U-Pb_Redux

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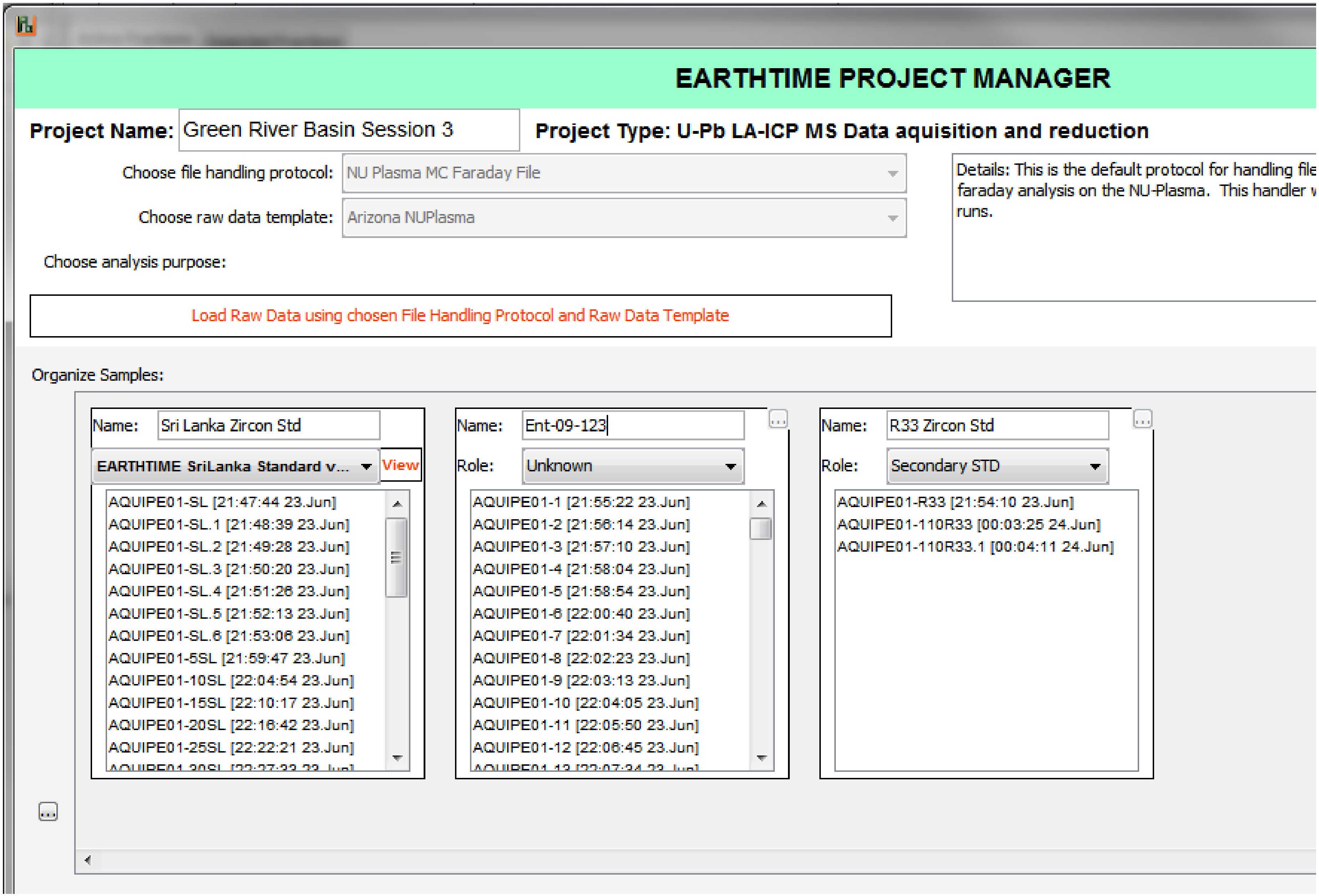
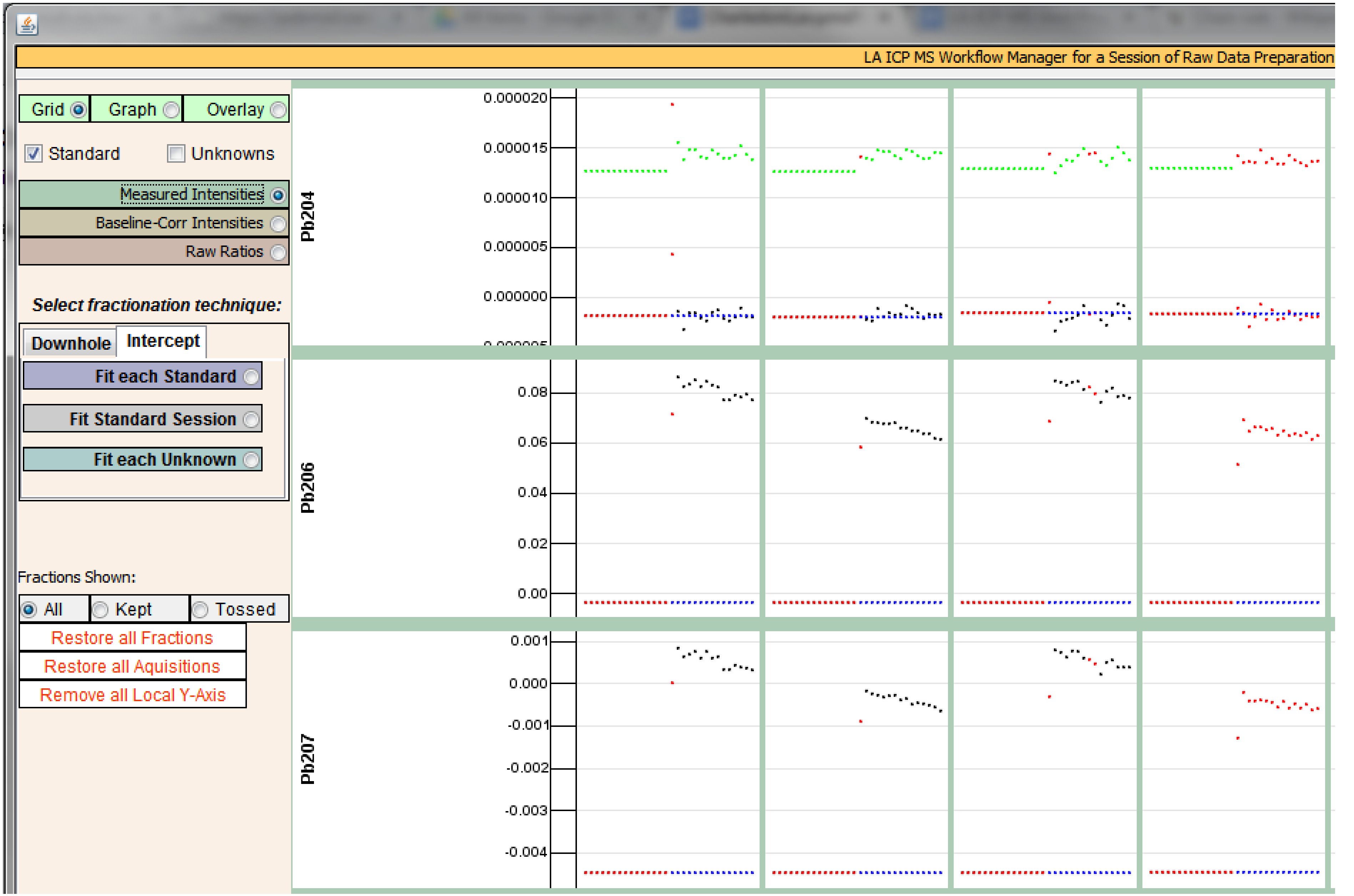
Outline:

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

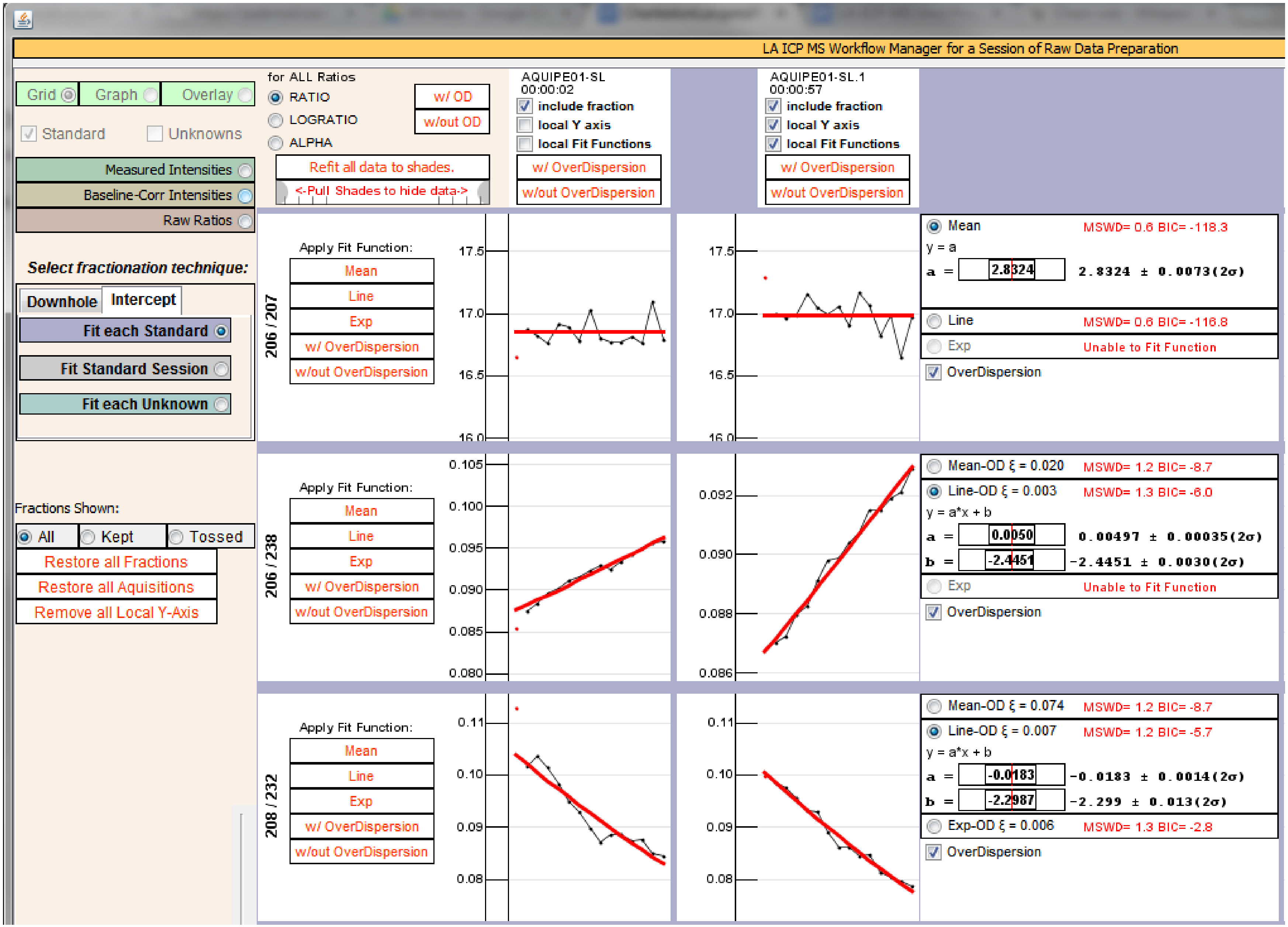
Workflow: Sample Setup



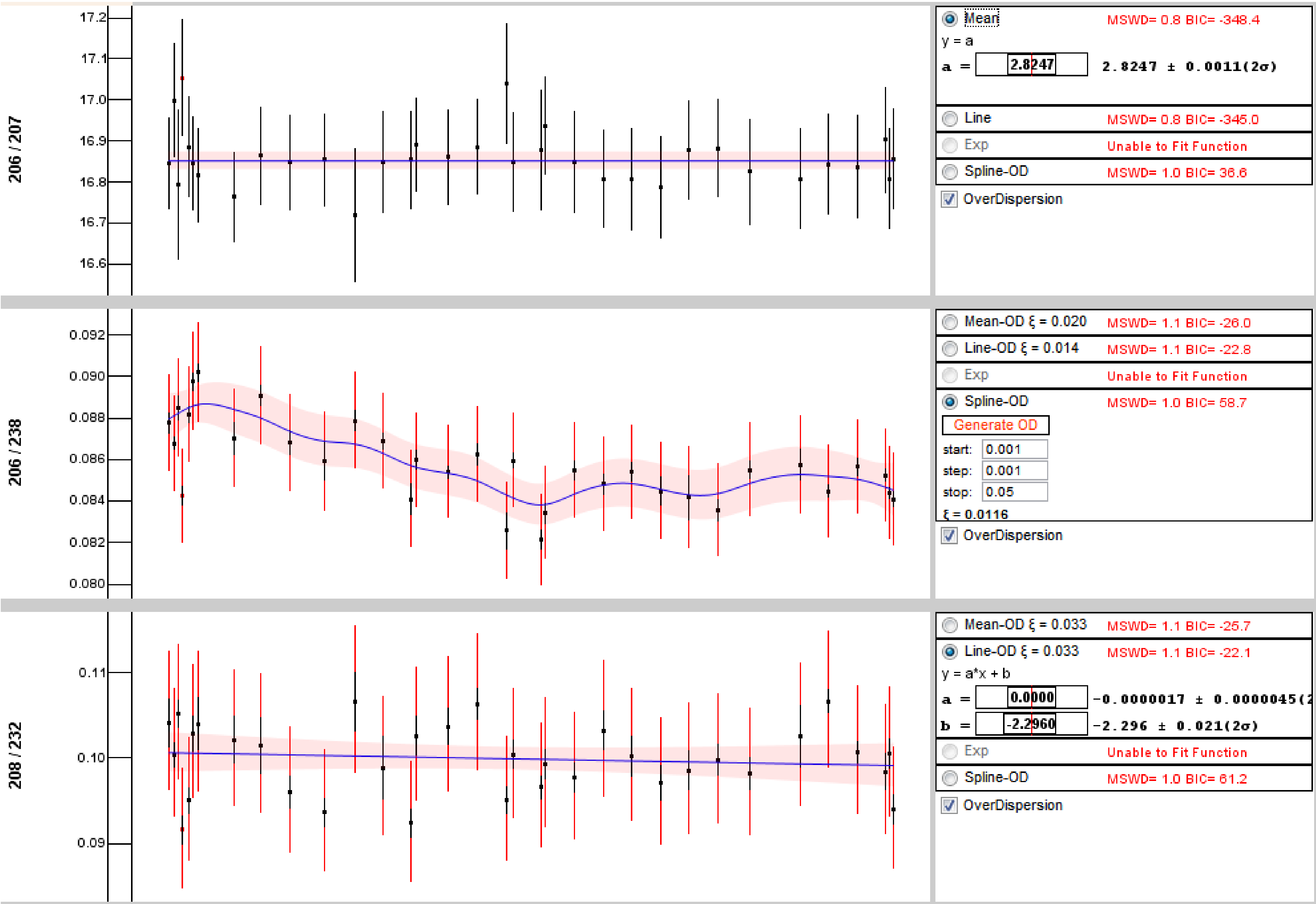
Workflow: Raw Ratios



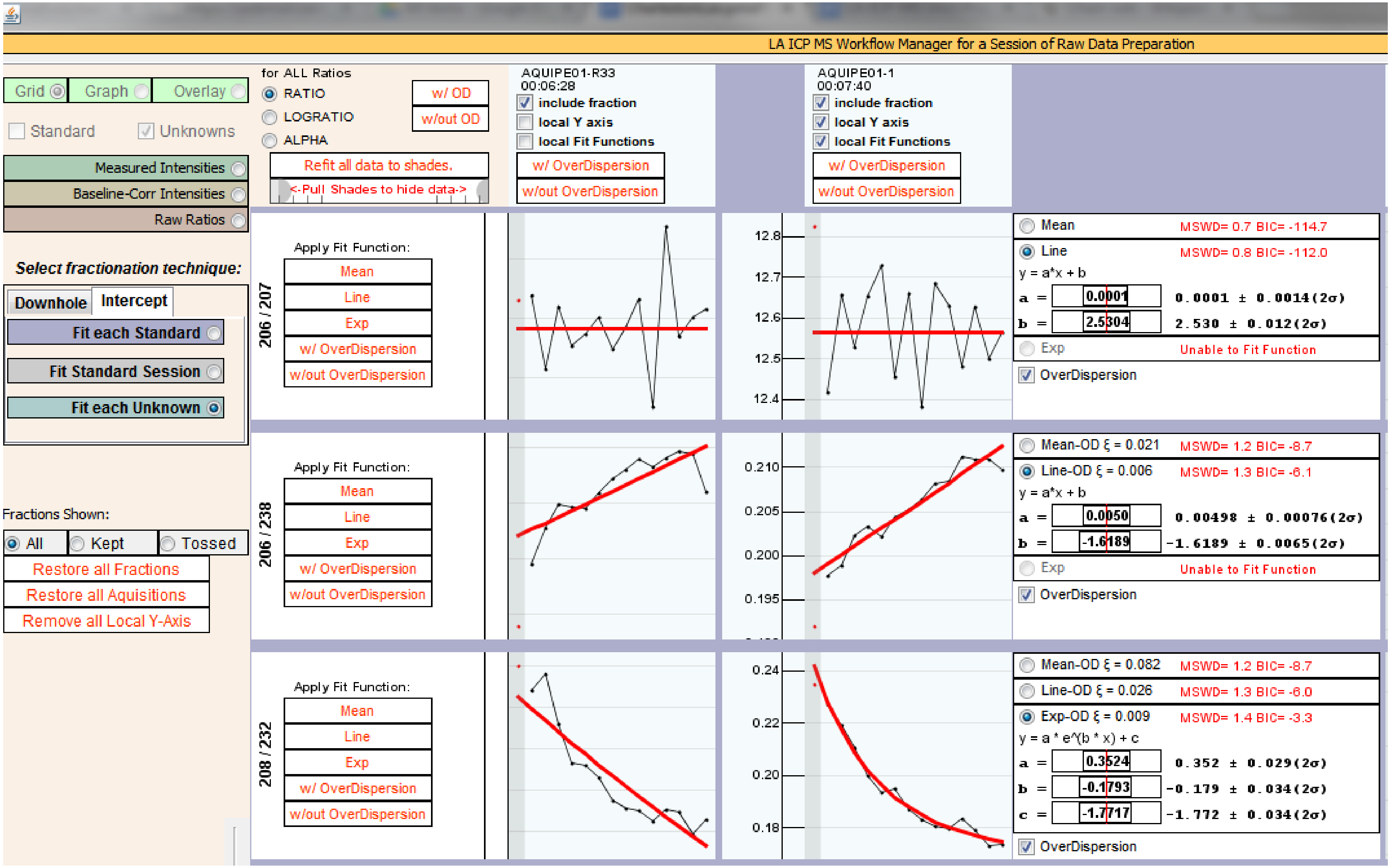
Workflow: Fit Standards



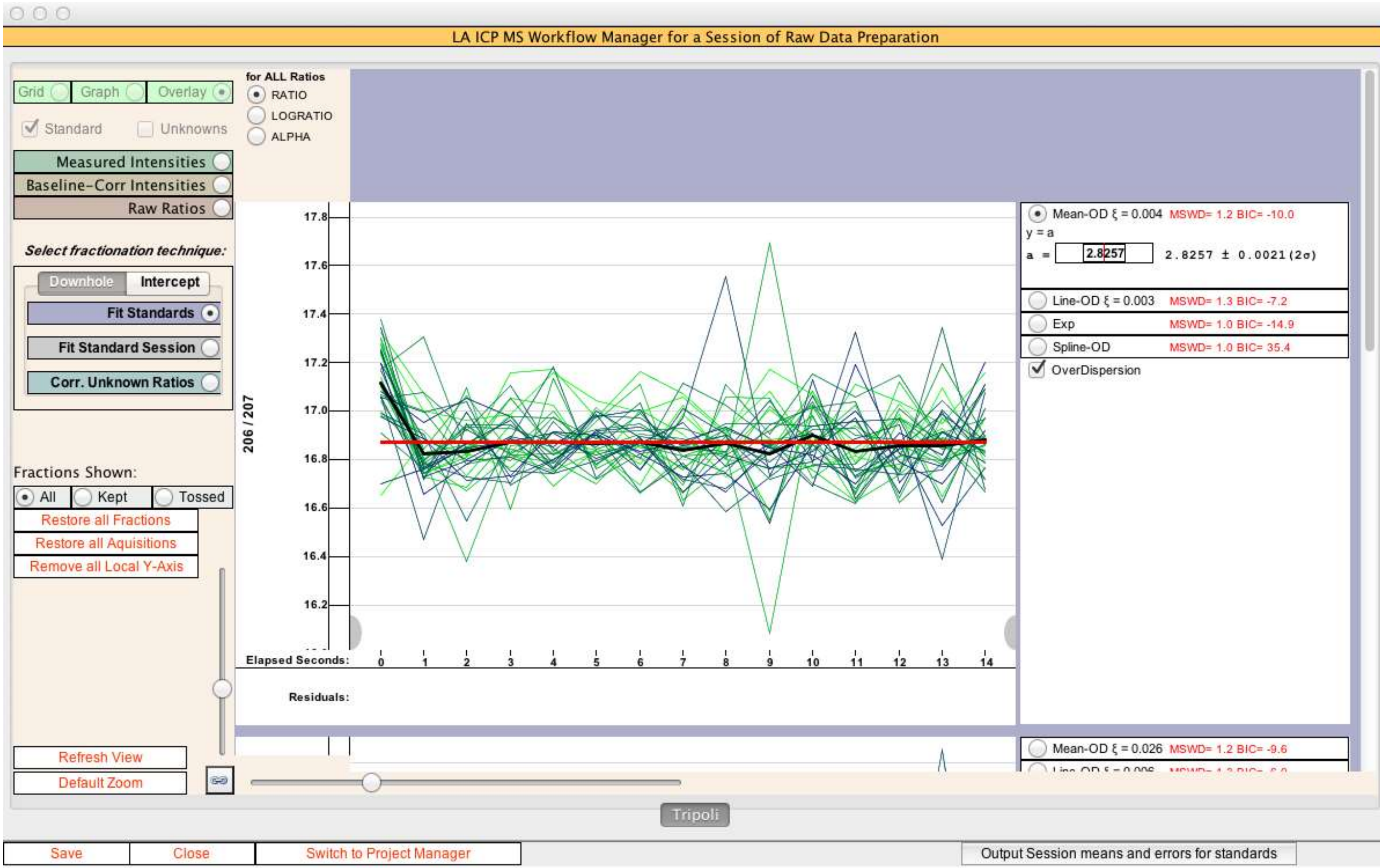
Workflow: Fit Session



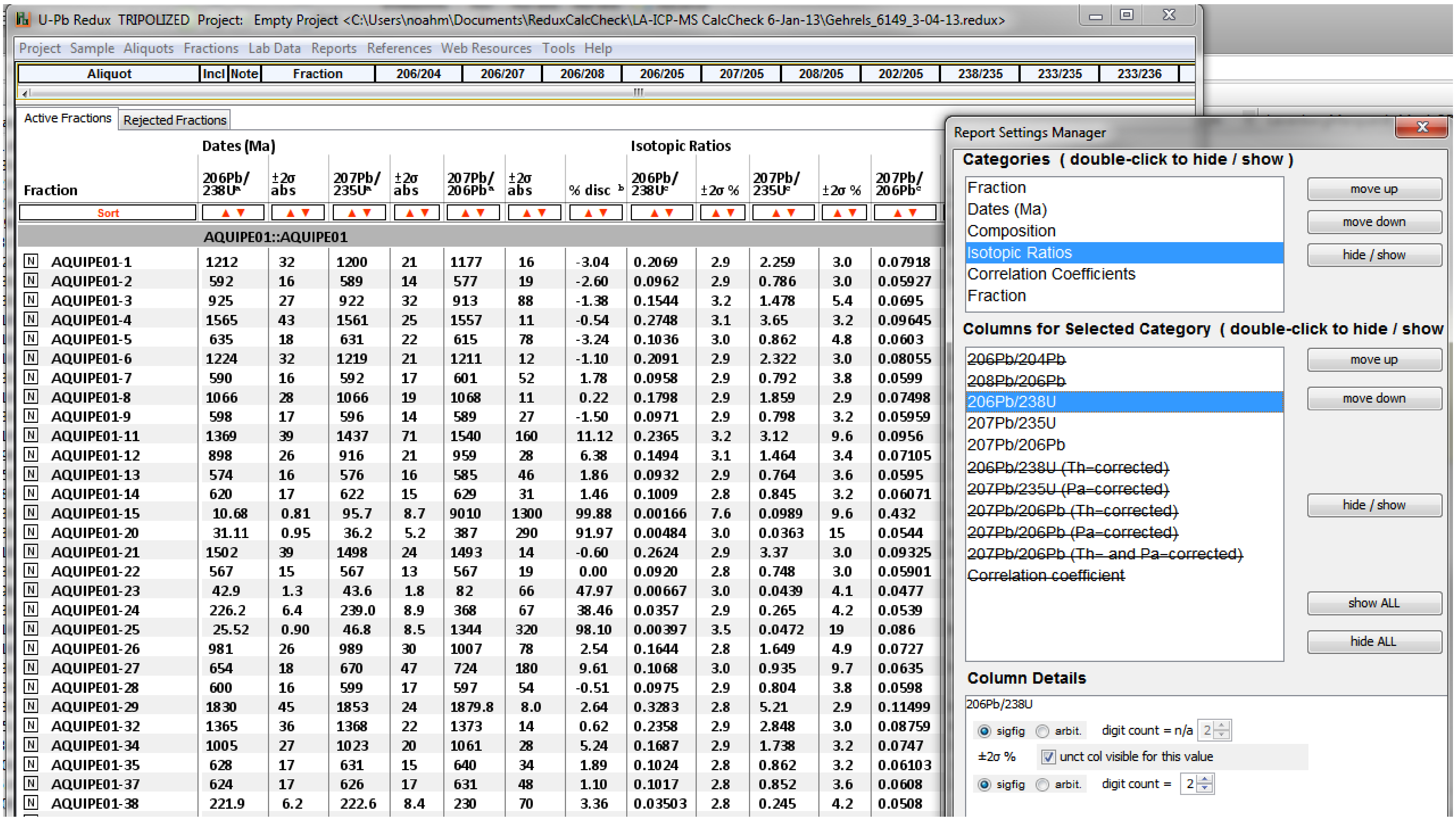
Workflow: Fit Unknowns



Workflow: Downhole (Iolite)

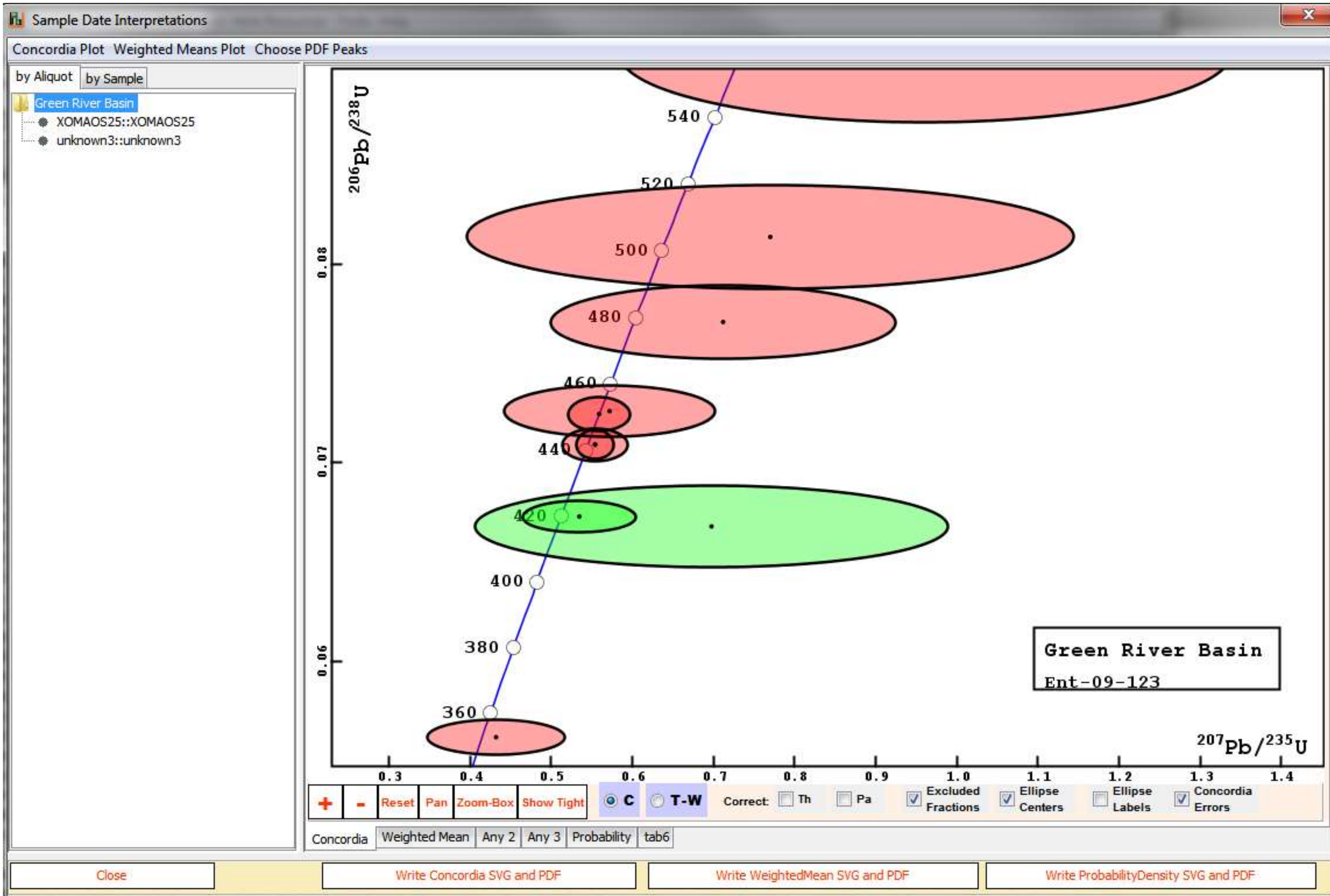


Workflow: Interactive Data Table

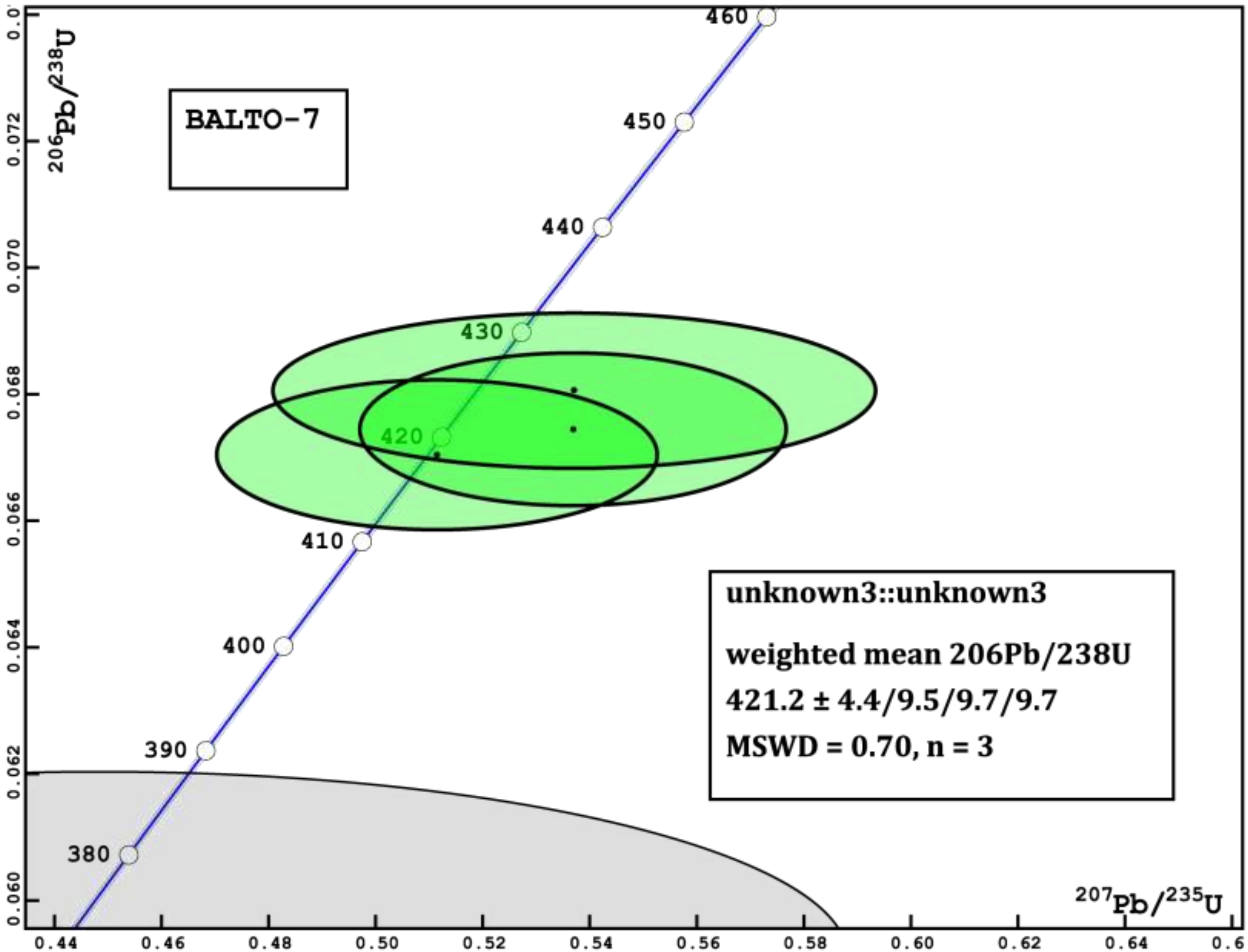


Fraction	206Pb/238U	±2σ abs	207Pb/235U	±2σ abs	207Pb/206Pb	±2σ abs	% disc	206Pb/238U	±2σ %	207Pb/235U	±2σ %	207Pb/206Pb
AQUIPE01-1	1212	32	1200	21	1177	16	-3.04	0.2069	2.9	2.259	3.0	0.07918
AQUIPE01-2	592	16	589	14	577	19	-2.60	0.0962	2.9	0.786	3.0	0.05927
AQUIPE01-3	925	27	922	32	913	88	-1.38	0.1544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

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

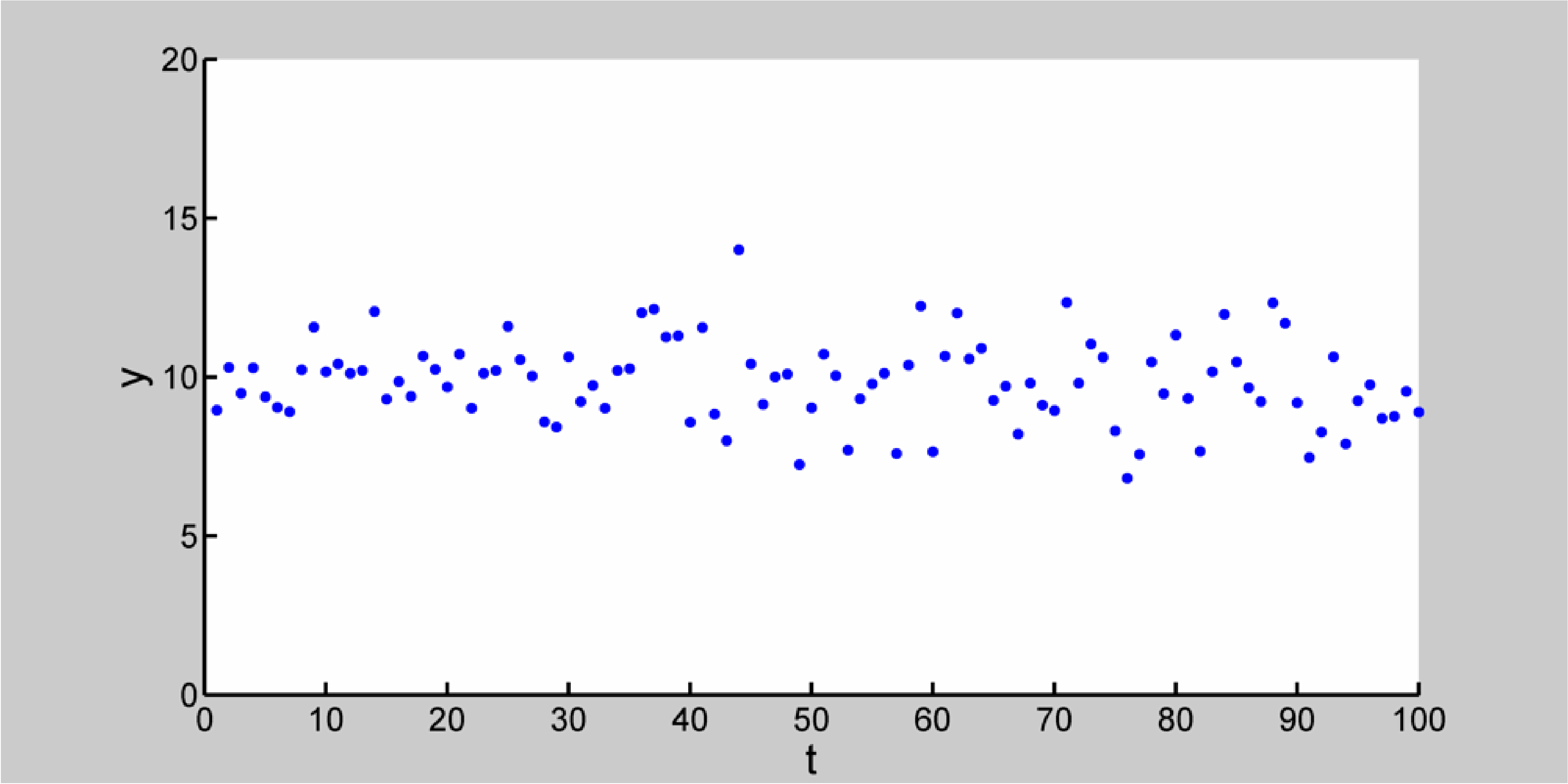
- Model stored publicly online as xml
  - Separately records radiogenic end-member and common Pb ICs, with covariance matrix to describe the uncertainties in each

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

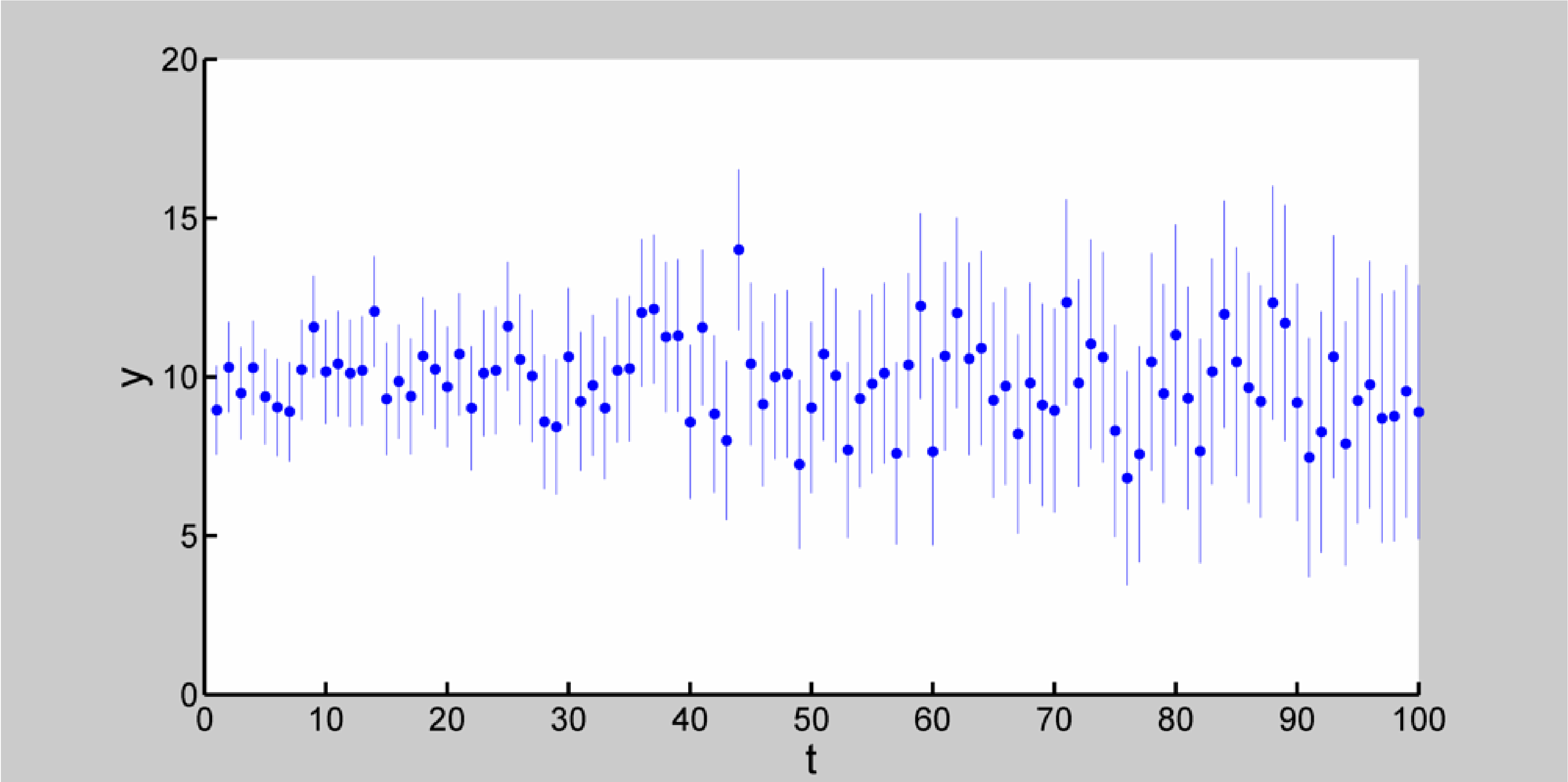


Mean: **9.86**

±2SE: **0.26**

A. Heteroscedastic data

- Uncertainty in each data point is different



Mean:	9.86	**Wtd Mean:**	**9.94**
±2SE:	0.26	**±2σ**	**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)

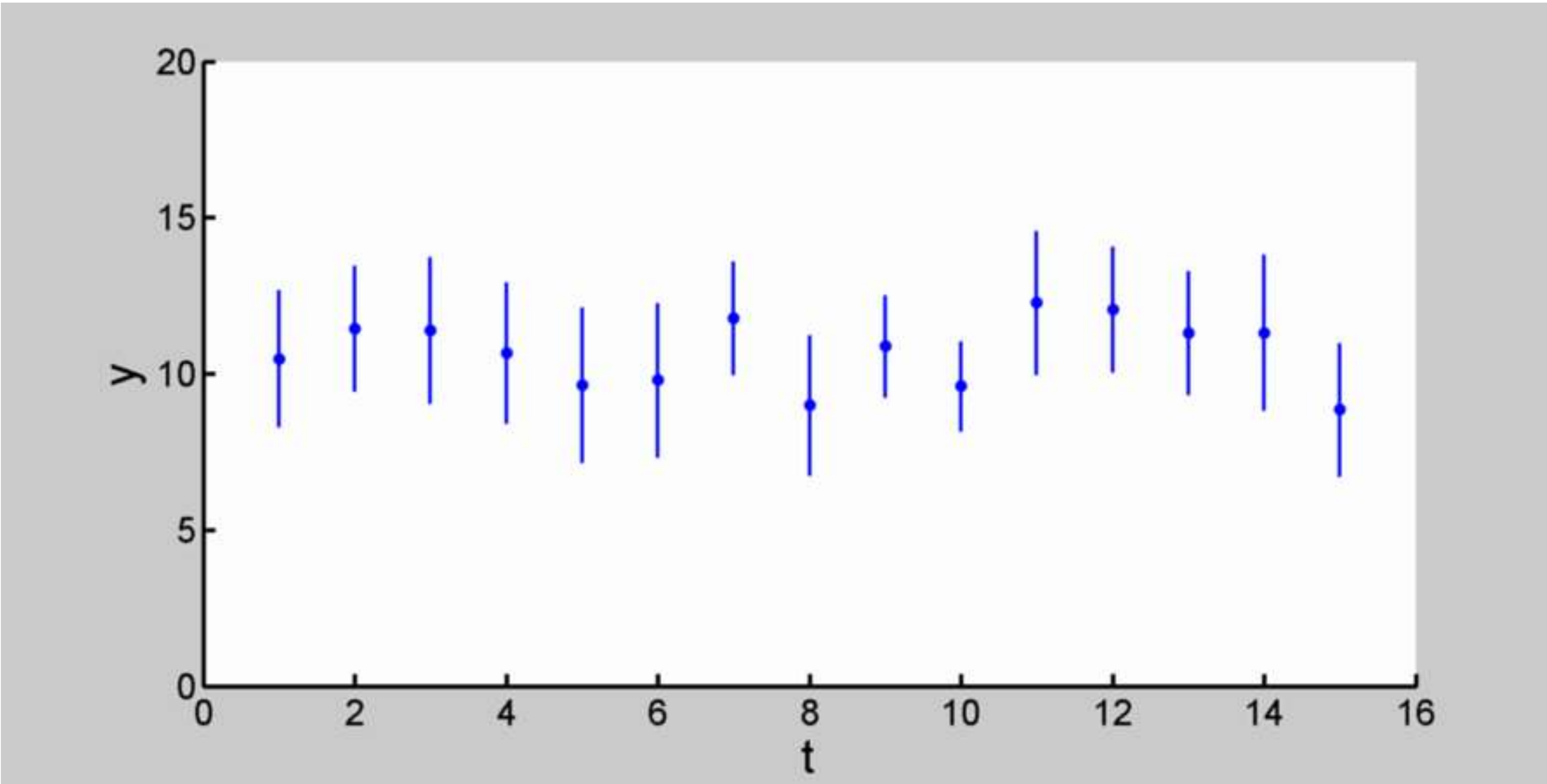
B. Log-ratios of compositional data

- 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

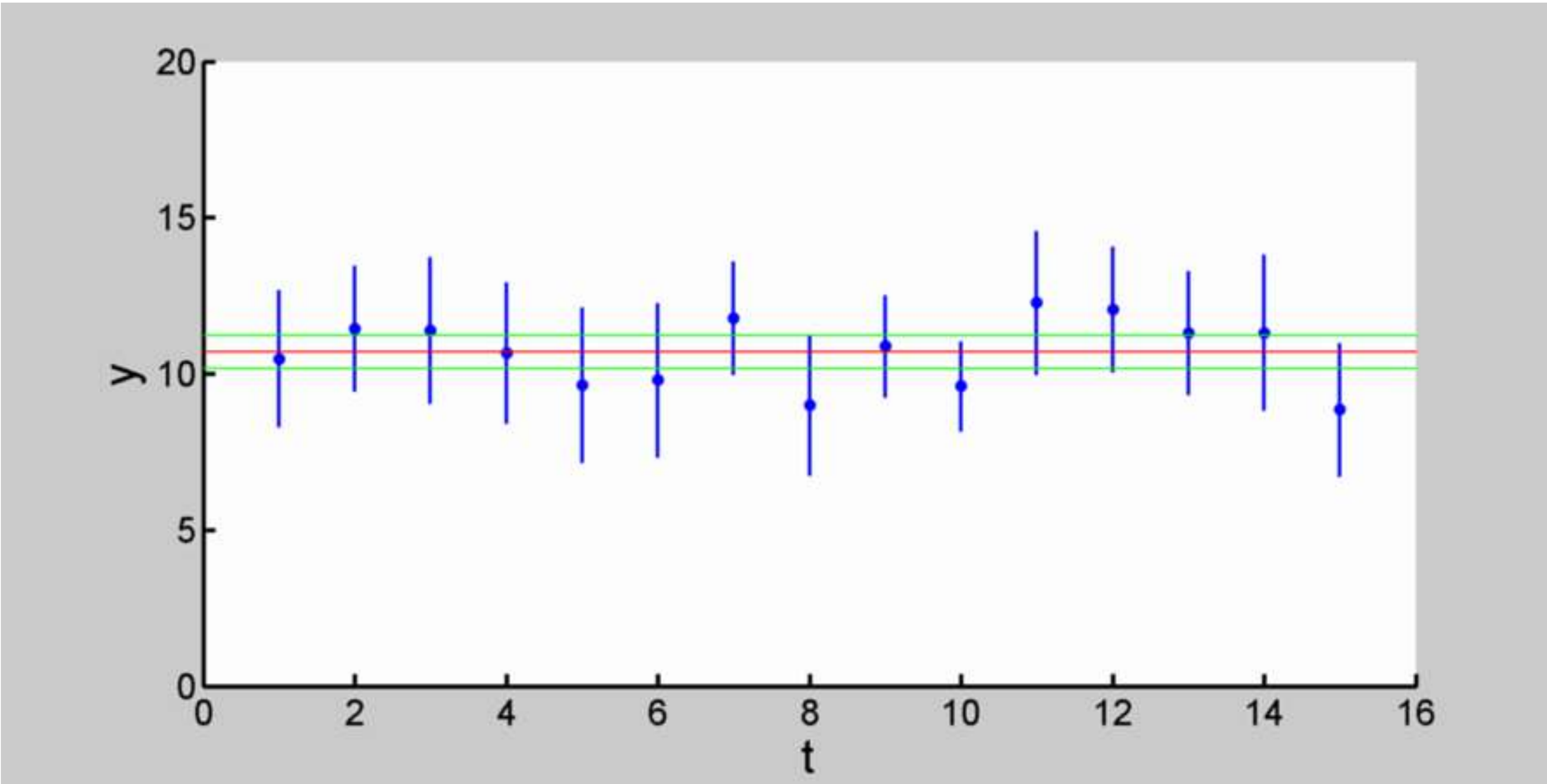
- Not as important for LA-ICP-MS at present, but will become more so as uncertainties continue to come down
- **Dead time**, ion counter non-linearity, gain inter-calibration between detectors.

D. Model Selection



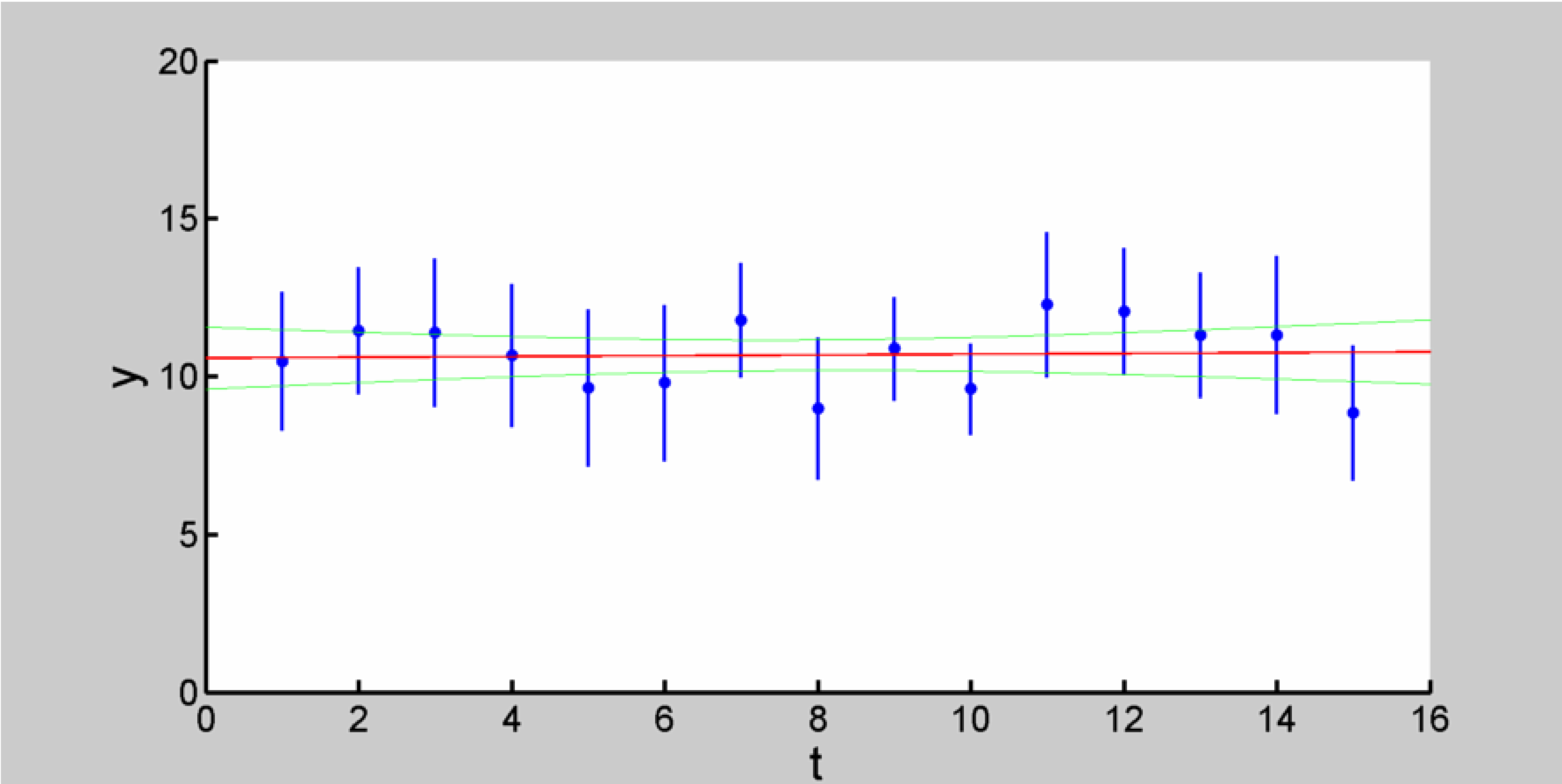
Do these measured data have a trend? Should I use a mean or a linear fit to describe the data?

D. Model Selection



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

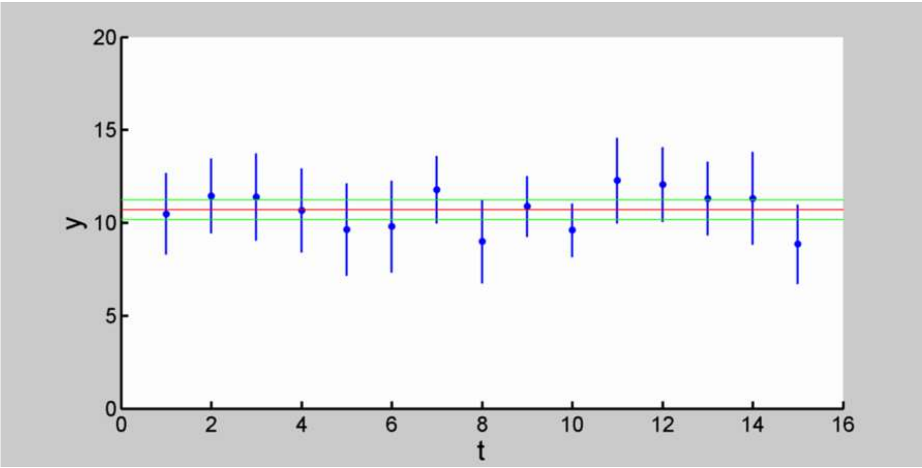
D. Model Selection



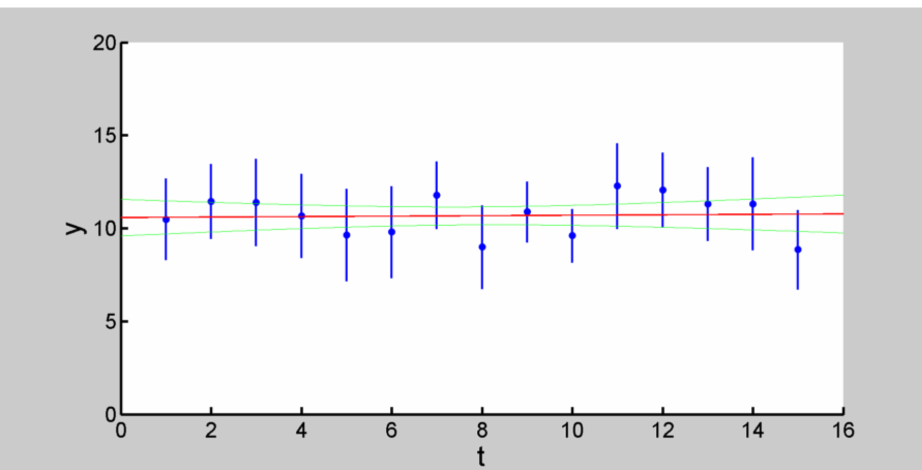
Line fit: $(0.012 \pm 0.11)t + (10.58 \pm 0.98)$, MSWD = 1.13

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

D. Model Selection



Weighted mean:
10.69 ± 0.53 (2σ),
MSWD = 1.38, **BIC = 20.7**

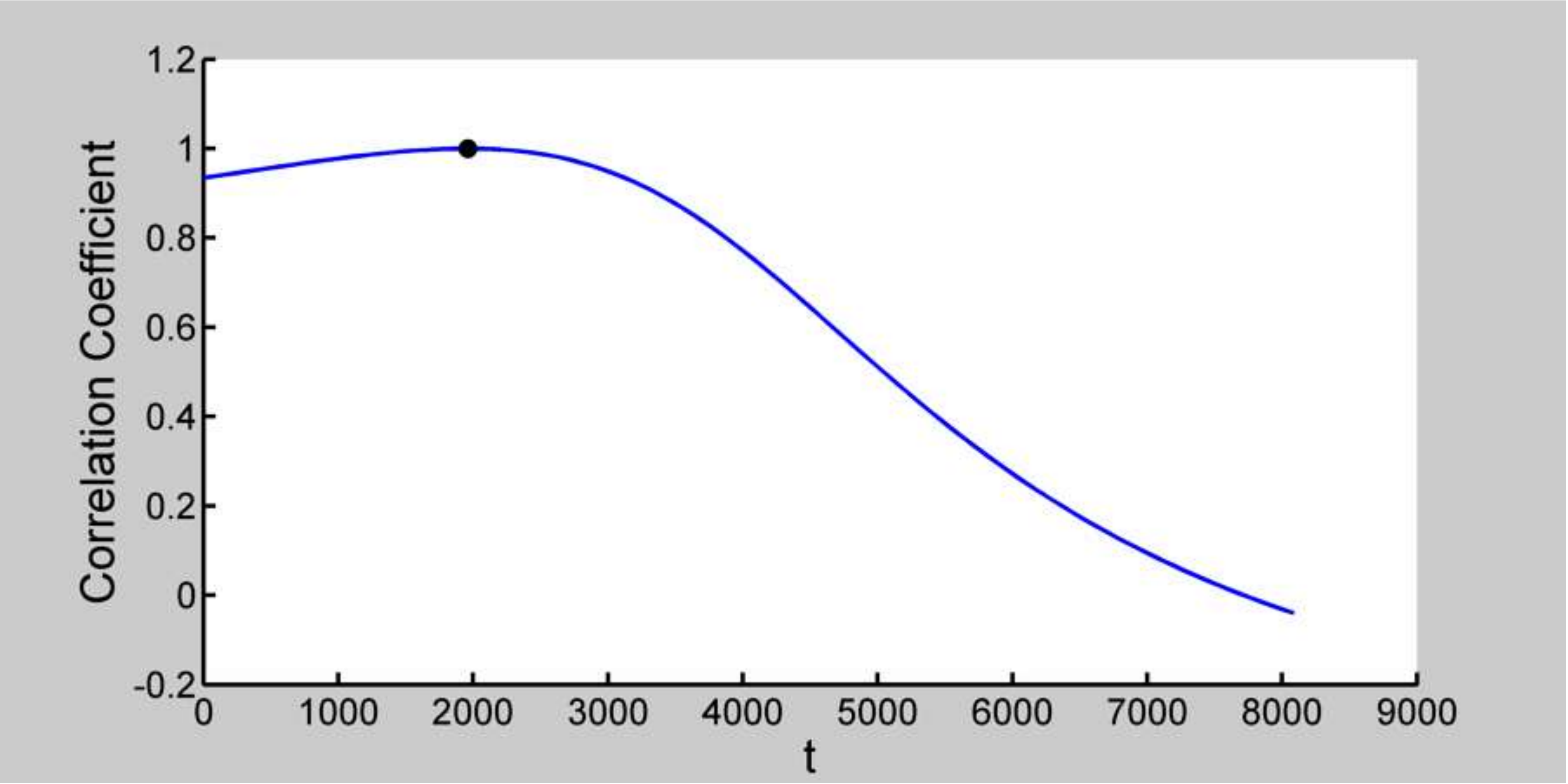


Line fit: (0.012 ± 0.11)*t* +
(10.58 ± 0.98),
MSWD = 1.13, **BIC = 19.9**

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

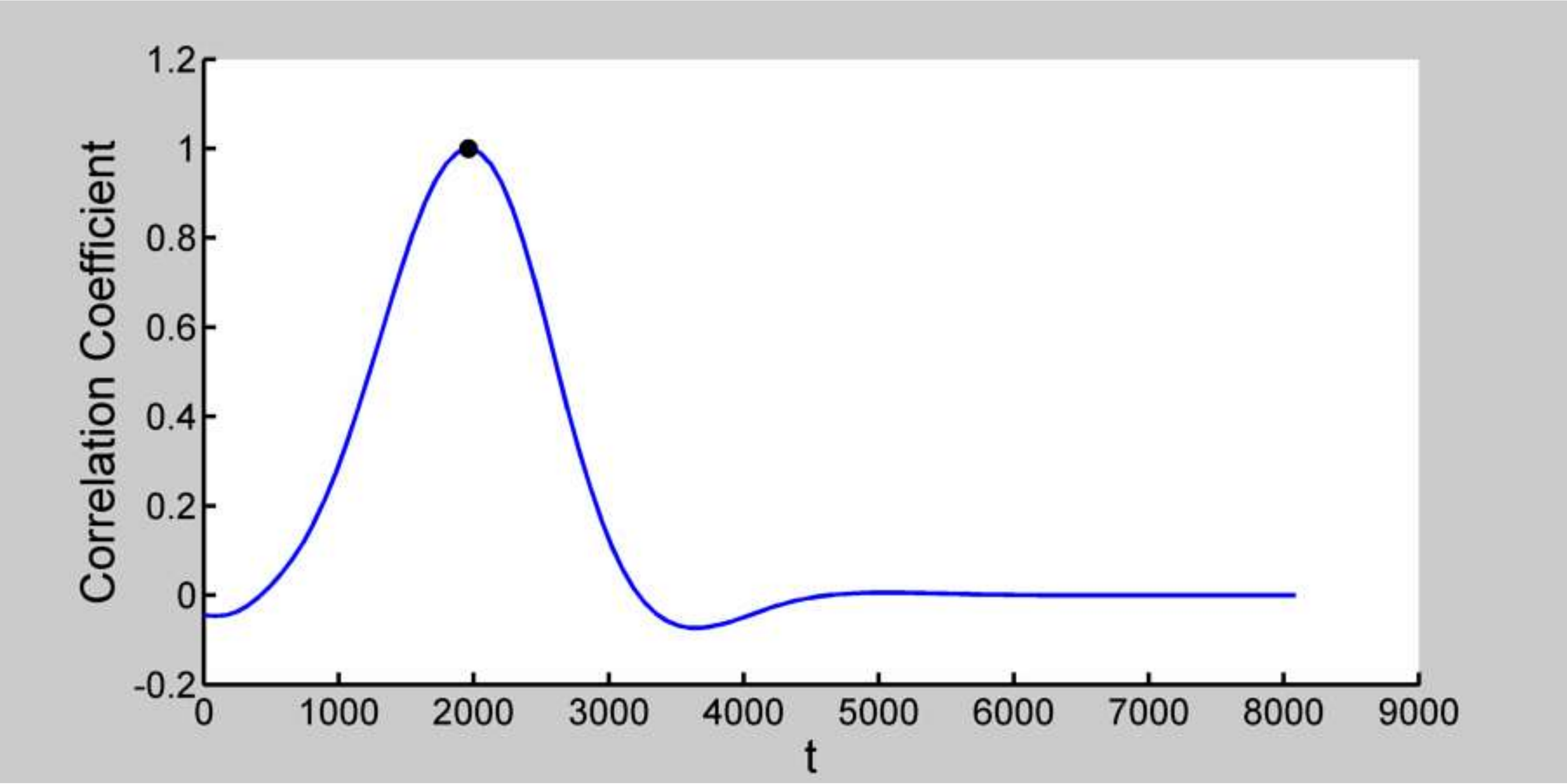
E. Sample-standard bracketing → Unct. correlation between unknowns

Line Fit:

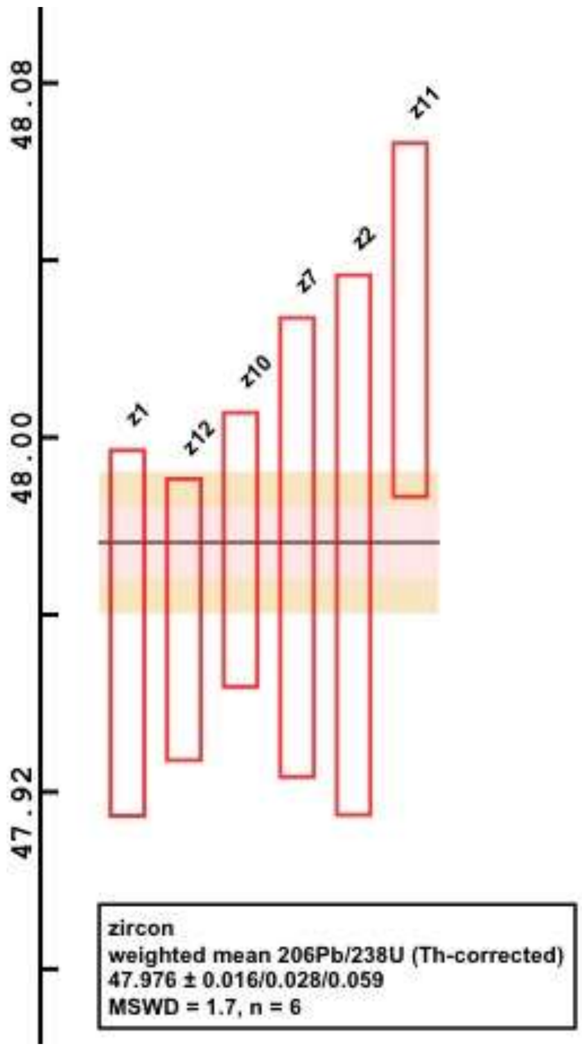


E. Sample-standard bracketing → Unct. correlation between unknowns

Spline Fit:



F. Calculating a weighted mean



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

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

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

Systematic uncertainties are covariance

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

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

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

McLean et al., 2011 (G^3)

Systematic uncertainties are covariance

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

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

$$\alpha = \mathbf{\Sigma}^{-1}\mathbf{1} \Big/ \left(\mathbf{1}^{\mathrm{T}}\mathbf{\Sigma}^{-1}\mathbf{1}\right)$$

McLean et al., 2011 (G^3)

Systematic uncertainties are covariance

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

$$\sigma^2_{\bar{t}} = \begin{bmatrix} \dfrac{d\bar{t}}{dt_1} & \dfrac{d\bar{t}}{dt_2} \end{bmatrix} \begin{bmatrix} \sigma^2_{t_1} & \sigma^2_{t_1 t_2} \\ \sigma^2_{t_1 t_2} & \sigma^2_{t_2} \end{bmatrix} \begin{bmatrix} \dfrac{d\bar{t}}{dt_1} \\ \dfrac{d\bar{t}}{dt_2} \end{bmatrix}$$

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

McLean et al., 2011 (G^3)

Photo courtesy of C. Frank Starmer July 2005

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]

EARTHTIME

calibrating earth history through teamwork & cooperation

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

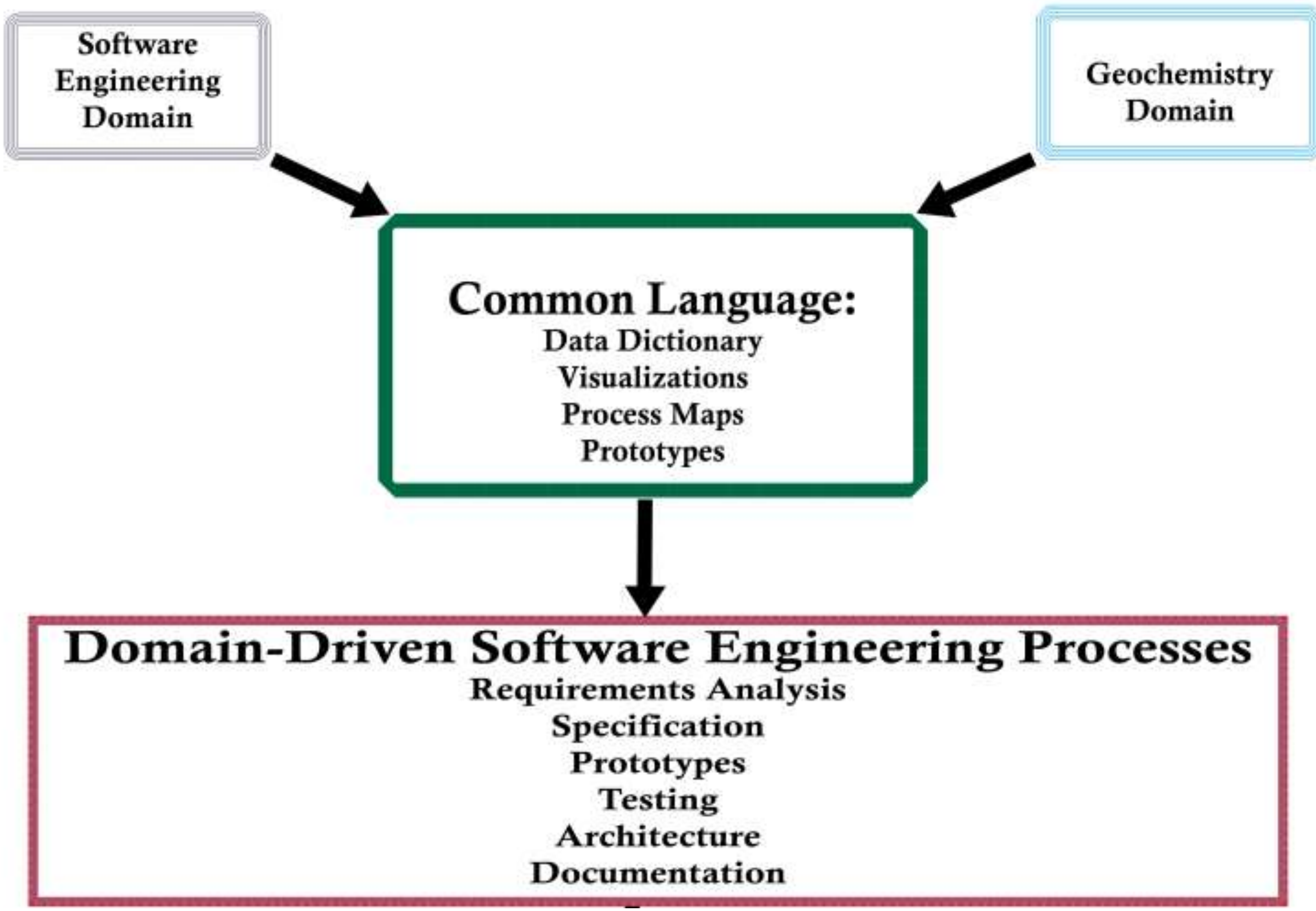
CIRDLES

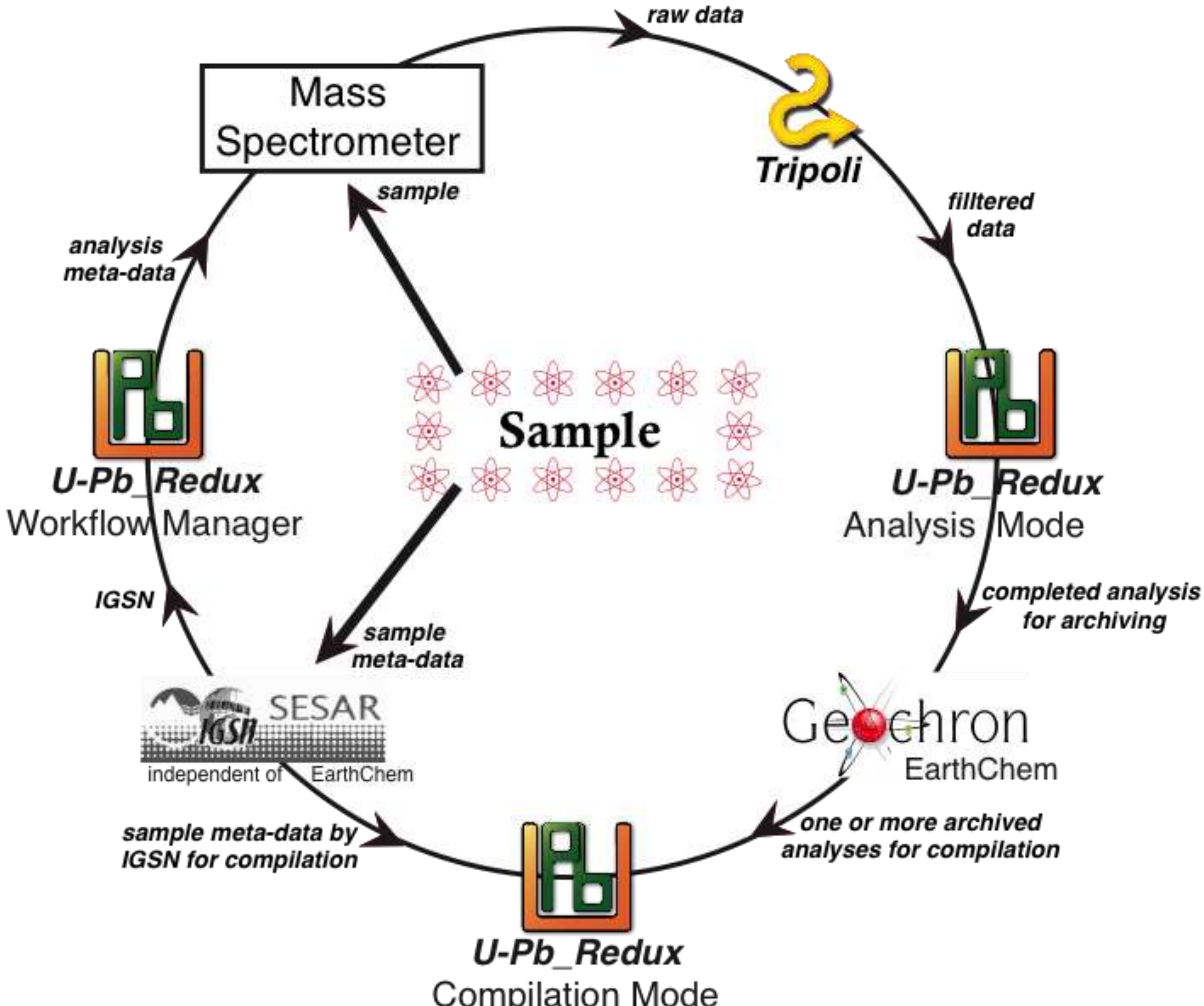
Cyber Infrastructure Research and Development Lab for the Earth Sciences

CIRDLES.org

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

Domain-Driven Development Process




raw data
Mass Spectrometer
Tripoli
filltered data
sample
analysis meta-data
Sample
U-Pb_Redux
Workflow Manager
U-Pb_Redux
Analysis Mode
completed analysis for archiving
IGSN
sample meta-data
SESAR
IGSN
independent of EarthChem
Geochron
EarthChem
one or more archived analyses for compilation
sample meta-data by IGSN for compilation
U-Pb_Redux
Compilation Mode

Questions ?