Numerous students working under five ERI PIs (Cottle, Gans, Hacker, Jackson, Spera) measure whole-rock major and trace element data to answer questions related to igneous and metamorphic petrology. The major elements are routinely measured by x-ray fluorescence (XRF) at Pomona College, whereas trace elements are typically measured in-house at UCSB by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). However, the current LA-ICPMS data reduction scheme is highly unsatisfactory: it relies on calibration to a single rock standard, yielding data that can be of questionable accuracy, especially if the chemical composition of unknowns deviates significantly from the standard composition. Alternative approaches involve the development of multi-point calibration curves, such that all measured rock standards are used to determine the composition of a given sample – but these schemes typically do not account for the time-varying nature of the calibration curve, i.e., instrumental drift, nor do they account for errors in regression. The absence of a fully robust and transparent data reduction routine presents a critical shortcoming for our laboratory.

To address these concerns, I have developed a coupled Iolite®- and Matlab®-based data reduction routine that i) develops robust three-dimensional calibration curves for every measured element, ii) accounts for non-linear instrumental drift, iii) propagates uncertainties from the calibration curve, and iv) yields demonstrably accurate trace-element data for rock standards that underwent the same whole-rock bead making method (i.e., the same process that is applied to unknowns). The first part of the routine is completed in Iolite®: backgrounds are subtracted and each element wave is ratioed to the internal standard wave (typically Ca, which is measured by XRF). The data are then output as a text file; after some user manipulation, the text file can be used as an input for the Matlab® reduction file. The routine prompts the user for certain information (e.g., which element is used as the internal standard), and then outputs a series of figures for each measured element with i) raw data and ii) curve fits to the raw data, including 95% confidence intervals for the fit (Figure 1). The final output is a spreadsheet that contains measured elemental concentrations and their uncertainties. Figure 1 shows that there are non-linear time-dependent drift effects on the measurement, and that the relationship between signal intensity and known concentration is not necessarily linear either – therefore six different fit types are tested that evaluate linear or squared fits between signal intensity and known concentration, and linear, squared, or cubic fits between signal intensity and time. A modified $r^2$ statistic calculated by Matlab’s® Curve-Fitting Toolbox is used as a loss function that penalizes higher-order fits, i.e., higher-order fits cannot just be better, but have to be significantly better than lower-order fits in order to be adopted. Therefore, this approach automatically and robustly fits a statistically defensible three-dimensional curve to each measured element, while transparently allowing the user to identify if the fit to the data is reasonable by visually examining the data and its calibration curve.

To test for method accuracy, I measured BCR-2 and BHVO-2 glasses that underwent the same bead-making routine as unknowns, i.e., they include lithium tetraborate flux. The results from this measurement are shown in Figure 2; of 47 measured isotopes, 36–40 of these are either within error of or within 10% of the published standard values. This approach shows that
combined errors from both the bead-making process and the data reduction routine yield accurate, defensible data for rock standards (and therefore unknowns).

The following tasks are in progress and will be completed as time allows:

i) I measured a standard round-robin run with ~15 USGS and MPI-DING whole-rock standards. As another accuracy test, I will run a Monte Carlo simulation in which I progressively remove standards from the calibration curve and run them as unknowns, thereby determining how much additional uncertainty should be added as the number of measured standards along the calibration curve decreases. This run also included the same lithium tetraborate-fired BCR-2 and BHVO-2 glasses, thereby providing a more robust accuracy check on our bead-making routine.

ii) The data used in the making of the routine was completed by making linear laser traverses, i.e., avoiding the complication of downhole spot fractionation. However, these traverses ablate significantly more material and take quite a bit longer than spot analyses, thus limiting the shelf life of our rock standards and using more instrument time. I do have additional whole-rock data that was completed using laser spots rather than lines, and I will complete additional work to assess if spot analysis yields accurate data – thus saving time and rock standards.

iii) I am currently writing up a user guide for ease of use; the guide will simply and transparently identify all working parts of the routine. As additional students test this routine, I will be on hand to troubleshoot any problems that arise, and intend to work with ERI PI John Cottle to ensure that the model statistics are defensible.

iv) I intend to apply this method not only to whole-rock glasses but also to individual phases (e.g., garnet and clinopyroxene), especially in cases where accurate determination of elemental concentrations is used for quantitative thermal or chemical modelling (e.g., thermobarometry).

v) Finally, I intend to write this up for publication within the next year, with the intent of making this tool available for the broader scientific community.

In sum, this data reduction routine represents a significant advance for our lab, and will ensure that whole-rock data published from UCSB are robust and defensible.
Figure 1: Raw data (top; counts per second signal intensity ratioed to the signal intensity of the internal standard vs. time vs. known concentration, colored by time) and the statistical fit to the data (bottom; including 95% confidence intervals as planes on top and bottom of the best fit) for Nd over the course of a ~12 hour LA-ICP-MS run. Note the clear time-varying effect of the calibration curve, as well as the non-linear relationship between signal intensity and known concentration – and how the fitted curve accounts for both considerations.
Figure 2: Combined accuracy test of the bead-making process and data reduction routine. The curves represent the % difference between measured and known concentrations for lithium-tetraborate-fluxed BCR-2 and BHVO-2 rock powders. Note that most of the measured elements are within uncertainty of their known values; even some elements with >10% deviation from their known values are still within error of them. Further, some major elements do deviate significantly, but these are typically measured by XRF rather than LA-ICPMS.