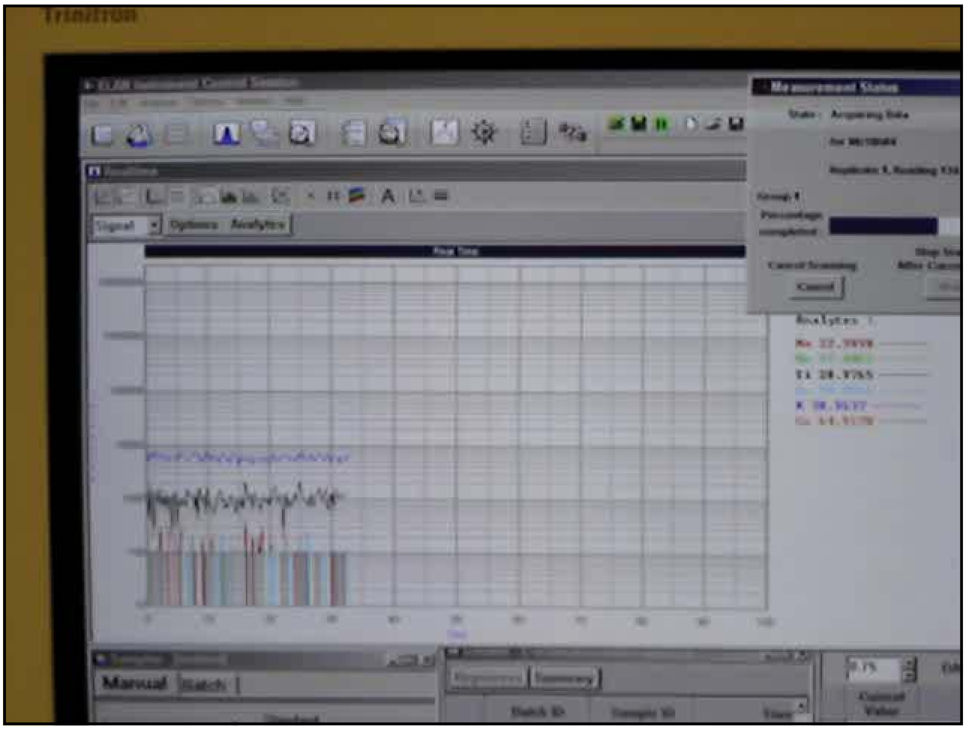
Thomas Pettke

UNIVERSITÄT BERN



Important parameters in LA-ICP-MS

- Transient (i.e., time-resolved or real time) data acquisition
- One detector; thus, sequential recording of analyte signals (except for isotope ratio measurements: MC-ICP-MS)
- Fast jumping from mass to mass required (i.e., mass filter settling time)
- One point per spectral peak to be recorded
- Dwell time (i.e., net measurement time on mass per sweep)
- One sweep comprises one measurement per specified mass (= analytes) across the entire mass range of interest
- Instrumental background intensities are recorded on peak immediately prior to LA sample signal
- Instrumental drift correction
- What we analyze is m/z, i.e., the mass of the isotope divided by its charge (e.g., $^{90}Zr^{++}$ sits on $^{45}Sc^{+}$, and ^{45}Sc is a 100% Isotope ...)

Signal quantification strategy

- Use an external standard to determine analyte sensitivities (i.e., cps / ppm)
- Assume (assumption justified by experiment for our LA-ICP-MS system) that element sensitivity RATIOS remain constant between external standard and samples.
- Use internal standardization to quantify sample element concentrations.
- Filter apparent element concentrations against the limits of detection, calculated individually for each element in every analysis.

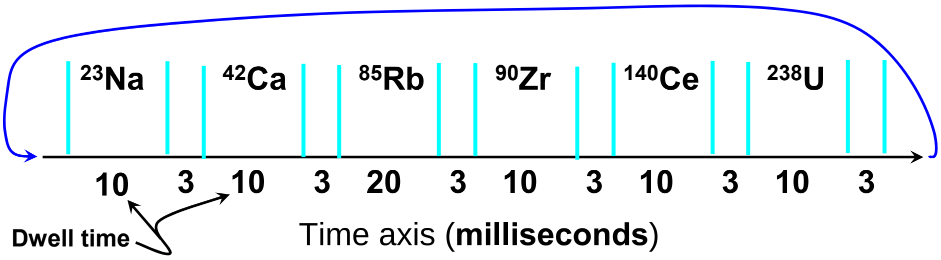
Significance of the internal standard (IS)

- **An IS is a MUST to convert the apparent element concentrations as derived from the external (bracketing) standardization (= reference material) into true sample element concentrations.**
- **The IS determines the sensitivity factor between the shots on the external reference material and sample shots.**
  Note: ONE sensitivity factor for ALL elements !
  Variable sensitivity between standard and sample results from:
  - variable ablation rate between reference material and sample (matrix dependent, since LA-conditions fixed)
  - the use of variable beam sizes for analysis
- **An internal standard is**
  - either an element of known concentration in the sample,
  - or it can be the sum of element oxides equaling 100 wt% minus the concentration sum of non-analyzed major element oxides (e.g., H_2O).

Definition of important parameters

- **Sensitivity (S):**
  This gives the *net count rate* obtained for an element per concentration unit; e.g., 1000 cps/(µg g^{-1})
- **Limit of detection (LOD):**
  This gives the minimal element concentration that can be "measured" in a sample (according to the LOD criteria defined).
  LOD = 3*"stderr"(bkg) / S
  → Why "stderr" ?
  We are interested in a measure of the distribution of the individual background measurements (i.e., the variability of the individual background measuerements) around the background mean intensity; thus "stderr"(bkg) = stdev(bkg) / sqrt(n sweeps)
- **Signal to background intensity ratios influence the LOD more than does simple sensitivity!**

One sweep: typical aquisition times



^{23}Na ^{42}Ca ^{85}Rb ^{90}Zr ^{140}Ce ^{238}U

10 3 10 3 20 3 10 3 10 3 10 3

Dwell time

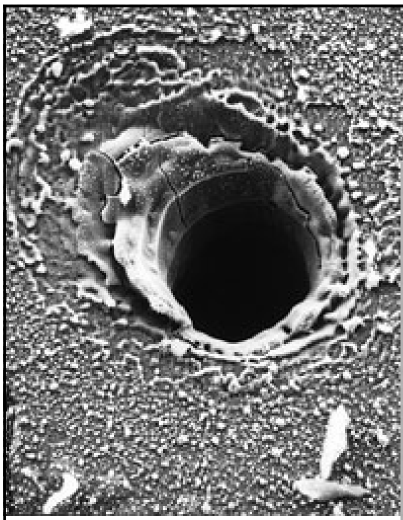
Time axis (**milliseconds**)

Total analysis time per sweep: 88 ms

Total analysis time per sample:
Limited by homogeneous signal section or - not seldom - by section thickness !!!

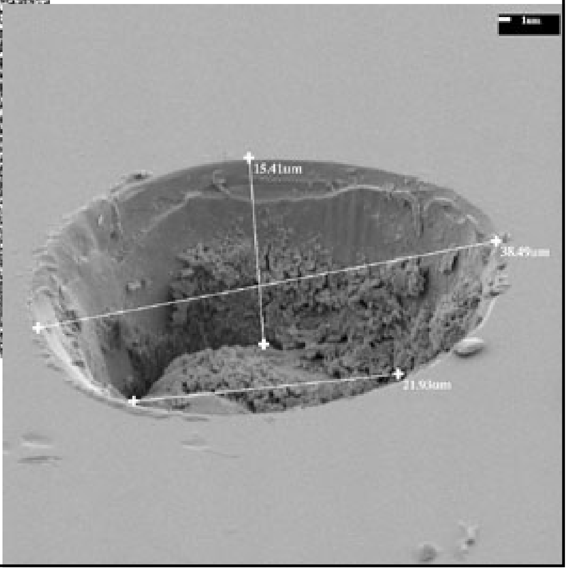
Key: measure each analyte often enough to obtain a statistically significant number of individual measurements (i.e., sweeps) per spot analysis

Duty cycle: This is the net measurement time per isotope in one sweep, e.g., for Ca = 11.4%, for Rb = 22.7%



Pit ca. 50 µm; 266 nm

Pit ca. 40 µm; 213 nm

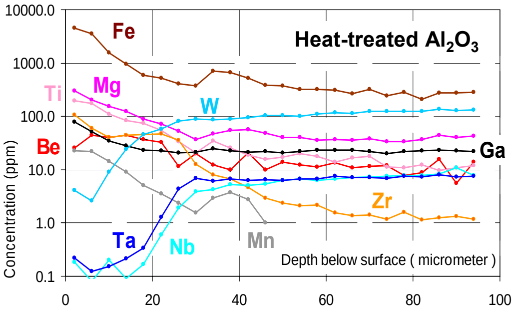


We always analyze a VOLUME

Analysis of VOLUME

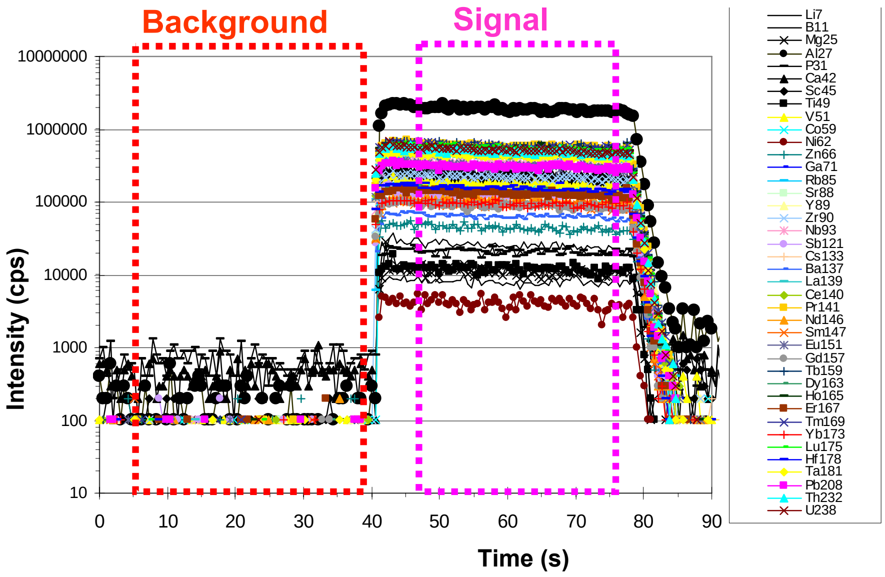
- This fact must be kept in mind all the time during sample preparation
  - BSE or CL images only represent the uppermost 2 µm of sample
  - Inspect sample interior during microscopic sample prep for the presence of inclusions, cracks, crap... *AT DEPTH* !!

  This is best done by using the condenser lens of your microscope
- For energy-homogenized laser systems producing flat-bottomed ablation pits (frying pan shape), huge potential for depth profiling

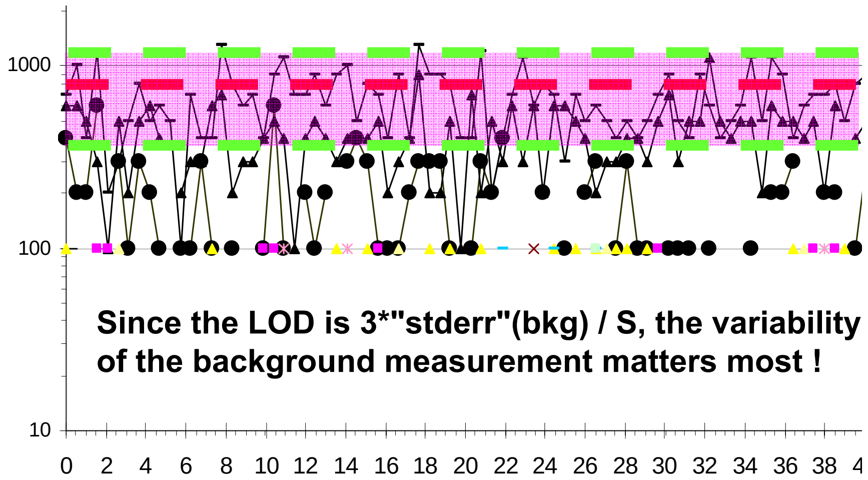


2 µm ablation intervals integrated, using 100 µm pit

Key signal features



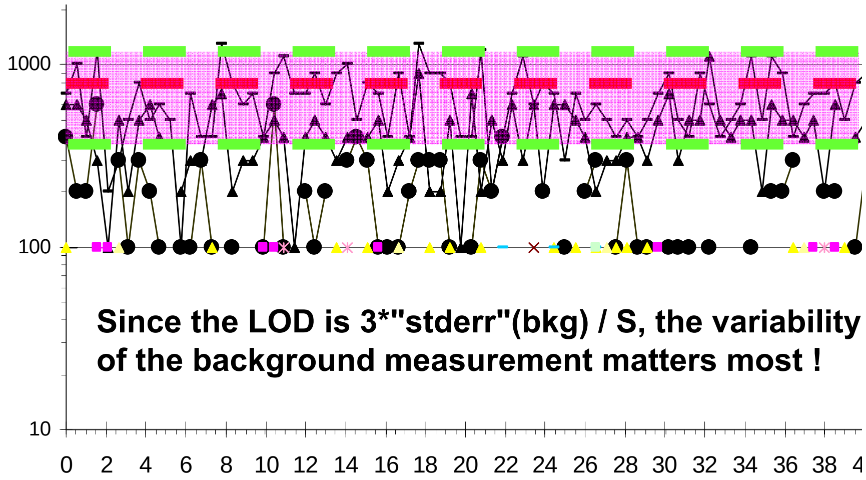
Background signal for —■—



Since the LOD is 3*"stderr"(bkg) / S, the variability of the background measurement matters most !

Low backgrounds "cannot" be more variable than high backgrounds unless they are spiky !

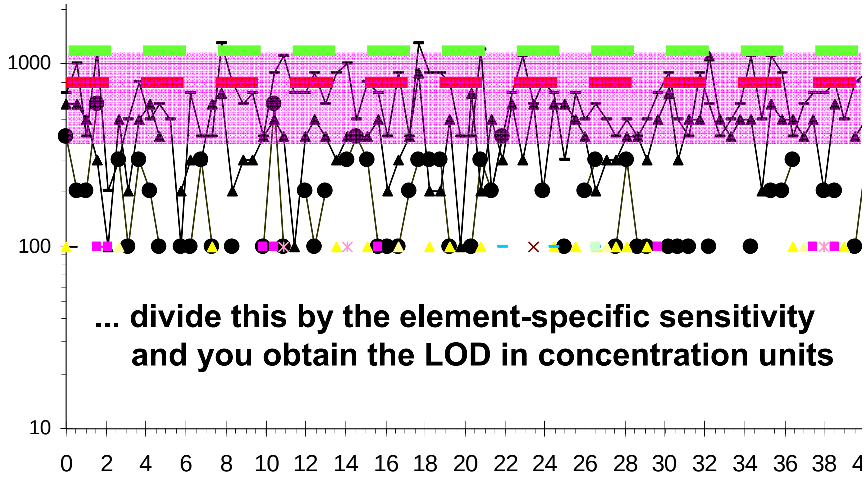
Background signal



Since the LOD is 3*"stderr"(bkg) / S, the variability of the background measurement matters most !

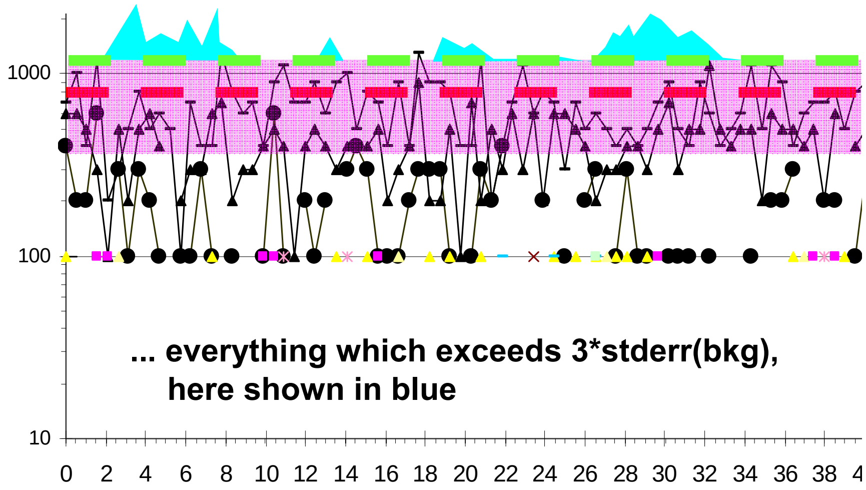
However, the background variability expressed as count rate increases with decreasing dwell time !

The LOD "signal" corresponds to a signal of average(bkg) + 3*"stderr"(bkg) (green line)



... divide this by the element-specific sensitivity and you obtain the LOD in concentration units

A significant signal is thus ...



... everything which exceeds 3*stderr(bkg), here shown in blue

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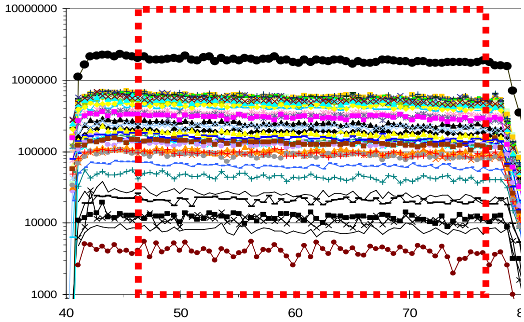
Analyte signal characteristics



Recall:

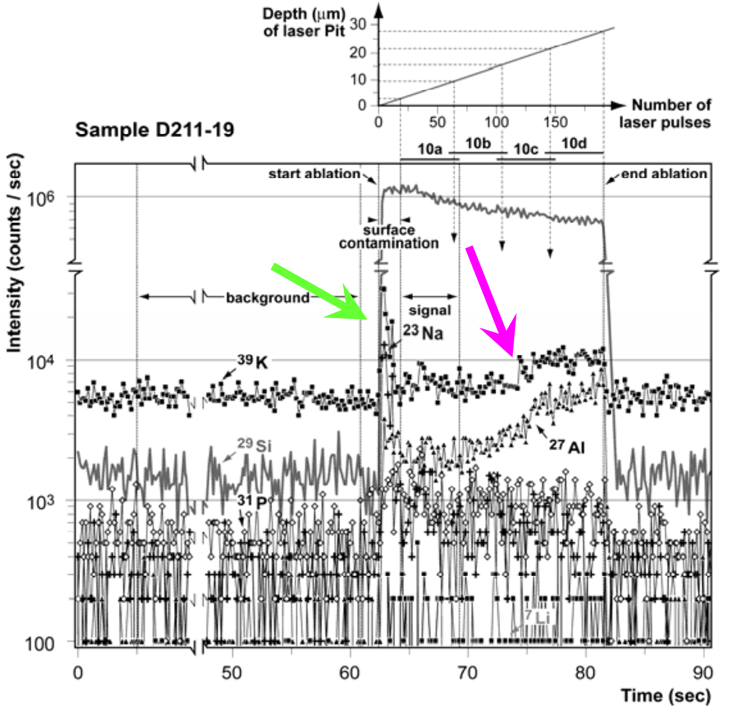
All analyte intensities **evolve parallel, i.e., intensity ratios constant**: no time-dependent elemental fractionation

Signal intensity decays with progressive ablation: drilling deeper and conical pit shape releases less aerosol

For such signals, the signal integration interval can be selected anywhere.

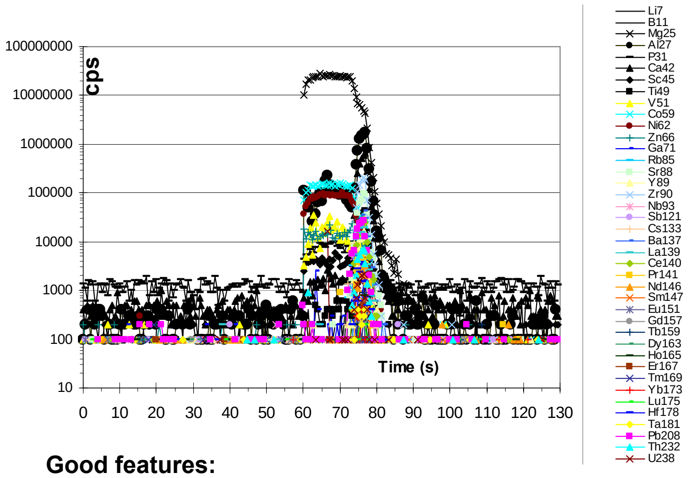
However, preferred are early signal sections because (i) signal to bkg ratio is maximized and risk of element fractionation in a shallow pit is minimized.

BUT: Watch out for SURFACE CONTAMINATION.
Moreover, it is advisable - if you can - to discard the first ca. 5 seconds of signal because it is here where most large particles are formed (recall element fractionation due to incomplete particle decomposition in the plasma).



Recall:
We analyze a sample VOLUME; thus, danger of zonation with depth!
(or: Potential for depth profiling)

Non-optimal analysis shot



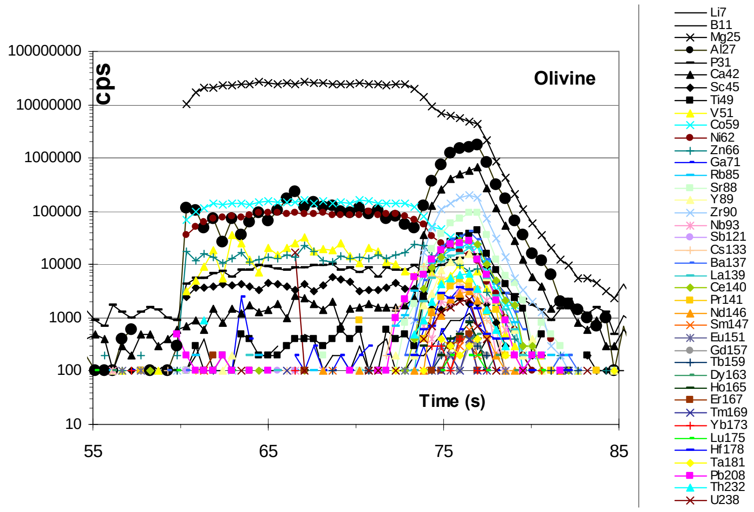
Good features:

- bkg ≥ 50s

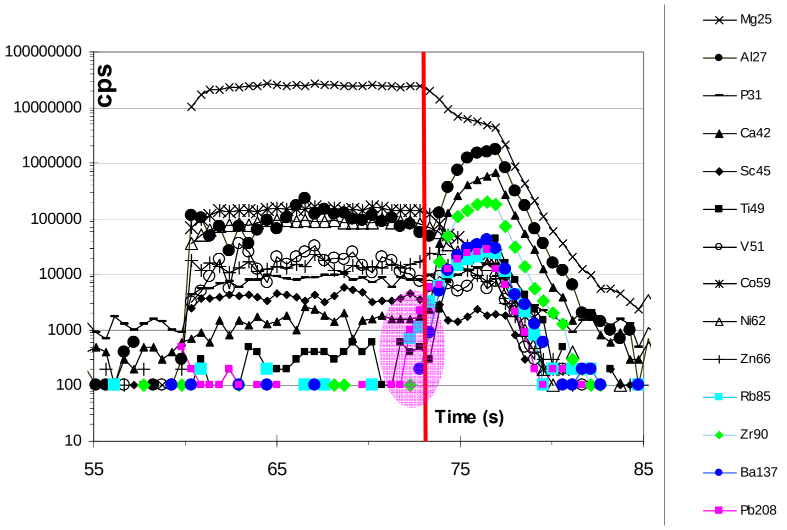
- bkg intensities very low

Non-ideal features:

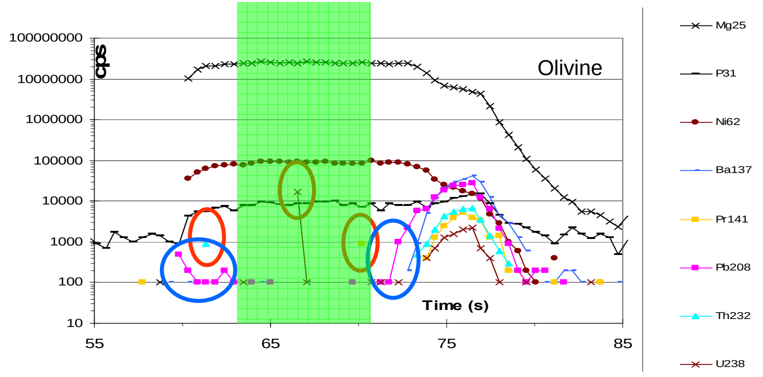
- short analyte signal



Drilled after ca. 12s into underlying section glass
40 elements measured;
thus, in 12s each element was recorded only 21 times
→ Statistics are not so good with only 21 individual determinations per element .....



Note that before we actually drill into the underlying glass support, signals of Pb and Rb raise, representing surface contamination of the lower section surface

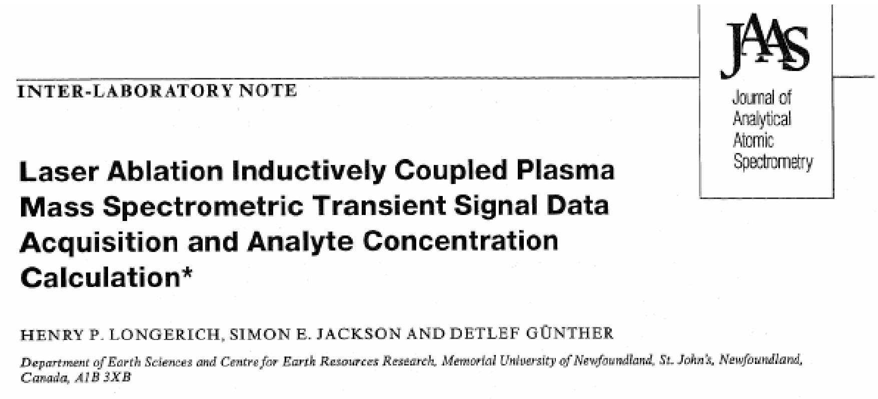


Signal "problems" include:

- Signal spikes - NOTE log-scale of intensity axis !!!
  (must be manually removed during data redution - see this afternoon)
- Surface contamination - must be avoided when setting the integration interval borders (recall: there are TWO SURFACES !)

→ optimal signal interval shown in green!

This selection is done on screen immediately after the analysis (i.e., during system flushing)



JAAS
Journal of Analytical Atomic Spectrometry

INTER-LABORATORY NOTE

Laser Ablation Inductively Coupled Plasma Mass Spectrometric Transient Signal Data Acquisition and Analyte Concentration Calculation*

HENRY P. LONGERICH, SIMON E. JACKSON AND DETLEF GÜNTHER

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Lamtrace and SILLS data reduction programs (and anything else useful) is based on this; SILLS further on Halter et al., 2002!

Essential steps in quantification

$\mathrm{Conc}_{X,sample} = \mathrm{CPS}_{X,sample} / S_{X,sample}$

$S_{X,sample}$ is the sensitivity for the elements (X) in the sample.

$\mathrm{LOD}_{X,sample} = (3 * \mathrm{stdev} / S_{X,sample}) * \mathrm{sqrt}(1/n_{bkg} + 1/n_{signal})$

where n_{bkg} and n_{signal} are the number of sweeps integrated
for the bkg and signal interval, respectively.

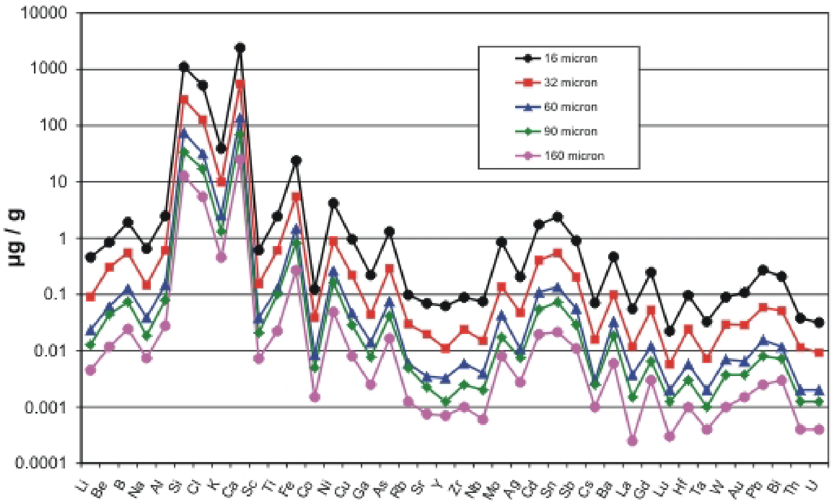
$S_{X,sample}$ must be derived from the sensitivity of the element
determined in the external standard.
It thus relates to the measurements of the bracketing standard
(std) via the expression:

$$S_{X,sample} = \mathrm{CPS}_{IS,sample} / \mathrm{Conc}_{IS,sample} * [(\mathrm{CPS}_{X,std} / \mathrm{Conc}_{X,std}) * (\mathrm{Conc}_{IS,std} / \mathrm{CPS}_{IS,std})]$$

What influences the LOD
of an element in the sample?

- Natural abundance of the isotope measured; e.g., Ca will give LOD in the range of tens of ppm because we have to measure mass 42 with a natural abundance of 0.65% !).
- Pit size. The larger the pit, the higher the sensitivity, because sensitivity is a count RATE per unit concentration. The instrumental background remains the same; thus, LOD becomes lower with increasing sensitivity.
- The quality of the background and signal measurements.
  The more sweeps recorded, the better. However, when each element in the background and signal intervals was measured > ca. 100 times, hardly anything can be gained by recording even more sweeps.
- The dwell time. The longer the dwell time, the less scatter there is between individual measurements of a given element (as background scatter is determined on count RATES); thus, LOD decreases.
  BUT: Since data recording is SEQUENTIAL, long dwell times
  bear the danger of non-representative sampling!
- Daily machine tuning, most importantly the system background
  (recall: $\mathrm{LOD} = 3 * \text{"sterr"}_{bkg} / S$)

Typical LOD achieved on in-house LA-ICP-MS



One order of pit size increase results in two orders of magnitude lower LOD!

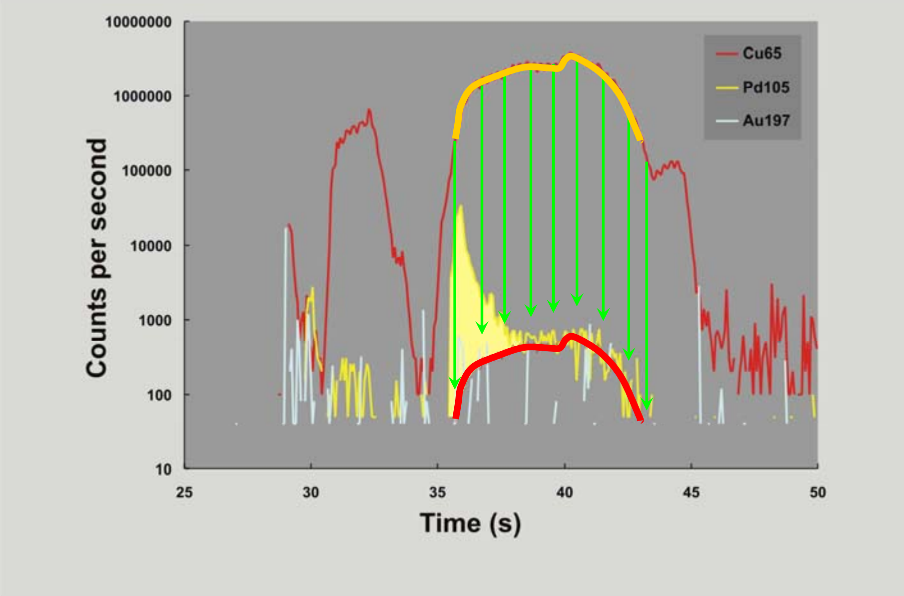
Minimal pit size

- Pit sizes NOMINALLY possible between 4 and 200 µm.
  Pit sizes >160 µm do no longer guarantee homogeneous energy distribution across the pit; hence, we will not use these.
- Pits smaller than ~5 µm are not providing acceptably precise and thus reliable data (recall useful signal duration).
- Pits between ~5 and ca. 25 µm may give acceptably precise data only for "short" element menues,
  e.g., up to ca. 20 elements.
- → Therefore, for small phases to analyze (i.e., pit sizes smaller than ca. 25 µm), a reduced element menue is mandatory
  (recall that we should not drill too deeply relative to pit diameter).

Choice of analyte masses

- Analyte masses must be interference-free (or else, a correction is required). Such corrections are linear provided that they are based on count rates. However, avoiding interferences is the safest bet!

$(^{65}Cu^{40}Ar)^+$ interference on ^{105}Pd



Choice of analyte masses

- **Analyte masses must be interference-free (or else, a correction is required). Such corrections are linear provided that they are based on count rates. However, avoiding interferences is the safest bet!**
- **Commonly, a non-interefered isotope with highest natural abundance is chosen. For cases of very high concentrations in the sample, isotopes of lower natural abundance may be better, e.g., ^{235}U (0.72% abundance) for uraninite (UO_2).**
- **Caution with radiogenic isotopes! The data reduction scheme calculates the element abundance from the analysed isotope assuming common (i.e., non-radiogenic) isotopic composition!**
- **More than one isotope for a given element can be analyzed to check for internal consistency or the accuracy of an interference correction!**
- **→ Do not worry too much: These issues are generally well controlled**

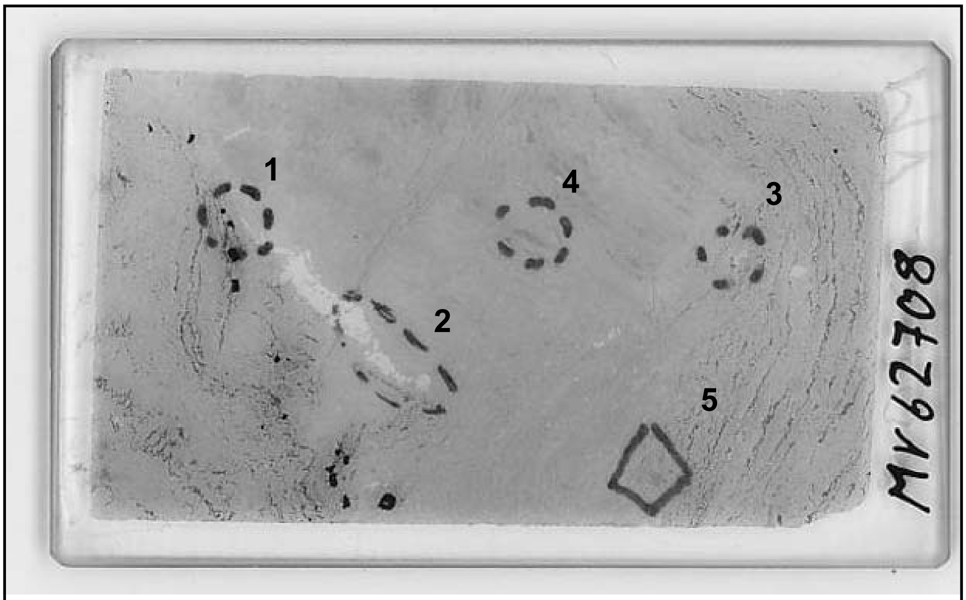
Analytical precision and accuracy

**Best measure for *analytical precision* is
the shot-to-shot reproducibility,
i.e., the external reproducibility**

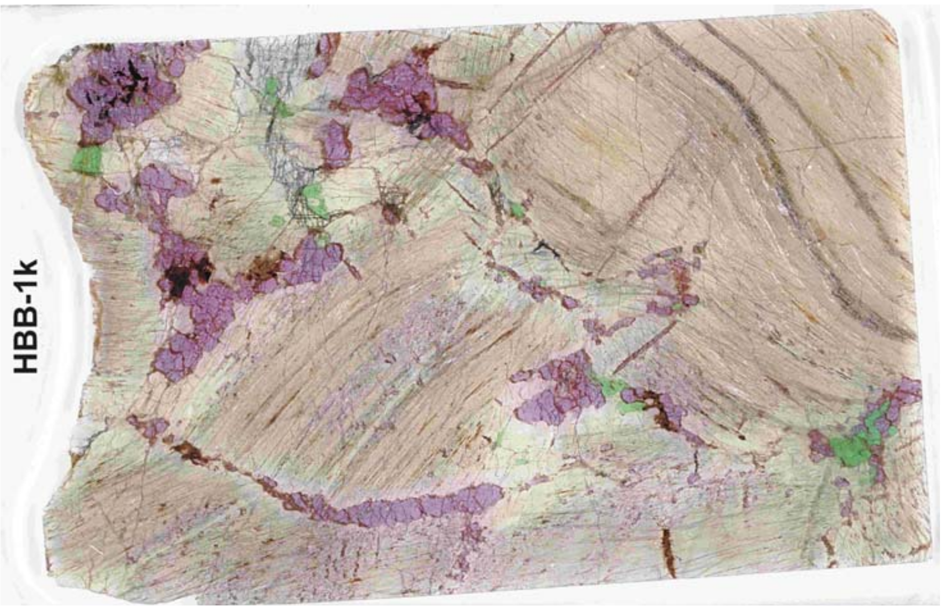
**Best measure for *analytical accuracy* is
to analyse a reference material closely matrix matching your sample material
(and *NOT* the external standard you use .....).**

**→ Think about this reference material for
your "personal" accuracy test!!**

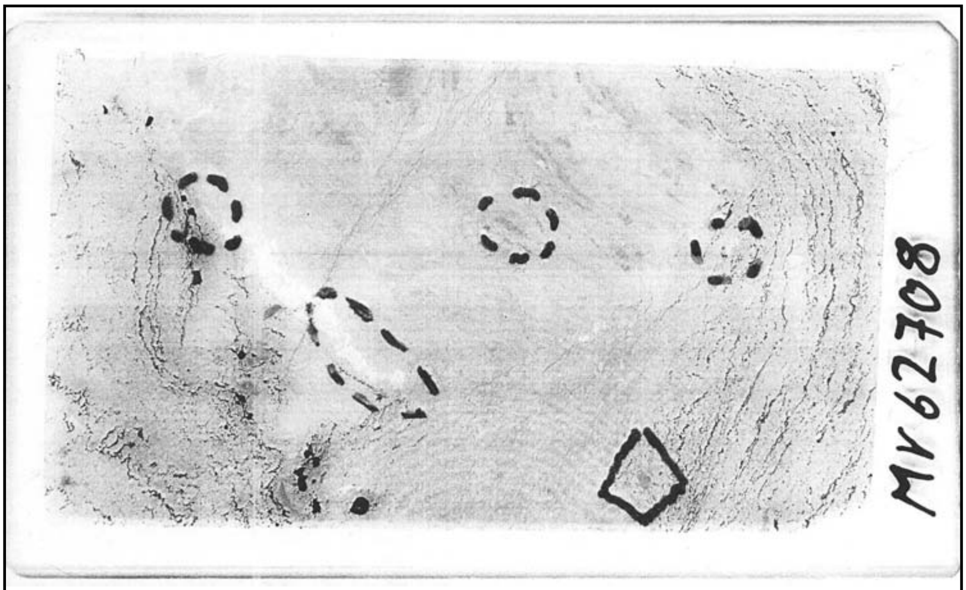
Some examples of sample preparation: analytical maps



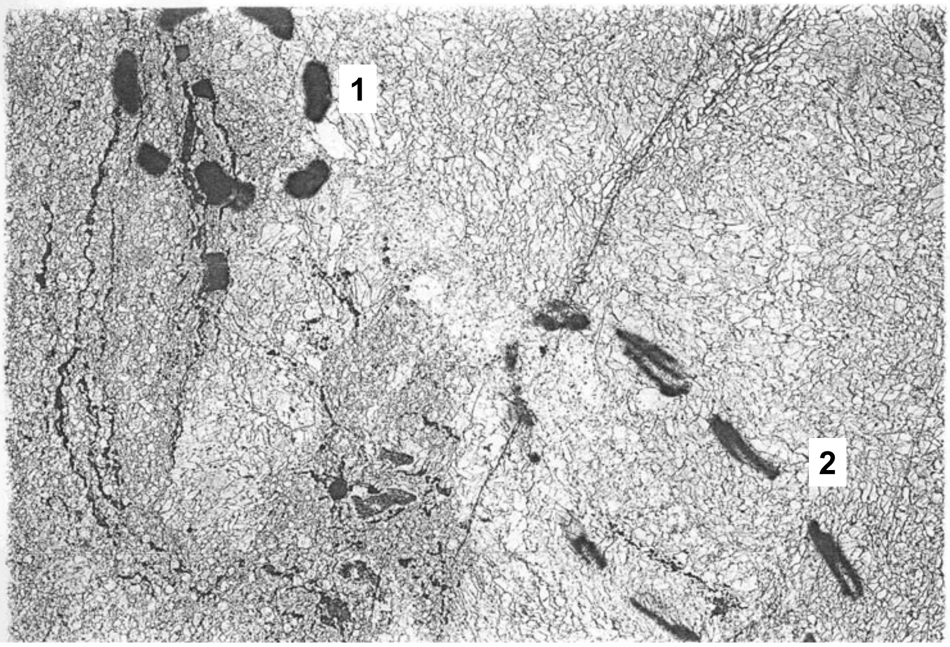
Grayscale thin section SCAN



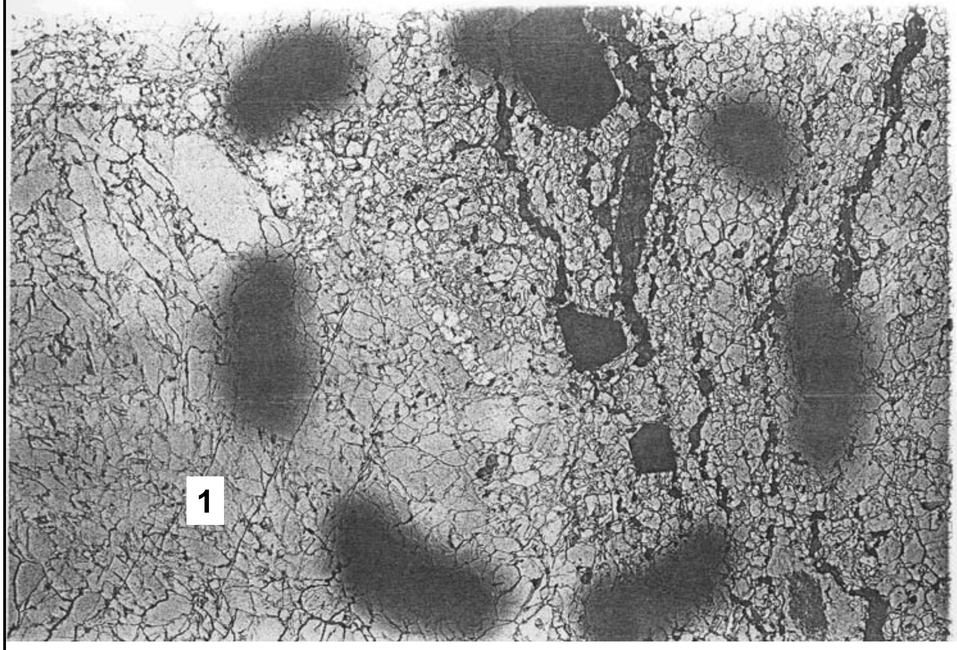
Colour thin section SCAN



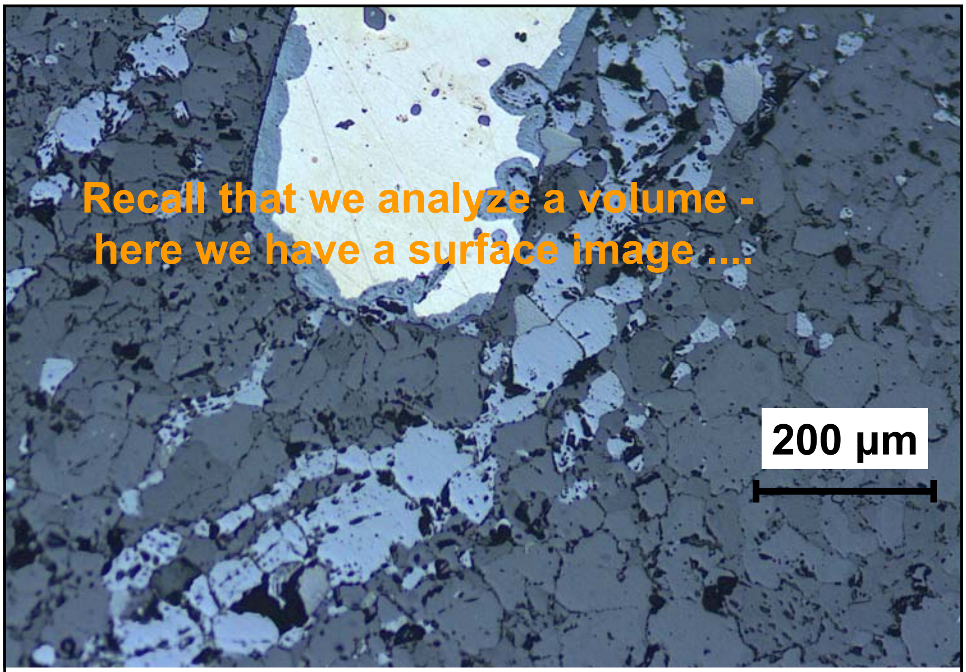
Scanned thin section PHOTOCOPY at 400x magnification



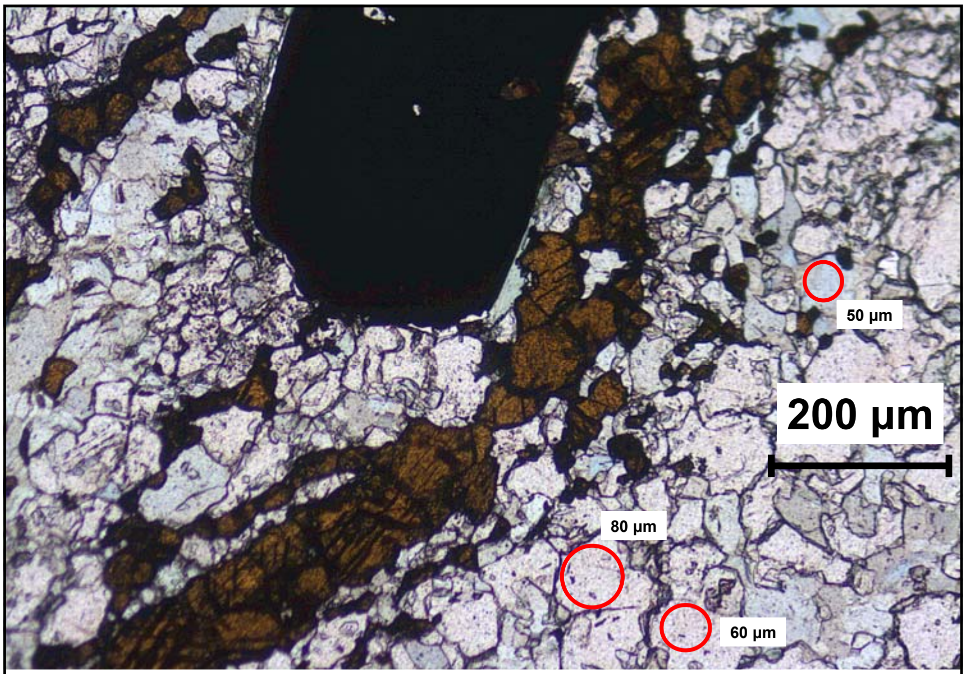
Scanned "FICHEN SCANNER" low-magnification image



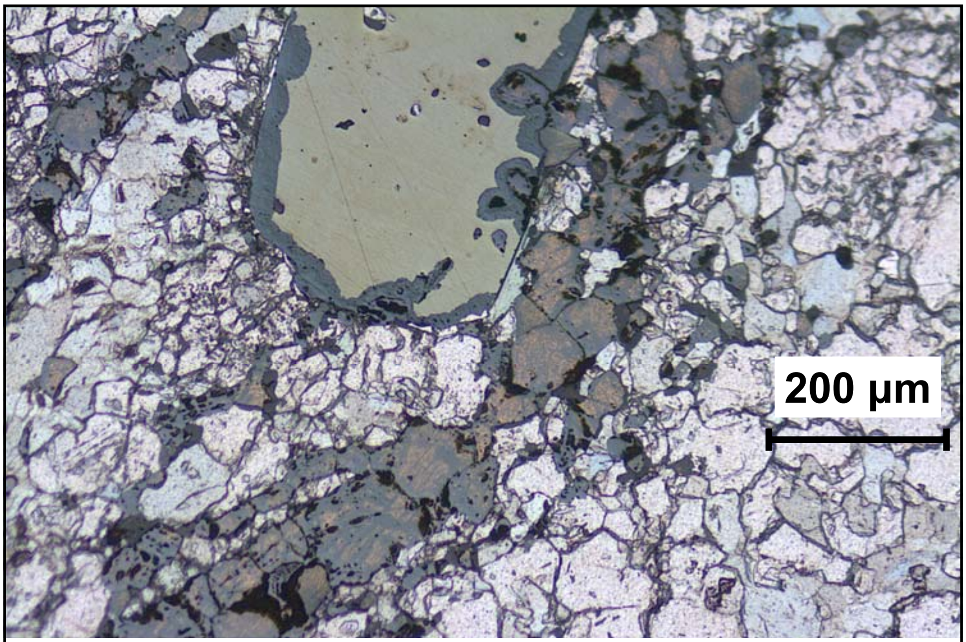
Scanned " FICHEN SCANNER " high-magnification image


Recall that we analyze a volume - here we have a surface image ....

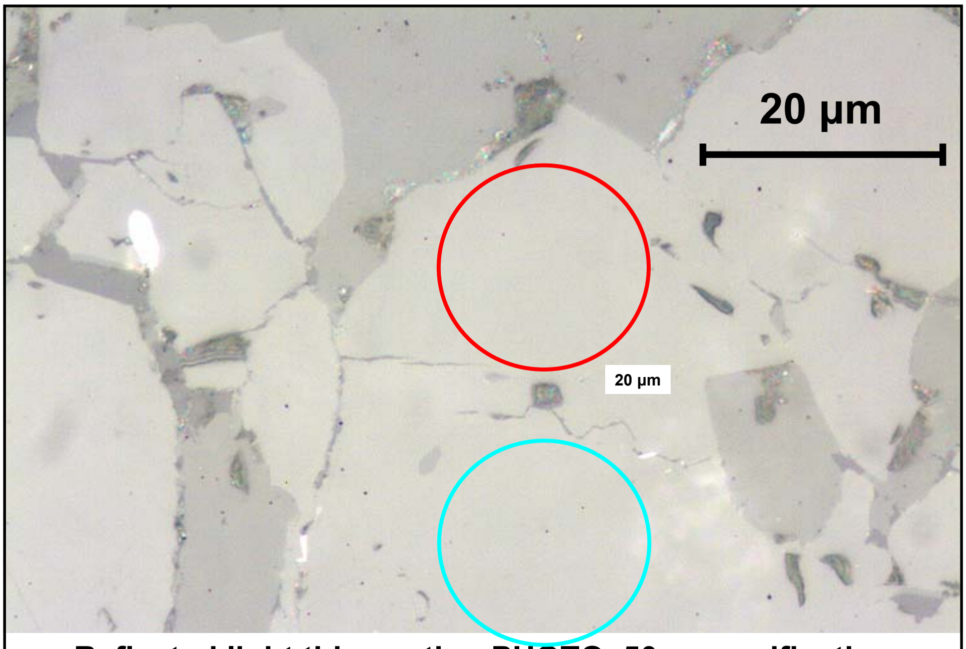
Reflected light thin section PHOTO, 4x magnification



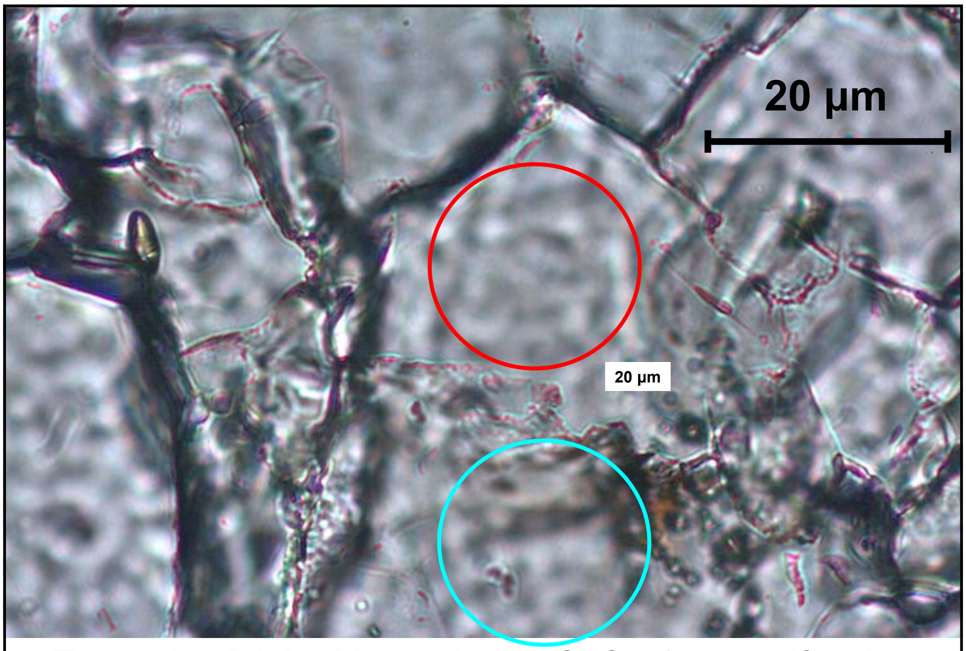
Transmitted light thin section PHOTO, 4x magnification



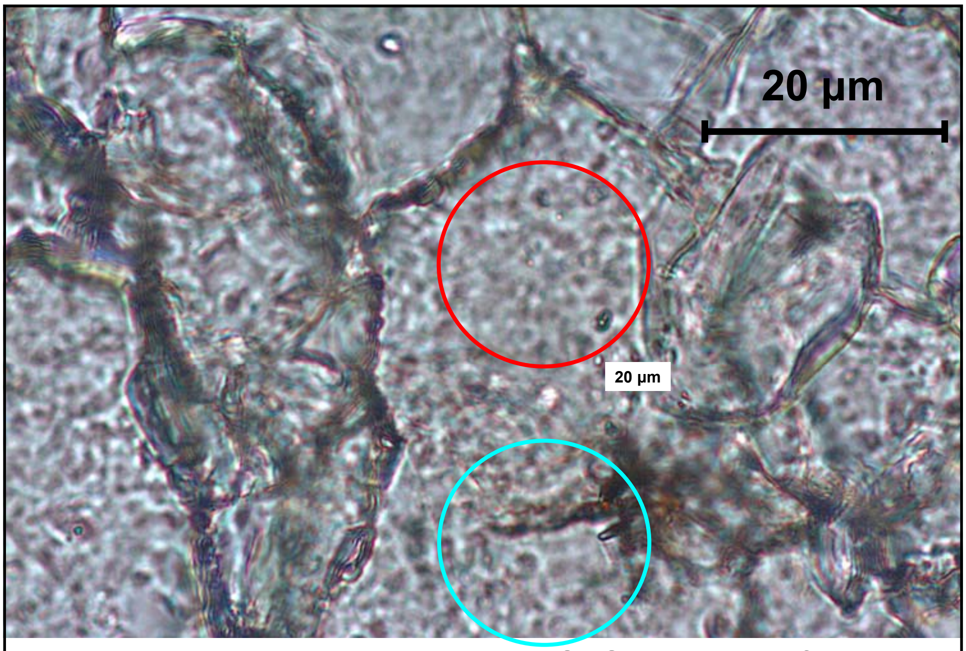
Transmitted plus reflected light thin section PHOTO,
4x magnification



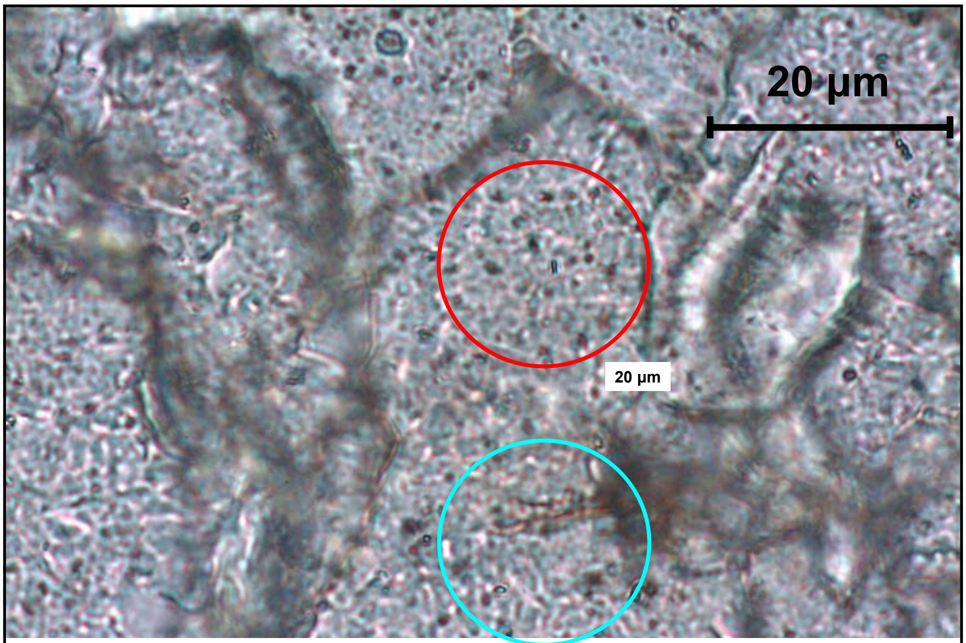
Reflected light thin section PHOTO, 50x magnification
"BSE equivalent"



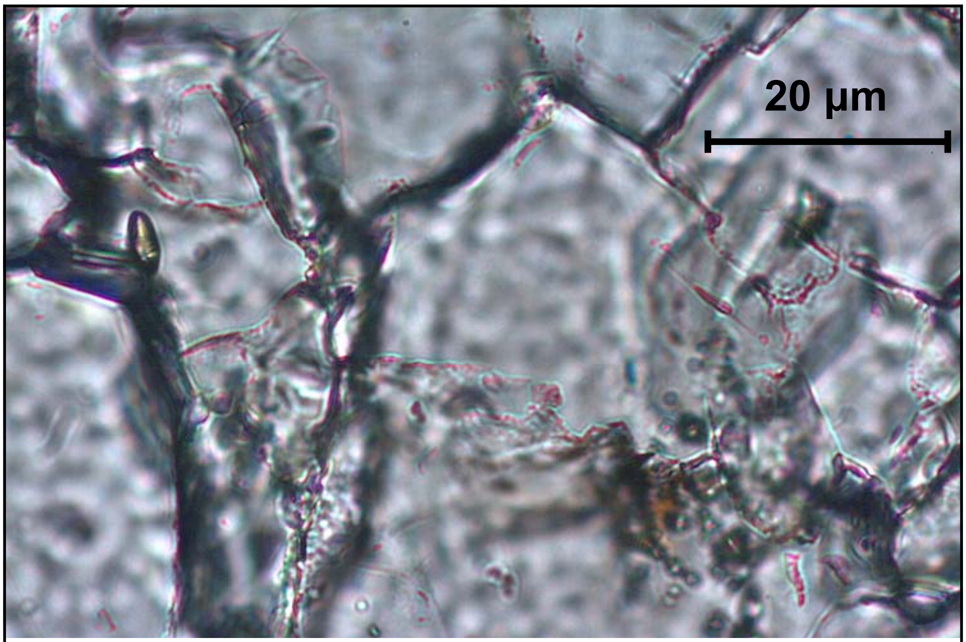
Transmitted light thin section PHOTO, 50x magnification
focus on sample surface



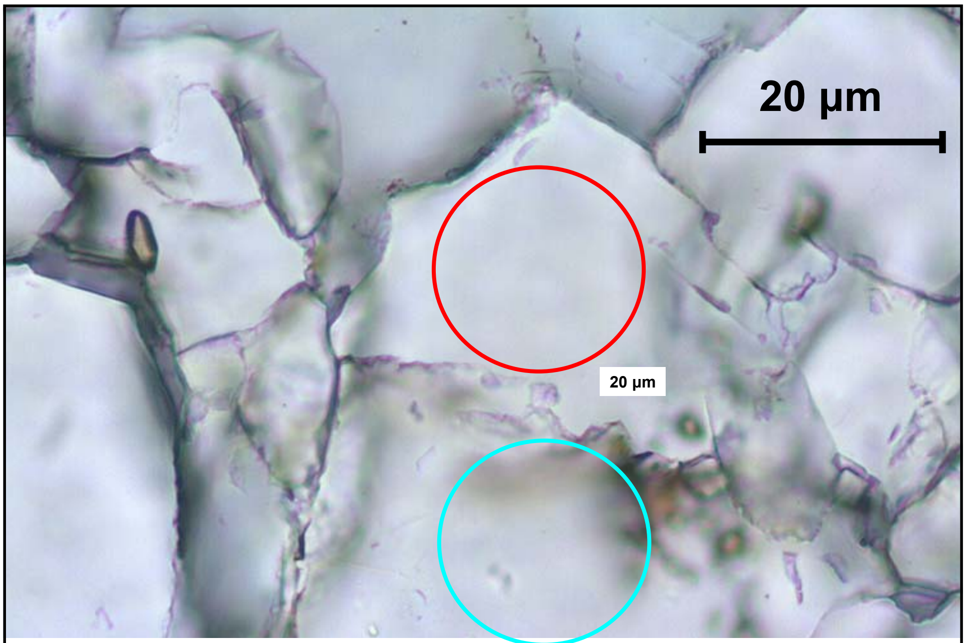
Transmitted light thin section PHOTO, 50x magnification
focus within sample



Transmitted light thin section PHOTO, 50x magnification
focus on LOWER sample surface



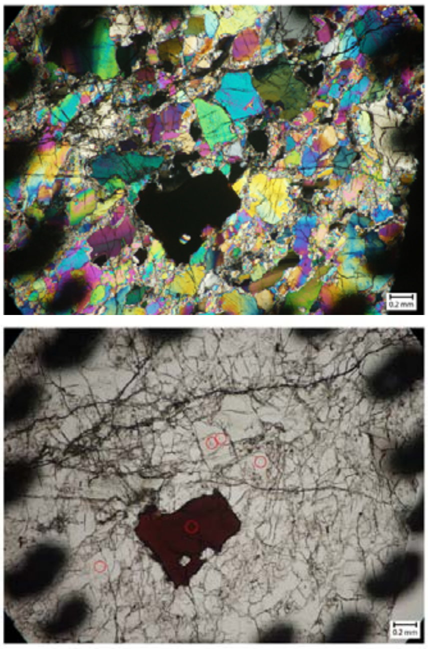
Transmitted light thin section PHOTO, 50x magnification
focus on sample surface

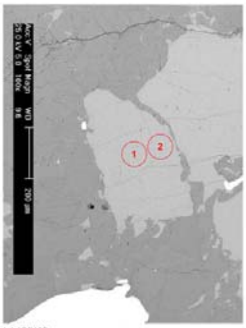


Transmitted light thin section PHOTO, 50x magnification
PLUS CONDENSER LENS, focus on sample surface

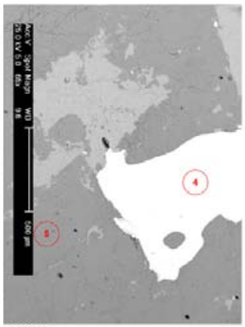
Pl2si cercle 1
IMAGE “A”

PHOTOS

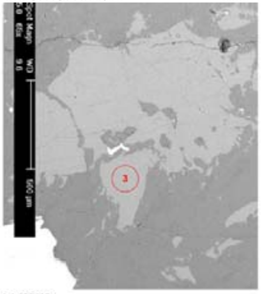




LA ICPMS
1. cpx coeur: p2c1cpxcc1 100µm
2. cpx bord: p2c1cpxcc1 100µm



LA ICPMS
4. spl coeur: p2c1splc1 100µm
5. ol coeur: p2c1olc1 100µm

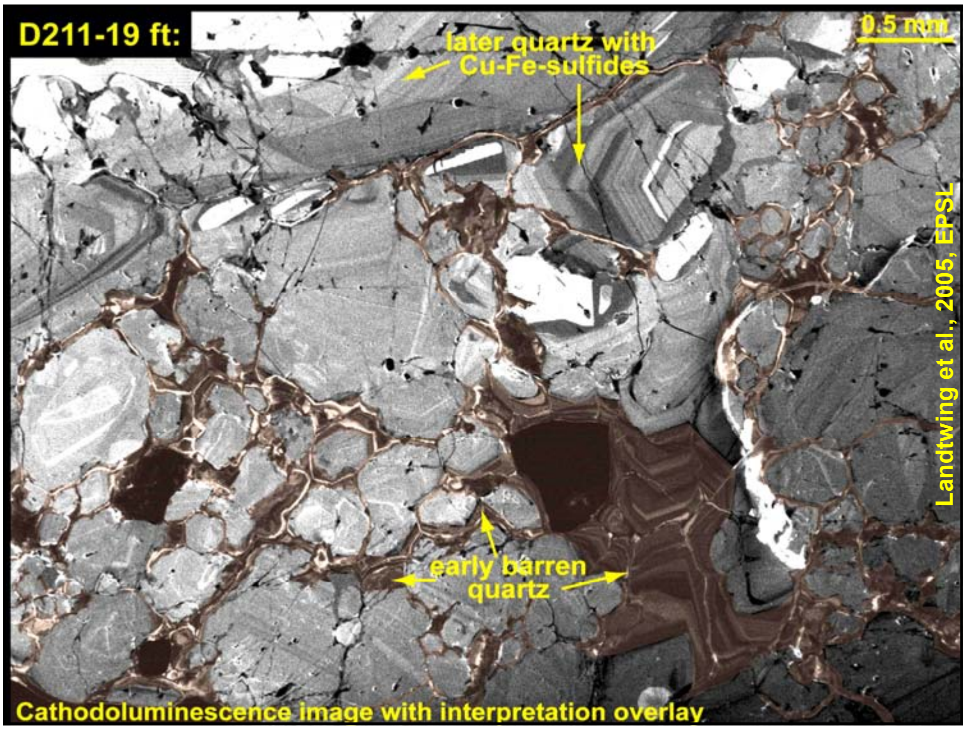


LA ICPMS
3. cpx coeur: p2c1cpxcc1b 100µm

BSE images

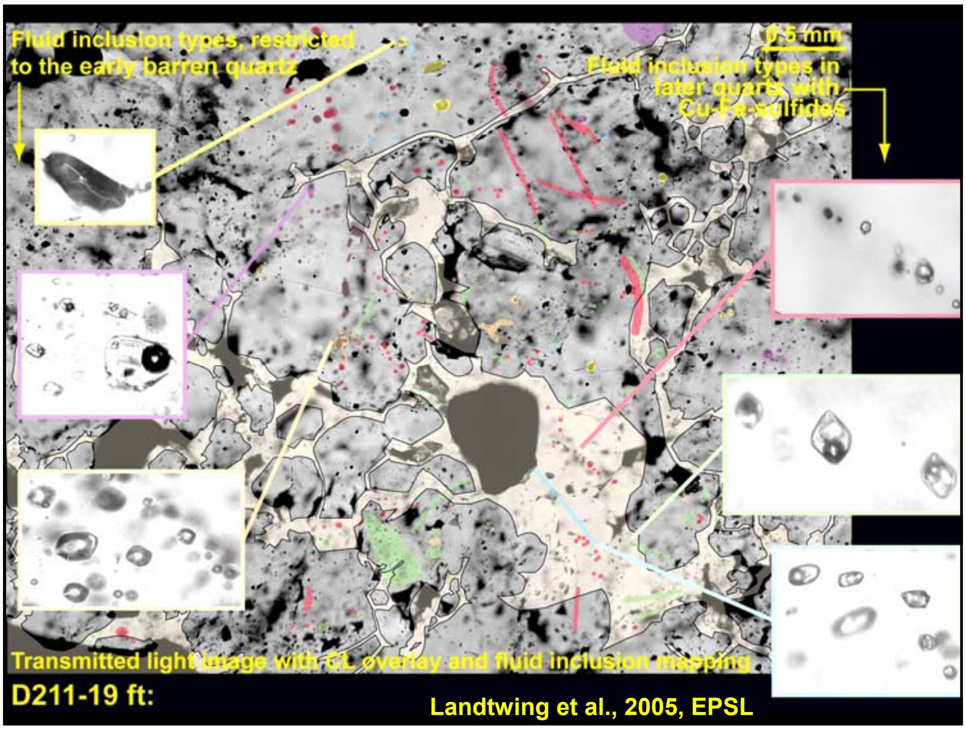
Thanks to
Laure Pelletier

D211-19 ft:



Cathodoluminescence image with interpretation overlay

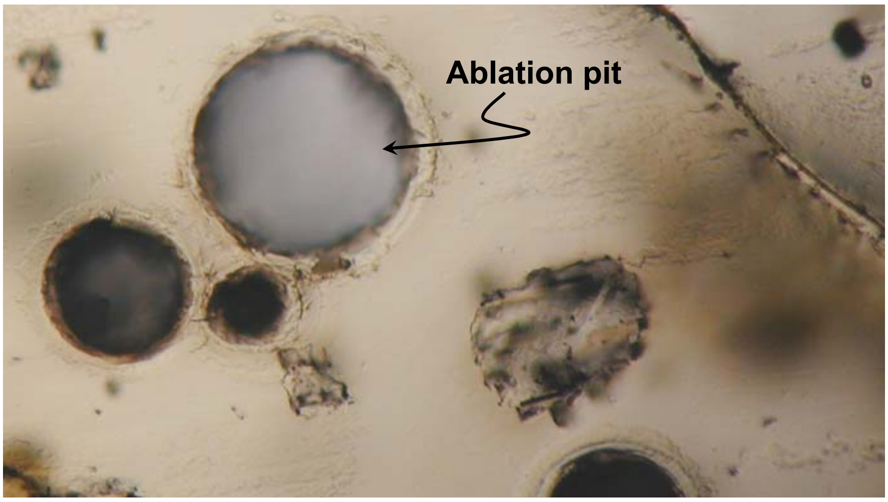
Landtwing et al., 2005, EPSL



Transmitted light image with CL overlay and fluid inclusion mapping

D211-19 ft:

Landtwing et al., 2005, EPSL

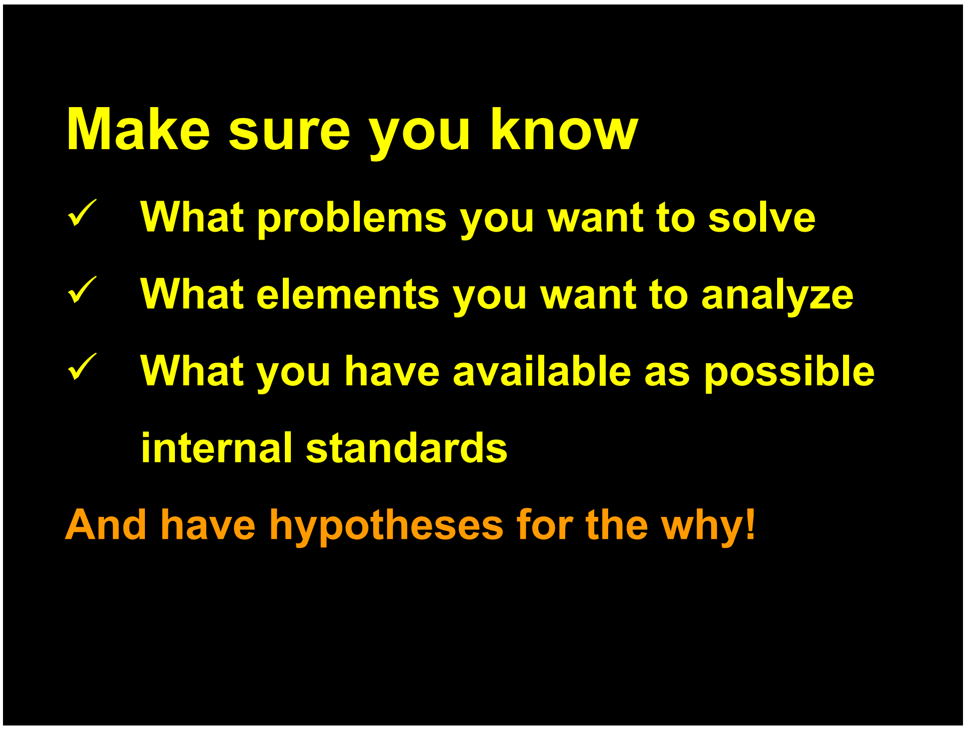


This analytical technique is destructive !!!
You need to perform all other analyses before you do LA-ICP-MS work on it!

I request a short written proposal (working hypothesis), detailing the problem, what data are already available and what the LA-ICP-MS analyses are expected to contribute.

Based on this we can then discuss the project, machine time and booking.

Requests for machine time are best done via email to pettke@geo.unibe.ch



Make sure you know

- ✓ What problems you want to solve
- ✓ What elements you want to analyze
- ✓ What you have available as possible internal standards

And have hypotheses for the why!

Prepare your sample well !!!

Thanks