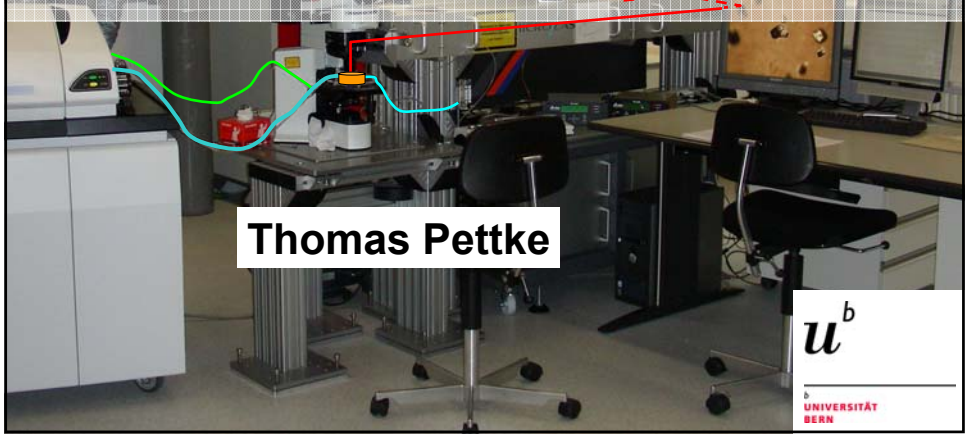
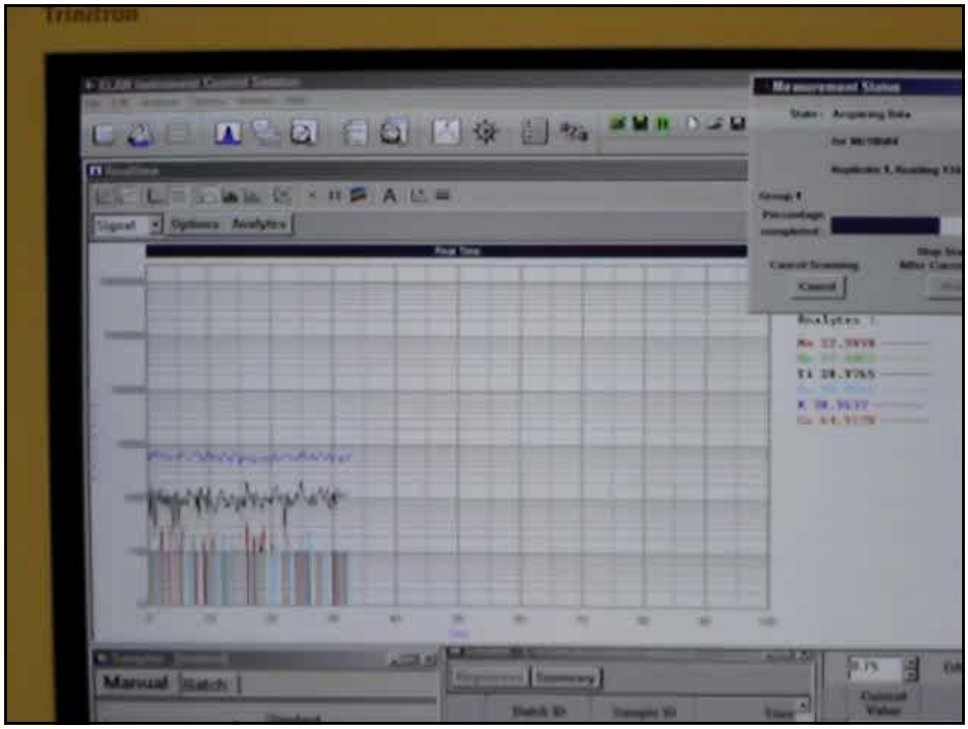
Principles of LA-ICP-MS high-precision analysis of trace element abundances and isotope ratios in minerals and fluids

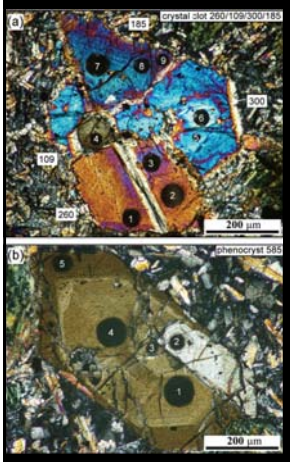


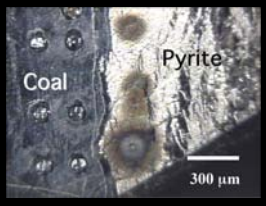
Thomas Pettke

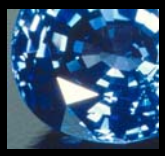
UNIVERSITÄT BERN

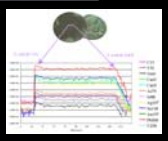


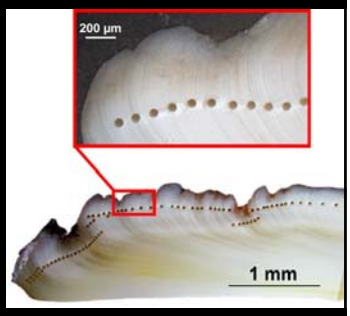
We measure major to trace elements and isotope ratios "in anything" in situ, down to mg/t for a 100 µm beam diameter



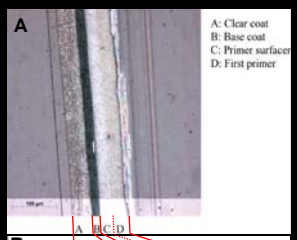




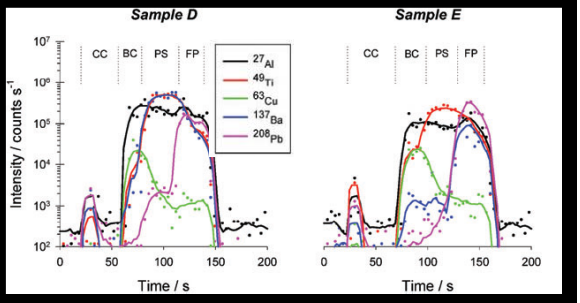




Instumental considerations
What LA-ICP-MS can analyze and what not
Data quantification strategies



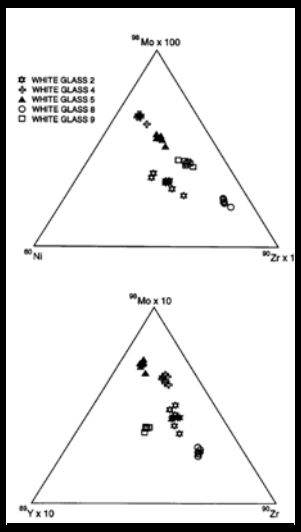
Forensic sciences: Car crash



Depth profiles for two green car paint samples (samples D and E), obtained with ICP-SF-MS: Intensity (log scale, cps) versus time. (CC: clear coat; BC: base coat; PS: primer surfacer; FP: first primer)

Deconinck et al. 2006

Materials sciences

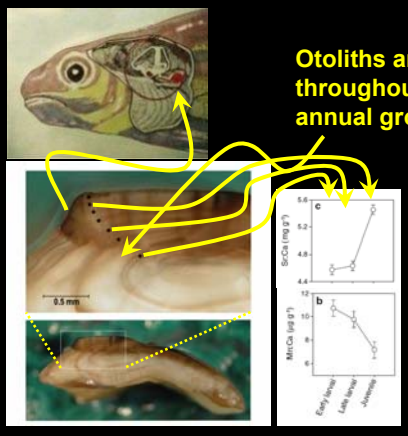


Watling et al. (1997)

Characteristic element concentrations (here: Car windows) determine materials properties (flexibility, breaking resistance, colour, ...).

The analysis of small splinters may thus provide diagnostic element signatures, and can be used in forensic sciences, too.

Otholit chemistry to track fish migration



Otoliths are mm-sized ear bones which grow throughout the life of an organism, displaying annual growth rings

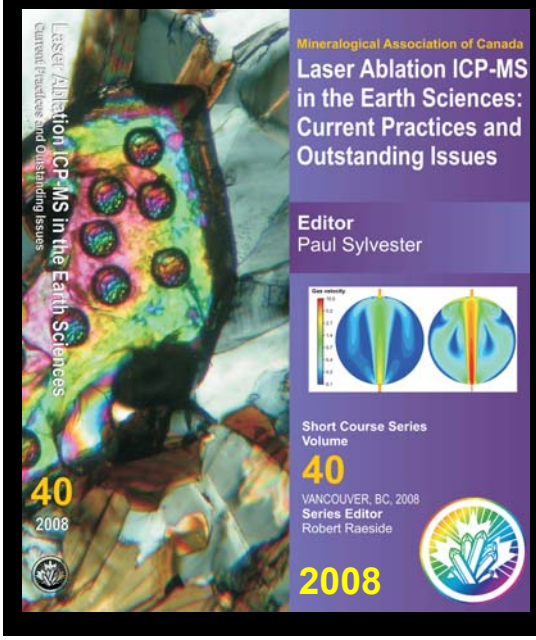
Selected trace element signatures are a proxy for temperature and water type (sea- vs. freshwater).

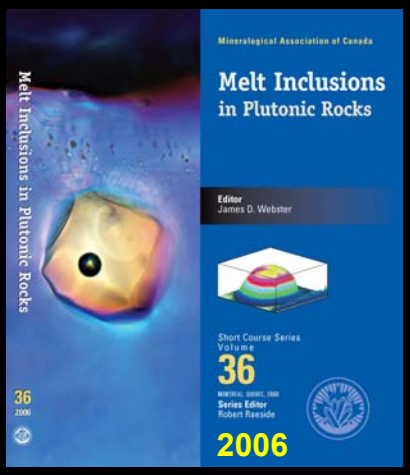
Migration of salmon can thus be tracked!

Otolithe of fossil fish can provide information about paleo-climate

(Miller, 2006)

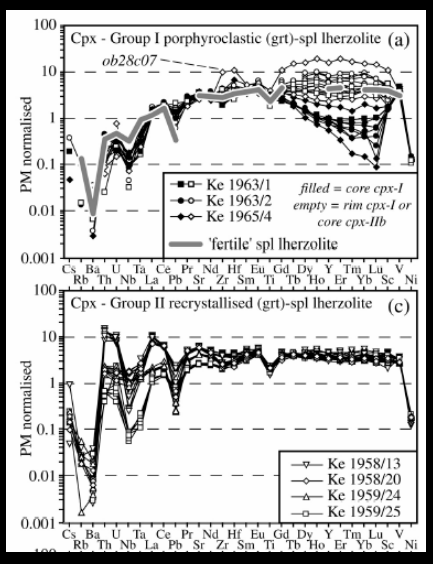
Recent literature

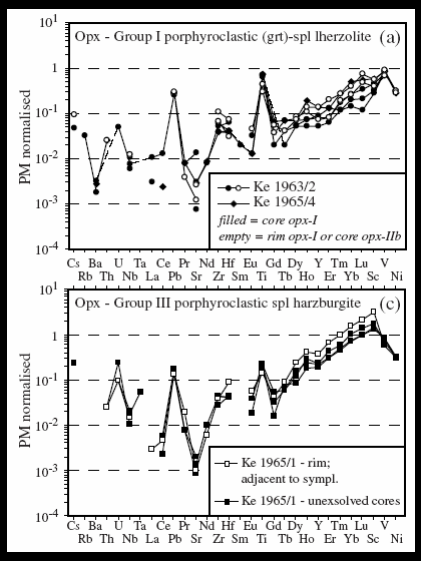




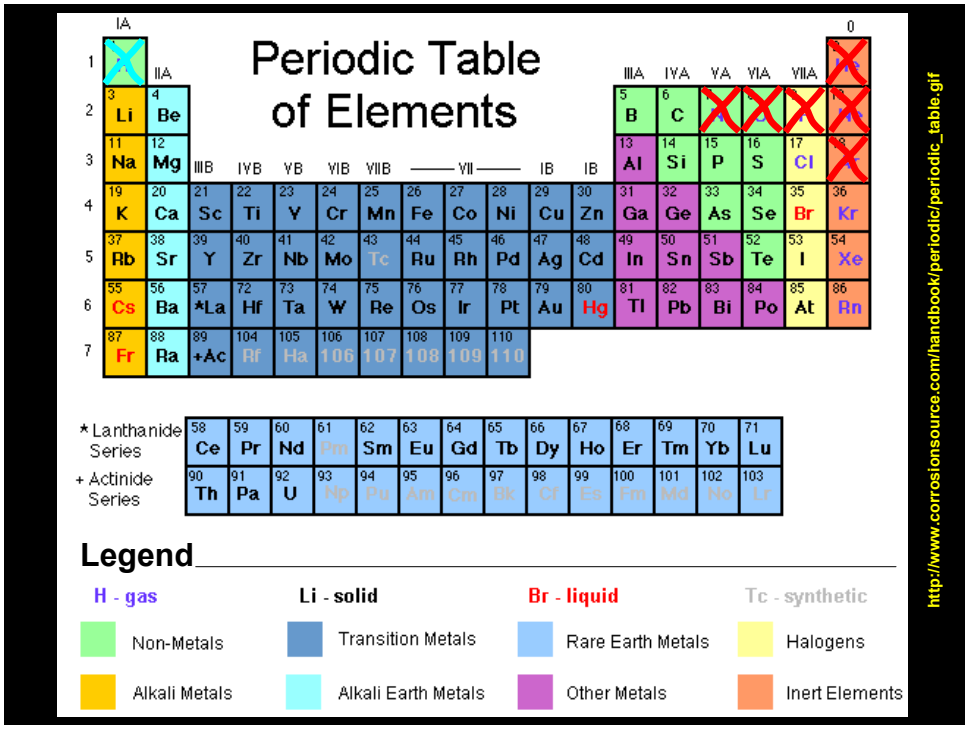
Two LA-ICP-MS chapters by Pettke, focusing on the analysis of heterogeneous inclusions in minerals

We can measure "all" trace elements in one analytical point



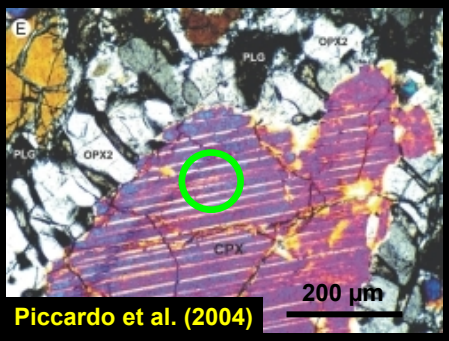


Kaeser et al., 2006, 2007, 2009

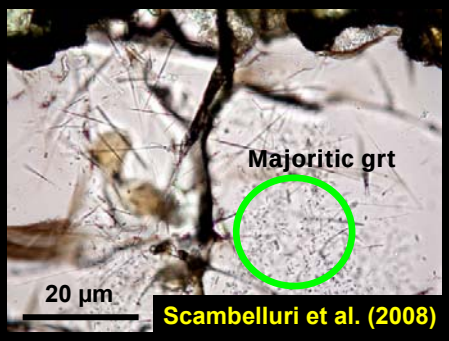

Periodic Table of Elements
IA
IIA
IIIB
IVB
VB
VIB
VIIB
VII
IB
IB
IIIA
IVA
VA
VIA
VIIA
0
1 H
2 Li Be
3 Na Mg
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba *La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Ra +Ac Rf Ha 106 107 108 109 110
B C Al Si P S Cl
* Lanthanide Series
+ Actinide Series
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Legend
H - gas
Li - solid
Br - liquid
Tc - synthetic
Non-Metals
Transition Metals
Rare Earth Metals
Halogens
Alkali Metals
Alkali Earth Metals
Other Metals
Inert Elements
http://www.corrosionsource.com/handbook/periodic/periodic_table.gif


We always analyze a VOLUME
465x

Heterogeneous phases



Piccardo et al. (2004)



Scambelluri et al. (2008)

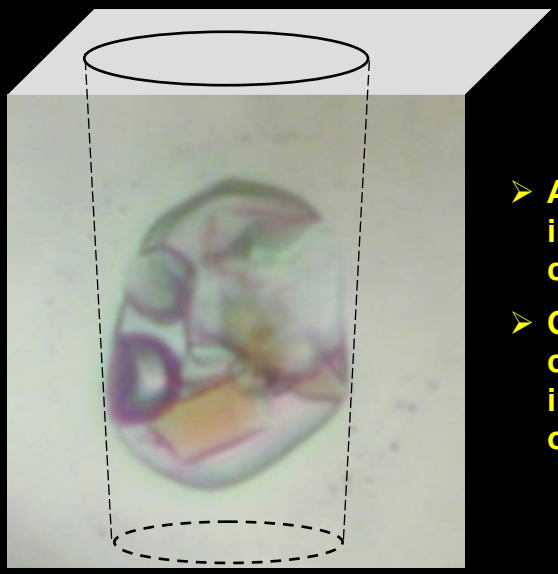
Unmixing:
OPx lamellae in CPx

Pyx exsolutions in Grt

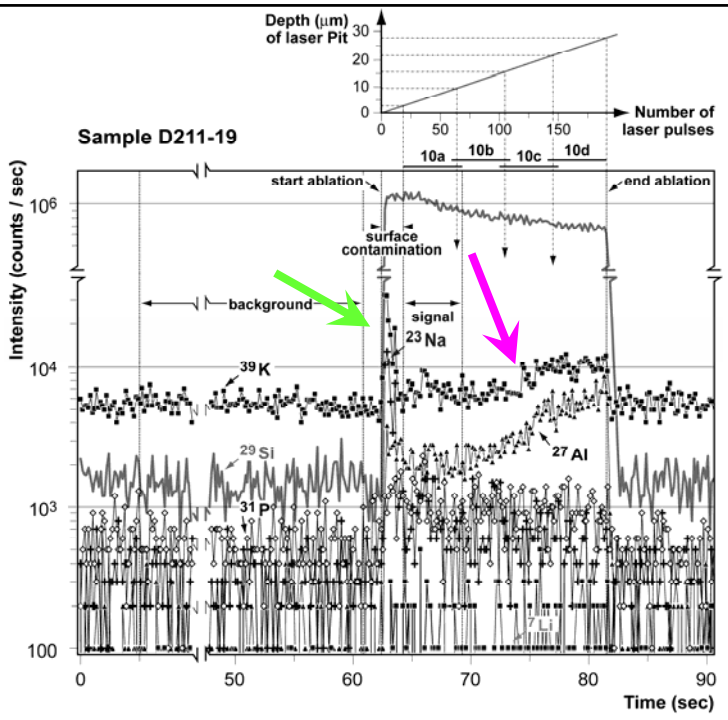
Reconstruction of homogeneous phase composition at formation conditions, i.e., high P and T !

Also essential in metallurgy

The unique possibility

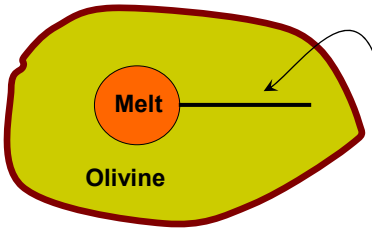


- **Analyze polyphase inclusions of confined volume**
- **Obtain bulk chemical composition of the inclusion trapped as one phase**



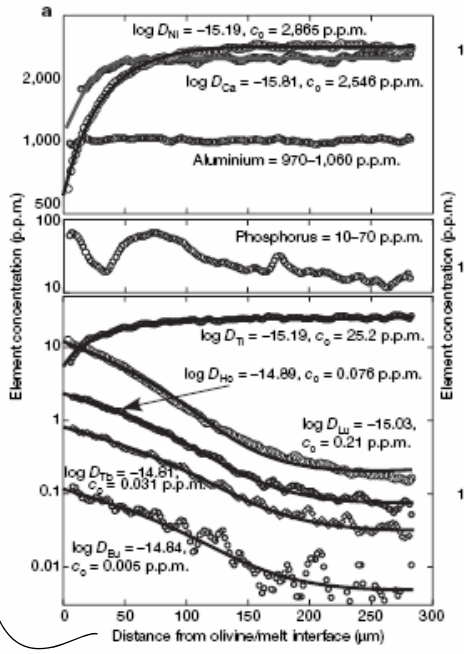
Recall:
We analyze a sample VOLUME; thus, danger of zonation with depth!
(or: Potential for depth profiling)

(Depth) profiling

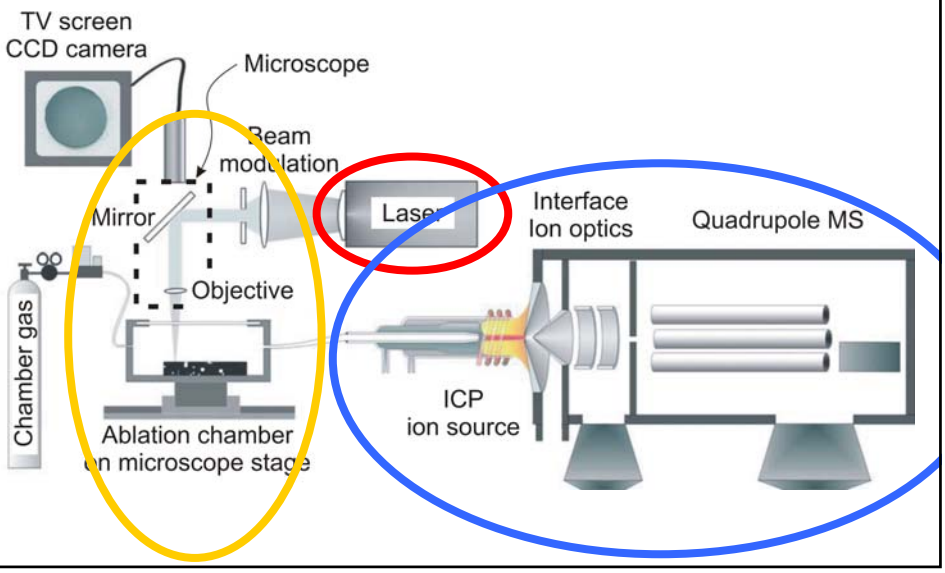


Diffusion profiles analyzed in line-scan mode away from melt - olivine interface (data, points; lines, fits): Determination of diffusion coefficients at experimental P, T, X.

Spandler et al., 2007



Typical LA-ICP-MS instrument



Laser

Light Amplification by Stimulated Emission of Radiation

produce coherent, collimated, monochromatic radiation, in free-running or Q-switched mode

Solid source

- **Nd-YAG (Nd-doped Y-Al garnet; 1064 nm), quadrupled or quintupled (266 or 213 nm).**
- **OPO lasers (Ti-Sapphire): down to <200 nm (Optical Parametric Oscillator)**

Gas source

Excimer = Excited dimer (noble gas – halogenides; e.g., ArF)
down to 157 nm with F_2, gas source lasers
(also named Exiplex)

Mass spectrometers

Quadrupole, Magnetic sector, Multiple collector, Time of flight

Fundamental principle of mass spectrometry

The analytes we measure are always mass-filtered according to their

MASS / CHARGE RATIO

$^{90}Zr^{++} = {}^{45}Sc^{+}$

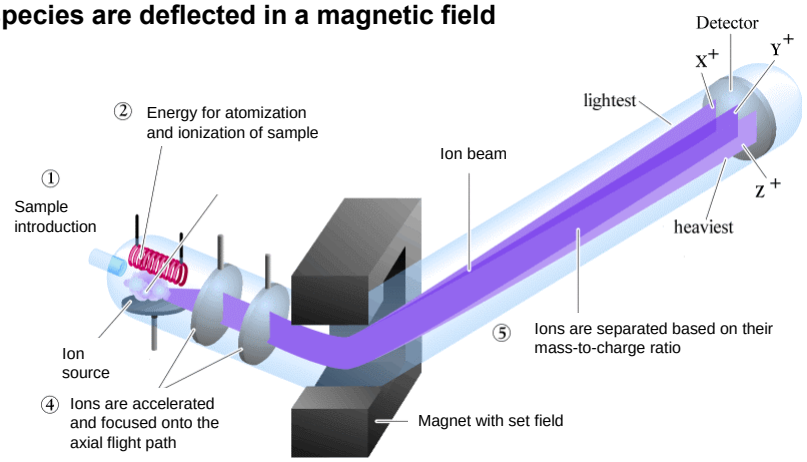
$^{28}Si^{+} = {}^{56}Fe^{++}$

Mass spectrometers

Quadrupole	Robust, fast scanning, sensitive, low mass resolution (interferences)
Time of flight	"Simultaneous" measurement, moderate sensitivity and backgrounds
Magnetic sector	Highly sensitive, moderate scanning speed, High mass resolution (loss of sensitivity)
Multiple collector	Simultaneous analyte measurements, limited number of isotopes (i.e., mass range), high to moderate sensitivity

Magnetic sector mass spectrometry

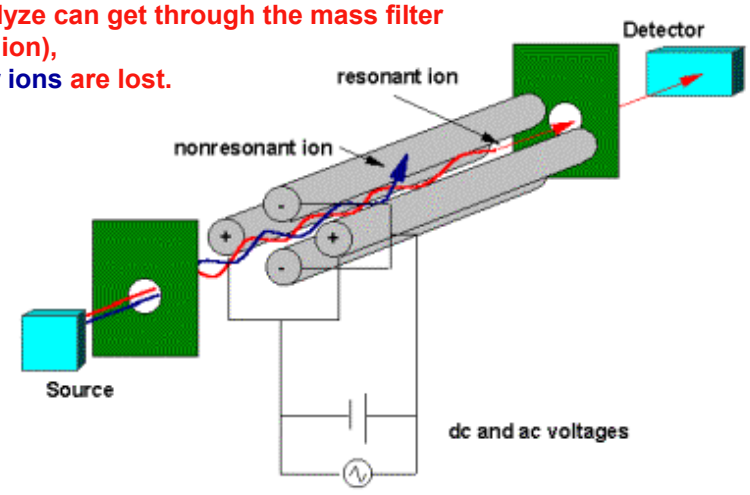
is based on the principle that moving charged species are deflected in a magnetic field



Quadrupole mass spectrometry

is based on the principle that moving charged species are (mass/charge)-filtered in an electrostatic field (between the rods).

Only the ion of the mass-to-charge ratio we want to analyze can get through the mass filter (= resonant ion), all the other ions are lost.



First LA-ICP-MS paper in 1985

ANALYST, MAY 1985, VOL. 110 *55* 1

Solid Sample Introduction by Laser Ablation for Inductively Coupled Plasma Source Mass Spectrometry

Alan L. Gray
Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, UK

The results are described of a preliminary study of the mass spectrometry of solid samples using a ruby laser to ablate the sample into an inductively coupled plasma (ICP) source mass spectrometer. Standard rock samples were used, pelletted with a binder into the form of a disc. Some 200 ablation pits could be accommodated on each sample. Laser pulse energies of 0.3-1 J were used in the fixed **Q** mode and the ablated material transferred from the ablation cell into the plasma torch by means of the plasma injector gas flow. The mass spectrometer was used in the fixed ion mode using mean ion current detection to evaluate the reproducibility of successive pulses on major constituents and in the scanning mode at the rate of 10 scans**s-1** to produce spectra using mean current detection for major elements and pulse counting detection for traces. Problems were experienced with saturation of the detection system in both the mean current and pulse counting modes owing to the transient nature of the sample pulse from the laser, when attempting to quantify major elements, but except where a major peak was saturated, reasonably uniform sensitivity for most elements across the mass range from 7 to 238 *m/z* was obtained. Isotope ratio measurements were made on lead at 29 pg g-1 and detection limits for the elements examined appear to be 10 ng g-1 or less.

Keywords: Solid samples; inductively coupled plasma source mass spectrometry; laser ablation

Comparison of LA-ICP-MS between

1985	2008
• 700 µm deep and wide craters	• 0.05 - 200 µm deep and 5 - 350 µm wide craters
• 40 shots = 200 µg per spot	• 300 shots = 0.X µg per spot
• LOD's in the 1000 - 0.1 µg/g range	• LOD's in the 10 - 0.0005 µg/g range

This is the SIGNIFICANT detection of one apple in 2'000'000'000 potatoes !!!

Characteristics of LA-ICP-MS

- All the matrix all the time
- Ablation rates not known a priori
- Ablation rates may vary with time
- Sample volume is analyzed
  → heterogeneity ?!?
- Occurrence of large particles
- Elemental analysis between 100 and 0.000'000'05 wt-% concentration possible from one spot

Interactive PARAMETERS in LA-ICP-MS

SAMPLE	LASER	AEROSOL TRANSP.	ICP-MS
Absorptivity of laser light	Wavelength	Ablation and carrier gas	Power, gas flows
Material robustness	Energy	Cell and tube volume	Torch position
	Pulse width	Cell flushing efficiency	Ion extraction
	Beam energy profile		Isotopes, dwell time
			Dual detector

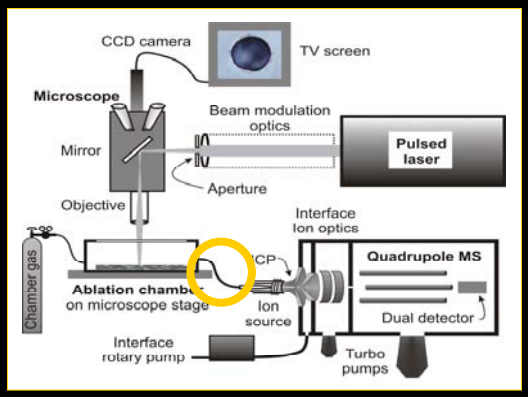
Interactive PROCESSES in LA-ICP-MS

ABLATION Responsible for:	TRANSPORT Responsible for:	IONIZATION Responsible for:
Material removal	Aerosol transport	Ion production
Particle production	Aerosol dispersion	Signal intensities
Condensation		Signal stability
Particle agglomeration	Particle agglomeration	Mass bias
Material loss	Material loss	Material loss

LA-ICP-MS

KEY ADVANTAGE:
Optimize aerosol generation and ion production independently!

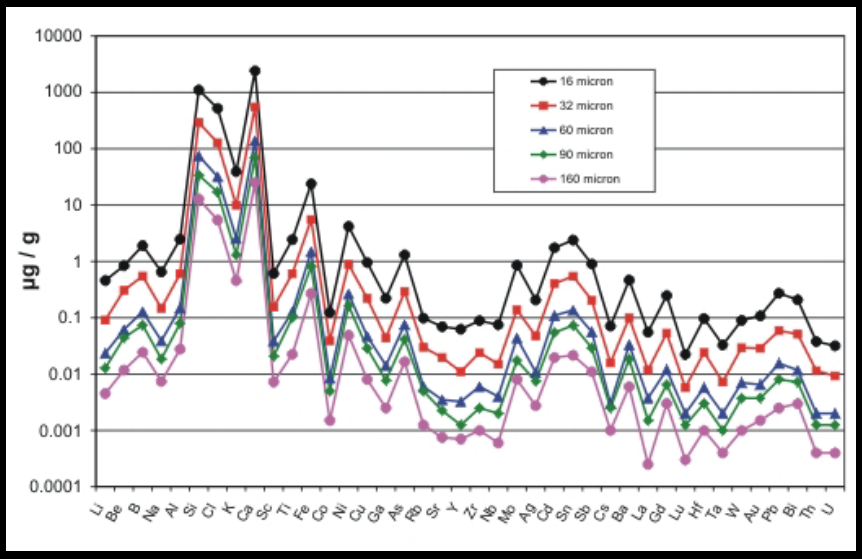
Air-tight plastic tube



Advantages of LA-ICP-MS

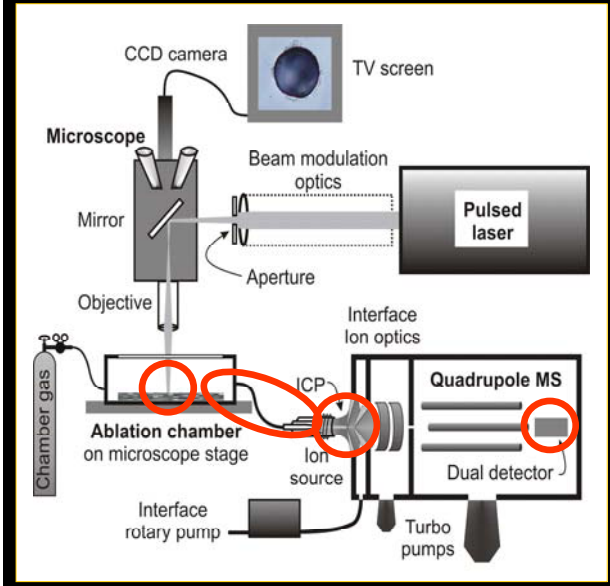
- In situ analysis (i.e., texturally controlled)
- Bulk mixtures
- Micro (≥5 µm spot size)
- From major to trace elements and isotopes
- High sensitivity
- Low backgrounds notably in high mass range
- Low limits of detection (LOD)
- "Easy" spectra (→ interferences)
- Chemists claim low sample prep:
  YES for actually producing numbers
  No for understanding and interpreting geoscientific data

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



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

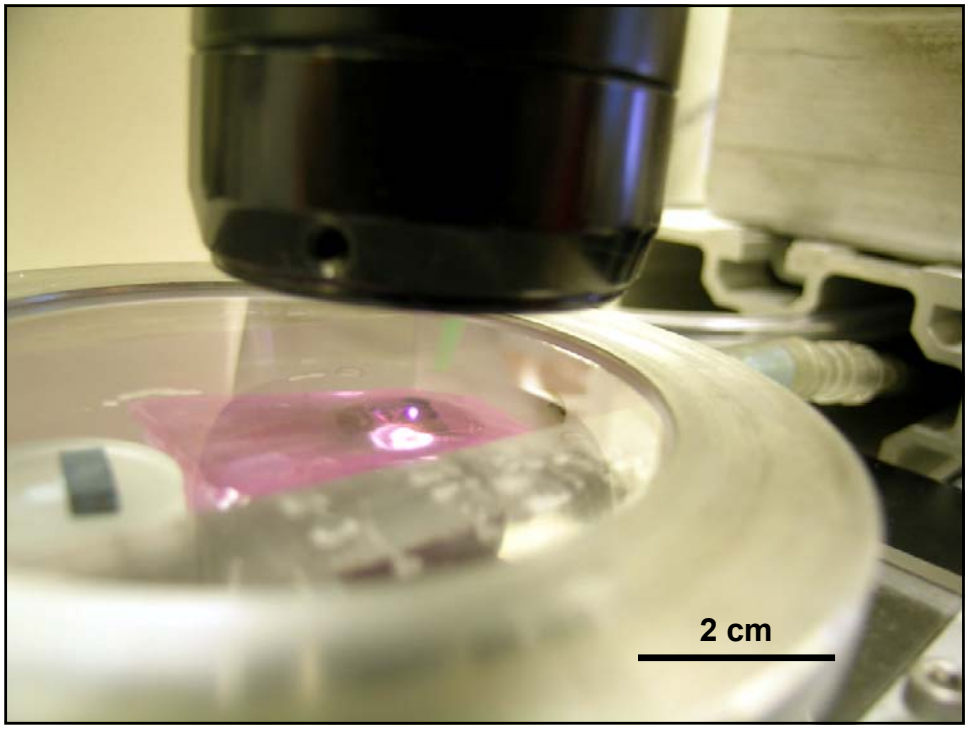
LA-ICP-MS Instrumentation



Hot spots:

- Ablation site laser - sample interaction
- Aerosol transport 100 %
- Aerosol ionization 100 %
- Signal recording 100 %

.. wishful thinking ..



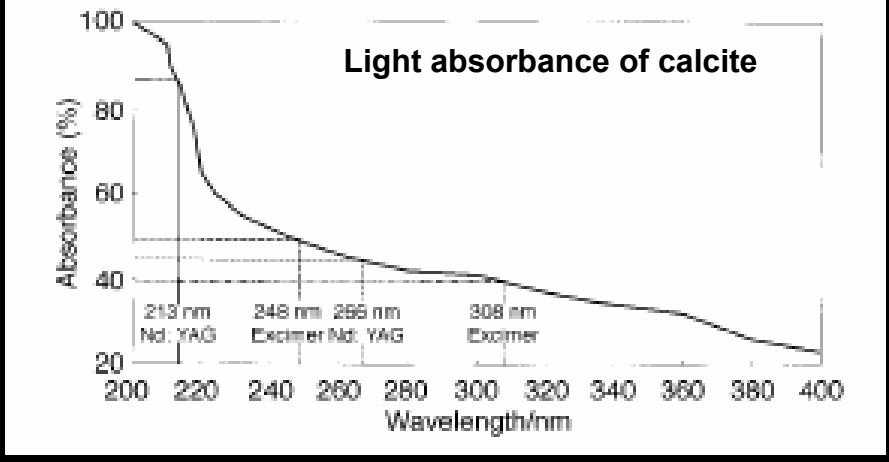
Laser ablation

- Produces sample aerosol with characteristic particle size and size distribution
  → shorter wavelength, smaller particles
  and narrower size distribution (at least for silicates)
- Absorbance of monochromatic light
  → Energy density in excited sample volume: irradiance
- Ablation energy threshold → "evaporation" (shattering)

Laser-sample interaction

Produce the smallest possible particles by:

- maximizing laser light absorbance
- thus maximizing sample irradiance
- unhindered expansion of ablation plume above spot (He-gas)

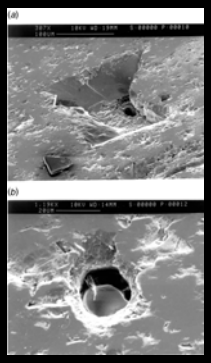


Jeffries et al. (1998)

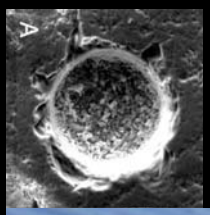
Laser ablation modes:
Single spot
versus
rastering or line scan

Rastering produces more large particles

Surface contamination always present
→ All the dirt all the time ...

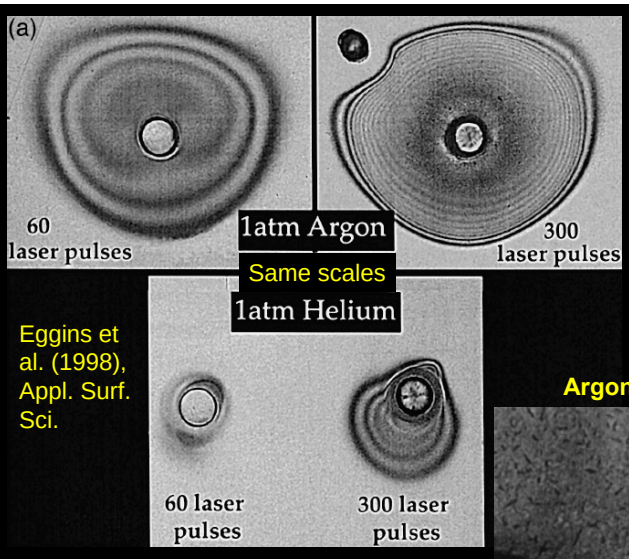


Jeffries et al., 1998:
LA in fluorite
with 266 nm (a)
and 213 nm (b)



Guillong et al., 2002:
266 nm energy-homogenized LA
in quartz (A) and SRM610 glass (B)

Our system, 2006:
193 nm energy-homogenized
LA in SRM610 glass,
several pit sizes superposed

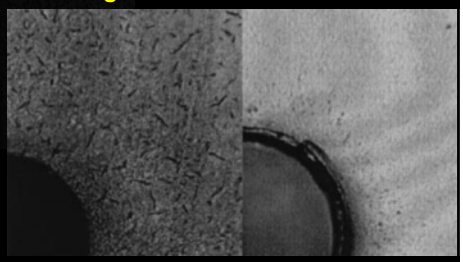


Eggins et al. (1998), Appl. Surf. Sci.

Ablation chamber gas

Argon

Helium



Günther and Heinrich (1999), JAAS

Use He gas in the ablation chamber

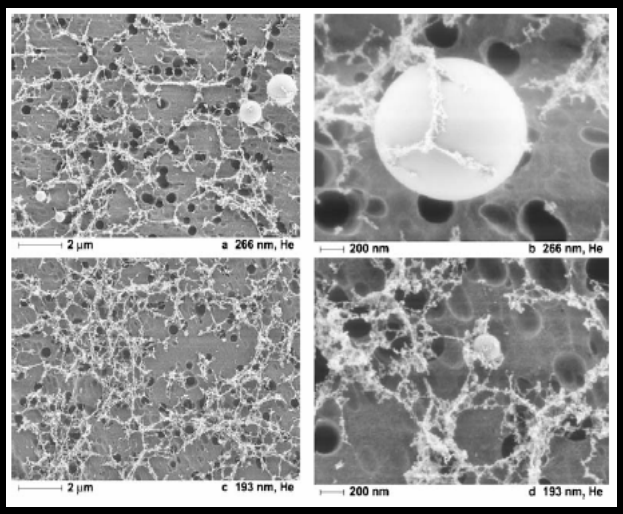
Terms in LA-ICP-MS

- Irradiance: Energy density in excited sample volume
- Laser fluence: Total energy per area (W/cm^2)
- Laser light pulse duration
- Ablation energy threshold
- Laser light absorbance

Irradiance increases with decreasing pulse duration for a given laser fluence.

Irradiance increases with increasing absorbance.

Laser aerosol particles from silicates

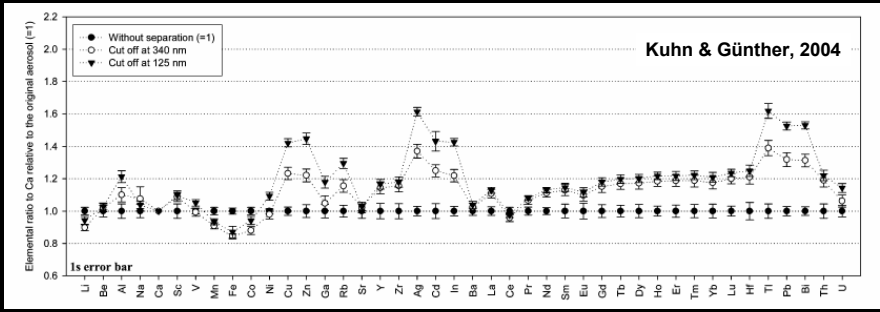


Filtered aerosol of NIST SRM 610 glass after 100 ablation pulses.

Note that with 193nm wavelength, no spherical particles are larger than 200 nm.
The pores of the filter are visible in the images as dark areas

Kuhn & Günther, 2005

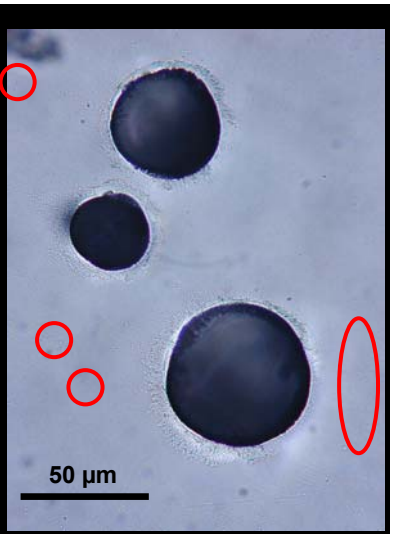
Different particle size fractions show variable chemical composition at least for some elements



266 nm, scanning ablation; SRM610 glass
(i.e., conditions to maximize the production of large particles !)

Aerosol transport

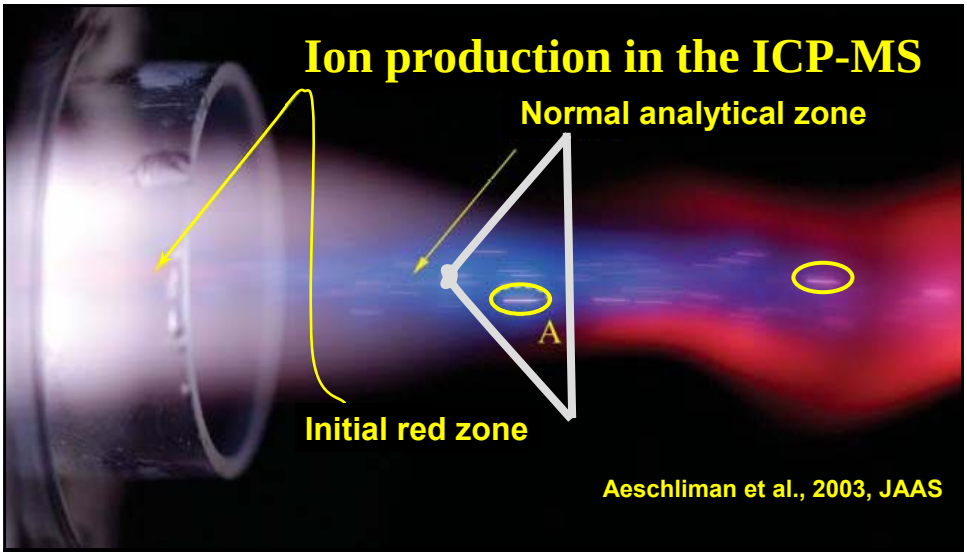
- Should be quantitative – but it is not ...
- Laser ablation particles all chemically identical ? – unfortunately not (Kuhn & Gunther, 2004)...
- Mass fraction of lost particles matters



Get as much small particles to the plasma as possible

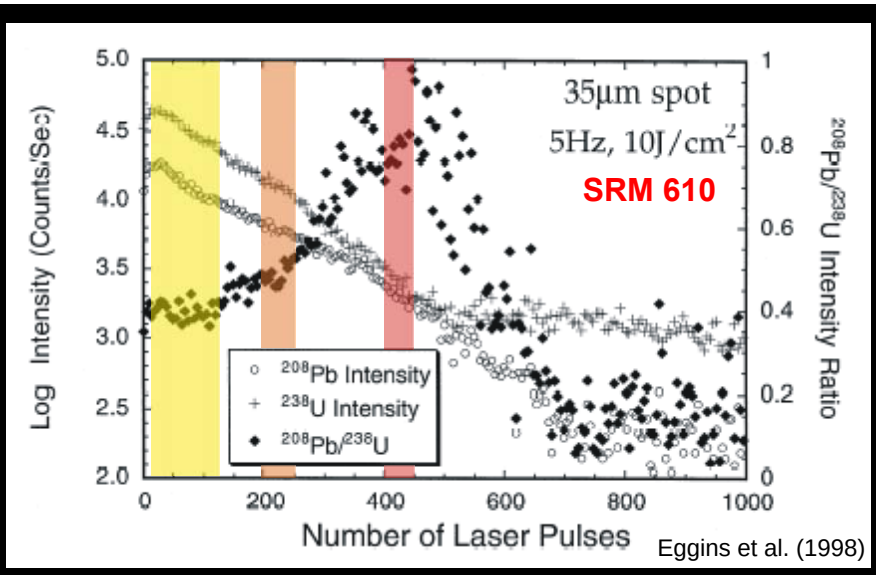
Aerosol transport efficiency

- The ablation chamber gas flow geometries dominate the aerosol dispersion
- Ablation chamber and transport tube volume has no influence on the amount of aerosol reaching the plasma (but: gas flow geometries)
- The smaller the particles, the "easier" the transport → particle size depends on sample irradiation (wavelength, matrix, ...)
- Particle loss must be minimized because of variable particle composition



Incomplete ionization:
large particles survive transition through plasma

Elemental fractionation likely .....

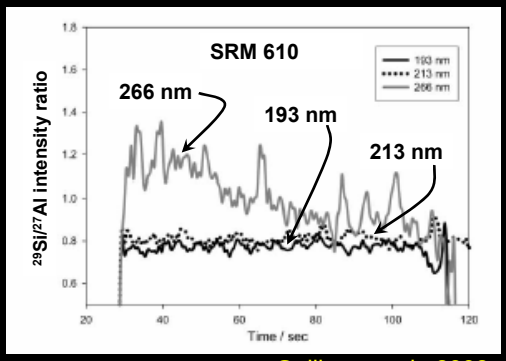


Eggins et al. (1998)

Elemental fractionation:
Analyte ratios evolve with time

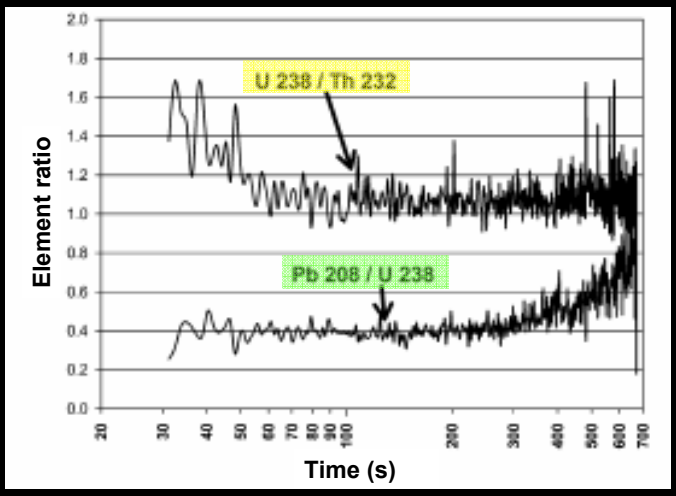
Elemental fractionation

- Collectively refers to changes in element responses (i.e., element sensitivity ratios) with changing LA-ICP-MS analytical conditions
- Occurs at the ablation site, during aerosol transport, and in the ICP
- Extent of element fractionation also matrix dependent
- Eliminate (minimize) element fractionation → achieve matrix independence



Guillong et al., 2002

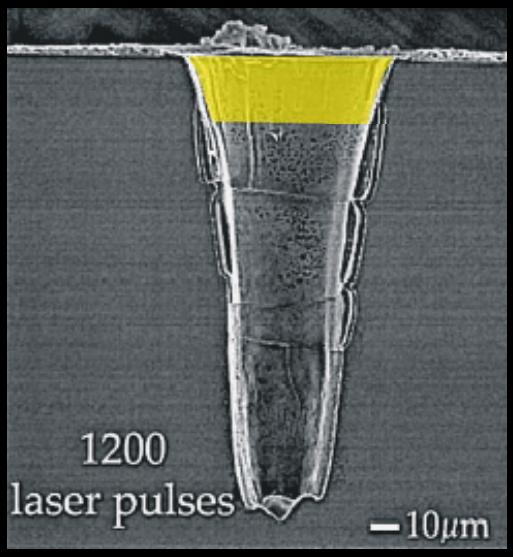
Two types of elemental fractionation

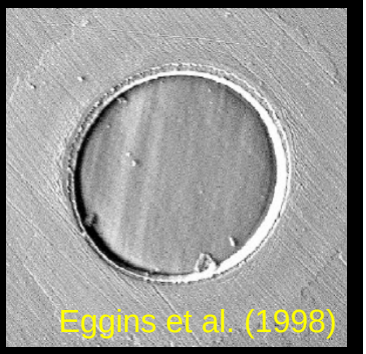


$^{238}U/^{232}Th$: monitors incomplete ionization in the ICP

$^{208}Pb/^{238}U$ monitors fractionation at LA-site

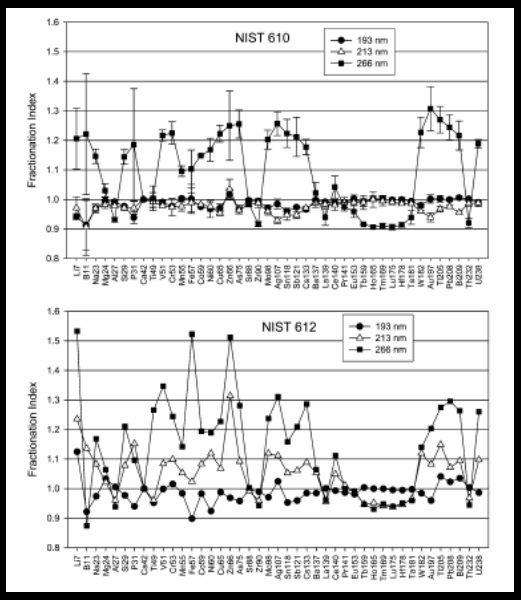
Fractionation at LA-site minimized ...





... by not drilling too deeply !!
depth / diameter < 1

Elemental fractionation



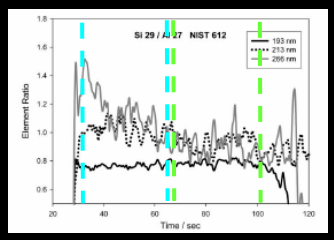
Fractionation index F:

$EI/Ca_{(2^{nd}\text{-}hs)}$ / $EI/Ca_{(1^{st}\text{-}hs)}$

(hs = half of signal)

is another expression for element response ratios that evolve with progressive ablation time (Fryer et al., 1995)

Guillong et al., 2003



Plasma processes

- **ICP temperature and plasma temperature structure**
  - higher rf-power → higher plasma temperature
  - lower gas flow rates → higher plasma temperature
- **Gas composition affects energy transfer to aerosol (e.g., H_2 promotes ionization)**
- **Sampling depth (i.e., position of sampler cone tip): Lower depth has higher temperature**
- **Ionization efficiency depends on**
  - ionization energies
  - plasma temperatures
  - particle residence time in the plasma

For accurate results: Easiest approach

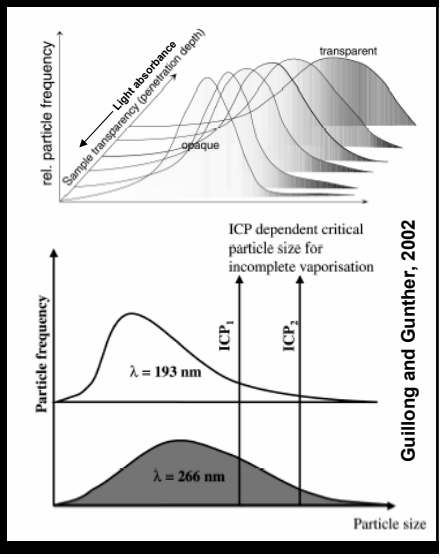
- Standards and samples should be matrix-matched
- Instrument parameters invariable between standard and sample analyses
- Ablation conditions should be selected to minimize the formation of large particles
- The first 5 seconds of the signal interval of a single spot ablation should be discarded

Do we really want this ?!?

Ion production in the ICP-MS

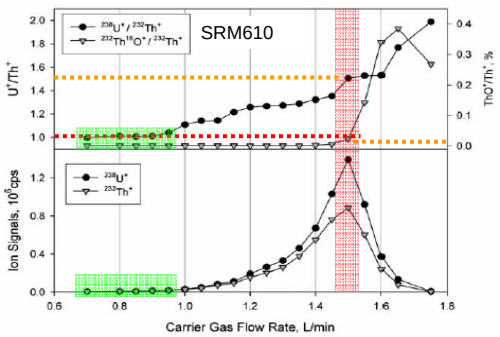
Complete ionization approached for:

- Small particles
- Narrow size distribution
- Optimized combination matrix – wavelength – pulse width
- Strong plasma (plasma load ...)
- ROBUST PLASMA analytical conditions



Robust plasma conditions

- Tune $(ThO)^+$ production rate to values < 0.5%
- Tune ICP-MS to maximum sensitivity



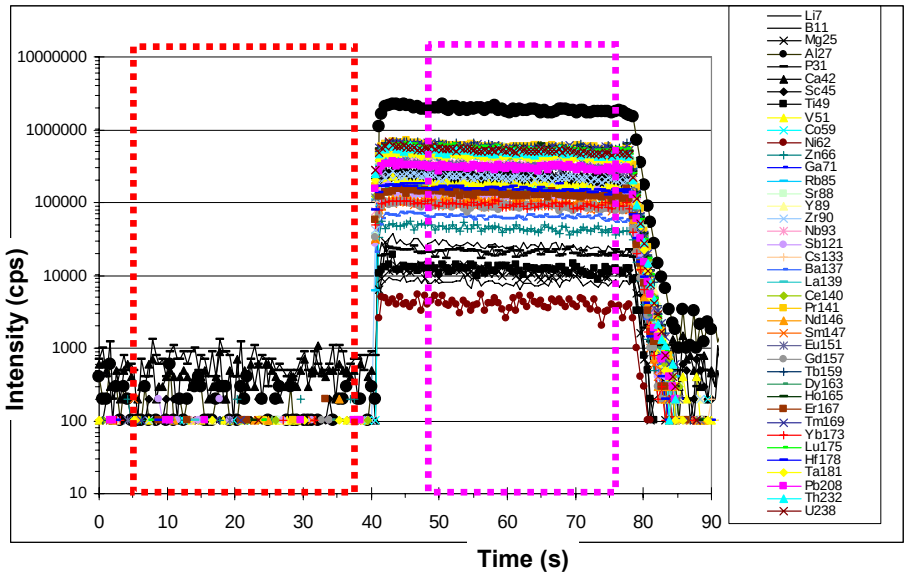
Summarized in Gunther and Hattendorf (2005) TrAC

U and Th: Elements with "equal" first ionization energies but different "volatility".

SRM 610: [U] = [Th] Tune U/Th sensitivity ratio to 1

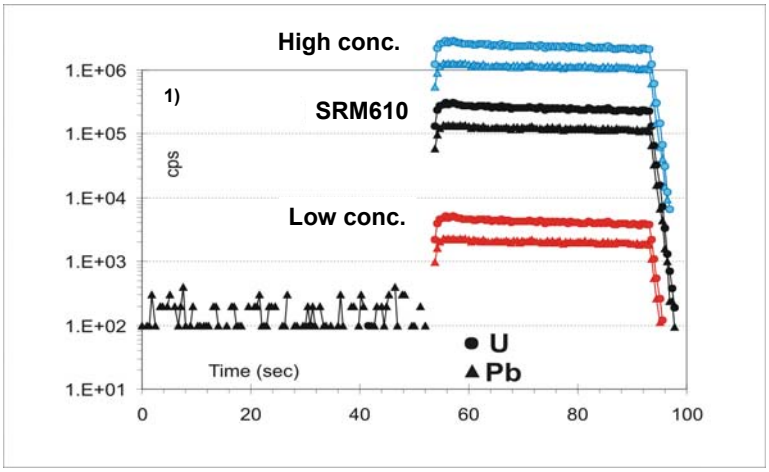
→ **MINIMIZE FRACTIONATION EFFECTS resulting from incomplete ionization**

LA-ICP-MS signal of homogeneous solid



Principles of signal quantification

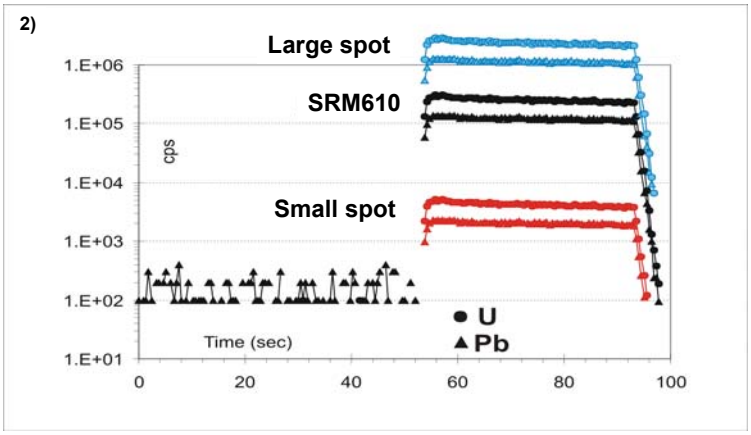
1) Variations in signal intensity are generated exclusively by variable analyte concentrations



→ External standardization alone quantifies the sample

Principles of signal quantification

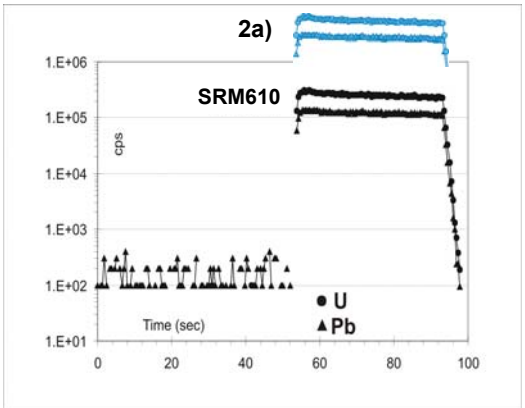
2) Signal intensities change in response to variables other than analyte concentrations (e.g., beam size)



→ External standardization alone fails to quantify the sample

2a) Signal intensities vary at CONSTANT SIGNAL INTENSITY RATIOS (blue case)

→ Combined *internal* and external standardization quantifies the sample (define SENSITIVITY FACTOR)



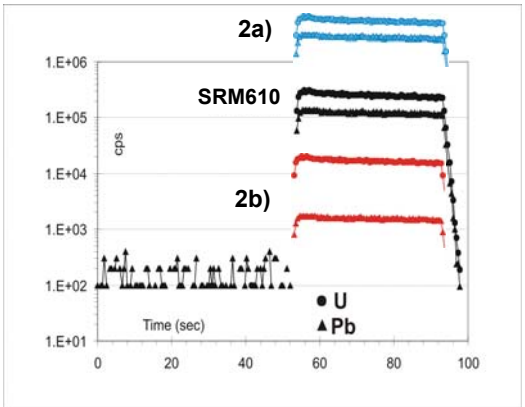
Key:

Element sensitivity ratios remain invariable!

→ ONE sensitivity factor for all analytes

2a) Signal intensities vary at CONSTANT SIGNAL INTENSITY RATIOS (blue case)

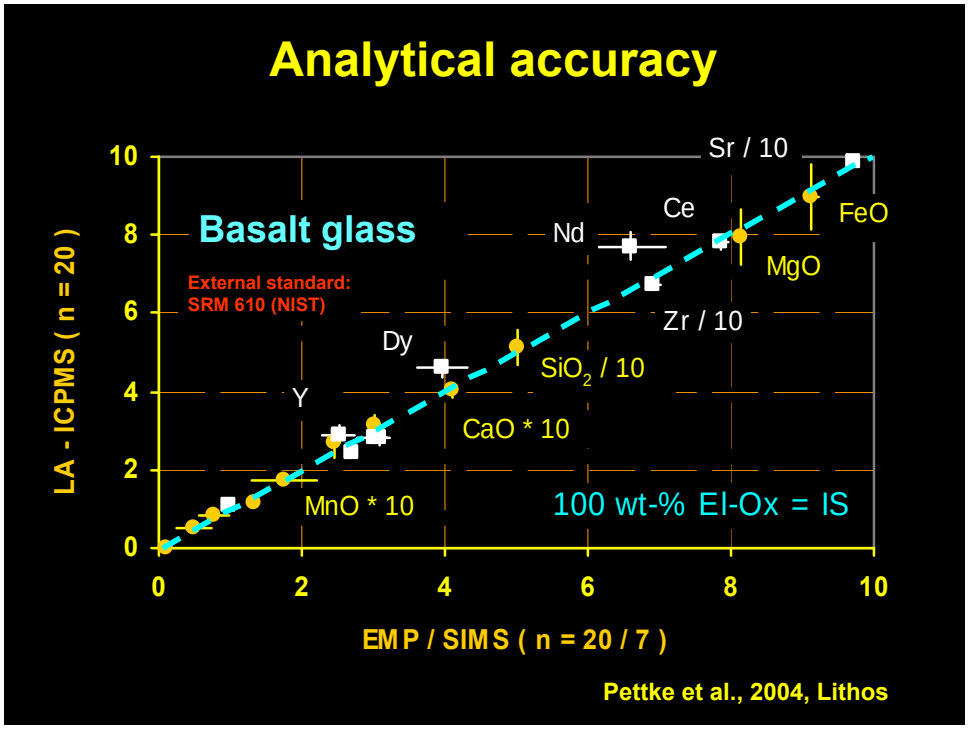
→ Combined *internal* and external standardization quantifies the sample (define SENSITIVITY FACTOR)

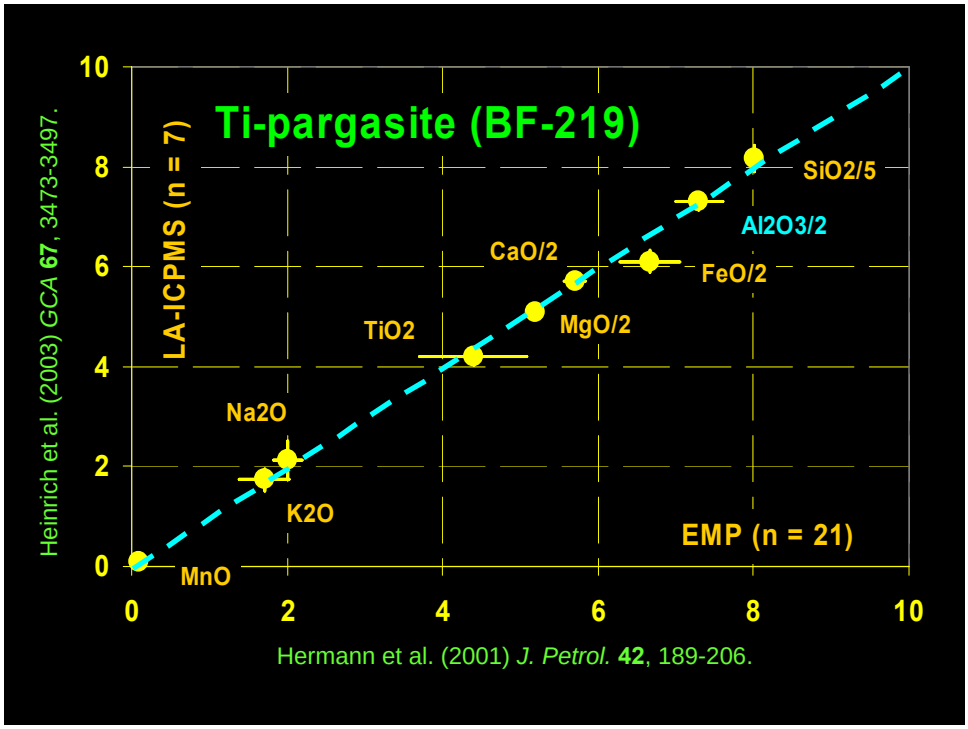


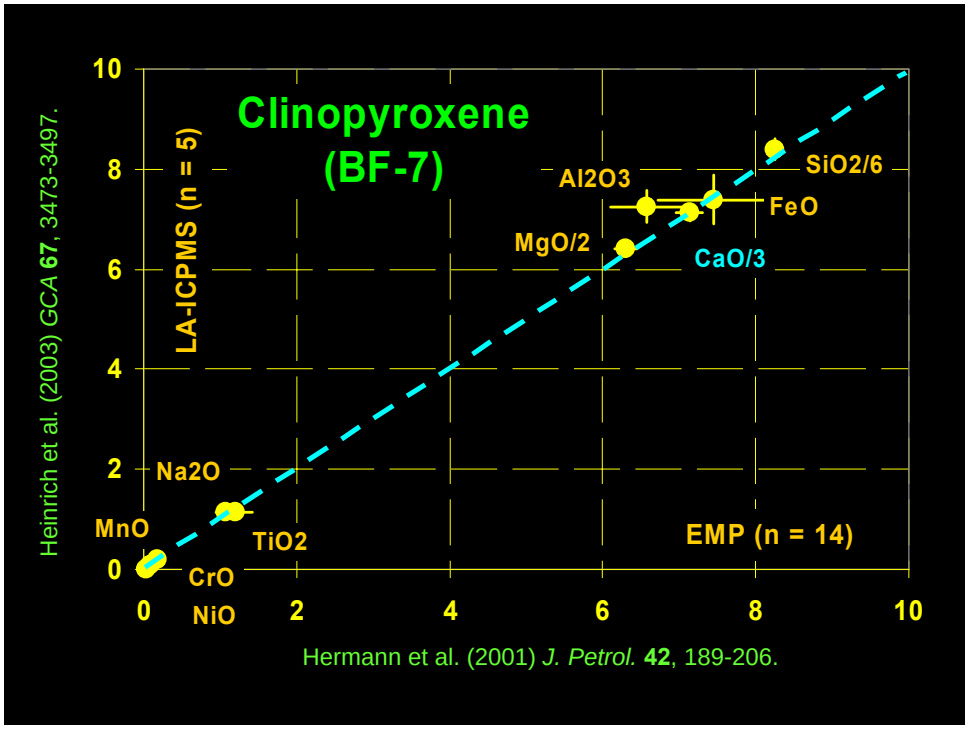
2b) Red case: Signal intensities and SIGNAL SENSITIVITY RATIOS ARE VARIABLE
→ cannot be quantified !
→ must be eliminated !

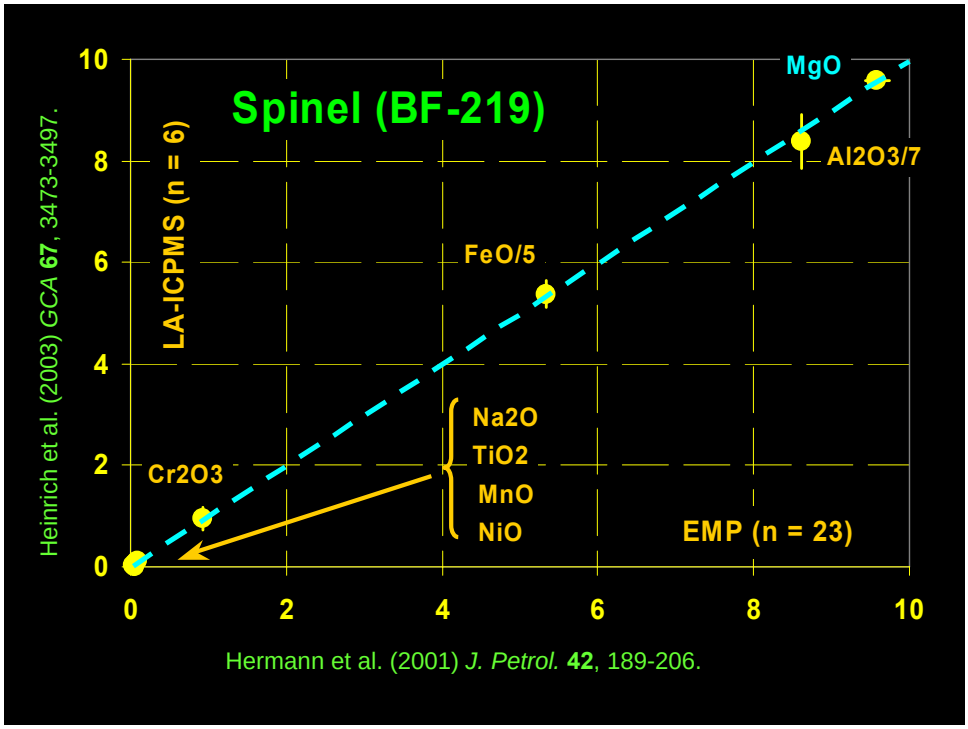
Commonly done by using identical analytical conditions and matrix matching

Impracticable for inclusion analysis by LA-ICP-MS

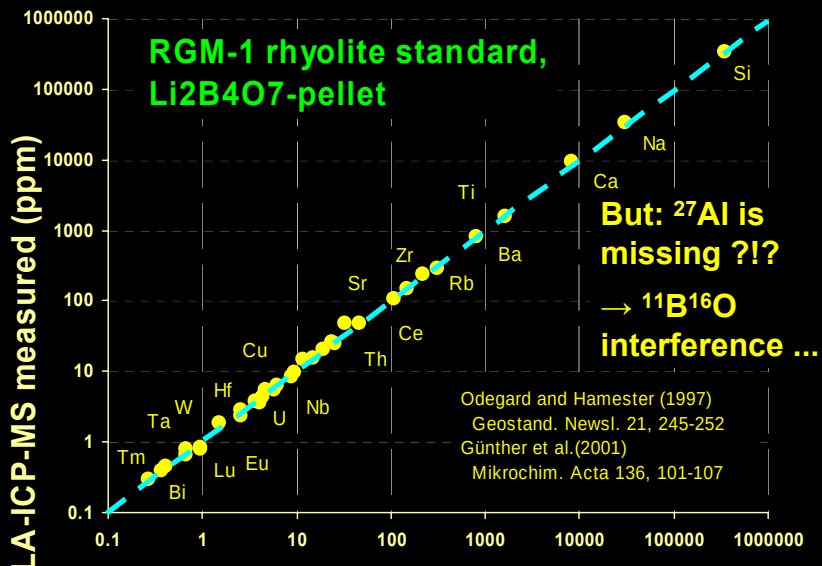

Analytical accuracy
Basalt glass
External standard:
SRM 610 (NIST)
Sr / 10
Ce
Nd
FeO
MgO
Zr / 10
Dy
SiO2 / 10
Y
CaO * 10
MnO * 10
100 wt-% El-Ox = IS
LA - ICPMS (n = 20)
EMP / SIMS (n = 20 / 7)
Pettke et al., 2004, Lithos


Ti-pargasite (BF-219)
LA-ICPMS (n = 7)
SiO2/5
Al2O3/2
CaO/2
FeO/2
TiO2
MgO/2
Na2O
K2O
MnO
EMP (n = 21)
Heinrich et al. (2003) GCA 67, 3473-3497.
Hermann et al. (2001) J. Petrol. 42, 189-206.

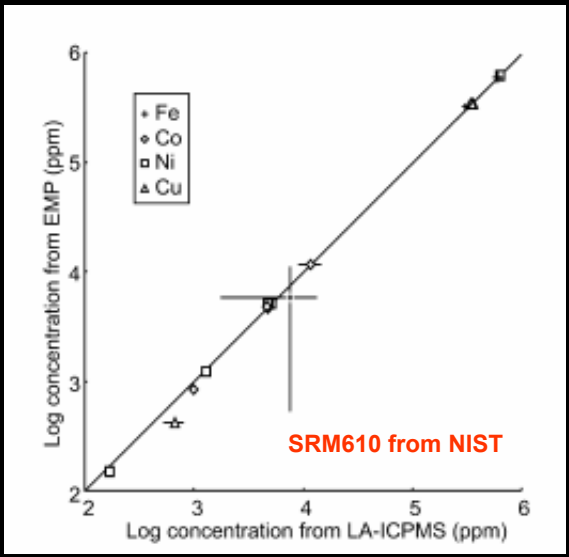

Clinopyroxene
(BF-7)
LA-ICPMS (n = 5)
EMP (n = 14)
Al2O3
SiO2/6
FeO
MgO/2
CaO/3
Na2O
TiO2
MnO
CrO
NiO
0
2
4
6
8
10
Heinrich et al. (2003) GCA 67, 3473-3497.
Hermann et al. (2001) J. Petrol. 42, 189-206.


Spinel (BF-219)
LA-ICPMS (n = 6)
EMP (n = 23)
MgO
Al2O3/7
FeO/5
Cr2O3
Na2O
TiO2
MnO
NiO
0
2
4
6
8
10
Heinrich et al. (2003) GCA 67, 3473-3497.
Hermann et al. (2001) J. Petrol. 42, 189-206.

Trace elements on XRF pellets



Analytical accuracy



Even for sulfides! (pyrrhotite, chalcopyrite and millerite)

Halter et al., 2004

Limitations on analytical accuracy

- Knowledge of external standards used, including most used SRM 610 and 612 from NIST (see Spandler et al., in review).
  - notably for "uncommon" elements, e.g., Be, Cl, Ge, Se, Mo, Sb, Nb, Ta, W, Au, ...

- Variability in ion production in ICP-MS as a function of elemental fractionation
  - Robust plasma conditions
  - Plasma aerosol load
  - Particle size and size distribution
  - Laser ablation conditions
  - .....

Interferences

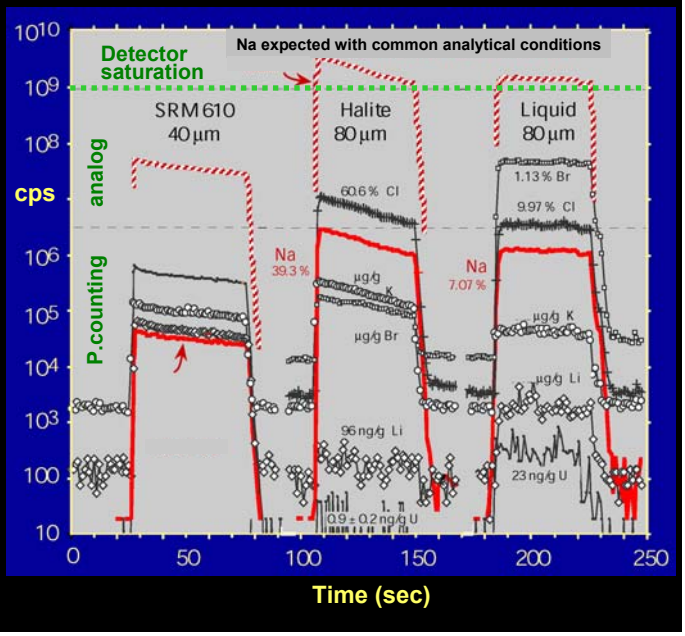
- Plasma-based gas interferences are, in principle, accounted for by background subtraction
- Isobaric interferences (e.g., ^{87}Rb on ^{87}Sr) avoided by proper analyte selection
- Polyatomic interferences are dangerous, e.g.,
  - matrix-gas-based: ($^{40}Ar^{16}O$) on $^{56}Fe^{+}$ in silicates
  - matrix-gas-based: Metal-argides on, e.g., $^{105}Pd^{+}$
  - matrix-based: ($^{44}Ca^{16}O$) on $^{60}Ni^{+}$ in carbonates, or ($^{16}O^{16}O$) on $^{32}S^{+}$ and ($^{16}O^{18}O$) on $^{34}S^{+}$ in silicates
- Doubly charged ions, e.g., $^{90}Zr^{++}$ on $^{45}Sc^{+}$ (recall: ions are measured as mass/charge ratio)

PAY ATTENTION IN ANALYTE SELECTION

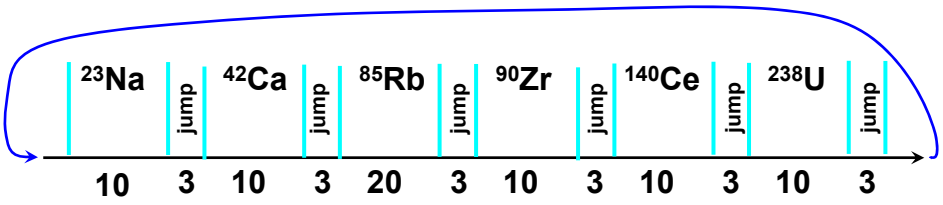
ICP-MS: Dynamic range and background

Major elements essential for quantification by internal standardisation

Some ICP-MS instruments allow for band passing



Measurement routine on a single collector intrument



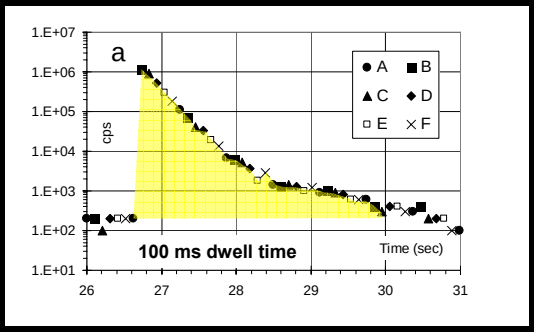
Time axis (**milliseconds**)

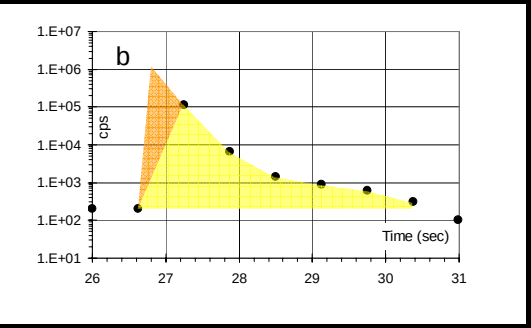
Total analysis time per sweep: 88 ms

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 analysis

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





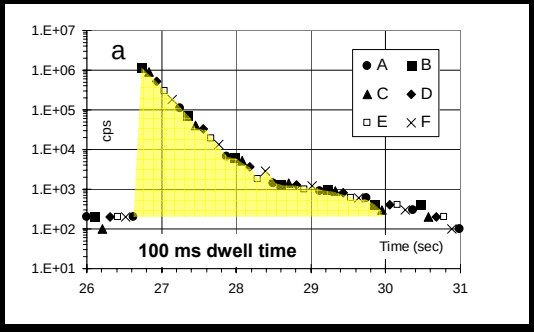
Representative recording of short, transient signals

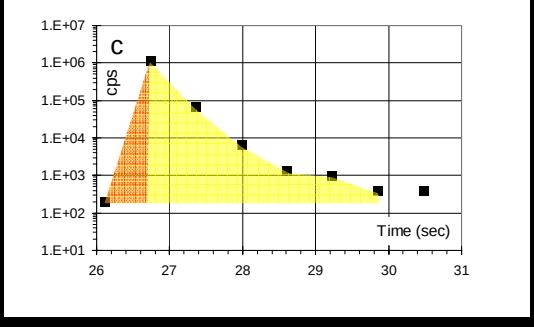
Net count rate: 106830 cps

Net count rate: 23840 cps

78% of the signal missed !!

Pettke et al. (2000) JAAS





Representative recording of short, transient signals

Net count rate: 106830 cps

Net count rate: 207692 cps

95% excess signal !!

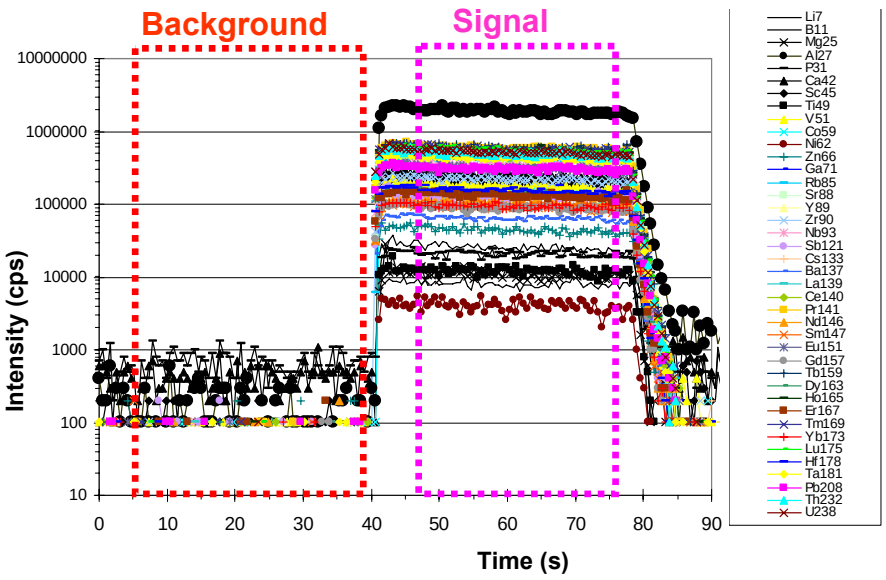
Pettke et al. (2000) JAAS

Matrix independent analytical conditions can be approached

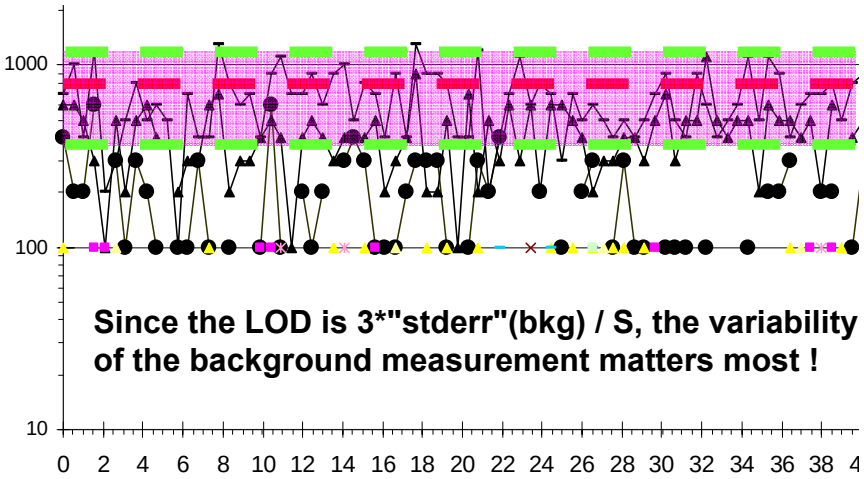
Matrix independent calibration strategies can provide accurate results

***In-situ* analysis of "any" materials possible (solid and even liquid)**

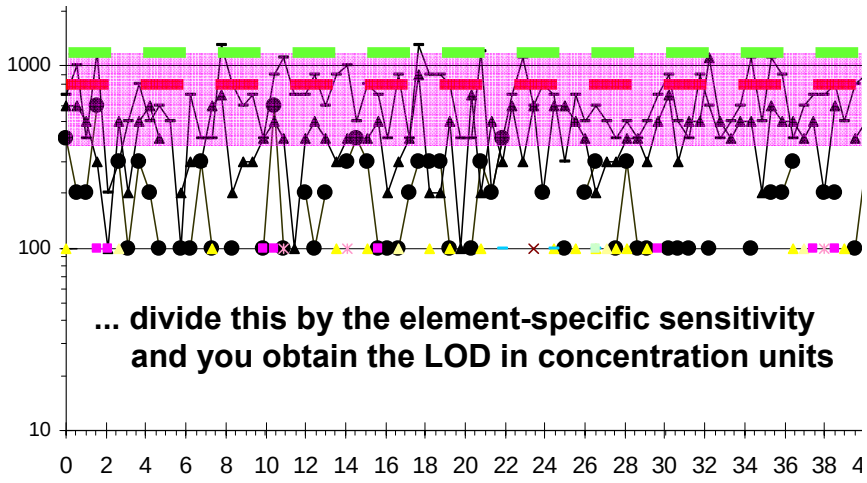
Signal



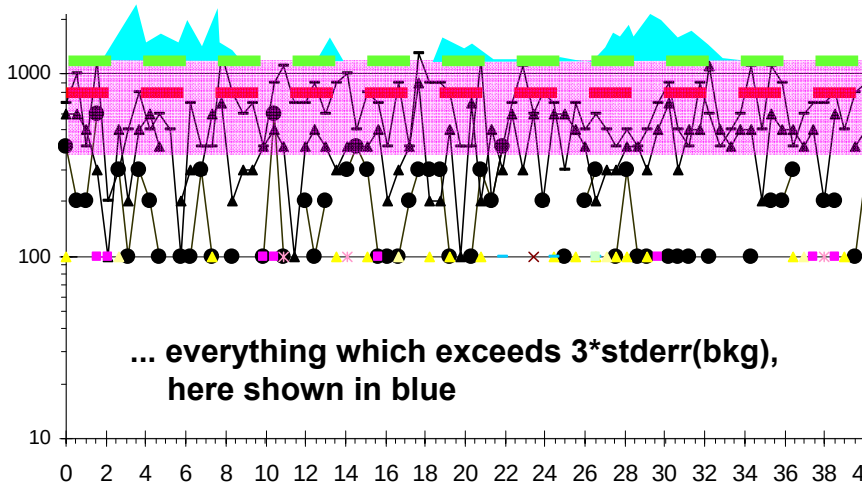
Background signal



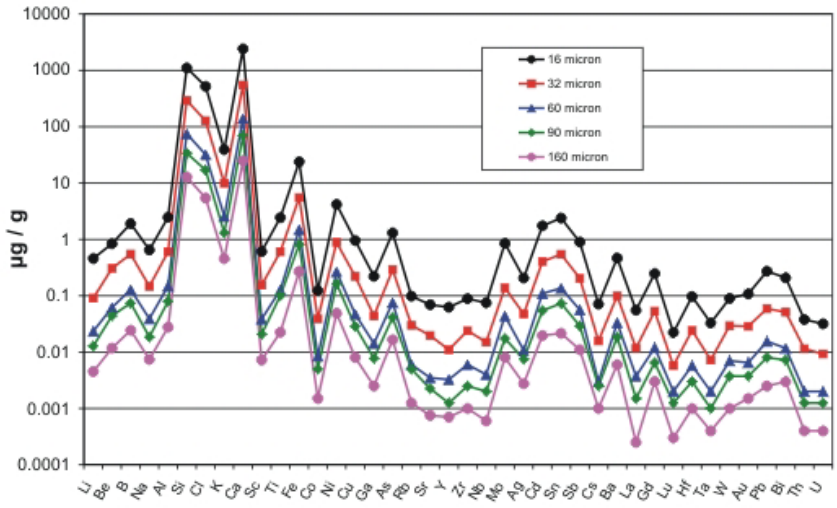
The LOD "signal" corresponds to a signal of average(bkg) + 3*"stderr"(bkg) (green line)



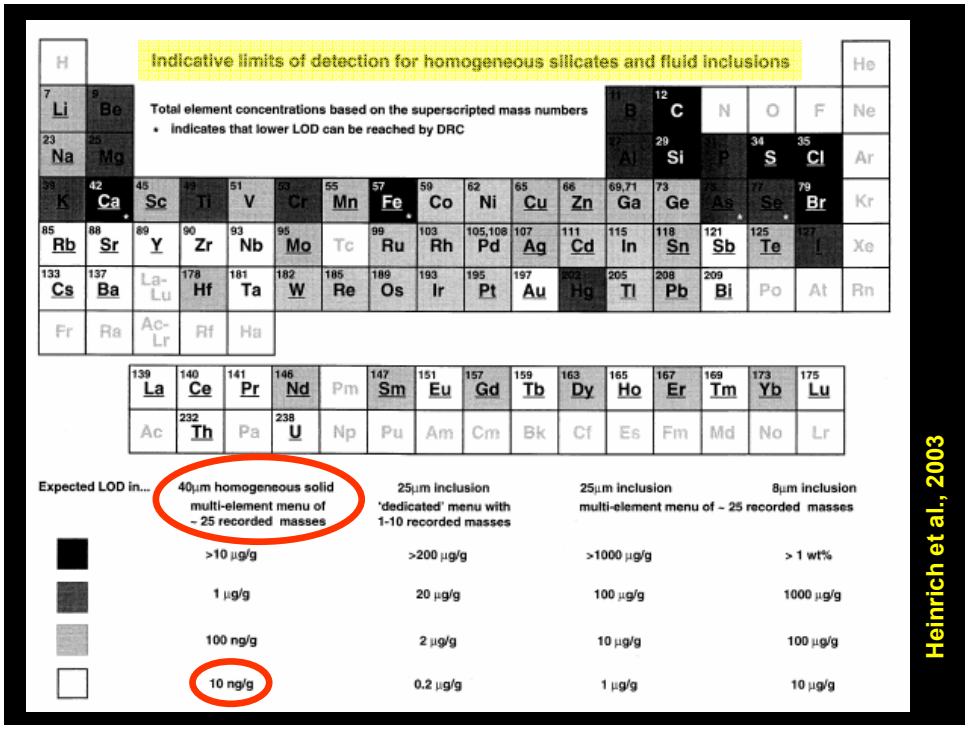
A significant signal is thus ...



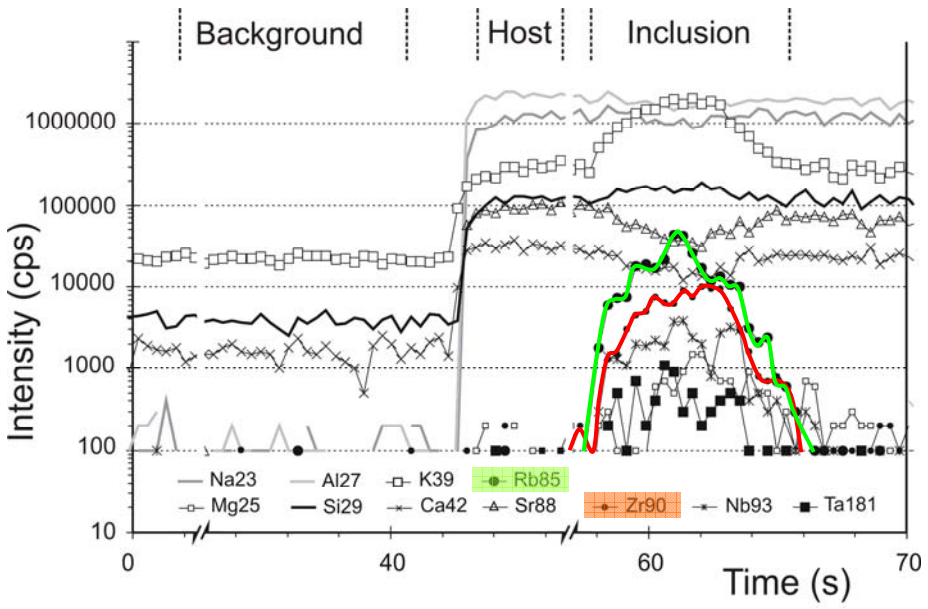
Typical LOD achieved on in-house LA-ICP-MS

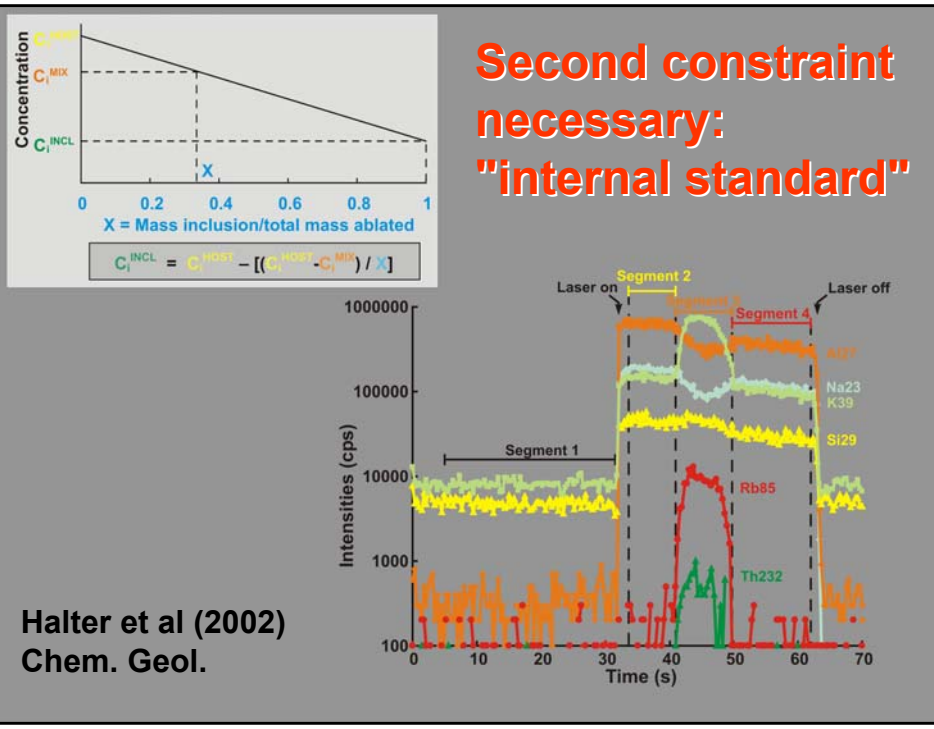


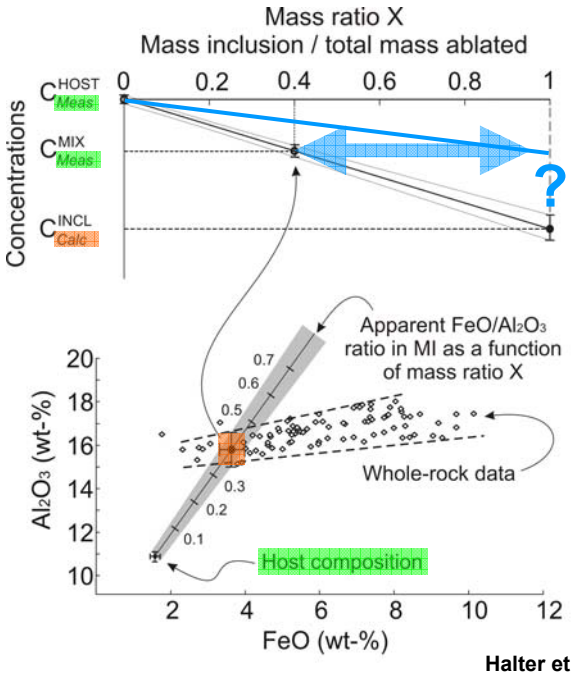
One order of pit size increase results in two orders of magnitude lower LOD!



Signal variability in heterogeneous MI







Second constraint:

Concentration of one element or an element ratio at MI entrapment known independently to determine MI-specific mass ratio,

e.g., whole rock data.

This mass ratio is then used to calculate the element concentrations of this MI

Halter et al (2002) Chem. Geol.

Limitations on analytical accuracy

- **Knowledge of external standards used, including most used SRM 610 and 612 from NIST (see Spandler et al., in review).**
  - **notably for "uncommon" elements, e.g., Be, Cl, Ge, Se, Mo, Sb, Nb, Ta, W, Au, ...**

- **Elemental fractionation during LA-ICP-MS analysis**
  → **The analyst should know what he/she is doing.....**

Some more essential considerations

Interferences

- Plasma-based gas interferences are, in principle, accounted for by background subtraction
- Isobaric interferences (e.g., ^{87}Rb on ^{87}Sr) avoided by proper analyte selection
- Polyatomic interferences are dangerous, e.g.,
  - matrix-gas-based: $^{40}Ar^{16}O$ on ^{56}Fe in silicates
  - matrix-gas-based: Metal-argides on, e.g., ^{105}Pd
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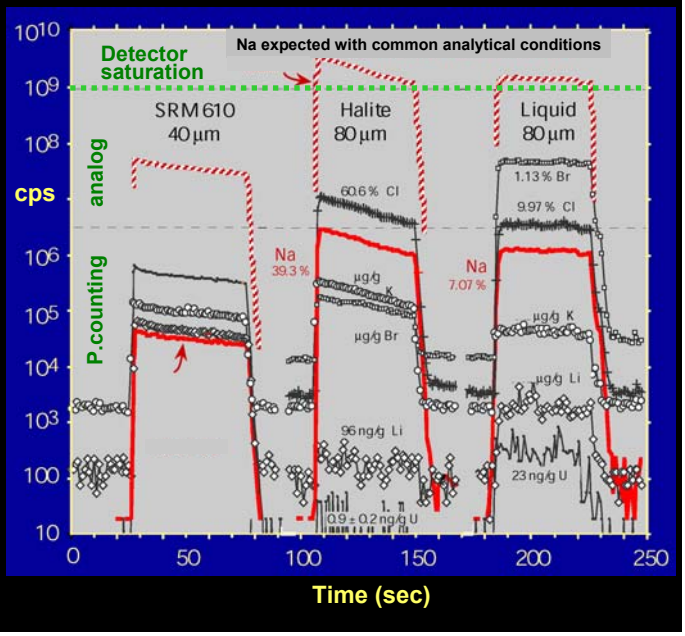

Matrix independent analytical conditions can be approached

Matrix independent calibration strategies can provide accurate results

***In-situ* analysis of heterogeneous samples in the Earth Sciences**