

2013 Workshop on

**Handling, Processing and Archiving of LA-ICP-MS U-Th-Pb Data:**  
***Statistical Interpretation of Age Information, LA-ICP-MS and***  
***Beyond***

College of Charleston  
Charleston, SC USA  
6-8 March 2013

**Organizing Committee:**  
Jim Bowring, Matt Horstwood, George Gehrels

Noah McLean, Chad Paton, Doug Walker

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## General Information

**Workshop title:** Handling, Processing and Archiving of LA-ICP-MS U-Th-Pb Data: *Statistical Interpretation of Age Information, LA-ICP-MS and Beyond*

**Location:** College of Charleston, Charleston SC, USA

**Date:** 6-8 March, 2013

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**Workshop Report:** This document published 1 May 2013.

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## Acknowledgements

NSF grant EAR-0930166

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College of Charleston Aramark Catering Services

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Lee Blackwell, College of Charleston, Computer Science

Clay McCauley, College of Charleston, Computer Science

Dr. Sam Bowring, MIT

## Attendee list and world map

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Jim Bowring	College of Charleston
Istvan Dunkl	University of Goettingen
Christopher Fisher	Washington State University
Dirk Frei	Stellenbosch University,S Africa
George Gehrels	University of Arizona
Axel Gerdes	Goethe-University Frankfurt
Chris Holm-Denoma	US Geological Survey
Matt Horstwood	British Geological Survey
Ryan Ickert	Berkeley Geochronology Center
Simon Jackson	Natural Resources Canada
Andrew Kylander-Clark	University of California Santa Barbara
Antonio Langone	University of Pavia
Noah McLean	British Geological Survey
Paul Mueller	University of Florida
Leonid Neymark	US Geological Survey
Jeff Oalmann	University of Kansas
Chad Paton	University of Copenhagen
Norm Pearson	Macquarie University, Sydney Australia
Nick Roberts	British Geological Survey
Keith Sircombe	Geoscience Australia
Luigi Solari	National Autonomous University of Mexico (UNAM)
Chris Spencer	Univ of St Andrews, Scotland
Alex Steely	UC Santa Cruz
Lisa Stockli	Univ Texas
Victor Valencia	University of Arizona
Pieter Vermeesch	University College London
Doug Walker	University of Kansas
Qing-Zhu Yin	UC Davis

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## Executive Summary

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This workshop represents the culmination of a three year National Science Foundation grant and of the ongoing efforts of the international community to improve comparability among U-Th-Pb geochronologic data acquired by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). It focused on the impact of data processing procedures in data reduction software packages and is the fourth in a series of workshops that has striven to improve the interpretation of these data.

Twenty-nine scientists from eleven countries across four continents attended the meeting (either directly or via Skype-link), contributing over 25 presentations during three days, with numerous additional discussion sessions.

The Charleston workshop goals were to:

- Identify and propagate the limiting uncertainties in LA U-Th-Pb dating
- Reassess the use of population statistics and the appropriate use of linear regressions and weighted means
- Identify software processing contributions to improving the 2% ( $2\sigma$ ) ILC uncertainty limit
- Understand interpretation limits in assessing ages and uncertainties of complex datasets, including the role of geological phenomena
- Identify how Isoplot-type functionality might be maintained for the future

The workshop achieved much more than these goals, and the notes in this document outline the presentations and discussions that took place.

The first day of the conference focused on the current state-of-the-art in LA-ICP-MS geochronology. A presentation of the 2011 LA-ICP-MS and SIMS interlaboratory comparison of detrital zircon results showed that resolvable biases exist (<1-5% range) in Pb-U and Pb-Pb data within these communities. Next, the authors of each major data reduction and uncertainty propagation software package used by the community presented their package. The authors emphasized the mathematical model used to describe and reduce the data and the statistical approach to propagating uncertainties. Discussion centered around the utility of various inter-isotope and inter-element fractionation models both during ablation (“down-hole”) and during the course of an analytical session. The problems inherent in comparing software outputs were discussed, and several ideas were put forward to design simple synthetic datasets to test all packages on the same footing.

Presentations of new and recent advances in defining, describing, and visualizing data in statistically accurate ways comprised the second day of the the conference. Significant spatial variability of Pb-U and even Pb-Pb fractionation within even those ablation cells considered to be best performers was demonstrated and the participants agreed that these effects should be documented and characterised for each laboratory and ablation cell type used. The minimum amount of information needed to fully describe the isotopic composition of a mineral standard

was then discussed, followed by an agreement that the publicly Internet-available versioned model (specified by an extensible markup language (XML) schema) as used in U-Pb\_Redux is suitable for distributing this information.

New statistical techniques and methods of data handling were highlighted such as log-ratio analysis of data, which was demonstrated to be the correct method for reducing compositional data, and key metric parameters such as the Bayesian Information Criterion which provides objective assessment of the quality of model fit. These optimised methods improve the accuracy of data quantification. Much discussion involved the benefits of kernel density estimations versus probability density distributions with particular reference to detrital mineral geochronology as well as the benefits of using very high-N data sets ( $N > 1000$ ) to better characterise these distributions.

The future requirements for data reduction and data/information integration were also discussed, highlighting the importance of combining U-Pb data with other isotopic, trace element, textural, and geological information to enhance and refine age interpretations particularly with respect to the discrimination of data populations. Presentation and discussion on the composition of the “ideal” software/data handling system for high-throughput data acquisition indicated the need for long-term storage of the raw time-resolved data to preserve transparency and traceability in datasets. Participants discussed implementing systems to support live importation of LA U-Th-Pb data into community databases for later processing. The need for ease of data entry and seamless incorporation into the operator’s workflow was highlighted as the biggest single requirement to promote uptake of a databased approach to data acquisition and processing.

Most of the geochronology community and other isotope geochemistry communities rely virtually entirely on the Isoplot add-in for Microsoft Excel written and maintained for many years by Prof. Ken Ludwig of the Berkeley Geochronology Center. With his retirement and the continuing transformation of Excel, the unsustainability of this approach was highlighted and suggestions solicited for how the community might take forward this capability. It was announced that NSF funding will be sought for the creation of a replacement package which will ensure the plotting and calculation requirements of the isotope community are met for the future and suggestions and comments were solicited during and after the workshop.

## Workshop Program

### **Wednesday - March 6, 2013 (Day 1)**

<b>Time</b>	<b>Event</b>
7:30 – 8:30	<b>Coffee and continental breakfast</b>
8:30 – 9:10	<b>Framing the Problems</b> <i>Jan Kosler and Matt Horstwood</i>

	<p>Implications from the 2011 LA U-Pb inter-laboratory comparison study (highlighting points from the 3 workshops and those to be discussed in this one)</p>
9:10 – 10:40	<p><b>Community Survey - Software Presentations, Part I</b>  (20 min presentations, 30min discussion at the end of the session)</p> <p>Data Reduction/Uncertainty Propagation Approaches in Existing Software Packages  To be addressed in each presentation:</p> <ul style="list-style-type: none"> <li>- Uncertainty propagation protocol/workflow</li> <li>- Common Pb correction methods, if applicable</li> <li>- Method of inter-element and inter-isotope fractionation correction</li> <li>- Weighted Mean/Linear regression support, if applicable</li> <li>- Rejection criteria</li> <li>- Handling/storage of reference values for normalization</li> <li>- Key differences from other available packages</li> </ul> <ul style="list-style-type: none"> <li>• AgeCalc</li> <li>• Glitter II</li> </ul>
10:40 – 11:00	<b>Coffee Break</b>
11:00 – 12:30	<p><b>Software Presentations, Part II</b></p> <ul style="list-style-type: none"> <li>• Frankfurt approach</li> <li>• Iolite and VizualAge</li> <li>• U-Pb_Redux</li> </ul>
12:30 – 13:30	<b>Lunch</b>
13:30 – 15:00	<p><b>Software Presentations, Part III</b></p> <ul style="list-style-type: none"> <li>• SQUID II</li> <li>• U-Pb Age for R</li> <li>• UranOS</li> </ul>

15:00 - 15:30	<i>Simon Jackson/Tonny Thomson</i> Some observations when comparing software packages: recommendations for standardization
15:30 – 16:00	<b>Coffee</b>
16:00 - 17:00	<b>Discussion &amp; Summary of salient points from presentations</b>
17:00 – 18:00	<b>Poster Session</b> Topic: Software packages and other relevant posters
18:30 - 21:00	<b>Dinner</b> Join us for dinner at the Francis Marion hotel (Pinckney Room) with guest speaker <a href="#">Dr. Norm Levine</a>

## **Thursday - March 7, 2013 (Day 2)**

<b>Time</b>	<b>Event</b>
7:30 - 8:30	<b>Coffee and continental breakfast</b>
8:30 – 10:30	<b>Recent Advances - Data processing</b> (25+15 min slots, discussion after each presentation/section as appropriate) <i>George Gehrels and Matt Horstwood</i> <ul style="list-style-type: none"> <li>- Reference Materials</li> <li>- What is the minimum amount of information we need?</li> <li>- What values should we be using?</li> <li>- Where/how should this information be archived for community access and use?</li> </ul> <i>Noah McLean</i> <ul style="list-style-type: none"> <li>- Log-ratio analysis of compositional data</li> </ul>



	- Analyzing choices in data reduction with respect to uncertainties and MSWD
10:30 – 11:00	<b>Coffee Break</b>
11:00 – 12:30	<i>Noah McLean</i> - The use and abuse of linear regressions and weighted means with ‘sample-standard’ bracketed data - How do we fractionation-correct using reference materials with (variable amounts of) Initial Common Pb?
12:30 – 13:30	<b>Lunch</b>
13:30 – 15:00	<b>Recent Advances - Uncertainties and Interpretation</b> <i>Pieter Vermeesch</i> - Kernel density estimation, probability density plots - Multi-dimensional scaling
15:00 – 15:30	<b>Coffee Break</b>
15:30 – 17:00	<i>Matt Horstwood</i> – Analytical limitations on age uncertainty – solution U/Pb & LA Pb-Pb (c.f. Stern & Amelin study)  <i>George Gehrels</i> - Geological limitations on age uncertainty
17:00	<b>End</b>
18:00 - 19:30	<b>Dinner</b>

### **Friday - March 8, 2013 (Day 3)**

<b>Time</b>	<b>Event</b>
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7:30 - 8:30	<b>Coffee and continental breakfast</b>
8:30 – 10:30	<p><b>Future directions for software and data handling in LA-ICP-MS geochronology</b> (Facilitator-led presentation (15mins) and discussion (30 mins))</p> <p><b><i>Statistics and data processing</i></b></p> <p><i>Pieter Vermeesch</i> - Are there applications for Bayesian stats in LA U-Pb data interpretation?</p> <p><i>Noah McLean</i> - How do we optimize measurement protocols to collect the most precise data in the least amount of time?</p> <p><i>Matt Horstwood</i> - The time-resolved interpretation of data: mapping, depth profiling, pulse-by-pulse interpretation and the impact of instrumental and analytical setup parameters</p>
10:30 – 11:00	<b>Coffee Break</b>
11:00 – 12:30	<p><b><i>Databases and data handling</i></b></p> <p><i>Doug Walker</i></p> <ul style="list-style-type: none"> <li>- The Geochron database</li> <li>- How do we ensure that U-Pb data are archived properly, or at all?</li> <li>- How do we record other geochemical data and imagery with U-Pb data? - database approaches</li> </ul> <p><i>Jim Bowring</i> - 'Isoplot 2020', Community requirements</p> <p><i>Andrew Kylander-Clark</i></p> <p>How do we integrate other geochemical data and imagery with U-Pb data? - software approaches</p>
12:30 – 13:30	<b>Lunch</b>
13:30 – 15:00	<i>Dirk Frei and George Gehrels</i>

	<p>What is the ultimate software solution for fully automated high-n dataset collection with interactive(?) quality control?</p> <p><b>Wrap-up</b></p> <p>Implementing conclusions and some actions</p> <p>Facilitating further community cooperation</p>
15:00	<b>End</b>

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## Detailed Summary

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### Wednesday Morning

#### Introduction: Jim Bowring

Jim Bowring opened the workshop with introductory comments explaining the history of the workshop in the context of the NSF grant awarded to himself as PI, and co-PIs Sam Bowring, Doug Walker, and George Gehrels. This workshop is a follow-up from the AGU-located workshop in 2009 and reported in EOS (\*Horstwood et al. (2009)). The PIs were awarded a three-year NSF grant to develop software and cyberinfrastructure: “Collaborative Research: Analytical Techniques and Software: Development of CyberInfrastructure to Support Laser-Ablation ICP Mass Spectrometry.” The funding for the 2013 workshop was included in the grant. Bowring also presented information about Charleston and the College of Charleston.

\*Horstwood, M., Gehrels, G. & Bowring, J. (2009) Improving Consistency in Laser Ablation Geochronology; Workshop on Data Handling in LA-ICP-MS U-Th-Pb Geochronology; San Francisco, California, 12–13 December 2009, Eos, Transactions American Geophysical Union, vol. 91, iss. 28, pp. 2324-9250; <http://dx.doi.org/10.1029/2010EO280003>

#### Framing the Problems: Matt Horstwood

Matt Horstwood spoke on behalf of Jan Kosler and himself about the implications from the 2011 LA U-Pb inter-laboratory comparison study that was presented in Prague 2011 and which focused on detrital zircon interpretations. A synthetic and well-defined detrital zircon mixture was made from available reference materials and sent to 10 laboratories to analyze. Samples were of several different ages from Mesozoic to Proterozoic. Labs were asked to analyze 100 grains out of the 208 on each mount. The U-Pb range of ages had a 3.5% to 5% total variation, although the youngest sample (213 Ma) had a 15% variation.

The results showed a consistent pattern in data from lab to lab. Pb/Pb ages were more scattered in accuracy than U-Pb ages. SIMS and LA-ICP-MS were similar, though only two SIMS laboratories reported. Those labs that were accurate in U-Pb were not necessarily the best in determining Pb/Pb ages. There was systematic variation from lab to lab; individual labs would generally report all ages either younger or older than the true ages. Two samples proved troublesome for interpreting the variation because of the inconsistency of reported results. The reasons for this were discussed. These two were removed from the comparison for statistical purposes to allow a clearer picture of the comparison. The community of labs had an accuracy of the U-Pb age of around 3%  $2\sigma$ . Some labs reproduced ages to better than 1%  $2\sigma$ . It was felt that 0.5%  $2\sigma$  is a realistic community goal for U-Pb, with 1%  $2\sigma$  for Pb/Pb. The study found a strong correlation between U concentration and range of accuracy in reported age values ~~relative to U concentration~~.

The determined age spectra were fairly similar between labs, with some interesting aspects. Some spectra showed 'ghost' peaks, some had side peaks. One lab missed the oldest peak that had a 3% presence in the sample. Two of the expected ages in the spectra were only 5% different at 1100 and 1150 Ma. These were not uniformly resolved by all labs.

Labs reported a wide variation in techniques, e.g., spot size, mass spectrometer type, ablation time, and reference materials. It appears that mass spectrometer type does not contribute to inter-lab variations, while data reduction programs appear to affect the values calculated for ages and their uncertainties. It was noted that in the highest Pb and U material that uncertainties are generally underestimated. Cell geometry and how reference materials are mounted relative to unknowns can play a role in this. It was reported that a SIMS comparison study gave similar results.

## **Community Survey - Software Presentations, Part I: various presenters**

### **AgeCalc - George Gehrels**

George Gehrels presented "AgeCalc", the software he wrote in Excel and that is currently used by his Arizona Laserchron Lab. The basic strategy is to mount reference materials with the sample and run a lot of secondary reference materials intermingled with the sample.

#### **Data reduction procedure**

- Background subtraction to start, no uncertainty propagated. Hg correction via measuring  $^{202}\text{Hg}$  to calculate  $^{204}\text{Hg}$  (would like to propagate  $^{202}/^{204}\text{Hg}$  variation).
- LIEF correction by  $t=0$  regression through last 12 of 15 1-second integrations for down hole fractionation, no down hole fractionation for Pb/Pb ratios.
- $^{204}\text{Pb}$ -based common Pb correction assuming a Stacey-Kramers composition at the apparent  $^{206}\text{Pb}/^{238}\text{U}$  age (only one pass).
- Propagate 10% uncertainty in common Pb  $^{206}/^{204}$  variation from Stacey-Kramers as a

systematic uncertainty.

- U-Pb normalisation conducted using a sliding window of the average of 6 reference materials around the sample of interest. Uncertainty in this is very important and the largest component of the systematic uncertainties.
- Disequilibrium correction for  $^{206}\text{Pb}/^{238}\text{U}$  applied using  $\text{Th}/\text{U}$  magma  $\approx 2.3$ . Th content of magma is uncertain in a detrital sample. Effect disappears at ages  $>10\text{Ma}$ .
- Calculate ages and uncertainties. Internal – due to grain measurement. External – due to reference material and common Pb composition. Individual analyses use internal only, but use external for dataset collected together. Age uncertainty never better than external uncertainty.
- Filter data for high  $^{202}\text{Hg}$ ,  $^{204}\text{Pb}$ , discordance or reverse discordance, and high uncertainties on any ratio.

Need to keep internal and external uncertainties separate.

Recommended to use various plots to explore data variation and potential problems.

### **Glitter - Norman Pearson**

Glitter is a realtime and online reduction package. The user can select the interval of signal to analyze in real time and can look at the downhole fractionation with this package. New version in the works. Trace element incorporation. Adapting to new mass spectrometer output. Glitter combines both internal and external uncertainties into the spot analysis. Internal uncertainties include counting statistics, elemental fractionation and instrument drift. External uncertainties include detector response and normalisation uncertainty as well.

Pb-Pb: Calculate mean of signal for each isotope and use this to calculate ratio (“ratio of the means” approach). Reference material normalization factor is determined and drift monitored over time. Reference material normalization uncertainty is added in quadrature.

U-Pb: Elemental fractionation seems to be the same from reference material to reference material. Then use mean of individual ratios in the integration interval and use this to compute uncertainties. Correlating sample and reference material integration interval is critical – these must be tied together to be able to do the down hole fractionation correction correctly otherwise substantial error can be introduced. Do the reference material normalization cycle by cycle and relate to unknown.

Use linear fit of reference material data for drift correction of samples for short runs. Can do higher order for long runs, and will in the future allow drift to be done piecewise.

Glitter does not do common Pb correction at present. Can do some data filtering for spikes, etc. Common Pb correction is performed off-line using Tom Anderson’s algorithm.

### **Group Discussion**

- Principle sources of uncertainty for Pb/Pb and U/Pb are different. For Pb/Pb this is the counting statistic uncertainty; for U/Pb it is the uncertainty associated with the downhole fractionation correction.
- Must be careful about what part of the signal for unknown is used. Can evaluate for instrument and geologic noise in the sample.
- Should we be able to move the interval over which the data is collected and ages computed? Doing this could lead user to bias results.
- Picking best bit of the signal is no worse than picking the actual zircons that are mounted and analyzed.
- Users must be educated to follow best practices. Review process may be the place that quality control should happen?
- Rather than drill down into the grain, perhaps do multiple spots on a grain to explore complexity.
- Zircon crystallography can be important in understanding the variation, especially if they are metamict.

## **Software Presentations, Part II**

### **Frankfurt Approach - Axel Gerdes**

Spot selection performed using CL images and live view. Spots are all numbered and correlated to images. Analyses are well tracked and time stamped. Also try to eliminate bias to the extent possible. Also do common Pb correction on everything. Do a cleaning shot to get rid of any common Pb signal. Signal is always defined in the same way.

640 ratios in 40 second scan. Data reduction program does linear  $t=0$  intercept for Pb/U fractionation. For each isotope subtract the background. Stacey-Kramers correction using  $^{204}\text{Pb}$  done first, then do a  $^{208}\text{Pb}$  based common Pb correction. Normalisation is based on the GJ1 reference material. All analyses and reference materials are acquired in a single file. Common Pb correction is the most time consuming step but also critical for getting good data. For  $^{208}\text{Pb}$  correction, must make assumption/estimate of radiogenic 208. Can go through and remove outliers of analyses with bad signals. Data reduction can take a lot of time. Can reject U-Pb and keep Pb/Pb.

GJ1 is used as the primary reference material with three secondary reference materials run for validation. Use of the  $t=0$  intercept method allows the flexible use of spot size depending on the elemental concentration (adjust as needed). Lab tries to use secondary reference materials of age similar to the age of the unknowns. Secondary reference materials are usually good to 2% accuracy. Use linear fit to reference materials and allow for time dependent correction to the data.

Need to do common Pb correction better to get reasonable results.  $^{208}\text{Pb}$  correction is particularly good to do. Using the intercept method for LIEF correction, must do common Pb correction prior to this.

Down hole fractionation depends on the spot size, so must monitor this effect when doing different spot sizes for different grains.

### **Iolite and VizualAge - Chad Paton (via Skype) and Andrew Kylander-Clark**

Presentation on workflow of data reduction, details of some specifics, and highlight strengths and weaknesses.

Stages in workflow: Data import, baseline subtraction, raw ratio calculation, down-hole fractionation correction, reference material normalization, uncertainty propagation, data export. Data is time resolved to the extent possible. Baseline is interpolated through out the entire session. Interpolation is flexible (linear or spline). Ratio calculation is done for every time slice of data. Can select the integrated time period for samples and reference materials but this is always linked to the requisite time period for LIEF correction. Down hole fractionation correction starts with combining the reference materials for the entire session into an average signal evolution. Start time is when the shutter opens. Can 'window' the reference zircon data if needed and software still combines. Reference normalization is separate from down hole fractionation correction. Spline fit to the reference data normalizes the data and corrects for time variation over session. Uncertainty propagation is done using the reference zircons treated as unknowns. This requires >15 analyses of the primary reference material to be reliable. Systematic uncertainties are not treated by this method. Data is exported as comma-separated values (CSV) so can put into Excel/Isoplot. Can also generate reports.

Iolite reduces data using 'mean of ratios' by default. Ratio of means can be less biased for very low counts. Ratio of means is not in Iolite at present.

Down hole fractionation correction method of Iolite allows for detection of variation within an analysis. It assumes reference materials and unknowns behave the same and that the down-hole fractionation model does not vary over the course of a session.

Session-based reduction treats an entire session of data at once.

Uncertainty propagation looks at whether the scatter in reference data can be explained by internal precision at  $2\sigma$ . If not, there must be another source of scatter. Use internal uncertainties and then compute the MSWD. If MSWD too high add some additional uncertainty to each analysis. Splines can cause some complications. The unsmoothed splines can create too much texture to the data correction. Use an "odd man out" method with the spline fit. Program can pick optimal spline for each intensity or ratio.

## **U-Pb\_Redux - Noah McLean and Jim Bowring**

Enter machine parameters to start. Then look at raw ratios. Baseline can be modeled or just used as a mean. Then fit the reference data. U-Pb\_Redux predicts uncertainty based on counting statistics and noise in instrument. Can add extra dispersion - is needed if data point uncertainty is too low. Next, fit the session data. U-Pb\_Redux calculates the uncertainty on each reference point, then analyzes the spline fit uncertainty, and finally the nature of the extra dispersion. Then fit unknowns. Uses the same down hole fractionation correction as Lolite at present. Data is then ported to interactive data table that can be customized. This also allows for Concordia plots that are also interactive.

Workflow at present is offline, not ready for real-time use at present for LA-ICP-MS. Common Pb correction not yet implemented.

Fractionation correction [  $\text{ref\_true} = \text{ref\_meas} * A$  ] is evaluated using log ratios [  $\log(\text{ref\_true}) = \log(\text{ref\_meas}) + \log(A)$  ]. This linear form is generally simpler to work with, especially for uncertainty propagation.

Weighted means/linear regression results are reported with four types of uncertainty, reported cumulatively. 1) Analytical uncertainty from isotope ratio measurements, within-session reproducibility of reference materials. 2) Lab-specific long-term observed variability in secondary reference materials. 3) Uncertainty in isotope composition of primary reference material used for normalization. 4) Decay constant uncertainties.

No automatic rejection of data yet (e.g.  $2\sigma$  rejection). However, the user can quickly, manually highlight and reject data points from consideration in fits.

Reference value for primary reference mineral isotopic compositions are available online in XML format, and can be downloaded and saved in U-Pb\_Redux. This ensures everyone is working with the same reference data, and version numbers provide for updates and revision. This reference data records both the radiogenic and common Pb components, useful for describing materials that have initial common Pb and heterogeneous U-Th distribution.

U-Pb\_Redux uses log-ratio analysis, which resolves the “ratio of means vs. mean of ratios” problem. Overdispersion can be assessed for both down-hole and session data sets, and the overdispersion is then included in the intercept/interpolation uncertainty. It provides model selection guidance for fitting data in the form of the Bayesian Information Criterion (BIC). Sample-calibrant bracketing uncertainty propagation takes into account that unknowns are not independent because each unknown uses a shared set of reference measurements for corrections. This means the uncertainties between unknowns must have some covariance, which invalidates the typical scalar weighted mean/linear regression approaches. However, the covariance is correctly incorporated into the generalized weighted mean already implemented in U-Pb\_Redux (McLean et al. 2011, [doi:10.1029/2010GC003478](https://doi.org/10.1029/2010GC003478)). Reduced data is then visualized/plotted/examined/reported by a well-developed toolset implemented already for TIMS



data (Bowring et al. 2011, [doi:10.1029/2010GC003479](https://doi.org/10.1029/2010GC003479)).

Software “chasm” means that we have a hard time making domain-specific software. Need software engineering approach to give scientific software scientific rigor.

U-Pb\_Redux software development is domain driven. This has been done for dating via the EARTHTIME effort. Software is open source, has graphical and statistical tools, reporting, and seamlessly archives data. The Cyber Infrastructure Research and Development Lab for the Earth Sciences ([www.CIRDLES.org](http://www.CIRDLES.org)) is the software engineering effort at the College of Charleston..

There was a long discussion on picking different portions of the signal evolution curve. Most agreed that this was ok in some circumstances, and may give useful geological information. For zircon, this may reflect different age zones. For titanite, this may come from variation in the relative abundance of common Pb.

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## Wednesday Afternoon

### Software Presentations, Part III

#### Squid II - Keith Sircombe

SHRIMP data processing. Some issues are similar between this method and ICP-MS. Data processing started with first SHRIMP in 1980, and has evolved over time. Squid 2000, Squid-2 in 2005. Different from the packages commonly used for LA-ICP-MS, but still time resolved data. Primary reference is Temora 2. Sessions typically last a week.

Workflow involves a text file from the instrument. There is a text file and an XML file that captures a lot of machine parameters. Uncertainties from counting statistics, common Pb, U-Pb discrimination, and age calibration. First normalize to secondary beam monitor and subtract background. Then do double interpolation for ratio calculation. Then produce mean value with rigorous calculation with rejection tested by MSWD. Normalize the signal and use Stacey-Kramers for common Pb correction. Monitor potential over counts on  $^{204}\text{Pb}$ . Next calculate the calibration constant. Check spot to spot uncertainty on reference material to add extra uncertainty if needed and then add that to the unknowns as well. Reference values are held in a user-editable worksheet in Excel.

Squid is Excel VB based/built on Isoplot, so it strongly depends on Isoplot's future.

Squid-2 has some issues. Distribution and installation can be problematic. Version control can be difficult. Office 2003 was required. Putting together a new application could take a lot of work and could be fraught with problems. Want to move Squid to open source, ensure that it is reproducible, and have a broad developer and maintenance community. Should be platform independent, cloud based.

Algorithms and user interface should be kept separate. This is interaction of code with interface with users, maintainers, and developers.

### **UPb.Age for R - Luigi Solari**

UNAM system built to reduce LA-ICPMS U-Pb data. Software aimed to be transparent and customizable. Written by Martin Tanner. Use statistical language R, which is free, open, and has many libraries.

Collect U-Pb data, but also trace and major element data. Use NIST glass as a reference for the elemental data.

Workflow is based on 2 files that are generated via the file transfer in CSV. UPB.AGE then takes this and does the data reduction. The program has an interface with a variety of options on data reduction parameters. Then displays the signal in visual mode so that users can select background and data windows. All analyses must be of the same duration. Then user checks for inclusions and zoning in the reference materials and then unknowns. For samples, the user can iterate on what part of the signal is analyzed. Next step is to check for outliers in reference materials and samples. After this do a linear regression for drift correction. Do downhole fractionation to  $t=0$  or using the mean. Now the user applies all the corrections and then recalculates the ratios. UPB.AGE then writes a results file with ratios, uncertainties, and rho, and a data file that includes counts on trace elements. Common Pb correction is not yet supported.

### **UranOS - Istvan Dunkl**

The graphical presentation is very important. Need to see the signal and how it evolves. Need to also visualize the ratios at the same time. Basic equations are all given in a PDF file. User sets a lot of default parameters that reflect material, time slices, outlier tests, data rejection, detection limit, etc. User can also define parameters that go into the export file.  $T=0$  uncertainty is critical to evaluate. User can decide how to do this. Can customize output results. Hg correction can have several different options.

Process reference materials first, and display so that users can compute fit to the data. It is important to worry about the Hg signal. Ratio can vary, and there is a Hg blank and signal option in the software.

For reference data you get a lot of statistical parameters that help to evaluate the uncertainties. User can define what goes into the export file.

Features include:

1. No plugins required
2. Window, Mac, Linux
3. Not real time
4. Universal input
5. Batch processing
6. Instrumental Hg correction
7. Outlier test
8. Common Pb correction

Finishing points:

1. Laser induced Hg emission – ablate Hg free material
2. Reliability of low counts – level of detection important
3. Zero counts – need to consider
4. Down-hole fractionation correction – mean and  $T=0$  for all data
5. Use more reference materials and define an average normalisation factor from these
6. Grouping of sequence can be an issue, not just ratio of reference to unknowns
7. Use prediction interval to propagate uncertainty in drift and fractionation

### **VizualAge - Andrew Kylander-Clark**

VizualAge is a plugin to Lolite. Can do histograms customizable for detrital data. Can do Concordia and Tera-Wasserburg diagrams. Can zoom in and pan around through the data. Can do a live Concordia plot that interacts with changing data reduction parameters.

### **All attendees: Discussion**

Horstwood stated he has never seen a true non-natural Hg composition during U-Pb work within the determined uncertainty levels. He related the documentation of apparent large Hg ratio variation (in U-Pb data) to measurement error/background subtraction at low counts. Lots of group discussion on this and how to look at the common Pb contribution to a change in the ratio.

### **Software package comparison - Tonny Thomson/Simon Jackson**

Initiative has two goals: determine best practices and provide a set of standardized procedures. Presentation reiterated San Francisco (2009) proposition to do a software round robin for comparison of software packages. An attempt at this was made by von Quadt and others and reported in 2009 and suggested that there were some problems. Hanchar round robin in samples showed that the community was underestimating uncertainties.

It would be logistically difficult to do the software round robin because many of the packages assume different data formats or have very specific data collection protocols. Some assume reference materials are analysed in specific positions in the sequence. Getting a single dataset together that all packages could use is difficult. Probably would have to acquire new dataset that would contain all the possible values that folks measure.

Aims: what are we evaluating? Is it a proficiency test of the software or just a comparison? How do we actually do the evaluation since different programs may have different strengths. Is it a good idea to do this comparison?

### **All Attendees: Further Discussion**

A file for testing software could be cloud-mounted for ease of use and low cost distribution.

Synthetic datasets can be hard to construct. Building these relies on a model for how the data works.

Collect new dataset with all possible values. Put it out as a simple CSV file that programs would have to be able to read.

For dataset not containing the whole suite of masses there are probably several of the programs that could accept these data. This comparison could be useful.

There is a lot of variation in results based on how the data are actually reduced by the user. Multiple people using same data and same program can get very different results depending on how they set parameters. The more flexible the package the more potential dispersion in results.

Many packages were built for lab specific protocols and possibly instrument behavior. Down hole fractionation can be nonlinear or linear. Packages may handle this very differently, e.g. only allowing linear down hole fractionation. Also, some packages assume single file for all samples, others take each sample as a single file.

Best synthetic dataset may be one generated from scratch that captures a typical aspect of the data evolution. Would construct intensities with time. This would probably be an enormous project. May be OK to just acquire some new (real) data and use these.

Start with one person analyzing the same dataset/session using all appropriate packages. This could be the first step.

Consensus is that this is a useful step. Want to know how software package outputs compare on the same simple dataset..

Approach: One user doing the same dataset in 5 packages. Would have to choose similar methods. Or several power users of each package analyzing the same dataset.

### **Consensus**

To move comparison forward, probably need to take small steps. Send dataset to the software developers/package authors and then compare results in a collegial way. Should use two materials, a reference and an unknown. Look at reference material with half of these processed as unknowns; the other aspect is to have a true unknown in the mix. Share the results in blog

form at [www.CIRDLES.org](http://www.CIRDLES.org) .

## Key Points, Day 1

Inter-laboratory comparison shows clear systematic variations between laboratories. The source and reason for the variation is not well understood. Data reduction process may play some role as do instrument and acquisition parameters. The community has yet to fully establish the basic best practices and these will vary between instrument types. Because of the wide range in acquisition and reduction parameters, defining a path to understand both the scatter in results and the systematic variation will be difficult.

The community is very split on using a common Pb correction. Some users consider this a critical part of data collection and data reduction. Others ignore the common Pb during processing and evaluate common-Pb components afterwards in a graphical fashion with a view to including or rejecting those data for interpretation purposes. This difference in approach seems to stem in part from observed lab-to-lab differences in the background Hg level and hence its impact on the  $^{204}\text{Pb}$  peak. Again, there is no absolute best practice in this area.

There is no consensus on using mean of ratios vs. ratio of means, although the former was demonstrated by Jackson (in the AGU 2009 workshop) to be more precise. McLean insists that both are incorrect, and will present further on Thursday morning. There is no consensus regarding using a down-hole fractionation model based on the reference materials to correct sample data vs. using a “time zero” correction for each analysis. Likewise, there is community disagreement on the validity of slicing out parts of the signal evolution for interpretation or rejecting the data if the evolution is complex.

Data reduction programs in general allow users to set a number of parameters for both data reduction and output. Users are generally happy with the program that they use and their overall interactions. Some reduction programs allow real-time analysis, others are used offline after data collection.

The participants consider a comparison study of the data reduction packages to be necessary. The path forward on this that seems best is to create a dataset consisting of one reference and one “unknown” to send to software developers (super users) to reduce. The dataset will have to be editable for measured ratios and mutable so that the various data entry approaches (e.g., file per session vs. file per sample) can be done. Two approaches will be taken. The first will simply deal with the primary reference material and process half of the analyses normalized to the rest. The second will present results (age and uncertainties) for the unknown. This work will be shared in a collegial and open manner and not be published or presented in published abstract until all contributors are satisfied with the outcomes.

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## Thursday Morning

### Recent Advances - Data processing

#### Managing U-Th-Pb Reference Materials - George Gehrels

Arizona uses HelEx cell with positions for 9 sample mounts. Tested reproducibility of 206/238 fractionation across the cell. Sri Lanka reference zircon placed in each of 9 mounts. Found that there was variation in ages based on position of the mount within the cell. Variation from center was up to 3 percent low in U-Pb age. This cell is a 2-volume cell. Some other users have similar experience with the same as well as different cells. This is why the Arizona group puts reference zircons on mounts with the unknowns. There was a long discussion on causes of variations.

How can we better use the secondary reference data? Labs should run at least one and possibly more secondary reference materials. Variation in the secondary reference materials gives information about the long term variability giving an uncertainty that needs to be added to the reported age uncertainty. Will hear more about this later.

From the 2009 AGU workshop - Wanted to compile info about reference materials, distribute reference materials to various labs, and compare results. LaserChron provides a lot of information about reference materials as well as offset plots for this lab. Information includes age, method, publication, nature of material, availability. There is a whole variety of methods used to get the age (ID-TIMS, CA-TIMS, SIMS, U-Pb, Pb-Pb). Offset plots show usually less than 2% variation from true value. There is systematic variation for each reference material from the true value. This could be due to the actual age or age method (comparing U-Pb vs. Pb-Pb for example).

LaserChron has this information for a lot of reference minerals. This sort of effort should be spread across lots of labs. Who should coordinate this effort? Each individual lab should be compiling their own data to start.

Noah McLean presented ideas about reference models using experience in ID-TIMS for U-Pb\_Redux. Can enter all relevant information about reference material or tracer. Reference materials are divided into radiogenic and common isotopic compositions with uncertainties. This is publicly available in XML format. This could be way for labs to contribute.

Matt Horstwood presented ideas about ages of reference materials. Most standards are not concordant due to common-Pb, Pb-loss or excess, so must use the correct reference ratio (U-Pb vs. Pb-Pb) for normalisation not a single age or concordia age. There is a lot of variability in the way labs currently approach this, which may be the source of some inter-lab variability.

## Log-Ratio Analysis of Compositional Data - Noah McLean

The Scottish statistician John Aitchison spent much of his professional career on the problem of how to correctly treat compositional data. His papers in Mathematical Geology in the 1980s and his seminal 1986 book The Statistics of Compositional Data provide an excellent starting point. What follows is heavily borrowed from him, and to my knowledge first recognized in the isotope geochemistry community by Pieter Vermeesch in his U-Th/He package Helioplot.

Domain – real numbers  $\mathbb{R}$  extend from negative to positive infinity. Physical variables defined on the real domain include voltages (potential fields), values measured relative to a reference (e.g.  $\delta^{18}\text{O}$ ) and rates of change. Other physical variables are only defined on  $\mathbb{R}^+$ , the positive real numbers, including distances areas and volumes, temperature (K), and abundances. Abundances for components that are present are defined in  $\mathbb{R}^+$ . We are mostly interested in relative abundances, also known as ‘compositional data’. Compositions always sum to a constant value (like 1, or 100%), and this constraint is best visualized and geometrically described on the simplex, an n-dimensional polytope which is the convex hull of its n+1 vertices (e.g. a 2D equilateral triangle in 3D, also known as a ternary diagram).

Compositional data presents several unique problems. First, we usually perform some normalization (e.g. normalize wt% oxides to 100% or calculate isotope ratios) and then calculate statistics like the mean and standard deviation. However using ratios, the de facto standard for the isotope geochemistry/geochronology community, then the means of different ratios can be inconsistent. Spreadsheet exercise: arithmetic vs. geometric means of A/B, A/C, B/C. Conclusion: if we perform our accustomed statistical analyses in log-ratio space, the inconsistencies in arithmetic means disappear.

Looking deeper into why this might be the case. The normal distribution is defined over all of  $\mathbb{R}$ . It extends to negative values, but ratios (or abundances) are not defined over negative values, so it is the wrong distribution to use. Even though means are calculated by summing and dividing by n, notionally they minimize the sum of the squared distances between the mean and the measured data points. All distances have six important properties, and differences between isotope ratios (subtraction) fail several of these. If we want to use normal distribution we need to transform out of the simplex into real numbers. The solution is to use log-ratios and assume that these are normally distributed. Lognormal distributions are asymmetric, and have zero probability at or below zero. They are roughly the same as a normal distribution away from the origin with relatively small uncertainties. Linear regression is also problematic for ratios--we must go to log space and use nonlinear regression (research in progress).

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**Thursday Afternoon**

## Recent Advances - Uncertainties and Interpretation

### Visualisation of detrital age distributions - Pieter Vermeesch

Selection of bin width in Probability Density Plots (PDPs) is arbitrary, MS Excel uses the square root of  $n$ , but the natural log of  $n$  is a better estimate when the peak is unimodal. More complex models are needed for age data.

PDPs were born in 1980s, implemented in Isoplot and Age Display, but without any published basis in statistics literature. PDPs break down under high precision and result in under-smoothed data, thus punishing imprecise data twice when  $n=10k$  leading to over smoothing of large data sets.

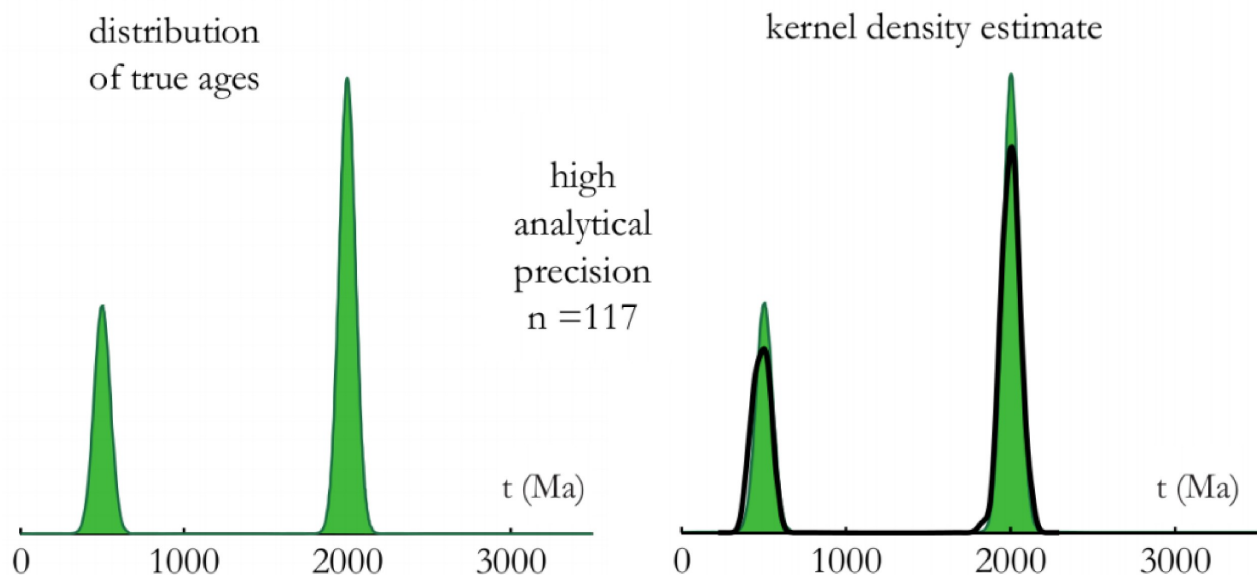
PDPs are a failed attempt to deal with heteroscedastic data, i.e. when the variance about the means of two samples is unequal. Radial plots can plot heteroscedastic data and calculate overdispersion. Can use radial plots to plot simple/unimodal U-Pb data but are not appropriate for detrital data sets

Should go back to histograms. Wikipedia has a good page on Kernel Density Estimation (KDE), there is no Wikipedia page for PDPs. No other scientific discipline uses PDPs, only geochronologists!

KDE estimates well, distributions in high and low precision data. But how do we choose the bandwidth of KDEs (equivalent to bin width)?

Botev algorithm incorporated into densityplotter.london-geochron.com

(<http://www.ucl.ac.uk/~ucfbpve/densityplotter/>)





## **Intercomparison of detrital age distributions - Pieter Vermeesch**

2025 analyses from 13 samples – N ranges from 58 to 772/sample

Quantile-quantile plot – 2 samples have the same distribution if they lie along the Q-Q line

$\chi^2$  stat – looking to get a small  $\chi^2$  for similarity. Statistic varies according to number of bins

Kolmogorov-Smirnov (K-S) statistic cumulative distribution – max vertical distance between 2 distributions on a K-S plot. Not sensitive to distributions at the tails of distributions.

Neyman-Pearson paradigm – formulate a null hypothesis (i.e. distributions are the same) and an alternate hypothesis (that they are different). Given a dataset, test the statistic. Reject, keep or re-test the null hypothesis. Cannot prove the null hypothesis, only reject it. If 2 samples are from the same distribution 95% of  $\chi^2$  will be <11.07. With  $\chi^2$  of 9 there is a probability (p) of 0.11 (=11%) that samples are similar. If  $p > 0.05$  cannot reject the null hypothesis.

3 factors affect the outcome of the statistic test – sample criterion, sample size, and effect size (the degree to which the null hypothesis is false – see J Cohen books)

Student t-test = difference between 2 averages / SE

Effect size = difference between 2 averages / (total N / 2)

p value is strongly dependent on sample size (N)

Effect size is independent of sample size

p-values should not be used in this setting (and many others); specifically, they should not be used to compare distributions because as n increases, they will inevitably find a small difference between the distributions... we are not interested in these very small differences.

Effect size should be used to quantify difference between two distributions.

### ***MDS: Multi-dimensional scaling***

Given a matrix of differences you can create an X-Y map of the data. For instance, using the distances between ten cities in the US, you can invert for their relative positions.

Shepherd plot – measured vs true X-Y

Can be used if values are non-negative, symmetric, and represent triangular inequality.  $\chi^2$ , K-S and effect size meet these requirements.

'Flavors' of MDS: Classical MDS (best for small data sets), metric MDS, and non-metric MDS,

generally the most robust and accurate.

Differences and similarities with PCA--MDS better suited for multi-sample comparisons of age distributions. PCA is a special case of classic MDS using Euclidean distances

MuDiSc – <http://mudisc.london-geochron.com/> free MATLAB GUI and simple R code to implement MDS – also allows combination of petrographic and geochron info.

## **Analytical limitations on age uncertainty - Horstwood and Gehrels**

### **Matt Horstwood (with input from Pieter Vermeesch)**

Solution ICP-MS measurements of Pb solutions and mixed U-Pb tracers provide a 'best-case scenario' for laser-ablation precision, because they don't incorporate the additional variability in laser-induced elemental and isotopic fractionation. Performing these experiments was a suggestion from the 2009 San Francisco workshop. NIGL performed several experiments, in particular on dilute solutions of NBS 981, to assess the best achievable precision on the measured  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio. Overall, the internal precision is largely limited by counting statistics, with uncertainties falling linearly with the square root of the intensity of the smallest ion beam. Radial plots provide a nice way to visualize this information, and to spot aberrant (e.g. overdispersed) data. An overdispersion at the 0.03% level was apparent in the data for measurements using a multi-ion counting array. For U-Pb measurements at the 3Mcps level using a Faraday array this overdispersion appeared to be ca.0.25%. These would then represent minimum uncertainties from the mass spectrometry limiting the interpretation of LA data.

Laser ablation experiments using single and multi-collector ICP-MS looked at the impact of measured ratio versus integration times on the achievable precision for the Pb/Pb ratio. One clear way to decrease the measured uncertainties in a given isotope ratio for a single-collector instrument is to adjust the integration times of the two isotopes so that approximately the same number of counts (ion arrivals) are observed for each. For instance, if a measured  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio is 0.05, then the integration time for  $^{207}\text{Pb}$  should be 20 times longer to achieve maximum precision on this isotope ratio. However, when inclusions containing common-Pb are encountered, or if older or other common-Pb containing phases are analysed without adjusting the dwell times appropriately, the achievable precision is compromised (by around a factor of 2-4) on a single collector instrument. Since prior knowledge of the age and/or composition can not be known this would require dwell times to be adjusted 'on the fly'.

Further group discussion centered on which isotope ratios to optimize to achieve the best precision in 'age'. McLean: The 'best' optimization depends on which age you wish to optimize (e.g. 206/238, 207/235, 208/232), how you plan to combine the age information (e.g. concordia age), and whether or not you wish to incorporate decay constant uncertainties into the weighting. All agree that some optimization is better than using the same integration time for all

isotopes--perhaps optimizing to the standard being used is the simplest procedure. Horstwood suggests that 'live' adjustment of dwell times could be a significant request to bring to the mass spectrometer companies.

### **George Gehrels**

Although automated U-Pb LA-ICP-MS data acquisition is becoming commonplace, it is still important to have an operator looking at the data.

Lots of different data types can be used with U-Pb to help interpret data but how should they be stored? And how used?

Large dataset, presented at GSA: Four second analyses, for N=1000 study, with ten seconds between each. The PDP with N=1000 is more reproducible than each of the ten subsets with N=100.

For a PDP with nine age groups, N=700-800 seems enough to see a match between two sets of data, for 3 age groups N=400-500 enough, for 1 age group N = 150-200.

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## **Friday Morning**

### **Future directions for software and data handling in LA-ICP-MS geochronology**

#### **Discussion - Vermeesch, McLean, Horstwood**

##### **Vermeesch:**

The name 'Laplacian Stats' is a more appropriate name than 'Bayesian Stats'. Outline of Bayes Theorem: incorporates new information and prior beliefs to update the state of knowledge. In many applications, Bayesian and frequentist statistical approaches yield the same answer.

The Bayesian approach is often used for complicated systems because it is easier to apply, especially through the use of Markov Chain Monte Carlo modeling.

Possible applications in geochron: mixture modeling. This can be visualized for heteroscedastic data with radial plots. Bayes's rule is used to select the number of peaks in prob distribution (using the BIC, as presented in model selection talk on Thursday). Bayes Mix (mixture modeling) can be applied to detrital geochron data (published Jasra et al. Mathematical Geology 2005).

#### **McLean - Optimizing measurement protocols**

Building on Matt Horstwood and Pieter Vermeesch's recommendations on Wednesday, those who use single-collector instruments should strongly consider optimizing dwell times. What represents the 'optimum' is up for debate: Is the object the most precise 206/238, 207/235, 207/206 date, or some combination of the above? Should we include decay constant uncertainties when we optimize for uncertainties? Failing to make a choice for dwell times (e.g. leaving them all equal) is a choice in itself.

Spacing of reference materials through session: Sample-standard bracketing necessarily creates uncertainty correlation between unknowns. These uncertainty correlations increase the estimated uncertainty in a weighted mean, and this increase can be calculated using a generalized weighted mean algorithm (published in McLean et al., 2011). However, for all session fits except a mean, the magnitude of correlation decreases as the farther apart in time the two reference materials are. Therefore, you can decrease overall uncertainty by spacing important samples (e.g. secondary reference materials) evenly through session for to minimize their correlation with one another.

Modeling down-hole fractionation accurately is essential. The fewer parameters you need to describe this process, the smaller your uncertainties will be. Therefore, the single-profile method of Paton et al. is capable of being the most efficient. However, if your data do not fit a single profile (e.g. slopes vary from standard to standard), then this approach will underestimate uncertainties. Use of MSWDs and BICs can help choose the appropriate model. The higher the precision you can achieve, the better you are able to determine whether your down-hole fractionation pattern is truly repeatable: this allows you to model fractionation accurately. Significant discussion on these points.

Discussion about strategy of analyzing standards & tossing outliers. All agree in principle that 2-sigma outlier rejection under-estimates calculated uncertainties.

### **Horstwood**

Pulse-by-pulse and short time-duration applications are becoming increasingly used and important. To achieve true resolution within these data the analytical set-up must have the appropriate time resolution. The need for quantifiable performance metrics for ablation cells was highlighted using information in Eggins & Shelley (2002). Importance of uniformity of performance across the cell has already been highlighted. Capabilities in depth & lateral resolution for high-time resolution data should be quantified.

Ales Steely and Qing-Zhu Yin provided applications highlighting the benefits of this approach.

### **Alex Steely**

Zircons and other U-bearing accessory minerals are often complexly zoned, with thin overgrowths and chemical zonation in trace elements and age. High volumetric resolution is required, not just high spatial resolution. During a long ablation, the volumes of successive

depths within the mineral being ablated are mixed in the sample chamber and gas lines, so that the mass spectrometer records a convolution of the actual variation in age/composition. Although some authors have proposed methods of deconvolution, 'single-shot' or 'pulse-by-pulse' techniques avoid the inherent uncertainties in deconvolution by instead ablating a small discrete volume, analyzing it, waiting for the system to wash out, then ablating another volume.

Discussed 'aliasing' - time off-set in data, and used a 5 laser-pulse burst to increase signal. Signal under peak integrated as one data point and represented 0.5um depth using a 35um spot. Used 5sec washout time. Uncertainty achieved was 4-6% (2s) using this method. Data reduction is performed in LabView, and the data reduction scheme is not limited to U-Pb data or a particular analysis style. Key innovation: treat observed isotope ratio data for the reference materials as a three-dimensional surface with the x- and y-axes being down-hole distance and time during the session. The difference between a point on this surface and the true isotopic composition of the reference material represents the fractionation. At any point during down-hole excavation and during the session, the predicted fractionation for an unknown can be interpolated. This approach was verified by analysis of Plesovice as a secondary reference material, and the results were uniformly good if parsed by time or burst.

Discussion of need to optimize duty cycle, pre-ablation, dwell-time. New research is focused on the relationship between Raman spectra and laser-induced fractionation. Group discussion also centered around the role of flexibility in innovation for data reduction and software development.

### **Qing-Zhu Yin**

Technique development and applications in recent papers (split-stream with Analyte G2, Neptune & ElementXR, 50 sec burst)

Analysis of 206/238 with Lolite – works great with simple grains but samples of interest often have highly variable 206/238 down-hole. First subtract out the fractionation patterns from reference materials – end up with big range of discordance. Use this to extract info from highly discordant analyses by plotting up a discordia by using each integration of the analysis.

Question about how to assign uncertainties for each parse of data – uses  $\sqrt{\text{cps}}$ .

Unlike U-Pb there is no change in Hf down-hole so this can be a powerful tool to work Hf in complicated zircons as well as U-Pb.

Good discussion of strategies – continuous acquisition, burst-acquisition down-hole, or different pits on surface (issues of correlation of errors, mixing of material, etc.).

### **Databases and data handling - Walker**

Database/archiving challenges in general:

- make data entry easy (organized, credited, usable)

-- need unique identifiers for samples (IGSNs): SESAR/IEDA ([www.geosamples.org](http://www.geosamples.org)) – sample identifier (inputs sample info, e.g., lat/long, type, collector, stratigraphic information)

Software implementation: seamlessly incorporate data archiving into analysts' workflow:

U-Pb\_Redux – process data, assign IGSN, then upload to Geochron (simple process)

Review of other communities – Ar/Ar, He, Ion microprobe, etc.

Demo of U-Pb\_Redux - processing & uploading to Geochron (igneous sample)

Geochron demo – already contains thousands of DZ records archived by Gehrels and Arizona LaserChron. Multiple visualizations possible, images of concordia and probability distribution plots (no kernel density estimates... yet) viewable online. Easy geographic search with interactive map interface.

### **ISOPLOT Replacement - Bowring**

Ken Ludwig has worked for years to provide and support his Isoplot software package for the isotope geochemistry community. A large number of scientists and students around the world have come to rely on Isoplot for visualizing and publishing a wide variety of geochronological data. Two major events have in recent months altered this landscape: 1) Ken has retired, and 2) Isoplot, which is written in Excel, is not compatible with recent releases of Excel for Windows and Mac platforms.

Bowring is soliciting requirements from workshop attendees and others for a new tool that will replace much of the functionality of ISOPLOT. The tool will likely be written in the Java programming language, run on any platform, and be available as a stand-alone application, an app, and a web service. All aspects of the development will be open-source, beginning with this document. We seek to lead the development effort by securing NSF funding for phase 1 - a tool set that will provide the community-requested functionality now available in ISOPLOT.

### **Discussion**

Concern was expressed about not having Excel functionality tied to the plotting/analysis program: this is one strength of Isoplot. A solution would be to have a new program that stands alone, but has outputs that can be shown in Excel.

Bowring would like input on what's needed, and possible collaborations (info sheet was passed out)

General initial discussion of moving forward:

Bowring asked about filtering on input of info for database – lots of discussion: Consensus is to upload everything that has essential info (info for concordia diagram, sample name, lat/long,

citation)

Existing mechanisms and new ideas for using U-Pb\_Redux/Isoplot to teach isotope geochem/geochron:

- pop-ups for equations
- would be nice to have same capability in 'Isoplot 2020'

Discussion on the availability of multiple data processing 'packages':

The ideal would be for one program for all users versus each group having their own program:

- one view is to have one that everyone contributes to
- alternative view is to have several packages that might be tailored to specific applications (e.g., detrital, high-precision igneous, complicated grains)
- view aired that having several packages going is healthy for innovation

No community conclusion, but consensus was for multiple programs at least in the short term, to encourage innovation.

### **Integrating Imagery with Databases - Kylander-Clark**

Minerals are commonly complex, but can be used to reconstruct history of growth. An application using rare earth element patterns of zircon that record growth/dissolution of other minerals was highlighted.

The ideal is to show isotopic & elemental data on SEM images – need to find better ways to display data (currently Matlab, Lolite, R Package from Martin Rittner. Ideally it should also be possible to archive laser and CL images – Resonetics software can do this.

SHRIMP users have CL images on screen while driving, but it's very complex...

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## **Friday Afternoon**

### **High Throughput Example - Dirk Frei**

Frei gave a review of high-throughput automated methods developed at the DLC, Copenhagen (Frei & Gerdes 2009). Each analysis consists of a 20-second background measurement followed by 15-second on-peak, then a 40 second washout. 45,000 analyses have been performed in 18 months at a rate of approximately 1000 per day. Automated SEM of grain ID & size/shape acquired for every sand sample. Data are uploaded to an internal database, that also has data-reduction routines (much of the data is proprietary as well).

View expressed that flexibility in data acquisition & reduction is essential. Also that raw data needs to be archived such that it can be re-processed. Not just processed data. This is essential for re-processing. Some government agencies require that raw data is also archived (Sircombe

and Pearson echo that this is true in Australia as well) to provide transparency of process and traceability of how the results were determined.

## **Wrap-up - Horstwood et al**

New statistical tools are available to better interpret data, e.g Log-ratios, KDEs, BICs, MDS, etc. Using these provides better quantification of data and objective metrics on their interpretation. Guidelines for their use will follow and/or be promoted by key advocates in due course.

### Recommendations

- All labs should check the variation in determined normalisation/inter-fractionation across the cells they use.
- CL images of reference material chips used for normalisation should be used to correlate image characterisation with performance/normalisation factor. Some 'bad zones' in some reference materials had been identified by users.
- All labs should confirm that correct reference ratios are being used during data reduction packages.

### Actions/activities

#### 1. Conduct Software comparison

- Synthetic data set created by Vermeesch & McLean
- Real data set created by Jackson & Kosler
- Data sent to: Simon Jackson, Luigi Solari, Alex Steely, Norm Pearson (Glitter), Istvan Dunkl, Jim Bowring, Axel Gerdes, Chad Paton & Andrew Kylander-Clark, Tonny Thomson/Zirchron, George Gehrels
- File format = CSV
- 202, 204, 206, 207, 208, 232, 235, 238, timestamp for each
- 20 ratios, 50 unknowns
- Use your personal preferences of selecting/rejecting

#### 2. Standard distribution:

- George Gehrels will gather, prepare materials for distribution (~100 grains of each standard; 50 packs for participating and developing labs)
- Horstwood will work with IAG for distribution
- Presume IAG will have nominal charge for admin & postage (participants possibly charged, other labs for sure). Suggestion to charge for package to generate a fund for characterising reference materials - to be investigated.

Fish Canyon (Gehrels will gather)

Plesovice (Jan Kosler will provide?)



Temora 2 (Keith will send Gehrels 2 buckets)  
R33 (Gehrels will provide)  
GJ-1 NP/SJ will see if there is a GJ1 that is large enough, and has been calibrated  
91500 (from IAG)  
FC-Z2 (Gehrels will provide, perhaps more needed from Minnesota)  
QGNG & OG-1 (KS will send 2 buckets of each to Gehrels for processing)

3. As part of the above two activities a 'library' of reference ratios for the commonly used reference materials will be constructed and made available to ensure that the community are using the same reference values for a particular reference material.

4. DZ database:

Gehrels will continue loading data in Geochron, but with no filters for precision or discordance. Will re-load data that has been filtered.

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## Conclusions and Objectives

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Some key conclusions and activities were decided upon at the workshop. An interlaboratory comparison of the data reduction software packages was designed in principle and will be implemented with initial results planned for discussion by the participating group prior to the Goldschmidt 2013 conference in Florence, Italy. The collegial approach agreed for this comparison demonstrates the goodwill within the community to address these problematic issues while disregarding any potential vested interests. The comparison will use two data files, one synthetic another containing real data, to highlight the variability in LA U-Th-Pb results attributable to the variable processing parameters in the data reduction software.

In order to validate the analytical performance of each lab and the community in general, it was agreed that best practice would be to release data from a range of reference materials. Arizona LaserChron currently demonstrates this and its data collation offers insight into some of the accuracy issues that limit achievable precision. In order to promote this best practice, a package of reference materials will be constructed (likely for purchase), helping to increase the number of laboratories openly reporting validation. As part of this exercise, a library of reference material values will also be assembled so that all users are using agreed values for data correction. This was hypothesized to be a potentially significant source of some of the reported biases.

Finally, it was agreed that users should map out the U-Pb performance of their own ablation cell configurations and characterise (at least by cathodoluminescence) the reference material chips utilized during data acquisition.

