Project Summary: New mass spectrometer technology, like linear ion counters (Noble et al., 2006; Richter et al., 2009), high-resistance amplifiers (Koornneef et al., 2014; von Quadt et al., 2016), and large-capacity vacuum pumping systems (e.g., Neptune+) have dramatically improved the precision of isotopic analyses and opened up the periodic table to new isotope systems. At the same time, sophisticated statistical data reduction and visualization software have improved the way we interpret isotope data in a scientific context (e.g., Bowring et al., 2011; McLean et al., 2011, 2016). These advances highlight the need for improving how we connect these two endpoints, starting with the raw intensity measurements output from the mass spectrometer and ending with the best possible estimates of the relative abundances of isotopes and their uncertainties.

Existing mass spectrometer software is not user-interactive and is statistically unsound in multiple ways, which we show often produces inaccurate results. For single collector isotope ratio measurements of low-abundance isotopes, existing software underestimates uncertainties (Ludwig, 2009). The next generation of algorithms should harness more available data, and the next generation of software should present real-time interactive visualizations.

We propose to expand the statistical toolbox isotope geochemists use to interpret high precision mass spectrometer data, which can then be output to any isotope-system-specific data reduction protocol. This includes integration of existing techniques, like log-ratio data analysis (e.g., McLean et al., 2016), highly cited algorithms new to isotope geochemistry, like the E-M algorithm for handling rejected data (Dempster et al., 1977), and methods for Bayesian inference recently adapted for geophysical problems, like reversible-jump Markov Chain and Adaptive Monte Carlo methods. Together, these can provide the next step in improving mass spectrometer precision and accuracy without costly instrument development. It is critical to encapsulate these algorithms into new robust open-source software with dynamic user interfaces that support new and existing scientific workflows. We also intend to develop open libraries for statistical analysis of mass spectrometer data and a new UI for interactive data visualization.

Intellectual Merit: The proposed work will systematically advance isotope geochemistry and geochronology with collaborations among earth scientists and software engineers. Our cyberinfrastructure ecosystem comprises open source sustainable software that supports workflows from field to archive. The three PIs are uniquely qualified to pursue this research. Bowring and McLean have a fifteen-year history of collaborating on the development of widely-used software Tripoli and ET_Redux for U-Pb geochronology by TIMS and LA-ICPMS. Bowring has been lead developer for 5 years of the Squid3 SHRIMP data reduction software for Geoscience Australia. PI Burdick brings expertise in inverse theory and experience developing Bayesian methods for seismic analysis. The proposed work will address the sustainability of software for science and innovate solutions, including introducing students to the importance of integrated teaching, research, and development.

Broader impacts: This proposal embodies key broader impacts criteria: (1) enhancing infrastructure for research through developing a new open source software tool, Tripoli, with synthetic data-sets for testing; (2) disseminating results broadly to enhance scientific understanding via two papers, a workshop, and an online training workshop; (3) promoting teaching, training, and learning while broadening the participation of underrepresented groups by providing trans-disciplinary undergraduate research opportunities and incorporating the new techniques into coursework. Burdick is an early career researcher, McLean mentors graduate researchers, and Bowring mentors undergraduate researchers, with a record of recruiting through the NSF-funded South Carolina Alliance for Minority Participation; and (4) clear benefits to society by developing and practicing software-sustainability regimens to protect the public's investment in this and other software development research projects.

Data Management Plan

Overview

In accordance with NSF philosophy and policy for the Dissemination and Sharing of Research Results, the PIs are committed to open and persistent access to data, services, documents, and software. The primary products of this research will be 1) software code including design documents, maintenance plans, test plans, user manuals, and development guidelines; 2) synthetic data sets developed for testing; 3) academic publications detailing the developed methodology and software as well as publications describing our sustainability efforts; and 4) video training materials. The software and other materials will be licensed under the Apache Software Foundation License version 2.0. The PIs are responsible for implementing this data plan and for ensuring its sustainability after the three years of this proposal. As part of the dissemination plan, the PIs will publicize the location of these repositories at professional meetings, and online at CIRDLES.org. The digital files for videos will be less than 100 gigabytes, and the volume of all data will be less than 10 gigabytes.

Data Product #1

Data type: Software System

Description: The PIs will maintain version-controlled repositories using "Git" at GitHub.com (or similar if GitHub were to one day become unavailable) of the software artifacts, including code, executables, design documents, maintenance plans, test plans, digital user manuals, and development guidelines produced during this research. These software products include the developed cyberinfrastructure and tools to assist with continuous improvement and sustainability.

Design documents, maintenance plans, test plans, and user manuals will be version-controlled using "Git" and published and maintained on the wiki for the Tripoli repository, providing a direct link between code and documentation.

Preservation plan: The PIs will use the no-cost academic license and storage of GitHub.com or similar to preserve and maintain these artifacts in the public domain. The PIs will also maintain backups of this repository on University of Kansas Research File Storage servers, which are in turn backed up to a remote location by University personnel.

Timeline for release: Continuous and immediate.

Data Product #2

Data type: Synthetic data

Description: Synthetic data and the software tools used to manage it produced during this research will support continuous testing of the software and be managed with version-controlled repositories at GitHub.com or similar. Synthetic datasets will be provided as delimited text files with a standard format compatible with the measured data file formats of the three major mass spectrometer companies. This will facilitate end-to-end testing of Tripoli algorithms, as well as easy comparison with existing and future mass spectrometer data reduction efforts. Additional documentation for synthetic datasets include the code used to create them (with 'true' values of measurement parameters like mean isotopic ratios, mass bias for internally normalized samples, collector gains, etc, and their statistical distributions), so that synthetic datasets can be reproduced and generalized. Full documentation and rich metadata will accompany the synthetic datasets.

Preservation plan: The PIs will use the no-cost academic license and storage of GitHub.com to preserve and maintain these artifacts in the public domain. The PIs will also maintain backups of

this repository on University of Kansas Research File Storage servers, which are in turn backed up to a remote location by KU personnel.

Timeline for release: Continuous and immediate.

Data Product #3

Data type: Academic publications

Description: Academic publications detailing the developed methodology and software, as well as publications describing our sustainability efforts.

Preservation plan: Open access pre-prints will be archived on the EarthArXiv server. Publishers will preserve typeset, publication versions of manuscripts.

Timeline for release: Upon publication.

Data Product #4

Data type: Video training materials

Description: The authors will record training videos demonstrating the use of Tripoli. We plan two series of videos. The first, led by PI McLean, will be a course in statistics as applied to mass spectrometry data, with an emphasis on how technical principles of mass spectrometry yield interpretable data patterns. The second series, led by PI Bowring, will provide end-to-end instruction in Tripoli workflows, customization, and options. Hyperlinks to training videos will be embedded in online software documentation and updated regularly during the software development process.

Preservation Plan: Videos will be uploaded to YouTube for public dissemination and comment, and all digital video files will be backed up on University of Kansas Research File Storage servers, which are in turn backed up to a remote location by KU personnel.

Timeline for release: Continuous and immediate.

Collaborative Research: Catalytic Track: Improving Accuracy and Efficiency of Multicollector Mass Spectrometry

1 Introduction

Mass spectrometry, the separation of atoms or molecules by mass, is used in geochemistry for a broad spectrum of applications. For instance, organic geochemists use mass spectrometry in tandem with gas/liquid chromatography (GC/LC-MS) to separate complex molecules by size, shape, and polarity, then use mass spectrometry to precisely analyze the outputs — or their breakdown products — by mass. Hydrologists, mantle geochemists, and geochronologists interested in noble gases interpret the time-dependent evolution of gases ionized and pumped from the source to the analyzer in gas-source mass spectrometer to measure abundances and isotope ratios. Geochemists working at small spatial scales can route aerosols created during laser ablation to inductively coupled plasma mass spectrometers for high-throughput analyses of trace elements and isotopes. These complex, time-dependent processes require sophisticated software to perform the calculations needed for data interpretation (e.g., Ross and McIntosh, 2012; McLean et al., 2016).

However, there are large segments of the geoscience mass spectrometer user community for whom no such software exists. These segments use methods with much slower time-dependent behavior, and the goal is to measure and interpret relatively stable mean isotope ratios and uncertainties. Prime examples include thermal ionization mass spectrometry (TIMS) and solution multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), both typically producing the highest precision isotope ratio data in geochemistry. Users rely on manufacturer-supplied software to transform measured instrumental parameters such as voltages and ion arrival rates into the isotope ratios that are interpreted in the service of science.

Due to the high precision that TIMS and solution MC-ICPMS can achieve, their use spans a broad spectrum of Earth Science applications. TIMS is the go-to tool for many 'traditional' stable and radiogenic isotope systems, including Sr, Nd, Pb, and Os, as well as popular high-precision geochronometers such as Rb-Sr, Sm-Nd, and U-Pb. U-Pb is the 'gold standard' for geochronology and underpins much of the geologic timescale. A partial list of other applications for just Sr includes using radiogenic Sr isotopic analysis to explore the chemical evolution of igneous processes, to correlate marine sections using Sr isotope stratigraphy, and to examine migratory patterns in animals with teeth, while the relatively new field of stable Sr isotopes has applications in hydrology (Neymark et al., 2014), archaeology (Knudson et al., 2010), and oceanography. Game-changing developments in MC-ICPMS instrumentation over the last decade have dramatically improved analytical precision and opened up much of the remaining periodic table of 'non-traditional stable isotopes.' Applications include exploring the physical and reaction pathways of fundamental earth processes, such as contaminant transport and fate, biogeochemical cycling in the critical zone, ore-body evolution, and subduction zone geochemical cycling at active plate margins and arc volcanoes (e.g., see reviews in Teng et al., 2017).

Therefore, despite occupying a small corner of the mass spectrometer user community, TIMS and solution MC-ICPMS applications address a broad range of fundamental and cutting-edge Earth Science undertakings. We show here that improved data handling will result in more precise and accurate output data, potentially reducing analytical times and increasing laboratory throughput.

2 Motivation

The central issue this proposal addresses is that mass spectrometer manufacturer companies provide few if any software tools for 1) reviewing, visualizing, and interacting with raw data; and 2) for accurately interpreting the measured data using modern statistical best practices to produce isotopic ratios. This means that data reduction tools don't receive the best data available from the mass spectrometer. **Improving the way all users interact with and interpret TIMS and MC-ICPMS data will improve the science of an entire international user community.**

The current state of the art is that older mass spectrometers — for instance the Sector 54 TIMS — measure isotope ratios but do not provide software to plot or interact with data. Outputs are text files with block and cycle data, displayed onscreen during measurement but without graphical support. The newest generation of mass spectrometers — the Isotopx Phoenix, Thermo Triton, and a new Nu for TIMS, as well as the Thermo Neptune and Nu Plasma (2 and 3) for ICP-MS — provide limited, non-interactive data visualization tools such as, for example, simple scatter plots of measured ratio vs. time with basic statistics that update during the run. However, it's impossible to visualize baseline data or to plot the correlation of two ratios as a diagnostic of isobaric interferences, isotopic fractionation, or simply counting (Poisson) statistics (see Sec. 2.1).

For statistical analysis, all generations of instruments have software that performs routine raw data reduction: baseline subtraction, automated (e.g., 2σ) outlier rejection, and arithmetic mean and standard error calculation. Unfortunately, and surprisingly, all of these practices are statistically dubious: baseline subtraction is a systematic error whose effect must be propagated into all data points that share a common baseline before evaluating their mean. Evaluating the arithmetic mean of compositional data like isotope ratios is statistically unsound. A 2σ outlier rejection protocol rejects many valid points, significantly degrading accuracy and precision, simultaneously making the calculated mean less accurate and underestimating its uncertainty. Finally, beam interpolation, one of the basic algorithms that especially thermal ionization mass spectrometers use to calculate ratios and uncertainties for single-collector data, is fundamentally flawed.

Below, we describe the novel solutions that our new software, Tripoli (replacing the current Tripoli), will implement to address the shortcomings of existing software.

2.1 Interactive visualizations – TIMS and solution MC-ICPMS

A key component of Tripoli will be its interactive data visualizations, provided both in real-time and post-analysis. The visualizations will support both the high-quality interpretation of the measured data and clear explanations of the resulting analyses in a number of ways. We will design toward the entire spectrum of mass spectrometer users, from beginner to expert, thereby assisting advancement along this spectrum. For example, on-demand interactive data visualizations can aid analysts' choices about when to increase the filament temperature on a TIMS, to dilute or concentrate a solution on ICPMS, and when to abort an analysis. These choices might reflect obtaining adequate analytical precision or reflect diagnosis of a data trend, like an isobaric interference or mass fractionation, or an evaluation of data quality.

Example visualizations for a static uranium analysis by TIMS are illustrated in Fig. 1. At the top left are three graphs typically provided by mass spectrometer software, which plot isotope ratios and intensities vs. analysis time. Also shown are examples of new plots for better understanding data. For instance, ratio vs. ratio plots (center of Fig. 1) can guide interpretation of temporal trends, like those pictured in the ratio vs. time plots. Two slopes are illustrated with black lines — the trend that results from positive correlation between the two isotope ratios that contain ^{235}U in the

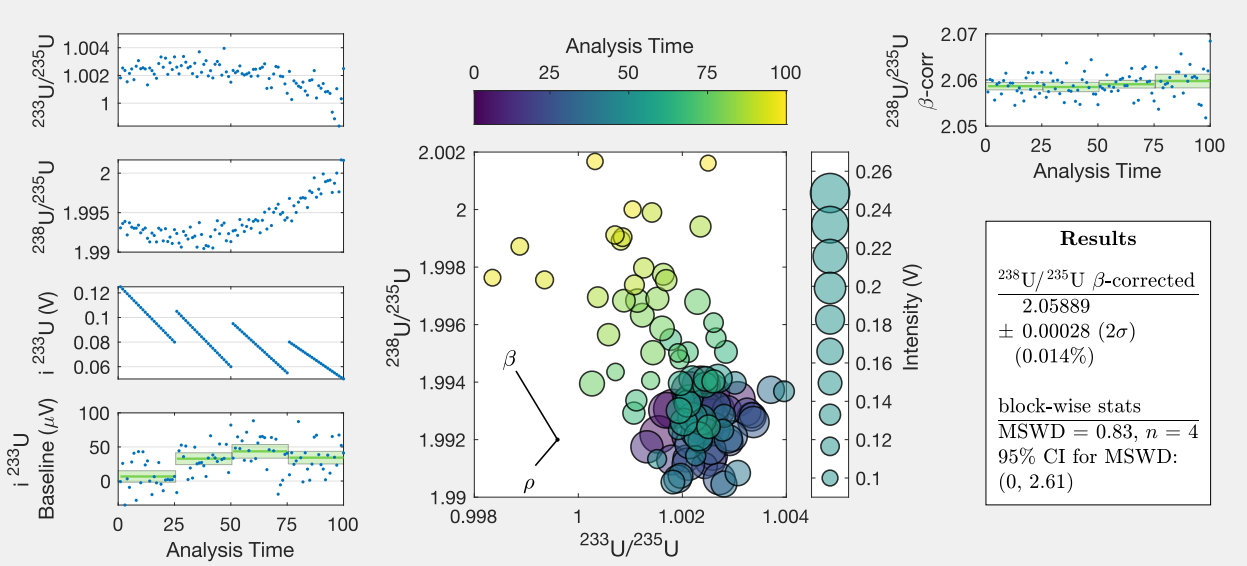

Figure 1: Examples of potential mass spectrometer data visualizations supported by Tripoli for a static Faraday analysis of U isotopes.

denominator, labelled ρ, and an exponential mass fractionation line, labelled β. It is clear that early measurements (purple to blue colors) show positive correlation between ^{233}U/^{235}U and ^{238}U/^{235}U, while later measurements (green to yellow) follow a mass fractionation trend. As expected, higher intensity measurements (larger circles) cluster more closely than lower intensity measurements (smaller circles). Because the sample is double-spiked with a ^{233}U-^{235}U tracer, internal normalization produces a fractionation-corrected ^{238}U/^{235}U (top right) whose block means become less precise as the ion beam intensity falls (green boxes illustrate 2σ uncertainties). Weighted mean statistics of those block means (results box, lower right) are a more accurate, precise, and informative synopsis than the typical mean and standard deviation/error reported by factory mass spectrometer software.

An interactive, educational example is to provide sliders that adjust the input deadtime to visualize its effect on ion-counter data, which depends on both ion beam intensities and the magnitude of the isotope ratio. Sliders that support exploration of changes in collector efficiencies or amplifier gains could illuminate the inner workings of multi-dynamic multicollector methods, helping users make connections between ratios measured in each sequence. Other ways of visualizing mass spectrometer data, like Figures 2 and 3, illustrate a valuable geophysical perspective for geochemical data. Active engagement with our user community will contribute additional ideas for Tripoli visualizations via workshops as detailed below. Color palettes will be optimized for color vision deficiency (Nuñez et al., 2018), like the viridis colormap in Figure 1.

Mass spectrometry represents a common entry point to data analysis in geochemistry and geochronology, and this project aims to take advantage by opening up the black box that turns measured ion beams into meaningful isotope ratios. Our idea is to provide interactive visualizations of each step, from baseline, isobaric interference, and abundance sensitivity corrections to beam interpolation and internal normalization. Interactive visualizations will illustrate tricky but fundamental concepts like covariance, intermediate concepts like log-ratio transforms, and more sophisticated techniques like Markov Chain Monte Carlo. Opening this black box will help develop

numerical and statistical tools in the next generation of geoscientists.

2.2 Peak-hopping: Bayesian inference – TIMS

Single-collector 'peak-hopping' methods are the most frequently used approach for measuring low-abundance isotopes.

2.2.1 Background - mass spectrometry

Ion counters are most precise for small ion beams but many instruments have only a single ion counter, so small ion beams must be measured one at a time. Measured intensities must then be corrected for the growth or decay of the beam during each cycle of mass measurements, a process known as beam interpolation. Beam interpolation algorithms used by current mass spectrometer manufacturers (e.g., Dodson, 1978) underestimate uncertainties by a factor of up to 1.4 for two, or 1.7 for three successive cycles of interpolation (Ludwig, 2009), and they don't efficiently utilize all measured data (see below). Rather than markedly underestimating every uncertainty or accurately inflating uncertainties, we propose a novel way to instead significantly improve precision by additionally utilizing Faraday detectors.

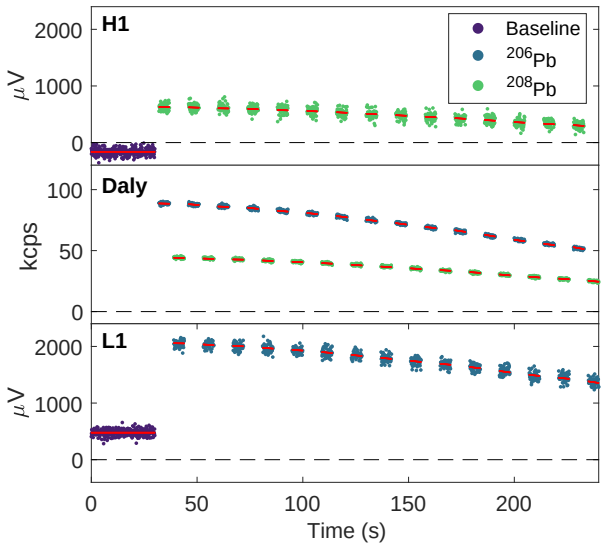

Figure 2: Example of raw mass spec data for peak-hopping two isotope test. Red lines show the best-fit model from MCMC algorithm.

New Faraday technologies such as 10^{13} Ω resistors on conventional amplifiers (e.g., von Quadt et al., 2016) and capacitance-based ATONA amplifiers (Hockley et al., 2018; Cox et al., 2018) have improved signal/noise ratios and might now help. However, beams less than ∼ 20 kcps still must be measured by ion counter, meaning that most low-abundance isotope applications (e.g., small samples of Pb, U, Th) still must contain a peak jump. Furthermore, ion counters have efficiencies that differ from Faradays – and from each other if there are multiple ion counters – and change with time. Calculating isotope ratios on mixed ion counter/Faraday arrays requires estimating these relative efficiencies by measuring the same ion beam on both types of detector. A complicated mass bias correction is also needed when the magnitude of bias is different for ion counters and Faradays, as commonly observed on TIMS. And finally, there is an awkward mismatch in the number of cycles for the higher-abundance isotopes that always appear on Faradays vs. the lower-abundance isotope(s) that are only measurable on an ion counter, making variance and covariance estimations complex. Both issues are universally ignored, but are important for accurate data.

2.2.2 New algorithms developed in the geophysics literature can help geochemists

To address all of these problems, we propose to refine and improve the data reduction pipeline for mass spectrometers using an approach borrowed from geophysics.

Specifically, we will apply Bayesian statistics using a reversible-jump Markov Chain Monte Carlo (rj-MCMC) approach (Green, 1995). In the past decade, rj-MCMC approaches have been frequently and fruitfully applied to geophysical problems, including surface wave tomography (e.g., Bodin and Sambridge, 2009; Bodin et al., 2012; Olugboji et al., 2017), receiver function surveys (e.g., Agostinetti and Malinverno, 2010), and body wave tomography with local earthquakes (Piana Agostinetti et al., 2015) and teleseismic phases (Burdick and Lekić, 2017; Young et al., 2013; Tkalcic et al., 2015).

Although it's more statistically and computationally intensive than currently used methods, the rj-MCMC technique has a number of strengths that make it uniquely applicable to our data. First, as a true data inversion technique, it is able to incorporate large quantities of data from multiple sources. This includes measured intensity data from all ion counters and Faradays and prior knowledge about how those detectors behave. We can then invert all of that data for a relatively small number of parameters of interest, like isotope ratios and their uncertainties.

The rj-MCMC method is also designed so that the measured data are not over- or under-fit by the model. For instance, a single straight line might inadequately fit a complex, non-linear ion beam evolution, but connecting every noisy data point with a line segment would be unrealistic. The transdimen-

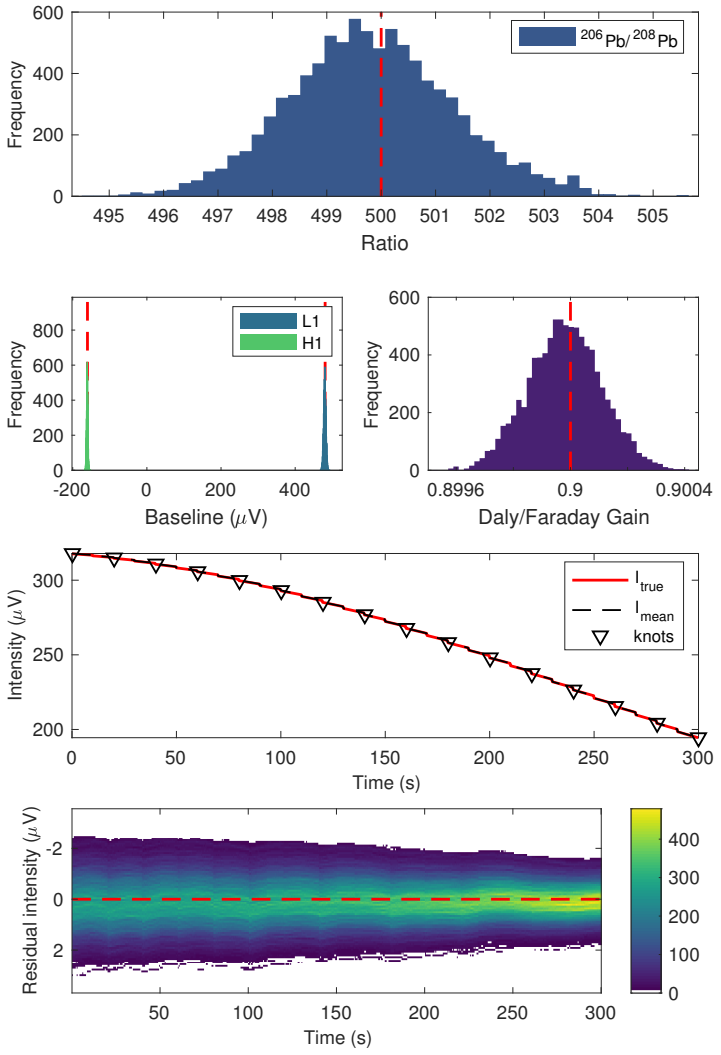

Figure 3: Example visualization of results from synthetic two-isotope test. Dashed red lines indicate true values. Row 1: histogram of $^{206}Pb/^{208}Pb$ ratios recovered in MCMC algorithm. Row 2, left: histogram of baseline estimates for Faraday amplifiers. Row 2, right: histogram of Daly/Faraday gain estimates. Row 3: Comparison between the true intensity (solid red) and mean intensity estimates recovered from algorithm (dashed black). Triangles show knots in continuous piecewise linear parameterization. Row 4: Heat map of intensity functions from ensemble (difference from true model). Yellow indicates more probable values.

sional approach (e.g., Malinverno, 2002) allows the number of parameters defining the model to vary. The resulting models are parsimonious, which is crucial for accurate uncertainty estimation.

The goal of the rj-MCMC approach is to determine the best fit model parameters — i.e., isotope ratios, ion beam intensity, Faraday/IC gain(s) — and their posterior probability distributions based on how well they explain observed data and agree with all prior knowledge of the system, like reasonable constraints on the Faraday/IC gain(s). The posterior probability is estimated by constructing Markov chains of models that explain the data. New models in the chain are proposed by adjusting or adding/deleting one model value at a time and are accepted or rejected based on the change in probability compared with the previous model (Metropolis et al., 1953). From the resulting model chains, useful statistics including the mean and modal values, uncertainties, and uncertainty correlations can be determined.

Thanks to dramatic improvements in computational resources, this technique has revolutionized the field and been applied to almost every outstanding problem. Transdimensional MCMC approaches have also been used to address problems in geochronology and thermochronology. For instance, Gallagher (2012) develops a method for inferring thermal history from low temperature thermochronology data, and Fox and Ickert (2015) apply it to sample-standard bracketing during a mass spectrometry session. These successes convince us that Bayesian inference using rj-MCMC is well-suited to the complex problem of raw mass spectrometer data reduction. Given that the raw data is the product of unknown isotope ratios and unknown beam intensity terms, it is difficult to linearize the problem and solve using standard inverse methods. The flexibility of the rj-MCMC approach provides the means for non-linear forward modeling of the data and furthermore can quantify both non-Gaussian posterior probabilities and the covariance between isotope ratios and other model variables.

2.2.3 Testing a preliminary model with real and synthetic data

We produce a preliminary rj-MCMC algorithm to recover the posterior probability of isotope ratios that fit raw multi-collector TIMS data. The algorithm was tested on synthetic and observed data for measurements with two and five isotopes. With assistance from the instrument manufacturer Isotopx, we acquired highly time-resolved data collected at 0.2s intervals. Peak-hopping data (figure 2) is forward modeled as a non-linear function of isotope ratios, time-dependent beam intensity, and the instrumental parameters (Faraday baseline voltages, Daly-Faraday gain). For n Pb isotopes, we include $n-1$ log-ratios parameters, with the most abundant isotope (here, ^{208}Pb) as the denominator. The raw data is then modeled as the product of the ratios and the ^{208}Pb intensity function. In this study, we model the intensity in each block with a piece-wise linear function, though this approach may not serve for quickly varying intensities. Finally, the Faraday baseline voltages are subtracted, and the Daly-Faraday gain is applied. The inclusion of Faraday baseline and Daly-Faraday gain allows us to address possible secular drift, but one major research task will be to determine whether these terms are stable or should be treated as variables.

The likelihood of a given model is proportional to the exponent of the χ^2 misfit between the modeled and observed data. The misfit includes a data covariance term that can vary within the algorithm (i.e. the hierarchical method, Bodin et al., 2012), which responds to beam strength and instrument noise. We estimate the posterior probability distribution by running the MCMC algorithm for one million iterations, saving every 100^{th} solution to the model ensemble following a burn-in period.

The ensemble solution for a two-isotope synthetic test is shown in Figure 3. Figures 3a-c show histograms of the ensemble values for isotope ratio, Faraday baseline and Daly-Faraday gain. The red lines represent the true values used to make the synthetic data. Figure 3d shows the true intensity function in red and the mean value derived from the MCMC process in black, while Figure 3e shows how the values cluster around the true intensity.

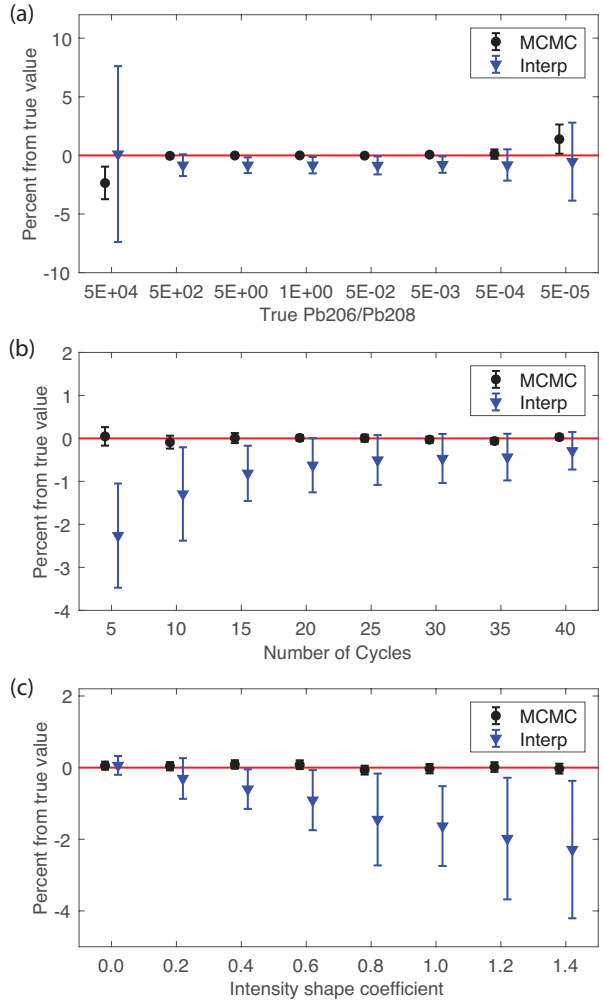

Figure 4: Synthetic data tests of calculations using our MCMC algorithm (black dots) versus standard Dodson beam interpolation (blue triangles). Uncertainty bars are ∼95% confidence intervals. (a) Mean $^{206}Pb/^{208}Pb$. (b) Block duration. (c) Complexity of intensity function, parameterized by a shape coefficient that increases with increasing non-linearity.

A comparison of results from our preliminary MCMC algorithm and the Dodson method is shown in Fig. 4. We test scenarios with varying values of isotope ratio, intensity, length of data collection, and complexity of the beam intensity function. In all cases, the new method outperformed double interpolation, which consistently underestimated measured ratios. The MCMC algorithm encountered difficulty when very low intensities resulted in a strong correlation between log-ratio and intensity in the models. The standard MCMC approach used here is known to have trouble with highly correlated variables, and we will survey alternate MCMC approaches to alleviate this problem.

Also of note are the large, percent-level discrepancies in Fig. 4 between the Dodson beam-interpolated results (blue triangles) to the true values (red lines) built into the modelling. The Dodson algorithm accurately interpolates beams whose intensity changes as first-order (linear) and second-order (parabolic) functions in time, but can badly miss on other functional forms. Here, the $I \propto \exp(-t^2)$ intensity function yields realistic-looking mass spectrometer data but large errors. Because real ion beam intensities do not follow linear or parabolic trajectories, it is important that the beam interpolation algorithm be as flexible as possible.

Initial results suggest that our new MCMC-based methodology improves upon current widely-used methods, but further development is necessary to improve the efficiency and robustness of the algorithm and incorporate it into an accessible software package that serves the community's needs.

2.3 Static/Dynamic Multicollector Data – TIMS and solution MC-ICPMS

A significant portion of mass spectrometer data derives from static (single-sequence) or dynamic (multi-sequence) scenarios, where each isotope is measured on one or more Faraday detectors. These scenarios are significantly less complex than those where one or more ion counters are utilized (see Sec. 2.2), but there are still opportunities for improving accuracy, precision, and the statistical rigor of data handling, and for creating new data visualizations, all facilitating better data interpretation.

2.3.1 Baselines – TIMS and solution MC-ICPMS

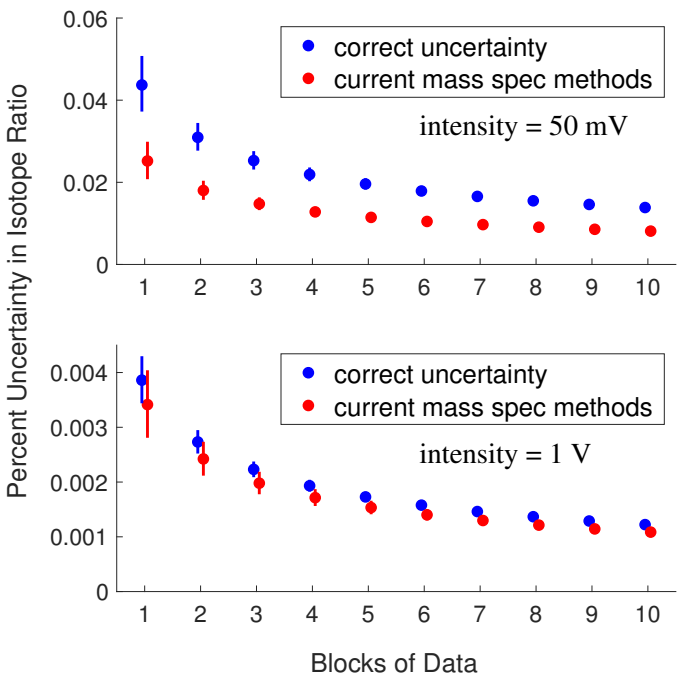

Figure 5: All current mass spectrometer software packages underestimate uncertainties for ratios of small isotope beams (top plot, simulated 50 mV signals) by neglecting baseline uncertainties. For larger ion beams (bottom plot, simulated 1 V signal), the effect is smaller but still statistically significant.

Isotopes of interest are measured as a difference between an 'on-peak' ion beam intensity and a 'baseline' measured without the ion beam in the collector. Baselines are measured, for instance, at half-mass while the sample is ionizing on TIMS. The baseline is subtracted from the following on-peak measurement, repeating for each block of data, and baseline-corrected intensities are used to calculate isotope ratios output to data reduction software.

The uncertainty from noise in the baseline and from noise in the on-peak measurement are equally important. But in all mass spectrometer software methods, it is not propagated, and on some platforms the raw data from the baseline is not even available for output. This likely explains higher-than-expected scatter for small samples, often blamed on blanks or small external effects. Fig. 5 shows the results of two simulations. The upper shows an isotope ratio where both ion beams are 50 mV signals on amplifiers with 10^{11} Ω resistors, and each block has a 10-second baseline and 30 seconds on-peak. The blue series shows the correct uncertainty, and the vertical line encompasses 95% of the expected variability from random effects. The red data series models the calculations currently employed in mass spectrometer software, subtracting only a mean baseline from each on-peak intensity. *The current approach underestimates uncertainties, here yielding only ∼33% of the true variance, or an uncertainty that's just 58% of its true size.* The lower trend illustrates the same measurement scenario for a ratio of 1 V beams, showing that the discrepancy decreases to 79% for variance or 89% for uncertainty for higher-intensity data. To remedy this, we will work with mass spectrometer companies (see letters of collaboration) to output relevant baseline intensity information for Tripoli. The variability in these baseline integrations acts as a systematic uncertainty in the on-peak data (McLean et al., 2016), and can be incorporated explicitly into plotted and calculated isotope ratio uncertainties.

2.3.2 Compositional Data – TIMS and solution MC-ICPMS

At present, mass spec users measure the ratio of two isotopes of interest, a and b, as (a/b) or (b/a). A method then measures this ratio several times and returns its mean and standard error. The table at right shows that the isotopic compositions calculated this way depend on the initial choice of numerator and denominator! The mean of (a/b) does not equal the reciprocal of the mean of (b/a) (e.g., McLean et al., 2016). **Both are wrong.** For three isotopes, the mean of (a/c) divided by the mean of (b/c) does not even equal the mean of (a/b). Synthetic data show arithmetic means do not match true ratios and can create confidence intervals that overlap negative values (antimatter?) for ratios near zero.

intensities		ratios	
a	b	a/b	b/a
3.70	2.32	1.59	0.63
1.61	1.89	0.85	1.17
2.25	3.74	0.60	1.66
0.91	2.67	0.34	2.93
1.06	2.95	0.36	2.78
1.17	2.02	0.58	1.73
2.24	1.75	1.28	0.78
1.48	1.57	0.94	1.06
2.09	1.95	1.07	0.93
2.07	1.10	1.88	0.53
arith. mean:		**0.950**	**1.421**
geo. mean:		**0.822**	**1.216**

The statistical field of Compositional Data Analysis, founded by Aitchison (1986), uses the geometric mean of relative isotope abundances expressed to a common denominator isotope. Aitchison's approach has been used for noble gas (e.g., Vermeesch, 2015) and LA-ICPMS (e.g., McLean et al., 2016) data, but has not yet been adopted by the TIMS or solution MC-ICPMS communities. We return to the point that sophisticated geochemical calculations and models currently rely on flawed statistics output by mass spectrometers, but that the fix is straightforward.

2.3.3 Outliers and missing data – TIMS and solution MC-ICPMS

Current mass spectrometer software implements data rejection by standard deviation or percentile, often automatically rejecting all data outside $\pm 2\sigma$ of the mean. This approach rejects $\sim 5\%$ of accurate Gaussian data and causes two problems. First, routine application of a 2σ filter underestimates the uncertainty of normally distributed data by about 12% (a true uncertainty of 1 becomes an underestimated uncertainty of ~ 0.88). Second, rejecting valid data actually *increases* the variability in the mean by about 10% (a standard deviation of 1 among measurements becomes about 1.1). The effects appear as excess scatter, attributed to e.g. geological causes rather than misguided data handling. We will use less aggressive filters, for instance the Chauvenet's Criterion used in the original Tripoli for TIMS, that have also been implemented successfully elsewhere (e.g., Vermeesch, 2018).

Missing data commonly result from transient isobaric interferences or instrument effects. This complicates estimating the statistical correlation between isotope ratios that occurs when they share a source of uncertainty, for instance a common denominator isotope. The prevailing way to calculate correlation coefficients — e.g., equation 19 of Schmitz and Schoene (2007) — assumes that no data have been rejected and leads to impossible correlation coefficients, with values > 1 or < -1. No available software treats this common occurrence. We plan to implement the popular EM algorithm of Dempster et al. (1977) to calculate self-consistent uncertainties and uncertainty correlations from isotope ratios with missing data.

2.3.4 Designing better methods – TIMS and solution MC-ICPMS

The statistical machinery used for testing the algorithms in this proposal can also be used to optimize mass spectrometer methods for maximum precision. The code used to calculate baseline uncertainties in Fig. 5, for example, can be used to calculate the optimal time spent measuring

baseline vs. on-peak during a TIMS analysis, where both must be measured while the sample runs. We propose an interactive utility that helps users define a measurement parameter to optimize (e.g., δ^{234}U, ^{87}Sr/^{86}Sr) and input the instrument and method setup (collector assignments, sequences) and expected ion beam sizes or isotope ratios. The utility will then solve for the user-defined method parameters, like baseline and integration times for each sequence, that yield maximum precision. These times are currently input by the user, but most would admit that their choices are not well informed.

Optimizing measurements on TIMS and MC-ICPMS has the potential to improve the precision for small samples, where uncertainties are often governed by achievable ion beam sizes and run times. The long-term community goals of increasing precision and decreasing sample sizes have often been accomplished with expensive new equipment, like updated electronics and larger interface pumps, but statistical optimization can improve measurements without instrument upgrades. For non-sample-limited applications like routine Sr, Nd, or non-traditional isotope work, optimization can decrease the time required to reach a desired precision, improving throughput.

2.4 Motivation: Summary

Mass spectrometry, and specifically TIMS and solution MC-ICPMS mass spectrometry, are critical tools for the geochronology and isotope geochemistry communities. Chronological and chemical from these labs are used to address every Priority Science Question articulation by the National Academies in the recent Earth In Time report (NASEM, 2020). Although data from these instruments support an array of sophisticated models, the data handling provided by instrument manufacturers and used by the community as a whole as inputs to these models is outdated and often incorrect. We propose bringing the same level of sophistication to TIMS and solution MC-ICPMS mass spectrometer data that we bring to the science that results from it.

3 Research Objectives

To address the challenges outlined above, we propose to 1) develop new data reduction protocols for raw mass spectrometer data, building on our initial investigations, and 2) develop a new software environment implementing this approach with end-to-end interactive visualizations. The resulting software tool, Tripoli (replacing the current Tripoli), will provide a seamless interpretive and analytical interaction with raw mass spectrometer data as or after it's produced. PI Bowring has over two decades of experience collaboratively building software (Tripoli and ET_Redux) with geochronologists, primarily with PI McLean (Bowring et al., 2011; McLean et al., 2011, 2016), and recently with Geoscience Australia developing Squid3 (Bodorkos et al., 2020). Tripoli will incorporate many of the mature procedures from these products.

The proposed project builds on previous work with three parallel and collaborative research objectives discussed below: Objective A is to develop Tripoli, Objective B is to develop the new algorithms, and Objective C is to develop a robust, sustainable infrastructure including supporting documents, web sites, videos, and integrations with existing infrastructure, and to sponsor community forums for training and ongoing collaboration.

A. Design and develop the software Tripoli.

Tripoli will be developed using a test-driven (Beck, 2003), agile (Beck and Andres, 2005) methodology and rely on the re-use of code from our existing products for the visualization framework. The overarching architecture has four components: 1) procedures for standardizing raw metadata and data inputs from mass spectrometers, 2) a logic core with an application programming interface

(API) that implements our algorithms for processing the standardized data, 3) a graphical user interface for providing interactive visualizations, and 4) procedures for exporting processed data and metadata. This architecture implements the Model-View-Controller architecture (Krasner and Pope, 1988), which enforces a separation of the basic logic and user interface(s) and thus supports sustainability through reuse by other developers. The testing environment will focus on the logical core and be informed with synthetic data. PIs Bowring and McLean have demonstrated the efficacy of synthetically-generated data sets to develop meaningful tests (Bowring et al., 2011). The agile approach provides for continuous iterations of artifacts informed by user evaluations, which is the successful development model the PIs have used in all projects.

1) Input-handling component: Because there is a wide variety of mass spectrometer output file formats, we need a data schema to standardize the inputs to Tripoli and mechanisms for users to transform their outputs to this schema. In collaboration with the community and mass spectrometer manufacturers, we propose to identify these formats and develop software adapters for each to render the data compliant with the new schema (see letters of collaboration from all three major mass spectrometer vendors in this space). This work removes a potential barrier to adoption in the community and provides exemplar software adaptor templates. This approach contributes to our plan for the long-term sustainability of this infrastructure as described in research objective C below.

2) Logic core component: The development of the logic component and API of Tripoli will occur in three iterative and parallel threads, each lasting the duration of this project. In thread I, we will implement initial versions of the algorithms. We will research, locate, and compare existing implementations of all or parts of reversible-jump Markov Chain Monte Carlo techniques to find a suitable candidate or to inspire development of a new domain-specific implementation based on the results of research objective A above. In thread II, we will work to maximize algorithm performance and to develop a set of snapshot approximations of the algorithms to support responsive real-time visual interactions. In thread III, we will design automated tests based on synthetic datasets to demonstrate, validate, and verify our work. The logic component will efficiently model entire data streams with a single set of isotope ratios and their uncertainties to support user-interface requirements for sensitivity testing. PIs Bowring and McLean have demonstrated the utility of interactive sensitivity testing in ET_Redux (Bowring et al., 2011). The logic component will also provide support for real-time 'live workflow' data acquisition and modelling in Tripoli, again previously demonstrated using the current Tripoli and ET_Redux for TIMS and LA-ICPMS.

3) Graphical user interface component (GUI): The development of the GUI will depend heavily on the reuse of the basic visualization frameworks developed and matured for use in the original Tripoli, ET_Redux, and Squid3. Using these frameworks, we will develop new visualizations for each step of the new data processing protocol, and Figures 1 and 2 are static prototypes for some of these new visualizations. The principal data processing steps requiring interactive visualizations are: 1) live data acquisition, 2) interaction with calculated models both as snapshots and as completed representations, 3) additional statistical filtering, 4) interpretation and analysis including interactive sensitivity testing, and 5) publication and archiving.

4) Output-handling component: We will extend the output schema of the current Tripoli with input from the user community to include additional parameters such as uncertainty correlations between isotope (log-)ratios of interest, the number of measured ratios for use in calculating effective degrees of freedom, method-specific information about which collectors were used and instrument- and run-specific metadata so that this information can be utilized by any and all future data

reduction software development efforts. This objective is straightforward but extremely critical to the success of Tripoli because it will define how other software products interact with Tripoli during and after its funded development period. As a demonstration project, we will develop a plug-in to export data to NSF EarthCube's *Sparrow* lab data and metadata management system. Integrating *Sparrow*, the next generation of lab-workflow cyberinfrastructure, will improve and extend the usability of both systems. See collaboration letter from *Sparrow* project scientist Daven Quinn.

B. Develop new algorithms for estimating isotope ratios.

Task 1: Identify and parameterize model variables: The initial task is to identify all factors involved in forward modeling the raw mass spectrometer output and assign an appropriate parameterization. Each instrument and mass spectrometer is different. We will determine which factors vary temporally during analysis (e.g., beam intensity, isobaric interferences), vary from analysis to analysis (isotope ratios), or are intrinsic to the instruments (Faraday baselines, ion counter dark noise). Next, we will assess whether each effect varies according to isotope or collector to determine whether separate parameters are necessary. Time-dependent variables will be classified as linear, piece-wise linear, or spline functions. For complex time-dependency, we will use a trans-dimensional approach.

Task 2: Develop and test MCMC algorithms: A broad spectrum of MCMC algorithms will be rigorously tested against real and synthetic data for accuracy, efficiency, and robustness over a wide range of scenarios. To date, exploration has focused on assessing two candidates: Trans-dimensional MCMC and Adaptive MCMC. The trans-dimensional approach allows for flexibility in dealing with arbitrarily complex intensity variations without over-fitting, but only provides for one model variable to change at a time, resulting in longer computational times and difficulty accommodating highly-correlated variables. The Adaptive MCMC approach, on the other hand, allows for the improved recovery of correlated variables. New models are proposed based on the (iteratively updated) model covariance, leading to a more efficient model search at the expense of flexibility. We will determine the range of scenarios to which each algorithm provides the best fit to our synthetic data.

Task 3: Real-time monitoring: Although the MCMC algorithm is currently implemented as a post-data collection step, we anticipate end users will seek to monitor the collection/analysis progress in real time. At present, the MCMC calculations take the same order time as the data collection. To improve efficiency and allow for real-time monitoring, we will explore two possible approaches. First, we will investigate the sequential addition of data into the inversion using Bayesian Updating. Model posteriors will be found at regular intervals by using the previous model as the prior and fitting new data, perhaps from each acquisition cycle (approximately 1-2 minutes). Second, in the event that the adjusted MCMC algorithms remain too time-intensive for real-time monitoring, we will develop more approximate algorithms to process and visualize the results as they accumulate, leaving the full analysis to be performed afterwards.

C. Develop a robust infrastructure for Tripoli.

We develop an infrastructure in several ways. First, software development will occur within the open-source social-coding platform GitHub.com. GitHub provides support for version-controlled repositories and tools for a development community to record plans, and to design and implement decisions, discussions, code, and documentation. Second, the proposed architecture of Tripoli separates the core logic and its API from the user interface so that other developers can easily provide their own user interface if desired. Third, we will employ test-driven development as

described above, and the published suite of test cases will serve to support development efforts by others as well as provide documentation for Tripoli. Fourth, we will conduct a community workshop during the development process to ensure that Tripoli meets the community's needs, and a recorded online software training workshop upon release, to teach others how to become part of the long-term software maintenance program. Fifth, we will produce training materials as part of our sustainability planning. Finally, we will engage with undergraduate and graduate students in our courses and labs to encourage and train them to participate in sustaining the software products they use in their scientific research.

4 Essential Elements

Modern cyberinfrastructure

Software and all documentation will be hosted on GitHub.com as an open-source project under the Apache 2 license. Schema for input and output data formats will provide open data standards satisfying FAIR: Findable, Accessible, Interoperable and Reusable. The coding language will be open source Java using the Open Java Development Kit, which runs on any platform (Windows, Mac, Linux, etc).

Engagement

The scientific community served by this project is large – a broad cross-section of geochemists and geochronologists using TIMS and solution MC-ICPMS methods, including faculty and staff at those labs, and also students and lab visitors from any geoscience field. Our outreach will include Tripoli-specific workshops, for which we will reach out to early career and underrepresented minority stakeholders through society programs like GSA's 'On to the Future' program. Because our software will be used by non-specialist laboratory users and visitors, we will explicitly incorporate this community during development in an effort to make Tripoli both usable and educational, opening up the current black box of mass spectrometer data interpretation. Further engagement opportunities may be provided by a proposed Geochronology RCN, GAIN, and the National Geochronology Consortium it envisions. There is significant overlap between this community and Tripoli users, and PI McLean, as part of its steering committee and Cyberinfrastructure Working Group, will solicit community feedback and participation in Tripoli as part of the broader GAIN initiative.

Community Workshops. Direct community engagement will be carried out via yearly workshops. In Year 1, we will hold a 3-day workshop in Charleston, SC to gather input from community members. Although we have previously established community interest, this workshop will allow us to determine the specific needs of the user base, including desired interface functionality, workflow requirements, input/output variables and formats, and connectivity with other software packages. We request funding to provide travel support for up to 50 participants. In Year 2, we will hold an online workshop to solicit feedback on the beta version of Tripoli. This meeting will also serve as an assessment checkpoint. Finally, in Year 3, we will hold a 2-day workshop prior to a major conference (e.g., GSA or AGU) to launch Tripoli and provide training in the functioning of the software. We will provide travel support for up to 50 participants.

Science motivation

As explored in Section 2, this grant would transform the relationship between a broad sector of geochemists and geochronologists, from research professionals to trainees and lab visitors, and the mass spectrometers they employ. We argue that better (more accurate and precise) measurements lead to better science.

Metrics

Metrics will include 1) count of GitHub issues generated, 2) count of issues closed and average time open, 3) count of downloads of each software release, 4) count of user contributions to code or documentation via pull requests per month, and 5) count of social media mentions per month. Data will be collected and published on a regular basis on the project's repository Wiki.

Sustainability plan

With reference to Research Objective C above, all PIs will contribute to sustainability planning. The PIs will consult regularly, with online web meetings at least once a month, and progress will be reported as part of the project's GitHub.com repository contents, an early community development workshop, and an online training workshop upon project completion and release. The PIs will encourage users to include modest budget line items in their future proposals to support the long-term maintenance of Tripoli. Realistic vehicles include funding computer science student research projects focused on maintaining and improving specific aspects of Tripoli and publicizing this need through organizations such as Teaching Open Source (TOS).

Management plan

Management of this project involves developing a working solution in the public domain that satisfies the needs of the community while demonstrating its correctness with testing, and providing for the long-term sustainability of the work through engagement of students and researchers. PI Bowring will be responsible for coordinating the development of the software components, PIs Burdick and McLean will develop the algorithms, and all three will collaborate on the visualizations, user interface, and testing. An important aspect of this project is that all artifacts will be continuously available via the public repositories used to host them so that the community can monitor progress and contribute ideas.

Year 1: Develop and test algorithms, consult with community members, develop schema for mass spectrometer raw data, and prototype software user-interface architectures for evaluation by community (All). Identify all time-dependent variables affecting raw data stream and choose appropriate modeling parameters (Burdick, McLean). Performance test different Monte Carlo algorithms (Burdick, Bowring) with real and synthetic U-Pb data (from McLean). Create visualizations for log-ratio statistics and Bayesian output parameters and prototype user interface (Bowring, McLean). Implement favored algorithm for integration into Tripoli (Burdick, Bowring). Identify architecture for live-workflow and prototype the logic layer (Bowring, McLean).

Year 2: Iterative development and testing of logic component software (Bowring, McLean). Develop and implement algorithm to support visualization of live data flows that update results and statistics. (Burdick, Bowring). Host a virtual community-development workshop (All).

Year 3: Iterative refinement of algorithms and software in response to community feedback from Year Two workshop and beta testers. Complete sustainability plan, conduct additional online training upon release to elicit feedback, improvements, and community engagement. Provide road map for generalizing methodology to other isotope systems and spectrometer systems. Publicize software and synthetic data. Develop supporting documents and how-to videos, etc. (All).

5 Broader Impacts

This proposal embodies broader impacts criteria: (1) enhancing infrastructure for research through developing a new open source software tool, Tripoli along with synthetic data-sets for testing; (2) disseminating results broadly to enhance scientific understanding through two planned

papers and a mid-project workshop; (3) promoting teaching, training, and learning while broadening the participation of underrepresented groups by providing trans-disciplinary undergraduate research opportunities and incorporating the proposed new techniques into undergraduate and graduate coursework — Burdick is an early career researcher, and Bowring mentors undergraduate researchers, with a track record of attracting students through the NSF-funded South Carolina Alliance for Minority Participation; and (4) clear benefits to society by developing and practicing software-sustainability regimens that will serve to protect the public's investment in this and other software development research projects.

6 Results from Prior NSF Support

PIs James Bowring and Noah McLean

NSF Award #1443037: $579,762 (**PI** Bowring: $334,730, SP McLean: $82,175); Sept 2014 to Aug 2019. **Title:** CIF21 DIBBs: Collaborative Research: Cyberinfrastructure for Interpreting and Archiving U-series Geochronologic Data. **Senior Personnel:** N. McLean, U. Kansas; A. Dutton, U. Florida; K. Rubin, U. Hawaii. Extending TIMS and LA-ICPMS cyberinfrastructure development to include U-series. Bowring coordinates development of software and McLean of algorithms. Interactive visualizations in ET_Redux support a work-flow that reprocesses archives of U-Th geochronology and sea level data. **Broader Impacts:** This work (1) enhances infrastructure for research by creating tools for archiving and interpreting geochronologic data; (2) has hosted three workshops for a broad user community; (3) has promoted teaching, training, and learning while broadening the participation of underrepresented groups by providing student research opportunities and incorporating the tools into undergraduate (College of Charleston) and graduate (U. Kansas, U. Florida, U Hawaii) coursework; and (4) benefits society by providing scientists who are not geochronologists with tools to construct time-lines for climate, sea level, and polar ice cap change and volcanic eruption histories. **Software:** ET_Redux is available on GitHub. **Publications:** Bowring et al. (2015); Chutcharavan et al. (2015); Hibbert et al. (2015); Ashe et al. (2015); McLean et al. (2016); Hibbert et al. (2016); Dutton et al. (2017); McLean and Bowring (2017); Chutcharavan et al. (2017, 2018).

PI Scott Burdick

Award No. NSF-EAR-1349771: $174,000; September 2014 to August 2016. **Title:** Constraining Continental Rifting Using a Novel Seismic Imaging Approach **PI:** Scott Burdick, University of Maryland, College Park. **Intellectual Merit:** This postdoctoral fellowship focused on deploying novel seismic methods to image the crust and upper mantle beneath the United States to better understand continental evolution, particularly the factors that control continental rifting. Under this project, novel trans-dimensional Bayesian methods were developed and applied to the problems of continental-scale body-wave tomography, refraction surveys, and regional receiver function imaging. Additionally, models of seismic velocity beneath the contiguous United States and Alaska were created and shared. **Broader Impacts:** This project supported mentoring of undergraduate researchers and the development of tomographic model visualizations for education and outreach. **Publications:** Burdick and Lekić (2017); Montgomery et al. (2017).

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