Preparation for your analytical session at the GZN LA-ICP-MS/MS facility

Laser ICP-MS/MS is a highly flexible and robust technique. However, preparation prior to your analytical session is essential for ensuring high quality results. This document is intended for new users to ensure that each analysis generates high quality data.

Prior to arrival at the GZN LA-ICP-MS/MS facility all users should have:

- Communicated their **sample types, analytical plan and goals** to Dr. Marshall (edward.w.marshall@fau.de) or the supervising analyst
- Prepared a **list of elements** need to be analyzed (note that longer lists of elements are analytically more challenging)
- Have a **physical or digital map** of the analysis locations
- Have ensured that their samples **fit into available drawer inserts**
- **Removed all carbon or gold coatings** from samples surfaces
- Measured the major element composition of the target(s) for analysis. For conventional quantitative LA-ICP-MS/MS analyses (e.g. trace elements in sulfides), **the major element composition of the material is needed for trace element data reduction** (e.g., through EMP analysis) for all locations of the object that are intended to be analyzed during LA-ICP-MS/MS. For more complex analyses (e.g., element imaging), contact Dr. Marshall or the supervising analyst.

Developing an Analytical Plan:

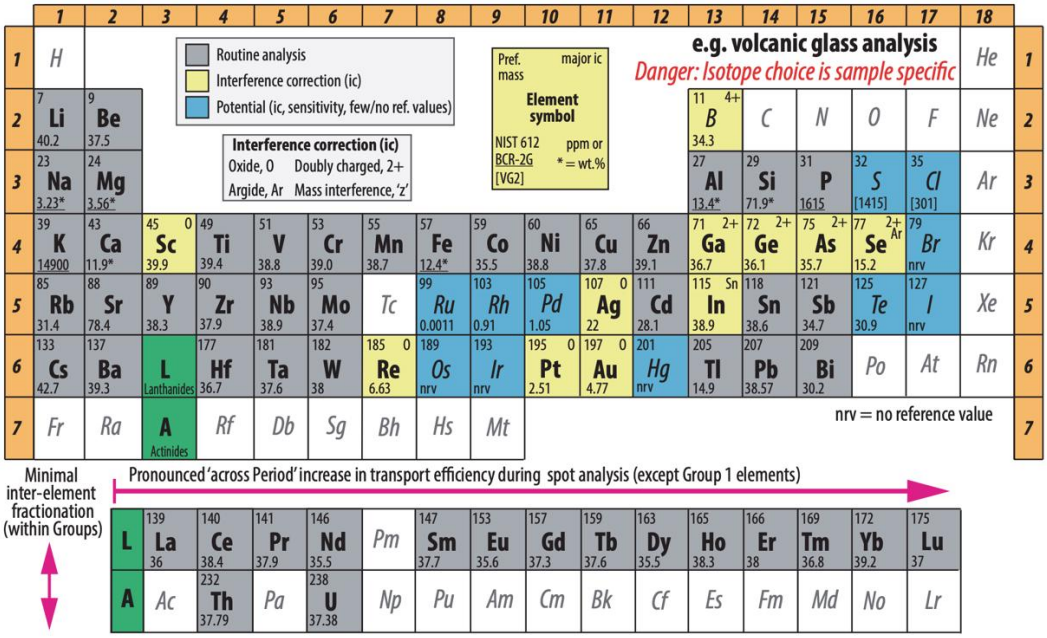
Quantity of Measurements:

The quantity of measurements depends primarily on the user. A single spot analysis on silicate minerals lasts about one minute. Because of the quick speed of analysis, much of the time in an analytical session is consumed during programming of the sample points (many users program points at a rate of ca. 1 spot per minute). Experienced, well-prepared users running in automated mode can analyze more than 200 sample spots (about 3.5 hours of measuring time) within an eight-hour work day. However, most users running in automated mode measure about 150 spots per day.

If each analysis needs to be run non-automated, for example in cases where extreme spatial precision is needed, this also slows down the number of spots that can be measured in a day. Here, the number of spots run per day may vary significantly.

Which Elements?

The selection of elements is entirely dependent on the project in question. However, some elements are more difficult to analyze than others (see below figure; from Jenner and Arevalo, 2016, Elements)



In the above figure, elements in grey are elements that are routinely measured in many materials at the GZN LA-ICP-MS/MS facility. The elements in yellow can be measured with some work. The elements in blue require specialized methods or standards. At the GZN LA-ICP-MS/MS, we actually specialize in measuring platinum group elements, S, and Te in sulfides, which are all outlined in blue here. However, for the most part, how easily an element can be analyzed also depends on the matrix and so it is best to have your list of elements checked by your LA-ICP-MS/MS analyst before the session.

What laser and ICP-MS parameters do I use? Element count times, Spot size, Fluence, etc: There are many detailed parameters for LA-ICP-MS/MS analyses, but these are best determined in collaboration with the LA-ICP-MS/MS analyst. Some parameters like spot size have strong tradeoffs between data quality and spatial resolution, and can be changed even in the middle of a session depending on need. Other parameters like laser fluence are simply related to the composition of the sample matrix and unlikely to change within a session.

Sample Preparation:

Routine laser ablation is most simply performed on flat, polished surfaces. If a user intends to measure a large number of points in a short time, we highly recommend mounting the sample in epoxy as a probe round or thin/thick section.

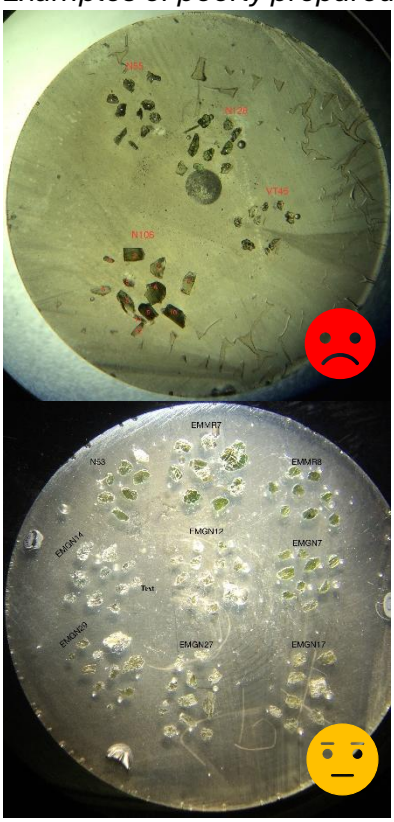
At the GZN LA-ICP-MS/MS facility, we have several different sample drawer inserts into the LA-ICPMS that permit a wide range of different sample preparation types:

Drawer 1: Nine 1'' (2.54mm) probe round slots and four 0.5'' (1.3mm) mini probe round slots

<u>Drawer 2</u>: Three 1'' (2.54mm) probe round slots, three 0.5'' (1.3mm) mini probe round slots, and two glass slide holders designed to accommodate four 28mm x 48mm glass slides or two 28mm x 96mm glass slides (thin or thick sections).

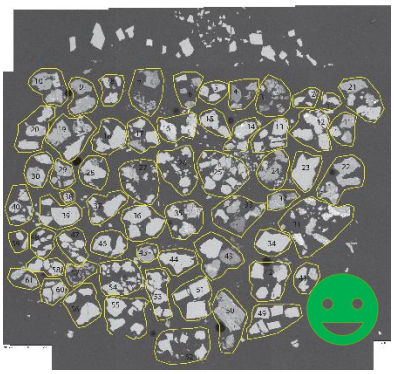
<u>Drawer 3</u>: An open-plan rectangular 100mm by 100mm tray for irregular samples. Samples can simply be placed onto the tray. Samples must not be more than 9mm in height. The drawback of using this sample chamber is that the laser can only perform analyses along a planar surface. Irregular samples must therefore be carefully placed at the particular height where they can be ablated. Because samples are not locked in place, as in the other holders, they can experience some movement during analysis. Therefore, we recommend that users that require high spatial precision do not use the open-plan drawer.

Examples of poorly prepared and good epoxy grain mounts



Poorly prepared mount: lots of wasted space, samples located all around the mount and not organized, grains not packed tightly together, only four samples in this mount.

Better prepared mount: samples are organized, each sample is more tightly packed, nine samples in this mount.



Best prepared mount: samples are organized, each sample is tightly packed, no wasted space, 61 samples in this mount.

Sample Chemical Characterization:

For conventional LA-ICP-MS/MS analyses, measurement of an internal standard is required in order to generate quantitative data.

Accurate analysis of trace elemental concentrations via LA-ICP-MS/MS nearly always requires preliminary major element analysis of the sample, such as via electron microprobe. This is because the data reduction for LA-ICPMS trace element analyses uses an "internal standard" which is an element that can be measured via LA-ICP-MS/MS and whose concentration is already known. For each analytical spot, the concentration of the internal standard element must be known and is used to quantify the abundances of all the trace elements explored in the LA-ICP-MS/MS analysis. Some common examples include: Fe or S in pyrite, Si or Ca in clinopyroxene, Si or Ca in basaltic glass, Al in corundum, or Ca in calcite. It is important that the internal standard be accurately and precisely determined, as all uncertainty from determining the internal standard is passed on the uncertainty in the trace element measurements.