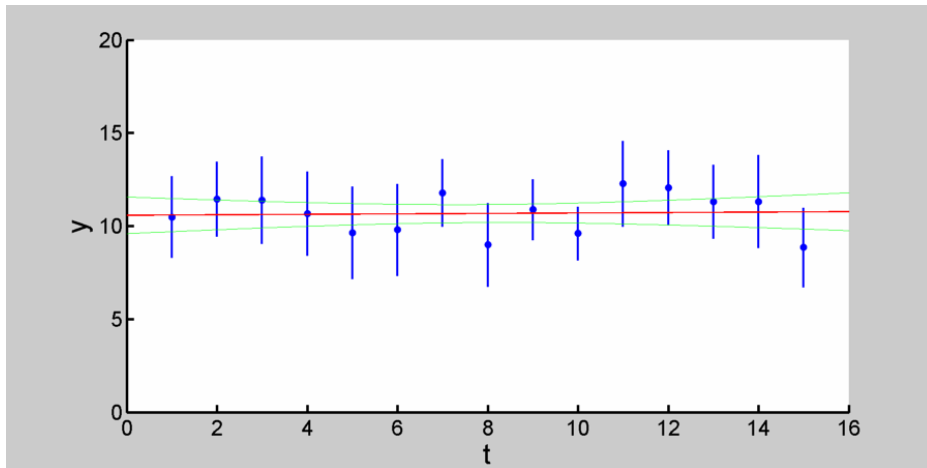
D. Model Selection



Weighted mean:

$10.69 \pm 0.53 (2\sigma),$

MSWD = 1.38, **BIC = 20.7**



Line fit: $(0.012 \pm 0.11)t +$

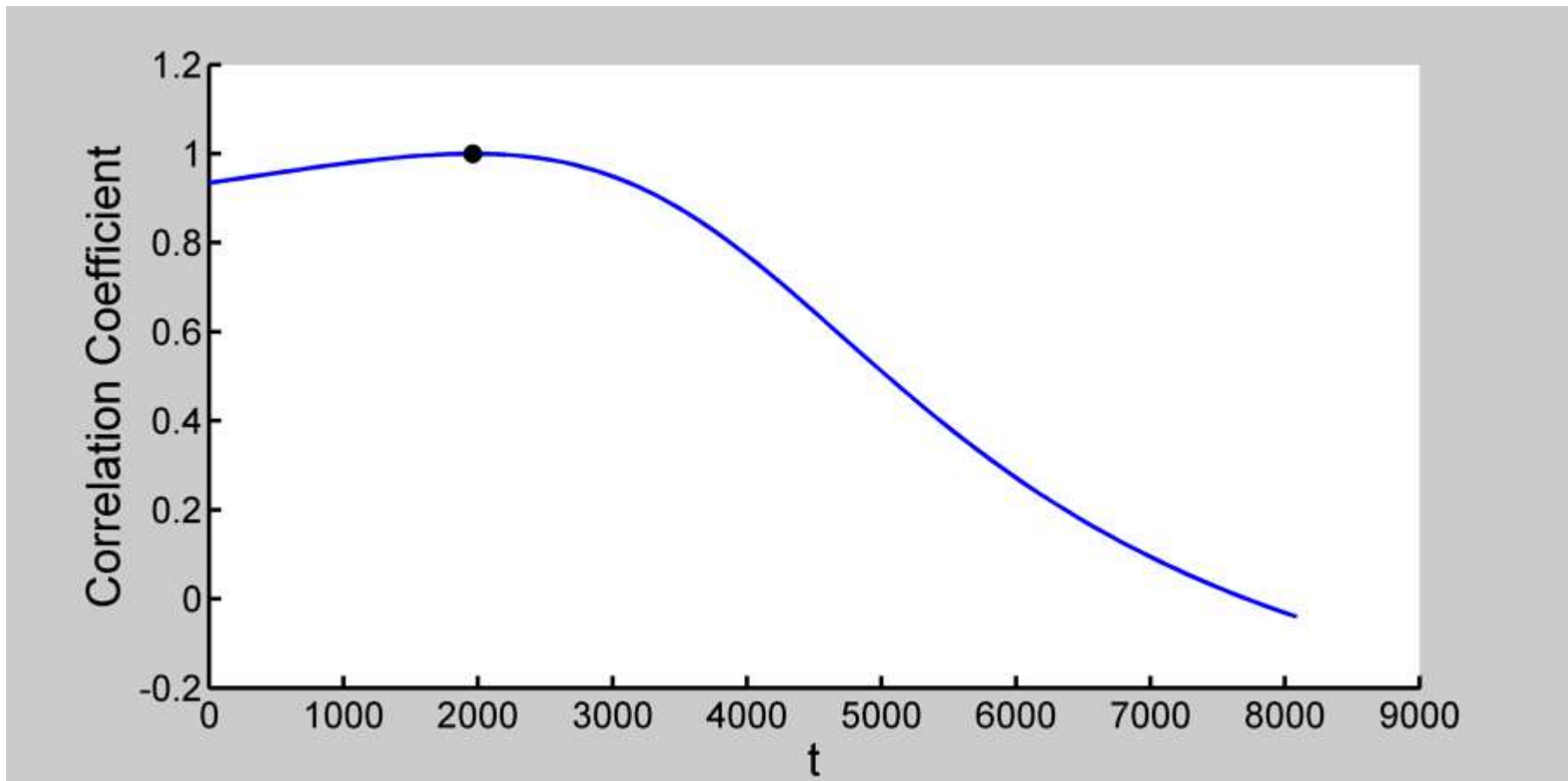
$(10.58 \pm 0.98),$

MSWD = 1.13, **BIC = 19.9**

*Lowest BIC wins: the **line** is most likely the best fit.*

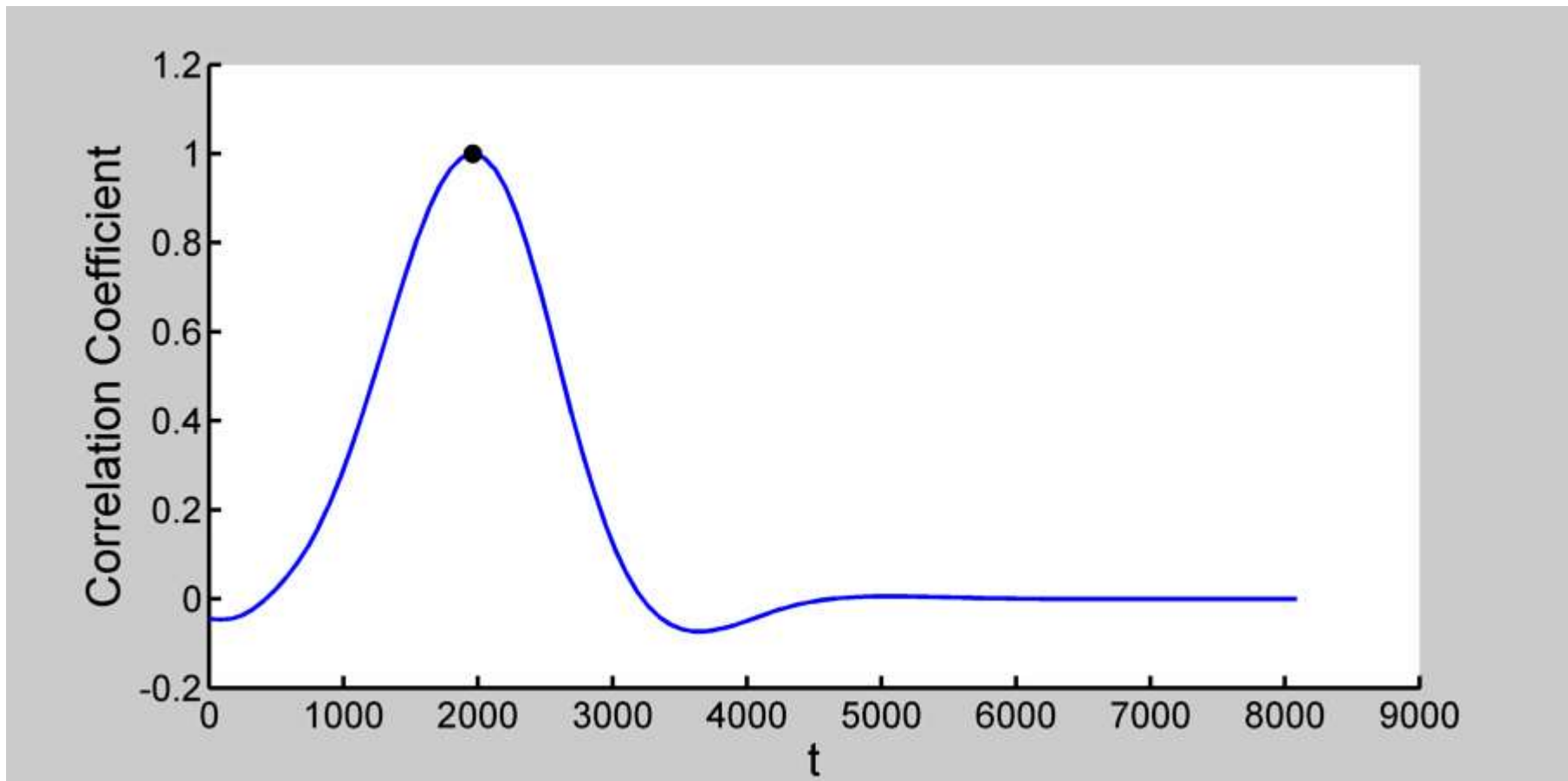
E. Sample-standard bracketing → Unct. correlation between unknowns

Line Fit:

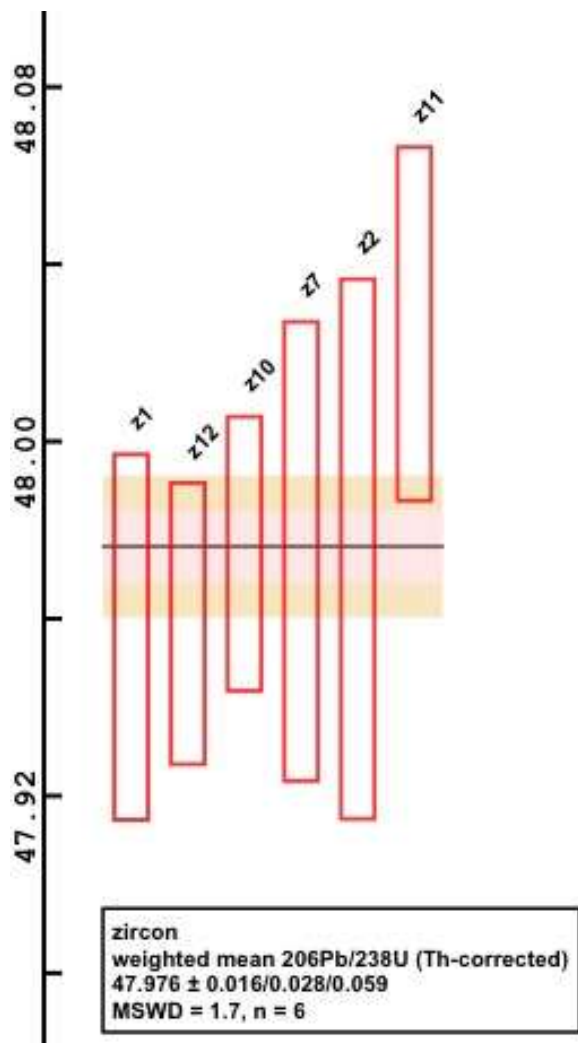


E. Sample-standard bracketing → Unct. correlation between unknowns

Spline Fit:



F. Calculating a weighted mean



- Gives more weight to more precise analyses, un-weights less precise analyses

$$\bar{t} = \sum_{i=1}^n \alpha_i t_i = \sum_{i=1}^n \left(\frac{t_i}{\sigma_i^2} \right) / \sum_{i=1}^n \left(\frac{1}{\sigma_i^2} \right)$$

- But there is no room here for systematic uncertainties, from sample-standard bracketing, standard ICs, decay constants...

Systematic uncertainties are covariance

$$\bar{t} = \alpha_1 t_1 + \alpha_2 t_2 \quad \alpha_1 + \alpha_2 = 1$$

$$\sigma_{\bar{t}}^2 = \begin{bmatrix} \frac{d\bar{t}}{dt_1} & \frac{d\bar{t}}{dt_2} \end{bmatrix} \begin{bmatrix} \sigma_{t_1}^2 & \sigma_{t_1 t_2}^2 \\ \sigma_{t_1 t_2}^2 & \sigma_{t_2}^2 \end{bmatrix} \begin{bmatrix} \frac{d\bar{t}}{dt_1} \\ \frac{d\bar{t}}{dt_2} \end{bmatrix}$$

- What are the weights that minimize the uncertainty in the weighted mean?

Systematic uncertainties are covariance

$$\bar{t} = \alpha_1 t_1 + \alpha_2 t_2 \quad \alpha_1 + \alpha_2 = 1$$

$$\sigma_{\bar{t}}^2 = \begin{bmatrix} \frac{d\bar{t}}{dt_1} & \frac{d\bar{t}}{dt_2} \end{bmatrix} \begin{bmatrix} \sigma_{t_1}^2 & \sigma_{t_1 t_2}^2 \\ \sigma_{t_1 t_2}^2 & \sigma_{t_2}^2 \end{bmatrix} \begin{bmatrix} \frac{d\bar{t}}{dt_1} \\ \frac{d\bar{t}}{dt_2} \end{bmatrix}$$

$$\alpha = \Sigma^{-1} \mathbf{1} / (\mathbf{1}^T \Sigma^{-1} \mathbf{1})$$

Systematic uncertainties are covariance

$$\bar{t} = \alpha_1 t_1 + \alpha_2 t_2 \quad \alpha_1 + \alpha_2 = 1$$

$$\sigma_{\bar{t}}^2 = \begin{bmatrix} \frac{d\bar{t}}{dt_1} & \frac{d\bar{t}}{dt_2} \end{bmatrix} \begin{bmatrix} \sigma_{t_1}^2 & \sigma_{t_1 t_2}^2 \\ \sigma_{t_1 t_2}^2 & \sigma_{t_2}^2 \end{bmatrix} \begin{bmatrix} \frac{d\bar{t}}{dt_1} \\ \frac{d\bar{t}}{dt_2} \end{bmatrix}$$

$$\bar{t} = \mathbf{1}^T \mathbf{\Sigma}^{-1} \mathbf{t} / (\mathbf{1}^T \mathbf{\Sigma}^{-1} \mathbf{1})$$



Software Chasm

Kelly: domain-independent software engineering solutions serve to isolate the scientific-computing community

[IEEE Software 2007]

Wilson: treat scientific software with scientific rigor

[American Scientist 2006]



Goal:

calibrate earth history and develop the geochronological techniques necessary to produce dates with uncertainties approaching 0.1 percent

Requires:

robust software for data reduction, analysis, and archiving to support both science and education

EARTHTIME

Software Requirements

open-source applications for full U-Pb data reduction and error propagation

provide graphical and statistical tools

produce publication-ready artifacts

produce a standardized record for transport to/from archival databases

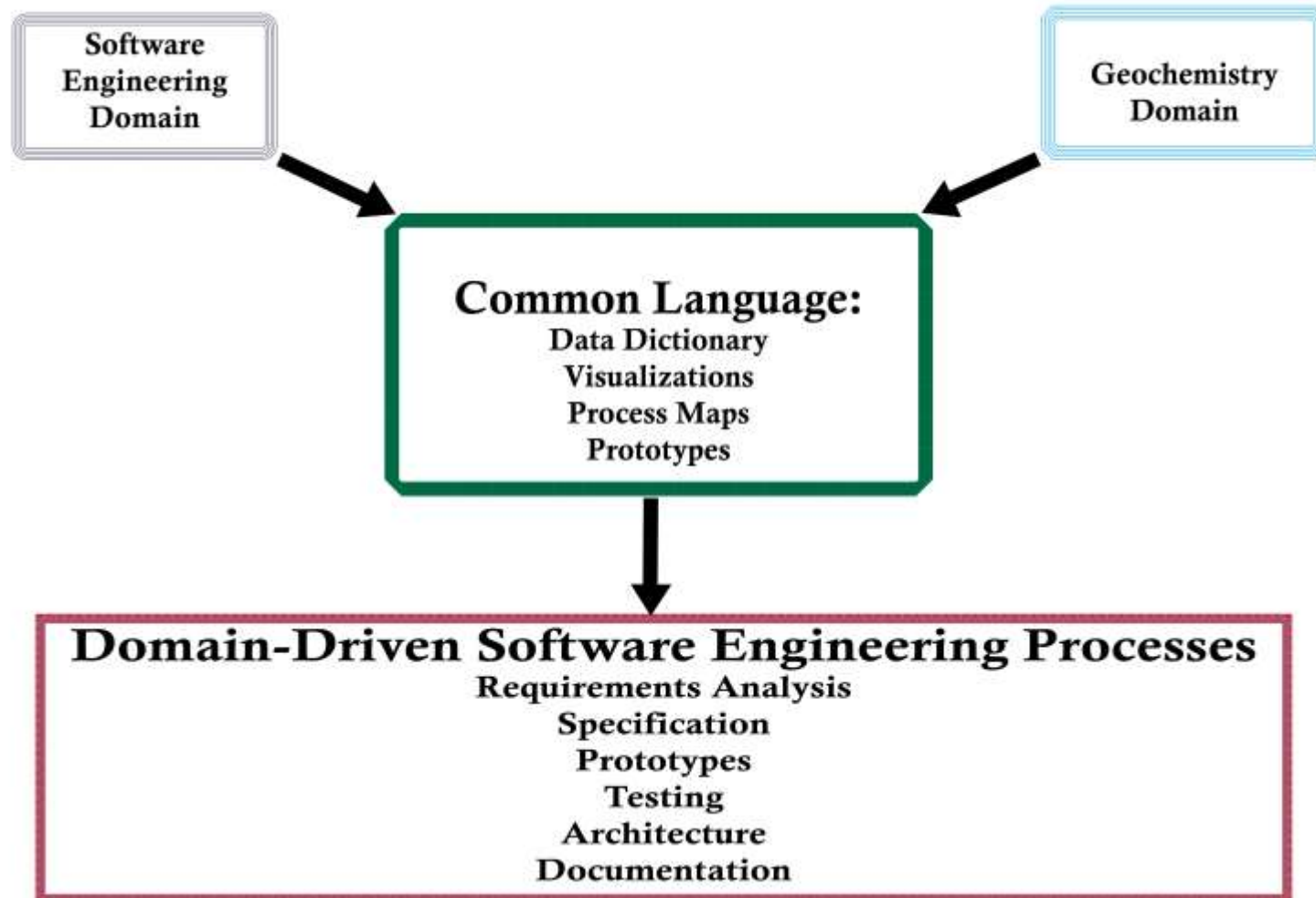
CIRDLES

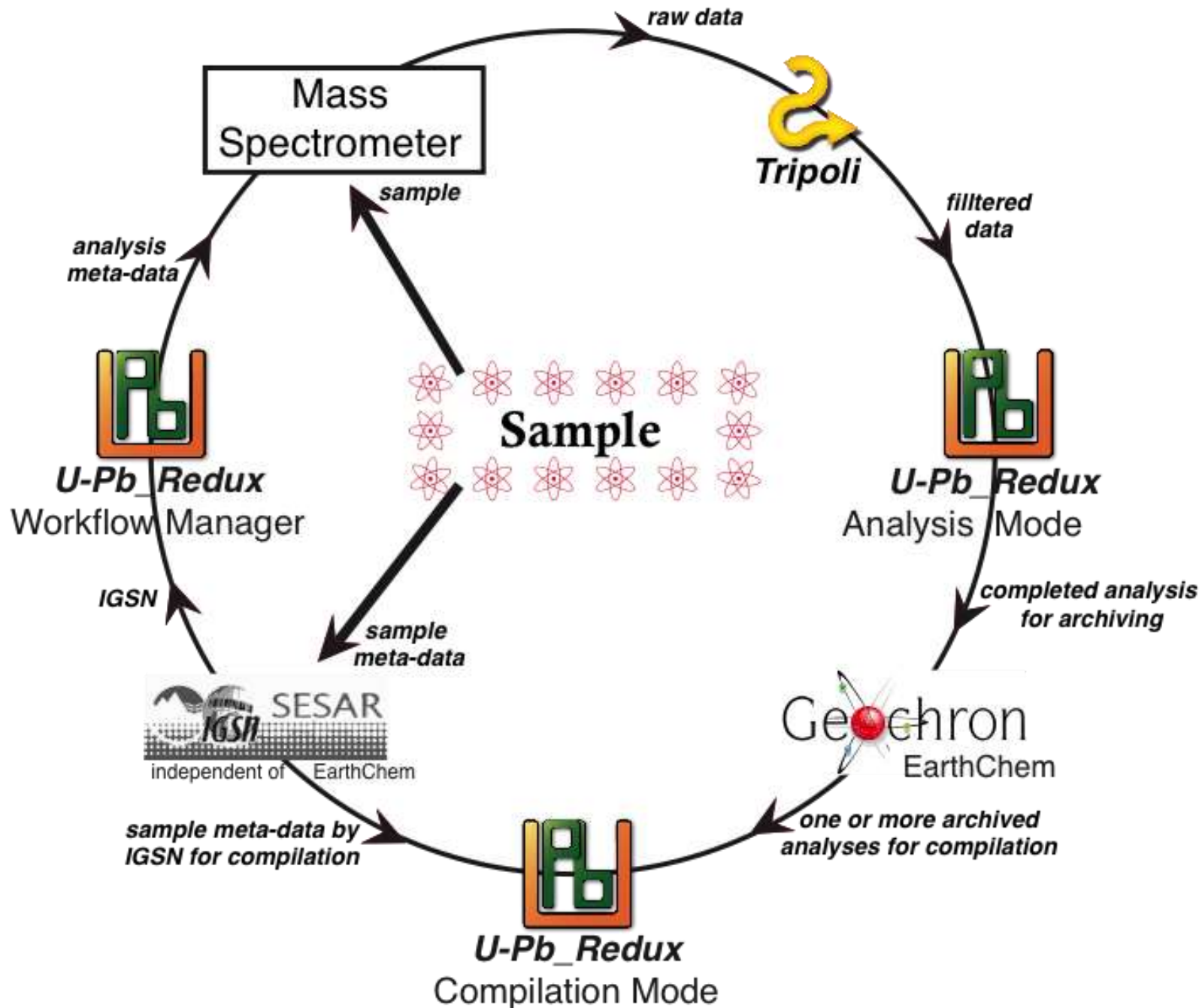
Cyber Infrastructure Research and Development
Lab for the Earth Sciences

CIRDLES.org

Collaborative domain-specific software
engineering research to produce tools that
advance science

Domain-Driven Development Process





Questions ?

