

Better Living Through Theoretical Mass Spectrometry: Tripoli

Noah McLean,¹ Scott Burdick,² and Jim Bowring³

1. University of Kansas
2. Wayne State University
3. College of Charleston



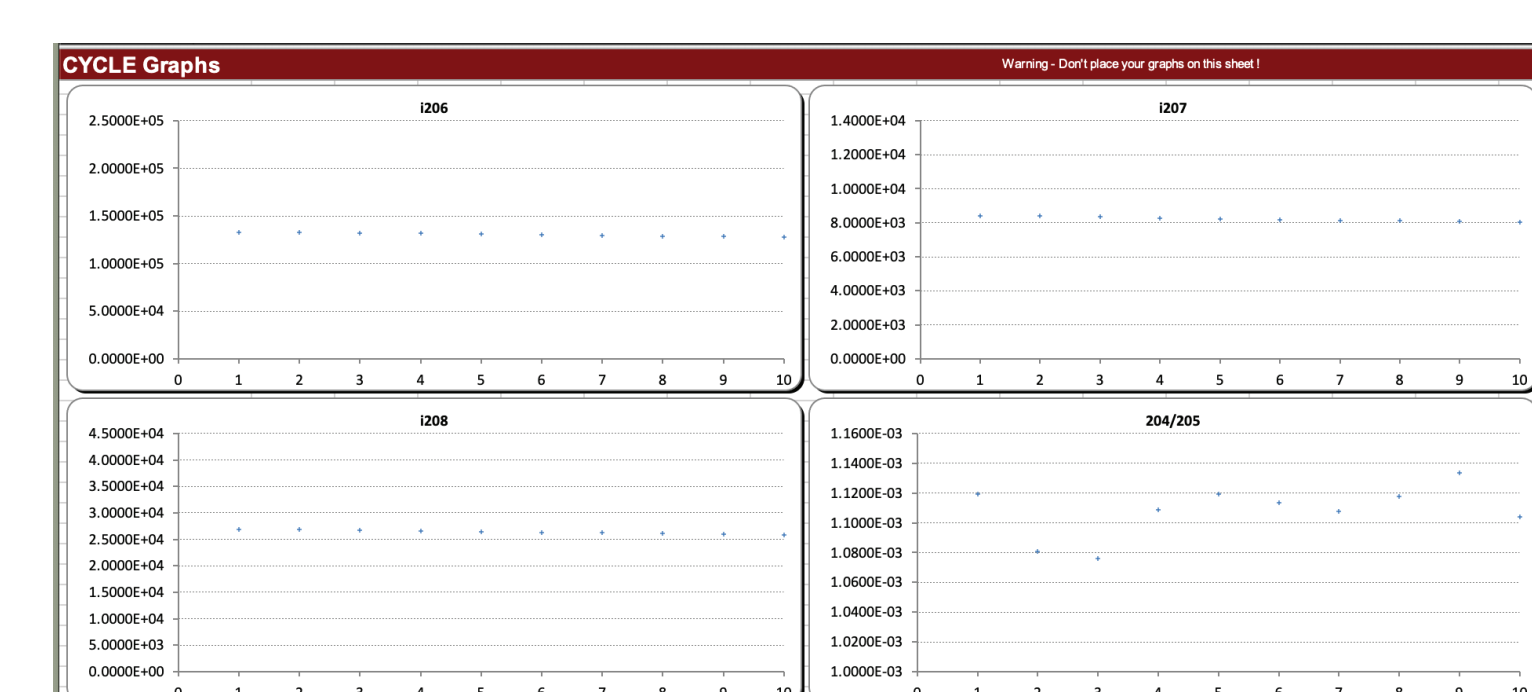
The Problem:

Multicollector mass spectrometers (TIMS and MC-ICPMS) have seen advances in electronics and components. **Statistical interpretation of mass spectrometer data** has not kept pace:

- Baselines uncertainties are often neglected.
- Beam interpolation algorithms underestimate uncertainties.
- Multicollector data is sometimes ignored.

Mass spectrometer data is rich and complex, ripe for **interactive visualizations** to lend insight to even routine workflows.

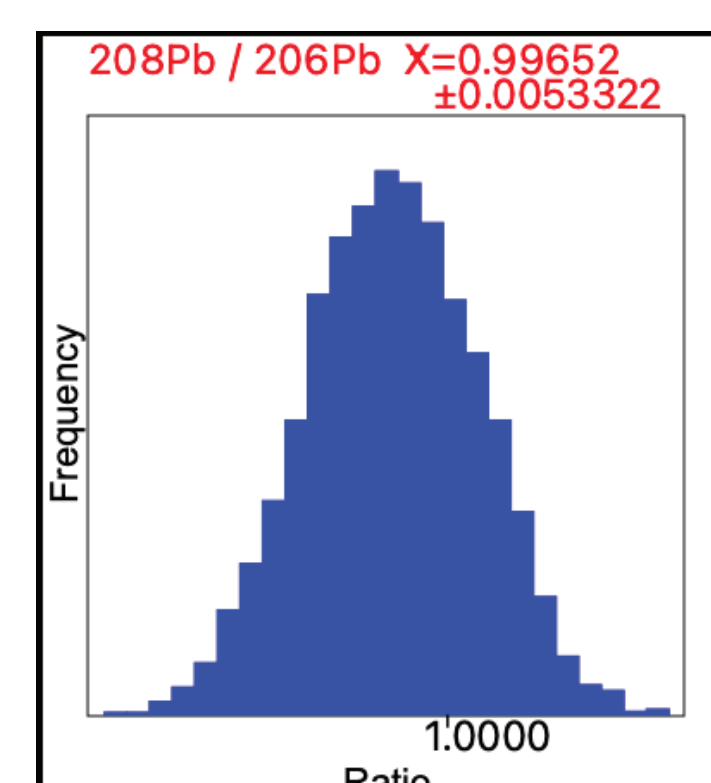
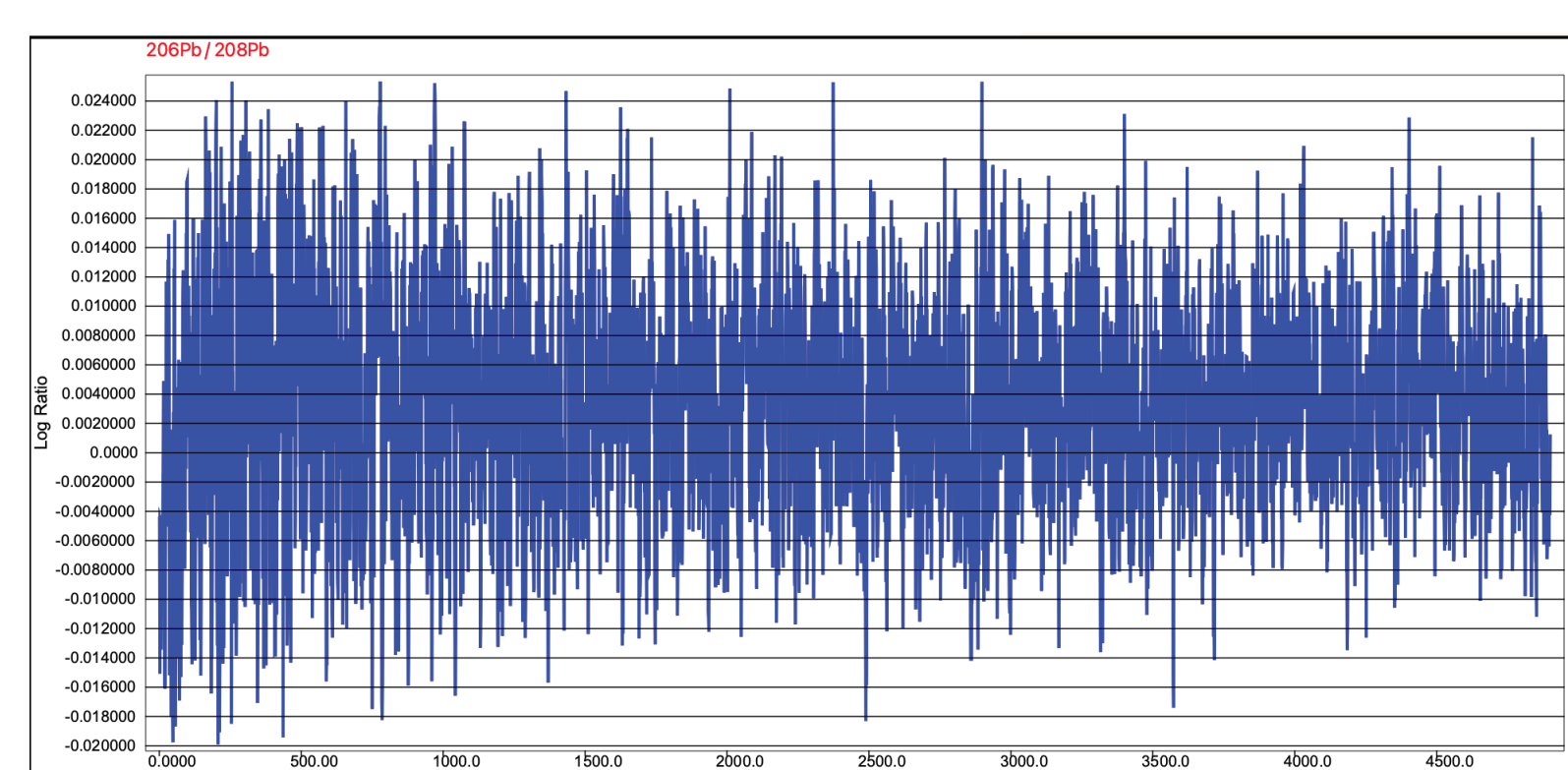
Finally measuring isotope ratios is just one step in a geochronology workflow, and **flexible output formats** need to communicate relevant data and metadata.



Mass spec software often leaves detailed data inspection and visualization up to the user. User workflows are often ad hoc and there's no documentation of the analytical choices made.

The Approach:

1. Handle the raw data output from the mass spectrometer as much as possible: parse method and raw data files (intensities with time stamps).
2. Use a combination of (quick, frequentist) maximum likelihood and (slower, Bayesian) Markov Chain Monte Carlo techniques to treat the mass spectrometer's collectors like a seismic network. Invert raw data for parameters (isotope ratios) of interest.
3. Visualize the results interactively to give the user better insight and control over the data.
4. Use synthetic data to test all of the above. Synthetic datasets are now publicly available!

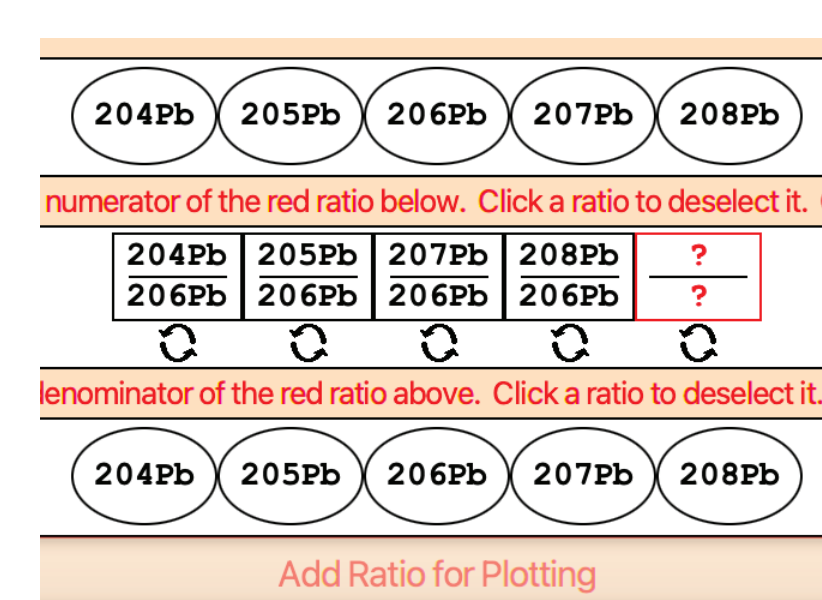


Markov Chain Monte Carlo outputs in Tripoli. The MCMC chain at left shows convergence after ~5000 saved iterations, and a histogram of samples illustrates the posterior distribution (uncertainty) of the measured ²⁰⁸Pb/²⁰⁶Pb ratio.

Early Workflows and Screenshots:

Method	Detector	Baseline	Sequence	Table	Select	Ratio	Plot
GPS	208Pb	206Pb	L3	L4	L3	L2	Av
GPS	208Pb	206Pb	L3	L4	L3	L2	Av
GPS	208Pb	206Pb	L3	L4	L3	L2	Av
GPS	208Pb	206Pb	L3	L4	L3	L2	Av

Loading in a method file means that Tripoli knows which isotope is on each collector at all times. Therefore Tripoli can control corrections for baselines and relative gains and propagate relevant uncertainties.



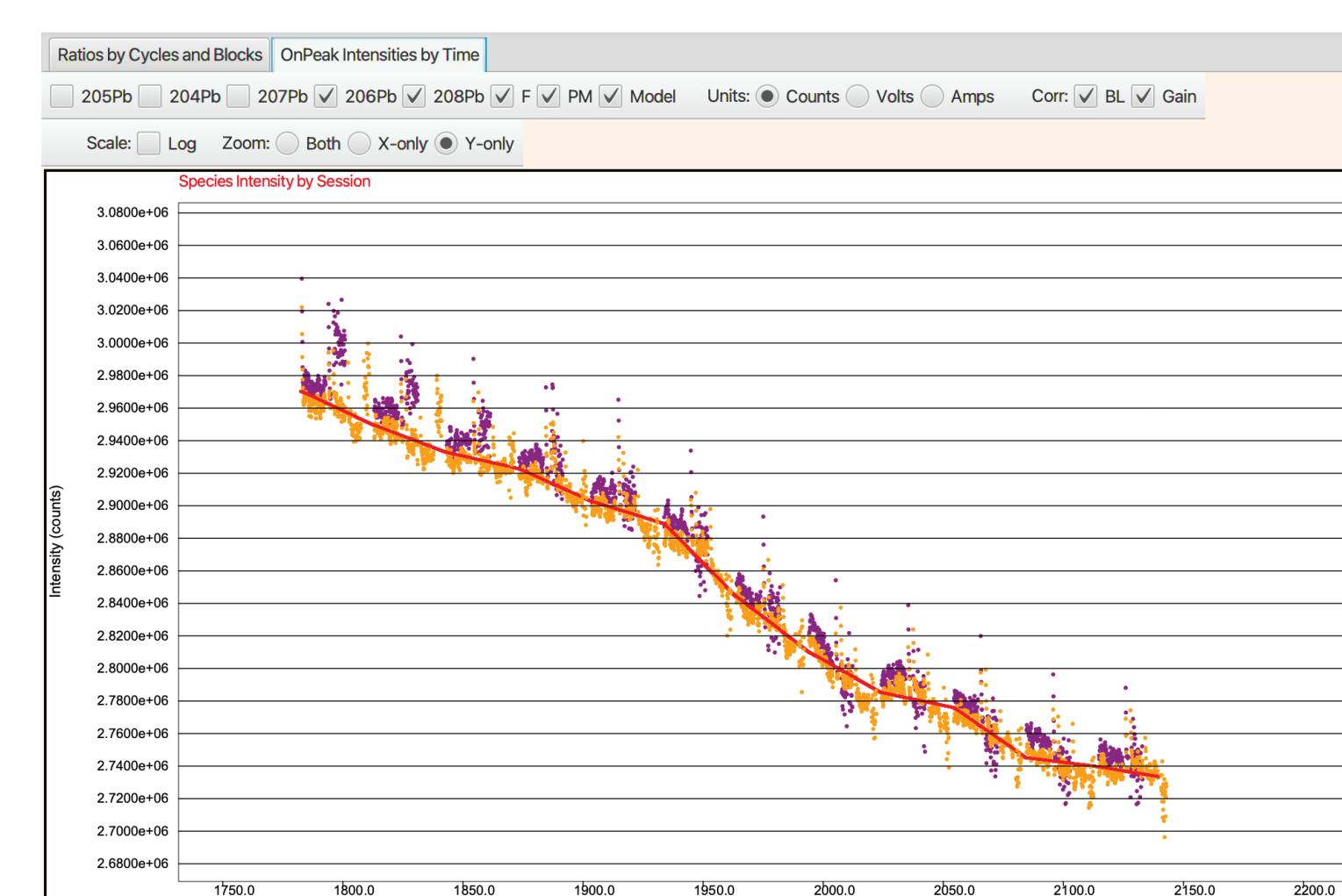
Method files contain a record of all species being measured, meaning you can pick which ratios you want to visualize, plot, and output, even after the analysis is complete.



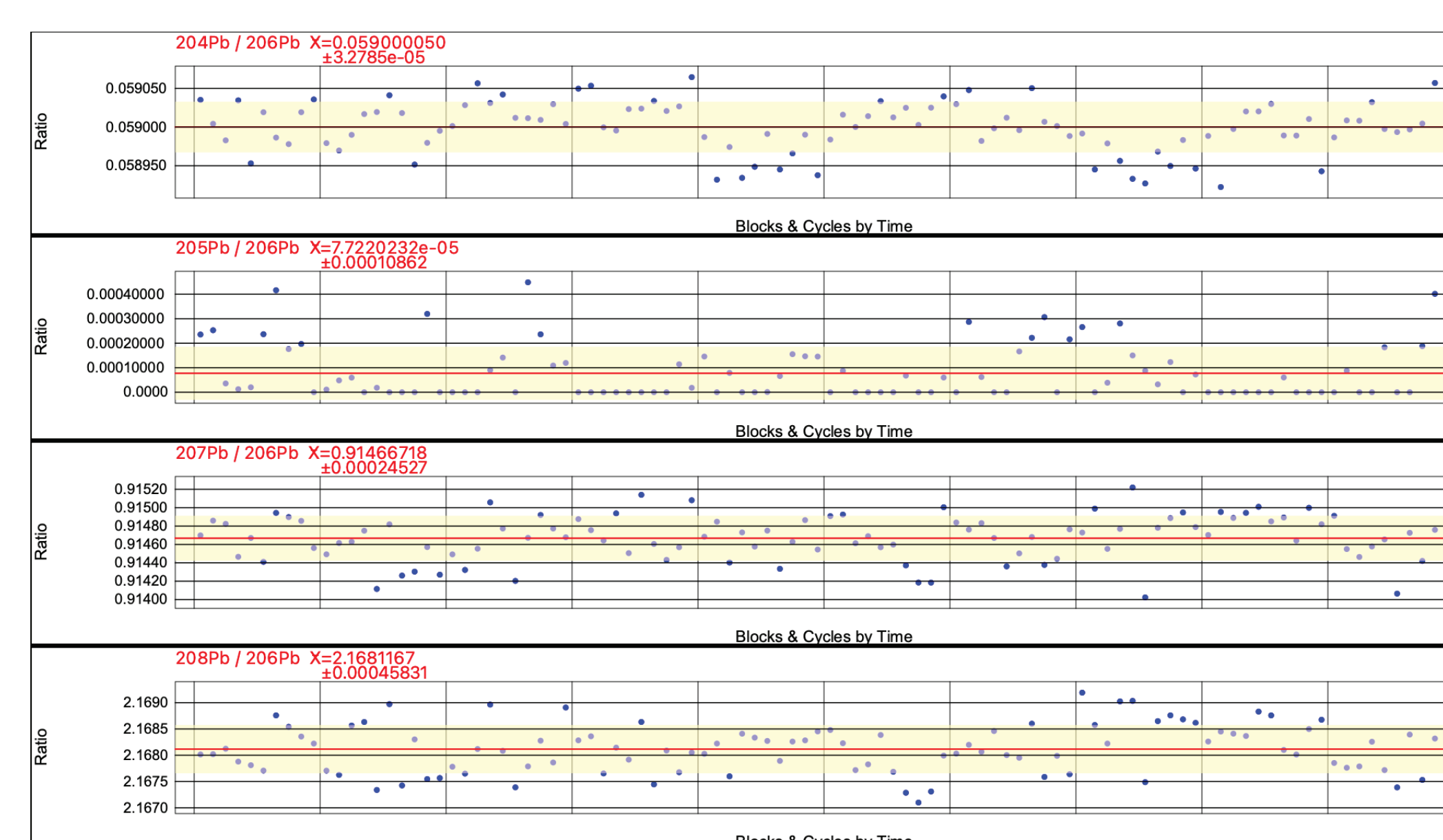
Reading in raw data can yield highly time-resolved data for measurements with short integration times. This helps estimate data uncertainties based on measured scatter.

Markov Chain Monte Carlo outputs in Tripoli. The MCMC chain at left shows convergence after ~5000 saved iterations, and a histogram of samples illustrates the posterior distribution (uncertainty) of the measured ²⁰⁸Pb/²⁰⁶Pb ratio.

Placing the Faraday detectors in line with ion beams that are not on the Daly yields a richer history of the intensity fluctuations and theoretically more precise beam interpolation.



A block of NBS982 Pb data, with ²⁰⁸Pb data in yellow and ²⁰⁶Pb data in purple. Additional, higher-noise data are from Faraday detectors. The excursions here indicate a too-short magnet settling time during some sequences (the peak shape was terrible too). Check out the demo for our new peak shapes visualization!



Once an intensity function is fit (by quick least squares or by MCMC methods), you can plot familiar cycle-by-cycle ratios and include/exclude data by block or cycle. Data inspection and rejection happens before and/or after the MCMC fit.

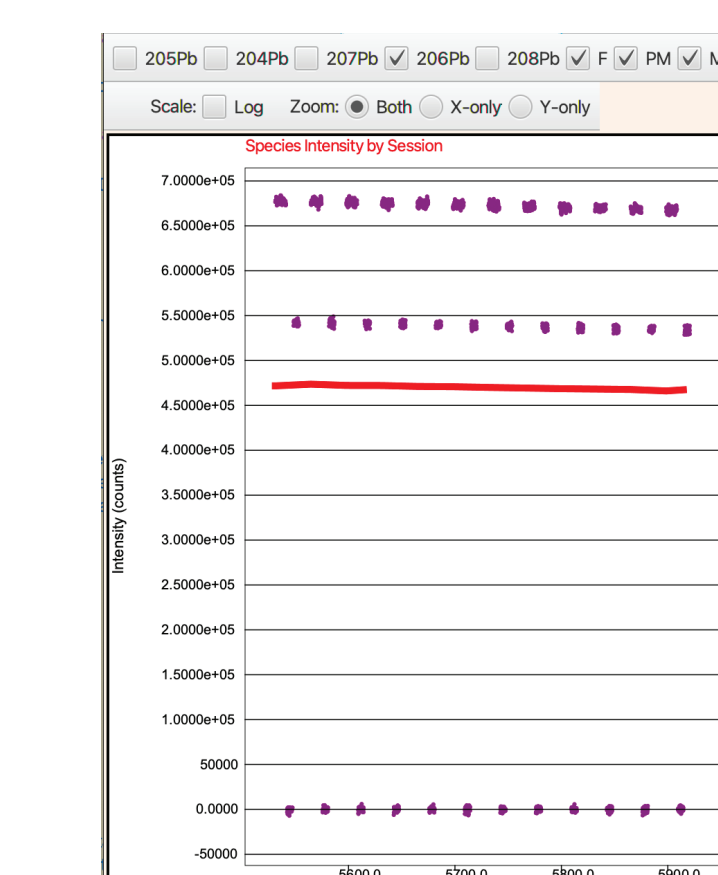
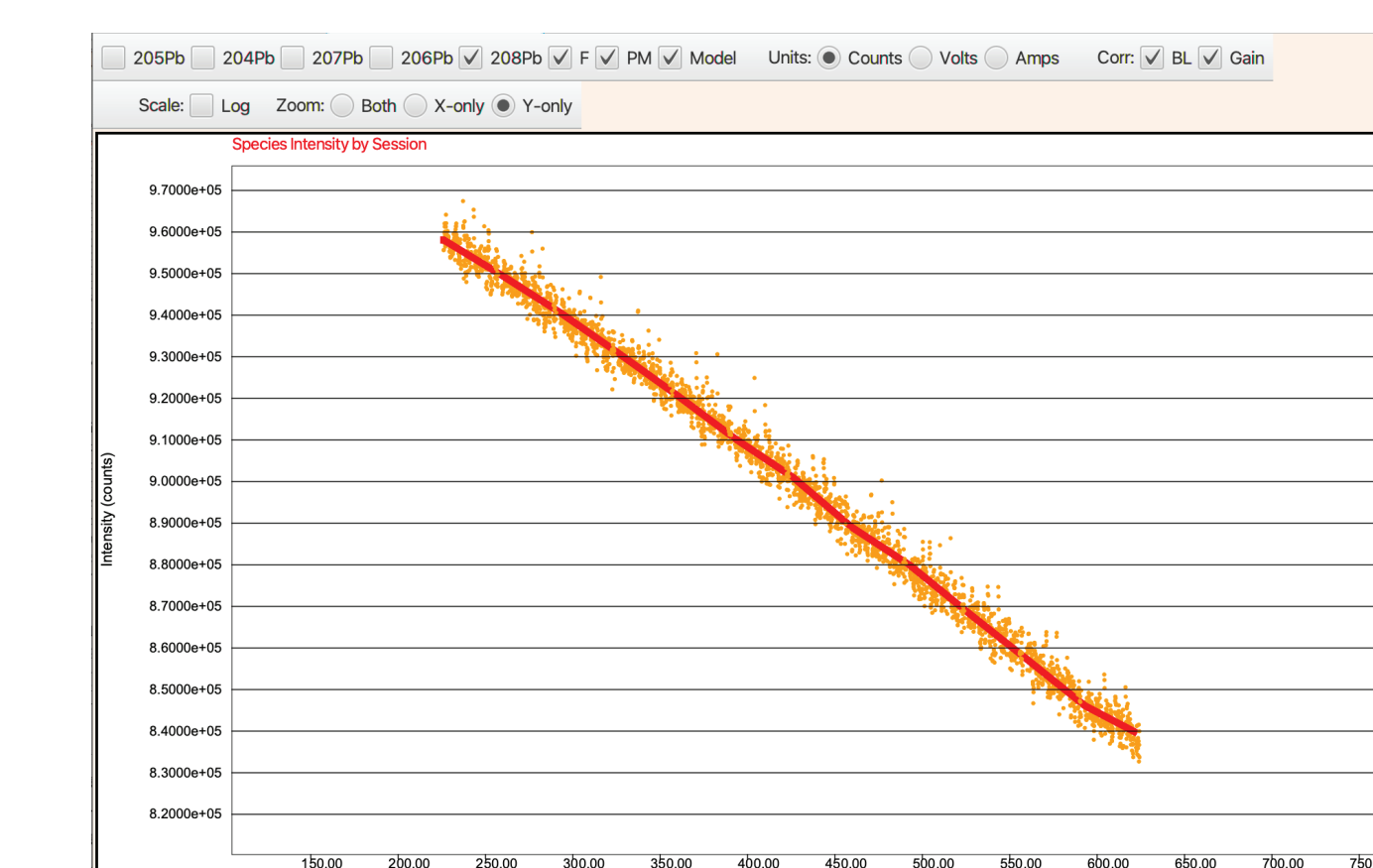
Lessons Learned:

Successes:

- MCMC approaches can be parallelized successfully to work on data from many blocks at the same time, reducing the time from data import to inspection.
- Initial tests show synthetic data results are accurate and precise (e.g., left, c.f., below).

Failures/Still Working On:

- Hierarchical models (estimating uncertainty in the data from its scatter around the model) is hard---there are tradeoffs among isotope ratios, baselines, and gains.
- Reversible Jump MCMC is also hard, but may be worthwhile for intensity functions.
- We have not yet compared our (freshly implemented) MCMC algorithms against standard practice on a range of synthetic datasets.



At left, a success: a simple ²⁰⁸Pb ion beam intensity changing with time, correctly modeled (red line) for beam interpolation. Knowing how the beam changes allows Tripoli to accurately calculate isotope ratios through time when beams are measured on different collectors at different times.

At right, a failure: a ²⁰⁶Pb ion beam (Daly on top, Faraday on bottom) corrected with the wrong gain, resulting in a model (red line) that doesn't fit the data.

Future Development, Ideas:

1. Add more mass spectrometer makes/models. We want your data! It doesn't matter what isotope system and it doesn't have to be perfect. Contact Noah at noahmc@ku.edu.
2. Visualization: Offer more visualization options (e.g., ratio vs. ratio plots), improve navigation of existing plots (they're brand new---try them out with a demo!)
3. Add multiple analyses to a session---useful for sample/standard bracketing, tracking long-term behavior of reference materials, or IC/ID pairs.
4. Add time series for baseline, isobaric interference, relative gains, isotopic fractionation/mass bias, peak tails, etc., all to make accurate and traceable corrections to isotope ratio measurements.

Get Involved:



GitHub
Repository



Tripoli
Homepage