Instructions for in-situ LA-ICP-MS Analysis

V. 2

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Purpose

The purpose of this lab/instruction manual is to introduce you to in-situ LA-ICPMS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) of accessory minerals of geochronologic interest and multi-element analysis of geological samples (For more information on LA-ICPMS see PDF file titled “Intro to LA-ICPMS” located in anonymous/LA_ICPMS/Intro to LA-ICPMS.)

Lab safety

Whenever working in a laboratory, safety should be the most important concern. LA-ICPMS work is no different. A number of simple rules to be followed in the ICPMS lab are listed here:

- Always wear eye protection
- No food or drink in the lab

General LA-ICP-MS operating procedures

Start-up (ICP-MS Vacuum System ON but not Plasma)

ICP-MS (internal schematics shown in Fig. 1)

- Turn on the cooling unit located under the laser ablation system. Wait 3 minutes before turning on the plasma.
- On the computer, go to the ‘ELAN’ software and click on the Front Panel of the Instrument window.
- Turn on the plasma.
- Go to optimization window, select manual optimization and adjust Nebulizer Flow to 0.7 L³/min
- Wait for 15 minutes to warm up the system.

Helium

Plug in GFC unit next to laser. Display should read 0.00 L³/min (this is the ‘set point’) Open valve on helium tank and adjust flow to ~5 psi.

Laser Ablation Unit

- Turn on the main laser power unit (located underneath the monitor table). The switch is on the back of the unit.
♦ Turn on the laser (switch on the back).
♦ Turn the key on the main power unit clockwise to ‘I’.
♦ On the computer, open the ‘MEO Laser’ software and let the system power up.
♦ Click ‘OK’ when you see the prompt after the XYZ calibration.
♦ Fire the laser at ZERO power.
♦ Warm-up the laser for 20 minutes.
♦ Click on ‘Purge’ after the ICP-MS plasma has warmed up and bring the system ‘Online’. Wait another 5 minutes before loading the sample chamber.

**Optimization**

- Load dark blue NIST Glass 610 (see loading samples below)
- Open method to be used in Elan. Change replicates to 1, and readings/replicate to 1000. This allows you view signal in real-time and thus optimize the settings. (Don’t forget to change the numbers back to 1000 replicates at 1 reading/rep to allow for GLITTER reduction)
- On the laser software select ‘line scan’ with speed of 5um/sec with a spot size the same as will be used in analyses.
- In the “real-time” window select 2-3 analytes to monitor during optimization.
- Open Optimization window and select ‘manual optimization”
- Plasma flow should be at 15 L/min, auxiliary flow should be set at Ca. 1.075 L/min.
- Start ICP and ablation…now with only the Manual Optimization and Real Time windows open…adjust the Nebulizer flow and He flow (see next page for how to adjust helium).
- Make adjustments such that signals viewed in real time window have the highest intensity, while maintaining low oxide formation (ThO⁺/Th⁺ <0.5%).

**Loading Samples**

- Stop firing the laser.
- Click on ‘Bypass’.
- Load the sample chamber (details see Appendix page 11).
- Process analysis (details of using software see Appendix Page 12-14).
**Shutdown**

**Laser Ablation Unit**

♦ On the computer, go to the ‘MEO Laser’ software and turn down the lamp.
♦ Make sure that the laser is not firing.
♦ Click on ‘Bypass’.
♦ Unload the sample chamber.
♦ Exit the software.
♦ Turn the key on the main power unit to ‘O’.
♦ Turn off the laser (if not using the next day).
♦ Turn off the power unit (if not using the next day).

**Helium**

* Shut off helium tank (do this BEFORE touching the GFC to avoid overheating).
* Next, turn adjustment screw on GFC counterclockwise until the display reads 0.00 (you’ve now successfully returned GFC to ‘set point” and unit should be properly calibrated for the next user)
* Unplug GFC

**ICP-MS**

♦ On the computer, go to the ‘ELAN’ software and click on the Front Panel of the Instrument window.
♦ Turn off the plasma.
♦ Wait for one minute and then turn off the cooling unit.

**Materials**

- 1” diameter epoxy mount, containing minerals for U-Th-Pb dating or materials for multi-element analysis. The mounts should be cleaned using diluted nitric acid.
- A map of each mount will be provided, these should be used during the ablation session to guide your selection of grains
- 213-nm Laser coupled to an ICPMS
Methodology of Zircon U-Pb dating

1. Isotope measured: \(^{202}\text{Hg}, {204}\text{Pb}, {206}\text{Pb}, {207}\text{Pb}, {208}\text{Pb}, {232}\text{Th}, (^{235}\text{U}, \text{optional}), {238}\text{U}\).

2. Low gas background signals for Pb are essential (Jackson et al. 2004). Typical gas blank \(^{208}\text{Pb}\) signals of ca. 30–40 cps can be achieved routinely. Backgrounds are <10 cps for the other elements of interest except Hg (ca. 300 cps on \(^{202}\text{Hg}\)). Usually, low Pb gas backgrounds were achieved by careful cleanliness of the LA system (acid cleaning sample cell and inserts, samples and tubes). If you find higher Pb backgrounds are present during U-Th-Pb dating using LA-ICP-MS, please stop analysis and contact Dr. Ayers or Yan for help.

3. The ICPMS is optimised using continuous ablation of a NIST 610 to provide maximum sensitivity of \(^{208}\text{Pb}\) while maintaining low oxide formation (\(\text{ThO}^+/{\text{Th}^+} <0.5\%\)). Table 1 lists typical operating conditions of LA-ICP-MS in VU.

4. For each analysis, backgrounds were acquired for ~30s prior to the beginning of the ablation. Signals were acquired ~ 40-60 s on the analyte signal. The first few ablation readings were rejected to avoid obtaining data from contamination on the sample surface. Time-resolved analysis data (a proxy for ablation depth) generally allow isotopic heterogeneity within the ablation volume to be clearly identified (e.g., zones of Pb loss or common Pb related to fractures or areas of radiation damage, inclusions, inherited cores, etc.).

5. The first analyses should be preformed on the standard with 4 data acquisitions of calibration material (AS3 and 91500), then up to 10 analyses will be of the unknown sample followed by 4 data acquisitions of calibration material again. If we define these analyses as “one run”, the subsequent “run” can always share the calibration materials that analysed at the end of the former run.

6. Save each run as separate folders.

7. These folders can be processed using GLITTER software installed in the workstation computer of Room 5708 (the calculation details see Appendix P15-18).
Table 1  LA-ICPMS typical operating conditions of U-Pb dating in EES, VU

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perkin-Elmer Sciex ELAN6100DRCII</strong></td>
<td></td>
</tr>
<tr>
<td>Forward Power</td>
<td>1350-1400 W</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td></td>
</tr>
<tr>
<td>Nebulizer</td>
<td>0.60-0.80 L min⁻¹</td>
</tr>
<tr>
<td>Auxiliary</td>
<td>0.6- 1.0 L min⁻¹</td>
</tr>
<tr>
<td>Plasma</td>
<td>~15.0 L min⁻¹</td>
</tr>
<tr>
<td>Lens Voltage</td>
<td>6-10.5 V</td>
</tr>
<tr>
<td>Auto Lens</td>
<td></td>
</tr>
<tr>
<td>Trace element analysis</td>
<td>ON (6.5-11.25V)</td>
</tr>
<tr>
<td>U-Pb age analysis</td>
<td>OFF</td>
</tr>
<tr>
<td>Oxide ThO⁺/Th⁺</td>
<td>&lt;0.5%</td>
</tr>
</tbody>
</table>

| **New wave 213 laser ablation system** | |
| Wavelength | 213 nm |
| Energy (26-30Kv, 10Hz) | >9 J cm⁻² |
| Laser frequency | |
| Trace element analysis of 91500 | 12 Hz |
| Spot size | |
| U-Pb age analysis | 30 µm~60 µm |
| Trace element analysis | 30-120 µm |
| He carrier gas flow | 0.6-1 L min⁻¹ |
| Pulse duration | 20 ns |

| **Data acquisition** | |
| Data acquisition protocol | Time resolved analysis |
| Scanning mode | Peak hopping, 1 point per peak |
| Dwell time per isotope | |

| **204Pb, 208Pb, 232 Th, 238 U** | 10 ms, respectively |
| **206Pb and 207Pb** | 20 ms, respectively |
| Quadruple settling time | ~30 s gas blank and 40 s ablation |
| Sweeps | 1 |
| Reading/Replicate | 450 ~810, depending on your analysis |
| Replicates | 1 |
Methodology of Monazite U-Th-Pb dating

This new methodology still needs testing for a long time precision. Currently, most steps are the same as zircon U-Pb dating, the main differences are

1. 44069 is used as calibration standard for U-Pb dating.

   Standard 554 is used as calibration standards for Th-Pb dating.

2. different modes of acquiring data.

Methodology of Trace elemental analysis

Analytical Protocol (Longerich et al., 1996; Gao et al. 2002; Luo et al. 2007)

1. All trace elemental measurements were carried out using time resolved analysis operating in a fast, peak jumping mode (one point per mass peak, 10 ms of dwell time per isotope and a quadruple settling time of 3 ms, one sweep per reading and 200 readings for one replicate.

2. Each spot analysis consisted of approximately 30 s background acquisition (gas blank) followed by 60 s data acquisition from the sample.

3. Gas blank was typically controlled as 1000-2000 cps for P, Ca and Mn; 100-500 cps for Na, Al, Sc and Sn; 50-100 cps for V; 50-20 cps for Li, Ti, Zn, Ga, Sb and Cs; 20-10 cps for Rb and Pb; and < 10 cps for Be, Mg, Co, Ni, Cu, Sr, Y, Zr, Nb, Mo, fourteen rare earth elements (REE), Ta, Th and U.

4. Calibration was performed using NIST SRM 610 as an external calibration sample (in most cases) in conjunction with internal standardization using 'naturally occurring' elements (e.g. Ca or Si etc). These are elements that are found in both the samples and calibration material, and for which the concentrations are known in both materials. The concentration of the internal standard can be obtained from an analysis using an alternative method (e.g. Electron microprobe) or from the known elemental stoichiometry when crystalline materials are analysed.

5. Choose the time intervals (replicates) over which to integrate (the mean is more convenient to calculate, noting that an integration is the mean count rate multiplied by time) the background and the ablation count rates. The first background interval is not used and 2-3 replicates immediately before the initiation of the LA are not used. The first few ablation replicates are generally rejected in order to avoid the effects of laser removal of surface contamination and to allow the signal to stabilize (see Fig. 1). Data integration is terminated at
the point when the laser starts to sample the support, an underlying mineral phase
or an inclusion or other anomalous chemical heterogeneity within the sample, or
the signal falls significantly (< FZ 50%), either because of termination of ablation
or laser defocusing.

6. Data are acquired in runs of up to 20 analyses. Each run starts and ends with two
data acquisitions on a calibration material (e.g. NIST 610). The 20 analysis limit
ensures that calibration is performed on no more than about two hours, in order to
monitor and correct for the drift of the inter-element sensitivities (i.e., analyte-
internal standard) with time. Reference materials (e.g. NIST612 or NIST614) are
also analysed at least twice during a run to monitor accuracy.

Fig. 1. Cited from Luo et al. (2007). Laser ablation ICP-MS spectra showing intensity (counts per second) vs. number of readings for
$^{42}$Ca, $^{59}$Co, $^{139}$La and $^{232}$Th of NIST612 glass. The dashed lines in the background and signal area demonstrate the selected time
interval which was used for integration. Backgrounds were acquired for ~30s (~60 readings) prior to the beginning of the ablation.
Signals were acquired ~60 s (~120 readings) on the analyte signal. The first few ablation readings were rejected to avoid obtaining
data from contamination on the sample surface.
7. Save raw data of each run as a separate folder. Use Glitter software to reduce data.

References


Appendix

Fig. 1  ICP-MS schematics
Load the samples

Making sure that the instrument is off line pull the loading bars up and slide the stage block out. In the center of the stage block is a sample loading hole. In the case of a mineral separate mount, the mount should be load in the hole so it is level with the stage block surface, see Fig 2. Wax plugs of differing size are available to set the mount at the right height. In the case of a thin section the slide will fit directly into the groove running across the stage block. After loading the stage block return it to the instrument making sure to press firmly while lowering the loading bars so a good seal is achieved. It is essential to achieve a good seal so no atmosphere can enter the chamber during the experiment run. Now that the sample is properly loaded it is time to turn to the computer interface.

Fig 2. The stage block and sample loading system.
Details of using LA-ICP-MS software

Fig. 3 is an image of the main screen for the laser control software. Initially the sample view portion of this screen will be dark. In the upper left corner of the tool bar there is a control button for illumination options. Click on the light bulb until it says the illumination source is coaxial, coax. Then, move the scale bar to about 75% and the stage light will illuminate the sample and it will become visible on the screen. Next, the image will need to be focused. The small bar on the left hand side of the sample image is used to focus the image and the laser, Z focus in Fig. 3. Clicking on the bar will allow a choice of magnifications, starting with the lowest setting and then using the drag bar to focus at that magnification will allow the sample surface to be seen clearly. Successively increasing magnification and refocusing will bring the sample into view for choosing a target. It is now possible to move the stage and find specific grains on the mount or thin section for ablation. Using the drag bar at the right of the image and the bottom of the image will allow navigation around the stage. Once the general location of sampling has been identified using the drag bars it is necessary to choose the exact spot for ablation. Using the mouse the cursor can be moved onto the sample image. Placing the cursor over the exact spot for ablation and left clicking will tell the laser to ablate that spot. The software will mark the spot on the image with an open yellow circle. After choosing your spot the words, Spot #1, will appear in the desired patterns box on the left of the screen. Right clicking on the text, Spot #1, in the desired patterns box and selecting Properties will allow the set up of both the preablation settings and the experimental run drag bar to focus at that magnification will allow the sample surface to be seen clearly. Successively increasing magnification and refocusing will bring the sample into view for choosing a target. It is now possible to move the stage and find specific grains on the mount or thin section for ablation. Using the drag bar at the right of the image and the bottom of the image will allow navigation around the stage. Once the general location of sampling has been identified using the drag bars it is necessary to choose the exact spot for ablation. Using the mouse the cursor can be moved onto the sample image. Placing the cursor over the exact spot for ablation and left clicking will tell the laser to ablate that spot. The software will mark the spot on the image with an open yellow circle. After choosing your spot the words, Spot #1, will appear in the desired patterns box on the left
of the screen. Right clicking on the text, Spot #1, in the desired patterns box and selecting Properties will allow the set up of both the preablation settings and the experimental run settings for the laser in the Pattern Properties window. The Pattern Properties window has two tabs, ablation and pre-ablation. Select the pre-ablation tab and set Passes to 1, depth/pass to 0, Energy to 80-100%, Rep Rate to 5, dwell time to 5, and Spot Size to one or two size setting greater than the size of spot intended for the analysis run. The left click on the button at the center of the box that says, Apply Settings To Laser, not seen in Fig. 3, then left click on OK. The Pattern Properties window will close and the laser will be set for preablation. Click on the run scans button and the Experiment window will open and the enable laser box must be checked. Once the enable laser box is checked the Run button may be clicked. The laser will now perform the preablation routine. Once the laser has preformed the pre-ablation routine and stopped firing it is essential to purge the system. This is accomplished by clicking on the purge icon located in the upper left of the screen, just below the illumination options, as seen in Fig. 4. The system will purge for a stated time while the system is purging it is important to slightly defocus the laser.

When choosing the original method for the experiments the number of replicates and count times for each isotope in question were determined. This then determines the total run time for the experiment. Since, it is important to know the background intensity of the analytes, background intensities are determined for one minute. This minute of time should be subtracted from the total time of analysis to determine the dwell time, or the period that the laser will actually be ablating. Thus the total time of analysis in seconds minus thirty seconds equals the dwell time, or time of ablation. This time is then entered in the dwell time box in the Patterns Properties window. After these boxes are filled click on Apply Settings...
To Laser button, then click on OK. The Pattern Properties window will now close and the Run Scans button can be clicked displaying the Experiment window. Again, make sure that the Enable Laser box in the Experiment window is checked. DO NOT CLICK RUN NOW. First it is necessary to choose an appropriate sample name. To name the sample it is necessary to switch to the ELAN software package. Fig. 6 shows the ELAN interface screen. The Screen shown in Fig. 4 allows for the entry of a sample name and contains the Start Analysis button. After entering an appropriate sample name in the sample box, it is time to start the analysis. First, switch back to the laser control software package and make sure the system is online, see Fig. 4. The online icon at the top left of the screen should be highlighted. Usually a clicking noise will be heard as the instrument comes on line, but it is necessary to check the icon as well. To start the analysis, click the Start Analysis button on the ELAN window. At this time a window will open in the lower left of the screen and will display a bar that tracks the progress of analysis. In addition, this window will also show a real time count of the number of replicates. After ~ 30 seconds of gas blank analysis, its time to switch back to the Laser interface software Experiments window that was left open. Again check to make sure the Enable Laser box is checked, and click on RUN. At this point the laser will begin to fire. Wait to see the laser is firing in the sample viewing window. Once the laser has begun to fire real time data acquisition can be monitored in the ELAN software package.

Return to the ELAN software and select the real time intensity window, seen in Fig. 6. This can be done by clicking on the icon with the blue curve at the top of the ELAN screen. This allows the user to see the actual intensities of the various analytes, and monitor the progress of the experiment. Once the experiment has run to completion the data will automatically be saved in a report file, and a new analysis can start. To begin new analyses return to the laser control software. Right click on the text, Spot #1, in the Desired Patterns window and select Delete from the menu. This removes the previous spot. Refocus the sample so it can be easily viewed. Now the drag bars to the right and the bottom of the sample view window can be used to locate the next ablation location. The above procedure can be repeated for each sample location.

Once all analyses have been completed it is necessary to retrieve the report output files from ELAN. These are located in C: elan/Report Output/ your files.
Details of Data Reduction

*Note that Glitter software can do this step automatically. This part is only for those who interests how Glitter reduce data.*

Now that you have made your analyses it is time to reduce the data. The instructions that follow illustrate how to data reduction can be done in an Excel spreadsheet.

1) Open the .rep files in Excel. First open the file containing the standard as a delimited, comma separated file. To do this first select OK on the first pop-up window (Task Import Wizard-Step 1 of 3), shown below (Fig. 7). Next select both Tab and Comma as delimiters and click on FINISH (Fig 8). The data should appear as shown below(Fig 9).

2) The next step is to sort the data. This is done by ‘cutting and pasting’ the title information to the side and highlighting the columns (C,D,E) containing the
‘intensities’ in counts per second of the isotopes of interest (Fig 10). Next sort in ascending order. Paste these values into a separate spreadsheet and organized by creating a column for each isotope as shown in Fig. 11. Close the original .rep file, but do not save. This will allow you go back to the original data if mistakes are made. (Note: the first intensity below the column header will be the first measurement made by ELAN, this is important since construction a simple line graph as described below shows how the intensity of each analyte varied during analysis.)

3) Next you will have to separate the gas blank data from the data collected during ablation. The gas blank data are easy to recognize since they should have very low counts relative to those measured during ablation of the sample. Take the average of the gas blank intensity of each isotope and subtract that number from the intensity measured during ablation. You have now successfully preformed the first correction, that of the gas blank.

4) You can now determine the ‘intensity’ of U235 by multiplying the U238 intensity by 1/137.88. Separate columns should be created for this data.

5) The next step is create columns for the isotope ratios of interest (for zircon these will be 207Pb/206Pb, 206Pb/238U, 207Pb/235U). Once these columns have been constructed you will need to make a ‘line’ graph of the data. (Go to ‘chart wizard’, select line graph and click on the upper left hand line graph choice). The data and line diagram look similar to those shown in Fig. 12.
6) The next step is to use the graph you just plotted to isolate the ‘steadiest’ portion of the signal (see red box above for an example of a steady signal). Create new columns containing the data you just isolated. *It is important to note that statistically, the more analyses used the more precise your average will be.*

7) Finally average these corrected values. These ratios will be ‘R(STD) meas’ which will be used to correct the raw data from the unknowns as discussed below.

The next step is to perform steps 1-8 above on each of your unknown analysis. (Note: it is probably easiest to copy the sorted data from each analysis into a separate worksheet in a single excel files. This should not be done if you plan on loading these analyses into the GLITTER software.

Once the most stable portion of the ratios is isolated and put into separate columns then the following equation is applied to each replicate of each ratio. (ie. create a separate column using the following equation.

\[
R(\text{Sample})_{\text{true}} = R(\text{Sample})_{\text{meas}} \times \frac{R(\text{STD})_{\text{true}}}{R(\text{STD})_{\text{meas}}}
\]

Note:
- STD=standard
- \(R(\text{STD})_{\text{meas}}\) was determined for each ratio of interest in step 9 above
- \(R(\text{STD})_{\text{true}}\) is given
Finally, take the average of these newly calculated ratios. *(At this stage the ratios have been corrected for the gas blank, instrumental mass bias, and ablation related fractionation).* The average of each ratio can either be plotted on Concordia or Tera-Wasserberg diagrams, or ages can be calculated for the individual ratios of interest. Templates for these calculations can be found in the directories below:

- Wetherill Concordia diagram… :anonymous/LA_ICPMS/ConcordiaTemp
- Tera-Wasserburg diagram……. anonymous/LA_ICPMS/TeraWasTemp
- 207Pb/206Pb age calc………… anonymous/LA_ICPMS/207_206agecalc
- 206Pb/238U and 207Pb/235U… anonymous/LA_ICPMS/U_Pbagecalc
Instructions for processing LA-ICP-MS data using Glitter

*Note: the Glitter file is c:\RSI\IDL53\Glitter.sav
One *.xl file for each analysis. Use Excel file created during analytical session to identify analysis "batches" that contain standard analyses, then samples, then standards. Create folder in c:\RSI\IDL53 for each batch. Most standard analyses occur in two folders, i.e., they are shared by consecutive batches, and are grouped with sample analyses run before and after them. Start Glitter, choose "Isotope ratios" for U-Pb geochronology. From pull-down list choose "Spreadsheet". "File: Load Data", Choose 91500 as reference material, Multiple dwells, set dwell times, click on each row that represent a standard analysis, click Save, then click Accept.

- "Window: Options", for "select signal marker mode" choose "All analyses markers independent".
- Window: Review Signal Selection", choose isotope ratios. Upper panel shows signal intensity for each isotope on a color scale from blue = low to white = high. Click "F" to filter out signal spikes. Click on display panels to set lower and upper limits of accepted time range; do this for blank (1st box with green outline on left) and sample (3rd box from left); middle box rejected.
- Tips: 1) for counts use log scale, and for ratios use linear scale. 2) Ideally all samples and standards should use the same time range; choosing a large time range reduces error but may reduce accuracy and make discordant. Only choose signal collected while the laser was firing (when Si cps are still high); once it stops firing Pb/U and age decrease because Pb is more volatile than U.
- Note that we did not choose an internal standard because don't need to calculate age or isotopic ratios.
- Window: Plot Results
- Can reject individual standard analyses by selecting their rows, and then choosing "Edit: Toggle Standard Off"
- Click on row, it is highlighted in plot; can choose which analyses to revisit for signal selection.
- "File: Export" to create a csv file.
- Use "ComPbCorr.xls" to correct for common lead
- Use the Isoplot add-in in Excel to create concordia diagrams, etc..

Tips:
1. If sample analyses are numbered sequentially and within a batch the number of digits in the sample I.D. changes then a zero must be added to make the number of digits the same. Example: samples 90-99 must be changed to 090-099 so that they appear in the correct order when sorted with 100-110.
2. For analysis batches in which two different spot sizes or frequencies used, must create a separate folder for each and include only standards measured using same parameters.
3. If the number of isotopes measured in an analysis batch changes then you need to add columns to the analyses that have fewer columns so that all of the output "xl" files have the same format (can add a column of zeros).
4. For our U-Pb session dwell times (ms) were Si29 10, Ti49 10, Pb204 10, Pb206 20, Pb207 20, Pb208 10, Th232 10, U238 10.