LA-ICP-MS U-Th-Pb Network Workshop

Prague Goldschmidt
15^{th}-16^{th} August 2015

Organisers:
Matt Horstwood, Simon Jackson, George Gehrels, Paul Sylvester, Norm Pearson

Workshop Goals

- To highlight progress in the zircon reference set and data processing software comparison initiatives.
- Defining the workflow and uncertainty propagation of common-Pb correction in LA-ICP-MS U-Pb geochronology.
- Defining the workflow and better practice guidelines for using annealing/chemical abrasion in LA-ICP-MS U-Pb geochronology.

Registered attendees (n=52)

Albrecht von Quadt	Kate Souders	Sebastian Tappe	Matthew Horstwood	Elton Dantas
Quentin Crowley	Urs Schaltegger	Azam Soltani Dehnavi	Victor A Valencia	Felipe Valença de Oliveira
Adriana Potra	Juliana Marques	Gabriela Solis-Pichardo	Norman Pearson	Paul Sylvester
Takafumi Hirata	Inga Sevastjanova	Donnelly Archibald	István Dunkl	David Chew
Martin Svojtka	André Poirier	Yuji Orihashi	Axel Gerdes	Jean Ping Mei Wong
Sebastien Meffre	Bodo Weber	Irina Tretiakova	Karina Zavala	Dirk Frei
Daniel Wiemer	Gavin Kenny	Ellen Kooijman	Ivan Belousov	Leonid Neymark
Yoshiaki Kon	Andreas Moeller	Charles W., Jr. Magee	Aleksey Sadekov	Noah McLean
Shuhei Sakata	Jean David	Matthijs Smit	Olawale Kayode Aromolaran	
Tonny B. Thomsen	Elena Belousova	Kyle Heron	Frank Tomaschek	
Jeffrey Oalmann	Morgan Blades	Pete Kinny	Simon Jackson	

Workshop Programme

Saturday – August 15th, 2015 (Day 1)

Time	Event
9:00 – 9:30	Introduction and tribute to Jan Košler *Matt Horstwood, Paul Sylvester & Simon Jackson*
9:30 – 10:30	Initial results from the zircon reference set 'offset plot' experiment – *Do we all see the same biases?* *George Gehrels & Matt Horstwood*
10:30 – 11:00	Coffee Break
11:00 – 12:30	Initial results from the data processing software comparison - *How significant are the biases introduced by different data processing packages and where do they occur in the processing workflow? Are the uncertainty outputs the same?* *Simon Jackson*
12:30 – 13:30	Lunch
13:30 – 16:00	Annealing/chemical abrasion in LA-ICP-MS U-Th-Pb geochronology – email discussion team synthesis and open floor discussion *Intro from Albrecht von Quadt* *Skype presentation from Luigi Solari* *Presentation from Quentin Crowley* *(with coffee around 3pm)*
16:00 - 17:00	Discussion summary – Defining better practice guidelines for using annealing/chemical abrasion – *when can we use it and how?*

Sunday – August 16th, 2015 (Day 2)

Time	Event
9:30 – 12:30	Common-Pb corrections in LA-ICP-MS U-Th-Pb geochronology - email discussion team synthesis and open floor discussion *Intro - Highlight questions (consider these through presentations)* *Iolite common-Pb DRS presentation from Chad Paton* *VizualAge DRS presentation from Dave Chew* *Presentation from Axel Gerdes* *Discussion around highlighted questions* *(with coffee around 10:30)*
12:30 – 13:30	Lunch
13:30 – 15:00	*Common-Pb in Redux presentation from Noah McLean* Discussion summary – Defining better practice for common-Pb corrections – *How are they best performed, what is the right uncertainty propagation and what are the limits to interpretation?*
15:00	Closing remarks
N.B.	Timings will be flexible to accommodate discussions and allow for over-run from the first day.

Notes from presentations and discussions

Initial results from the zircon reference set 'off-set plot' experiment – George Gehrels & Matt Horstwood

Following the 2013 Charleston Workshop a set of 10 reference zircons was compiled and distributed to 46 labs to investigate potential systematic off-sets noted between the determined and expected ages for some of these materials. George Gehrels has led this effort, organising the picking and packaging of 100,000 zircon grains!

The purpose of the exercise was two-fold:

- to investigate whether different labs saw the same biases, and
- for each lab to use these materials to quantify the systematic, long-term variance uncertainty component required in the uncertainty propagation protocol defined at previous workshops (see recommended uncertainty propagation protocol on www.Plasmage.org)

To date, only 10 labs have submitted data and so the presentation represented only a recent snap-shot of the compilation results. Assessment of the data will continue and further submissions were requested.

The data were reported as weighted means of 9-10 points with 2s uncertainties without propagation for systematic uncertainties since most labs did not report this component when requested.

Initial conclusions seem to be that the younger (<100Ma) samples were challenging with fairly scattered Pb/U and Pb/Pb results. Pb/U for Plesovice was reported as systematically higher than the expected (chemically abraded (CA-)TIMS) value by around half of the labs with the other half much nearer the expected value. Temora 2 showed a more even spread of values around the expected age with limited scatter (+/- 2% range) whilst R33, of similar age and U concentration, demonstrated a much greater scatter of values and assigned uncertainties. 91500 returned Pb/U results systematically young by around 1% whilst Pb/Pb results were more accurate. FC1 (Duluth Gabbro) returned Pb/U results systematically high by ca. 1%, again with more accurate Pb/Pb results on the whole. On the whole the results returned for Oracle were more accurate with possible biases to young Pb/U ages and older Pb/Pb ages. Pb/U results for Tan-Br were somewhat mixed, possibly a little old, whilst the Pb/Pb results began to clearly demonstrate the need for systematic uncertainty propagation. OG-1 appeared to return Pb/U results around 1% older than expected whilst the Pb/Pb results scattered around the expected value but with underestimated uncertainties.

The results were compared to both chemically abraded and non-chemically abraded TIMS values where these were available. On the basis of the evidence so far, LA-ICP-MS U-Pb data from non-chemically abraded reference materials appear to better match the non-chemically abraded TIMS reference values. Since the Pb/Pb ID-TIMS results are very similar for both CA and non-CA reference values, LA-ICP-MS Pb/Pb agree with both.

Clear anomalies seemed to be:

- OG1: LA Pb/U ages are older than both CA and non-CA reference values
- FC-1: LA Pb/U ages are older than the CA reference values as indeed are the non-CA reference values
- 91500: LA Pb/U ages are younger than both the CA and non-CA reference values

Although not intended as an interlaboratory comparison, taking the statistics as such indicated a ca. 3% 2SD uncertainty on the reported Pb/U accuracy (for the >100Ma samples, rising to 4.5% for the <100Ma samples). This was better for the Pb/Pb results on average which scaled with the age of the sample.

It was noted that the present data set is too small to document any offsets with certainty and the return of more data was requested. Assessment of these systematic offsets will continue as more data are returned. It was also reiterated that systematic uncertainty components should be reported with the returned data and that these materials should be used by each laboratory to document the long term variance of their results. No more materials will be distributed until more data from this exercise has been assessed.

Discussion

The reason for the more scattered results for R33 compared to Temora 2 was questioned. It was noted that R33 was developed as a reference material for SIMS and that the SIMS community recognise fractures and heterogeneities in this material that might impact deeper LA analysis. Optical and CL imaging of R33 is therefore important in targeting LA analyses and R33 is likely more useful as a validation material rather than a primary LA reference. It was also noted that the TIMS community have considerably more difficulty in reproducing R33 and that there might therefore be some small scale age variation. It was suggested that comparing the offsets with count rate might also be revealing.

The systematically young Pb/U results for 91500 were discussed. This material is used as a primary reference by a number of labs. At least 4 labs have observed very young chips of 91500 in the past (presumably from the original aliquot of material rather than that being distributed more recently) with some suggesting Pb/U ages down to 950Ma. It was also noted that there is a colour difference between the original (coloured) and newer (clear) batches of 91500 being distributed and that this may be related to U concentration.

It was questioned and confirmed that this uncertainty level of 3% is the uncertainty level at which data need to be compared in the literature. For an individual lab, the propagation of their long term variance represents their accuracy.

It was noted that this was a worst-case scenario since the reporting labs utilised the full range of mass spectrometry and laser ablation equipment with related variability in acquisition methodology.

In light of this it was noted that the relevant metadata needed to be submitted with data for this exercise and all journal submissions and that a Community-recommended metadata table was available on www.Plasmage.org

It was also highlighted that accurate ion counter deadtime corrections were important and that this was possibly an issue with the Pb/U results for OG1. It was also noted that FC-1 was known to be available through some alternative sources but it was confirmed that the material used had come from a reliable source.

Tribute to Jan Kosler – Paul Sylvester

Paul gave a compelling tribute to our departed colleague Jan Kosler who is greatly missed by the community and who was a key figure in the LA U-Th-Pb Network activities. Paul highlighted Jan as a creative and broad-thinking scientist, describing his contributions outside of geochronology and his love for Canada, seeing analogies with science in the openness and frankness of exchange found there. Jan's mischievous sense of humour was also highlighted and his love for his family. This was also later highlighted by Simon Jackson who described a recent canoe trip with family where, ever the innovative scientist, Jan dispensed with paddle-power mocking-up sail-power for more efficient progress! Paul led the audience in a round of applause to remember Jan and noted that the workshop was set-up in his honour and dedicated to his work and contribution to LA-ICP-MS geochronology. Rest peacefully Jan.

Evaluation of U-Pb laser ablation ICPMS data reduction software: an inter-laboratory comparison – Simon Jackson and Jan Kosler

Simon described an experiment in which Jan was instrumental, conducted as a result of discussions held at the Charleston 2013 workshop. The experiment centred around generating a LA U-Pb data-set which would then be distributed to key data processing software package authors/practitioners to process using their respective packages.

The goals were:

1) to determine best practice in LA-ICP-MS U-Pb data processing
2) to provide a set of reasonably standardised procedures
3) to publish these as a paper

A key aim was to evaluate and improve existing data-reduction packages

30 analyses of an unknown zircon (Z9910), previously dated by ID-TIMS at the GSC, were distributed to software package authors. These were analysed in 5 blocks of 6 analyses interspersed with analyses of reference materials 91500, GJ-1 and Temora 2. Ablations were 60seconds long with a 30second baseline measurement. There was some common-Pb in the sample. The weighted average 206Pb/238U result for the ID-TIMS data (not CA) was 441.15 +/- 0.69 (95% conf, MSWD =1.3, n= 5). Some aliasing effects were apparent in the laser ablation data distributed which had been deliberately left in to challenge the exercise. Some samples had drilled through during the 60sec ablation, some spikes of common-Pb were apparent, alumina-silicate inclusions and U data spikes.

The software packages evaluated as part of this study were: Iolite (v2.3 & 2.5) with and without VizualAge, UPb.Age for R, GLITTER, UranOS and UPb Redux.

The ID-TIMS data suggested very little Pb-loss in the sample.

Considering the output for each of the 30 individual sample analyses, it was noted that although there had been submissions from multiple users using the same package, no two submissions resulted in the same output for the processed data, indicating the presence of user bias as well as any package-related effects. There was at least a 2% range (up to 8%, median 3.1%) in the determined 206Pb/238U age reported by each package for a single data point. Equally, there was a 2% range (up to 18%, median 2.8%) in the determined 207Pb/206Pb age, however it should be noted that a common-Pb correction was not routinely applied by most participants so a large degree of this variance will likely be assigned to this.

Excluding the result from an earlier version of UranOS (and UPb Redux which had only been submitted immediately prior to the presentation), all weighted mean 206Pb/238U results were within a 0.6% range (i.e.+/- 0.3%) but all were systematically younger and outside of uncertainty compared to the ID-TIMS result (except the earlier UranOS result which was younger but within uncertainty). The UPb Redux result was the more accurate result at 440.8 +/- 4.8 (2s, MSWD ~3, excluding 3 points). It was noted that Redux had used the intercept method of downhole fractionation correction unlike the rest of the packages. This was discussed later but not thought to be a significant factor. It was noted that the MSWD values for all the returned results were all >1 (1.4-13), probably due to the lack of common-Pb correction but that this could also reflect the aliasing effects in the data. The reported 207Pb/206Pb ratios were mostly high due to common-Pb.

Conclusions

Processing of LA-ICP-MS U-Pb data typically induces a median ca.3.1% variations on an individual 206Pb/238U age (2.8% on an individual 207Pb/206Pb ratio) and up to 1.4% range on the weighted mean 206Pb/238U age (1.3% on a weighted mean 207Pb/206Pb ratio).

Encouragingly, excluding 1 result (and the recently submitted UPb redux result), the spread (i.e. range) of weighted mean 206Pb/238U ages is only 0.6% (+/- 0.3%) but all results are biased low (by 0.6-2%) compared to the ID-TIMS results (except the excluded result which was within uncertainty at the 95% conf. level).

It would appear that all the various approaches to correct Pb/U fractionation operate equally well giving precise but inaccurate results. However, this bias could also be a function of the original analysis rather than reflecting a bias in the data processing.

Results are both software and operator dependent.

MSWD's for weighted mean 206Pb/238U ages are all >1, mostly >2, indicating excess variance over and above the quoted uncertainties, likely caused by variable Pb/U fractionation, single channel spikes in U and common-Pb. For 207Pb/206Pb, MSWD's are >1 except for one package where both users appear to have screened out common-Pb effects resulting in MSWD's <=1. No reported data were common-Pb corrected despite significant evidence of its presence. These differences in processing of single data points are sufficient to cause significant differences in interpreted ages for data populations when using unconstrained regressions or when interpreted as detrital data.

Observations from this exercise were that a common-Pb correction needs to be more widely applied during data processing, even for small amounts of common-Pb, greater care needed to be taken to omit problem parts of the TRA signal when selecting integrations and that judicious and painstaking processing of data was instrumental to avoid common-Pb, zones of Pb-loss and other artefacts. More robust uncertainty propagation still needed to be applied.

Points raised in Discussion

- Chemically abrade the sample material to remove common-Pb issues and repeat the exercise.
- Use only the 1st 20secs of data to mitigate against downhole fractionation variations to see if closer agreement to the ID-TIMS result was achieved.
- The same primary reference value had been used by all participants.
- Quantification of laser fluence each day was important in documenting laser performance.
- GLITTER applies the same uncertainty to the primary reference ratios for 207Pb/206Pb and 206Pb/238U
- It was commented that the downhole corrected Pb/U profiles of most sample analyses were not flat.
- The MSWD of the secondary reference material results limit that which can be expected for the samples
- For a 15-20Ma old material, geological variations will begin to impact results
- Marillo-Sialer et al 2015 demonstrates variability in the downhole Pb/U fractionation with each material and even each analysis.
- OG1 fractionation effects are really problematic. This could be a sub-sampling scale problem linked to mobility of U and Pb.
- There may be a lack of flexibility in the software packages which is constraining processing. However, greater flexibility also leads to greater potential variability due to the larger number of variables and selection bias/variability by the user.
- Two sets of data could be generated, one strongly fractionated (acquired at ca. 6J.cm-2) the other not (acquired at ca. 1J.cm-2), with no aliasing effects, and the experiment repeated.
- Discussion of Pb/U fractionation correction using the 'intercept method' vs 'downhole correction' ensued following the Redux result. It was noted that a 'downhole correction' provides a fit to the data with the fewest parameters and assumptions and is a correction model which can then be tested since the resulting Pb/U profile should be flat if the sample and reference material match. However, any remaining variation could reflect a real age variation. The 'intercept method' requires more assumptions and parameters to fit the data and assumes that there is no internal variation of the material (or data) during ablation. However, consensus appears to be growing that each material fractionates differently and that, in detail, equality with the primary reference material may not be the norm.
- Since their packages were both equipped with the capability, Istvan Dunkl and Noah McLean agreed to produce both 'downhole corrected' and 'intercept method' corrected results for comparison.
- Comparison of scatter of weighted mean results using 6-10 data points instead of the 30 used in this study, might be a more realistic demonstration of the data scatter usually reported.

Istvan Dunkl highlighted the 'decision tree' of data processing and noted strongly that the variation in output results was much more due to variations made in selections by the user rather than software related. A suggestion was put forward to use multiple reference materials for standardisation to more realistically assess the range of biases between reference materials and apply this to samples. A counter-argument was that this simply masked these biases, preventing our resolution of them so that we might understand their origin.

Suggestions and actions

One goal of this exercise was to look at the uncertainty contribution from data processing variations.

The results are very similar between packages using a downhole correction method (+/- 0.3% range for weighted mean data, n=30). Using n=6-10 is more reflective of the number of data points used in an age calc. It is likely that this variation would then increase a little, perhaps 0.4%? (but some of this will be down to common-Pb). – **When comparing published weighted mean dates, data processing variations likely contribute ca.0.4% to the systematic uncertainty limit (2-3% 2s).**

For single data points the range was 2% (for clean data) to 8% (with common-Pb) (median 3.1%) – **+/- 1% then represents the single data point variation from data processing alone! This represents an uncertainty limit for comparing detrital U-Pb data point ages in the literature. A +/- 1% (2% range) limit was also noted for 7/6 data (but these contain common-Pb……)**

Only the one result using an intercept method gave an accurate result. This needs proving as cause and effect

Actions

1) **Noah to give the downhole correction result from Redux to see if this really is different in the same package;**
2) **Istvan to generate an intercept method corrected resulted to go with his downhole corrected one for the same reason;**
3) **Axel to return a result (intercept) to see if agrees with Noah & Istvan;**
4) **Put file on Plasmage.org for people to download and try out their processing practice/package**
5) **Use first 20secs of data and try again…..lower degree of LIEF should give more accurate end result for downhole method, also negates some of the variation with depth issues for downhole method. Does this make the outputs more similar?**

Intercept vs Downhole correction thought-tree

- If you have reason to think that the downhole fractionation is purely related to LIEF, use the intercept method; if it could be age variation or there are other complications in the fractionation profile, use the downhole correction.

Downhole correction is the safest method – uses least assumptions – but more likely to be inaccurate for internally simple samples.

Intercept correction makes more assumptions of the fractionation profile but should be more accurate for simple analyses. For more internally complex samples the intercept method is more likely to be inaccurate.

Since drill rate varies for each ablation causing a change in Pb/U fractionation behaviour, we need another proxy for drill rate/ablation volume variation that isn't Pb/U. If we corrected the downhole fractionation using this, this would be an accurate correction. Norm Pearson suggested that the decay in signal profile during an ablation and the difference of this between ablations, could be used as a proxy for drill rate.

Annealing/Chemical Abrasion in LA-ICP-MS U-Th-Pb geochronology

Prior to the workshop an e-mail discussion team addressed some questions regarding the role of annealing and chemical abrasion (A-CA) in LA-ICP-MS U-Pb geochronology. A summary of the e-mail discussion is presented below.

Annealing/Chemical Abrasion (A-CA) E-mail discussion team summary

A-CA team – Albrecht von-Quadt, Quentin Crowley, Luigi Solari, Charlotte Allen, Estephany Marillo-Sialer, Martin Whitehouse, Matt Horstwood

1) ***What are the appropriate reference values to use during the A-CA approach?***
    a) Agreement that ratio specific reference values should be used (i.e. 206Pb/238U reference ratio to normalise 206Pb/238U sample data, not a conversion from an assumed age).
    b) Suggestion that the community should fix on ONE reference value regardless of whether material is A-CA or non-A-CA.
    c) Another suggestion that non-A-CA is the reference value to use for non-A-CA AND annealed-only material
    d) Suggestion that for non-A-CA reference materials, the discordance difference in age (i.e. between the 207Pb/206Pb and 206Pb/238U ages) should be propagated as a systematic uncertainty (e.g. ca. 0.3% difference between Pb/U and Pb/Pb age in 91500) to reflect the potential for some parts of the crystal to be concordant whilst others might be more discordant than the TIMS reference value.
    e) Noted that the effectiveness of the A-CA procedure is grain size dependent and that larger A-CA'd chips can be unaffected in their centres. The effectiveness of the A-CA procedure needs to be proven for a specific size of reference chip.

2) ***Does the A-CA approach make samples and reference materials more similar or can it introduce more variability?***
    a) Some do CA, most just annealing. Annealing takes 48-60 hours. CA 1-2 days. **When is CA required rather than just annealing?**
    b) CA reduces scatter in the data set
    c) Raman studies show there are still physical differences in crystals after annealing possibly resulting in variable ablation rates even after annealing. Ablation rates are never the same between samples and reference materials but A-CA improves things. Ablation rate variation not the same for all samples
    d) Observation – 91500 has significantly higher alpha dose and ablation rate than most zircons (but still used as a primary)

e) Suggestion that process of metamictisation fractionates U-Pb in zircons and therefore is not just a downhole effect and affects raster scans also.

3) ***Considering the factors above, when is it appropriate to utilise annealing and/or CA, when will it fail, which assumptions might not be fulfilled after annealing and what are the potential 'false positive' interpretations which might be generated?***
   a) Suggestion to A-CA everything….but some high-U grains wont survive
   b) Suggestion that annealing doesn't improve accuracy significantly
   c) Note from above – effectiveness of A-CA process is grain-size dependent. If the process hasn't A-CA'd the whole grain then the reference value used wont reflect the material ablated causing over/under correction of the sample data point.
   d) CA isn't guaranteed to get rid of all Pb-loss
4) ***Can we define 'better practice' in using and interpreting data treated by annealing and/or CA?***
   a) No too early to state this for laser work
   b) Independent LIEF correction for each analysis overcomes ablation rate variations. Can the data processing packages be modified to do this?
   c) Recommendation for an A-CA procedure for a specific grain size?

At the workshop, members of the e-mail team gave presentations to show further details on the subject.

Albrecht von Quadt gave an introduction to this topic, highlighting that annealing conditions commonly used were on the order of 850C for 48hrs, requiring cooling of the sample for 0.5 day before further processing. Chemical abrasion then took 12hrs (commonly overnight) at 180C and another 0.5 day for cooling. A further wash with 6N HCl on a hot plate at 80C for 24hrs was needed prior to rinsing. Albrecht highlighted a TIMS data example and noted that the effectiveness of CA was crystal size specific and didn't always get through to the centre of large grains or chips of reference material. CA did however appear to improve the accuracy and reproducibility of LA data by reducing scatter up to 50%.

Luigi Solari discussed his work over a skype link, highlighted the advantages of annealing without the need for the full CA process. This required only the step requiring 48hrs at 850C with no other washing or preparation and several hours cooling. Luigi studied annealed and non-annealed grains mounted together and analysed at the same time. A range of elements (Si, P, Ti, Y, Nb, REE's, Hf, Pb, Th, U) were determined on a Q-ICP-MS with laser fluence checked at the beginning and end of the analysis session. Iolite and VizualAge were used for data processing with 91500 used as the primary reference material, Plesovice as validation, both annealed and not-annealed. Ages for Plesovice were significantly different between material annealed (337-338Ma) and not-annealed (ca.340Ma). Two pegmatite samples showed significantly improved scatter in the data sets although all data were slightly younger than the expected age based on TIMS. Annealing was found not to change the elemental content, overgrowth structure or REE pattern and abundance. An apparent improvement in precision for Hf isotope data from annealed material needs confirming and could relate to a better tuned instrument and improved sensitivity on the session (annealed and non-annealed data were gathered 2yrs apart). SEM images demonstrate that the structure of zircon material is much improved by annealing with cleaner ablation pits resulting.

Quentin Crowley presented more CA work, specifically addressing the question of whether the full CA process is needed or just annealing. The time investment involved in the CA wasn't considered excessive and to a certain extent the time spent could be regained through less time spent collecting discordant data. Older high-U grains were considered troublesome with care needed. CL zoning was still distinct after CA with the bonus that CA eliminated common-Pb (whereas annealing doesn't). It was noted that this was akin to excluding the common-Pb through judicious ablation signal integration. Optical interferometry was used to measure differences in zircon ablation rates on the nm scale, it being a cheap, rapid and easy to use technique. A difference of around 5% was noted in the degree of downhole fractionation seen in annealed (less) vs non-annealed (more) material. It was recommended that samples and reference materials were treated alike, i.e. CA'd reference materials should be used for CA'd samples. Using Mud Tank, a slight correlation of age and alpha dose was suggested. **Estephany Marillo-Sialer**'s work was also noted, showing a strong positive correlation between increasing pit depth (expressed as aspect ratio) and resultant age as laser fluence was increased. It was noted that annealing reduced ablation rate but did not make all ablation rates equal and that CA was an effective pre-treatment for LA work, reducing Pb-loss and common-Pb.

In discussion afterwards, it was noted that absolute calibration between interferometers will vary resulting in different pit depths between materials measured on different interferometers. Also, the alpha dose calculation depends heavily on the complexity of the cooling history and that mostly this is unknown. Clearly annealing would improve the resolution of inaccuracy but the increased time required for collection and reduction of extra non-annealed data may outweigh the time investment in doing the whole CA process. A benefit for detrital samples where large volumes of data need to be interrogated, is that CA might highlight some populations that would otherwise not be visible from non-CA'd discordant data. It was suggested CA can be applied to 1000 grains just as easily as 1 grain so little time is lost CA'ing more material.

Jeff Oalman highlighted the change of Raman response when zircons were annealed, noting that Mud Tank possessed perfect crystallinity without annealing but that this was never achieved for the other reference materials even after annealing.

Leonid Neymark highlighted his annealing experiments which appeared to show results biased to older ages after annealing when prior to annealing any bias was within uncertainty of the expected value. It was suggested that this might reflect a heterogeneity that had occurred in the primary reference material since it affected the results of more than one sample.

Paul Sylvester showed the results of some experiments on Jack Hills and Mount Narryer detrital zircons which appeared to show no effect on concordance after annealing.

<u>A-CA Discussion Summary</u>

Ablation rate varies with each material and correlates with U-Pb fractionation. Annealing reduces ablation rate (= LIEF)(but doesn't make all ablation rates equal) and U-Pb fractionation and is therefore beneficial. Annealing appears to reduce scatter in data points for a sample.

Conclusion – There is strong evidence indicating annealing is a beneficial first step in LA sample prep

Match the state (annealed, not-annealed) of samples and reference materials

Recommendation – use non-CA'd reference values for annealed materials (Pb-loss still present in annealed grains)

There is a need to calibrate-out ablation rate variations. This represents a failure of the downhole correction method. Subtle variations of laser focus affect ablation rate/LIEF (Marillo-Sialer et al 2014). – *can we standardise our focussing better? Autofocussing mechanisms?*

Should we chemically abrade all LA materials (or just anneal)? Chemical abrasion is clearly a useful tool in LA work – improving precision and accuracy. Doesn't eliminate ablation rate variations. By CA'ing, we might lose some poorly constrained age information but should we "just let it go" since we can't interpret much from it anyway??

CA is not 100% effective for all materials. Some Pb-loss can remain (based on CA-TIMS data). Can Pb-loss profiles be useful? Rarely. Common-Pb trajectories are useful….but only for correcting/regressing data; should we just CA it?! Can't do CA on non-zircon materials or thin sections – have to live with effects there so need to understand the potential inaccuracies and limits to interpretation for these instances.

Common-Pb corrections in LA-ICP-MS U-Th-Pb geochronology

Prior to the workshop an e-mail discussion team addressed some questions regarding common-Pb corrections and assessment in LA-ICP-MS U-Pb geochronology. A summary of the e-mail discussion is presented below.

Common-Pb corrections e-mail team discussion summary

Team members – Axel Gerdes, David Chew, George Gehrels, Andrew Kylander-Clark, Chad Paton, Noah McLean, Axel Schmitt

1) ***What acquisition strategies are appropriate for different instrument types?***
   a) Variety of instruments and acquisition methods too great to give generalised guidelines

2) ***Data can be corrected for common-Pb during TRA processing of the data or after this stage on the mean value. What are the pro's and con's of these two approaches and when is one more valid than the other?***
   a) If common-Pb is variable through the run, time slice correction is required
   b) When 204 is small then using a mean value at the end may be beneficial (using RoM)

3) ***What are the strategies for dating common Pb phases where the standards contain appreciable (and variable) common Pb?***
   a) See Iolite DRS – presentation by Chad
   b) See VisualAge DRS – presentation by Dave

4) ***How should common-Pb corrections of data be applied in both TRA and mean data point scenarios? What is the appropriate uncertainty propagation for each of these?***
   a) 'Double regression' of data (where data are regressed on a T-W plot and the defined 207Pb/206Pb used to then 'correct' the data points prior to a weighted mean calculation) is invalid since it ignores the uncertainty on the 207Pb/206Pb used AND the intercept uncertainty defined in the original regression. The resulting age uncertainties are far below reality.
   b) Agreed. These double-corrections should no longer be used.
   c) Common-Pb assessment should use a Tera-Wasserburg plot to maintain resolution of scatter in the common-Pb regression. This is lost if a common-Pb correction is applied and propagated into each data point as standard procedure.
   d) There is no additional information gained by correcting the data to concordia, so it cant improve the derived age. The correction to concordia actually uses up information - we lose potentially useful details about the variability in common-Pb fraction and composition, and scatter between individual analyses.
   e) Where a Tera-Wasserburg age gives a frustratingly large uncertainty we need to add more information to the system - either by making an assumption about the common-Pb composition, or by analysing a cogenetic common-Pb rich phase.
   f) Unless the common-Pb composition in the sample is variable with each point, the correction uncertainty is a systematic component and should be propagated into the regression result.

5) ***Can we recommend some uncertainties for the Stacey-Kramers values?***
   a) Survey of room at workshop. What uncertainty values and how did you arrive at them?

6) ***How should common-Pb corrected data be quantified and interpreted?***
   a) State the Pb correction method applied, the initial Pb composition used (and its uncertainty), and the rationale for employing that initial Pb composition.

At the workshop, members of the e-mail team gave presentations to show further details on the subject.

Chad Paton demonstrated a new Iolite DRS which allows downhole correction in conjunction with common-Pb assessment in Tera-Wasserburg (T-W) space. For common-Pb containing materials there is a need to separate the common-Pb content variation from the U-Pb fractionation. There are 3 scenario's that need to be dealt with:

1) no common-Pb
2) a constant amount of common-Pb - a conventional downhole correction will still work here
3) a variable amount of common-Pb

The new DRS doesn't 'correct' for common-Pb but removes it temporarily from the ablation profile to allow correction of the downhole fractionation. A T-W projection can then be used to calculate the age intercept on Concordia.
Chad showed the new DRS and talked over the pro's and con's of the approach.

Dave Chew showed a similar approach using a new VizualAge DRS (UcomPbine) for Iolite. Here though, a common-Pb correction is first made to reveal the downhole fractionation. The common-Pb correction can be based on 204Pb, 207Pb or 208Pb and assumes the age of the reference material is homogeneous and that its common-Pb composition is constant.

Axel Gerdes described his approach using his own 'in-house' spreadsheet calculations. A 204Pb-based correction is first made before an intercept correction of U-Pb fractionation. For young samples a 207Pb-based correction is used.

It was noted that a common-Pb correction must first be made if an intercept correction is used, to help conform to the inherent assumptions of this model (that the profile represents only U-Pb fractionation). A T-W assessment cannot therefore be employed after using an intercept correction. Using a downhole correction (where the sample correction is based on that of the reference material), a T-W assessment can be employed. For high common-Pb minerals (e.g. carbonates) where a T-W assessment is a better mechanism for interpreting age, a downhole correction method must be used.

Dave Chew then highlighted some examples of dating of common-Pb containing accessory minerals. Common-Pb correction in rutile utilises 208Pb due to the low Th content of most rutiles. But some samples do contain Th. This raises the question of calibration of Th/Pb in rutiles when the reference materials have little Th. Calibrating to NIST seems like the only realistic option at this point. Four scenarios of T-W regressions were highlighted:

1) well constrained regressions – data set with a large spread of U/Pb requiring no further constraints
2) moderately constrained regressions – require anchoring to a sensible common-Pb composition with a large uncertainty
3) poorly constrained regressions, data mostly common-Pb – require anchoring to common-Pb with conservative uncertainty
4) poorly constrained regressions, data close to Concordia as a 'bullseye' – require anchoring to common-Pb with conservative uncertainty

When to use a 204Pb or 207Pb-based correction was highlighted. 207Pb corrections assume concordance so should not be used for materials which may have experienced Pb-loss. It was suggested that for zircons, a 207Pb-based common-Pb correction was only appropriate for zircons <20Ma.

Noah McLean discussed the propagation of uncertainties on common-Pb compositions and highlighted a little of how Redux deals with this. In contrast to the apparent accuracy of the intercept corrected Redux result in the software comparison exercise, it was noted that the original off-set plot of George Gehrels which originally highlighted apparent biases between different samples, was also based on intercept corrected data. A note of caution was added with regard to using feldspar to determine a common-Pb composition for a sample, since the lowest mu (238/204) zones need to be used for this to avoid radiogenic ingrowth in those higher U zones. Redux allows for random and systematic uncertainties to be assigned to the common-Pb composition. It is also important to consider correlations between 207/204 and 206/204 which reduce the uncertainty on such diagrams to the width of the uncertainty ellipse rather than its length in either axis. Statistical reasons for why 'double regressions' of common-Pb containing data were wrong, were also highlighted. In answer to a question regarding the appropriate level of uncertainty that should be applied to common-Pb ratios, it was noted that the Earthchem database could be used to assess this and that George Gehrels had previously investigated this in a paper (2008) and decided on conservative uncertainty levels of 1, 0.3 & 2 (2s) for the 206/204, 207/204 & 208/204 respectively.

<u>Common-Pb Discussion summary</u>

Recommendation – 'Double regressions' of common-Pb containing data should not be used. Instead T-W regressions with appropriate uncertainty propagation on the regression intercept result more accurately reflect the scatter in the data constituting the regressed population.